PCBs: HUMAN AND ENVIRONMENTAL HAZARDS

Edited by

Frank M. D'Itri
and
Michael A. Kamrin

BUTTERWORTH PUBLISHERS
Boston • London
Sydney • Wellington • Durban • Toronto
An Ann Arbor Science Book

MONS 004771

PCBs: HUMAN AND ENVIRONMENTAL HAZARDS

MONS 004772

RA
1242
P7
P22
1983

Ann Arbor Science is an imprint of Butterworth Publishers

Copyright © 1983 Butterworth Publishers
All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior written permission of the publisher.

ISBN 0-250-40598-9
Library of Congress Catalog Card Number 83-14249

10 9 8 7 6 5 4 3 2 1

Butterworth Publishers
10 Tower Office Park
Woburn, MA 01801

Printed in the United States of America

MONS 004773





Frank M. D'Itri is Professor of Water Chemistry, Institute of Water Research and Department of Fisheries and Wildlife, Michigan State University in East Lansing. With a Ph.D. in analytical chemistry, his primary research emphasizes the analytical aspects of water and sediment chemistry, especially the transformation and translocation of phosphorus, nitrogen, heavy metals and hazardous organic chemicals in the environment.

Professor D'Itri is listed in *American Men of Science, Physical and Biological Science*. He is the author of *The Environmental Mercury Problem*, co-author of *Mercury Contamination: A Human Tragedy* and *An Assessment of Mercury in the Environment*, and editor of *Wastewater Renovation and Reuse*. Dr. D'Itri is also the editor of *Land Treatment of Municipal Wastewater: Vegetation Selection and Management*, published by Ann Arbor Science. In addition, he is the author of more than forty scientific articles on a variety of environmental topics.

Dr. D'Itri has served as chairperson for the National Research Council's panel reviewing the environmental effects of mercury and a number of symposia dealing with the analytical problems related to environmental pollution. He has been the recipient of fellowships from Socony-Mobil, the National Institutes of Health, the Rockefeller Foundation and the Japan Society for the Promotion of Science.

Michael A. Kamrin is currently a Professor at the Center for Environmental Toxicology, Michigan State University in East Lansing. Dr. Kamrin holds a Ph.D. in biophysical chemistry, and his primary research interests focus on the assessment of the scientific evidence used to evaluate the benefits and risks of substances that affect human health.

He has served as Visiting Scientist in the Legislative Office of Science Advisor, Lansing, Michigan; Visiting Lecturer in the Department of Zoology at the University of Turku (Finland); and he has held positions as Assistant Professor, Associate Professor, and Professor in the Department of Natural Science at Michigan State University. Dr. Kamrin is also the author of numerous articles published in professional journals.

MONS 004774

LIST OF CONTRIBUTORS AND PARTICIPANTS

*Thomas Anderson (375), Michigan Representative (Retired), 13726 Sycamore Street, Southgate, MI 48195

*Shoji Asano (241), Research Scientist, Otsuka Pharmaceutical Company, Ltd., 31, 2 Chome, Otedori, Higashi-ku, Osaka, JAPAN

Steven D. Aust, Professor, Department of Biochemistry, Michigan State University, East Lansing, MI 48824-1319

*Willard M.J. Baird (91), Lansing Bureau Chief, (Retired), Gannett News Service, 6684 Lakeview Drive, Lake City, MI 49651

W. Emmett Braselton, Associate Professor, Department of Pharmacology and Toxicology, Michigan State University, East Lansing, MI 48824-1317

*Karl E. Bremer (367), Toxic Substances Coordinator, U.S. Environmental Protection Agency, Region V, Chicago, IL 60604

*John E. Cantlon (51), Vice President for Research and Graduate Studies, Michigan State University, East Lansing, MI 48824-1046

Burton D. Cardwell, Michigan Department of Agriculture, P.O. Box 30017, Lansing, MI 48909

*Chia-Cheng Chang (241), Associate Professor, Department of Pediatrics and Human Development, College of Human Medicine, Michigan State University, East Lansing, MI 48824-1317

*William E. Cooper (423), Chairman, Department of Zoology, Michigan State University, East Lansing, MI 48824-1115

Frank M. D'Itri, Professor, Institute of Water Research, Department of Fisheries and Wildlife, Michigan State University, East Lansing, MI 48824-1222

*Steven J. Eisenreich (49), Associate Professor, Environmental Engineering Program, Department of Civil and Environmental Engineering, University of Minnesota, Minneapolis, MN 55455

MONS 004775

Carlos M. Fetterolf, Jr., Executive Secretary, Great Lakes Fishery Commission, 1451 Green Road, Ann Arbor, MI 48105

*Greta G. Fein (311), College of Education, University of Maryland, College Park, MD 20742

*William R. Gaffey (279), Monsanto Company, 800 N. Lindberg Boulevard, St. Louis, MO 63167

*Andrew P. Gilman (115), Environmental Health Directorate, Health Protection Branch, Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario, CANADA K1A OL2

*Jay I. Goodman (179), Professor, Department of Pharmacology and Toxicology, Michigan State University East Lansing, MI 48824-1317

*Donald L. Grant (383), Foods Directorate, Health Protection Branch, Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario, CANADA K1A OL2

Rolf Hartung, Professor, School of Public Health, University of Michigan, Ann Arbor, MI 48109

*Alan L. Hoeting (393), U.S. Food and Drug Administration, 1560 East Jefferson Avenue, Detroit MI 48207

Jerry B. Hook, Director, Center for Environmental Toxicology, Michigan State University, East Lansing, MI 48824-1206

*Harold E.B. Humphrey (299), Michigan Department of Public Health, Environmental Epidemiology, 3500 N. Logan, P.O. Box 30035, Lansing, MI 48909

*Joseph L. Jacobson (311), Department of Psychology, Wayne State University, Detroit, MI 48202

*Sandra W. Jacobson (311), Department of Psychology, Wayne State University, Detroit, MI 48202

*Thomas C. Johnson (49), Department of Geology, University of Minnesota-Duluth, Duluth, MN 55812

Allan F. Johnson, Water Resources Branch, Ministry of the Environment, 135 St. Clair Avenue, West, Toronto, Ontario, CANADA M4V 1P5

Michael A. Kamrin, Professor, Center for Environmental Toxicology, Michigan State University, East Lansing, MI 48824-1206

*Albert C. Kolbye, Jr. (77), Nutrition Foundation, 888 17th Street, N.W., Washington, DC 20006

MONS 004776

*John J. Lech (187), Department of Pharmacology and Toxicology, Medical College of Wisconsin, P.O. Box 26509, 8701 Watertown Plank Road, Milwaukee, WI 53226

John A. Liddle, Chief, Toxicology Branch, Centers for Disease Control, Atlanta, GA 30333

*H.B. Matthews (203), National Toxicology Program, Systemic Toxicology Branch, National Institute of Environmental Health Sciences, Research Triangle Park, NC 27709

*William E. McCracken (123), Michigan Department of Natural Resources, Permit Section, Surface Water Quality, P.O. Box 30028, Lansing, MI 48909

*Michael D. Mullin (165), Research Chemist, Large Lakes Research Station, U.S. Environmental Protection Agency, 9311 Groh Road, Grosse Ile, MI 48138

*Richard E. Peterson (187), Department of Pharmacology and Toxicology, School of Pharmacy, University of Wisconsin, Madison, WI 53706

*Cynthia M. Pochini (165), Large Lakes Research Station, U.S. Environmental Protection Agency, 9311 Groh Road, Grosse Ile, MI 48138

*Robert K. Ringer (227), Department of Animal Science, Michigan State University, East Lansing, MI 48824-1225

*Stephen H. Safe (165), College of Veterinary Medicine, Department of Physiology and Pharmacology, Texas A&M University, College Station, TX 77843

*Lorna M. Safe (165), College of Veterinary Medicine, Department of Veterinary Physiology and Pharmacology, Texas A&M University, College Station, TX 77843

*Pamela M. Schwartz (311), School of Public Health, University of Michigan, Ann Arbor, MI 48109

*Stuart D. Sieight (215), Professor, Department of Pathology, Michigan State University, East Lansing, MI 48824-1316

*Wayland R. Swain (111), Professor, Vakgroep Aquatische Oecologie, University of Amsterdam, Kruislaan 320, 1098 SM, Amsterdam, THE NETHERLANDS

*Daniel R. Talhelm (409), Professor, Department of Fisheries and Wildlife, Michigan State University, East Lansing, MI 48824-1222

*Howard A. Tanner (347), Director, Michigan Department of Natural Resources, P.O. Box 30028, Lansing, MI 48909

MONS 004777

*James E. Trosko (241), Professor, Department of Pediatrics and Human Development, Michigan State University, East Lansing, MI 48824-1317

*Gen Tsushimoto (241), Research Scientist, Otsuka Pharmaceutical Company, Ltd., 31, 2 Chome, Otedori, Higashi-ku, Osaka, JAPAN

*Eileen O. van Ravenswaay (353), Assistant Professor, Department of Agricultural Economics, Michigan State University, East Lansing, MI 48824-1039

*Claude Ver Duin (109), Executive Director, Great Lakes Fisheries Development Foundation, 619 Washington Avenue, Box 656, Grand Haven, MI 49417

*Bailus Walker, Jr. (3), Director, Michigan Department of Public Health, P.O. Box 30035, Lansing, MI 48909

*Thomas L. Washington (101), Executive Director, Michigan United Conservation Clubs, P.O. Box 30235, Lansing, MI 48909

*Frank Welsch (253), Chemical Industry Institute of Toxicology (CIIT), P.O. Box 12137, Research Triangle Park, NC 27709

Wayne A. Willford, Chief, Section of Physiology and Contaminant Chemistry, Great Lakes Fisheries Laboratory, Ann Arbor, MI 48105

*Matthew J. Zabik (141), Professor, Pesticide Research Center, Michigan State University, East Lansing, MI 48824-1311

* Authors of papers published in this book.

MONS 004778

CONTENTS

Part I
Scientific, Social, and Political Overview 1

1. Introduction 3
B. Walker, Jr.

2. The PCB Problem: An Overview 5
J.E. Cantlon

3. An Overview of the Scientific Basis for Concern with Polychlorinated Biphenyls in the Great Lakes 11
W.R. Swain

4. PCBs in the Great Lakes: Sources, Sinks, Burdens 49
S.J. Eisenreich and T.C. Johnson

5. Regulatory Considerations Regarding Limiting Human Exposures to PCBs 77
A.C. Kolbye, Jr.

6. Responding to Public Concern over Environmental Pollution Hazards 91
W.M.J. Baird

7. The Environmentalist's View of the PCBs Problem in the Great Lakes 101
T.L. Washington

8. The Commercial Fishermen's View of the PCBs Problem in the Great Lakes 109
C. Ver Duin

MONS 004779

Part II
PCBs: Analysis and Monitoring 113

9. Monitoring for PCBs in Fish: The Human Health Perspective 115
A.P. Gilman

10. Edible Tissue Sampling for Fish Contaminant Analysis 123
W.E. McCracken

11. The Photochemistry of PCBs 141
M.J. Zabik

12. Analysis of PCBs Using Specific Isomer High Resolution Capillary Gas Chromatography 165
M.D. Mullin, C.M. Pochini, S.H. Safe, and L.M. Safe

Part III
Metabolism and Toxicology of PCBs 177

13. Concepts in Toxicology and Carcinogenesis: A Basis for Discussing the Potential Environmental Hazard Posed by PCBs 179
J.I. Goodman

14. Biotransformation and Persistence of Polychlorinated Biphenyls (PCBs) in Fish 187
J.J. Lech and R.E. Peterson

15. Metabolism of PCBs in Mammals: Routes of Entry, Storage, and Excretion 203
H.B. Matthews

16. Pathologic Effects of PCBs in Mammals 215
S.D. Sleight

17. Toxicology of PCBs in Mink and Ferrets 227
R.K. Ringer

MONS 004780

18. Inhibition of Intercellular Communication by Various Congeners of Polybrominated Biphenyl and Polychlorinated Biphenyl 241
G. Tsushimoto, S. Asano, J.E. Trosko, and C-C. Chang

19. Effects of Polychlorinated Biphenyls on the Expression of Embryotoxicity Caused by Model Teratogens 253
F. Welsch

Part IV
The Effects of PCBs on Human Health 277

20. The Epidemiology of PCBs 279
W.R. Gaffey

21. Population Studies of PCBs in Michigan Residents 299
H.E.B. Humphrey

22. Intrauterine Exposure of Human Newborns to PCBs: Measures of Exposure 311
S.W. Jacobson, J.L. Jacobson, P.M. Schwartz, and G.G. Fein

Part V
Regulation of PCBs 345

23. Regulation of PCBs in Michigan 347
H.A. Tanner

24. The Science-Policy Interface in Regulatory Decision-Making 353
L.O. van Ravenswaay

25. Dealing with Multi-Agency and Multi-State Regulation of Polychlorinated Biphenyls 367
K.E. Bremer

26. The Role of the Legislature in the Regulation of Toxic Materials 375
T. Anderson

MONS 004781

27. Regulation of PCBs in Canada 383
D.L. Grant

28. FDA Regulation of PCB in Food 393
A.L. Hocting

29. Economic Impacts of PCB Regulation in Food Fish 409
D.R. Talhelm

30. Problems in Legislating and Regulating Toxic Materials: Panel Discussion 423
W.E. Cooper, Moderator

Index 435

MONS 004782

PREFACE

Polychlorinated biphenyls (PCBs) have been used for industrial purposes for over 50 years. Nonetheless, except for the occupational exposure first reported in the early 1940s, concern about the ecological and human health impact did not become an environmental issue until 1966 when S. Jensen published "Report of a New Chemical Hazard" in the *New Scientist* (Volume 32, page 612). Research since then has offered insights into major aspects of the problem; and this volume presents the reader with varied viewpoints, the latest research findings, and an overview of the steps that are being taken to solve these problems, particularly in the Great Lakes region.

The material in this book is based on papers given at an International Symposium on PCBs in the Great Lakes held at Michigan State University March 17-19, 1982. At that time, scientists and other concerned citizens presented and evaluated data regarding PCBs to help develop a basis for regulations to protect human health.

The book is divided into five parts. Chapters 1 through 8 present background, scientific, social, and political information that is important to understand the PCB contamination problem. Chapters 9 through 12 describe the current state of the art with respect to chemical analyses and monitoring. Chapters 13 through 19 summarized the information on the metabolism, biotransformation, toxicology, and persistence of PCBs. Chapters 20 through 22 present the data on the effects of PCBs on human health. Chapters 23 through 30 address the roles of federal and state agencies in the regulation of PCBs.

While much remains to be learned about the effects of chronic low levels of PCB exposure on human beings and animals, it is hoped that the information presented in this volume will stimulate further research and encourage the readers to formulate conclusions about the essential issues and the necessary related actions.

Frank M. D'Itri
Michael A. Kamrin
East Lansing, Michigan

MONS 004783

ACKNOWLEDGMENTS

The success of the International Symposium on PCBs in the Great Lakes, presented by the Michigan State University Center for Environmental Toxicology, was due to the interest and dedication of the many individuals and organizations involved; and it is our pleasure to acknowledge as many of them as possible. First, a grateful acknowledgment is extended to Jerry B. Hook, Director of the Center for Environmental Toxicology, for his early conceptualization of the plan for this symposium and subsequent contributions to its implementation. Second, we would like to give special thanks to the members of the symposium planning committee: John Hesse and Harold E.B. Humphrey of the Michigan Department of Public Health, William E. McCracken of the Michigan Department of Natural Resources, and Burton D. Cardwell of the Michigan Department of Agriculture. Third, our special appreciation is extended to all of the authors whose written presentations made this book possible. Every attempt was made to reproduce their manuscripts accurately; however, the editors accept responsibility for any errors. Fourth, we would like to thank the Michigan State University Agricultural Experiment Station and Cooperative Extension Service, which actively supported this meeting. We would also like to express our appreciation for the support provided by the Michigan State University Institute of Water Research; the Michigan Departments of Agriculture, Natural Resources, and Public Health; the Michigan Toxic Substance Control Commission; and the Michigan Sea Grant College Program. Finally, we would like to acknowledge and thank Terry Waters, Mary Robinson, and Carole Abel for their expert secretarial and typing skills; and Donna Taxon for her editorial assistance.

MONS 004784

PART I

SCIENTIFIC, SOCIAL, AND POLITICAL OVERVIEW

MONS 004785

CHAPTER 1

INTRODUCTION

Bailus Walker, Jr.
Director
Michigan Department of Public Health
Lansing, Michigan 48909

Historically, two factors have greatly affected the cost of illness and disease. One is the personal health care provided by hospitals and private physicians; the other is environmental health services, including traditional public health work. The diseases that tend to generate the greatest cost are the complex ones and the basic knowledge of their etiology or causes is sometimes lacking. The cause and effect relationships between communicable diseases are fairly easy to identify, but when we are dealing with the effects on health of chemicals, and of environmental impurities, these are very, very poorly understood. As one chemical effect on health comes to be understood, others are used in an even wider spiral.

In public health, we try to stress prevention from three different approaches. The first, by one's own personal behavior; that is, we can smoke less or not at all. We can drink less alcohol or not at all. Secondly, by some institutional means, when our personal behaviors are inadequate for the problems we face. In this case, the state, in the broadest sense, can supply safe water and help insure the adequate disposal of wastes. The third approach is none of the above. For example, neither industry nor government, or we as individuals, can do much about some of these social pressures that tend to increase susceptibility to disease. Finally, there seems to be a genetic component of susceptibility, but we know that our ancestors are very hard to change.

The complexity of the polychlorinated biphenyl (PCB) issues argues that some institutional action is necessary; and if history is to be believed, it is likely to be the most effective means for preventing PCB induced illnesses. As a

MONS 004786

regulatory agency, I think we know that the regulation and control of PCBs and other toxic chemicals are fraught with many difficulties. Human epidemiological data are often unavailable, and conclusions from them are uncertain because of population limitations. Animal tests, as many of you well know, are extremely costly; and even then they only provide information at high dosages in one or two species. Short-term tests are useful but they are not necessarily definitive.

Now, against that background, I think it is also recognized that decision-making at all levels of government presupposes the availability of a body of information on the basis of which the relative merits of alternative policies can be analyzed and considered. If this information, or the data base, is constrained or invalid, resulting decisions must also be constrained or invalid, and sometimes this threatens the whole fabric of democratic government. So we would hope that the discussions here for the next few days would clarify many of the issues on the health effects as well as the ecotoxicological effects of PCBs and, at the same time, reduce some of the constraints on data generation as well as on data interpretation. We know that widely different opinions have been expressed on several of the topics which will be discussed here in the next three days. In such instances, the organizers of this Symposium have tried to select speakers who are most qualified to explain each of two or more different points of view. Finally, a glance at the contents of this Symposium gives us some idea about the broad spectrum of topics which specify the extent of the PCB issue. While these three days are rather full and comprehensive, this Symposium, as you well know, is not all inclusive but it is certain to contribute to a new perspective on PCBs and thus engender a renewed vigilance about other chemicals which are pervasive in our biosphere.

MONS 004787

CHAPTER 2

THE PCB PROBLEM: AN OVERVIEW

John E. Cantlon
Vice President
Research and Graduate Studies
Michigan State University
East Lansing, Michigan 48824-1046

This International Symposium on Polychlorinated Biphenyls (PCBs) in the Great Lakes addresses a class of problem that is not much older than many of us gray-beards in the audience. However, chemical contamination of man's environment by his technology is almost as old as civilized man (e.g., there is skeletal evidence of probable lead poisoning in sites of very ancient mining and smelting activity). But global contamination with toxic organics began with the burgeoning of industrial chemistry between World Wars I and II and picked up substantially both in the diversity of hazardous materials and in the tonages that were released into the earth's hydrosphere, atmosphere, lithosphere, and biosphere after World War II.

Global contamination by hazardous materials came into sharp focus as atmospheric testing of nuclear weapons by the United States and the U.S.S.R. reached high levels prior to the 1963 Limited Nuclear Test Ban Treaty. International research by a wide range of disciplines established that testing presented risks to man of cancer, birth defects, and genetic change from radionuclides contained in fallout. Other scientists assembled data on global circulation, atmospheric residence times, fallout patterns, deposition on land and water surfaces, and movement of radionuclides through natural and human ecosystems and into man and his tissues.

The 1963 Limited Nuclear Test Ban Treaty was an early triumph of environmental sanity even though it has been honored by only the major testing nations.

MONS 004788

The halogenated hydrocarbons were manufactured for various kinds of industrial uses from pesticides to paints and inks, from cutting oils to heat exchange fluids, among many other uses. It wasn't long after these compounds entered uses which resulted in widespread releases to the atmosphere and to surface waters that they began to appear in fish, birds, food animals, and indeed, in man himself. DDT and its related persistent halogenated pesticides received much attention as contamination was demonstrated to be virtually world wide and that body burdens were carried by most living organisms including man. The scientific data on presence, accumulation, and effects began to appear in the scientific literature in the 1950s; but Rachel Carson's dramatic book, "Silent Spring," published in 1962, drew public attention to this global contaminant.

Similar global and ecosystem quantification approaches to those for nuclear fallout were used to assess the transport, fate, and effects of these broad spectrum pesticides on non-target organisms and to assess the potential risk to man's ecosystems and his health. Unlike the case with atmospheric testing of nuclear weapons, DDT and related pesticides had high utility in food production and infectious disease suppression. The debate and political and judicial processes that eventually led to the 1972 ban on the use of DDT in the United States was provided with a broad array of research data. Up to and even following the Environmental Protection Agency's (EPA) decision to ban the use of DDT after December 31, 1972, in the United States, scientists continued to debate the interpretations of the research cited as the basis of the decision. Indeed, the late Phil Handler, former President of the National Academy of Sciences and a respected biochemist, argued to his last year that the human health data cited for that decision would not stand careful bias-free scrutiny.

In a somewhat different category of global contamination, we note that the very light weight chlorofluorocarbons have been said to be associated with damage to the earth's stratospheric ozone layer (NAS, 1976). Here the hazard to man would be indirect, coming from reduced screening of ultra violet radiation and a possible increase in skin cancer for man, as well as potential biological and climatic effects. The atmospheric transport, upper atmospheric and stratospheric physics, and photochemistry, the sampling problems and modeling are difficult and costly. In the most recent reassessments (Norman, 1981), there continues to be ambiguity about the relationship between releases of chlorofluorocarbons and changes in the ozone layer. Nevertheless, in 1979 the United States placed a ban on uses of these chemicals which result in significant release to the atmosphere.

MONS 004789

In the case of the polybrominated biphenyls (PBBs) we have an array of compounds that were widely used in ant control and as fire retardants, but they are not in the same class as DDT and the PCBs as global contaminants. The PBBs did seriously contaminate several areas of the United States, including Michigan's food animal industry through the now famous error in mixing Firemaster rather than a chemical food additive into animal feeds.

The gathering and use of research data in making various regulatory agency and legislative decisions in Michigan's PBB episode again demonstrate that the setting of specific standards, establishing disposal specifications, and many other aspects are made in contexts where the scientific data could equally support other standards and other specifications.

The story of PCBs is one of major global contamination by a group of highly useful chemicals which now appear in the tissues of most living creatures as well as in the air, water, soils, and sediments over most of the earth. The Great Lakes have been a particularly interesting contamination area with substantial food-chain concentration of these highly fat soluble chlorinated hydrocarbons.

While the manufacture of PCBs is now prohibited in the United States, the size of the environmental burden in waters, sediments, soils, disposal sites, and in deployed transformers and other containers of PCBs is very large, having been estimated by the National Academy of Science (1979) study to be 82 million kg.

The reduction of the DDT body burdens of animals and man following its 1972 banning by EPA gives some encouragement that the PCBs will also eventually decrease to trivial levels in systems such as the Great Lakes. However, PCBs exhibit differences in mobility, biodegradability, waste storage, continuing uses, and other characteristics that suggest we are likely to have to cope with this hazardous pollutant for some time to come (NAS, 1979).

As we look at the challenge of continuing to live with an environment and food chain that is contaminated with PCBs, we need to refine our assessments of the risk it poses for man; and where those risks are significant, seek options for mitigating them. The economic and political aspects of these alternatives will continue to be significant issues in the Great Lakes region for some time to come.

Much of the program of this symposium addresses research pertinent to these questions by highly capable scientists in a

MONS 004790

broad array of disciplines. I would like to make some observations about decision making in these complex areas where the research is pressed to the limits of our current knowledge, and where the political and economic ramifications of the decisions are substantial. These observations come from over 20 yr of participation in environmental research and various, mostly federal, scientific advisory bodies and professional organizations.

First, research results that bear on urgent decisions rarely have the luxury of science's normal process of rigorous peer review prior to publication with the journal articles then subjected to broad international scrutiny and commonly replicated by others and the resulting confirmation or refutation published.

Under the very best of these urgent decision conditions, we find highly competent scientists doing first class research; and almost as soon as it is available, it is provided to decision makers for use in the decision process. Under less satisfactory conditions we may find over-worked, in-house researchers performing rushed, last-minute, poorly conceived research or contracting with readily available, marginally capable individuals who generate scientifically questionable results which are added to the decision pool with no, or inadequate, review. Under the least desirable circumstances, we may have studies set up "to prove" a previously arrived at conclusion; and inadequate care allows such bias to shape experimental design and the results, often without overt dishonesty, but certainly reflecting poorly on the role of science in decision making.

Secondly, my long exposure to the process has given me the impression that decision makers in developmental agencies or regulatory agencies often have the unenviable problem of being subject to very strong public or not-so-public pressures, predominantly from one side or the other in arriving at their decisions. In spite of the popular mythology, we get rather stout-hearted and honest people in these roles in our state and federal agencies. However, their decisions can (as we would assume) reflect the people they feel they represent. Regulatory agencies, all else being equal, tend to make decisions that are "fail safe" while developmental agencies would tend to make decisions that protect large prior investments by major sectors of the economy.

When the body of scientific data is equivocal, it is occasionally the case that such decisions cite data that do not represent what the scientific community--given its normal slow

MONS 004791

processes--would agree to constitute unequivocal support of the decision.

By these over-simplifications of an exceedingly difficult societal process, I'm not sketching a good guys-bad guys picture. Rather, developmental agencies tend to draw their scientific data from a group of scientists who come at questions differently from those chosen by regulatory agencies. If there is plenty of time and if both groups publish their studies in high quality, broadly read journals, these perspective biases tend to be worked out and a balanced picture emerges. In today's fast paced world,this is not always the case with environmental decision making.

A third observation. On occasion one agency holds both developmental and regulatory responsiblities and we find scientists of one section taking issue with scientists of the other. Many of us will remember the early Atomic Energy Commission (AEC) in this connection. Internally in our better chemical manufacturing companies, the toxicology section researchers may on occasion take issue with product development researchers. I personally remember participating in an environmental issue and providing opposing testimony to colleagues in other departments here at the University.

Experienced scientists are not surprised that perspectives do influence research programs, but they are frequently surprised that a decision may be made by a public official in spite of the absence of convincing specific data. However, we need to appreciate that the political processes in representative governments reflect the perceptions of the constituencies who impact government. When a wide spectrum of a population is frightened and believes they are at great risk, regulatory agencies find it very difficult to be in the position of trying to convince them the risk is small or negligible. Thus, regulatory agencies--whether of executive, legislative, or judical bodies--will tend to take a "fail safe" posture under conditions they perceive to reflect high public apprehension.

I trust that these over-simplified observations based on long exposure to these processes are not interpreted as reflecting a cynical perspective. I intend these remarks simply to underline the role that I believe the scientific community must play in these complex societal processes. This is an important, indeed an essential role. The collective product of the scientific enterprise must be the gathering of data, the evaluation of that data, and the rendering of judgments supported by the data, with clearly identified assessments of the confidence with which the data, the evaluation, and the judgment may be taken. Most of us have conducted experiments,

MONS 004792

the results of which we were later unable to repeat or confirm. Most of us have also conducted experiments which failed to control or even to take cognizance of a particular variable which later proved to be highly significant. Science moves ahead by this process of improvement, correcting errors, and international discourse over results.

Environmental decision making which considers both scientific data and the perceptions of citizens about risk also moves in ways that aren't precisely straight lines or point events. While connected, scientific research and political decision making are far from one and the same process. As scientists, we must provide high quality research as our product; and even when it is unpopular to do so, we must question poor research, recognizing always that the agency's decision is a very different product than those of research.

I wish you well in this very interesting symposium on PCBs in the Great Lakes. The complexity of the science questions that bear on the important regulatory and developmental issues insures that this is no open-and-shut issue. As citizens of the Great Lakes basin we are affected by the recreational, economic, and health questions its PCB burdens pose. But, as scientists, our obligation is to provide the highest quality science as expeditiously as good science will permit so as to better understand the various questions. We can be thankful we aren't also burdened with responsibility for making the key decisions that have and will be made.

LITERATURE CITED

Carson, R. 1962. Silent Spring. Houghton Mifflin, NY.

NAS. 1976. Halocarbons: Effects on Stratospheric Ozone. National Research Council/National Academy of Science, Washington, DC.

NAS. 1979. Polychlorinated Biphenyls. National Research Council/National Academy of Science, Washington, DC.

Norman, C. 1981. Satellite Data Indicate Ozone Depletion. Science 213:1085-1089.

MONS 004793

CHAPTER 3

AN OVERVIEW OF THE SCIENTIFIC BASIS FOR CONCERN WITH POLYCHLORINATED BIPHENYLS IN THE GREAT LAKES

Wayland R. Swain
Vakgroep Aquatische Oecologie
University of Amsterdam
Kruislaan 320 1098 SM
Amsterdam, The Netherlands

The ubiquitous distribution of residue forming xenobiotic substances, particularly organochlorine compounds, is rapidly becoming apparent. Widespread dissemination is suggested by a variety of studies of areas presumably remote from the direct industrial and/or cultural influences attributable to man, including melting snow in the Antarctic (Peterle, 1969; Peel, 1975), mammals of the Arctic (Bowes and Jonkel, 1975; Clausen et al., 1974); in the surface waters and atmosphere above the Sargasso Sea (Bidleman and Olney, 1974); the waters of the Gulf of Mexico (Giam et al., 1973); remote island sites (Swain, 1978); rainfall over the Hawaiian Islands (Benvenue et al., 1972); and the sediments of Siberian Lake Baikal (Swain, 1980). Although a number of these compounds have been banned outright, or had their utilization severely restricted in the 1969 to 1971 time period, they still are routinely reported in the Great Lakes Basin (International Joint Commission, 1977, 1978). Strachan and Huneault (1979) note three principal reasons for this continued occurrence:

(1) the widespread geographic occurrence of organochlorine substances;
(2) their persistence and relatively long biological half-lives; and
(3) the demonstration of long range atmospheric transport of these substances.

The persistence of many of the xenobiotic compounds of concern is measured in years or decades (International Joint Commission, 1975). This fact, combined with hydraulic detention times of the order of centuries for the sequentially coupled

MONS 004794

St. Lawrence Great Lakes (Rainey, 1967), yields a potential for bioaccumulation and bioconcentration virtually unparalleled elsewhere in North America. When one considers that the Great Lakes represent 20 percent of the world's freshwater and 95 percent by volume of the freshwater of the adjacent United States (McGrath, 1980), the problem is of even greater interest.

Current estimates suggest that more than 30,000 chemicals of commercial and/or industrial significance are used in the Great Lakes Basin, and in excess of 1,000 new compounds are developed each year (Maugh, 1978; Ames, 1979; Costle, 1980). Even if only a small proportion of these compounds are toxic in nature (<1.0%), and if a similarly small percentage enters the Great Lakes ecosystem, the magnitude of the problem is readily apparent.

It is not surprising, then, that contamination by toxic organic substances of anthropogenic origin have been suggested as the major environmental concern confronting both the scientific community and the management structure associated with the Great Lakes (Sonzogni and Swain, 1980).

Because of the complexity of the issue; the multiplicity of substances and their metabolities, daughter compounds, and degradation products; the size and scope of the ecosystem in both spatial and temporal scales; and the intricacy and interdependence of the trophic system in the Great Lakes, it has been reasoned that an ecosystem approach to the problem was the method of choice for examining the relationships and proportions of these interdependent entities (Swain, 1981). The use of such a conceptual framework related to toxic substances has been previously suggested (Gillett et al., 1974; Metcalf et al., 1975; Thomann, 1978, 1980; Bierman and Swain, 1978; and Weininger, 1978). However, few of these approaches have considered man as an integral part of the environmental structure, and none have regarded him as both an interactive and reciprocal part of the ecosystem. The intent of this overview is to use an ecosystem approach to address the basis of scientific concern surrounding polychlorinated biphenyls (PCBs) and their impact on environmental quality and human health in the Great Lakes Basin.

Polychlorinated biphenyls are a group of chlorinated hydrocarbons manufactured by the controlled chlorine substitution of the biphenyl molecule. More than two hundred arrangements of components are theoretically possible, but in actual practice, slightly more than 100 formulations have been used. PCBs have been manufactured and used on a worldwide basis. In the United States, PCBs were produced under the trade name Aroclor. The Japanese produced not only Aroclors, but also

Sanotherm and Kaneclor; in Germany the trade name Clophen was used, as was Pyralene and Phenoclor in France, Fenclor and Phenoclor in Italy, Sovol in the USSR, and Delor in Czechoslovakia.

The chemistry, properties, and characteristics have been previously described in detail (Hutziger et al., 1974; Brinkman and De Kok, 1980) and need not be reiterated here.

In general, however, PCBs were first synthesized in 1881, but did not see industrial application in the United States until 1929. For nearly 50 yrs until cessation of production in 1977, U.S. industry manufactured and used PCBs because of their high dielectric constant, their chemical and thermal stability, their non-flammability, and their low cost.

Their uses included insulating fluids in electrical transformers and capacitors in the power industry, heat transfer substances, cutting oils, hydraulic fluids, lubricating oils, and plasticizers for making brittle plastic pliable. Application was also found for these compounds in paints, printing inks, carbonless copy paper, sealants, adhesives, and the like.

Regrettably, the identical characteristics which made the PCBs industrially desirable, also make them persistent and accumulatible in the environment. The chemical stability of the PCB compounds is unique. They are resistant to acid-base reactions, hydrolysis, chemical oxidation, photodegradation, thermal changes, and most chemical agents. As a result of this stability, they are generally poorly metabolized by biologic systems. PCB solubility in water is very low, and appears to decrease with increasing chlorination (Hutzinger et al., 1974). They have relatively low vapor pressures, but in general, the lower the chlorine content, the more likely the compound is to volatilize.

PCBs tend to bond tightly to particulate matter, notably soils and sediments. Thus, surface waters with low particulate loads may have barely detectable levels of PCB in the water mass, but high concentrations in the bottom sediments. Of further concern is the effective half-life of these substances. Present estimates of PCB half-life fall into a range of 8 to 15 yrs in environmental samples.

Since PCBs are poorly soluble in water and extremely soluble in oils and fats, they tend to partition out of the aquatic ecosystem into biologic tissue. Because of their persistence and the fact that they are poorly metabolized, these substances bioaccumulate in the food chain, often increasing

several orders of magnitude in concentration at each succeeding trophic level.

Because PCBs bioaccumulate so successfully through the food chain, and because the components of the Great Lakes ecosystem are inexorably linked and interrelated, it is possible, at least in theory, if not in actual fact, to trace the PCBs added to the atmosphere as a result of burning waste oil to heat a building through the Great Lakes ecosystem to exposure of man and his progeny. To accomplish this end, an ecosystem approach to the problem provides a means of organizing the massive amount of existing information (Figure 1).

The upper lakes--Superior, Michigan, and Huron--are the most susceptible. This increased susceptibility is a function of:

(1) large surface areas,
(2) extreme depth,
(3) low suspended sediment loads per unit volume,
(4) low autochthonous production of particulates,
(5) highly sensitive biota, and
(6) extreme hydraulic detention times (Sonzogni and Swain, 1980).

Of the upper lakes, Lake Michigan currently has the largest mass of PCB residue contained within its basin. The principal sources of PCB to this ecosystem are three:

(1) atmospheric inputs,
(2) tributary loads, and
(3) direct discharges.

The preponderance of scientific evidence suggests that the atmosphere can be a major source of PCBs to the Great Lakes. While there is currently scientific controversy over the exact magnitude and the extent of atmospheric deposition, all estimates suggest that it is the principal source. Murphy and Rzeszutko (1977) estimated that 80 percent of the PCBs contributed to Lake Michigan were from atmospheric sources, and Eisenreich et al. (1981), using more recent data, estimate a value approaching 50 percent. Regardless of the exact percentage, it is clear that the bulk of the contributions of PCBs to the upper lakes is derived from atmospheric sources.

Earlier estimates (Swain, 1981) suggested that these loadings drive the water mass concentrations to the extent of 2-10 ng/l (ppt). Recent measurements for open Lake Huron, however, indicate values nearly an order of magnitude below these levels; in a range of from 0.2-1.0 ng/l (Swain et al.,

MONS 004797

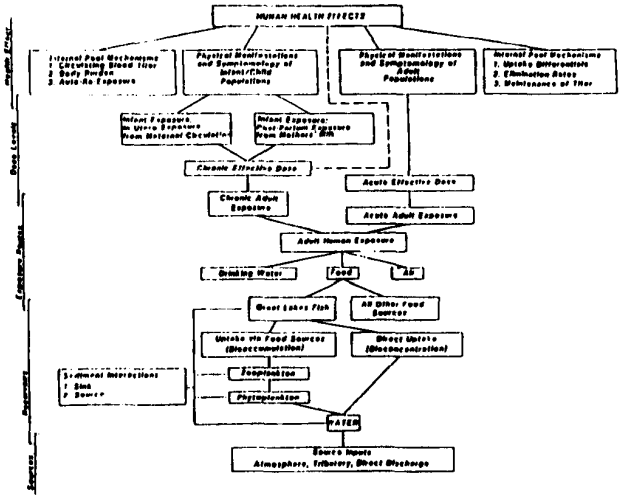


Figure 1. A conceptual framework for toxic substances in the Great Lakes ecosystem.

1982). While the samples taken from the rest of the Great Lakes yet await analysis, similar declines in observed PCB levels in these bodies of water may reasonably be anticipated.

Planktonic constituents living in the surrounding milieu tend to biomagnify the level of PCB to the order of 20 to 200 ng/g (ppb). Glooschenko et al. (1976), working on Superior, observed PCBs in 7 of 15 section samples in concentrations ranging from 0.5 to 1.3 mg/kg. Of the eight remaining samples, three had levels that were below the threshold of detection, while the remaining five were detectable, but below the level of quantification. Veith et al. (1977) report from 0.05 to 0.12 mg/kg PCB, and 0.04 to 0.05 mg/kg of DDT residues and 2.0 ug/kg of dieldrin in the samples of the opossum shrimp Mysis relicta taken from the Minnesota north shore of western Lake Superior during 1973-1974.

While the sediments act alternately as both a sink and a source of pollutant materials depending on a variety of naturally occurring processes--adsorption, desorption, sinking rates, wind driven resuspension, and the like--the planktonic constituents of the second trophic level, in turn, fall prey to the consumers of the next trophic level, the Great Lakes fish.

Because of their widespread availability throughout the Great Lakes ecosystem, their persistence, their lipophilicity, and the long hydraulic detention times of the coupled system, polychlorinated biphenyl compounds tend to biomagnify in Great Lakes biota; either through food chain transfer (bioaccumulation) or as a function of direct uptake across gill or other surface membranes (bioconcentration). While there is some question as to the exact magnitude of contribution of each of these phenomena to the body burden of Great Lakes fish--Weininger (1978) estimates approximately 95 percent food chain transfer and 5 percent direct uptake; Thomann (1978) calculates 75 percent bioaccumulation and 25 percent bioconcentration--there is no argument that the higher trophic levels show substantially increased levels of PCBs as compared with the water masses, the primary producers, and the primary consumers.

As a result of these phenomena, and because of the relative ease of quantifying organochlorine compounds at the mg/kg level, as compared with levels in the ug/kg or ng/kg range, Great Lakes fish have been extensively utilized as both monitoring and indicator organisms. While an exhaustive analysis of extant data is beyond the scope of this effort, a synopsis of historic studies is provided in Table 1 and summarized in Table 2.

The fish of particular concern, the sports species can be expected to achieve levels in an approximate range of 2 to 20

MONS 004799

TABLE 1

Polychlorinated Biphenyls Observed in Fish of the Great Lakes

Location	Species	Date	Quantity in mg/kg	Reference
Lake Superior				
Nearshore, Ontario	Lake Trout	1974	0.387-1.796	Upper Lakes Ref. Group, 1977
	Walleye	1974	0.243-3.635	Upper Lakes Ref. Group, 1977
	Whitefish	1974	0.125-3.635	Upper Lakes Ref. Group, 1977
	Herring	1974	0.193-0.757	Upper Lakes Ref. Group, 1977
Nearshore, Minnesota	Mottled Sculpin	1974	0.035-0.600	Upper Lakes Ref. Group, 1977
Nearshore, Michigan	Lake Trout	1974	N.D.-0.46	Upper Lakes Ref. Group, 1977
	Siscowet Trout	1974	1.95-8.37	Upper Lakes Ref. Group, 1977
	Whitefish	1974	0.27-0.89	Upper Lakes Ref. Group, 1977
	Herring	1974	0.22-1.03	Upper Lakes Ref. Group, 1977

MONS 004800

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Mottled Sculpin	1974	N.D.-0.46	Upper Lakes Ref. Group, 1977
Nearshore, Wisconsin	Bullhead	1974	0.017-0.050	Upper Lakes Ref. Group, 1977
	Northern Pike	1974	0.020-0.030	Upper Lakes Ref. Group, 1977
	Walleye	1974	0.080-0.218	Upper Lakes Ref. Group, 1977
	Yellow Perch	1974	0.046-0.05	Upper Lakes Ref. Group, 1977
	White Sucker	1974	0.024	Upper Lakes Ref. Group, 1977
	Rainbow Smelt	1974	0.202-0.263	Upper Lakes Ref. Group, 1977
	Brown Trout	1974	0.145	Upper Lakes Ref. Group, 1977
	Rainbow Trout	1974	0.065-0.110	Upper Lakes Ref. Group, 1977
Open Lake	Slimy Sculpin	1974	0.16-0.36	Upper Lakes Ref. Group, 1977
	Burbot	1974	1.40-1.59	Upper Lakes Ref. Group, 1977

MONS 004801

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Lake Trout	1974	0.80-4.32	Upper Lakes Ref. Group, 1977
Nearshore, Apostle Islands	Lake Trout (Fillets-Whole Fish)	1974	1.68-1.80	Upper Lakes Ref. Group, 1977
Nearshore, Wisconsin	Rainbow Smelt	1974-1976	0.250-0.270	IJC, 1978
	Rainbow Trout	1974-1976	0.40-0.110	IJC, 1978
	Brown Trout	1974-1976	0.130-0.235	IJC, 1978
	Perch	1974-1976	0.02-0.450	IJC, 1978
	Northern Pike	1974-1976	0.03-0.65	IJC, 1978
	Bullhead	1974-1976	0.003-0.03	IJC, 1978
	Carp	1974-1976	0.19-1.34	IJC, 1978
Isle Royale Area	Siscowet Trout	1975	2.06-6.90	IJC, 1978
	Whitefish	1974	0.72-3.77	IJC, 1978
Nearshore, Michigan	Lake Trout	1975	0.62-2.58	IJC, 1978
	Siscowet Trout	1975	2.06-31.20	IJC, 1978
	Herring	1974	0.22-1.03	IJC, 1978
	Chubs	1974	0.62-0.69	IJC, 1978

MONS 004802

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
Nearshore, Wisconsin	Lake Trout	1974	2.7	U.S. Fish & Wildlife Ser., 1974
	Lake Whitefish	1974	0.7	U.S. Fish & Wildlife Ser., 1974
	Bloater	1974	1.2-2.7	U.S. Fish & Wildlife Ser., 1974
Nearshore, Michigan	Lake Trout	1974	3.7-4.5	U.S. Fish & Wildlife Ser., 1974
	Herring	1974	1.1	U.S. Fish & Wildlife Ser., 1974
	Bloater	1974	0.61-0.79	U.S. Fish & Wildlife Ser., 1974
Isle Royale	Lake Trout	1974-1976	0.3-1.72	Swain, 1978
	Siscowet Trout	1974-1977	5.4-8.4	Swain, 1978
	Whitefish	1974-1976	0.37	Swain, 1978
Lake Michigan				
	Bloater	1972	3.12-8.17	Willford et al., 1976
	Bloater	1973	4.20-6.33	Willford et al., 1976
	Bloater	1974	4.83-6.22	Willford et al., 1976
	Coho Salmon	1972	4.93-15.4	Willford et al., 1976

MONS 004803

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Coho Salmon	1973	8.24-16.6	Willford et al., 1976
	Coho Salmon	1974	6.99-16.3	Willford et al., 1976
	Lake Trout	1972	3.53-25.3	Willford et al., 1976
	Lake Trout	1973	9.36-30.6	Willford et al., 1976
	Lake Trout	1974	7.05-47.4	Willford et al., 1976
Vicinity Saugatuck & East-Central Lake Area (annual mean values)	Bloater	1972	5.66	U.S. Fish & Wildlife Ser. in IJC, 1978
	Bloater	1973	5.24	U.S. Fish & Wildlife Ser. in IJC, 1978
	Bloater	1974	5.57	U.S. Fish & Wildlife Ser. in IJC, 1978
	Bloater	1975	4.58	U.S. Fish & Wildlife Ser. in IJC, 1978
	Bloater	1976	4.11	U.S. Fish & Wildlife Ser. in IJC, 1978
	Coho Salmon	1972	10.93	U.S. Fish & Wildlife Ser. in IJC, 1978
	Coho Salmon	1973	12.17	U.S. Fish & Wildlife Ser. in IJC, 1978
	Coho Salmon	1974	10.45	U.S. Fish & Wildlife Ser. in IJC, 1978

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Coho Salmon	1975	10.77	U.S. Fish & Wildlife Ser. in IJC, 1978
	Coho Salmon	1976	9.21	U.S. Fish & Wildlife Ser. in IJC, 1978
	Lake Trout	1972	12.86	U.S. Fish & Wildlife Ser. in IJC, 1978
	Lake Trout	1973	18.93	U.S. Fish & Wildlife Ser. in IJC, 1978
	Lake Trout	1974	22.91	U.S. Fish & Wildlife Ser. in IJC, 1978
	Lake Trout	1975	22.28	U.S. Fish & Wildlife Ser. in IJC, 1978
	Lake Trout	1976	18.68	U.S. Fish & Wildlife Ser. in IJC, 1978
Nearshore, Michigan	Salmon	1974	0.22-1.64	Mich. Dept. Agr. in IJC, 1978
	Lake Trout	1974-1975	0.99-27.80	Mich. Dept. Agr. in IJC, 1978
	Chub	1974	2.87-3.74	Mich. Dept. Agr. in IJC, 1978

MONS 004805

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
Nearshore, Wisconsin	Carp	1976	16.3	Kleinert, 1976
	Lake Trout	1976	2.9-33.8	Kleinert, 1976
Lake Huron				
Vicinity of Bay Port, Michigan	Yellow Perch	1974	2.2-3.9	U.S. Fish & Wildlife Ser. in IJC, 1978
	Carp	1971	3.0-4.7	U.S. Fish & Wildlife Ser. in IJC, 1978
Vicinity of Alpena, Michigan	Yellow Perch	1974	0.65-0.94	U.S. Fish & Wildlife Ser. in IJC, 1978
	White Sucker	1974	0.73	U.S. Fish & Wildlife Ser. in IJC, 1978
	Whitefish	1974	0.46	U.S. Fish & Wildlife Ser. in IJC, 1978
Nearshore, Michigan	Brown Trout	1974	0.35-1.93	Mich. Dept. Agr. in IJC, 1978
	Carp	1974	1.06-4.30	Mich. Dept. Agr. in IJC, 1978
	Chinook Salmon	1974	1.29-2.97	Mich. Dept. Agr. in IJC, 1978
	Yellow Perch	1974	0.02-0.23	Mich. Dept. Agr. in IJC, 1978

MONS 004806

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Brown Trout	1975	0.64-1.70	Mich. Dept. Agr. in IJC, 1978
	Carp	1975	0.92-2.75	Mich. Dept. Agr. in IJC, 1978
	Lake Trout	1975	0.99-5.7	Mich. Dept. Agr. in IJC, 1978
	Rainbow Smelt	1975	0.69-0.80	Mich. Dept. Agr. in IJC, 1978
	Whitefish	1975	0.20-0.43	Mich. Dept. Agr. in IJC, 1978
Nearshore, Michigan	Brown Trout	1974-1975	1.1-1.3	Upper Lakes Ref. Group, 1977
	Perch	1974-1975	N.D.-0.20	Upper Lakes Ref. Group, 1977
	Rainbow Trout	1974-1975	0.94	Upper Lakes Ref. Group, 1977
	Whitefish	1974-1975	N.D.-0.34	Upper Lakes Ref. Group, 1977
	Chinook	1974-1975	2.31	Upper Lakes Ref. Group, 1977
Nearshore, Ontario	Perch	1974-1975	0.003-0.40	Upper Lakes Ref. Group, 1977

MONS 004807

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	White Sucker	1974-1975	0.125-1.53	Upper Lakes Ref. Group, 1977
	Rainbow Trout	1974-1975	0.09-2.17	Upper Lakes Ref. Group, 1977
	Walleye	1974-1975	0.258-0.827	Upper Lakes Ref. Group, 1977
	Northern Pike	1974-1975	0.024-0.085	Upper Lakes Ref. Group, 1977
Huron Lake	Burbot	1974-1975	0.77-2.35	Upper Lakes Ref. Group, 1977
	Bloater Chubs	1974-1975	0.89-361	Upper Lakes Ref. Group, 1977
	Slimy Sculpins	1974-1975	0.52-0.77	Upper Lakes Ref. Group, 1977
Lake Erie				
Nearshore	Shad	1977	0.69-1.72	Herdendorf et al., 1978
	Perch	1977	0.35-1.34	Herdendorf et al., 1978
	Catfish	1977	3.4-3.85	Herdendorf et al., 1978
	Drum	1977	0.26-0.36	Herdendorf et al., 1978
Nearshore, Michigan	Carp	1974	3.7-3.9	Mich. DNR in IJC, 1978
	Catfish	1974	2.97-3.0	Mich. DNR in IJC, 1978
	Drum	1974	0.52	Mich. DNR in IJC, 1978

MONS 004808

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Yellow Perch	1974	0.03	Mich. DNR in IJC, 1978
	Walleye	1974	0.22	Mich. DNR in IJC, 1978
	White Bass	1974	2.19	Mich. DNR in IJC, 1978
	Carp	1975	3.17-3.9	Mich. DNR in IJC, 1978
	Catfish	1975	3.29-5.65	Mich. DNR in IJC, 1978
	Drum	1975	0.11	Mich. DNR in IJC, 1978
	Salmon	1975	0.38	Mich. DNR in IJC, 1978
	Walleye	1975	0.34	Mich. DNR in IJC, 1978
	White Bass	1975	0.55-1.78	Mich. DNR in IJC, 1978
	Rainbow Trout	1975	0.70	Mich. DNR in IJC, 1978
	Chinook Salmon	1975	0.25	Mich. DNR in IJC, 1978
Lake Ontario				
Nearshore	American Eel	1976	0.12-14.77	IJC, 1977
	Largemouth Bass	1976	0.09-2.92	IJC, 1977
	Smallmouth Bass	1976	0.45-10.93	IJC, 1977
	White Bass	1976	0.83-5.17	IJC, 1977
	Black Crappie	1977	0.51-0.89	IJC, 1977
	Brown Bullhead	1977	0.30-2.81	IJC, 1977
	Muskellunge	1977	1.93-4.05	IJC, 1977
	Northern Pike	1977	0.58-4.17	IJC, 1977
	Yellow Perch	1977	0.22-1.72	IJC, 1977
	White Perch	1977	0.86-9.70	IJC, 1977

MONS 004809

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Coho Salmon	1977	1.60-10.27	IJC, 1977
	Chinook Salmon	1977	2.36-13.47	IJC, 1977
	Brown Trout	1977	1.31-15.14	IJC, 1977
	Lake Trout	1977	1.38-18.30	IJC, 1977
	Rainbow/Steelhead	1977	10.64	IJC, 1977
	Walleye	1977	0.08-1.21	IJC, 1977
St. Lawrence River	Smallmouth Bass	1976	0.25-16.17	IJC, 1977
(edible portions of fish)	Northern Pike	1976	1.18-3.93	IJC, 1977
	Yellow Perch	1976	0.46-4.26	IJC, 1977
	White Perch	1976	0.66-11.80	IJC, 1977
	Walleye	1976	1.41-6.52	IJC, 1977
Eastern Nearshore Area	Catfish	1976	7.9-12.42	IJC, 1977
(edible portions of fish)	Pike	1976	0.22-0.89	IJC, 1977
	Coho Salmon	1976	2.0-5.38	IJC, 1977
	Sucker	1976	0.96-1.15	IJC, 1977
	Carp	1976	1.3-3.29	IJC, 1977
	White Perch	1976	0.82-2.8	IJC, 1977
	American Eel	1976	4.4-8.5	IJC, 1977
	Yellow Perch	1976	0.28-0.52	IJC, 1977
	Bullhead	1976	0.21-0.41	IJC, 1977
	Rainbow Smelt	1976	1.12-1.22	IJC, 1977

MONS 004810

Table 1 (cont.)

Location	Species	Date	Quantity in mg/kg	Reference
	Sheepshead	1976	0.89-6.6	IJC, 1977
	Rock Bass	1976	0.11-5.21	IJC, 1977
Adjacent to Credit River	Coho Salmon	1975	2.1-22.5	IJC, 1977
Various Nearshore Areas	Alewife	1975	0.14-381	Haile et al., 1975
	Smelt	1975	1.40-3.49	Haile et al., 1975
	Slimy Sculpin	1975	1.58-9.17	Haile et al., 1975
	Rock Bass	1976	N.D.-2.60	IJC, 1978
	White Perch	1976	4.5-6.4	IJC, 1978
	Yellow Perch	1975	1.7-3.3	IJC, 1978
	Rock Bass	1975	2.0-2.4	IJC, 1978

MONS 004811

TABLE 2

Representative Mean Contaminant Ranges Summarized From Literature Values in Selected Great Lakes Fish

Lake	Species of Fish	DDT (mg/kg)	PCB (mg/kg)
Superior	Lake Trout	0.5-1.0	2.0-4.0
	Siscowet Trout	5.0-10.0	8.0-15.0
	Yellow Perch	0.01-0.05	0.02-0.05
Michigan	Lake Trout	5.0-10.0	18.0-20.0
	Coho Salmon	3.0-10.0	7.0-17.0
	Yellow Perch	--	0.5-1.0
Huron	Lake Trout	2.0-4.0	3.0-5.0
	Yellow Perch	0.04-0.4	0.04-0.4
Erie	Coho Salmon	0.3-0.5	0.5-1.5
	Yellow Perch	0.1-0.5	0.03-0.1
Ontario	Lake Trout	2.0-4.0	6.0-8.0
	Coho Salmon	1.0-2.0	6.0-8.0
	Yellow Perch	0.03-0.1	0.5-3.0

mg/kg. For the first time in 50 yrs of science on the Great Lakes, it has become necessary to consider man as a truly reciprocal and interactive part of the Great Lakes ecosystem. Up to now, man has had the luxury of regarding himself as simply contributing to "source inputs" in the ecosystem equation. Suddenly, it is becoming painfully evident that as "top predators" in the Great Lakes food web, mankind has collectively become a "reservoir" or "sink" term in the ecosystem toxic substances mass conservation expression.

Public exposure to orally ingested PCBs is rather effectively controlled through the United States Food and Drug Administration's tolerance levels set for these substances. Established in 1973, the FDA levels restrict fish, shellfish, and the fat portions of poultry above 5.0 mg/kg; require levels no greater than 2.5 mg/kg (fat portion) in milk and dairy products; 0.5 mg/kg in eggs; 0.2 mg/kg in infant and junior foods; and limit PCBs in packaging materials to 10 mg/kg. At

MONS 004812

the time of the preparation of this summary, FDA has undertaken steps to reduce the tolerance levels/permissible amounts to 2.0 mg/kg in fish and shellfish; 1.5 mg/kg in milk and milk products; 0.3 mg/kg in eggs; and 3.0 mg/kg in poultry. Establishment of these reductions in acceptable values has been delayed in part by action enjoining the activities of the agency. The lower levels for eggs, milk and dairy products, and poultry went into effect on August 28, 1979, but the National Fisheries Institute filed objections to the proposed standards for fish and requested a hearing. Hence, the implementation of this guideline has not occurred.

The theoretical effects of adopting and implementing regulatory standards of this sort are two:

(1) reduction of the absolute magnitude of exposure per unit of time, and hence measurable levels of body burdens among the general population, and

(2) a tendency toward a leveling effect in exposure potentials throughout the population-at-large, leading to a more nearly uniform exposure experience across a population.

While exposure among the general population via food sources has been demonstrated, particularly prior to the 1972 limitations imposed by the Food and Drug Administration (Kolbye, 1972; Biros et al., 1970; Finklea et al., 1972), there appears to be no data from "market basket" studies supporting substantial differences in current levels of exposure from food sources between one area of the country and another. Jelinek and Corneliussen (1976) report that "the occurrence of PCBs has narrowed to the point where freshwater fish are now the primary source of PCBs in our diet." They further note that "the daily intake of PCB for the average citizen is low, since his consumption of freshwater fish is low." They also add, however, "PCB intake could be quite different for those people whose diets include substantial quantities of sports fish." Thus, if the exposure potential from food sources for the general population can be assumed to be approaching a uniform level, and that, as a result of FDA limitation, that level is at least an order of magnitude below the exposure potential for consumption of Great Lakes fish, an argument for consideration of the health consequences of Great Lakes Basin residents is raised.

As was previously noted, public consumption of Great Lakes fish heavily contaminated with PCBs is regulated through the embargo of commercial catches in the United States by the

MONS 004813

counties of the State of Michigan that border on and abut lake Michigan, there are presently well over a third of a million licensed sports fishermen. As a group, these sports fishermen and their families consume more than three times the national average of fish per year. Preliminary studies by the Michigan Department of Public Health (Humphrey, 1976; Humphrey, 1983) have demonstrated what appears to be a direct, nearly linear relationship between the total amount of Great Lakes fish consumed and the absolute circulating titer of PCBs in the blood of these individuals.

For humans, as well as Great Lakes biota, there are two major routes of toxic action--acute toxicity and chronic toxicity. The acutely toxic activity is dose/time dependent. A very high exposure over a very short period of time to exceed the "critical dose" or "effective dose level" is sufficient to produce physical manifestations and symptomology in adult human populations.

The effects of long-term chronic exposure are less well known. Such phenomena can be assumed to be dose/time dependent, and to involve a very long lag phase. Typically, with organic toxicants, this period may be in excess of 25 to 35 yrs.

Of present critical concern, however, is the potential for serious and significant impacts upon selected "high risk" populations. A mother, belonging to the group of consumers who eat large quantities of Lake Michigan sports species of fish, selectively increases her own circulating blood titer of PCBs as a result of additional exposure to fish.

Transplacental passage of the PCB molecule has been repeatedly demonstrated (Kodama and Ota, 1980; Masuda et al., 1978; Polishuk et al., 1977; Funatsu et al., 1972; and Jacobson et al., 1983). As a result, the mother's unborn child is also exposed to PCB as a result of maternal circulation. Literature values and early Great Lakes experimental efforts suggest that, for the period of 9 months of gestation, the unborn infant may be exposed to a significant level of his mother's blood burden (Kuwabara et al., 1978; Jacobson et al., 1983). This exposure comes at a time of unprecendented growth and development, and critical maturation of tissues.

At birth, the child may be exposed to an additional source of PCB as a result of nursing. A recent nationwide survey of 1,038 nursing mothers in the United States (summarized in Ames, 1979) demonstrated that approximately a third (309) of the women had PCB in measurable amounts in their breast milk. A more recent study of 1,057 Michigan mothers reported PCB in breast

milk of all participants (Wichizer et al., 1981). In this latter survey, an average level of 2.3 mg/kg was found.

Among individuals consuming Lake Michigan fish who participated in the early phase of the Michigan blood level PCB study, a single analysis of breast milk was made (Humphrey, 1976). The sample was received from a mother in the low exposure class who had consumed 12.73 kg of Lake Michigan fish during a two year period (1973-74), approximately one-half of the maximum recommended by the Michigan Department of Public Health.

This woman had a circulating blood titer of 0.053 ug/kg PCB. A breast milk sample collected the same month as the blood sample contained 4.0 ug/kg PCB on a fat basis (2% fat content), equivalent to 80.0 ug/kg PCB on a whole milk basis. This value is substantially above the level reported in the literature for the general population, and for that portion of Michigan residents unexposed to large quantities of Lake Michigan fish. On the basis of present work, the value reported for this sample is not unusual for breast milk from women exposed to substantial quantities of Lake Michigan fish (Humphrey, 1981, personal communication).

It can be reasonably assumed that a nursing infant will consume 1 kg of breast milk per day. At a level of 80 ug/kg, the child could be exposed to 80 ug of PCB each day.

Dose, as contrasted with exposure, is calculated upon mass of compound per mass of body weight per unit of time. To carry the analogy of exposure to dose, it is necessary to make only one further assumption; i.e., that a reasonable birth weight is 3-4 kg (approximately 6-8 pounds). Thus, the dose rate for a child of these proportions would be between 20 and 26.6 ng/kg/day, some 20 to 25 times the maximum daily dose rate of 1 ug/kg/day PCB recommended by the U.S. Food and Drug Administration for adult intake.

Internal pool mechanisms may be very important in the long view; however, at present their effects are unknown. It is known, however, that as the child undergoes natural growth and developmental cycles, he is repeatedly subjected to intensive spurts of growth in which most of the available fatty materials are drawn into circulation and metabolized to aid in the provision of energy for the tremendous anabolic activites that are going on. Since PCBs are lipophylic in nature, it is to be expected that the stored contaminant will be mobilized with the body fat, potentially producing a selective form of autore-exposure.

MONS 004815

The effect of this activity is unknown. It is known, however, that much of the mobilization would occur at the times when the myelin sheathes surrounding the central nervous system are being laid down. Myelin, of course, is an insulating substance and is composed largely of lipid materials. Thus, it may be reasonably expected that some impact on the body's centers of higher integration will result (Fein et al., 1982; Jacobson et al., 1983).

It has also been suggested from recent studies that PCBs and their congeners have a major impact on reduction of sperm production and motility in males (Dougherty et al., 1980).

The problem is inordinately complex. It is not currently possible to project or calculate the absolute risks associated with exposure to PCBs and their congeners. However, it is possible to estimate a relative risk of exposure for those individuals who consume Great Lakes fish, as compared with those who do not.

It appears that the major source of PCB for Lake Michigan Basin resident populations is derived from Great Lakes sports species of fish. To place this contaminant burden in perspective, it is necessary to examine the relative contribution of other kinds of sources. For PCBs and their congeners, among non-occupationally exposed individuals, the sources are two: respired ambient air and potable drinking water.

Estimates of the average annual intake from orally ingested drinking water suggest very minimal exposure levels, even assuming that mean raw water values at approximately 4 ng/l are used (Table 3). Finished drinking water levels are at least an order of magnitude below that of raw water values; hence, the 4 ng/l estimates represent a very conservative upper mean.

TABLE 3

Estimated Oral Exposure to PCB From Great Lakes Drinking Water

Average Raw Water PCB Content	4 ng/l
Average Daily Water Intake Per Person	2 l
Maximum Daily Oral Exposure	8 ng/day
Maximum Annual Oral Exposure	2.9 ug/yr

MONS 004816

When one examines the potential for respiratory exposure, similar relationships are observed. Assuming complete and instantaneous sorption and selective uptake of PCBs at the alveolar surface of the lung, based on an average tidal volume of approximately half a liter, the annual uptake of PCBs through the respiratory route is only on the order of 5 to 10 ug annually (Table 4).

In terms of exposure potential using maximum exposure values, it is possible to breathe the air in the Lake Michigan Basin (outside of the metropolitan centers) and drink its polished drinking water for a very long time before you would achieve the same effective exposure from eating a single one-pound fish meal of Lake Michigan lake trout. The length of time required for equivalent exposure, of course, is a function of the concentration of contaminants in the fish (Table 5). If 12 mg/kg may be taken as a reasonable mean for Lake Michigan lake trout currently, more than 500 yrs would be required for an equivalent exposure from air and water. If the contaminant level in fish is reduced to 5 mg/kg, the currently applicable tolerance limit for interstate sales, a 200 yr equivalent exposure is received from each 0.45 kg of fish. At the current Canadian standard, and the guideline proposed for the U.S., 2

TABLE 4

Estimated PCB Exposure from the Atmosphere

Level of PCB in the Atmosphere[1]	1.5 ng/m^3
Average Rate of Respiration	20 respirations/min 1,200 respirations/hr 28,800 respirations/day
Mean Tidal Volume of the Lungs	500 ml
Total Daily Air Volume Respired	14,400 l/day 14.4 m^3/day
Average Daily Respiratory Exposure	14.4 m^3/day x 1.5 ng/m^3 = 21.6 ng/day
Annual Exposure	7.8 ug/yr

[1]Eisenreich, S. (1981)

MONS 004817

TABLE 5

Relative Exposure to PCB from Great Lakes Fish Compared With Irreducible Sources

A. Relative exposure to PCB from consumption of Lake Michigan lake trout:

Scenario No. 1: 12 ppm PCB in lake trout flesh

12 ppm = 12 mg/kg; since 1 lb = 0.45359 kg, 12 mg/kg x 0.45359 kg/lb = 5.443 mg/lb. Thus, lake trout at 12 ppm PCB contain 5,443 ug PCB per pound of fish.

Scenario No. 2: 5 ppm PCB in lake trout flesh

5 ppm = 5 mg/kg; 5 mg/kg x 0.45359 kg/lb = 2.267 mg/lb. Thus, lake trout at 5 ppm PCB contain 2,267 ug PCB per pound of fish.

Scenario No. 3: 2 ppm PCB in lake trout flesh

2 ppm = 2 mg/kg; 2 mg/kg x 0.45359 kg/lb = 0.907 mg/lb. Thus, lake trout at 2 ppm PCB contain 907 ug PCB per pound of fish.

B. Total estimated mean ambient exposure to PCB from drinking water and respired air:

Estimated total annual exposure = 2.92 ug/yr (water) + 7.88 ug/yr (air) = 10.8 ug/yr

C. Estimated time required for equivalent exposure from ambient sources as from consumption of one pound of fish:

$$\text{Estimated time for equivalent exposure} = \frac{\text{Quantity of PCB in one pound of fish (ug)}}{\text{Estimated total annual ambient exposure (ug/yr)}}$$

From Scenario No. 1:

$$\text{Estimated time for equivalent exposure} = \frac{5,443 \text{ ug}}{10.8 \text{ ug/yr}} = 503.9 \text{ yr}$$

From Scenario No. 2:

$$\text{Estimated time for equivalent exposure} = \frac{2,267 \text{ ug}}{10.8 \text{ ug/yr}} = 209.9 \text{ yr}$$

From Scenario No. 3:

$$\text{Estimated time for equivalent exposure} = \frac{907 \text{ ug}}{10.8 \text{ ug/yr}} = 83.98 \text{ yr}$$

MONS 004818

mg/kg, an equivalent exposure of more than 80 yrs is acquired per 0.45 kg of fish.

Yet another perspective is gained by taking the same contaminant values and comparing them against recommended PCB intake rates for full grown adults. As was noted earlier, the Federal Food and Drug Administration has recommended a maximum daily dose rate of 1 ug/kg/day PCB for adult intake. If this daily value can be assumed to be an annual average, then a 70 kg adult may ingest no more than 25,550 ug of PCB annually (Table 6).

Assuming that the average lake trout from scenario number 1 contains 12 mg/kg PCB, the sports fishermen may consume approximately four and one-half 0.45 kg meals per year, or nine 0.23 kg meals per annum, and not violate the maximum recommended dose rate. Similarly, at 5.0 mg/kg PCB in lake trout, eleven 0.45 kg or twenty-two 0.23 kg fish meals may be consumed, and at 2.0 mg/kg, twenty-eight 0.45 kg meals or a net amount of a single 0.23 kg fish meal per week may be eaten and not exceed the guidelines.

TABLE 6

Total Consumption of Great Lakes Fish at Varying Concentrations of PCB Permissible Within Established Guidelines

---

Federal Food and Drug Administration recommended maximum adult intake of PCB
1 ug/kg/day
Average annual exposure limits for a 70 kg adult
25,550 ug/annum (1 ug x 70 kg x 365 day/yr)
From Scenario No. 1, lake trout at 12 mg/kg PCB:
Allowable consumption = $\frac{25,550 \text{ ug/yr}}{11,975 \text{ ug/kg}}$ = 2.13 kg/yr,
or approximately 9 meals containing 0.45 kg of fish.
From Scenario No. 2, lake trout at 5 mg/kg PCB:
Allowable consumption = $\frac{25,550 \text{ ug/yr}}{4,987 \text{ ug/kg}}$ = 5.12 kg/yr,
or approximately 22 meals containing 0.45 kg of fish.
From Scenario No. 3, lake trout at 2 mg/kg PCB:
Allowable consumption = $\frac{25,550 \text{ ug/yr}}{1,995 \text{ ug/kg}}$ = 12.81 kg/yr,
or approximately 56 meals containing 0.45 kg of fish.

MONS 004819

Because of calculations of this sort, the Michigan Department of Public Health established a Public Health Advisory related to fish consumption. This Advisory recommends limitation of the absolute amount of fish consumed per year, and recommends against consumption by children, women who expect to bear children, pregnant women, and nursing mothers.

A major question facing the scientific/regulatory/managerial community is the length of time that this problem will persist. The final answer is, at present, unknown. At best, only estimates can be made. The accuracy of the estimate is directly proportional to the quality of the initial data being utilized. The limiting data in this case are the loading values of PCB to the lakes, the initial concentrations in the water, the lake-wide mean water column concentrations of PCB, and internal loss velocities. The available fish data can be assumed to be more accurate.

The most remarkable data set in existence for Great Lakes fish is the information contained in the U.S Fish and Wildlife Service's Contaminant Monitoring Program (Willford, 1982). These data represent the only historical time sequence information on toxic contaminants in the Great Lakes by species of fish, for which sampling, analytical methodologies, and data handling have been carefully controlled to represent an accurate trend.

The data on corregonid fishes, in this case bloater chubs, shows a relatively continuous downward trend after 1974 (Figure 2). It was reasoned that these fish with their relatively short life cycle, as compared with lake trout for example, ought to reasonably reflect levels of PCB in the water column at the time the sample was taken. The rationale for this judgment is presented in Bierman and Swain (1982). Because of the lack of historically reliable time-sequence measurements of water column concentrations, it is necessary to infer concentrations from available fish data. Figure 3 suggests that concentrations in lake trout also seem to be declining, as do the PCBs in coho salmon shown in Figure 4.

When the body burden of individual species in the Fish and Wildlife Service data set are internally normalized (Figure 5), the apparent trends become clearer. It appears that for the salmonid fishes--the lake trout and coho salmon--real decreases have begun, but they appear to lag the corregonid fish by a substantial margin, perhaps 1 to 3 yrs. The decrease in all three species of fish suggest an overall reduction in the loads of PCB applied to Lake Michigan.

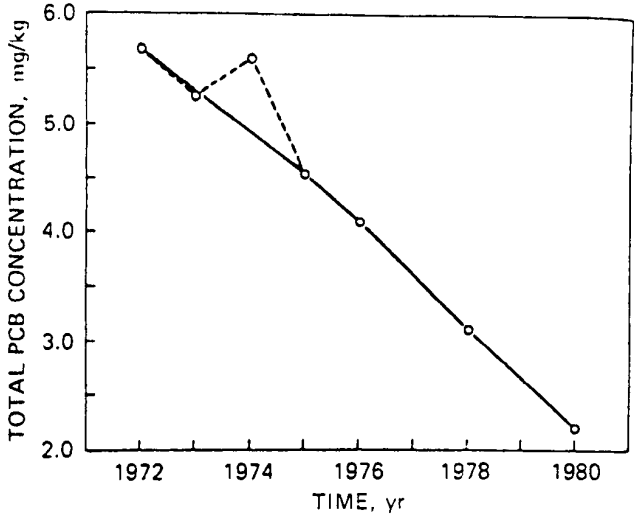


Figure 2. PCB concentrations in Lake Michigan bloater chubs.

If numerical simulation is then used, applying a least-squares fit to determine the net loadings of PCB to Lake Michigan necessary to produce each of the historic data points in the bloater chub curve (Figure 2), the sequential reductions in historical total loadings can be estimated. Extrapolating these reductions into the future, it is possible to estimate the loss rate for PCBs in each species of fish (Figure 6).

The calculation suggests that under the scenario projecting continuously decreasing loadings similar to those that have apparently occurred historically, coho salmon consistent with those in the data set would have reached the 5.0 mg/kg level in 1980, and lake trout with size and age characteristics similar to those previously collected will achieve 5.0 mg/kg by 1984 (Table 7). The projected times to 2.0 mg/kg are 1986 and 1989 for coho and lake trout, respectively.

MONS 004821

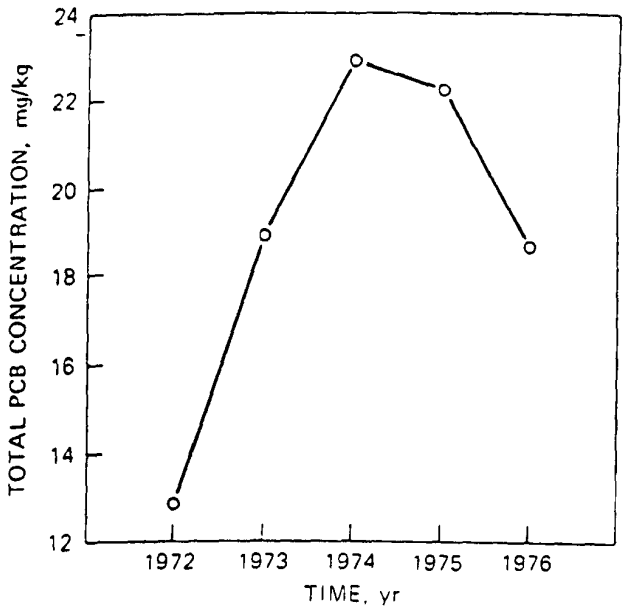


Figure 3. PCB concentrations in Lake Michigan lake trout.

However, if the loading of PCB is not continuously reduced incrementally, and instead of a continuous decrease, the load estimated for 1980 of slightly less than two and one-half metric tons per year is maintained, it appears that lake trout would not achieve the 5.0 mg/kg level until 1998, and coho and lake trout would not achieve 2.0 mg/kg until 1998 and 2006, respectively (Table 8).

If PCBs in Lake Michigan fish are truly declining at the rates the data would seem to indicate, why is there a continued concern over this compound? There are several reasons. Probably the most important involves human consumption. If humans consuming fish from Lake Michigan follow similar loss patterns for PCB, the human loss curve can be reasonably

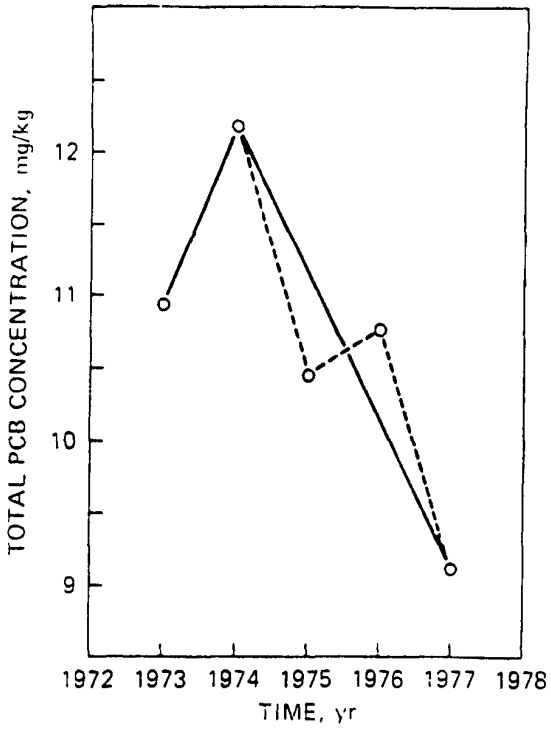


Figure 4. PCB concentrations in Lake Michigan coho salmon.

expected to lag the curve for lake trout by some 5 to 15 yrs--a decade being a reasonable approximation--since the human life cycle is four to five times longer than that of the lake trout, and it appears that PCBs are as poorly metabolized in humans as they are in fish. Given the longer human life cycle, the retention probably increases proportionately.

Thus, even with the projected declines in the aquatic environment, we are faced with the possibility of PCB persisting in the human population from this source for as long as 5 to 8

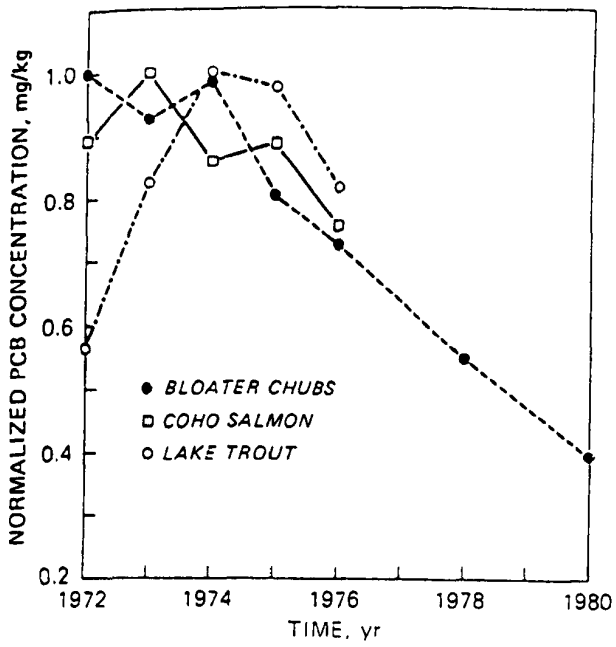


Figure 5. Normalized PCB body burdens in Lake Michigan fish.

generations into the future. Any consideration of the toxicological impacts of this compound should be set against the incredible persistence of this substance in the environment, and in human tissue.

Beyond this issue, it is necessary to remember that it has been estimated that only about one-third of all the PCB manufactured has reached the environment to date. It is to be hoped that the rest has been successfully contained. In addition, recent information suggests that some of the compounds being proposed as PCB substitutes may not differ markedly from the original compound. All of this information suggests that the PCB problem is likely to continue at least into the foreseeable future.

MONS 004824

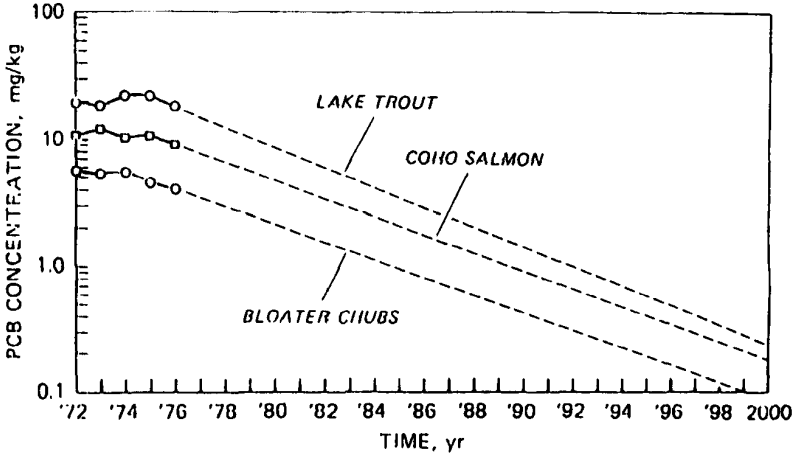


Figure 6. Estimated loss rates for PCB in Lake Michigan fish.

MONS 004825

TABLE 7

Estimated Year When Various Guideline Values of PCB Will be Achieved in Lake Michigan Fish, Based on Continuous Load Reductions

Guideline Value Achieved mg/kg	Species of Fish		
	Bloater Chubs	Coho Salmon	Lake Trout
15.0	--	--	1977-1978
10.0	--	--	1979-1980
5.0	--	1979-1980	1983-1984
2.0	1980-1981	1985-1986	1988-1989
1.0	1984-1985	1989-1990	1992-1993
0.5	1989-1990	1994-1995	1997-1998

TABLE 8

Estimated Year When Various Guideline Values of PCB Will Be Achieved in Lake Michigan Fish, Under a Steady-State Load of 2.4 Metric Tons Per Year After 1980

Guideline Value Achieved mg/kg	Species of Fish		
	Bloater Chubs	Coho Salmon	Lake Trout
5.0	--	1981	1998
2.0	1981	1998	2006

LITERATURE CITED

Ames, B. 1979. Identifying Environmental Chemicals Causing Mutations and Cancer. Science 204:587-593.

MONS 004826

Benvenue, A., J.N. Ogata, and J.W. Hylin. 1972. Organochlorine Pesticides in Rainwater, Oahu, Hawaii, 1971-1972. Bull. Environ. Cont. Toxic. 8:238-241.

Bidleman, J.F. and C.E. Olney. 1974. Chlorinated Hydrocarbons in the Sargasso Sea Atmosphere and Surface Water. Science 183:516-518.

Bierman, V.J. and W.R. Swain. 1978. DDT Loss Rates in Low Lipid Fishes of the Great Lakes. International Association for Great Lakes Research, Abstracts and Papers, 21st Conference on Great Lakes Research, p. 12.

Bierman, V.J. and W.R. Swain. 1982. Mass Balance Modeling of DDT Dynamics in Lakes Michigan and Superior. Environ. Sci. and Tech. 16:572-579.

Biros, F.J., A.C. Walker, and A. Medberry. 1970. Polychlorinated Biphenyls in Human Adipose Tissue. Bull. Environ. Cont. Toxic. 5:317-323.

Bowes, G.W. and C.J. Jonkel. 1975. Presence and Distribution of Polychlorinated Biphenyls (PCB) in Arctic and Subarctic Food Chains. J. Fish Board Can. 32:2111-2123.

Brinkman, U.A.T. and A. DeKok. 1980. Production Properties and Usage. In: Kimtrough, R.D. (ed.), "Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products," pp. 1-40. Elsevier/North-Holland Biomedical Press, Amsterdam.

Clausen, J., L. Braestrup, and O. Berg. 1974. The Content of Polychlorinated Hydrocarbons in Arctic Mammals. Bull. Environ. Cont. Toxic. 12:529-534.

Costle, D.M. 1980. A Reveille, Not a Requiem. Address before the Energy and Environmental Policy Center, Harvard University, Cambridge, MA. April 2, 1980. Released as USEPA Bull. OPA 109/0.

Dougherty, R.C., M.J. Whittaker, S. Tang, R. Bottcher, M. Keller, and D.W. Huehl. 1980. Sperm Density and Toxic Substances: A Potential Key to Environmental Health Hazards. Environmental Health Chemistry, Ann Arbor Science Publishers, Ann Arbor, MI.

Eisenreich, S.J., B.B. Looney, and J.D. Thornton. 1981. Airborne Organic Contaminants in the Great Lakes Ecosystem. Environ. Sci. and Tech. 15(1):30-38.

MONS 004827

Fein, G.G., S.W. Jacobson, P.M. Schwartz, and J.L. Jacobson. 1982. Intrauterine Exposure to Environmental Toxins: Behavioral Effects in the Human Newborn. Unpublished manuscript, University of Michigan, Ann Arbor, MI.

Finklea, J., L.E. Priester, J.P. Creason, T. Hauser, T. Hinners, and D.I. Hammer. 1972. Polychlorinated Biphenyl Residues in Human Plasma Expose a Major Urban Pollution Problem. Amer. J. Pub. Health 62(5):645-651.

Funatsu, I., F. Yamashita, Y. Ito, S. Tseugama, T. Fanatsu, T. Yoshikane, M. Hayashi, T. Kato, M. Yakushiji, G. Okamoto, S. Yamasaki, T.Arima, T. Kuno, H. Ide, and I. Ibe. 1972. Polychlorinated Biphenyls (PCB)-Induced Fetopathy. Kurme Medical Journal 19:43-51.

Giam, C.S., M.K. Wong, A.R. Hanks, and W.M. Sackett. 1973. Chlorinated Hydrocarbons in Plankton from the Gulf of Mexico and Northern Caribbean. Bull. Environ. Cont. Toxic. 11:376-382.

Gillett, J.W., J. Hill, A.W. Jarvinen, and W.P. Schoor. 1974. A Conceptual Model for the Movement of Pesticides Through the Environment: A Contribution of the EPA Alternative Chemicals Program. USEPA Ecol. Res. Series, EPA-660/3-74-0234, p. 79.

Glooschenko, W., W.M.J. Strachan, and R.C.J. Sampson. 1976. Distribution of Pesticides and Polychlorinated Biphenyls in Water Sediments and Seston of the Upper Great Lakes-1974. Pestic. Monit. J. 10(2):61-67.

Haile, C.M., G.D. Veith, G.F. Lee, and W.C. Boyle. 1975. Chlorinated Hydrocarbons in the Lake Ontario Ecosystem (IFYGL). USEPA Ecolog. Res. Series, EPA-660/3-75-022, p. 28.

Herdendorf, C.E., C.L. Cooper, and M. Gessner. 1978. Lake Erie Water Quality Status Report for 1977-Nearshore. Center for Lake Erie Area Research Technical Report No. 80, Ohio State University.

Humphrey, H.E.B. 1976. Evaluation of Changes of the Level of Polychlorinated Biphenyls (PCB) in Human Tissue. Unpublished manuscript, Michigan Department of Public Health, Lansing, MI.

Humphrey, H.E.B. 1981. Personal communication. Michigan Department of Public Health, Lansing, MI.

Humphrey, H.E.B. 1983. Population Studies of PCBs in Michigan Residents. In: F.M. D'Itri and M.A. Kamrin (eds.), "PCBs: Human and Environmental Hazards," pp. 299-310. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

MONS 004828

Hutzinger, O., S. Safe, and V. Zitko. 1974. The Chemistry of PCBs. Chapters 1 and 2, CRC Press, Cleveland, OH.

International Joint Commission. 1975. Water Quality Objectives Sub-Committee Report: Persistent Compounds. Water Quality Board Report (1974) to the International Joint Commission. Appendix A, p. 123, and Appendices.

International Joint Commission. 1977. Great Lakes Water Quality. Status Report on the Persistent Toxic Pollutants in the Lake Ontario Basin by the Implementation Committee, p. 95.

International Joint Commission. 1978. Great Lakes Water Quality. Status Report on Organic and Heavy Metal Contaminants in the Lakes Erie, Michigan, Huron, and Superior Basins. Great Lakes Water Quality Board Appendix E, p. 373.

Jacobson, S.W., J.L. Jacobson, P.M. Schwartz, and G.G. Fein. 1983. Intrauterine Exposure of Human Newborns to PCBs: Measures of Exposure. In: F.M. D'Itri and M.A. Kamrin (eds.), "PCBs: Human and Environmental Hazards," pp. 311-343. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Jelinik, C.F. and P.E. Corneliussen. 1976. Levels of PCBs in the U.S. Food Supply. National Conference on Polychlorinated Biphenyls, November 19-21, 1975, Chicago, IL. NTIS PB-253-248, pgs. 147-154.

Kleinert, S.J. 1976. The PCB Problem in Wisconsin. A report prepared for the Joint Hearing of the Assembly, Environmental Quality Committee with the Senate and Assembly Natural Resources Committees on NR212 Administration Rules for PCB Effluent Standards.

Kodama, H. and H. Ota. 1980. Transfer of Polychlorinated Biphenyls to Infants from their Mothers. Arch. of Environ. Health 35:95-100.

Kolbye, A.C. 1972. Food Exposure to Polychlorinated Biphenyls. Env. Health Persp. 1:85-88.

Kuwabara, K., T. Yakushiji, I. Watanabe, S. Yoshida, K. Koyama, N. Kunita, and I. Hara. 1978. Relationship Between Breast Feeding and PCB Residues in Blood of Children Whose Mothers Were Occupationally Exposed to PCBs. Int. Arch. Occup. Environ. Health 41:189-197.

MONS 004829

Masuda, Y., R. Kagawa, H. Kuroki, M. Kuratsune, T. Yoshimura, I. Taki, M. Kusuda, F. Yamashita, and M. Hayashi. 1978. Transfer of Polychlorinated Biphenyls from Mothers to Fetuses and Infants. Bull. Environ. Cont. Toxic. 16:543-546.

Maugh, T.H. 1978. Chemicals: How Many Are There? Science 199:162.

McGrath, M. 1980. The Fourth Coast. EPA Journal 6(5):22-24.

Metcalf, P.L., J.R. Sanborn, P. Lu, and D. Nye. 1975. Laboratory Model Ecosystem Studies of the Degradation and Fate of Radiolabeled Tri-Tetra- and Penta-Chlorobiphenyl Compared with DDE. Arch. Environ. Cont. and Toxic 3(2):151-165.

Murphy, T.J. and C.P. Rzeszutko. 1977. Precipitation Inputs of PCBs to Lake Michigan. J. Great Lakes Res. 3:305-312.

Peel, D.A. 1975. Organochlorine Residues in Antarctic Snow. Nature 154:324-325.

Peterle, T.J. 1969. DDT in Antarctic Snow. Nature 224:620.

Polishuk, Z.W., D. Wasserman, M. Wasserman, S. Cucos, and M. Ron. 1977. Organochlorine Compounds in Mother and Fetus During Labor. Environ. Res. 13:278-284.

Rainey, R.H. 1967. Natural Displacement of Pollution from the Great Lakes. Science 155:1242-1243.

Sonzogni, W.C. and W.R. Swain. 1980. Perspectives on U.S. Great Lakes Chemical Toxic Substances Research. J. Great Lakes Res. 6(4):265-274.

Strachan, W.M.J. and H. Hanesult. 1979. Polychlorinated Biphenyls and Organochlorine Pesticides in Great Lakes Precipitation. J. Great Lakes Res. 5(1):61-68.

Swain, W.R. 1978. Chlorinated Organic Residues in Fish, Water, and Precipitation from the Vicinity of Isle Royale, Lake Superior. J. Great Lakes Res. 4(3-4):398-407.

Swain, W.R. 1980. Unpublished data.

Swain, W.R. 1981. An Ecosystem Approach to the Toxicity of Residue Forming Xenobiotic Organic Substances in the Great Lakes. Ecotoxicology Working Papers: Testing for the Effects of Chemicals on Ecosystems. National Research Council, National Academy of Sciences, pp. 194-257.

MONS 004830

Swain, W.R., M.D. Mullin, and J.C. Filkins. 1982. Refined Analysis of Residue Forming Organic Substances in Lake Trout from the Vicinity of Isle Royale, Lake Superior. International Association for Great Lakes Research, Abstracts of Papers, 25th Conference on Great Lakes Research, p. 18.

Thomann, R.V. 1978. Size Dependent Model of Hazardous Substances in Aquatic Food Chains. USEPA Ecol. Res. Series, EPA-600/3-78-036, p. 39.

Thomann, R.V. 1980. Steady State Model of Fate of Chemicals in Diverse Aquatic Food Chains. Manhattan College, Bronx, NY (typescript), p. 46.

United States Fish and Wildlife Service. 1974. National Pesticide Monitoring Program-Fish-1974. Fall 1974 Analytical Results.

Upper Lakes Reference Group, International Joint Commission 1977. The Waters of Lake Huron and Lake Superior. Volume III, Parts A and B.

Veith, G.D., D.W. Kuehl, F.A. Puglisi, G.E. Glass, and J.G. Eaton. 1977. Residues of PCBs and DDT in the Western Lake Superior Ecosystem. Arch. Environ. Cont. and Toxic. 5:487-499.

Weininger, D. 1976. Accumulation of PCBs by Lake Trout in Lake Michigan. Ph.D. Thesis, University of Wisconsin, Madison, WI, p. 232.

Wickizer, T.M., L.B. Brilliant, R. Copeland, and R. Tilden. 1981. Polychlorinated Biphenyl Contamination of Nursing Mothers' Milk in Michigan. Amer. J. of Pub. Health 71:132-137.

Willford, W.A., R.J. Hesselburg, and L.W. Nicholson. 1976. Trends of Polychlorinated Biphenyls in Three Lake Michigan Fishes. National Conference on Polychlorinated Biphenyls, November 19-21, 1975, Chicago, IL. NTIS PB-253-248, pgs. 177-181.

Willford, W.A. 1982. Evaluating the Presence and Effects of Contaminants in Fish of the Great Lakes. Agenda Item 14.6, presented before the Great Lakes Fisheries Commission, 1982 Annual Meeting, Green Bay, WI, June 9-10, 1982.

MONS 004831

CHAPTER 4

PCBs IN THE GREAT LAKES: SOURCES, SINKS, BURDENS

Steven J. Eisenreich
Department of Civil and Mineral Engineering
University of Minnesota
Minneapolis, Minnesota 55455

Thomas C. Johnson
Department of Geology
University of Minnesota-Duluth
Duluth, Minnesota 55812

INTRODUCTION

Polychlorinated biphenyls (PCBs), as a class of synthetic, chlorinated organic chemicals, are ubiquitous in the marine and freshwater environments of our planet (NAS, 1979; Nisbet and Sarofim, 1972; Ballschmiter and Zell, 1980). The global distribution of PCBs is demonstrated by their occurrence in fish and fish products from as dissimilar environments as the Antarctic Ocean, the North Atlantic Ocean, North Sea, and Alpine Lakes (Zell and Ballschmiter, 1980; Ballschmiter and Zell, 1980; Ballschmiter et al., 1981). Since 1929, approximately 2×10^9 kg of PCBs have been commercially produced, and about 2×10^8 kg remain in mobile environmental reservoirs (31%) and in landfills or equipment dumps (58%) (NAS, 1979). The voluntary and projected legislative bans instituted since 1971 by the Monsanto Chemical Company to restrict production, sale, and use of PCBs to closed systems suggests that the tropospheric and hydrospheric burdens should be decreasing. Indeed, decreasing concentrations in certain fishes from the Great Lakes (Hartig, 1981), sediment (Eisenreich et al., 1980), and atmosphere (Eisenreich, 1982a; 1982b) support this hypothesis. However, PCBs are refractory compounds resisting chemical and biological degradation and will remain active for decades to come (Ballschmiter et al., 1978).

MONS 004832

The National Academy of Sciences (1979) issued a report on PCBs in which estimates of the environmental load for the U.S. and Atlantic Ocean were made (Table 1). The major environmental reservoirs for PCBs in the northern hemisphere were concluded to be marine sediments and water and freshwater sediments, especially those of the Great Lakes. The data indicate that the North Atlantic Ocean is the ultimate sink for PCBs emitted in North America, and atmospheric transport/deposition is the major input mode. Similar information on the sources, sinks, and burdens in the Great Lakes is only now becoming available and is summarized in this chapter, although considerable uncertainty still exists in estimating fluxes at air/water and sediment/water interfaces.

MASS BALANCE APPROACH

One approach to viewing the "PCB status" of the Great Lakes is to construct a model describing the inputs, outputs, and compartmental burdens. A mass balance model provides an understanding of the transport and distribution of PCBs in the lakes and an estimate of the residence time that the pollutant remains in the ecosystem or in any compartment. The mass balance

TABLE 1

Environmental PCB Load Estimates for the United States and Atlantic Ocean (NAS, 1979)

Environmental Compartment	PCB Loading (10^6 kg)
Atmosphere	0.018
Hydrosphere	
Freshwater	0.012-0.035
Freshwater Sediments	1.4-7.1
Freshwater Biota	0.03
Marine Water	6.0-66
Marine Sediment	0.66-27
Marine Biota	0.03
Lithosphere	0.14-2.8

MONS 004833

approach has been applied to the cycling of PCBs in Lake Michigan (Weininger and Armstrong, 1981) and Lake Superior (Eisenreich *et al.*, 1980, 1981b).

Figure 1 schematically describes the mass balance model of pollutant cycling in a Great Lake ecosystem and will be used as a paradigm for discussing PCB transport and distribution. The time-dependent change in the PCB concentration in a lake may be given by:

$$d(C_tV)/dt = \Sigma Q_iC_i - Q_oC_t - V_sC_dK_p/h - k_dCd - k_vC_d$$

where:

- C_t = total PCB concentration in water (mass/volume)
- Q_i = inflow volume (volume) at influent concentration, C_i (mass/volume)
- V = lake volume (volume)
- Q = outflow volume (volume/time)
- V_s = apparent net settling velocity for particles (length/time)
- C_p = particulate PCB concentration (mass/volume)
- h = lake depth (length)
- k_d = first-order rate constant for PCB degradation ($time^{-1}$)
- C_d = dissolved PCB concentration (mass/volume)
- K_v = PCB volatilization rate (length/time)
- K_p = PCB partition coefficient (volume/mass)

The ΣQ_iC_i signifies the summation of all inputs of PCBs. The sources of PCBs to the Great Lakes are atmospheric deposition, tributary inputs, municipal/industrial discharges, and sediment resuspension/pore water advection. Available data and theory do not presently permit an estimation of sediment resuspension and pore-water advection although Rogers (1982) and Chambers and Eadie (1981) have addressed the former while Eadie (personal communication, GLERL, NOAA, 1982) is addressing the latter. The outputs of PCBs are tributary outflow (Q_oC_t), sedimentation ($V_sC_dK_p/h$), biological degradation (k_dC_d), and volatilization (k_dC_d). PCB burdens in the Great Lakes are expressed as mass accumulated in the atmosphere, water, sediment, and biota.

PCB Concentrations and Burdens

Atmosphere

The atmosphere does not represent a significant reservoir of PCBs for the Great Lakes but is a major input pathway. The

MONS 004834

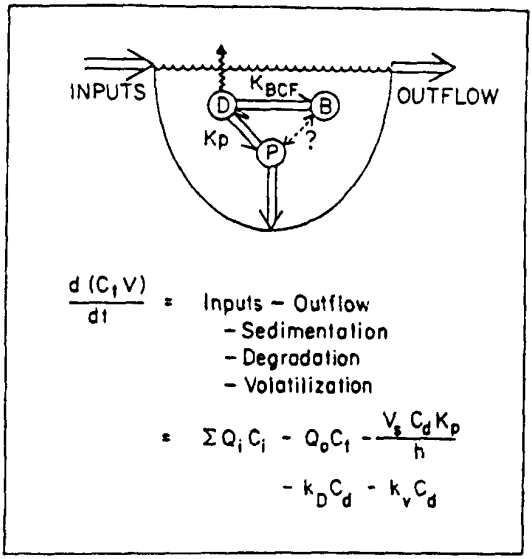


Figure 1. Mass balance model of pollutant cycling. See text for definition of symbols.

concentrations of PCBs in air have been summarized by Eisenreich et al. (1981b) and updated in MacKay et al. (1982). Airborne PCBs have been primarily measured in Lakes Superior and Michigan by Eisenreich et al. (1981a), Eisenreich et al. (1982b), Doskey and Andren (1981a), Rice et al. (1981a), and Murphy and Rzeszutko (1977). Doskey and Andren (1981a) have reported that the mean PCB concentration in the atmosphere over Lake Michigan during 1977-78 was approximately 1 ng/m^3 with a range of 0.5-1.5 ng/m^3. Rice et al. (1982) have reported higher PCB concentrations in 1979-80 ranging from 1.0 to 5.4 ng/m^3. Airborne PCB concentrations over Lake Superior were approximately 1.5 ng/m^3 in 1978 (Eisenreich et al., 1981; Hollod et al., 1982) but have apparently decreased to a mean of about 0.3 ng/m^3 in 1981 (S.J. Eisenreich, unpublished data). Airborne PCBs occur at concentrations of 0.3 to 2 ng/m^3 in the Great Lakes (Table 2), occur primarily in the vapor phase (up to 100%), and are dominated by the lower chlorinated isomers such as Aroclor 1242

MONS 004835

TABLE 2

PCB Concentrations in the Air, Rain, Water, and Sediments in the Great Lakes Basin

Environmental Compartment	Lake Superior Median	Lake Superior Range	Lake Michigan Median	Lake Michigan Range	Lake Huron Median	Lake Huron Range	Lake Erie Median	Lake Erie Range	Lake Ontario Median	Lake Ontario Range
Air (ng/m^3)	0.3	--	1.0	--	--	0.5-1.0	2.0	--	2.0	--
Rain (ng/l)	--	10-30	--	20-50	--	10-50	--	10-50	--	20-50
Water (ng/l)	--	1-2	--	1-5	--	1-3	--	2-10	--	2-6
Sediments (ng/g)[a]	3.3±5.7	2.2-57	9.7±15.7	2-190	13±10[b]	3-90	95±114	4-800	57±56	5-280

[a]From Frank et al., 1977; 1979a; 1979b; 1980; 1981.
[b]PCB concentration in sediment of Georgian Bay is 11±11 ng/g.

MONS 004836

(approximately 60-80%). Reasonable atmospheric fluxes (Mackey et al., 1983) and observed atmospheric burdens lead to the conclusion that atmospheric residence time over an individual lake is approximately 1 to 5 days.

Even less is known about PCB concentrations in precipitation (Table 2). Although levels in urban/industrial-impacted areas such as southern Lake Michigan may exhibit rain concentrations up to approximately 100 ng/l (Murphy and Rzeszutko, 1977), present day values over the whole basin probably average about 10 to 50 ng/l. Support for this is provided by field data (Davis, 1980; Swain, 1978; Strachan and Huneault, 1979; Murphy et al., 1981). Frank and Braun (1981) found PCB concentrations in rain during 1975 in 6 agricultural watersheds in southern Ontario to be 20 to 100 ng/l, similar to the concentrations found in stream water. PCB concentrations in air and rain should be highest close to and downwind of populated areas, but in fact, are rather well dispersed over the whole basin implicating atmospheric transport as a principal distribution process.

Hydrosphere

Few data are available on PCB concentrations in the water of the Great Lakes. Konasewich et al. (1978) summarized the literature prior to 1978 and found wide discrepancies in the reported concentrations. Little attention has been paid to the hydrospheric burden of PCBs, even though the dissolved species supports the elevated biotic burdens often reported. For example, total PCB concentrations in Lake Superior over the last ten years have been reported from 0.8 to about 110 ng/l in the open waters, and perhaps up to 200 ng/l in nearshore waters and harbors (Swain, 1978; Reinert, 1970; Konasewich et al., 1978; Veith et al., 1977). By comparison, the concentrations of PCBs in Lake Michigan have been reported to range from 1 ng/l to as high as 200 ng/l in open waters, and higher in harbors and embayments. PCB concentrations in the contaminated Waukegan Harbor of southern Lake Michigan ranged from 20 to 1000 ng/l in 1979, while 0.5 km offshore, 1 to 10 ng/l values were found (Thomann and Koutaxis, 1981). The present day concentration in Lake Michigan is probably much closer to 1 to 5 ng/l, while Lake Superior has PCB levels of 1 to 2 ng/l. Tables 2 and 3 show the measured and estimated concentrations of total PCBs in the Great Lakes on a whole-lake average. The entire range of mean values is 1 to 10 ng/l, with locally higher concentrations likely near point sources.

Eisenreich et al. (1983a) have found that PCB concentrations in Lake Superior averaged 1.3 ± 1.3 ng/l in 1978 (n =

MONS 004837

TABLE 3

PCB Concentrations in Water

Watercourse	Concentration (ng/l)	
	Median	Range
Great Lakes		
1. Superior	1-2	0.2-8.4
Michigan	1-5	0.5-10
Huron	1-3	0.5-10
Erie	2-10	5-20
Ontario	2-6	1-20
2. Open Waters	-	0.5-5
Embayments	-	1-10
Harbors	-	5-50
Marine	0.1-1.0	0.1-5.0
Rivers		
Undisturbed	1	1-5
Disturbed	-	10-200

30), 3.6 ± 1.8 ng/l in 1979 (n = 35), and 0.9 ± 0.4 ng/l in 1980 (n = 62). Concentrations in Lake Michigan have tentatively been assessed at about 2 ng/l (Armstrong, 1982, personal communication) and 2 to 5 ng/l (Rice et al., 1982). The distribution of isomeric mixtures is about 50 ± 20 percent Aroclor 1242 (1016) with 60 to 80 percent operationally existing in the dissolved phase. Although hydrophobic pollutants such as PCBs are known to partition into suspended matter (Steen et al., 1978; Paris et al., 1978; Karickhoff et al., 1979; O'Connor and Connolly, 1980), partitioning favors the dissolved phase in waters of low suspended concentrations (SS) even though K_p may be 10^5 to 10^6 l/kg.

The relatively uniform PCB concentrations in the open waters of the Great Lakes are attributed to the interaction of

MONS 004838

varying concentrations of suspended solids with dissolved PCBs, with subsequent particle loss to the sediments. In Lake Erie where PCB loadings are likely elevated, high sedimentation rates remove a greater mass to the sediment. In Lake Superior, lower PCB loadings are balanced by inefficient removal processes because suspended solids concentrations are low and sedimentation rates are slow. The net effect of variable PCB loadings, suspended solids and sedimentation rates is low, and relatively uniform water-column concentrations. In all cases, the fraction in the particle phase (i.e., CdK_p/C_t) is that portion of the PCB burden influenced by loss to the sediments.

Sediments

Sediments represent the ultimate sink for PCBs and other hydrophobic pollutants in the Great Lakes. As a result, numerous studies on the distribution of PCBs in the surficial sediments have been conducted, primarily to assess the extent of environmental degradation and insult. The most ambitious and wide-ranging study to date was conducted in 1968 to 1976 by the Ontario government in which more than 1200 surficial sediment samples (upper 3 cm) were collected and analyzed for PCBs and organochlorine insecticides. The intent of the study was to establish baseline levels and identify sources to enable future trends to be assessed. The surficial sediment concentration of PCBs were reported for Lake Erie (Frank et al., 1977), Lake Ontario (Frank et al., 1979a), Lake Huron (Frank et al., 1979b), Lake Superior (Frank et al., 1980), and Lake Michigan (Frank et al., 1981). Table 2 depicts the mean, standard deviation, and range of PCB concentrations observed in the 0 to 3 cm surficial sediments. The lower lakes, especially Erie and Ontario, have the highest mean and range of concentrations averaging 50 to 60 ng/g. The Upper Great Lakes exhibit surficial sediment concentrations of 3 to 10 ng/g. Eisenreich et al. (1979; 1980) have observed concentrations 10 to 20 times greater in the upper 0.5 cm of Lake Superior sediments. There is evidence to suggest that actual surficial concentrations in areas of low sedimentation may be substantially higher than those given in Table 2. However, overall sediment burden may be calculated using these data, and certainly the sedimentary and lake-to-lake trends may be evaluated. Table 4 lists the PCB concentrations observed in surficial sediments of the Great Lakes by several authors. PCB concentrations are higher in depositional vs. non-depositional zones within the same lake, and the Upper Lakes exhibit lower concentrations than the Lower Lakes, presumably due to proximity to sources.

The historical input of PCBs to the sediments of the Great Lakes has not been generally reported, but is presently being

MONS 004839

TABLE 4

PCBs in Great Lakes' Sediments

Watercourse	Whole Lake (ng/g)	Non-Deposition Zones (ng/g)	Deposition Zones (ng/g)	Range (ng/g)	Reference
Superior	4.8	3.9		<2.5-57	Frank et al., 1980
	(5.5)	(2.1)			
	130	80	180	5-290	Eisenreich et al., 1979; 1980
	(110)	(40)	(110)		Veith et al., 1977
	7.0			5-1300	Glooschenko et al., 1976
Michigan	9.7	6.3	17.3	<2-190	Frank et al., 1981
	(15.7)	(8.1)	(23.9)		
				3.7-133	Schacht, 1978
				5-200	Weininger and Armstrong, 1981
				2-7	Simmons et al., 1980
Huron	13	11	15	<3-90	Frank et al., 1979a, 1979b
	(10)	(7)	(13)		
Georgian Bay-North Channel	11	11	11	<3-43	Frank et al., 1979a, 1979b
	(11)	(13)	(8)		

MONS 004840

Table 4 (continued)

Watercourse	Whole Lake (ng/g)	Non-Deposition Zones (ng/g)	Deposition Zones (ng/g)	Range (ng/g)	Reference
Erie	95 (114)	64 (105)	115 (114)	4-800	Frank et al., 1977
Lake St. Clair	10 (6)	--	--	ND-28	Frank et al., 1977
Ontario	57 (56)	31 (40)	85 (57)	5-280	Frank et al., 1979a, 1979b
Bay of Quinte	48 (43)	47 (45)		<2-260	Frank et al., 1980

Numbers in parentheses indicate one standard deviation.

MONS 004841

constructed by this author for the Great Lakes, and D.E. Armstrong for Lake Michigan. PCB accumulation in sediments over time can only be determined by carefully examining detailed cores. Figure 2 shows the depth profile of four sediment cores taken in Lake Superior with a box corer and carefully fractionated into approximately 0.25 cm segments in the uppermost sediments. The right vertical axis shows the dates of specific depth segments as determined by ^{210}Pb geochronology (Evans et al., 1981). The profiles are typified by high surficial concentrations (0-0.5 cm) followed by a rapid decrease with depth, such that no detectable values were observed at depths greater than 1 to 5 cm depending on the core. In general, PCB concentrations appeared in the sediment profile in 1940 to 1950. However, careful examination of sediment cores least disturbed by bioturbation indicate that the PCBs entered the Lake Superior system about 1950. All cores exhibit 20 to 100 percent lower PCB concentrations in the upper 0 to 0.25 cm than in the 0.25

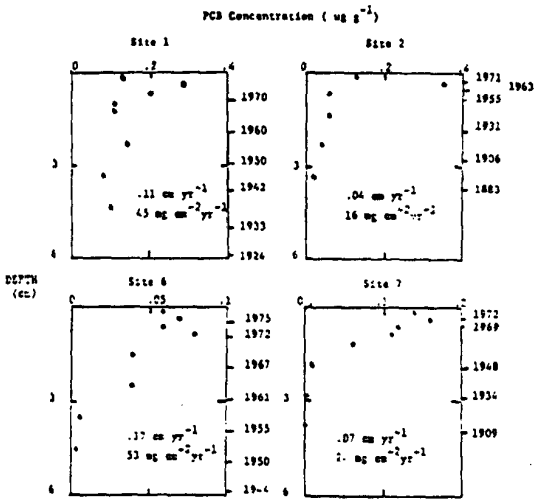


Figure 2. PCB concentration profiles (ug/g) in sediment cores from Lake Superior in areas with sedimentation rates $\geq$ 0.04 cm/yr.

MONS 004842

to 0.5 cm segment. This behavior implicates a mechanical loss of the most flocculant sediment during sampling or provides evidence for a recent decrease in sedimentary PCB flux in response to decreased loadings. Both possibilities are being carefully examined using sediment cores in zones of more rapid deposition.

Environmental PCB Burdens

The PCBs accumulated or stored in the major environmental reservoirs of the Great Lakes may be estimated from concentrations in the atmosphere, lake water, and sediments. The biotic compartment contributes no more than a few percent at most to the whole lake burden. Table 5 lists the physical characteristics of the Great Lakes needed, in part, to estimate compartmental burdens of PCBs for each of the Great Lakes shown in Table 6. The sediment burden for each of the lakes was estimated from the sediment concentrations in the upper 0 to 3 cm provided by Frank et al. (1977; 1979a; 1979b; 1980; 1981), assuming that all PCBs resided in that depth increment, and the density was 2.5 g/cm^3. Studies of depth profiles in cores of the Upper Lakes suggest that most of the PCB burden is contained in the 0 to 3 cm segment, while PCBs extend to greater depths in the high sediment flux areas of the Lower Lakes. Therefore, sediment burdens listed in Table 6 likely underestimate actual values. The water burden of PCBs was calculated from mean lake concentrations and lake volume. Atmospheric burdens assumed a constant air concentration to a 1 km mixing height over the lake surface area. A conservative estimate of the total mass of PCBs in the Great Lakes is 473 x 10^3 kg of which 88 percent

TABLE 5

Physical Characteristics of the Great Lakes

	Volume (10^{12} m^3)	Area (10^{10} m^2)	Mean Depth (m)	Annual Discharge (10^{10} m^3/yr)	RT_{H_2O} (yr)
Superior	12.1	8.21	147	6.72	179
Michigan	4.92	5.78	85	3.60	137
Huron	3.54	5.96	59	16.1	22
Erie	.484	3.56	19	18.2	2.7
Ontario	1.64	[illegible]7	83	21.2	7.7

MONS 004843

TABLE 6

PCB Burden in the Great Lakes

Lake	Sediments		Water		Atmosphere	
	Concentration ng/g	Burden 10^3 kg	Concentration ng/l	Burden 10^3 kg	Concentration ng/m^3	Burden 10^3 kg
Superior	3.3±5.7	20	1-2	12-24	0.3	0.025
Michigan	9.7±15.7	42	1-5	4.9-25	1.0	0.058
Huron	13±10	58	1-5	3.5-18	0.5	0.030
Erie	95±114	182	2-10	1-9.7	2.0	0.051
Ontario	57±56	115	2-6	3.3-9.8	2.0	0.039
TOTAL	--	417	--	25-87	--	0.20

Total PCB Burden: 442 to 504 MT

MONS 004844

is contained in the top 3 cm of sediment. It is unlikely that this estimate is inaccurate by more than a factor of 2. Inclusion of the PCB burden contained in the sediments of Waukegan Harbor and North Ditch, southwestern Lake Michigan, would more than double the Great Lakes burden. If the PCB burden had been deposited in the lake at a constant rate over the last 30 yrs, a long-term average net input of 1300 kg/yr would be added to Lake Superior to 6200 kg/yr for Lake Erie. Note that the mass of PCB in Lakes Erie and Ontario exceed that in the remaining lakes by more than 100 percent. The sedimentary PCB burden in the Lower Lakes may be much higher. There is no doubt that even conservative estimates show that lakes near urban/industrial centers suffer a massive environmental insult due to the input of anthropogenic organic chemicals such as PCBs.

Detailed estimates of the PCB burden have been made for Lake Michigan (Weininger and Armstrong, 1981) and Lake Superior (Eisenreich et al., 1982)(Table 7). The total PCB burden of Lake Superior was estimated as 39,000 kg, fortuitously close to the value listed in Figure 3. The total PCB burden of Lake Michigan was estimated as approximately 70,000 kg, about 20 percent higher than estimated before. About 60 and 86 percent of the PCB mass has accumulated in the sediments of Lake Superior and Lake Michigan, respectively.

PCB SOURCES AND SINKS

The principal sources of PCBs to the Great Lakes are atmospheric deposition, tributary input, and municipal/industrial discharges. Atmospheric transport and deposition of PCBs has been implicated as a primary input pathway to freshwater and marine ecosystems as a result of its presence in marine (Harvey and Steinhauer, 1974; Bidleman and Olney, 1974; Giam et al., 1980; Atlas and Giam, 1981) and Great Lakes' atmospheres (Doskey and Andren, 1981; Eisenreich et al., 1981; 1982b). For example, the North Atlantic Ocean (water + sediments) is the principal sink for PCBs produced in North America from 1930 to 1976 (NAS, 1979; Table 1). A second major sink is freshwater sediment, primarily in the Laurentian Great Lakes, where atmospheric inputs may be partially responsible for sedimentary accumulation. Eisenreich et al. (1979) concluded that atmospheric inputs could support their accumulation in surficial sediments.

Early studies of PCBs in precipitation by Murphy and Rzeszutko (1979) in the Lake Michigan Basin clearly showed that atmospheric deposition was an important pathway. Later studies

MONS 004845

TABLE 7

PCB-Burdens in Lakes Superior and Michigan, 1980

	Lake Burdens	
	Superior[1]	Michigan[2]
Lake Water (kg)		
PCB_T	1 ng/l	2 ng/l
Dissolved (approx. 80%)	9,600	8,200
Particulate (approx. 20%)	2,400	1,600
	12,000 kg	9,600 kg
Sediments (kg)		
Approx. 0.1 ug/g	15,300 kg (0-.5 cm)	30,000 kg (0-2 cm)
Approx. 0.025 ug/g	11,600 kg (.5-2 cm)	30,000 kg (2-5 cm)
	26,900 kg	60,000 kg
Atmosphere (kg)		
Approx. 1 ng/m^3 1 km hm	82 kg	58 kg
Biota (kg)	Approx. 5-10 kg	Approx. 10 kg
TOTAL	Approx. 39,000 kg	Approx. 70,000 kg

[1]Eisenreich *et al.* (1982b)
[2]Weininger and Armstrong (1981)

by Murphy *et al.* (1981) and Doskey and Andren (1981b) also showed that wet and dry deposition were important. The magnitude of the PCB problem is properly viewed in the context of recently published input-output models for PCBs in Lake Superior (Eisenreich *et al.*, 1981a, 1981b) and Lake Michigan (Weininger and Armstrong, 1981). For both systems, atmospheric deposition is the dominant input pathway and sedimentation is the dominant

MONS 004846

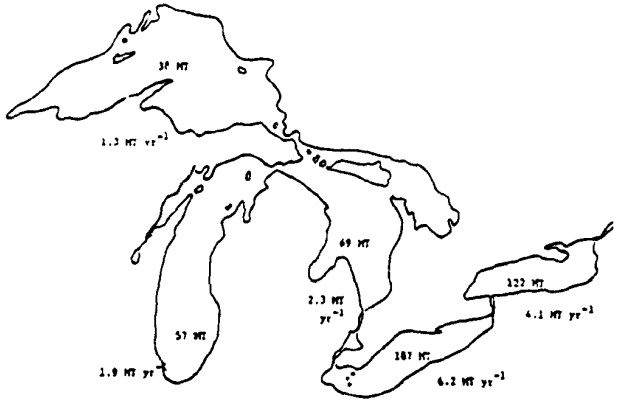


Figure 3. PCB burden (10^3kg) and mean annual input rate over 30 years to the Great Lakes (10^3kg/yr)

loss pathway. The input-output values require that the net annual accumulation of PCBs is 6300 to 8600 kg and 3950 kg for Lake Superior and Lake Michigan, respectively, corresponding to increases in water-column concentrations of approximately 0.5 to 0.7 ng/l/yr and approximately 0.8 ng/l/yr. Since fish, sediment, and atmospheric PCB concentrations seem to be slowly decreasing, then either atmospheric inputs are too high or other loss mechanisms have not been considered. A brief discussion of the problem follows.

Atmospheric deposition can be derived from the scavenging of particulate or gaseous PCB in the atmosphere by precipitation and the dry flux of particulate and gaseous PCB. The wet inputs have been measured in the field by collecting and analyzing rain and snow. As shown in Table 2, PCB concentrations in precipitation on a volume-weighted basis range from 10 to 50 ng/l. Thus, wet deposition may be estimated by:

$$F_W = C_{rain} \cdot J = C_{air} \cdot J \cdot W$$

MONS 004847

where:

F_W = wet flux (mass area^{-1} time^{-1})
C_{rain} = PCB concentration in air (mass volume^{-1})
J = precipitation intensity (length time^{-1})
W = scavenging coefficient (dimensionless)

For the Upper Great Lakes, 10 to 30 ng/l PCB in rain and 74 cm/yr annual precipitation yield wet fluxes of 7.5 to 23 ug/m^2/yr. For the Lower Great Lakes, 20 to 50 ng/l PCB in rain and 85 cm/yr annual precipitation yield wet fluxes of 17 to 43 ug/m^2/yr.

Interestingly, the PCB flux to the sediments of Lake Superior and Lake Michigan is approximately 10 to 19 ug/m^2/yr and approximately 45 ug/m^2/yr, respectively. Note that the wet flux of PCBs to Lake Superior is close to the sediment flux, while additional sources are evident for Lake Michigan.

Estimation of the dry flux of particles and gases to the Great Lakes, however, is not nearly so manageable a task. Recall that 80 to 100 percent of the airborne PCBs occur in the vapor phase, although this may be an overestimate since PCBs trapped on a back-up solid absorbent (e.g., XAD-2, polyurethane foam) may collect vapor desorbed from particles retained upstream on a filter. As a result, both particle flux and vapor-phase exchange across the air/water interface need be considered. A detailed examination of the particle and gas-flux questions is beyond the scope of this paper, but the reader may consult excellent discussions of these topics in Doskey and Andren (1981), Slinn and Slinn (1981), MacKay and Yuen (1981), and Eisenreich *et al.* (1981). Recently, Andren (1983) addressed the dry flux of PCB-laden particles to water surfaces in some detail and will not be considered here. The gas-phase flux of PCB vapor across the air-water interface is given by:

$$F_{D_1} = K_{oL} (C - P/H),$$

$$1/K_{oL} = 1/K_L + RT/HK_g$$

where:

F_D = dry vapor flux
K_{oL}, K_L, K_g = mass transfer coefficients (m/hr)
C = aqueous PCB concentration (mol/m^3)
P = atmospheric partial pressure of PCB (atm)
H = Henry's Law Constant = P/C at saturation (atm m^3/mol)
RT = 0.0245 at 25°C (mole/atm/m^3)

MONS 004848

MacKay et al. (1979) have shown that resistance lies 95 percent in the gas phase if $H \geq 5 \times 10^{-3}$ atm m^3/mol, lies 95 percent in the liquid phase if $H \leq 5 \times 10^{-6}$ atm m^3/mol, and occurs in both phases between these values. Gas-phase control implies air-to-water transfer, and liquid-phase control implies the opposite. Considerable confusion as to the value of Henry's Law Constant existed until recently. The Henry's Law Constant for PCBs is approximately 10^{-3} to 10^{-4} atm m^3/mol and varies little between isomers (Murphy et al., 1983). However, laboratory (Doskey and Andren, 1981a, 1981b) and field data suggest that H = 10^{-6} to 10^{-7} atm m^3/mol in natural aquatic systems. What is the source of the conflict? Recently, Eisenreich et al. (1983a) reported total PCB and isomeric depth profiles in the water column of Lake Superior. They concluded that although surface profiles supported atmospheric transfer as a source, calculations showed that air and surface water PCBs were in near equilibrium with H = 10^{-3} to 10^{-4} atm m^3/mol. Briefly, this suggests that (1) atmospheric inputs are primarily a result of precipitation inputs; (2) net vapor-phase transfer is presently negligible; (3) atmospheric PCB concentrations are buffered by air/water exchange; and (4) volatilization is only a minor loss mechanism. A modified tentative PCB mass balance for Lake Superior (Table 8) shows that inputs only slightly exceed outputs, which could easily be balanced by low biodegradation and/or volatilization rates. Similar models for the other lakes require better estimates of tributary, municipal, and industrial inputs.

Since the major loss of PCBs from the lakes is sedimentation, accurate estimates of sediment fluxes are critical. The PCB flux to the sediments of Lake Superior and Lake Michigan determined from analysis of sediment cores are approximately 1000 to 1600 and 2600 kg/yr, respectively. An alternate method of estimating sediment fluxes is given by:

$$F_{sed} = V_s C_d K_p A_x$$

where:

F_{sed} = PCB sediment flux (mass/time)
V_s = net apparent particle settling velocity (length/time)
C_d = dissolved PCB concentration (mass/volume)
K_p = PCB partition coefficient (volume/mass)
A_s = lake surface area ($length^2$)

The V_s values were obtained from Bierman and Dwain (1982). Calculated sediment fluxes from above agree reasonably well

MONS 004849

TABLE 8

Tentative Mass Balance of PCBs in Lake Superior

Input (kg/yr)			Output (kg/yr)	
Tributary			Tributary	
1300			140	
Municipal			Biodegradation	
66			100	
Industrial			Volatilization	
2			0	
Atmospheric			Sedimentation	
Wet	620-1850		1000-1600	measured
Dry	200-1000	particle	1600-200	calculated (v_g)
	0	vapor		
Total	820-2850			
TOTAL INPUT			TOTAL OUTPUT	
2200-4200			1840	

with measured PCB fluxes to the sediments (Table 9). Another method of estimating PCB losses to the sediments is to examine the decrease in concentration in certain fish (and therefore burden) over recent years. Hartig (1981) has provided the concentrations of total PCBs in Lake Michigan bloater chubs from 1972 and 1980. Figure 4 clearly shows that PCB values in this short-lived species decreased linearly over the 8 yrs of study, supposedly in response to decreasing inputs and water concentrations. Assuming the total PCB concentration in water was between 1 and 3 ng/l, then bioconcentration factors (BCF) are approximately 2.2×10^6 to 7.3×10^5. Since fish concentration ought to be linearly related to water concentration, the PCB concentration in Lake Michigan water was back calculated as between 2.5 and 6.4 ng/l in 1972. Assuming that the decreasing fish concentration represented an annual loss to the sediments, 900 to 2000 kg/yr PCBs were sedimented out, closely matching previous estimates (Weininger and Armstrong,

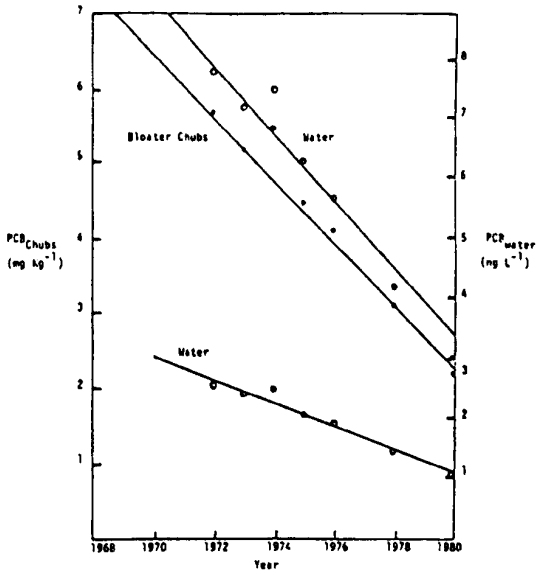


Figure 4. Estimation of historical PCB concentrations in water and sediment losses from trends of PCB levels in Lake Michigan bloater chubs, 1972-1980.

1981). If correct, this analysis shows that the PCB water burden is decreasing. There is no reason to suspect that this is not occurring for Lake Superior as well.

One measure of the response time of a lake to changing inputs/outputs of contaminants, and lifetime of chemicals is to consider residence times. Table 10 shows four different methods of estimating the PCB residence time in Lakes Superior and Michigan. The conventional calculation is to divide the water burden by the input or output rate. If the system is at steady-state, the residence times calculated by either method are equal because inputs equal outputs. The estimated residence time for PCBs in Lake Superior is between 2 and 7 yrs, while similar values for Lake Michigan are between 1.5 and 4 yrs. The residence time estimated by Eisenreich and Swain (1982) for

MONS 004851

TABLE 9

Estimating PCB Fluxes to the Sediments

Parameters	Lake Superior	Lake Michigan
v_s (m/yr)	120-150[a]	69-84[a]
C_{ss} (mg/l)	0.2	1.0
$C_{PCB,T}$ (ng/l)	1.0	2.0
K_p	10^6	2.5×10^5
A_s ($10^{10} m^2$)	8.2	5.8
$F_{PCB} = V_s C_d K_p A_s$		
Calculated F_{PCB} (kg/yr)[b]	1600-2000	1600-2000
Measured F_{PCB} (kg/yr)	1000-1600	2600[c]

[a]Bierman and Swain (1982)
[b]$F_{PCB} = V_s C_d K_p A_s$
[c]Weininger and Armstrong (1981)

DDT in Lake Michgian of about 1.7 yrs, and the 2.2 yrs estimated from data on bloater chubs given here agrees very well with the mass balance calculations. The PCB residence times of a few years are in sharp contrast to the water residence times of 100 (Lake Michigan) and 172 yrs (Lake Superior). The lakes apparently respond quite quickly to inputs of toxic, hydrophobic pollutants by removing them to the sediment. However, re-mobilization from sediments may maintain elevated concentrations in the biota for many decades.

ACKNOWLEDGMENTS

This research was supported in part by the U.S. Environmental Protection Agency under grants R805172-01 and R806084-01, and the Minnesota Sea Grant Program via an institutional grant to the University of Minnesota by the National Oceanic and Atmospheric Administration (Grant No. DOCNA81, AA-D00114). The cooperation, critical discussions, and assistance of M.R. Hoffman, B.B. Looney, P.D. Cape, G.J. Hollod, D.E. Armstrong, C. Rice, and A.W. Andren are greatly appreciated. The first author was a visiting professor at

MONS 004852

TABLE 10

Residence Time of PCBs in Lakes Superior and Michigan

Environmental Compartment	Residence Time	
	Lake Superior (yr)	Lake Michigan (yr)
Water Burden Input Rate	2.9-5.5	1.5[a]
Water Burden Output Rate	6.9	3.6[a]
DDT Decrease in Fish	2.0	1.7[b]
PCB Decrease in Chubs	--	2.2[c]
Water Volume Water Output	172	100

[a]Weininger and Armstrong (1981)
[b]Bierman and Swain (1982)
[c]Eisenreich et al. (1982a, 1982b)

the California Institute of Technology during the period of manuscript preparation, and special thanks are extended to Environmental Engineering Sciences and the Environmental Quality Laboratory.

LITERATURE CITED

Andren, A.W. 1983. Processes Determining the Flux of PCBs Across Air/Water Interfaces. In: D. Mackay, S. Paterson, S. Eisenreich, and M. Simmons (eds.), "Physical Behavior of PCBs in the Great Lakes," pp. 127-140. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Atlas, E.L. and C.S. Giam. 1981. Global Transport of Organic Pollutants: Ambient Concentrations in the Remote Marine Atmosphere. Science 211:163.

MONS 004853

Ballschmiter, K., M. Zell, and H.J. Neu. 1978. PCBs: Will They Never Degrade? Chemosphere 1:173.

Ballschmiter, K. and M. Zell. 1980. Baseline Studies of the Global Pollution. I. Occurrence of Organohalogens in Pristine European and Antarctic Aquatic Environments. Internat. J. Environ. Anal. Chem. 8:15-35.

Ballschmiter, K., H. Buchert, S. Bihler, and M. Zell. 1981. Baseline Studies of the Global Pollution. IV. The Pattern of Pollution by Organochlorine Compounds in the North Atlantic as Accumulated by Fish. Fresnius Z. Anal. Chem. 306:323-339.

Bidleman, T.F. and C.E. Olney. 1974. Chlorinated Hydrocarbons in the Sargasso Sea Atmosphere and Surface Water. Science 183:516-518.

Bierman, V.J., Jr. and W.R. Swain. 1982. Mass Balance Modeling of DDT Dynamics in Lakes Michigan and Superior. Environ. Sci. Tech. 16:572-579.

Capel, P. and S.J. Eisenreich. 1983. PCB Dynamics in Lake Superior Water. Areal, Vertical, and Temporal Distribution. Submitted for publication.

Chambers, R.L. and B.J. Eadie. 1981. Nepheloid and Suspended Particulate Matter in South-Eastern Lake Michigan. Sedimentology 28:439-447.

Connolly, J.P. and D.J. O'Connor. 1980. Effect of Concentration of Adsorbing Solids on the Partition Coefficient. Water Res. 14:1517.

Davis, A.R. 1981. The Canadian Network for Sampling Organic Compounds in Precipitation. Inland Waters Directorate, Ottawa, Canada.

Doskey, P.V. and A.W. Andren. 1981a. Concentrations of Airborne PCBs Over Lake Michigan. J. Great Lakes Res. 7:15-20.

Doskey, P.V. and A.W. Andren. 1981b. Modeling the Flux of Atmospheric PCBs Across the Air/Water Interface. Environ. Sci. Tech. 15:705-711.

Eisenreich, S.J., C.J. Hollod, and T.C. Johnson. 1979. Accumulation of PCBs in Surficial Lake Superior Sediments. Atmospheric Deposition. Environ. Sci. Tech. 13:569-573.

MONS 004854

Eisenreich, S.J., G.J. Hollod, T.C. Johnson, and J.E. Evans. 1980. PCB and Other Microcontaminant-Sediment Interactions in Lake Superior. In: R.A. Baker (ed.), "Contaminants and Sediments," pp. 67-94, Vol. 1, Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Eisenreich, S.J., G.J. Hollod, and T.C. Johnson. 1981a. Atmospheric Concentrations and Deposition of PCBs to Lake Superior. In: S.J. Eisenreich (ed.), "Atmospheric Pollutants in Natural Waters," Chapter 21, pp. 425-448, Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Eisenreich, S.J., B.B. Looney, and J.D. Thornton. 1981b. Airborne Organic Contaminants in the Great Lakes Ecosystem. Environ. Sci. Tech. 15:30-38.

Eisenreich, S.J., P.D. Capel, and B.B. Looney. 1983a. PCB Dynamics in Lake Superior Water. In: D. MacKay, S. Paterson, S. Eisenreich, and M. Simmons (eds.), "Physical Behavior of PCBs in the Great Lakes," pp. 181-211. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Eisenreich, S.J., B.B. Looney, and G.J. Hollod. 1983b. PCBs in the Lake Superior Atmosphere - 1978-1980. In: D. MacKay, S. Paterson, S. Eisenreich, and M. Simmons (eds.), "Physical Behavior of PCBs in the Great Lakes," pp. 115-125. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Evans, J.E., T.C. Johnson, E.C. Alexander, Jr., R.S. Lively, and S.J. Eisenreich. 1981. Sedimentation Rates and Depositional Processes in Lake Superior from ^{210}Pb Geochronology. J. Great Lakes Res. 7:299-310.

Frank, R., M. Holdrinet, H.E. Braun, R.L. Thomas, A.L.W. Kemp, and J.M. Jaquet. 1977. Organochlorine Insecticides and PCBs in Sediment of Lake St. Clair (1970 and 1974) and Lake Erie (1971). Sci. Total Environ. 8:205-227.

Frank, R., R.L. Thomas, M. Holdrinet, A.L.W. Kemp, and H.E. Braun. 1979a. Organochlorine Insecticides and PCB in Surficial Sediments (1968) and Sediment Cores (1976) from Lake Ontario. J. Great Lakes Res. 5:18-27.

Frank, R., R.L. Thomas, M. Holdrinet, A.L.W. Kemp, and R. Dawson. 1979b. Organochlorine Insecticides and PCB in the Sediments of Lake Huron (1969) and Georgian Bay and North Channel (1973). Sci. Total Environ. 13:101-117.

MONS 004855

Frank, R., M. Holdrinet, R.L. Braun, J. Rasper, and R. Dawson. 1980. Organochlorine Insecticides and PCB in Surficial Sediments of Lake Superior (1973). J. Great Lakes Res. 6:113-120.

Frank, R., M. Holdrinet, D.L. Gross, and T.T. Davies. 1981. Organochlorine Insecticides and PCB in Surficial Sediments of Lake Michigan (1975). J. Great Lakes Res. 7:42-50.

Frank, R. and H.E. Braun. 1981. Residues from Past Uses of Organochlorine Insecticides and PCB in Waters Draining Eleven Agricultural Watersheds in Southern Ontario, Canada, 1975-1977. Sci. Total Environ. 20:255-276.

Glooschenko, W.A., W.M.J. Strachan, and R.C.J. Sumpson. 1976. Distribution of Pesticides and PCBs in Water, Sediments, and Seston of the Upper Great Lakes - 1974. Pestic. Monit. J. 10:61-67.

Giam, C.S., E.L. Atlas, H.S. Chan, and G. Neff. 1980. Phthalate Esters, PCB, and DDT Residues in the Gulf of Mexico Atmosphere. Atmos. Environ. 14:65-69.

Hartig, J.H. 1981. Highlights of Water Quality and Pollution Control in Michigan. Department of Natural Resources, State of Michigan, Publication No. 4833-9804.

Harvey, G.R. and W.G. Steinhauer. 1974. Atmospheric Transport of PCBs to the North Atlantic. Atmos. Environ. 8:777-782.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Res. 13:241-248.

Konasewich, D., W. Traversey, and H. Zar. 1978. International Joint Commission, Water Quality Board, Appendix E, Windsor, Ontario, Canada.

MacKay, D., W.Y. Shiu, and R.P. Sutherland. 1979. Determination of Air-Water Henry's Law Constants for Hydrophobic Pollutants. Environ. Sci. Tech. 13:333-337.

MacKay, I. and A.T.K. Yuen. 1981. Transfer Rates of Gaseous Pollutants between the Atmosphere and Natural Waters. In: S.J. Eisenreich (ed.), "Atmospheric Pollutants in Natural Waters," Chapter 3, pp. 55-65, Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

MONS 004856

MacKay, D., W.Y. Shiu, J. Billington, and G.L. Huang. 1983. Physical-Chemical Properties and Behavior of PCBs. In: D. MacKay, S. Paterson, S. Eisenreich, and M. Simmons (eds.), "Physical Behavior of PCBs in the Great Lakes," pp. 59-69. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Murphy, T.J. and C.P. Rzeszutko. 1979. Precipitation Inputs of PCBs to Lake Michigan. J. Great Lakes Res. 3:305-312.

Murphy, T.J., A. Schinsky, G. Paolucci, and C.P. Rzeszutko. 1981. Inputs of PCBs from the Atmosphere to Lakes Huron and Michigan. In: S.J. Eisenreich (ed.), "Atmospheric Pollutants in Natural Waters," Chapter 22, pp. 445-458, Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Murphy, T.J., J.C. Pokojowczyk, and M.D. Mullin. 1983. Vapor Exchange of PCBs With Lake Michigan: The Atmosphere as a Sink for PCBs. In: D. MacKay, S. Paterson, S. Eisenreich, and M. Simmons (eds.), "Physical Behavior of PCBs in the Great Lakes," pp. 49-58. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

National Academy of Sciences (NAS). 1979. Polychlorinated Biphenyls. National Academy of Sciences, Washington, DC. 182 pp.

Nisbet, I.C.T. and A.F. Sarofim. 1972. Rates and Routes of Transport of PCBs in the Environment. Environ. Health Persped. 1:21-38.

O'Connor, D.J. and J.P. Connolly. 1980. The Effect of Concentration of Adsorbing Solids on the Partition Coefficient. Water Res. 14:1517.

Paris, D.F., W.C. Steen, and G.L. Baughman. 1978. Role of Physico-Chemical Properties of Aroclors 1016 and 1242 in Determining Their Fate and Transport in Aquatic Environments. Chemosphere 4:319-325.

Reinert, R.E. 1970. Pesticide Concentrations in Great Lakes Fish. Pest. Monit. J. 3:233-249.

Rice, C.P., B.J. Eadie, and K.M. Ersfeld. 1982. Enrichment of PCBs in Lake Michigan Surface Films. J. Great Lakes Res. 8:265-270.

Rogers, P.W. 1983. Model Simulation of PCB Dynamics in Lake Michigan. In: D. MacKay, S. Paterson, S. Eisenreich, and M. Simmons (eds.), "Physical Behavior of PCBs in the Great Lakes," pp. 311-327. Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

MONS 004857

Schacht, R.A.- 1974. Pesticides in the Illinois Waters of Lake Michigan. U.S. EPA, Ecol. Res. Ser., EPA 660/3-74-002.

Simmons, M.S., D.I. Bialosky, and R. Rossman. 1980. PCB Contamination in Surficial Sediments of Northeastern Lake Michigan. J. Great Lakes Res. 6:167-171.

Slinn, S.A. and W.G.N. Slinn. 1981. Modeling of Atmospheric Particulate Deposition to Natural Waters. In: S.J. Eisenreich (ed.), "Atmospheric Pollutants in Natural Waters," Chapter 2, pp. 23-53, Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Steen, W.C., D.F. Paris, and G.L. Baughman. 1978. Partitioning of Selected PCBs to Natural Sediments. Water Res. 12:655-657.

Strachan, W.M.J. and H. Huneault. 1979. PCBs and Organochlorine Pesticides in Great Lakes Precipitation. J. Great Lakes Res. 5:61-68.

Swain, W. 1978. Chlorinated Organic Residues in Fish, Water, and Precipitation from the Vicinity of Isle Royal, Lake Superior. J. Great Lakes Res. 4:398-407.

Thomann, R.V. and M.T. Koutaxis. 1981. Mathematical Modeling Estimates of Environmental Exposure Due to PCB-Contaminated Harbor Sediments of Waukegan Harbor and North Ditch. U.S. EPA, Ind. Env. Res. Lab., Cincinnati, OH, by Hydr Qual., Inc., Mahwah, NJ. 109 pp.

Weininger, D. and D.E. Armstrong. 1981. Organic Contaminants in the Great Lakes. In: "Restoration of Lakes and Inland Waters," pp. 364-372, EPA 440/5-81-010.

Veith, G.D., D.W. Kuehl, F.A. Puglisi, G.E. Glass, and J.G. Eaton. 1977. Residues of PCBs and DDT in the Western Lake Superior Ecosystem. Arch. Envir. Cont. Toxic. 5:587-599.

Zell, M. and K. Ballschmiter. 1980. Baseline Studies of the Global Pollution. III. Trace Analysis of PCBs by ECD Glass Capillary Gas Chromatography in Environmental Samples of Different Trophic Levels. Fresnius Z. Anal. Chem. 304:337-349.

MONS 004858

CHAPTER 5

REGULATORY CONSIDERATIONS REGARDING LIMITING HUMAN EXPOSURES TO PCBs

Albert C. Kolbye, Jr., M.D., J.D., M.P.H.
Nutrient Foundation
Washington, D.C.

INTRODUCTION

Back in 1969, I was associated with the Mrak Commission on Pesticides and Their Relationship to Environmental Health (HEW, 1969); and, of course, the focus there was on the chlorinated hydrocarbons that were being used as pesticides, mainly DDT. At the time, we were facing some very serious questions about the benefits of chemicals in the service of man as compared to the deleterious effects of chemicals on the environment. As many of you know who waded through some or all of the Mrak Commission report, the main emphasis and degree of concern with those chemicals was not really the health of man. The main emphasis was on protecting the ecology against the various effects that these biopersistent compounds could have. Well, about that time, when we were focusing on DDT, we began to hear the term, or at least I began to hear the term, polychlorinated biphenyls (PCBs), and I wondered what they were. There was a stray report here or there in 1969 and there was a beginning awareness of an accident in Japan. As I left the Mrak Commission and joined the Food and Drug Administration (FDA) in February of 1970, it became evident that we were going to have to familiarize ourselves with whatever these chemicals were that were called PCBs, because the more we looked in foods the more residues we found. I think most of us are familiar with the history and the purpose of these compounds, so I won't dwell on these in great detail, except to say that by the time the federal agencies had a beginning awareness of the nature

---

Formerly: Associate Bureau Director for Toxicology, Bureau of Foods, Food and Drug Administration, Washington, D.C.

appreciate that we were starting "behind the curve". It's questionable in a situation like this whether you can catch up fast enough so that you can get on top of the curve and start controlling human exposure. Now I won't necessarily say that I am happy to be back in Michigan because there were many tensions and frustrations directed at the FDA on several problems, not the least of which was polybrominated biphenyls. Again, we were behind the curve on that problem, not because the FDA was slow, but because a chemical got loose in the environment and contaminated the food supply. Staying with PCBs, the main problem that we found was similar to the problem in Japan: besides all of the open ended uses of the compounds, the stuff was being used in heat exchangers used for food processing. And that, of course, was the cause of the Yusho incident.

EPIDEMIOLOGY: YUSHO

I would like to briefly describe the information that became available to us in the early 1970s as we dealt with Yusho to give you a feel for the kinds of information that were available and an appreciation of some of the considerations; and then I will gradually lead you into the regulatory perspective. First, the information concerning these contaminants in the rice oil was pretty iffy. From our calulations, the oil contained about 2,000 mg/kg of PCB compounds. We knew that it was a mess because there were other things in there: chlorinated naphthalene derivatives and, as was later appreciated, also chlorinated dibenzofurans. In addition, there were other chlorinated complex structures that later were identified as quaterphenyls. But initially, all we could really get a handle on was the chlorinated biphenyl series of compounds. On reviewing the exposure in Yusho, you could make a few simplifications in order to deal with the problem a little bit further. You would estimate that the duration of exposure that led to chronically obvious illness in the Yusho incident was about 100 days. Based on this, you calculate that it took about 2,000 mg in adults before the appearance of the disease. With regard to, I think it was about an 8 yr old boy, we figured that it took about 500 mg exposure before the appearance of overt disease. We didn't know what a no-effect level was because as we looked at the data provided by the Japanese, we found the data were not of the quality of a good classical, prospective epidemiological study. The data were from a retrospective study, "catch as catch can," and the Japanese did the best they could.

TOXICOLOGICAL DATA

Looking at animal data, we attempted to determine the pattern of what happened in animals exposed to various PCBs and we attempted to find levels that were associated with no adverse effects. I suppose it is important to repeat and to keep clear in our mind that every compound is toxic at some level. And with few exceptions, the converse should be true: that every compound is not toxic at some level. But the kinds of problems posed by PCBs have turned out over the years to be a little more extraordinary than we thought they were at the time. In terms of the animal data, one could see fairly obvious effects in rodents at 100 mg/kg in the diet. At around the 10 mg/kg level in the diet, according to the information we had then, was the no-adverse effect level. In between these two levels, you had an increase in probability of picking up metabolic disturbances due to the enzyme induction and inhibition powers, if you will, of these chemicals. And if we did some calculations based on a no-adverse effect of 10 mg/kg using the more classical rules for dealing with food additive and 100-fold safety, we came up with an acceptable daily intake roughly of 150 ug/person/day for an adult.

TOLERABLE DAILY INTAKE

As we looked at the Yusho data, coming back to the humans, we thought we had every reason to believe that this stuff has a long biological half-life, but we did not know how long. And we did not know what a no-effect level was in humans. We wondered if there were some way that we could approximate a 100-fold safety rule to see where we would come out. When you are dealing with a situation of widespread environmental contamination by a biopersistent compound, you have to think down the road a little bit because nobody has a magical wand to wave so that these residues immediately disappear from the food supply. In contradistinction to a food additive (where your recourse is simply not to permit the intentional or negligent addition of a compound into food while it is being processed), when you are dealing with an environmental contaminant in many food products, your only recourse is not to permit the ingestion of particular products as food. Looking at the Yusho data, we thought, what happens if we take one-tenth of the level that is associated with overt disease in adults and spread that over a ten times greater time period to provide some coverage for the unknown biopersistence of this compound. A tenth of the 2,000 mg is 200 mg; and if you spread that over 1,000 days, which is about 3 yrs, you come up with a 200 ug/adult/day type of exposure. That wasn't very far from the 150 ug/adult that was calculated from the more or less

classical approaches using rodent data. In effect, that's what we did.

REGULATORY PERSPECTIVE

Back in those days we were besieged, bothered, and bewildered because every place we looked we were bumping up against these residues. Just to refresh your memory, they were found in paper used as food packaging. They were found in fish, of course. They were found in fish meal that was being used for poultry feed. There was leakage from heat exchangers that had been using PCBs, and so we had several major incidents involving contamination of poultry and eggs. Then we began to look in milk and milk products and we found that the PCBs had been used as silo coatings and that they would flake off in the silage and contaminate dairy products. In reality, we did our best to try to prevent human consumption of as much of these contaminated food products as we felt we reasonably could. We could not turn off the food supply. We had to come to a level based on a particular food commodity, a level where we would decide that we were going to get tough. So what we did in the early 1970s was to set up a series of what we tried to clearly state as temporary action levels, or guidelines, or whatever you want to call them. The resources of the FDA were expended nationwide and internationally going after food, doing a lot of sampling, and taking food products off the market if they were above our action level and also in interstate commerce.

FACTORS REGARDING HUMAN EXPOSURE

The problem that anybody concerned with protecting public health from chemicals in food faces boils down to several questions. What levels of the residues are actually occurring in a food commodity? The answer is going to be a frequency distribution of data, because all food is not equally contaminated. Then comes the question of what is a typical serving size of that food. Again you are up against a frequency distribution curve. The third question is how frequently people eat that volume of product contaminated with X level of residue. So you are dealing with another probability curve. Believe me, that gets very complex. You have to look at your data, and all other available data, and then you have to make a decision which you may have a little difficulty defining as the right decision. The decision is difficult because you are dealing with a spectrum of considerations; and if you go too high on the spectrum, you may over react to the problem. So in terms of interstate commerce, we made some assumptions and set out action levels as I indicated earlier, and we enforced them.

MONS 004862

SPORADIC VERSUS SYSTEMATIC EXPOSURES

If one looks at the United States from the viewpoint of the FDA, one looks at a variety of regional and ethnic eating habits; but one usually can count on most people getting food from a store of some kind. Much of the food that they buy in the store comes from various parts of the country at various times so the probability of a systematic human exposure is usually limited, unless a particular purchaser has a brand preference and that particular brand of product is always made from certain sources. However, if one talks about sport fishing people who go to a particular lake or stream, and consistently fish that particular area, and those fish are consistently contaminated, and they eat those fish frequently, quite obviously they are getting a very systematic exposure. So from one extreme of the nationwide probability that you are not getting a systematic exposure, you go to the other extreme of the sport fishing family frequently ingesting a highly contaminated product. In between there are certain considerations which deal with intrastate commerce, for which the state authorities have the authority and for which we in FDA only try to render advice when it is appropriate; we try to do that also if asked with respect to the problems associated with sport fishing people.

As I look back on the approach that was taken by FDA in the early 1970s, I've been reasonably well satisfied with the rather substantial decrease in PCB residues in most foods. That part of it is a success story; not perfect, but very substantial progress was made. The fish situation over the past decade has, of course, not been ameliorated nearly as much. We have had in some localities systemtic human exposure progressing over time. I guess it was around 1974 when I heard people in a sister agency criticizing me because they felt I was too tough on PCBs; then I found out that they were permitting pollution of receiving bodies of water by PCBs leading to levels of up to 5 mg/kg in the edible portion of the fish. I couldn't believe it. That sister agency changed its attitude and started turning off the faucet a little bit more aggressively with respect to PCBs as effluents in the receiving bodies of water such as the Great Lakes. That was a surprise which I am not sure many of you are fully cognizant of and I am not assigning blame to anybody, but it did happen. Because the efforts to cut off the PCB effluents were not as aggressive as they should have been, the data that you saw earlier today on fish might have looked even brighter, had these efforts been undertaken earlier in time. Just as it is difficult sometimes for the various agencies within a state to get their act together, it happens in Washington, D.C., too.

MONS 004863

CHEMICAL AND BIOLOGICAL CONSIDERATIONS

We know that many PCBs have a long biological half-life, especially the higher chlorinated isomers. Conversely, we know that the lower chlorinated isomers have far greater acute toxicity. We know that many compounds will inhibit or induce enzymes, including many natural substances in our diet; but the difference is that most of those natural substances in our diet have relatively short biological half-lives.

In dealing with PCBs, it is important to get a good approximation of which PCB isomers humans are actually getting exposed to. For example, it doesn't make much sense to study Arochlor 1248 if the residue pattern that is occurring in fish is an approximation of a mixture of Arochlor 1254 and 1260. The reason is that 1248 has a tremendously high percentage of the lower chlorinated isomers as compared to 1254 or 1260 and so you are dealing with substantially different spectrums of toxicity than what the humans of concern are ingesting. Probably none of us has a very accurate idea of what really did cause Yusho because we had a "glop" there, if I may use that term, a real mess. We had the chlorinated naphthalenes; we had the PCBs; the quaterphenyls; the dibenzofurans; and for all I know, some other stuff. This type of incident, unfortunately, has been repeated from time to time with similar effects, notably in Taiwan. But in this country I haven't heard of any appreciable presence of quaterphenyls in foods and I haven't heard of any appreciable presence of dibenzofurans in fish, per se, that I would call a substantial problem. A lot also depends on which dibenzofurans we are talking about, as it depends, in similar fashion, on which dioxin we are talking about if the subject of this meeting was dioxins.

The reproductive work that was done by Jim Allen using Arochlor 1248 on rhesus monkeys that caused such a tremendous national uproar, where people were politicking to ban all breast feeding of babies, was something that I felt was inappropriate and not fully relevant to the human situation. I would ask any of you who are dealing with monkeys, or are considering data from non-human primates, to remember that there is a very substantial difference between the rhesus monkey and certain other monkeys like the chimp; some of these differences deal with the fundamental sensitivity and feedback of the pituitary circuit and estrogen, estradiol, etc. It will take additional research using different monkeys using a mixture of 1254 and 1260 to get a better handle on what's really happening with pregnant monkeys. If you want to find out what's really happening with the fetus, expose the mother monkey but don't intoxicate the mother monkey; don't poison her, because if you poison any pregnant animal, you're going to have problems with

the offspring. The real clue is to approach this study with what I call a sub-toxic approach in the maternal animals.

That ends this part of the talk. You'll notice that I have not yet spoken about the cancer risk factors. What I don't want us to lose sight of, aside from the human considerations, is that we have some real concerns with the ecology and with some very fundamental aspects of the biology of reproduction, not only with humans, but with just about all other forms of animal life.

FUNDAMENTALS OF CHEMICAL CARCINOGENESIS

I'd like to go back to some fundamentals. This formula, I equals V/R (or a function of V/R), reflects a very simple fundamental: that the incidence of a disease is a reflection of both the challenge (V) to and the biological resistance (R) of that human, or any animal, to the disease. The same is true for cancer. There can be an increase in the incidence of a disease, either by an absolute increase in V or by a decrease in R, or both. In my judgment, very few people really think about this relationship.

Table 1 gives a shorthand version of classical carcinogenesis theory: if there are initiated cells, those cells have to be promoted by some process if cancer is going to result. The process of tumor promotion, and I am using the term somewhat broadly, can be effected by classical tumor promoters or by other forms of toxicity which approximate the adverse biological effects associated with tumor promoters. The process involves a selective pressure on cell reproduction over a considerable period of time in order to complete the promotion phase. And, it usually requires substantial dosing that is performed consistently. Said differently, if you interrupt the substantial dosing before the critical effect of promotion actually is attained, there is either an arrest or, in many cases, a substantial degree of reversibility of the so-called promotion process.

The term potentiator in Table 2 is used in almost a mathematical sense to reflect enhancement of the I in the I equals V/R relationship. If you have a compound which increases the activation of electrophiles, and those electrophiles are carcinogenic initiators, you will enhance the risk of cancer. Classical promoters under certain circumstances enhance the risk for cancer by a different mechanism. If you chop out part of the liver of an experimental animal, you will have an effect similar to tumor promotion. If you intoxicate that liver, you will also have an effect similar to promotion. Suc.

TABLE 1

Shorthand Version of Classical Carcinogenesis Theory

NORMAL MODE		
DNR in Normal Cell	Normal Replication - - - - - - - - - - - Normal Repair	Replicated DNA Replicated Normal Cells
CARCINOGENESIS		
Critically Damage DNA (Genotoxicity)	Abnormal Replication - - - - - - - - - - - Abnormal Repair	Initiated Cells (Potential for Malignant Transformation)
Initiated Cells	Promotion or - - - - - - - - - - - Toxic Hyperplasia Selective Pressure Through Succeeding Generations of Cell Line	Cancer (Malignant Characteristics)

intoxication can occur by poisoning various defense mechanisms or it can occur by a hyperplastic-like process, or by both. Under certain conditions, many other factors, including hormones, can enhance the risk of cancer. Nutritional aberrations, such as a deficiency of vitamin A, can have a powerful ultimate effect on risk, as can a very high level of unsaturated fatty acids in the diet. I am just trying to give you some perspective here.

Table 3 shows some of the changes that have been associated with classical promoters, and what I want you to take home is that there are many forms of toxicity that can be caused by a variety of compounds, some of which do not fulfill all the criteria for classical promoters. Figure 1 is just a different way of looking at this, but I want to draw your attention to the histones because they act to protect mammalian DNA, along

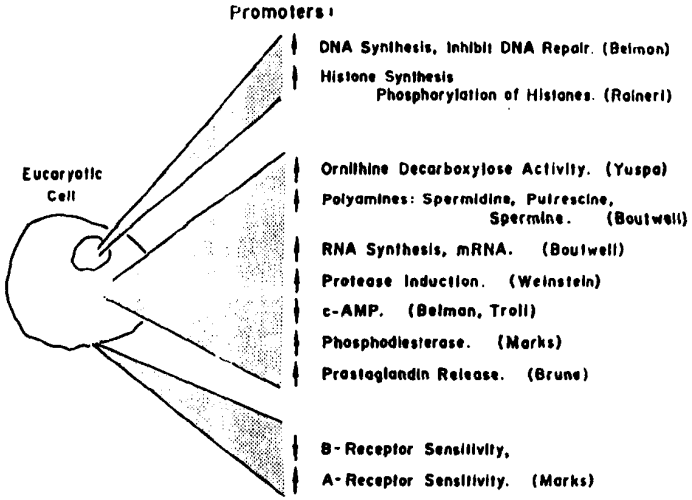


Figure 1. Factors influencing and/or influended by promotion.

MONS 004867

TABLE 2

Carcinogenic Sequence

Chemical Precursor	Activation	Electrophilic Carcinogen
Electrpohile and DNR		Damaged DNR
DNA Damage	Normal Repair and Replication	None or Some Initiated Cells
DNA Damage	Abnormal Repair and Replication	More Initiated Cells
Initiated Cells	Abnormal Replica-Through Many Cells Cycles	Malignant Cells
	Repetitive Exposure to Promoters or Agents Which Cause Toxic Hyperplasia	

with other nucleoproteins. The list of promoters on Table 4 is not perfect and I should have labeled it indirect carcinogens, but the word promoter in the broad sense will do. I include PCBs more in a category of a promoting-like compound than an initiating-type of carcinogen. As you study the effects in liver when you apply promoters (and please remember that the liver is an organ that has cells initiated independently, probably from many sources, not the least of which may be endogenous nitrosamines from the intestinal tract), you can follow the progression of critical lesions by looking for enzyme-altered foci. If human beings showed such effects, then they would be entering what I would call a substantial zone of risk: but in order to get this kind of a risk, you need that

TABLE 3

Promoter Induced Cellular Changes

Altered Surface Tension	↑Deacylation of Cellular Lipids
↓Lipid Microviscosity	↑Prostaglandins
↓In Cell Surface Charge	↑m-RNA Activity
Loss of Contact Inhibition	↑Protease
↓Chalone Responsiveness	↑Polymorphonuclear Leukocyte Degranulation
↓B - Receptors	Stimulates T-Cell
Inhibits Binding of Epidermal Growth Factor	↑Ornithine Decarboxylase
↓Na^+ · K^+ ATPase	↑Putrescine Levels
↓Mg^{++} · Ca^{++} ATPase	↑Protein Production
↑Phosphodiesterase Synthesis	γ - Glutamyl Transpeptidase
↓c - AMP	↑DNA Synthesis
↑c - GMP	↑Histone Phosphorylation and Synthesis
↑Uptake of Hypoxanthine	Stimulates Synthesis of 2 New Proteins
↑Uptake of Choline	↑5' Nucleotidase
↓Glucose-6-Phosphate	Inhibition of DNA at Endonuclease Step
↑Phospholipids	↑Levels of Sister Chromatid Exchange
↑Arachidonic Acid Metabolism	↓Histidase

TABLE 4

General List of Promoters

Deoxycholate	Lithocholic Acid
Sodium Chloride	Glucose
Ethanol	Cholesterol
Saccharin	Tryptophan
Sodium Oleates	Fatty Acid Esters:
Citrus Oil	Oleic Acid
Sodium Cyclamate	Lauric Acid
Vitamine A-Palmitate	Retinyl Acetate
Caffeine	High Fat Diet
High Meat Diet	Catechols
BHT	Surface Agents
Sulphur Dioxide	Tweens
Paraffin	Spans
Glass	Carbon Tetrachloride (CCl_4)
Iodoacetic Acid	Anthralin 2-Naphthylamine
DDT	(Trichloro-2 Propene Oxide)
Hydroquinones	TCPO
Asbestos	($ChCl_3$) Methyl Chloride
Dieldrin	Thioacetamide
Thiourea	3-Aminotriazole
Linear Alkanes (10,12,14-C)	PVP
Iron Dextran	Phenobarbital
Chloroform	Phorbol Esters:
Diterpenes:	Croton Oil
Tigliane	TPA
Ingenane	PMA
Daphnane	Sodium Laurel Sulfate
Aluminum Hydroxide	Cholestyramine
PCB	Prolactin
Pyrilamine Maleate	Hormones
Injury	

which I mentioned: substantial, consistent, and repetitive dosing.

CONCLUSIONS

What I am trying to say is that the ordinary human in the United States is probably in pretty good shape. For low exposure, and for infrequent or inconsistent exposures to PCBs,

I don't think that there is any need to get excited or to have any fear. At the other end of the spectrum, there are people who may be getting very substantial repeated exposures to PCBs; here I am again talking about sport fishing people. An action level doesn't apply to them in the legal sense. To the best of my knowledge, some of the people who have had substantial, repetitive exposures to PCBs do show some changes in enzymes like the gamma-glutamyltranspeptidase, which can also be influenced by many other factors such as alcohol intake. I think people who are getting high, repeated exposures to PCBs should have some sort of medical follow-up. If their serum enzyme levels indicate problems, I think somebody ought to tell them to live a little differently (i.e., reduce exposure to PCBs and alcohol, etc.), because there may be a secondary promotional-like process underway. I do not think that PCBs should be treated like primary carcinogens.

CHAPTER 6

RESPONDING TO PUBLIC CONCERN OVER ENVIRONMENTAL POLLUTION HAZARDS

Willard M. J. Baird
Lansing Bureau Chief, Retired
Gannett News Service
Lake City, Michigan 49651

Many in this audience probably remember a phase in our recent history when scarcely a week went by without a news report of a laboratory discovery somewhere that another product or substance might cause cancer or some other human affliction. The theme became so repetitive we began to hear it said, half-seriously, "Everything causes cancer." As in the story of the boy who cried "Wolf!" once too often, I fear the dismal warnings we were then hearing began to lose some of their urgency. Not because the wolf wasn't there, but because people came to fear there were so many wolves lurking around us that there was really no chance of escape. Our environment and our food supply, so it seemed, were laced with a great variety of alien substances which could imperil our health and more of these hazards were being identified with alarming frequency.

The steady flow of these reports of ominous laboratory findings portending an adverse impact, immediate or potential, on human health appear to have occasioned misunderstanding and confusion in the public mind about the exact meaning and significance of the findings. With so many potential health perils reportedly threatening us, it is readily understandable why some people may have concluded they have stumbled into an environmental trap from which they cannot break loose. We hear them say: Why get excited? Why worry?

Perhaps, if you are a research specialist or a government administrator working day by day on matters involving pollution of the environment, you may have occasionally experienced a sense of dismay because the public doesn't seem to take your

MONS 004872

work or your warnings seriously. If you happen to feel that way, that would be understandable, too. But perhaps an obvious reminder is in order: Because the experts know, it doesn't follow that everyone knows the danger or appreciates the extent of a particular type of contamination or exposure.

It may also be well to remember that all of us are continually buffeted by a variety of relentless pressures and demands competing for our attention and our concern. Is it realistic to expect each individual to become intensely alarmed about every threat to his health and every assault on the environment that he hears about? If so, I fear we would soon become prime candidates for psychiatric attention. And if not, then each of us must devise a personal scale of priorities for our individual concerns and fears.

But let us not forget a basic rule of behavioral psychology--the one that says a squeaking wheel gets the grease. Popular attention can and will be focused on whatever topics are dominant at the time in the news media. In fact, the degree of media attention a given topic may arouse can be a powerful factor in shaping our own reaction and determining where that particular subject fits in our personal scale of priorities.

PCB POLLUTION OF THE GREAT LAKES

We are concerned at this symposium with environmental pollution hazards associated with polychlorinated biphenyls (PCBs) in the Great Lakes. Are most of the people residing in Michigan and in other Great Lakes states and provinces concerned? I would like to think the answer is, "Yes, to some extent--some more so than others, of course." But are they deeply worried at this time about PCBs in the Great Lakes? I doubt it. Should they be? I don't know. Others at this symposium may be able to tell us whether we should be mildly concerned or greatly alarmed, or something in between.

But if the public should be genuinely disturbed, or perhaps even fearful, then the public is entitled to straight talk on the issue from responsible and reliable sources. A well-informed people given reliable information can be expected to react positively and responsibly in their own best interest to the efforts of official agencies to bring a serious environmental hazard under control.

I will not go into the techniques for mobilizing that kind of public response at this time because this is not the appropriate forum for that discussion. But the agencies of govern-

ment, as well as the universities and others in the arena of social and political action, know there are ways of developing public support for goals which are broadly perceived as worthwhile and desirable.

PUBLIC CONCERN OVER PCBs IN THE GREAT LAKES BASIN

To the people from regulatory agencies and to the scientists and researchers in our midst who may feel frustrated by what appears to be a low level of public awareness or concern about PCBs in the Great Lakes basin, may I suggest let's pause for a moment to review the situation. If you believe there is inadequate public recognition and support for your work, is anything to be gained by blaming other people for being confused or indifferent, given the bewildering array of warnings, demands, restrictions, and requirements all of us face?

What is needed, I suggest, is a carefully drawn definition of the problem as the experts see it and reflecting their consensus and a clearcut statement of needed remedial or protective action. In the course of taking those two steps, it can be reasonably determined what types and levels of public involvement are advisable and the means of generating popular support.

The initiative should come, as I see it, from the appropriate official agencies. But if for some reason they cannot or do not act, it is likely that aroused citizen groups will assert leadership at least until government finally accepts responsibility. Supportive resources will be found in educational institutions, in social and political action organizations, and in the field of communications.

I am convinced the public will listen when you have something to say that needs to be said; and when it is said clearly enough, to be readily understood.

PCB CONTAMINATION OF GREAT LAKES FISHES

In 1969, we are told, PCB contamination was found in Great Lakes fish; more so in Lake Michigan than in any of the other Great Lakes, and more so in the southern part of Lake Michigan than in the upper part (Humphrey, 1975; NRC, 1975). The latter observation regarding contamination in southern Lake Michigan cannot be said to be surprising considering the heavily industrialized and urbanized regions of Michigan, Indiana, Illinois, and Wisconsin adjoining the southern portion of that lake.

After discovery of the contamination, the official agencies recognized a possible threat to health among those people, sports fishermen and their families in particular, who were eating trout and salmon and some of the other species of fish taken from Lake Michigan (MDPH, 1971). If the health of sports fishermen alone were the only concern, it would be cause enough for responsive government action. But isn't there more to be considered?

What assurance can be offered about the quality and purity of water taken from the Great Lakes, and from Lake Michigan especially, when that water is used for community water supplies, for agricultural irrigation, for domestic and commercial food processing and canning, and for other types of industrial processing?

What is the impact, now and for the future, of PCB contamination on the commercial fishing industry in the Great Lakes region and on the workers and their families who rely on that industry for their livelihood?

Are we concerned about the possibility of an adverse impact on the tourist industry of the Great Lakes region?

And what may be the effect eventually on government resources and government costs in providing health protection, health care services, pure food protection, and the regulatory controls and mechanisms for monitoring or preventing environmental hazards (McCracken, 1982; MDA, 1981; Walker, 1981)?

As these questions come to mind, responding to them on the basis of information shared with the public up to this point may lead us to feel there is no cause for great alarm. If for some reason PCBs in Great Lakes waters are seen as a serious menace in the future, however, they may easily become a highly disturbing factor in the lives of countless people throughout the Great Lakes basin.

RESPONDING TO PUBLIC CONCERN

In responding to public concern about the hazards of environmental pollution, it would seem almost axiomatic that we must know, more or less specifically, what the public is concerned about. Similarly, if we are dealing with a situation in which, to our dismay, the public appears to be apathetic and unconcerned, we may want to know why.

MONS 004875

In either case, the answer, in oversimplified terms, is two-fold: ask and listen.

To discover the degree of public awareness about an issue or the tone of public reaction to that issue, a good approach is to ask. There are numerous techniques available for doing so, including questionaires and neighborhood canvassing. If no other means are at hand, or as a supplemental device, you might try a public opinion survey conducted by a qualified and reputable polling organization.

Or, you might wish to develop a system for listening to what the public is saying about a given topic. How? By routinely noting the essence of complaints, questions, or suggestions reaching your agency in letters and telephone calls relating to the topic under consideration; or by observing the frequency and content of news media attention to the subject; or by noting the points of view expressed in published editorials and letters to the editor; or by noting attitudes expressed and positions taken by citizen groups, adversary organizations, and political leaders. Regional and district field offices of government departments could be asked for periodic summaries of their perception of citizen interest and attitudes in their area as an indication of public awareness and concern about the given topic.

I am not suggesting for a moment that anyone in a position of official responsibility should react spontaneously to every straw fluttering in the wind. I do suggest that a responsible administrator should have the full benefit of his agency's observations and perceptions of public attitude and concern when evaluating alternative courses of action, and perhaps also when he is considering the possibility of altering a plan or compromising on a procedural approach to avoid counter-productive controversy.

May I point out, too, that if some of the comments and complaints voiced by the public reveal their authors are poorly informed or arriving at ill-advised judgments, no benefit results from dismissing these points of view out of hand. Rather, it could be productive to interpret them as an indication of the educational challenge which needs to be faced and of the communications job which has to be done. This is all the more important, I believe, when government agencies are about to impose restrictions or prohibitions and need broad acceptance and compliance to achieve effective results.

MONS 004876

PBB OPINION RESEARCH

A few years ago, in the midst of the polybrominated biphenyl (PBB) exposure incident we were then experiencing in Michigan, I was associated with the Michigan Department of Public Health (MDPH) for several months as a communications consultant. The department was then preparing to undertake a statewide study to determine the extent and degree of exposure to PBB among Michigan residents and to search for demonstrable links between exposure and its effect on human health. As organized by the MDPH with federal and state funding, one of the major components of the study was to be conducted by medical researchers from Mt. Sinai School of Medicine in New York and another by the School of Public Health, with the assistance of the Survey Research Center of the University of Michigan. Results of the work of both groups were to be monitored by the Wayne State University School of Medicine.

Before proceeding with a study of that magnitude and cost, the MDPH wished to be certain that a sufficient number of people in all parts of the state would willingly participate in it if asked. It so happened that Market Opinion Research (MOR), a Detroit polling organization, was about to conduct one of its quarterly surveys of Michigan residents. Arrangements were made to have 10 questions relating to the PBB situation included in the MOR survey. The responses were reassuring and yet in some respects surprising. MOR's survey report indicated that it had indeed been worthwhile to ask people what they knew or thought about the matter (MOR, 1978).

The MOR cross sectional statewide survey was conducted over a two week period in December of 1977 by telephone interviewers who questioned 800 adult respondents selected by the polling organization to provide a statistically valid sampling of the Michigan population. The reported results were said by MOR to be subject to possible error of plus-or-minus three percentage points. Here are some of the results of that survey:

To the first question: How concerned would you say you are about food additives, preservatives, or contaminants in your food?

--47 percent said they were very concerned;
--28 percent said they were somewhat concerned;
--25 percent said they weren't concerned at all or didn't know.

Note that 75 percent of the respondents were sufficiently aware of the matter to express concern, and nearly half were "very concerned". Moreover, younger people showed greater

concern about the matter than older people. Of the respondents in the 18 to 24 age group, 86 percent expressed concern compared to 70 percent or less in older age brackets.

Among the respondents expressing concern, 44 percent mentioned food additives, 32 percent mentioned PBB, and 2 percent mentioned PCB (identified in the MOR report as PCP). Both PBB and health perils associated with food additives had been prominently in the news shortly before the MOR survey was taken; PCB had not. Even so, we can see some awareness of PCBs indicated in that sampling despite the absence of current news media emphasis. Interestingly, too, the greatest awareness of PCBs was evidenced in the age group of 25 to 44, although the percentage was small (4%).

Responding to another question, some 35 percent of those interviewed (or more than a third) feared that food additives, preservatives, and contaminants can cause cancer, while 27 percent feared they could cause other health problems.

Among all the persons contacted and questioned in the survey, 48 percent thought they had some of these substances in their bodies, including 29 percent who thought they had PBB. It may be pertinent at this point to note that at the conclusion of the General Population Study, the Mt. Sinai School of Medicine researchers reported that 70 percent of Michigan's population had levels of PBB of more than 0.3 ug/kg in their blood, including 11 percent with more than 3 ug/kg (Selikoff and Anderson, 1979). In other words, the breadth of exposure was much greater than most Michigan residents had thought.

And finally, nearly 52 percent of those who were questioned said that if selected as part of a random sample of Michigan residents to study the effects of PBB on the general population, they would be willing to participate. Interestingly, among the respondents who felt they had PBB in their bodies, 93 percent said they were willing to participate in a general population health study.

Subsequently, the PBB General Population Study was conducted with adequate numbers of Michigan residents willingly taking part--7,711 questioned in two random sample telephone surveys conducted by the University of Michigan School of Public Health, and 1,738 individuals examined by the Mt. Sinai medical research team at six clinics throughout the state (UMSPH, 1979; Selikoff and Anderson, 1979). I mention the PBB polling survey by way of indicating what can be learned about public attitudes and reactions when using that technique.

CONCLUSION

If anyone at this symposium is interested at this time in involving the public to a greater extent in dealing with the matter of PCBs in the Great Lakes, I would suggest as one approach that you first try to determine what the public may already know about the subject and what concerns there may be in the popular mind, if any at all, about PCBs. Then, having asked and listened, you may be better prepared to proceed with your plans. And if there is still a question in your mind about what the public can do, or what you might wish people would do, go public with the story and tell all of us what needs to be done.

ACKNOWLEDGMENT

The assistance of Theodore R. Ervin, John L. Hesse, and Dr. Harold Humphrey of the Michigan Department of Public Health in providing reports and other background material on PCBs in the Michigan environment is gratefully acknowledged.

LITERATURE CITED

Humphrey, H.E.B. 1975. Evaluation of Changes of the Level of Polychlorinated Biphenyls (PCB) in Human Tissue. Final Report on FDA Contract 223-73-2209, Michigan Department of Public Health, Lansing, MI.

MOR. 1978. Data From Survey on Food Additives and Contaminants Collected as a Supplement to Market Opinion Research (MOR) Quarterly Survey. Report to Michigan Department of Public Health, Market Opinion Research, Detroit, MI.

McCracken, W.E. 1982. Economic Impacts of Lowering the Allowable Level of PCBs in Commercial Fish. Michigan Department of Natural Resources (interoffice communication), Lansing, MI.

MDA. 1981. PCB in Fish. Michigan Department of Agriculture (MDA), Lansing, MI.

NRC. 1975. PCB Use in Michigan. Policy Statement of Michigan Natural Resources Commission (NRC), Lansing, MI.

MDPH. 1971. News release of September 30, 1971, and periodic advisory notices issued subsequently regarding PCBs and other contaminants in fish taken from Michigan waters, including "Material for 1982 Fishing Law Digest". Michigan Department of Public Health (MDPH), Lansing, MI.

MDNS 004879

Selikoff, I.J. and H.A. Anderson. 1979. A Survey of the General Population of Michigan for Health Effects of PBB Exposure. Final Report-Summary to Michigan Department of Public Health, Environmental Sciences Laboratory, Mt. Sinai School of Medicine of The City University of New York, New York, NY.

UMSPH. 1979. Overall Summary of University of Michigan School of Public Health PBB Investigations. Report to Michigan Department of Public Health, Ann Arbor, MI.

Walker, B., Jr. 1981. Health/Medical Support for a Reduced PCB Guideline in Fish. Michigan Department of Public Health memorandum to the Governor, Lansing, MI.

MONS 004880

CHAPTER 7

THE ENVIRONMENTALIST'S VIEW OF THE PCBs PROBLEM IN THE GREAT LAKES

Thomas L. Washington
Executive Director
Michigan United Conservation Clubs
P. O. Box 30235
Lansing, Michigan 48909

INTRODUCTION

It is my pleasure to address you as part of this International Symposium on PCBs in the Great Lakes. I bring to this program the non-scientific perspective of a layman and the concerns of the people I represent through the Michigan United Conservation Clubs (MUCC)--the sports anglers and their families of Michigan.

We welcome this symposium. It is my hope that the questions I bring you today will be answered through this meeting or through new initiatives which come out of these deliberations. We are rapidly coming to the realization that the future of quality recreational fishing rests on our ability to safely manage chemical discharges to air and waters of the Great Lakes Basin.

MUCC AND PCBs

The interest of our organization in water quality problems actually dates back to our founding in 1937. MUCC now represents over 100,000 members and 400 affiliated organizations. Nearly all our members (95%) are anglers and half fish the Great Lakes. Since we know there is a direct relationship between the quantity of Great Lakes fish eaten and the polychlorinated biphenyl (PCB) levels found in human blood (Humphrey, n.d.), our interest is obvious.

MONS 004881

Let me mention to you a few of the recent actions of MUCC regarding PCBs. In 1976, we prompted the Michigan Department of Natural Resoruces (MDNR) to include the first "Public Health Advisory" regarding consumption of contaminated fish on the 1977 Michigan Fishing Guide, a brochure distributed with all sports fishing licenses. That same year MUCC was instrumental in passage of the nation's first ban on PCBs through a state law (Act 60 of 1976). In 1977, we blew the whistle on one of the most flagrant cases of PCB pollution in the Great Lakes Basin at Cast Forge on the South Branch of the Shiawassee River. Record PCB levels of 345 mg/kg in biota and 530 mg/kg in sediments a mile below the plant were known by the state but not publicized. The river is still closed to fishing, but a $1 million clean-up plan is now underway, the first such restoration effort we know of.

In 1978, we helped force the closing of a toxic liquid waste incinerator on the Saginaw Bay (Hartley & Hartley at Kawkawlin, Michigan) operated by SCA Services, Inc. This company operated its liquid disposal business in the 1960s by storing the waste liquids in open ponds in the Tobico Marsh and periodically setting them on fire. Then in 1971, the state licensed an uncontrolled incinerator at the site. SCA's advertising was revealing:

> Now you can get rid of your troublesome chemical wastes EASILY, CONVENIENTLY, ECONOMICALLY, SCIENTIFICALLY . . . Ship us your waste or we will pick it up and we will process it in accordance with federal, state, and local regulations, relieving you of liability as well as relieving you of a burdensome task. We will process such chemical wastes as: PCBs, cyanides, pesticides, chlorinated solvents . . . carcinogens, heavy metal wastes, . . . mercury sludges . . . and so on.

This was a <u>legal</u> operation; no one was ever prosecuted for this environmental travesty. No wonder the Great Lakes have toxic chemical problems; no wonder no one trusts government regarding toxic chemical management.

I should also note that MUCC has been active in seeking solutions to the PCB problem. We have bucked local opposition and vocally supported proposed PCB incineration at the Peerless Cement kiln in Detroit and at the General Motors Chevrolet plant in Bay City. We have supported various PCB treatment technologies in the region. And we have been active in virtually all phases of hazardous chemical management and regulation in our state.

I mention these examples only by way of background to demonstrate how seriously MUCC takes PCB contamination of the Great Lakes. Our membership has demonstrated its commitment to toxic chemical control over and over with money and energy. And this public support is consistently underestimated by public agencies and politicians.

GREAT LAKES PCBs AND MICHIGAN ANGLERS

PCBs in the Great Lakes are particularly important for the state of Michigan and our anglers. We own title to 40 percent of the area of the Great Lakes. Michigan has a higher ratio of our area covered by freshwater compared to land than any other state or country--two square miles of Great Lakes surface water for every three of land.

Tourism and travel, much of it related directly to the Great Lakes, is over a $9 billion annual industry in Michigan. The Great Lakes sports fishery is a $350 million annual business in our state alone. This fishery is one of the best and most exciting in the world. Michigan has 1.5 million licensed anglers, not including the many children and spouses who don't need licenses to fish.

The salmon fishery continues to expand. For example, Lake Michigan salmon (and steelhead) now run up the Grand River to the state capitol and may eventually be caught on this campus of Michigan State University. Those fish are being caught and eaten in huge quantities. Many families catch and can hundreds (some thousands) of pounds of salmon every year and eat those fish all year long.

In the midst of this expanding recreational fishery, sports anglers are faced with this ironic note of warning on their fishing law digest:

> Certain Great Lakes fish should not be eaten--by children, women who are pregnant, nursing, or expect to bear children. Limit consumption by all others to no more than one meal per week.

Incidentally, this warning includes those salmon and steelhead I mentioned now migrating to Michigan State University.

What does this warning mean to the sports anglers and their families of Michigan? This very distinct population in Michigan is at very distinct risk from long-term exposure to PCBs. I can assure you that many anglers do not take seriously the warnings about limiting consumption of Great Lakes fish. You've

heard the rationale: "Everything causes cancer. I'm not a white rat. Remember the cranberry scare. Everyone's got to die from something." Perhaps most pathetic of all: "I've been eating these fish all my life and it never hurt me." One outdoor writer in the region is spreading the good word to sportsmen that concern over PCBs is a "fright scene orchestrated by environmental extremists and their kneejerk media handmaidens" and that PCBs and table salt "may well be about equally toxic" (Spiers, 1981). It makes good copy and this kind of nonsense is just the excuse many sportsmen need to justify what they want to believe that nothing bad has been proven about PCBs.

The public, and especially the majority of the sports fishing public, is crying for information and answers to questions. It is my conclusion that government and public unversities have failed miserably in providing information and answers to questions of vital public concern.

FISH MONITORING DATA

If you want an exasperating experience, try to find basic information on what fish species and what size classes from what waters have or do not have various contaminants. The cursory information provided in Michigan's Public Health Advisory is better than nothing, and that is about the best you can say for it.

There is, however, no comprehensive document available to the public summarizing all available data on fish contaminants in Michigan. I suspect other states are no better off. In fact, we finally were forced to compile all the data we could find ourselves for publication in our magazine, Michigan Out-of-Doors (Schmidt, 1981).

Why hasn't the MDNR, and until recently the Michigan Department of Public Health (MDPH), shown any interest in publicizing data on contaminants? No one wants to be the bearer of bad news about poisoned fish. But the public is demanding better information about environmental contaminants from its public servants. It is deplorable how little we know about fish contaminants, not only in Great Lakes fish but from fish in inland waters as well. It is inexcusable how poorly the limited data we have has been made available to the public.

For example, the 1982 Public Health Advisory states that musky from Lake St. Clair should not be eaten. From this you would assume that all other species in any size class from Lake St. Clair are safe. Yet we know from Ontario data that this sanguine conclusion is dead wrong. Doesn't anyone from Michigan

agencies talk to anyone in Ontario agencies? As another example, all Lake Huron trout and salmon are lumped in a single advisory. Aren't any of the small fish safe?

The Ontario program for monitoring and publicizing fish contaminants is the best model we can point to. It is an honest attempt by the provincial government to point out to the public exactly what we do and do not know about fish contaminants. Michigan can claim that we can't afford the program. I suggest that until state governmental agencies first demonstrate concern and recognize the importance of collecting and publicizing such monitoring data, the money will never be available. It may also be time for sports anglers to begin thinking about using fishing license money to partially fund such programs.

PUBLIC HEALTH AND PCBs

The public is demanding answers to complex questions on public health impacts from long-term exposure to PCBs. We recognize that Michigan has done some of the only research in this area, but it is pitifully inadequate. And there are some basic questions for which answers may already be available that are not being translated into plain English.

What do we know about the effects of PCBs on animals? What do the studies already completed demonstrate? If people are reminded what happens to mink fed Lake Michigan salmon, it has an impact on their attitudes. Somehow results of animal studies seldom get translated into reports average people can relate to and understand.

If I interpret the data correctly, I read that a woman eating only 6.4 kg of Lake Michigan fish/yr could typically expect to have 4 mg/kg PCBs in her breast milk (Swain, 1981). Further, her nursing infant would then be exposed to 20 to 25 times the maximum daily dose rate recommended by the U.S. Food and Drug Administration (FDA) for adult intake. This is shocking. Why isn't this type of common sense information widely publicized? Women want to know. I have seen other data concluding that nursing infants of heavy fish eaters could receive a total body burden of PCBs from nursing of up to 3.44 mg/kg (Harger, 1980). Women are looking for honesty from state government, no matter how incomplete the information may be or how unpalatable it may sound.

Again, I have to point to Ontario for the best model for public information on this issue. Their publication, "Health Implications of Contaminants in Fish" (OMOE, 1978) is the best

summary on this question we know of. To my knowledge, no comparable publication is available from any of the Great Lakes states.

The other frightening question we raise concerns our ignorance on possible additive or synergistic effects of Great Lakes contaminants. Virtually everyone in Michigan already carries a body burden of PCBs and polybrominated biphenyls (PBBs). And PCBs in fish are not often a single pollutant but can be found in combination with mercury, DDT, PBB, chlorinated dioxins, dibenzofurans, chlorinated benzenes, and/or various other chemicals. The International Joint Commission has now identified 468 chemical contaminants in the Great Lakes system. PCBs cannot be treated as a single contaminant in an otherwise sterile environmental laboratory. How does this stuff all add up? We can't even get our MDPH to set a safe limit for dioxins in fish (Walker, 1981), let alone tell us what these exotic combinations may mean for the public health of our state.

REDUCING PCBs IN FISH

I recognize that some questions I raise may be beyond the limits of epidemiology to answer today. So let me try some simpler ones. If a salmon steak is canned with the skin on, eaten six months later with the skin off, how much are PCBs reduced or increased in the meat? If a salmon is smoked, what happens to PCBs in the skin and fat? If a salmon is broiled in butter with the skin on, what happens to the PCB level in the meat? It is hard to believe, with all the great minds concerned about public health implications of PCBs that no one has even cooked up a few salmon in different ways to answer these and related questions.

IMPACTS OF PCBs ON FISH AND WILDLIFE

We are also greatly concerned about direct impacts of PCBs on fish and wildlife, as well as public health. Research such as is being conducted by the U.S. Fish and Wildlife Service Great Lakes Fish Laboratory in Ann Arbor on lake trout reproduction is of great interest to sportsmen. But like so much research, it is communicated poorly, if at all, to the general public. Then when the budget ax falls, no one is sure what we would be losing if all the Great Lakes research facilities were closed. That is exactly what is happening today on the Great Lakes and I suggest these labs are themselves in part to blame for their political problems due to their dismal public relations with their constituency.

MONS 004886

But what do PCBs in the environment mean to native fur bearers? If reproduction in commercial mink are affected by diets of Lake Michigan salmon, what of the native populations feasting on spent salmon every fall? What of other predatory species in waters affected by PCBs, such as snapping turtles? What of fish eating birds (see, for example, Haseltine et al., 1981)? I suspect there is more information available than we see, but what good is it buried in a research volume?

POLITICS

I will conclude with one comment on the politics of toxic substances in the Great Lakes. Most of my questions have dealt with the need for public information and public accountability for government programs. We are making progress in Michigan. The single biggest factor in this progress towards honesty and public accountability has been the over-sight functions provided by the Michigan Toxic Substance Control Commission (TSCC). It has made numerous contributions to resolving toxic substance problems in Michigan, raising issues no one else will confront (see, for example, Holcomb, 1981). But its most important contributions have been two intangible ones:

(1) Independent over-sight of the politics and priorities of state agencies regulating PCBs and other hazardous chemicals.

(2) Providing a forum--the only one available--for the public to voice the concerns such as I have raised today.

The TSCC has been a force for positive change in this state.

Yet there are powers within the executive and legislative branches of state government today with the avowed objective of eliminating the TSCC. This objective is totally contrary to the public interest and the public's broad support for the continuation of the TSCC. It is terribly frustrating to be fighting these petty factional squabbles while the real questions of public health and environmental quality go begging for attention.

SUMMARY

Let me summarize with just two statements:

(1) The public, especially the sport fishing public, is crying for more information on PCBs and other

MONS 004887

environmental contaminants. There is a need for a vastly improved information base on PCBs and other contaminants in the Great Lakes environment and a vastly improved delivery system to get that information to the general public.

(2) People want honesty from their government. They want government to level with them in language they can understand about what we know and what we don't know about PCBs. If you aren't straight forward with people, no one trusts anyone.

LITERATURE CITED

Harger, J.R.E. 1980. PCBs and General Low Level Contaminants in Fish. Michigan Toxic Substance Control Commission, P.O. Box 30026, Lansing, MI 48909 (memorandum, November 17, 1980).

Haseltine, S.D., G.H. Heinz, W.L. Reichel, and J.F. Moore, 1981. Organochlorine and Metal Residues in Eggs of Waterfowl Nesting on Islands in Lake Michigan Off Door County, Wisconsin, 1977-78. Pest. Monit. J. 15(2):90-97.

Holcomb, L.C. 1981. PCBs in Salmon. Michigan Toxic Substance Control Commission, P.O. Box 30026, Lansing, MI 48909 (internal issue paper, October, 1981).

Humphrey, H.E.B. N.D. Evaluation of Changes of the Level of Polychlorinated Biphenyls in Human Tissue. Michigan Department of Public Health, Final Report on FDA Contract 223-73-2209. 66 pp.

OMOE. 1978. Health Implications of Contaminants in Fish. Ontario Ministry of the Environment, Rexdale, Ontario. 132 pp.

Schmidt, W. 1981. Special Report: Are Your Fish Safe to Eat? Michigan Out-of-Doors 35(9):36-37, 53-54.

Spiers, A. 1981. PCB Scare Stories Being Revived. The Great Lakes Steelheader 5(10):6.

Swain, W.R. 1981. Ecosystem Monitoring in the Great Lakes: Research Needs, Public Health Implications. Great Lakes Focus on Water Quality 7(1):1-2, 8-12.

Walker, B., Jr. 1981. Personal Communication to T.L. Washington, Director, Michigan Department of Public Health, Lansing, MI 48909 (December 30, 1981).

MONS 004888

CHAPTER 8

THE COMMERCIAL FISHERMEN'S VIEW OF THE PCBs PROBLEM IN THE GREAT LAKES

Claude Ver Duin
Great Lakes Fisheries Development Foundation
Grand Haven, Michigan 49417

It is a pleasure to talk to you about the effects that polychlorinated biphenyls (PCBs) have upon our commercial fisheries. First of all, I want to emphasize that the industry does not want to produce a product that will adversely affect human health, and that we applaud all efforts to reduce contaminants in the lakes. Having said that, I want to point out that it is the commercial fishing industry that has probably suffered the most from contaminants in their products. They have seldom, if ever, had any direct role in causing the contaminant pollution, yet in only a few cases have they been compensated for their losses. When contaminants occur in fish, and these contaminants cause disease, the public knowledge of this may reduce the attractiveness and price of these products in the market. Any time there is mention of the PCB problem in the news media, sales in the retail fish markets and supermarkets go down. The public is so sensitive that I am sure that even the publicity associated with this symposium will cause some people to think again about the fish they are eating and forego fish for at least a period of time.

A government, motivated either by known or feared consequences of eating contaminated fish, may take a number of different steps. It may determine the maximum sizes that may be taken, as occured in Muskegon last year. The fishermen there were advised that whitefish weighing more than 1.8 kg (4 lb) could not be sold. This year, because the levels have come down, fishermen will be permitted to take whitefish up to 2.7 kg (6 lb). A government may legally close certain fisheries, as has been done in western Michigan. The area from approximately Montague south to the Indiana line is closed for chub fishing because of high levels of dieldrin. Another step a

MONS 004889

government can take is to set action levels and ban the sale of fish which exceed this level. Alewives, the predominant species in Lake Michigan, can't be harvested because of high levels of PCBs. It is estimated that at least 455,000 kg of these fish, which could be used as sardines, could be harvested out of just the Wisconsin ports on Lake Michigan. A government may issue advisories that the more contaminated species should not be eaten, except occasionally. This is the way that the sports fisheries have been handled. Sports fishermen are warned against eating highly contaminated fish too often or in too large amounts.

This different treatment of sports and commercial fishermen has been bothersome for some time. Let's look at a situation that is repeated daily when commercial fishermen and sports fishermen are on the same fishing grounds. A lake trout is brought aboard a commercial vessel as the fisherman lifts his net that was set for a different species of fish. He is not permitted in the state of Michigan to have this incidental catch. He must throw it back in the lake because, under the Food and Drug Administration (FDA) standard, the fish is not fit for human consumption. Now, let's assume that an hour later this same fish is caught by a sport fisherman and is declared legally acceptable as human food in the state of Michigan. There is something wrong with this situation. The fish is either fit to be eaten regardless by whom it is taken or it is not safe to be eaten. If the current concern over PCBs indicates that fish with certain levels of contamination are not fit to be eaten, then no one should be eating them.

When I was first asked to participate in this symposium, I wondered why Michigan was concerned over the present situation. PCB levels have been declining faster than anyone had expected them to. A few years ago, when PCB levels ranged in the high teens and low twenties, individuals who caught their own fish, and consumed their catch, were merely warned not to eat fish too often. From what we known, a lot of fish were eaten. I ate my share. Now that PCB levels, in many species and in many places, are as low as 5 mg/kg, there is an expressed concern over the effects of PCBs in humans. Perhaps there is new evidence that will be presented in the next two days that will tell us why there is new concern.

I also wonder why this symposium is being convened, and why Michigan is considering unilateral action to establish a lower guideline for PCB in fish, when this same issue is being considered in Washington. For the past 15 months, the FDA, various environmental groups, the National Conservation Council, the National Fisheries Institute, the National Marine Fisheries Service, and other associated commercial fishery

interests have been arguing the case before Administrative Law Judge Daniel J. Davidson (FDA Hearing Examiner). At first, a decision was expected on January 11, 1982, but there was so much evidence presented that he postponed his decision and it is now expected around the first of May.

At these hearings, consideration has been given not only to the level at which human beings can be adequately protected, but also the required level that can be established without causing economic disruption to an industry. The law judge has made a determination that in deciding whether to drop the guidelines for PCBs from 5 mg/kg to a new legal level of 4, 3, or 2 mg/kg, there must also be a consideration of the economic loss to industry. Judge Davidson also ruled that you cannot take the dockside value of the fish and use this to represent the economic loss. Instead, the dockside value must be multiplied by 6 to determine the economic loss to the industry on a national level. This multiplier takes into account that the fish doesn't stay on the dock, but instead moves through transportation to wholesalers, processors, and canners to the ultimate consumer, whether it be through a restaurant, a club, a fast-food outlet, or in your own dining room.

The factor of 6 might be a little high considering the total economic loss to the industry in Michigan because, obviously, we do not have canneries as they do on both the East and West coasts. Also, there may be another process or step eliminated but it would be fair to say that a multiplier of 4 to 5 is a reasonable figure to use. William McCracken, chairman of the Fish Contaminants Advisory Committee, has made a study to determine the economic impact of lowering the allowable level of PCB in commercial fish harvested in Michigan from 5 to 2 mg/kg. He said that the effect on the commercial market would be $4.2 million. He did not take into consideration a million pounds of chubs that could be produced were it not for dieldrin. They are currently selling for a dollar a pound on the dock. So if we take the $4 million, add another million to it, and multiply by 4.5, we are up to about $22 million. Mr. McCracken had another interesting figure and that was the increased regulatory cost to the state of Michigan of policing a 2 mg/kg level if it were not also adopted by the neighboring states. This cost would be high because much of the fish sold in Michigan comes from other states. He estimates that the cost to the state would be $500,000.

Additional economic losses may occur if contaminants reduce the biological productivity of fish stocks. Some years ago our chub fishery in Lake Michigan began to decline and there was a great deal of concern about this. Was the fishery being overfished? The problem, however, was not overfishing but a

MGNS 004891

lack of recruitment over a period of years. The fishermen were reducing the standing stock and there was no recruitment of young coming up to offset that. It was determined that the presence of DDT was either making the eggs infertile or killing off the little fish with the yolk sacs still attached. When the DDT levels came down, the recruitment of stocks went up. This incident provided dramatic evidence that contaminants in fish could materially affect their ability to reproduce.

We hope that out of this symposium may come a closer surveillance of the uses of PCBs. We know that some of it is still being used. We hope that the state would determine where this PCB is getting into the lakes and the fish. I am sure a lot of good can come from this symposium.

MONS 004892

PART II

PCBs: ANALYSIS AND MONITORING

MONS 004893

CHAPTER 9

MONITORING FOR PCBs IN FISH: THE HUMAN HEALTH PERSPECTIVE

Andrew P. Gilman
Environmental Health Directorate
Health and Welfare Canada
Tunney's Pasture
Ottawa, Ontario
Canada K1A 0L2

INTRODUCTION

I have always been impressed with the opening quotation provided by Dr. David B. Peakall of the Canadian Wildlife Service in a presentation that concerned monitoring in the aquatic environment (Peakall et al., 1980). He walked to the podium with a bible tucked under his arm and read the following excerpt from Deuteronomy (Chapter 14:11-17):

> Of all clean birds ye shall eat. But these are they of which ye shall not eat: the eagle, the ossifrage, and the osprey, . . . and the pelican, and the gier eagle, and the cormorant.

The audience was left rather quiet, some fidgeted. Dr. Peakall continued with his talk. He made no further mention of the bible passage, but its relevance to his presentation of the Herring Gull monitoring program in the Great Lakes was suitably clear.

I am sure that the authors of Deuteronomy did not have access to gas chromatographs, high pressure liquid chromatographs, or mass spectrometers; however, they may have sensed a danger associated with the consumption by the public of these fish-eating birds. It is remarkable that all of these birds are currently under the strictest of protection in North America although the rationale for their protection is conservation of the species rather than concern for public health.

MONS 004894

This paper is not about fish-eating birds; rather, it concerns fish-eating people. Specifically, this paper provides the perspective of the human health evaluator on the need for polychlorinated biphenyls (PCBs) monitoring data in Great Lakes fish and also the benefits for man of the application of results of surveillance and monitoring programs.

ENVIRONMENTAL SURVEILLANCE AND MONITORING

Despite large resource expenditures for surveillance and monitoring, there remains considerable confusion over the definitions of these two activities (Berlin, 1979; Holdgate, 1979). Surveillance is usually defined as "the repeated measurement of a variable in order that a trend may be detected." Monitoring, on the other hand, is more action oriented and "designed to tell us how well our regulations are working and how far standards are being met." The line between these two activities is not always distinct. A preliminary survey of contaminant levels, or their effects, in the environment at one point in time may be repeated (surveillance) to identify trends. These trends may indicate control actions are required and the surveillance program is continued as monitoring to determine the impact of the control actions on environmental levels of the contaminant(s) and to assess compliance with regulations. For the purposes of this paper I have used the above definitions of surveillance and monitoring. The identification of new, previously unrecognized contaminants I have put as part of the surveillance activity; determining levels of PCBs in fish, now that PCB use is carefully controlled in North America, I have considered monitoring.

Man's interest in monitoring has largely been self-serving. In the past, the canary was carried down the mine shaft by generations of miners to warn of the presence of toxic gases. Today there are a variety of rationales for surveillance and monitoring programs (Gray, 1980; Nielsen et al., 1980). Furthermore, we have adopted more sophisticated terminology (Hytteborn, 1979). For example, surveillance and monitoring programs with biota are now described in terms of the use of active species (i.e., those species put in place in the zone of contamination and subsequently sampled) and passive species (i.e., those species that are residents of the zone of contamination and are subsequently sampled). Some species have extensive ranges, are long lived, and accumulate pollutants that are found over large areas; these species are "integrators" of pollutants that are "widespread". Other species are restricted in their habitat and range and serve as indicators of "point-source" or "local" contamination. Still other species

can more adequately provide data on the effects of pollutants as opposed to the levels (Gilman, 1983).

Only sometimes does the rationale for surveillance and monitoring pertain to human health concerns. Currently, federal, state, and provincial programs in the Great Lakes basin are partially coordinated through the International Joint Commission (IJC)(Anon., 1978). The programs are primarily passive, they identify both local and widespread pollution problems, they ascertain contaminant levels, and, to a lesser extent, their effects on biota. To provide the data necessary for evaluation of human health risks from environmental contaminants, it is vital that specialists in health assessment contribute to the modification of existing programs and the design of future programs.

SELECTION OF FISH FOR PCB MONITORING

The strongest rationale for monitoring fish for levels of PCBs is also the most simple rationale: PCBs are toxic, they accumulate in fish, and people eat fish. Monitoring programs that are to provide useful data for health risk evaluation must meet the following four basic criteria:

Criterion 1. Monitoring programs must sample fish species that are consumed by the public.

PCBs from the Great Lakes basin will be ingested by sport fishermen, commercial fishermen, and the public through consumption of Great Lakes fish. To assess the health impact for man of PCBs in Great Lakes fish, it is essential to have information on the species of fish consumed, the amounts consumed, the frequency of consumption, and the preferences of "special groups" for certain species. These special groups include various ethnic, religious, socio-economic, and native sub-populations. Application of this knowledge to the selection of fish species for monitoring and in the calculation of average annual intake of PCBs will enhance the relevance of monitoring programs for public health.

Criterion 2. Fish species to be sampled must be collected at the same time of year and location that they are commonly caught for consumption.

The PCB content of fish can vary significantly because their body lipid levels can fluctuate (seasonal and sex related), their diets can vary, and their migratory patterns can expose them to varying concentrations of PCBs at

specific times of year. Hence, assessments of public exposure to PCB must be based on data obtained from fish that have been sampled when and where these species are caught for consumption by the public. The usefulness of sampling data forthcoming from monitoring programs carried out at arbitrary times of the year is diminished because of the need to estimate levels of PCB at the time of public exposure.

Criterion 3. Monitoring programs must sample and analyze enough fish to ensure that reliable PCB concentrations can be calculated for the species and size classes consumed.

Suitable sample size is dictated by the amount of variation between the individual analyses. Currently, a sample size of 20 fish of any one size class (each fish analyzed individually) from any one location is adequate to detect a 10 to 20 percent change in PCB concentration from one year to the next (Anon., 1978). When standardization of size class is not possible, then statistical comparisons of concentration cannot be based on mean PCB concentration per size class. Instead, levels of PCB in individual fish must be plotted against the size class for that fish. When the analytical and measurement data for a large number of fish have been plotted, it is possible to compare PCB concentrations between years via linear regression analysis.

Criterion 4. Analysis of fish for PCB must be carried out on the consumed portion of the fish.

There is unanimous agreement between the Great Lakes jurisdictions of the need to analyze "edible portions" of fish when addressing public health concerns. However, definition of edible portion has become a contentious issue within and between analytical groups and between jurisdictions. Debates over skin-on and skin-off fillets, dorsal or whole fillets, belly-fat-on or belly-fat-off fillets, etc., continue. Detailed discussion of this complex issue appears in this volume (McCracken, 1983). The significance of consistent analyses of similar portions of fish between programs cannot be overstated from the perspective of health risk evaluation. Without agreement between the jurisdictions on a standard edible portion, comparisons of data collected from Great Lakes fish are almost impossible.

Application of these four criteria in the development of monitoring programs tailored to health concerns and addressing

MONS 004897

PCBs in fish must be tempered by several practical considerations.

Consideration 1. Cost of sampling.

Monitoring programs are expensive. When considering species capable of reflecting human exposure to PCB, it is necessary to examine existing programs. Do these programs sample for species that might be capable of providing data useful to public health officials? What is the ease and cost of sampling for the selected species (e.g., Rainbow Smelt, Osmerus mordax, are far cheaper to sample than Lake Trout, Salvelinus namaycush)?

Consideration 2. Availability of species.

Historical data and trends in PCB levels are significant when assessing impact on human health. Is there the potential for multi-year sampling or is the fish stock dwindling?

Consideration 3. Biological data base for species.

The best monitoring species are those with well known life cycles, feeding habits, population dynamics, migratory patterns, etc. Knowledge of PCB uptake and depuration rates, sex differences, and the relationship between size and level of contamination is useful. Also, is the selected species amenable to laboratory studies?

The need to integrate monitoring criteria and practical considerations underscores the importance of interagency and interdisciplinary consultation. The fisheries biologist, analytical chemist, health risk evaluator, and monitoring coordinator must be willing to cooperate and compromise to prepare a program that will produce meaningful data on exposure of man to PCBs. Furthermore, the data must be available in a format that can be used by health biometricians (i.e., the levels of PCB by species, size class, location, and season must be provided).

BENEFITS OF MONITORING AND SURVEILLANCE PROGRAMS

Do the benefits of contaminant surveillance and monitoring programs justify their costs? From the human health perspective, no quantitative answer is possible unless a value is assigned to "good health". Nevertheless, in qualitative terms and in full recognition of the desire to optimize public health, these programs are a bargain; some specific benefits from Great

Lakes monitoring have been thoughtfully described by Swain (1981).

Data resulting from monitoring programs designed to determine PCB levels in fish enable us to:

--assess exposure of the public (especially critical sub-populations) to PCBs in fish;

--inform the public whether or not the current PCB guidelines are being met;

--identify previously undetected or new PCB sources;

--determine the effectiveness of abatement programs and the need to modify pollution control schemes to meet changing conditions.

Multi-contaminant monitoring and surveillance programs for both levels and effects provide the above advantages for other contaminants and also enable us to:

--identify "new" or previously unrecognized contaminants in media or food of direct importance to man;

--identify population effects in biota that may provide an early warning of the cumulative impact of environmental contaminants on living tissue;

--direct limited resources toward contaminants of highest priority and optimize the output of research, data gathering, and assessment activities.

As monitoring programs shift toward providing data that meet the needs of health risk evaluators, the task of making good use of the data comes into sharp focus. The end point in contaminant levels monitoring is not a listing of hundreds of mean contaminant levels in media and biota; rather, it is the determination of the effects of these levels of contaminants in man. Other papers in this proceedings address the impact of multi-media exposure to contaminants, contaminant interactions, and the assessment and regulatory processes.

CONCLUSIONS

Thoughtfully considered and carefully conducted monitoring and surveillance programs that provide suitable data for human health risk evaluations are urgently needed. Most important is the development of an agreement between the jurisdic-

MONS 004899

tions to analyze similar edible portions of fish to facilitate comparisons of data collected throughout the Great Lakes basin. The ultimate outcome of these programs will be better risk evaluations and enhanced utilization of environmental resources by North Americans.

The IJC has recently published a report of a Roundtable meeting on the detailed requirements for data adequate for health risk assessment (Anon., 1982). This document will, hopefully, stimulate the production of more useful data for the assessment of human health risks from environmental PCB and other chemicals in the Great Lakes basin.

LITERATURE CITED

Anon. 1978. Great Lakes International Surveillance Plan. International Great Lakes Joint Commission, Windsor, Ontario. 522 pp.

Anon. 1982. Proceedings of the Roundtable on the Surveillance and Monitoring Requirements for Assessing Human Health Hazards Posed by Contaminants in the Great Lakes Basin Ecosystem. International Great Lakes Joint Commission, Windsor, Ontario. 72 pp.

Berlin, A., A.H. Wolff, and Y. Hasegawa. 1979. The Use of Biological Specimens for the Assessment of Human Exposure to Environmental Pollutants. Proc. of Intern. Workshop, Luxemburg, April 18-22, 1977, Martinus Nijhoff, Hague. 366 pp.

Gilman, A.P. 1983. The Selection of National Biological Monitoring Species. Canadian Wildlife Service Red Report Series No. 43 (in press).

Gray, J.S. 1980. Why Do Ecological Monitoring? Marine Pollut. Bull. 11(3):62-65.

Holdgate, M.W. 1979. A Perspective of Environmental Pollution. Cambridge University Press, Cambridge, MA. 278 pp.

Hytteborn, H. 1979. The Use of Ecological Variables in Environmental Monitoring. Proc. of the First Nordic Oikos Conference, Uppsala, Sweden. National Swedish Environmental Protection Board Report PM 1151. 350 pp.

McCracken, W.E. 1983. Edible Tissue Sampling for Fish Contaminant Analysis. In: F.M. D'Itri and M.A. Kamrin (eds.), "PCBs: Human and Environmental Hazards," pp. 123-139, Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Nielsen, S.W., G. Migaki, and D.G. Scarpelli. 1979. Animals as Monitors of Environmental Pollutants. National Academy of Science, Washington, DC. 421 pp.

Peakall, D.B., G.A. Fox, A.P. Gilman, D.J. Hallett, and R.J. Norstrom. 1980. Reproductive Success of Herring Gulls as an Indicator of Great Lakes Water Quality. In: B.F. Afghan and D. MacKay (eds.), "Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment," pp. 337-344, Plenum Publishing Corp., New York, NY.

Swain, W.R. 1981. Ecosystem Monitoring in the Great Lakes: Research Needs, Public Health Implications. Focus (Great Lakes Focus on Water Quality) 7(1):1-2, 8-12.

MONS 004901

CHAPTER 10

EDIBLE TISSUE SAMPLING FOR FISH CONTAMINANT ANALYSIS

William E. McCracken
Surface Water Quality Division
Michigan Department of Natural Resources
P. O. Box 30028
Lansing, Michigan 48909

INTRODUCTION

There has been disagreement for years about how fish should be prepared for contaminant analyses. Whole fish, skin-on fillets, and skin-off fillets are three of the many types of sample portions which have been recommended and hotly debated as the "proper" methods of sample preparation. The State of Michigan has looked into this issue in some depth and is proposing a rationale for selecting the portion to use in the analysis when the investigator desires to characterize the edible portion of fish. This paper presents Michigan's reasoning on this issue.

FISH CONTAMINANT MONITORING IN MICHIGAN

Michigan has three state agencies involved in fish contaminant monitoring. The Michigan Department of Agriculture is the state agency responsible for regulating the state's food supply. The Michigan Department of Agriculture coordinates its work with the U.S. Food and Drug Administration (FDA) which has the corresponding federal responsibility. Under their joint authority, regulation of fish and fish products in the food supply has been carried out for a number of years. Sampling by these agencies includes commercial catches of fish, fish and fish products as sold in wholesale and retail outlets, and fish served by restaurants.

MONS 004902

The Michigan Department of Natural Resources (DNR) is the state agency responsible for management of environmental protection programs and for management of the state fishery for commercial and sport fishing. Sampling includes fish from lakes and streams.

The Michigan Department of Public Health (DPH) is the state agency responsible for evaluating human health effects of eating contaminated fish and issuing health advisories as needed. The Michigan DPH does not have fish sampling responsibilities, but uses data from the Departments of Agriculture and Natural Resources and other sources in evaluating potential health effects.

Michigan carried out the Great Lakes Environmental Contamination Survey (GLECS) for about 9 yrs during the 1970s. GLECS was a cooperative program involving the Michigan Departments of Natural Resources, Public Health, and Agriculture, the U.S. FDA, and the U.S Fish and Wildlife Service. GLECS was hampered by the lack of a consistent funding source. This ultimately caused it to be discontinued in 1980.

The state established a Fish Contaminant Advisory Committee (FCAC) in January, 1981, to ensure that the fish contaminant monitoring efforts of the Michigan Departments of Agriculture, Natural Resources, and Public Health are coordinated. Among other things, the FCAC was charged with developing and maintaining a fish contaminant monitoring plan to guide the state's efforts in this area, and to resolve any technical issues relating to fish contaminant monitoring. The FCAC completed the fish contaminant monitoring plan in January, 1982. Most of the plan cannot now be carried out because funding is not available. However, it will serve as the state's blueprint for fish contaminant monitoring if and when the resources become available. The most difficult technical problem which faced the FCAC in developing the plan was how fish should be prepared for analysis, particularly when attempting to characterize the edible portion.

FISH CONTAMINANT MONITORING OBJECTIVES

The type of fish sample to be taken for contaminant analysis depends on the objective of the study. The importance of the objectives cannot be over-emphasized. The principal objectives that the Michigan fish contaminant monitoring plan is designed to achieve are:

MONS 004903

(1) To provide information for assessing potential human exposure to toxic materials due to consumption of commercial and sport fish.

(2) To determine chronological trends in fish contaminants.

(3) To identify new or previously unrecognized contaminant residues in fish.

(4) To communicate results to appropriate government agencies for regulation of commercial food supplies, for determination of human exposure and public health advisories, and for determination of the need for new remedial measures or the success of completed remedial measures. Also, to communicate any resulting public health advisories to the general public.

The first objective is to determine amounts of consumable contaminants present in fish. Therefore, it makes sense for the edible portion of fish to be used for contaminant analysis when carrying out this objective.

The second objective is to determine chronological trends in fish contaminants. Again, the FCAC decided the edible portion should be used for carrying out this objective because the trends in edible portions are of most interest in Michigan.

The third objective is to identify new or previously unrecognized contaminant residues in fish. In this case the FCAC decided that the whole fish would be most appropriate because, when looking for "hot spots" or areas of previously unrecognized contaminant residues, the sample would include parts of the fish that may contain those residues even if these are not the edible parts of the fish.

The fourth objective is simply to communicate results from studies carried out to achieve the first three objectives.

JURISDICTIONAL INCONSISTENCY IN EDIBLE PORTION SAMPLING

A survey of other jurisdictions in the Great Lakes region indicates there is much inconsistency in what portions of fish are sampled for contaminants analysis. Sampling done by the other jurisdictions is summarized below. The persons from the various jurisdictions who provided information for the survey are listed following the jurisdiction in parentheses and are listed as references at the end of the paper:

MONS 004904

Illinois

The Illinois Department of Conservation, in conjunction with other federal and state agencies, has established a fish contaminant monitoring program with the following objectives:

(1) To assess fish toxicity and public health implications due to the build-up of contaminants in fish.

(2) To determine the impact on fish species diversity and abundance.

(3) To locate sources of contaminant discharges and evaluate the long-term effects of environmental controls and land use changes.

Composites of scales-off, skin-on, boneless fillets are used for analysis; however, catfish are prepared as skinless, boneless fillets. Whole fish samples are also required from specified contaminant sites in addition to the fillets. The whole fish are analyzed by the U.S. Environmental Protection Agency (EPA) for a broad range of contaminants (Mick, 1982).

Indiana

The Indiana DNR and the State Board of Health monitor contaminants in Lake Michigan salmonids and other commercial species to determine the suitability for human consumption and to evaluate trends in contaminant levels. Composites of skin-on, one-inch thick, cross-sectional steaks are used for salmonid analysis, while individual whole fish of other commercial species are utilized.

The State Board of Health also sampled nineteen stream stations as part of the U.S. EPA Basic Water Monitoring Program. Composites of whole fish are analyzed. However, an "edible portion", which is usually a skin-off fillet, may also be analyzed when whole fish are found to contain contaminants above FDA action levels (James, 1982; Bridges, 1982).

Minnesota

The Minnesota Departments of Natural Resources and Public Health and the Minnesota Pollution Control Agency have developed a cooperative effort for fish contaminant monitoring. The short-term objectives of the monitoring program include: defining locations, species, and size of fish which contain residues exceeding safe consumption levels; assessing the environmental

MONS 004905

integrity of the state's fish populations; and locating discharges of priority pollutants. Long-term objectives include the assessment of pollution abatement programs and compilation of a tissue data bank.

"Edible portions", which are usually skin-off fillets, are used to assess human health impacts; while whole fish are analyzed to address the environmental integrity of the fishery. In certain cases, specific organs (liver, kidney) may be analyzed to monitor pollutants known to selectively accumulate (Helwig, 1982).

New York

The New York Department of Environmental Conservation has a diverse fish contaminant monitoring program. Some current program objectives include heavy metal, pesticide and industrial organic contaminant trend analyses, and tracking of sources of polychlorinated biphenyl (PCB) and mercury contamination in marine and fresh-water species.

A standard fillet, defined as a boneless, skin-on, scales-off portion is used for all analysis. The standard fillet is used to supply a baseline reference from which judgments on human fish consumption can be made (Skinner, 1982).

Ohio

The Ohio DNR annually samples coho salmon from the Grand and Huron Rivers in connection with the Great Lakes International Surveillance Plan (GLISP). These fish are supplied to the U.S. EPA for analysis. These samples are skin-on fillets and provide information for evaluating the hazard that toxic substances pose to the fish-consuming public (Atgear, 1982).

Ontario

The Ontario Ministries of Natural Resources, Environment, and Labour sample and analyze approximately 15,000 fish/yr. Skinless, lean dorsal muscle is used for analysis. The data are used to develop lake-by-lake, species-specific tables listing consumption recommendations which are designed to protect public health.

In a separate program, the Ontario Ministry of the Environment samples whole fish to provide contaminant trend information

MONS 004906

and to identify any additional potentially hazardous contaminants (Johnson, 1982).

Pennsylvania

The Pennsylvania Department of Environmental Resources and the Erie County Health Department are involved in a cooperative effort to provide fish samples for the U.S. EPA Basic Water Monitoring Program and the GLISP. Composites of whole fish of both bottom feeders and perch are used to determine trends in contaminant levels.

The same whole-fish composites of perch also provide information for assessing human health impacts. Also, under the GLISP, skin-on fillets of coho salmon are used to provide information for evaluating the hazard that toxic substances pose to the fish-consuming public (Frey, 1982; Wellington, 1982).

Wisconsin

The Wisconsin DNR monitors contaminants in fish from the Great Lakes and their tributaries and inland lakes and rivers. Program objectives include the review and update of the fish contaminant advisory, identification and elimination of point sources of contaminants, and evaluation of commercial fish stocks. Both skin-on, boneless fillets and whole fish are utilized.

The Wisconsin Department of Agriculture and Consumer Protection routinely monitors PCB concentrations in smoked fish and PCB and chlorinated pesticide concentrations in chubs taken from markets and commercial fisheries. A skinless, boneless fillet is used for analysis (Sheffy, 1982; Merdol, 1982).

U.S. EPA - Region V (Chicago)

The U.S. EPA fish contaminant monitoring program consists of four elements. This effort is part of the GLISP, and a cooperative plan with Great Lakes jurisdictions. Several references to the plan are noted above. The first element involves open lake fish monitoring to define contaminant trends and identify new contaminants. Whole fish are homogenized for analysis. The second element includes analysis of skin-on fillets from game fish to evaluate potential human health hazards. The third element involves detection of new problem areas and contaminants in Great Lakes tributaries and embayments. Composites of whole

MONS 004907

fish are scanned for a broad range of organic and metal contaminants. The fourth element is designed to follow-up on data gathered for element three. Contaminant concentrations found to be significantly above background levels or FDA action levels in the whole fish composites will then also be monitored in skin-on fillets of game fish from these problem sites (DeVault, 1982).

U.S. FDA (Detroit)

The U.S. FDA is currently sampling commercial and potentially commercial species from 48 Great Lakes locations. At present, the FDA lab manual provides the following guidance for sampling raw fish for contaminant analysis: "Use the edible portion." The "edible portion" is defined to mean skin-on fillets in general, but allows for judgment to be used and often cross-sectional steaks or skin-off fillets are allowed. However, in reality, most samples prior to 1981 were prepared as skin-off fillets (Schneider, 1982).

Based on the above information, the jurisdictional sampling methods have been grouped under two general classes of objectives, shown in Table 1 (Sections A and B). Section A shows the sample types used when the objective is to determine the condition of the environment with respect to toxic materials. Section B shows the sample types used when the objective is to determine amounts of contaminants consumed when eating fish.

Most jurisidictions agree that whole fish should be analysed when the objective is to determine the condition of the environment (Section A). However, there are many inconsistencies in the sample portion used to determine amounts consumed (Section B). Most jurisdictions use, at one time or another, skin-on fillets or skin-off fillets. There are also other types of samples. Skinless dorsal muscle is used in Ontario. This is the sample portion which would contain a minimum of fat and which would, therefore, contain the least fat-soluble contaminants, such as PCBs and other non-polar organics. It can be considered a "best case" sample portion. On the other hand, some jurisdictions use the "worst case" sample portion. Indiana uses whole fish and cross-sectional steaks which would contain a maximum of fat and fat-soluble contaminants. So, indeed there is much variation.

MONS 004908

TABLE 1

Jurisdictional Methods of Fish Sampling

Jurisdiction	Type of Sample				
	Whole Fish	Cross-Sectional Steak	Skin-On Fillet	Skin-Off Fillet	Skinless Dorsal Muscle
A. Objective: Environmental Monitoring for Toxic Materials					
Illinois	X				
Indiana	X				
Michigan	X				
Minnesota	X				
New York			X		
Ohio			X		
Ontario	X				
Pennsylvania	X				
Wisconsin	X		X		
U.S. EPA (Chicago)	X				
B. Objective: Assessing Human Exposure; Determining if Fish Are Safe to Eat					
Illinois			X	X	
Indiana	X	X		X	
Michigan			X	X	
Minnesota				X	

MONS 004909

Table 1 (cont.)

Jurisdiction	Type of Sample				
	Whole Fish	Cross-Sectional Steak	Skin-On Fillet	Skin-Off Fillet	Skinless Dorsal Muscle
U. (continued)					
New York			X		
Ohio			X		
Ontario					X
Pennsylvania	X		X		
Wisconsin	X		X	X	
U.S. EPA (Chicago)			X		
U.S. FDA (Detroit)				X	

MONS 004910

THE NEED FOR STANDARDIZATION

There are several reasons why standardization of edible tissue sampling is needed. The first is simply because of the differences among the jurisdictions as indicated above. Michigan salmon data show that the skin-on fillet contains from 2 to 4 times as much DDT and PCB as the skin-off fillet (Rohrer et al., 1981). Thus, assuming that the action levels (contaminant concentrations used to determine if fish are safe to eat) do not vary among the jurisdictions, fish may pass in one jurisdiction and fail in another.

As discussed above, the U.S. FDA's guidance for sampling raw fish is to "use the edible portion", but is somewhat vague as to exactly what this means. In those jurisdictions and those programs where this is the only guidance for preparing samples, differences may occur among laboratories, and perhaps even among analysts at a single lab when they interpret what the "edible portion" is.

The same sample portion should be used for determining the commercial salability of fresh fish as for determining when warnings should be issued to sport anglers. This is because it is likely that persons purchasing fresh fish would prepare and eat the fish much as they would if they caught the fish themselves. However, sampling for these two purposes has often not been done consistently in the past.

One of the reasons that there are so many differences among the jurisdictions may be that no single portion serves to characterize contaminants in the edible portions of all species. For example, smelt are normally eaten as headless, gutted whole fish. Catfish are usually eaten as skin-off fillets. Therefore, the Michigan PCAC reached the conclusion that a species-specific standard edible portion is needed.

Although this seemed to be a sensible approach, the controversy was not over. Some fish are cooked with the skin on, but the skin is not eaten. Three examples of this are salmon, large trout, and whitefish. Since cooking prior to sampling is not practical, and since the information on precisely what happens to fat soluble contaminants during various cooking methods is incomplete, the debate has continued on what should be the edible portion. The debate has centered on two main points: should the "worst case" be used in order to be most protective, or should the "most likely case" be used to be credible with the most people? When sampling raw fish, the "worst case" is where the skin-on, high-fat portion which is to be cooked is used in order to obtain the highest concentration of fat-soluble contaminants. The "most likely case" is where

MONS 004911

the portion which would be eaten, after cooking, is used. This portion would contain lower concentrations of fat-soluble contaminants.

THE STANDARD EDIBLE PORTION PROPOSAL

To resolve these dilemmas, Michigan proposes that:

(1) there should be a standard edible portion which is specific for each species; and

(2) the "most likely case" should be used, that is, the portion of the raw fish which would actually be eaten after cooking.

In order to determine just how certain fish are prepared, cooked, and eaten, Michigan is making a survey of fish eaters. The survey will request information on those species for which there is the greatest difference of opinion regarding these questions. Included are Great Lakes salmon, whitefish, and catfish, and trout from both Great Lakes and inland waters. Figure 1 shows that form which is being used in the survey. It has been mailed to a 1 percent sample of those holding Michigan fishing licenses. Several thousand responses are expected. The results will be used to determine the official species-specific standard edible portion for these species.

In the meantime, a preliminary listing of standard edible portions has been prepared, based on the best judgments of the FCAC. It is shown in Table 2. The three types of standard edible portions are skin-on fillet, skin-off fillet, and headless, gutted whole fish. Only three kinds of sample portions are included in order to keep it relatively simple. The only fish in the category of headless, gutted whole fish is smelt. However, for skin-on fillets, there are a number of different kinds of fish including perch, walleye, bass, and the panfish group including bluegills and sunfish. The skin-off fillet group includes catfish, northern pike, whitefish, trout, salmon, and carp. The belly flap, which contains much of the fat, will be left on for skin-on fillets and will be taken off for skin-off fillets. The scales can be either left on or taken off because they should not have a significant effect on contaminant concentration.

There are several major advantages to this concept:

(1) It provides standardization among laboratories and jurisdictions. Of course, this advantage will occur regardless of whether the concept is "best case,"

1. PREPARATION

Do you trim away the dorsal and belly fat areas?

	FISH FROM THE GREAT LAKES				Trout From Other Waters
	Trout	Salmon	Whitefish	Catfish	
ALWAYS					
USUALLY					
SOMETIMES					
RARELY					
NEVER					

2. COOKING METHODS

a. Indicate how you cook each species of fish. Check a method only if you use it at least 20% (1/5) of the time.

	FISH FROM THE GREAT LAKES				Trout From Other Waters
	Trout	Salmon	Whitefish	Catfish	
PAN FRIED					
BROILED					
STEAMED					
DEEP FRIED					
CANNED					
SMOKED					
OTHER					

b. Do you cook the fish with the skin on?

	FISH FROM THE GREAT LAKES				Trout From Other Waters
	Trout	Salmon	Whitefish	Catfish	
ALWAYS					
USUALLY					
SOMETIMES					
RARELY					
NEVER					

3. CONSUMPTION

Do you eat the fish skin along with the fish flesh?

	FISH FROM THE GREAT LAKES				Trout From Other Waters
	Trout	Salmon	Whitefish	Catfish	
ALWAYS					
USUALLY					
SOMETIMES					
RARELY					
NEVER					
DO NOT EAT					

Figure 1. The Michigan Fish Eaters Survey Form.

"most likely case," etc., as long as it is standardized.

(2) The "most likely case" is believed to provide a more realistic measurement of the contaminants which would actually be consumed when eating the fish. Although the actual information on the effect of cooking is somewhat incomplete and sketchy at this time, studies have shown (see list of references) that many methods of cooking do reduce contaminants to some extent because fat will drip off or otherwise escape from the fish.

TABLE 2

Standard Edible Portions of Michigan Fishes

Standard Edible Portion	Common Name	Scientific Name
Skin-on Fillet	Yellow Perch	Perca flavescens
	Walleye	Stizostedion vitreum
	Sauger	Stizostedion canadense
	Largemouth Bass	Micropterus salmoides
	Smallmouth Bass	Micropterus dolomieui
	Bluegill	Lepomis macrochirus
	Pumpkinseed	Lepomis gibbosus
	Rock Bass	Ambloplites rupestris
	White Bass	Morone americana
	Black Crappie	Pomoxis nigromaculatus
	White Crappie	Pomoxis annularis
	Green Sunfish	Lepomis cyanellus
	Longear Sunfish	Lepomis megalotis
	Warmouth	Lepomis gulosus
	Sucker Family	Catastomidae
Skin-off Fillet	Black Bullhead	Ictalurus melas
	Brown Bullhead	Ictalurus nebulosus
	Yellow Bullhead	Ictalurus natalis
	Channel Catfish	Ictalurus punctatus
	Muskellung	Esox masquinongy
	Northern Pike	Esox lucius
	Lake Whitefish	Coregonus clupeaformis
	Round Whitefish (Menominee)	Prosopium cylindraceum
	Lake Herring	Coregonus artedii
	Chubs	Coregonus hoyi
	Lake Trout (lean & siscowet)	Salvelinus namaycush
	Steelhead	Salmo gairdneri
	Brown Trout	Salmo trutta
	Brook Trout	Salvelinus fontinalis
	Splake	Salvelinus fontinalis X Salvelinus namaycush
	Atlantic Salmon	Salmo salar
	Coho Salmon	Oncorhynchus kisutch
	Chinook Salmon	Oncorhynchus tshawytscha
	Pink Salmon	Oncorhynchus gorbuscha
	Carp	Cyprinus carpio
	Sheepshead	Aplodinotus grunniens

MONS 004914

Table 2 (cont.)

Standard Edible Portion	Common Name	Scientific Name
	Buffalo	Ictiobus cyprinellus
	Burbot	Lota lota
	Quillback	Carpiodes cyprinus
	Sturgeon	Acipenser fulvescens
Headless, Gutted Whole Fish	Rainbow Smelt	Osmerus mordax

(3) The "most likely case" is understandable and credible to fish eaters. It is understandable because the edible portion is simply the portion eaten, rather than the portion cooked. This should help prevent people from ignoring advisories which are based on how fish are cooked. For example, a person might say, "Why should I pay attention to a warning based on a skin-on portion when I don't ever eat the skin?"

(4) The "most likely case" corresponds with fish preparation recommendations from the state. Michigan advises people to avoid eating or even cooking contaminated fish with the skin on.

There is one disadvantage to the concept. In certain instances it may underestimate contaminants contained in the portion of fish that is eaten. However, in general, the difference in contaminant concentrations between skin-on and skin-off fillets are small in relation to the uncertainty of knowledge about human health effects. Thus, the disadvantage to this concept is minimal. Michigan believes that it is important to standardize so that everyone will be able to understand what is meant by a contaminant concentration from an edible portion, and not have to wonder what portion of the fish was used in the analysis.

The standard edible portion will be most advantageous if it is adopted by all the jurisdictions in the Great Lakes region. In order to pursue this, Michigan's first step will be to

MONS 004915

petition the U.S. FDA to establish the concept in its national lab manual. Also, Michigan will be recommending it to the U.S. EPA, to working groups under the direction of the International Joint Commission, and to the other jurisdictions.

In conclusion, Michigan believes that the "most likely case" standard edible portion is a good common-sense approach to fish contaminant sampling when the objective is to determine amounts of consumable contaminants present in fish.

ACKNOWLEDGMENTS

This paper is a formal statement of the proposed standard edible portion concept developed by the Michigan Fish Contaminant Advisory Committee. The author is greatful for the assistance of the other members of that committee: Dr. James Bedford, Mr. David Borgeson, Mr. Albert Hafner, Dr. Harold Humphrey, Mr. David Kenaga, and Mr. Thomas Rohrer. Thanks are also extended to Ms. Janice Swanson for her assistance in compiling the survey information on jurisdictional fish sampling methods, and to the jurisdictional respondents listed below.

SURVEY RESPONDENTS

Atgear, Barry. Ohio Department of Natural Resources, telephone communication to Michigan DNR, February 10, 1982.

Bridges, Lee. Indiana State Board of Health, telephone communication to Michigan DNR, February 17, 1982.

DeVault, Dave. U.S. Environmental Protection Agency. letter to Michigan DNR, February 19, 1982.

Frey, Robert. Pennsylvania Department of Environmental Resources, letter to Michigan DNR, February 18, 1982.

Helwig, Daniel. Minnesota Pollution Control Agency, letter to Michigan DNR, March 8, 1982.

James, William. Indiana Department of Natural Resources, telephone communication to Michigan DNR, February 16, 1982.

Johnson, Allan. Ontario Ministry of the Environment, telephone communication to Michigan DNR, February, 1982.

Mick, James. Illinois Department of Conservation, letter to Michigan DNR, March 4, 1982.

MONS 004916

Merdol, Jerry. Wisconsin Department of Agriculture and Consumer Protection, telephone communication to Michigan DNR, February 12, 1982.

Schneider, Felix. U.S. Food and Drug Administration, telephone communication to Michigan DNR, February, 1982.

Sheffy, Tom. Wisconsin Department of Natural Resources, letter to Michigan DNR, February, 1982.

Skinner, Larry. New York Department of Environmental Conservation, letter to Michigan DNR, February 22, 1982.

Wellington, Robert. Erie County Pennsylvania Health Department, telephone communication to Michigan DNR, February 26, 1982.

LITERATURE CITED ON EFFECT OF PREPARING AND COOKING ON FISH CONTAMINANTS

Cichy, R.F., M.E. Zabik, and C.M. Weaver. 1979. Polychlorinated Biphenyl Reduction in Lake Trout by Irradiation and Broiling. Bull. Environ. Contam. Toxicol. 22:807-812.

Dice, E.F. 1971. Getting Your Salmon Ready for Dinner. Ext. Bull. E-663, Michigan State University Cooperative Extension Service, East Lansing, MI. 4 pp.

New York State Department of Environmental Conservation. 1979. Quarterly Report on Toxic Substances Impacting on Fish and Wildlife 3(1), June 1979. Division of Fish and Wildlife.

Reinert, R.E., D. Stewart, and A.L. Seagran. 1972. Effects of Dressing and Cooking on DDT Concentrations in Certain Fish From Lake Michigan. J. Fish. Res. Bd. Canada 29:525-529.

Rippen, T.E. 1980. Understanding Contaminants in Fish. MICHU-SG-80-510, Michigan Sea Grant Publication. Ext. Bull. E-1434, Michigan State University Cooperative Extension Service, East Lansing, MI. 6 pp.

Smith, W.E., K. Funk, and M.E. Zabik. 1973. Effects of Cooking on Concentrations of PCB and DDT in Chinook and Coho Salmon From Lake Michigan. J. Fish Res. Bd. Canada 30:702-706.

MONS 004917

Wanderstock, J.J., W.W. Iskat, W.H. Gutenmann, and D.J. Link. 1971. Effect of Several Cooking Methods on Concentration of DDT Residues in Lake Trout and Coho Salmon. N. Y. Fish Game J. 18(1):70-72.

Zabik, M.E., P. Hoojjat, and C.M. Weaver. 1979. Polychlorinated Biphenyls, Dieldrin, and DDT in Lake Trout Cooked by Broiling, Roasting, or Microwave. Bull. Environ. Contam. Toxicol. 21:136-143.

OTHER LITERATURE CITED

Rohrer, T.K., J.H. Hartig, and J.C. Forney. 1981. Organochlorine and Heavy Metal Residues in Coho and Chinook Salmon of the Great Lakes. Michigan Department of Natural Resources Publ. No. 3730-0031, Lansing, MI. 23 pp.

MONS 004918

CHAPTER 11

THE PHOTOCHEMISTRY OF PCBs

Matthew J. Zabik
Pesticide Research Center
Michigan State University
East Lansing, Michigan 48824-1311

Within the last few years, a sudden interest has developed in a hitherto relatively unknown class of industrial organochlorine compounds: the polychlorinated biphenyls (PCBs). Figure 1 give the structures of some selected symmetrical and unsymmetrical PCBs.

Traces of these compounds have been reported in environmental samples since 1966 (Anon., 1966). In the following years, PCB contamination was found to be almost universal (Risebrough et al., 1968; Gustafson, 1970; Peakall and Lincer, 1970; Veith and Lee, 1970; Richardson et al., 1971; Edwards, 1971) including human milk (Acker and Schulte, 1970), human adipose tissue (Biros et al., 1970), and brain tissue of infants (Hutzinger et al., 1972). Little is known about the toxic effects of PCB after long-term exposures, as observed in the endemic poisoning resulting from PCB contaminated rice oil (Kuratsune et al., 1971).

Polychlorobiphenyls are prepared commercially from the iron catalyzed chlorination of biphenyl. The product is a complex mixture containing at least sixty different PCB isomers with varying chlorine content. Table 1 lists some glc retention times of some selected PCBs.

The characteristic properties of PCBs which make them desirable for industrial use are their high dielectric constant and their thermochemical stability up to 900°C. Their stability, coupled with the ease with which they are taken up by living organisms and accumulated at higher levels of the food web, has resulted in environmental problems.

MONS 004919

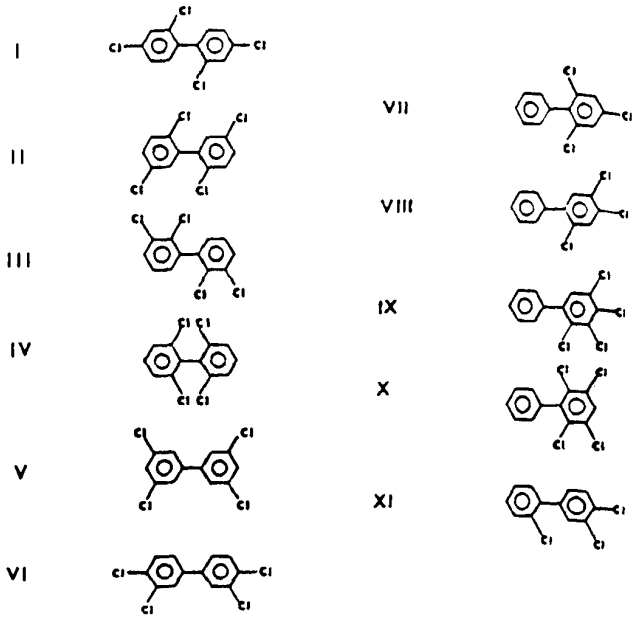


Figure 1. Structures of symmetrically substituted tetrachlorobiphenyls (I-VI) and unsymmetrical tri- and tetrachlorobiphenyls (VII-XI).

They were used as dieletric fluids in capacitors and transformers; as industrial fluids in hydraulic systems, gas turbines, and vacuum pumps; as plasticisers in adhesives; in textiles, surface coatings, sealants, and copy paper; as heat transfer agents, fire retardants, and fruit preservers. With such a variety of uses, it is not surprising that industrial leaks are largely responsible for the presence of PCB in the ecosystem.

MONS 004920

TABLE 1

Gas Chromatographic Retention Times of Polychlorinated Biphenyls in Cyclohexane[a]

PCB	R_t	PCB	R_t	Designation
Monochloro		Trichloro		
2-	0.60	2,4,6-	1.55	(VII)
3-	0.82	2,2',6-	1.65	
4-	0.85	2,2'5-	1.85	
Dichloro		2,4,5-	2.20	(VIII)
2,6-	0.92	2,3',5-	2.45	
2,2'-	1.00	2,4'-	2.60	
2,5-	1.15	3,4,2'-	2.75	(XI)
2,4-	1.25	3,4,5-	3.60	
2,3-	1.40	3,3',4-	4.30	
3,5-	1.50	Tetrachloro		
3,3'-	1.75	2,2',4,4'-	3.70	(I)
3,4-	1.80	2,2',5,5'-	3.65	(II)
4,4'-	1.95	2,2',3,3'-	4.80	(III)
		2,2',6,6'-	2.30	(IV)
		3,3',5,5'-	5.70	(V)
		3,3',4,4'-	8.90	(VI)
Methoxylated PCB		2,3,4,5-	4.80	(IX)
2,4,4'-Trichloro-2'-methoxy	5.05	2,3,5,6-	3.35	(X)
4,4'-Dichloro-2,2'-dimethoxy	6.30			

[a] R_t relative to cyclohexane

There is evidence that PCBs are metabolized slowly in some organisms to their hydroxy derivatives (Block and Cornish, 1959). However, little is known about the efficiency of uptake and excretion and it is considered probable that a steady-state situation exists in some areas.

Even though all the available commercial PCB mixtures are toxic to some extent, those containing four or less chlorine substitutents have the highest toxicity, as reported in a study of their interaction with tissue culture cells (Hoopingarner et al., 1972).

MONS 004921

The uv spectra of the PCBs I-XI were obtained in cyclohexane solution. Scanning was carried out in the 220-320 nm region. Typically, PCB solutions were 0.1-1.0 x 10^{-4}M except in cases where higher concentrations had to be used in order to obtain the molar absorptivity (ε) in 280-300 nm region. The values of ε were calculated at 290 nm and at the maximum wavelength of the conjugaton band (240-270 nm). In cases where this band disappeared, the extinction coefficient was calculated at 255 nm.

Since PCB absorption in the uv conformed to Beer's Law, ε was calculated using equation 1.

$$\log I_0/I = A = \varepsilon bM \qquad (1)$$

Those PCB containing para and no ortho chlorines exhibited a band in the 240-270 nm region of greater intensity than that of biphenyl itself. PCB containing ortho chlorines showed decreased intensity relative to that of unsubstituted biphenyl. When only meta chlorines were present, the intensity of absortion was similar to biphenyl. Extinction coefficients are listed in Table 2.

In 1971, the first study of PCB photochemistry appeared in the literature (Safe and Hutzinger, 1971). Dechlorination of 2,2',4,4',5,5'-hexachlorobiphenyl at wavelengths greater than 300 nm in hexane yielded more than ten products containing two to five chlorines per molecule. The individual isomers were not identified beyond establishing their parent peaks M$^+$ from the mass spectra.

Our studies of the photolysis of 3,3',4,4'-tetrachlorobiphenyl showed stepwise dechlorination to be the only reaction undergone by this compound in hexane (Ruzo et al., 1972). At about the same time, 2,2',5,5'-tetrachlorobiphenyl was photolysed in dioxane-water and hydroxy substitution was obtained in addition to small amounts of condensation and reductive dechlorination products. 2,2',5,5'-, 3,3',4,4'-, and 2,2',6,6'-tetrachlorobiphenyls were found to decompose at about the same rate in non-degassed solutions. However, no accurate kinetic values were obtained and no photoproducts were identified beyond their molecular weight.

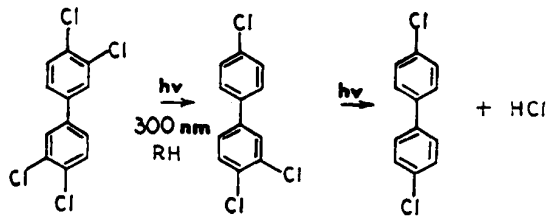
The photolysis of 2,2',4,4',6,6'-hexachlorobiphenyl in oxygen saturated methanol solution has been found to yield oxygenated, methoxylated, and dechlorinated products (A,B,C) (Anderson et al., 1973) in small amounts. These compounds arise from cleavage of ortho chlorines and subsequent radical reactions with oxygen. None of them are observed in degassed solutions.

MONS 004922

TABLE 2

Molar Extinction Coefficients of PCB in Cyclohexane Solution

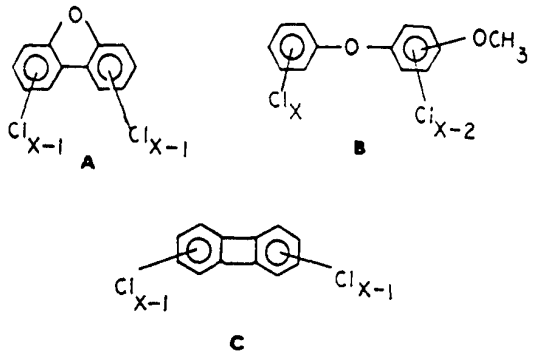
PCB	ε(290 nm)	ε(240-270 nm)	λ_{max}
I	320	10,000	253
II	300	1,200	(255)
III	170	1,500	(255)
IV	50	300	(255)
V	950	18,000	252
VI	6,000	22,000	262
VII	85	4,800	(255)
VIII	1,200	11,800	260
IX	1,100	19,200	260
X	390	2,800	(255)
XI	730	13,100	252
Biphenyl	900	15,000	249



All these results point to the intermediacy of biphenyl-free radicals, either abstracting hydrogen from the solvent, or combining with triplet oxygen to give peroxides and subsequently ethers.

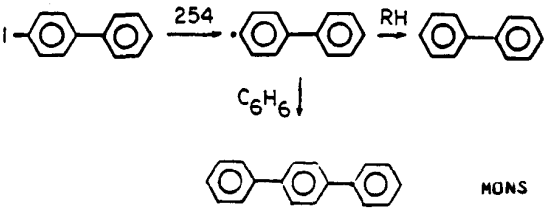
The methoxylated or hydroxylated products observed may be formed in a manner similar to that of several haloaromatic systems studied (Earltrop et al., 1967; Kharasch, 1967).

MONS 004923



At the beginning of our research (1970), no reports existed in the literature concerning the photochemical behavior of PCB. Several chloroaromatics had been studied; and in every case, either chlorine cleavage with subsequent free radical hydrogen abstraction (Forbes and Dearden, 1959; Latowska and Latowski, 1966; Majer and Simmons, 1964; Henderson and Zweigh, 1967) or nucleophilic displacement of chlorine (Barltrop et al., 1967; Crosby and Yu-Li, 1966; Havinga and Kronenberg, 1968) occurred.

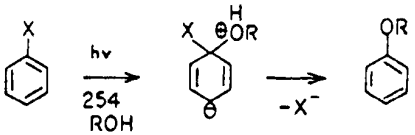
The photochemistry of iodobiphenyls at 254 nm in benzene and hydrocarbon solvents was reported in 1968 (Kharasch and Sharma, 1968). Kharasch found that iodine cleavage resulted in the formation of a biphenyl radical which could then either attack the solvent to yield terphenyl or abstract hydrogen and form biphenyl.



MONS 004924

In the presence of oxygen, the recombination reaction becomes negligible and p-hydroxybiphenyl is obtained. Further proof of the intermediacy of free radicals is obtained when the reaction is run in the presence of nitric oxide (NO), a known radical scavenger which can inhibit the back reaction; thus the quantum yield of iodobiphenyl reaction increases.

The photolysis of iodobenzene in fluorocarbon solvents at 77° K has been studied by ESR. The results also suggest the formation of free phenyl radicals upon photolysis (Ingalls *et al.*, 1964).



R = CH_3, H X = Cl, Br, I

The ionic intermediate can be stabilized by electron withdrawing groups *ortho* or *para* to X. The reaction usually has a low quantum yield (<0.1), and the preferred course is elimination of X before nucleophilic attack takes place. Tables 3-9 give the photoproducts of some selected biphenyls.

Haloterphenyls have also been found to dechlorinate photochemically with subsequent formation of terphenyls and cyclization products (Sato *et al.*, 1969).

In 1933, Adams showed that those derivatives of biphenyl which had substituents above a certain limiting size in the *ortho* position could be resolved into stereoisomers (Adams and Yuan, 1933). This phenomenon was explained as a result of restricted rotation of the two benzene rings by interference from the substituent groups.

The ultraviolet absorption spectra of several 2,2'-disubstituted biphenyls showed unexpected differences with their benzene analogs (Pickett *et al.*, 1936). The band maxima in the benzene derivatives corresponded to similar ones in the

MONS 004925

TABLE 3

Photoproducts of 2,2',4,4'-Tetrachlorobiphenyl (I) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
2,4,4'-Trichlorobiphenyl	256	2,4,4'-Trichlorobiphenyl	256
4,4'-Dichlorobiphenyl	222	4,4'-Dichlorobiphenyl	222
4-Chlorobiphenyl[b]	188	4-Chlorobiphenyl[b]	188
		$C_{12}H_6Cl_3(OCH_3)$	256
		$C_{12}H_6Cl_2(OCH_3)_2$	282
		$C_{12}H_7Cl_2(OCH_3)^6$	252

[a]Combined methoxylated products constitute <5% of total product formation.
[b]Product constitutes <1% of total product formation.

TABLE 4

Photoproducts of 2,2',5,5'-Tetrachlorobiphenyl (II) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
2,3',5-Trichlorobiphenyl	256	2,3',5-Trichlorobiphenyl	256
3,3'-Dichlorobiphenyl	222	3,3'-Dichlorobiphenyl	222
3-Chlorobiphenyl[b]		$C_{12}H_6Cl_3(OCH_3)$	256
		$C_{12}H_6Cl_2(OCH_3)_2$[b]	252

[a]Combined methoxylated products constitute <3% of total product formation.
[b]Product consitutes <1% of total product formation.

biphenyl compounds which are displaced toward lower energies. Absorption was nearly additive for the two rings. With 4,4'-dichlorobiphenyl, the red shift was greater and the band intensity showed a 10^3-fold increase compared to that of

TABLE 5

Photoproducts of 2,2',3,3'-Tetrachlorobiphenyl (III) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
2,2'3'-Trichlorobiphenyl[b]	256		
2,3,3'-Trichlorobiphenyl	256	2.3.3'-Trichlorobiphenyl	256
3,3'-Dichlorobiphenyl	222	3,3'-Dichlorobiphenyl	222
3-Chlorobiphenyl[b]	188		
		$C_{12}H_6Cl_3(OCH_3)$	286
		$C_{12}H_6Cl_2(OCH_3)_2$	282

[a]Combined methoxylated products constitute <3% of total product formation.
[b]Product constitutes <1% of total product formation.

TABLE 6

Photoproducts of 2,2',6,6'-Tetrachlorobiphenyl (IV) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
2,2',6-Trichlorobiphenyl	256	2.2',6-Trichlorobiphenyl	256
2,2'-Dichlorobiphenyl	222	2,2'-Dichlorobiphenyl	222
		$C_{12}H_6Cl_3(OCH_3)$[a]	286

[a]Product constitutes <1% of total product formation.

2,2'-dichlorobiphenyl. At the time (1936), no explanation was offered for this phenomenon.

In 1938, the geometry of biphenyl derivatives was studied on the basis of their dipole moments (LeFevre and Vine, 1938). the carbons 4-1-1'-4' were found to be colinear in a large majority of the compounds studied. X-ray studies confirmed these findings (Pickett, 1936).

MONS 004927

TABLE 7

Photoproducts of 3,3',5,5'-Tetrachlorobiphenyl (V) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
3,3',5-Trichlorobiphenyl	256	3,3',5'-Trichlorobiphenyl	256
		3,3'-Dichlorobiphenyl	222

[a]Product constitutes <1% of total product formation.

TABLE 8

Photoproducts of 3,3',4,4'-Tetrachlorobiphenyl (VI) in Cyclohexane and Methanol Solutions

Products (Cyclohexane)	m/e	Products (Methanol)[a]	m/e
3,4,4'-Trichlorobiphenyl	256	3,4,4'-Trichlorobiphenyl	256
3,3',4'-Trichlorobiphenyl	256		
4,4'-Dichlorobiphenyl	222	4,4'-Dichlorobiphenyl	222
4-Chlorobiphenyl[a]	188	4-Chlorobiphenyl[a]	188
		$C_{12}H_6Cl_3(OCH_3)$[a]	286

[a]Product constitutes <1% of total product formation.

The earliest observations with regard to the actual excited state of biphenyls were given by Lewis and Kasha in 1944. The triplet energy (E_t) of several haloaromatics was calculated from their phosphorescence spectra. E_t values were lowest for 4,4'-disubstituted biphenyls (< 66 kcal) and highest for the ortho substituted PCB (>70 kcal).

The solution spectrum of biphenyl shows a single structureless band with λ_{max} around 250 nm and ε_{max} of 18,000. Presumably, this band represents the 208 nm transition of benzene, which is shifted by conjugation with the chromophoric phenyl substituent. The forbidden benzene transition at 25[illegible]

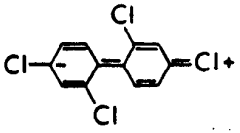
MONS 004928

TABLE 9

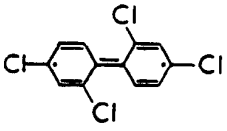
Photoproducts of Unsymmetrical PCB (VII-XI)
in Cyclohexane Solution

PCB	Products	m/e
VII	2,4-Dichlorobiphenyl	222
	4-Chlorobiphenyl	188
VIII	3,4-Dichlorobiphenyl	222
	4-Chlorobiphenyl	188
IX	3,4,5-Trichlorobiphenyl	256
	3,4-Dichlorobiphenyl	222
X	2,3,5-Trichlorobiphenyl	256
	3,5-Dichlorobiphenyl	222
XI	3,4-Dichlorobiphenyl	222

nm is probably hidden below the main biphenyl band. The additional weak band displayed at 270-290 nm by some halobiphenyls is probably the result of interactions between the substituent's free electrons in the π system (Beaven and Hall, 1956;. The electron distribution in the excited state can be represented by 1 or 2:



1



2

MONS 004929

Thus, if the excited state of PCB is a dipolar or diradical species with coplanar rings and a C-C linkage of essentially complete double bond character, then the short wave shift in the conjugaton band of an ortho chlorinated PCB would arise from an increase in the transition energy resulting from the raising of the triplet energy. The excited triplet is thus shown to be more sensitive to steric effects than the ground state.

On this basis, a correlation may exist between the steric requirements of the triplet and the photochemical lability of the ortho chlorines, relative to that of those in the meta or para positions.

Studies of deuterium isotope effects have been carried out (Bartell, 1961). A molecule such as biphenyl d_{10} would be expected to be closer to planarity than normal biphenyl h_{10} owing to the shorter length of the C-D bond compared to the C-H bond. The extinction coefficient of biphenyl d_{10} reflects the increase in resonance between the rings, in hexane solution a ratio of $\varepsilon_H/\varepsilon_D = 0.96$ has been obtained (Leffek, 1967).

In 1967, Wagner (1967) reported the actual triplet energy of biphenyl. He found that there was a 10 kcal difference between the highest energy phosphorescence band at 65.5 kcal and the lowest energy absorpton band at 75.5 kcal. This case of non-overlapping emission and absorption spectra is a direct result of the Franck-Condon principle (Pringheim, 1949). Quenching experiments relative to benzophenone would indicate an E_t value of 69.5 kcal.

The most stable conformation of ground state biphenyl depends strongly on the medium. The dihedral angle between the rings is 40-50° in the gas phase (Bastiansen, 1949), 20-25° in solution (Suzuki, 1959), and 0° in the crystalline state (Trotter, 1961; Hirota, 1966). Since ortho substituents increase this angle, better quenching could be expected if the excited state was non-planar, and worse quenching if planar. Wagner found that the quenching efficiency of substituted biphenyls was less than expected when quenching a series of ketones.

One advantage liquid-phase photochemistry has over the gas phase is that several kinetic simplifications can be made. Absorption of light by a PCB can produce several excited singlets with many corresponding vibrational levels. In solution, decay to the lowest excited singlet occurs almost instantaneously (10^{-12} sec)(Wilkinson and Dubosis, 1963). Thus, it may be assumed that all singlet processes happen from the lowest singlet (S_1).

MONS 004930

Experiments using mono- and di-chlorobiphenyls show that inter-system crossing quantum yields (Φ_{isc}) increase with increasing number of chlorine substituents (Wagner and Scheeve, unpublished results). Though small, chlorine has a measurable heavy atom effect (HAE). With iodine and bromine, HAE values are greater (McGlynn et al., 1963; Medinger and Wilkinson, 1965). Such effects on $S-\bar{T}$ transitions are quite general and are probably the result of spin orbit coupling which causes mixing of singlet and triplet states (Robinson and Frosch, 1963). The singlet then acquires a small amount of triplet character and the triplet some singlet character, so the transition loses some of its forbidden character. HA effects are responsible for large phosphorescence/fluorescence ratios obtained with haloaromatics (Dewar and Gleicher, 1965). It has also been pointed out that HAE involving $\pi - \pi^*$ excited state are quite pronounced since normally negligible amounts of spin orbit coupling are present in symmetrical aromatics (El-Sayed, 1964).

For kinetic calculations in solution, the rate of phosphorescence can usually be ignored since it is much slower than the rates of other triplet processes. The following mechanistic scheme can be written for the photochemical processes of PCB (A) in solvent (SH), with quencher (Q).

SCHEME 1

Process	Rate	
$A_0 + h\nu \xrightarrow{I_a} A_1^* \xrightarrow{isc} A_3^*$	a (if $\Phi_{isc} = 1$)	(1)
$A_3^* \rightarrow A_0$	$K_d\ (A_3^*)$	(2)
$A_3^* \rightarrow A^\cdot + Cl^\cdot$	$K_r\ (A_3^*)$	(3)
$A^\cdot + SH \rightarrow A-H + S^\cdot$		(4)
$S^\cdot + S^\cdot \rightarrow S-S$		(5)
$A^\cdot + A^\cdot \rightarrow A-A$		(6)
$Cl^\cdot + SH \rightarrow H-Cl + S^\cdot$		(7)
$Cl^\cdot + A^\cdot \rightarrow A_0$		(8)
$A^\cdot + S^\cdot \rightarrow A-S$		(9)
$A_3^* + Q \rightarrow A_0 + Q_3^*$	$K_q\ (Q)(A_3^*)$	(10)

MONS 004931

Under steady-state conditions, $dA^{*3}/dt = 0$ and the only directly measurable parameter is the quantum yield of reaction. Using the definition of Wagner (1971), the quantum yield for a particular photoprocess is given by:

$$\Phi_i = \Phi_{ES}\, \Phi_R\, P_i. \tag{11}$$

Assuming $\Phi_{isc} = 1$ for PCB containing three or more chlorines:

$$\Phi_i = P_i \frac{K_r}{K_r + K_d} \tag{12}$$

so that Φ_i becomes the quantum yield of reaction.

When a triplet quencher is used, equation 12 becomes:

$$\Phi_i = P_i \frac{K_r}{K_r + K_d + K_q(Q)} \tag{13}$$

Dividing equation 12 by equation 13, the familiar Stern-Volmer relationship is obtained:

$$\frac{\Phi}{\Phi_Q} = 1 + K_q t(Q) \tag{14}$$

Where Φ_Q represents the quantum yield of reaction in the presence of quencher (Q). The lifetime of the triplet (t) is the reciprocal of the sum of the rates of all the reactions undergone by the triplet.

$$t = (K_r + K_d)^{-1} \tag{15}$$

A plot of the relative quantum yield versus quencher concentration is linear with a slope equal to the product $K_q t$ and an intercept of 1, if only one excited state is reacting and being quenched.

The photoreactions of PCB were found to be zero order when >99 percent of the incident light was absorbed. The following equation gives the rate constant for a zero order reaction (k):

$$(PCB)^o - (PCB)^t = k\, t \tag{16}$$

MONS 004932

where t is the time of irradiation and (PCB) is the substrate concentration at 0 and t times. Plots for I-VI are shown in in Figures 13 through 15. The k values are given in Table 10.

For compounds VII-XI, one point rate constants were determined (Table 11). The k values obtained in cyclohexane were found to be slightly lower than those in methanol solution.

The largest k values were obtained for PCBs containing ortho-para chlorination (I, VII-IX, XI). Compounds with ortho-meta chlorination showed intermediate k values (II-IV, X), and those with meta-para substitution (V-VI), the lowest.

TABLE 10

Reaction Rate Constants (k) and Quantum Yields (δ_r) for PCB in Cyclohexane

PCB	k, 10^{-9}M sec^{-1}	δ_r
I	74.5	0.100
II	7.4	0.010
III	5.0	0.007
IV	3.8	0.006
V	1.2	0.002
VI	2.8	0.005

TABLE ··

One Point Reaction Rate Constants (k) for Unsymmetrically Substituted PCB in Cyclohexane Solution

PCB	k, 10^{-9}M sec^{-1}	δ_r
VII	14.0	0.02
VIII	42.4	0.05
IX	29.3	0.04
X	6.0	0.01
XI	12.0	0.02

MONS 004933

Absolute quantum yields of reaction ($\bar{\delta}_r$) were determined for I-XI. Degassed cyclohexane solutions of PCBs containing an internal standard were irradiated in parallel with actinometer solutions at 300 ± 10 nm. Values for $\bar{\delta}_r$ are given in Tables 10 and 11.

The quantum yields obtained correlated well with the rate constants. The extremely low values of $\bar{\delta}_r$ found for V and VI by necessity must contain a relatively large error and were calculated basically for comparison purposes.

In order to determine the lifetime of the excited state of I-VI, quenching of the dechlorination reaction was carried out. 1,3-Cyclohexadiene (E_t = 50 kcal/mole) was found to be an appropriate quencher for the systems under study.

Vpc analysis of PCB reacted permitted the calculation of relative quantum yields, $\bar{\delta}^o/\bar{\delta}$. The Stern-Volmer plots obtained were linear with unity intercepts. The slopes are equal to $k_q t$. The diffusion rate constants in cyclohexane and methanol are known (Wagner and Kochevar, 1968); however, some change is expected in their value at 30°C, according to the Debye (1942) equation.

Using these values, the excited state lifetimes were calculated (Table 12). The t values were the same in both solvents within experimental error.

TABLE 12

Lifetimes of the Triplet Excited States of Polychlorinated Biphenyls

PCB	Solvent	$k_q t$	$t, 10^{-8}$ sec
I	Methanol	101.4	0.78
I	Cyclohexane	68.8	0.85
II	Methanol	87.1	0.67
III	Methanol	100.1	0.77
IV	Methanol	91.0	0.70
IV	Cyclohexane	76.9	0.95
V	Methanol	248.3	1.91
V	Methanol	286.0	2.20

MONS 004934

The sensitized isomerization of cis → trans piperylene was used to determine isc for several PCB. Reproducible results were only obtained for 3,3',4,4'-tetrachlorobiphenyl (VI) indicating a-value of unity by comparison with benzophenone. The sensitized phosphorescence of biacetyl gave better results allowing the calculation of isc for I, III, V, and VI.

Benzene solutions of PCB and biacetyl were degassed and their phosphorescence emission at 521 nm compared with that of benzene solutions of benzophenone/biacetyl. In all cases, $\Phi_{isc} = 1$ (Table 13).

With the exception of most fluoroaromatics, the primary process in haloaromatics involves cleavage of the C-X bond to yield radicals. In some of the early experiments, the presence of free halogen atoms was observed from transient spectra due to formation of ClO, BrO, IO, following the flash photolysis of the halogenated compound (Majer and Simmons, 1964).

The formation of dechlorinated PCB in hydrogen donating solvents such as cyclohexane and methanol points to the presence of a free radical species capable of hydrogen abstraction. Cleavage of the C-Cl (83 kcal/mole) in the triplet yields a phenyl radical in a primary rate determining step. Formation of HCl is detected during irradiation in keeping with such a mechanism.

It is preferentially the ortho chlorines that cleave. Some meta cleavage was also observed (III), but could be considered negligible compared to ortho dechlorination. In the absence of ortho substituents, meta dechlorination occurs preferen-

TABLE 13

Intersystem Crossing Quantum Yields of Selected Polychlorobiphenyls

PCB	Φ_{isc}
I	1.00 ± 0.01
III	0.97 ± 0.03
V	0.99 ± 0.02
VI	0.99 ± 0.00

MONS 004935

tially (VI, VIII, IX). These results point to the importance of steric and resonance effects in determining the course of the reaction.

Dechlorination in I-VI was in a stepwise manner, chlorine cleaving first on one ring, then in the same position in the other ring. In none of the cases studied was one ring dechlorinated preferentially over the other.

The methoxylated products obtained in methanol solution most likely arise from nucleophilic attack of the solvent with intermediacy of an ionic species stablized by charge delocalization over the biphenyl system.

Since no methoxylation occurs at the para position, it must be concluded that bond weakening of the ortho chlorine plays an important part in this process. Attack of the nucleophile can be visualized as occurring on an already partially ionized C-Cl bond, where carbon has developed a partial positive and chlorine a partial negative charge. This weakening of the bond would not occur at the para carbon-chlorine position since it does not destabilize the excited state.

The linearity of the Stern-Volmer plots (Wagner, 1971) and the absence of fluorescence from tetrachlorobiphenyls indicate the existence of only one reactive excited state, a triplet.

Quantum yields give a more dramatic demonstration of the substituent effects as shown in Tables 10 and 11. The value of Φ_r for 2,2',4,4'-tetrachlorobiphenyl (0.100) is greater by a factor of 10-50 than those obtained for II-VI. The unsymmetrical PCB VII-IX and XI also show larger values. The lowest values obtained are for those compounds containing no ortho chlorines (V and VI). It is clear that the reactivity of PCB could at least partially be explained on the basis of the "ortho" effect; however, the large difference between the 2,4 and 2,3 substituted PCB could not be explained without calculation of the k_d and k_r values. The ratios of decay/reaction for six PCB triplets are listed below:

PCB	k_d/k_r
I	9
II	100
III	120
IV	150
V	520
VI	200

MONS 004936

In all cases decay is preferred to reaction; however, this tendency grows more pronounced in the order 2,4, 2,3, 3,4, and 3,5 substitution. In compounds having 2,4 substitution, the reaction becomes a competitive path to reversion to the ground state.

Transannular effects are shown to be present in the reaction of 3,4,2'-trichlorobiphenyl (XI) to yield, 3,4-dichlorobiphenyl (ϕ_r = 0.02). This quantum yield is the smallest of those obtained for 2,4 PCB; but still greater than those of the rest, the highest of which is 0.01 (II). It can be concluded that the driving force for the reacting is greatest when both the ortho and para chlorines are on the same ring and that the rates increase when the effects arise from both rings.

Since PCBs are thermally and biologically non-degradable, their presence in the environment, either by misuse or accidenal leakage, constitutes a long-term problem. Photochemical degradation is shown to be a major, if not the only, degradation pathway since solar radiation of the wavelength required is present.

The prevalent substitution patterns of tetrachlorobiphenyls found in Arochlor 1242 and 1248 (42 and 48% chlorine, respectively) are 2,5; 2,3; 2,4; and 3,4 (Hutzinger et al., 1972). Of these, the only ones that can be degraded with relative ease are the 2,4 substituted isomers.

The photochemical introduction of biological "handles", which make metabolic degradation possible, is shown to take place in methanol and in water. Methoxy and hydroxy groups are introduced rather slowly; this detracts from their environmental significance. Furthermore, since PCB introduction in the aquatic environment usually takes place in the presence of other hydrophobic substances (oils), contact with the potential nucleophile, water, would be minimized.

LITERATURE CITED

Acker, L. and E. Schulte. 1970. Uber das Vorkommen von Chlorienten Biphenylen and Hexachlorbenzol neben Chlorierten Insektiziden in Humanmilch and Menschlichem Fettzeweke. Naturwiss 57:497.

Adams, C. and L. Yuan. 1933. The Stereochemistry of Diphenyls and Analogous Compounds. Chem. Rev. 12:261-338.

MONS 004937

Anderson, K., A. Norstrom, C. Rappe, B. Rasmuson, and H. Swahlin. 1973. Photochemical Degradation of PCB. Abstracts of the 166th Meeting of the American Chemical Society, Chicago, IL, p. Pest-11.

Anon. 1966. Report of a New Chemical Hazard. New Scientist 32:612.

Barltrop, J.A., N.J. Bunce, and A. Thompson. 1967. Organic Photochemistry. Part IV. Photonucleophilic Substitution Reactions of Monosubstituted Benzenes. J. Chem. Soc. (c):1142-1145.

Bartell, L.S. 1961. The Role of Non-Bonded Repulsions in Secondary Isotope Effects. I. Alpha and Beta Substitution Effects. J. Amer. Chem. Soc. 83:3567-3571.

Bastiansen, O. 1949. The Molecular Structure of Biphenyl and Some of Its Derivatives. Acta Chem. Scand. 3:408-414.

Beaven, G.H. and D.M. Hall. 1956. The Relation Between Configuration and Conjugation in Diphenyl Derivatives. Part VII. Halogenodiphenyls. J. Chem. Soc.:4637-4646.

Biros, F.J., A. Walker, and A. Medbery. 1970. Polychlorinated Biphenyls in Human Adipose Tissue. Bull. Environ. Contam. Toxicol. 5:317-323.

Block, W.D. and H.H. Cornish. 1959. Metabolism of Biphenyl and 4-Chlorobiphenyl in the Rabbit. J. Biol. Chem. 234:3301-3302.

Crosby, D.G. and H.O. Tutass. 1966. Photodecomposition of 2,4-Dichlorophenoxyacetic Acid. J. Agr. Food Chem. 14:596-599.

Debye, P. 1942. Reaction Rates in Ionic Solution. Trans. Electrochem. Soc. 82:265-272.

Dewar, M.J.S. and G.J. Gleicher. 1965. Self-Consistent Field Molecular Orbital Calculations for Cyclobutadiene. J. Amer. Chem. Soc. 87:3255-3256.

Edwards, R. 1971. The Polychlorobiphenyls, Their Occurrence, and Significance: A Review. Chem. and Ind.:1340-1348.

El-Sayed, M.A. 1964. Vanishing First- and Second-Order Intramolecular Heavy-Atom Effects on the (n^* → n) Phosphorescence in Carbonyls. J. Chem. Phys. 41:2462-2467.

Forbes, W.F. and J.C. Dearden. 1959. Light Absorption Studies. Part XVI. The Ultraviolet Absorption Spectra of Fluorobenzenes. Can. J. Chem. 40:1977-1985.

MONS 004938

Gustafson, C.G. 1970. PCB's - Prevalent and Persistent. Environmental Science and Technology 4:814-819.

Havinga, E. and M.E. Kronenberg. 1968. Some Problems in Aromatic Photosubstitution. Pure and Appl. Chem. 16:137-152.

Henderson, W.A. and A. Zweigh. 1967. Photolytic Rearrangement and Halogen-Dependent Photocyclization of Halophenylnaplthalenes. J. Amer. Chem. Soc. 89:6778-6779.

Hirota, N. 1966. Use of Triplet-State Energy Transfer in Obtaining Singlet-Triplet Absorption in Organic Crystals. J. Chem. Phys. 44:2199-2200.

Hoopingarner, R., A. Samuels, and D. Krause. 1972. Polychlorinated Biphenyl Interactions With Tissue Culture Cells. Environ. Health Perspect. 1:155-158.

Hutzinger, O., S. Safe, and V. Zitko. 1974. The Chemistry of PCB's. CRC Press, Cleveland, OH, pp. 197-220.

Ingalls, R.B., W. Wolfe, and N. Kharasch. 1964. An ESK Study of the Photolysis of Iodobenzene of 77°K. Abstracts of the 146th Meeting of the American Chemical Society, Denver, CO, p. 6D.

Kharasch, N. 1967. Formation of Benzynes by Photolysis of 1,2-Di-iodoarenes. Chem. Comm.:492-493.

Kharasch, N. and R.K. Sharma. 1968. The Photolysis of Indoaromatic Compounds. Ang. Chem. Int. Ed. 7:96-98.

Kuratsune, M., T. Yoshimura, J. Matsuzaka, and A. Yamaguchi. 1971. Epidemological Study on Yusho, A Poisoning Caused by Injection of Rice Oil Contaminated With a Commercial Brand of Polychlorinated Biphenyls. Environ. Health Perspect. 1:119-128.

Latowska, E. and T. Latowski. 1966. Badania Nod Fotochemia Chloroweopochodnych. VII. Fotoliza Wielochloropochadnych Benzenu Oraz Isomerow Roznych Dwuchlorowcobenzenow w Roztworze Metanolowizn. Rocz. Chem. 40:1977-1981.

LeFevre, R.J. and H. Vine. 1938. The Configuration of Certain Diphenyl Compounds Indicated by Their Dipole Moments. J. Chem. Soc.:967-972.

Leffek, K.T. 1967. Deuterium Isotope Effect on the Ultraviolet Spectrum of Biphenyl. Can. J. Chem. 45:2115-2117.

MONS 004939

Lewis, G.N. and N. Kasha. 1944. Phosphorescence and the Triplet State. J. Amer. Chem. Soc. 66:2100-2116.

Majer, J.R. and J.P. Simmons. 1964. Photochemical Processes in Halogenated Compounds. In: Noyes, W.A., G.S. Hammond, and J.N. Pitts, Jr. (eds.), "Advances in Photochemistry," pp. 137-181, Vol. 2. John Wiley and Sons, Inc., New York, NY.

McGlynn, S., J. Daigre, and F.J. Smith. 1963. External Heavy-Atom Sping-Orbital Coupling Effect. IV. Intersystem Crossing. J. Chem. Phys. 39:375-679.

Medinger, T. and F. Wilkinson. 1965. Mechanism of Fluorescence Quenching in Solution. Part 1. Quenching by Bromobenzene. Trans. Faraday Soc. 61:620-630.

Peakall, D.B. and J.L. Lincer. 1970. Polychlorinated Biphenyls - Another Long-Life Widespread Chemical in the Environment. BioScience 20:958-964.

Pickett, L.W., G. Walter, and H. France. 1936. The Ultraviolet Absorption Spectra of Substituted Biphenyls. J. Amer. Chem. Soc. 58:2296-2299.

Pickett, L.W. 1936. An X-Ray Study of Substituted Biphenyls. J. Amer. Chem. Soc. 58:2299-2303.

Pringheim, P. 1949. Fluorescence and Phosphorescence. Interscience Publishers, Inc., New York, NY. p. 299.

Richardson, A., J. Robinson, A. Crabtree, and M.K. Baldwin. 1971. Residues in Fish, Wildlife, and Estuaries - Residues of Polychlorobiphenyls in Biologcal Samples. Pesticide Monitoring Journal 4:169-176.

Risebrough, R.W., P. Rieche, D.B. Peakall, S.G. Herman, and M.N. Kirvan. 1968. Polychlorinated Biphenyls in the Global Ecosystem. Nature 220:1098-1102.

Robinson, G.W. and R.P. Frosch. 1963. Electronic Excitation Transfer and Relaxation. J. Chem. Phys. 38:1187-1203.

Ruzo, L.O., M.J. Zabik, and R.D. Schuetz. 1972. Polychlorinated Biphenyls: Photolysis of 3,4,3',4'-Tetrachlorobiphenyl and 4,4'-Dichlorobiphenyl in Solution. Bull. Environ. Contam. Toxicol. 8:217-218.

MONS 004940

Safe, S. and O. Hutzinger. 1971. Polychlorinated Biphenyls: Photolysis of 2,4,6,2',4',6'-Hexachlorobiphenyl. Nature 232:641-642.

Sato, T., S. Shimada, and K. Hata. 1969. Photo-Aryl Coupling and Related Rections. II. The Formation of Triphenylenes from Halogeno-o-terphenyls. Bull. Chem. Soc. Jap. 42:766-772.

Suzuki, H. 1959. Relations Between Electronic Absorption Spectra and Spatial Configurations of Congugate Systems. I. Biphenyl. Bull. Chem. Soc. Jap. 32:1340-1361.

Trotter, J. 1961. The Crystal and Molecular Structure of Biphenyl. Acta Crystallogr. 14:1135-1140.

Veith, G.D. and G. Lee. 1970. A Review of Chlorinated Biphenyl Contamination in Natural Waters. Water Research 4:265-269.

Wagner, P.J. and J. Scheeve. Unpublished results, Department of Chemistry, Michigan State University, East Lansing, MI.

Wagner, P.J. 1967. Conformational Changes Involved in the Singlet-Triplet Transitions of Biphenyl. J. Amer. Chem. Soc. 89:2820-2825.

Wagner, P.J. and I. Kochevar. 1968. How Efficient is Diffusion-Controlled Triplet Energy Transfer? J. Amer. Chem. Soc. 90:2232-2238.

Wagner, P.J. 1971. Energy Transfer Kinetics in Solution. In: A.A. Lamola (ed.), "Creation and Detection of the Excited State," pp. 173-212, Vol. 1, Part A. Marcel Dekker, Inc., New York, NY.

Wilkinson, F. and T. Dubosis. 1963. Energy-Transfer Studies by Spectrophotofuorometric Method. J. Chem. Phys. 39:377-385.

MONS 004941

CHAPTER 12

ANALYSIS OF PCBs USING SPECIFIC ISOMER HIGH RESOLUTION CAPILLARY GAS CHROMATOGRAPHY

Michael D. Mullin
Cynthia M. Pochini
U.S. Environmental Protection Agency
ERL-D at Grosse Ile
Grosse Ile, Michigan 48138

Stephen H. Safe
Lorna M. Safe
Department of Veterinary Physiology & Pharmacology
Texas A&M University
College Station, Texas 77843

HALOGENATED AROMATICS

Polychlorinated biphenyls (PCBs) are one of a number of groups of chemical compounds referred to as halogenated aromatics. These groups of compounds include the polychlorinated naphthalenes (PCNs), polychlorinated benzenes (PBs), polychlorinated terphenyls (PCTs), polybrominated biphenyls (PBBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-p-dioxins (PCDDs). The difficult problems associated with the toxicology and analytical chemistry of these compounds are due to the large numbers of theoretically possible isomers of each group (Table 1). For example, the commercial PCB formulations are complex mixtures of PCB isomers that have not yet been completely identified (Hutzinger et al., 1974; Sissons and Welti, 1971; Ballschmiter and Zell, 1980; Jensen and Sundstrom, 1974). In addition, the variable partitioning of the isomers between different trophic levels in the environment and within different members of the same trophic levels, in conjunction with preferential biological degradation of certain isomers, makes the composition of PCBs in these samples quite different from the commercial mixtures (Jensen and Sundstrom, 1974;

MONS 004942

TABLE 1

Multiplicity of Isomers in the Halogenated Aromatics

Halogenated aromatic	PCB	PBB	PCN	PCDD	PCDF
Number of isomers	209	209	135	75	135

Yakushiji et al., 1978; Kuroki and Masuda, 1977; Safe, 1980). Compared to the commercial PCB formulations, precipitation samples are almost void of the early eluting isomers as are lake trout from the Great Lakes. Human blood samples also evince a lack of the early eluting isomers and, in addition, contain fewer isomers than the lake trout implying a more rigorous degradation and/or elimination of selected PCB isomers from humans than from fish. The toxicity of PCBs is a function of the structure of the individual isomer. Therefore, it is not sufficient to quantify the total amount of PCBs present in an environmental sample, but the concentrations of the isomers which are potentially more toxic must also be determined.

TOXICOLOGY OF PCB ISOMERS

Recent toxicology studies on PCBs have concentrated on the use of these compounds to induce a microsomal cytochrome P-448 dependent monooxygenase enzyme designated aryl hydrocarbon hydroxylase (AHH)(Parkinson and Safe, 1981; Goldstein, 1979; Poland et al., 1979; Poland and Glover, 1977). An evaluation of the structure-activity relationship among halogenated aromatics indicates a correlation between those compounds which induce AHH activity and their structure. Table 2 indicates all the PCB isomers which are known AHH inducers (Parkinson and Safe, 1981; Poland and Glover, 1977; Goldsetin et al., 1977; Parkinson et al., 1980a; 1980b; 1981a; 1981b; 1981c). The toxicity of the following isomers have been confirmed: 3,3'4,4'-tetra-; 3,3',4,4',5-penta-; 2,3,3',4,4'-penta-; 2,3,4,4',5-penta; 3,3',4,4',5,5'-hexa-; and 2,3,3',4,4',5-hexachlorobiphenyls (Parkinson and Safe, 1982; Yoshimura et al., 1979; Goldstein, 1979; Poland et al., 1979; Yamamoto et al., 1976; Ax and Hansen, 1975; Poland and Glover, 1977; Goldstein et al., 1977; Parkinson et al., 1980a; Yoshihara et al., 1979; Stonard and Greig, 1976). The isomers listed in Table 2 should be of concern to environmental toxicologists, analytical chemists,

MONS 004943

TABLE 2

A Summary of PCB Isomers Which Induce AHH Activity

Number of Chlorine Substituents							
1		2		3		4	
Peak Number	Structure	Peak Number	Structure	Peak Number	Structure	Peak Number	Structure
077	3,3'4,4'	126	3,3',4,4',5	169	3,3',4,4',5,5'	189	2,3,3',4,4',5,5'
081	3,4,4',5	105	2,3,3',4,4'	156	2,3,3',4,4',5	170	2,2',3,3',4,4',5
		118	2,3',4,4',5	157	2,3,3',4,4',5'		
		114	2,3,4,4',5	166	2,3,4,4',5,6		
		123	2',3,4,4',5	158	2,3,3',4,4',6		
				128	2,2',3,3',4,4'		

MONS 004944

and others who are concerned with the contamination of the environment by anthropogenic materials.

LOW VS. HIGH RESOLUTION GAS CHROMATOGRAPHIC ANALYSIS OF PCBs

The majority of laboratories analyzing environmental samples for PCBs are using some form of packed column gas chromatography coupled with either an electron capture detector (ECD) or a mass spectrometer (MS) and are indicated in Table 2 as low or medium resolution techniques. The results from these techniques are quantified by comparison with commercial PCB formulations (Hutzinger et al., 1974; Cairns and Siegmund, 1981; Sawyer, 1978) and provide semi-quantitative concentrations. However, low and medium resolution PCB analyses have several disadvantages: the lack of sufficient resolution masks some of the subtle changes in the distribution of PCBs within an ecosystem; the difficulties in making an accurate quantitative estimate of the PCB concentration when the PCB composition in the sample has been subjected to extensive degradation; the inability to provide quantitative data on individual isomers; and the lack of quantitative data on the potentially toxic PCB isomers.

High resolution specific isomer capillary gas chromatograph PCB analysis (Ballschmiter and Zell, 1980; Ballschmiter et al., 1978; Albro and Parker, 1979; Mullin and Filkins, 1981;

TABLE 2

Resolution Characteristics of Various Instrument Combinations

Column Type	Detector	Quantitation Method	Resolution
Packed column	EC	Peak matching or pattern matching	Low
	MS	Peak matching or pattern matching	Medium
Capillary column	EC	Isomer response	High
	MS	Isomer response	High

MONS 004945

Albro et al., 1981; Mullin et al., 1981) is now a viable analytical technique which utilizes a high resolution fused silica capillary column as the medium of separation, couples it with either an electron capture detector or a mass spectrometer and requires all 209 PCB isomers as reference standards for initial instrument calibration (Table 3). The synthesis of all of the PCB isomers is an awesome task and a great deal of progress has been made in achieving this goal (Mullin et al., 1981). Of the 209 possible isomers, 182 have been synthesized using the Cadogan coupling (Cadogan et al., 1962) of a chlorinated aniline with a chlorinated benzene (in excess) in the presence of amyl nitrite. Proton magnetic resonance (PMR) and mass spectrometry (Mullin et al., 1981) are used on the purified products to characterize the isomers synthesized.

The proposed numbering scheme (Ballschmiter and Zell, 1980) is used to more easily discuss the individual PCB isomer by relating them to an integer from 1 to 209. The relative retention times (RRTs) and relative molar response factors have been determined for most of the PCB isomers available using octachloronapthalene (OCN) as an internal standard.

ANALYSIS OF SAMPLES USING HIGH RESOLUTION CAPILLARY GAS CHROMATOGRAPHY

A number of commercial formulations and environmental samples have been analyzed and quantified for PCBs by using the individual PCB isomers as reference standards. The following analytical conditions were used on a Varian model 3700 gas chromatograph[1] equipped with an electron capture detector:

Column - 50 meter narrow bore fused silica capillary coated with SE-54 (Hewlett-Packard)

Injector Temperature - 270°C

Detector Temperature - 330°C

Oven Temperature - 100°C to 240°C (280°C with 32 minute final hold for precipitation samples) at 1°C per minute with a 2 minute final hold

Sample Volume - 6 ul injected vented from 0.75 to 1.75 minutes at a ratio of 10:1

---

[1]The use of trade names does not constitute an endorsement by the U.S. Environmental Protection Agency of these products.

Carrier Gas - Hydrogen at a constant pressure to yield a linear velocity of 45 cm/second at 100°C oven temperature

The high resolution capillary gas chromatographic separation of a mixture of Aroclor® 1016 plus 1254 plus 1260 (5:3:2 by weight), a composite human blood sample, a composite precipitation sample from the Great Lakes shoreline and a lake trout sample from the Great Lakes are shown in Figures 1, 2, 3, and 4, respectively. Using the isomeric PCB standards to calibrate the mixture of Aroclors as a reference standard, the relative retention times of the above samples were compared to the RRTs of the standard enabling the identification of many of the peaks in the samples as specific PCB isomers. Figure 4 illustrates the more complex chromatogram obtained from the lake trout which the high resolution capillary technique is able to resolve sufficiently to qualitatively identify many of the peaks and quantify those identified peaks; this would not have been possible using the low or medium resolution techniques.

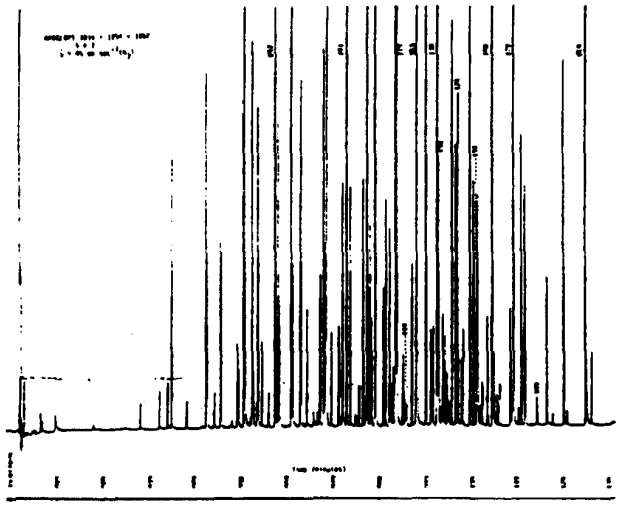


Figure 1. High resolution capillary gas chromatographic separation of a mixture of Aroclors 1016 plus 1254 plus 1260.

MONS 004947

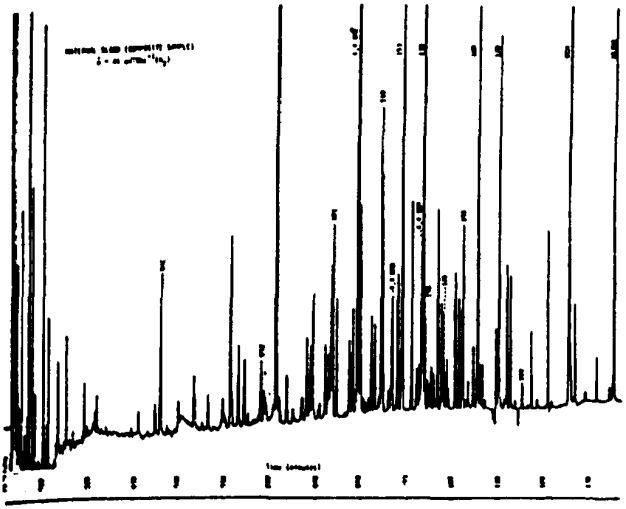


Figure 2. High resolutions capillary gas chromatographic separation of chlorinated hydrocarbons in a composite human maternal blood sample.

CONCLUSION

The use of high resolution capillary gas chromatography, in conjunction with the use of PCB isomers as reference analytical standards, presently is a viable analytical technique for the analysis of commercial PCB formulations and environmental samples from many different matrices. Future efforts will address the application of this technique to a greater variety of samples to determine the effects of PCB structures on the dynamics of PCB persistence in the environment.

ACKNOWLEDGMENTS

The financial assistance of the U.S. Environmental Protection Agency is gratefully acknowledged (S.S.).

MONS 004948

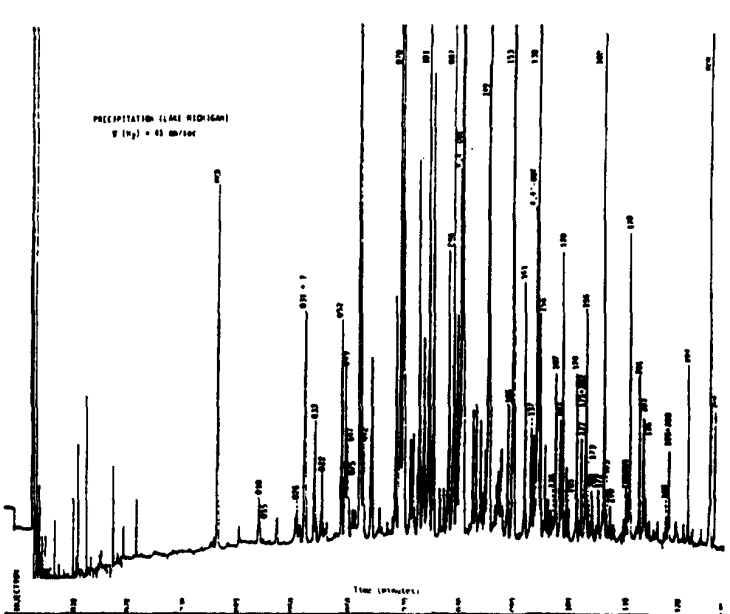


Figure 3. The high resolution capillary gas chromatographic separation of a composite precipitation sample from Lake Michigan.

LITERATURE CITED

Albro, P.W., J.T. Corbett, and J.L. Schroeder. 1981. Quantitative Characterization of Polychlorinated Biphenyl Mixtures (Aroclors 1242, 1254, and 1260) by Gas Chromatography Using Capillary Columns. J. Chrom. 205:103-111.

Albro, P.W. and C.E. Parker. 1979. Comparison of the Composition of Aroclor 1242 and Aroclor 1016. J. Chrom. 169:161-166.

Ax, R.L. and L.G. Hansen. 1975. Effects of Purified PCB Analogs on Chicken Reproduction. Poultry Sci. 54:895-900.

MONS 004949

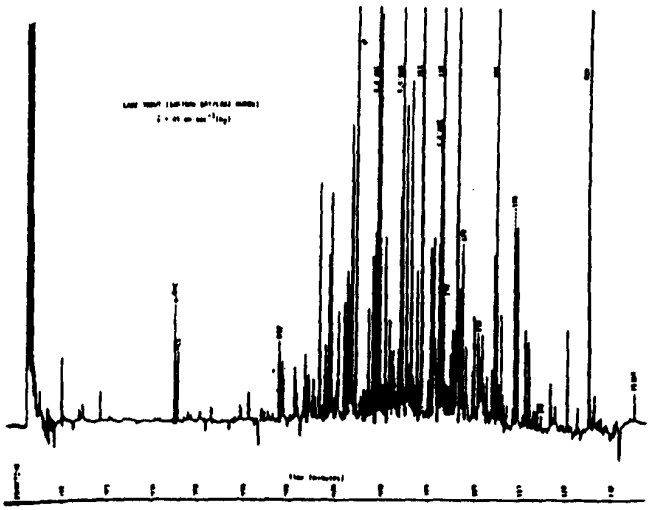


Figure 4. High resolution capillary gas chromatographic separation of chlorinated hydrocarbons in a lake trout from Saginaw Bay/Lake Huron.

Ballschmiter, K. and M. Zell. 1980. Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography. Composition of Technical Aroclor- and Chlophen-PCB Mixtures. Fresenius Z. Anal. Chem. 302:20-31.

Ballschmiter, K., M. Zell, and H.J. Neu. 1978. Persistence of PCBs in the Ecosphere: Will Some PCB-Components Never Degrade. Chemosphere 7:173-176.

Cadogan, J.I.G. 1962. A Convenient New Method of Aromatic Arylation. J. Chem. Soc. (London):4257-4258.

Cairns, T. and E.G. Siegmund. 1981. PCBs-Regulatory History and Analytical Problems. Anal. Chem. 53:1183A-1193A.

Goldstein, J.A. 1979. The Structure-Activity Relationship of Halogenated Biphenyls as Enzyme Inducers. Ann. N. Y. Acad. Sci. 320:164-178.

Goldstein, J.A., P. Hickman, H. Bergman, J.D. McKinney, and M.P. Walker. 1977. Separation of Pure Polychlorinated Biphenyl Isomers Into Two Types of Inducers on the Basis of Induction of Cytochrome P-450 or P-448. Chem.-Biol. Interact. 17:69-87.

Hutzinger, O., S. Safe, and V. Zitko. 1974. The Chemistry of PCBs. CRC Press, Inc., Cleveland, OH, pp. 22-39.

Jensen, S. and G. Sundstrom. 1974. Structures and Levels of Most Chlorobiphenyls in Two Technical PCB Products and In Human Adipose Tissue. Ambio 3:70-76.

Kuroki, H. and Y. Masuda. 1977. Structures and Concentrations of the Main Components of Polychlorinated Biphenyls in Patients With Yusho. Chemosphere 8:469-474.

Mullin, M.D. and J.C. Filkins. 1981. Analysis of Polychlorinated Biphenyls by Glass Capillary and Packed Column Gas Chromatography. In: L.W. Keith (ed.), "Advances in the Identification and Analysis of Organic Pollutants in Water at the Second Chemical Congress of the North American Continent, Las Vegas, Nevada," pp. 187-196, Vol. 1. Ann Arbor Press, Ann Arbor, MI.

Mullin, M., G. Sawka, L. Safe, S. McCrindle, and S. Safe. 1981. Synthesis of Octa- and Nonachlorobiphenyl Isomers and Congeners and Their Quantitation in Commercial Polychlorinated Biphenyls and Identification in Human Breast Milk. J. Anal. Toxicol. 5:138-147.

Parkinson, A., R. Cockerline, and S. Safe. 1980a. Induction of Both 3-Methylcholanthrene- and Phenobarbitone-Type Microsomal Enzyme Activity by a Single Polychlorinated Biphenyl Isomer. Biochem. Pharmacol. 29:259-261.

Parkinson, A., R. Cockerline, and S. Safe. 1980b. Polychlorinated Biphenyl Isomers and Congeners as Inducers of Both 3-Methylcholanthrene- and Phenobarbitone-Type Microsomal Enzyme Activity. Chem. Biol. Interact. 29:277-289.

Parkinson, A., L. Robertson, L. Safe, and S. Safe. 1981a. Polychlorinated Biphenyls as Inducers of Hepatic Microsomal Enzymes: Effects of Diortho Substitution. Chem. Biol. Interact. 31:1-12.

Parkinson, A., L. Robertson, L. Safe, and S. Safe. 1981b. Polychlorinated Biphenyls as Inducers of Hepatic Microsomal Enzymes: Structure-Activity Rules. Chem. Biol. Interact. 30: 271-285.

MONS 004951

Parkinson, A., L. Robertson, and S. Safe. 1980c. Hepatic Microsomal Enzyme Induction by 2,2', 3,3', 4,4'-, and 2,2', 3', 4,4',5-Hexachlorobiphenyl. Life Sciences 27:2333-2337.

Parkinson, A. and S. Safe. 1981. Aryl Hydrocarbon Hydroxylase Induction and Its Relationship to the Toxicity of Halogenated Aryl Hydrocarbons. Toxicol. Environ. Chem. 4:1-46.

Poland, A. and E. Glover. 1977. Chlorinated Biphenyl Induction of Aryl Hydrocarbon Hydroxylase Activity: A Study of the Structure Activity Relationship. Mol. Pharmacol. 13:924-938.

Poland, A., W.F. Greenlee, and A.S. Kende. 1979. Studies on the Mechanisms of Toxicity of the Chlorinated Dibenzo-p-dioxins and Related Compounds. Ann. N. Y. Acad. Sci. 320:214-230.

Safe, S. 1980. Metabolism, Uptake, Storage, and Bioaccumulation. In: R. Kimbrough (ed.), "Halogenated Biphenyls, Naphthalenes, Dibenzodioxins, and Related Products," pp. 77-107, Elsevier/North-Holland.

Sawyer, L.D. 1978. Quantitation of Polychlorinated Biphenyl Residues by Electron Capture Gas-Liquid Chromatography: Collaborative Study. J. Assoc. Offic. Anal. Chem. 61:272-281.

Siasons, D. and D. Welti. 1971. Structural Identification of Polychlorinated Biphenyls in Commercial Mixtures by Gas Liquid Chromatography, Nuclear Magnetic Resonance, and Mass Spectrometry. J. Chrom. 60:15-32.

Stonard, M.D. and J.E. Greig. 1976. Different Patterns of Hepatic Microsomal Enzyme Activity Produced by Administration of Pure Hexachlorobiphenyl Isomers and Hexachlorobenzene. Chem.-Biol. Interact. 15:365-379.

Yakushiji, T., I. Watanabe, K. Kuwabara, and S. Yoshida. 1978. Identification of Low Chlorinated Biphenyls in Human Milk by Gas Chromatography-Mass Spectrometry. J. Chrom. 154:203-210.

Yamamoto, H., H. Yoshimura, M. Fujita, and T. Yamamoto. 1976. Metabolic and Toxicologic Evaluation of 2,3,4,3',4'-Pentachlorobiphenyl in Rats and Mice. Chem. Pharm. Bull. 24:2168-2174.

Yoshihara, S., K. Kawano, H. Yoshimura, H. Kuroki, and Y. Masuda. 1979. Toxicologcal Assessment of Highly Chlorinated Biphenyl Congeners Retained in the Yusho Patients. Chemosphere 8:531-538.

MONS 004952

Yoshimura, H., S. Yoshihara, N. Ozawa, and M. Miki. 1979. Possible Correlation Between Induction Modes of Hepatic Enzymes by PCBs and Their Toxicity in Rats. Ann. N. Y. Acad. Sci. 320:179-192.

MONS 004953

PART III

METABOLISM AND TOXICOLOGY OF PCBs

MONS 004954

CHAPTER 13

CONCEPTS IN TOXICOLOGY AND CARCINOGENESIS: A BASIS FOR DISCUSSING THE POTENTIAL ENVIRONMENTAL HAZARD POSED BY PCBs

Jay I. Goodman
Department of Pharmacology and Toxicology
Center for Environmental Toxicology
Michigan State University
East Lansing, Michigan 48824-1317

All of us who are attending this conference have an interest in addressing the question of what is a "safe" level of an environmental chemical. We are concerned with a rational approach towards setting acceptable levels of environmental pollutants. Scientific input is just one of several avenues feeding into this decision-making process. The deliberations involved in the establishment of acceptable levels for a chemical in the environment must take into account political considerations, social considerations, economic considerations, and scientific considerations.

While we can be proud of our scientific accomplishments in the area of toxicology it is also important, if we wish to maintain our credibility, to put our limitations up front. The science of toxicology is an exciting and dynamic field. We have made some very significant strides towards understanding the mechanisms of action of toxic chemicals and using this information to try to arrive at rational decisions relative to the establishment of acceptable levels for environmental chemicals. However, we are far from our ideal goal. While we are reasonably good at making qualitative predictions, we have quite a ways to go when it comes to quantitative predictions.

I would like to develop for you some basic concepts in traditional toxicology and compare and contrast this with problems that we face in modern aspects of toxicology specifically related to carcinogenesis. I shall then discuss some current concepts in chemical carcinogensis and show you how this impacts

MONS 004955

on the question of deciding what is and what is not a "safe" or "acceptable" level of a particular chemical.

The basic concepts upon which traditional toxicology is based were derived from classical pharmacological studies. In clasical pharmacology we picture a drug (or in our case toxic chemical) interacting with a receptor located on the target cell membrane or within target cells, giving us a drug receptor complex which causes an effect. The magnitude of the effect is often thought to be directly related to the amount of drug receptor complex that is formed (Gilman et al., 1980). We can use this paradigm to try to explain dose-response type data. In classical pharmacological or toxicological studies as we increase dose we observe increased intensity of effects. In pharamcological studies we would be talking about a therapeutic effect, in toxicology an adverse effect. When one looks at a classical type dose effect relationship, taking a sedative hypnotic drug as an example, we see that if we focus on sedation as the therapeutic effect, as one increases dose an increased percent of individuals in the treated population respond to the therapeutic effect. We eventually arrive at a dose where 50 percent of the population responds to the therapeutic effect and we call this the "effective dose$_{50}$", the ED_{50}. If we continue to increase the dose, we produce toxicity, in this case death. Eventually we reach a point where 50 percent of the population will die. We refer to this later dose as the LD_{50} or lethal dose for 50 percent. A measure of safety called the "therapeutic index" is obtained on dividing the LD_{50} by the ED_{50}. This represents a ratio of the dose required for the beneficial effect vs. harmful effect in the average of the individuals comprising the test population. These principles of pharmacology have led to the basic concepts in "traditional" principles of toxicology (Saffiotti, 1977). In traditional toxicology we are primarily concerned with terminal toxic effects; LD_{50}, for example. These toxic effects have the following characteristics. First, they appear early--dose your animals, inspect them a few hours later, perhaps a couple of days later, and ascertain whether or not they are alive. Second, the intensity of the induced pathology can be directly correlated with the intensity of toxic exposure. Third, manifestations of toxicity are due to altered functional products, degenerative changes, or death of target cells. Let us contrast this with the situation that we face when dealing with the cancer problem. This is one area, along with mutagenesis and teratogenesis, which can be considered among the "modern" aspects of toxicology. We can think of these as self-replicating toxic effects as opposed to terminal toxic effects (Saffiotti, 1977). The general characteristics of carcinogenic effects are the following:

MONS 004956

(1) their appearance is delayed. Delayed by months to years in animals, delayed by perhaps decades in the human;
(2) the frequency of the expression of injury (i.e., tumor incidence) in the exposed population is directly correlated with the intensity of exposure. However, the intensity of the induced pathology is independent of the intensity of exposure to the carcinogenic substance. That is, once the cancer is formed in a specific individual, it makes little difference whether it took a high dose to do it, a medium size dose, or a low dose, the ability of that tumor to spread, to metastasize, to express its malignant potential is independent of the dose of the chemical that it took to start the process in the first place;
(3) the manifestations of toxicity are due to proliferation of a new cell population.

There are many chemicals which are recognized as carcinogens. Today it is known that many of these are not cancer causing in and of themselves but must be metabolized to a reactive, electrophilic, form which is then capable of initiating the cancer process (Miller and Miller, 1981). These chemicals are mutagenic. It is also quite possible to metabolize these chemicals to inactive metabolites. The relative ability to metabolically activate vs. inactivate can at least in part explain some of the selectivity that we see in terms of species/sex susceptibility, and probably some of the reasons for organ selectivity of different carcinogenic chemicals.

Carcinogenesis appears to be a multi-stage phenomenon (Boutwell, 1974). The hypothesis that carcinogenesis can be divided into a stage of initiation and a promotion stage has gained a high degree of credibility. The basic studies began with Berenblum and Shubik (1947) in the 1940s. They reported that they could apply coal tar, one application, to the skin of mice and skin cancer would arise. They then decreased the dose of coal tar used down to a level at which one application did not result in skin tumors being formed. So far, this fits nicely with the classical toxicology concept of a "no effect" level. They then asked, "what would happen if we took this low, 'safe dose', of coal tar and added a second chemical to the system." The "low" dose of coal tar was applied to the skin of mice and followed by repeated applications to the skin of an irritant, croton oil. They observed that this low dose of carcinogen, the initiating dose, when followed by the croton oil treatment results in the production of tumors. Berenblum and Shubik termed the low dose of carcinogen the "initiator" and the croton oil the "promoter". The next question asked was "how reversible is this process?" What happens if after

applying the initiator one waited a few months before promoter application? When this experiment was performed, tumors arose. This was the first indication that initiation of carcinogenesis is probably a "permanent" and perhaps heritable event. Next, the question as to the reversibility of the effects of promoter treatment was investigated. Is this reversible or is each dose analogous to a turn of a ratchet wrench. That is, does it require multiple applications but never "slips" back? If, after initiation a few doses of promoter are applied and one waits a month or so prior to completing the process (i.e., the same total number of doses but spread out), no tumors are formed. Therefore, while the initiation process appears to be heritable, the promotion process, at least in part, is reversible. The initiation-promotion hypothesis appears to be widely accepted due to a considerable amount of scientific evidence supporting it (Boutwell, 1974; Miller and Miller, 1981). We now do not simply think of "chemical carcinogens". We think of them in terms of initiators and promoters of carcinogenesis. Some chemicals are capable of acting as a complete carcinogens (i.e., capable of carrying out both the initiation and promotion steps). In "low" doses a complete carcinogen may serve as an initiator. Promoters do not appear to be mutagenic. These compounds are capable of altering gene expression and might, therefore, act through an epigenetic mechanism (Weinstein, 1981). How good are we at discerning carcinogens, and specifically, how good are we at discerning carcinogens which are effective in man? Today the basic approach is the National Cancer Institute/National Toxicology Program Rodent Bioassay (Page, 1977). This assay involves exposing two species of rodents (usually rats and mice), male and female of each, to the test compound for most of their life. The question asked in this assay is are these chemicals carcinogenic or not? This is aqualitative test. How good are these tests as predictors of human carcinogens? Let us consider carcinogenicity data compiled by the International Agency for Research on Cancer (IARC)(IARC, 1979). Based upon epidemiology studies, industrial exposure accidents and medical exposure, there is reasonable evidence indicating that those chemicals listed below are carcinogenic to man:

Aflatoxins
4-Aminobiphenyl
Arsenic compounds
Asbestos
Auramine (manufacture of)
Benzene
Benzidine
N,N-bis(2-chloroethyl)-2-naphthylamine
Bis(chloromethyl) ether
Cadmium oxide
Chloramphenicol (strong suspicion)

MONS 004958

Chromium(chromate-producing industries)
Cyclophosphamide
Diethylstilboestrol
Haematite (mining)
Isopropyl oil
Melphalan
Mustard gas
2-Naphthylamine
Nickel (refining)
Oxymetholone (strong suspicion)
Phenacetin
Soot, tars, and oils (polycyclic aromatic hydrocarbons)
Vinyl chloride

With the exception of arsenic compounds and benzene, all of the chemicals listed above are carcinogenic in at least one laboratory animal species. In addition, for five of these chemicals, aflatoxins, 4-aminobiphenyl, diethylstilboestrol, melphalan and mustard gas, and vinyl chloride, evidence of carcinogenicity in experimental animals preceded evidence of carcinogenicity in man (Rall, 1979). From these data we can conclude that there are clear historical examples which show that if there is strong evidence that a chemical is carcinogenic in appropriate laboratory animal test systems, it must be treated as if it were carcinogenic in man. What about the question of organ specificity? There appears to be solid data for 109 chemicals which are carcinogenic in both rats and mice; and out of these, 70 have at least one common target organ (Purchase, 1980). Put another way, approximately one-third of them attack totally different target organs.

At this point it would be appropriate, within the context of this conference, to consider the definitions of some basic terms in toxicology. When employing the word toxicity, the toxicologist talks about the capacity of a chemical to produce injury. The term hazard refers to the probability that injury will result from a chemical under specific conditions of exposure. The toxicologist uses the term safety to connote the reciprocal of risk, that is the probability that harm will not occur under specific conditions of exposure. The toxicologist is able to make some reasonable judgments about hazard or safety under specific conditions of exposure (i.e., dose, sex, age, what chemicals has the animal previously been or currently being exposed to). It is important to keep the above discussion in mind when contemplating the question of whether or not a chemical is going to be carcinogenic. We picture the initiator of carcinogensis as transforming normal cells into initiated cells probably by virtue of causing a mutation. A rather prolonged treatment with promoter is then required for expression of malignancy, to transform the initated cells into frank cancers.

MONS 004959

There are many places in this scheme when a second chemical can interact with the carcinogen. For example, what if an animal is treated such that its capacity for oxidative metabolism is enhanced. Do we increase the ability to metabolize precarcinogens to initiators? Do we increase the ability to form inactive metabolites? Pretreatment of animals with a microsomal enzyme inducer or the combined administration of the inducer and a carcinogen usually inhibits the tumorigenic effect of the chemical administered (Conney, 1982). Let us look, for example, at a selected group of chemicals which can inhibit carcinogensis. Prior administration of phenobarbital (Peraino et al., 1971), butylated hydroxytoluene (Ulland et al., 1973), butylated hydroxyanisol (Wattenberg, 1973), 3-methylcholanthrene (Miller et al., 1958), polybrominated biphenyls (Schwartz et al., 1981), and polychlorinated biphenyls (PCBs) (Hendricks et al., 1977; Nishizumi, 1976; Makiura et al., 1974) have a protective effect on chemically-induced carcinogenesis. These agents are effective in a wide variety of carcinogens including azodyes (Makiura et al., 1974; Miller et al., 1958), aromatic amines (Makiura et al., 1974; Miller et al., 1958; Schwartz et al., 1981; Ulland et al., 1973; Peraino et al., 1971), alkylating agents (Nishizumi, 1976; Wattenberg, 1973), and aflatoxins (Hendricks et al., 1977). We must keep in mind the fact that several inducers of microsomal enzymes have been shown to be capable of promoting carcinogenesis if they are administered after initiation has taken place (Conney, 1982). In this situation the induction of microsomal enzymes and tumor promotion might not be causally related.

What is the usual carcinogenicity data which we derive in laboratory animal studies? Generally, we are dealing with something between 50 and 100 percent tumor incidence. In some of the best laboratory studies we are dealing with 10 percent tumor incidence as our low value. When we try to extrapolate from this observed 10 percent incidence down to zero tumor incidence, we encounter a large mathematical error. In addition, there is the question as to whether or not it is justifiable to draw a straight line through the origin in the first place. We are really making a guess, albeit an educated guess, with some very significant errors. The conclusion one can draw from this is that we must not lose sight of the fact that in toxicity testing we use the animals as surrogates for humans and that attempts to quantify responses beyond the realm of scientific or biological certainty are open to some very serious questions.

What we will try to do for you in the next series of presentations is to give you a feel for selected aspects of the toxicology of PCBs and an indication of what levels we are at in regard to assessing the toxicological potential of these compounds.

MONS 004960

ACKNOWLEDGMENT

Research in the author's laboratory is currently funded by grant number CA-30,635 awarded by the USPHS, National Institutes of Health, National Cancer Institute.

LITERATURE CITED

Berenblum, I. and P. Shubik. 1947. A New Quantitative Approach to the Study of the Stages of Chemical Carcinogenesis in the Mouse's Skin. Brit. J. Cancer 1:383-391.

Boutwell, R.K. 1974. The Function and Mechanisms of Promoters of Carcinogenesis. CRC Crit. Rev. Toxicol 2:419-443.

Conney, A.H. 1982. Induction of Microsomal Enzymes by Foreign Chemicals and Carcinogenesis by Polycyclic Aromatic Hydrocarbons: G.H.A. Clowes Memorial Lecture. Cancer Res. 42:4875-4917.

Gilman, A.G., S.E. Mayer, and K.L. Melmon. 1980. Pharamacodynamics: Mechanisms of Drug Action and the Relationship Between Drug Concentration and Effect. In: A.G. Gilman, L.S. Goodman, and A. Gilman (eds.), "The Pharmacological Basis of Therapeutics," pp. 28-39. MacMillan, NY.

Hendricks, J.D., T.P. Putnam, D.D. Bills, and R.O. Sinnhuber. 1977. Inhibitory Effect of a Polychlorinated Biphenyl (Aroclor 1254) on Aflatoxin B_1 Carcinogenesis in Rainbow Trout (Salmo gairdneri). J. Natl. Cancer Inst. 59:1545-1551.

IARC. 1979. Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man. Vols. 1-21 (1972-1979), International Agency for Research on Cancer, Lyon.

Makiura, S., H. Aoe, S. Sugihara, K. Hirao, M. Arai, and N. Ito. 1974. Inhibitory Effect of Polychlorinated Biphenyls on Liver Tumorigenesis in Rats Treated With 3'-Methyl-4-Dimethylaminoazobenzene, N-2-Fluorenylacetamide, and Diethylnitrosamine. J. Natl. Cancer Inst. 53:1253-1257.

Miller, E.C. and J.A. Miller. 1981. Mechanisms of Chemical Carcinogenesis. Cancer 47:1055-1064.

Miller, E.C., J.A. Miller, and J.R. Brown. 1958. On the Protective Effect of Certain Polycyclic Aromatic Hydrocarbons Against Carcinogenesis by Aminoazo Dyes and 2-Acetylaminofluorene. Cancer Res. 18:469-477.

MONS 004961

Nishizumi, M. 1976. Enhancement of Diethylnitrosamine Hepatocarcinogenesis in Rats by Exposure to Polychlorinated Biphenyls or Phenobarbital. Cancer Lett. 2:11-16.

Page, N.P. 1977. Concepts of a Bioassay Program in Environmental Carcinogenesis. In: H.F. Kraybill and M.. Mehlman (eds.), "Environmental Cancer, Advances in Modern Toxicology," Vol. 3, pp. 87-171. Hemisphere Publishing Co., Washington, DC.

Peraino, C., R.J. Fry, and E. Staffeldt. 1971. Reduction and Enhancement by Phenobarbital of Hepatocarcinogenesis Induced in the Rat by 2-Acetylaminofluorene. Cancer Res. 31:1506-1512.

Purchase, I.F.H. 1980. Range of Experimental Evidence in Assessing Potential Human Carcinogenicity. In: J. Clemmesen, D.M. Conning, D. Henschler, and F. Oesch (eds.), "Quantitative Aspects of Risk Assessment in Chemical Carcinogenesis," pp. 295-305. Arch. Toxicol. (Suppl. 3):295-305.

Rall, D.P. 1979. The Role of Laboratory Animal Studies in Estimating Carcinogenic Risks for Man. In: W. Davis and C. Rosenfeld (eds.), "Carcinogenic Risks Strategies for Intervention," pp. 179-190. International Agency for Research on Cancer, Lyon.

Saffiotti, U. 1977. Scientific Basis for Environmental Carcinogenesis and Cancer Prevention. J. Toxicol. Environ. Hlth. 2:1435-1442.

Schwartz, E.L., W.M. Kluwe, S.D. Sleight, J.B. Hook, and J.E. Goodman. 1981. Inhibition of N-2-Fluorenylacetamide-Induced Mammary Carcinogenesis in Rats by Dietary Polybrominated Biphenyls. J. Natl. Cancer Inst. 64:63-67.

Ulland, B.M., J.H. Weisburger, R.S. Yamamoto, and E.K. Weisburger. 1973. Antioxidants and Carcinogenesis: Butylated Hydroxytoluene But Not Diphenyl-P-Phenylenediamine Inhibits Cancer Induction by N-2-Fluorenylacetamide and by N-Hydroxy-N-2-Fluorenylacetamide in Rats. Fd. Cosmet. Toxicol. 11:199-208.

Wattenberg, L.W. 1973. Inhibition of Chemical Carcinogen-Induced Pulmonary Neoplasia by Butylated Hydroxyanisole. J. Natl. Cancer Inst. 50:1541-1548.

Weinstein, I.B. 1981. The Scientific Basis for Cancer Detection and Primary Cancer Prevention. Cancer 47:1133-1141.

MONS 004962

CHAPTER 14

BIOTRANSFORMATION AND PERSISTENCE OF POLYCHLORINATED BIPHENYLS (PCBs) IN FISH

John J. Lech
Department of Pharmacology and Toxicology
Medical College of Wisconsin
Milwaukee, Wisconsin 53226

Richard E. Peterson
Department of Pharmacology and Toxicology
School of Pharmacy
University of Wisconsin
Madison, Wisconsin 53706

INTRODUCTION

In addition to the workplace, important routes of exposure of the human population to chemicals are by way of the atmosphere and the diet. Consumption of chemically contaminated aquatic species, such as fish, is probably one of the major routes of dietary exposure in the human population since fish and many other aquatic species which dwell in aquatic environments are ultimately the final common destiny for many chemicals. Due to several unique features, the polychlorinated biphenyls (PCBs) are taken up from lower members of the food chain in the water and are found in concentrations in consumable fish species which far exceed levels which can be measured in the water itself (Norstrom et al., 1978).

While it is now known that not all of the over 200 PCB congeners behave in the same manner in different biological systems, the general properties of high lipid solubility and lack of biotransformation of certain PCB congeners has led to the bioaccumulation and persistence of this class of compounds. The relative composition of PCB mixtures is based on the degree and position of chlorination (Hutzinger et al., 1974). While, in general, the higher chlorinated congeners of the PCBs are more persistent, the actual structure of a specific congener is more important in determining persistence and toxicity than

MONS 004963

is the absolute number of chlorine atoms in the molecule (Kato et al., 1980). It was not until specific chemical structures of the chlorinated biphenyl components of these complex mixtures became known that details of the toxicity, biotransformation, and bioaccumulation of these compounds could be investigated (Fishbein, 1972).

BIOACCUMULATION

The information presented in Figure 1 illustrates the time-dependency and magnitude of bioaccumulation of Aroclor 1254 and 1248 by channel catfish exposed to these mixtures in water (Mayer et al., 1977). It can be seen that even after 77 days of exposure the concentration of PCBs in fish had not reached the steady state, even though bioaccumulation had proceeded to over 60,000 times the concentration of these mixtures in the exposure water. Based upon first order kinetic theory, an approximation of the time to reach the steady state would be five times the half-life for each Aroclor component.

It is important to note that data concerning bioaccumulation of chemicals, including the PCBs, can be expressed on an absolute amount of chemical in the body at any given time, or the concentration, that is, mg/kg, ug/g, or ppm. This is an important concept since in long-term exposure studies the fish are growing, and one must deal with the combination of constant intake of chemicals and the tendency toward dilution of the concentration in the animal by growth (Lieb et al., 1974). This is illustrated in Figure 2 in which A represents the PCB concentration in fish in mg/kg, B represents the total PCB content of the fish in ug, and C illustrates the body weight measured over the exposure period. It is clear that while the concentration in the fish begins to level off at approximately 2½ weeks of dietary exposure, the absolute amount of PCBs in the animals continued to increase. This data illustrates that although a steady state may be reached in terms of concentration in the animal during the exposure, total PCB content in absolute ug/animal may continue to increase. The concentration in the animal may not increase since the body weight continues to increase and reduces the concentration by dilution. The information presented in Figure 3 further illustrates this point. When trout were fed a diet containing 15 mg/kg of Aroclor 1254 for 16 weeks, and then were switched to a control diet, the fish which continued to receive PCBs in the diet continued to accumulate PCBs (A), but the trout removed from the PCB-containing diet had no further increase in PCB content (B). It is important to recognize that the absolute amount of PCBs expressed as ug/fish did not change significantly from the 16-32 weeks while on the control diet. This data dramatically

MONS 004964

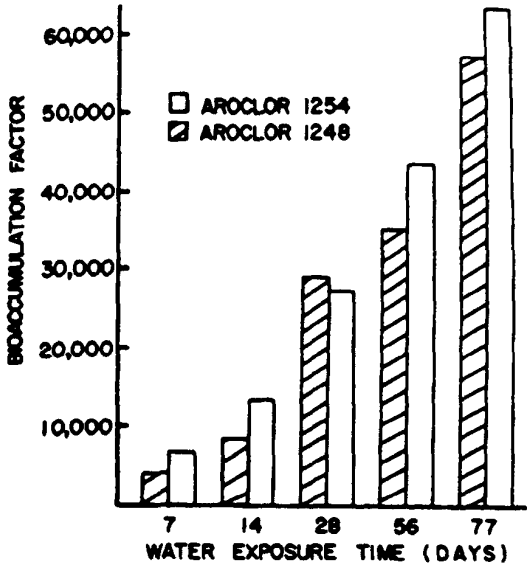


Figure 1. Bioaccumulation of Aroclor 1248 and 1254 by channel catfish during chronic water exposure. The concentration of Aroclor 1248 and 1254 in the water was 5.8 and 2.5 ug/l, respectively. The bioaccumulation factor was defined as the PCB concentration in the whole fish divided by the PCB concentration in the water. This figure was adapted from Mayer et al., 1977.

illustrates the lack of elimination of Aroclor 1254, even when animals were fed a control diet. However, if the data are expressed as concentration, that is mg/kg, the situation is quite different. This is illustrated in Figure 4 in which PCB concentration in lipid is plotted against the average fish weight and the time in weeks after removal from the PCB-containing diet. These data show that the PCB concentration decreased over time after removal of the fish from the PCB-containing diet, and this decrease in concentration can be

MONS 004965

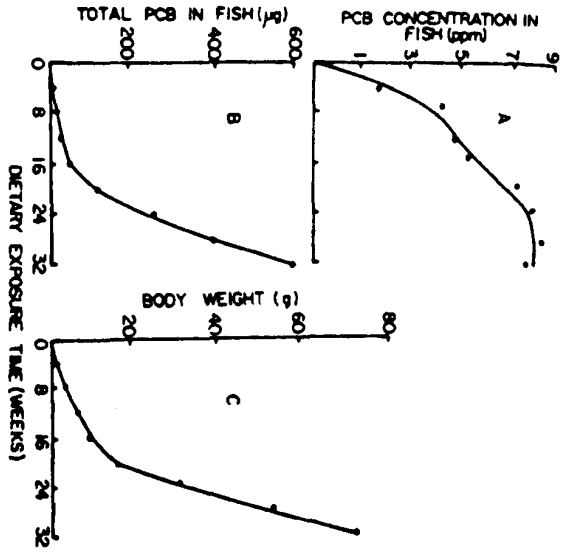


Figure 2. Bioaccumulation of Aroclor 1254 by rainbow trout during chronic dietary exposure. The fish were exposed to 15 mg/kg of Aroclor 1254 in the diet for 32 weeks. This figure was adapted from Lieb et al., 1974.

Accounted for almost entirely on the basis of dilution through the weight gain of the fish. These experiments indicate that when rainbow trout are removed from a diet containing Aroclor 1254, there is essentially no excretion of PCBs, but the concentration in the animal decreases by dilution because of weight gain.

In general, the tendency of PCBs to accumulate in fish is greater when animals are fed PCB mixtures containing higher chlorinated congeners (Mayer et al., 1977), and this is illustrated in Figure 5. It should be noted, however, that this data illustrates total PCB levels and does not indicate which congeners are present. Much of the work on bioaccumulation of

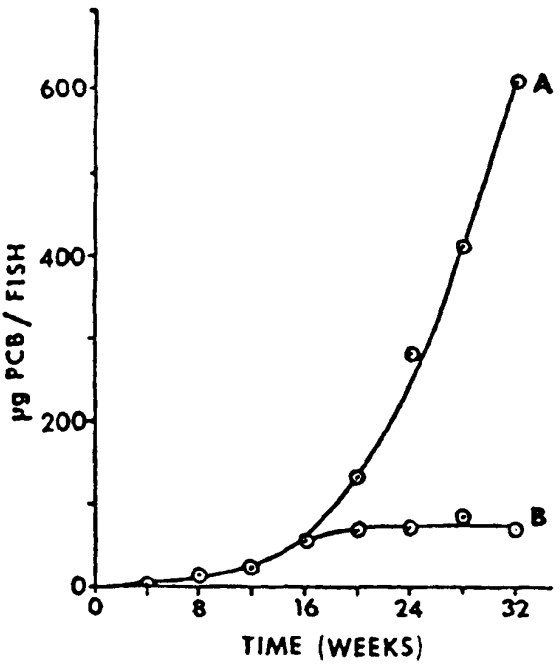


Figure 3. Persistence of Aroclor 1254 in rainbow trout after stopping chronic dietary exposure. This figure was adapted from Lieb et al., 1974.

PCB mixtures had been done in parallel when other studies were pursuing the molecular structure of specific PCB components in these complex mixtures. It is apparent from work that has been carried out over the past several years that there is a great deal of species differences in the biotransformation of PCB congeners to more readily excreted chemical forms. Since a major driving force in the elimination of any specific PCB congener is its rate of metabolism to a form which may be excreted in the urine or bile, the process of biotransformation

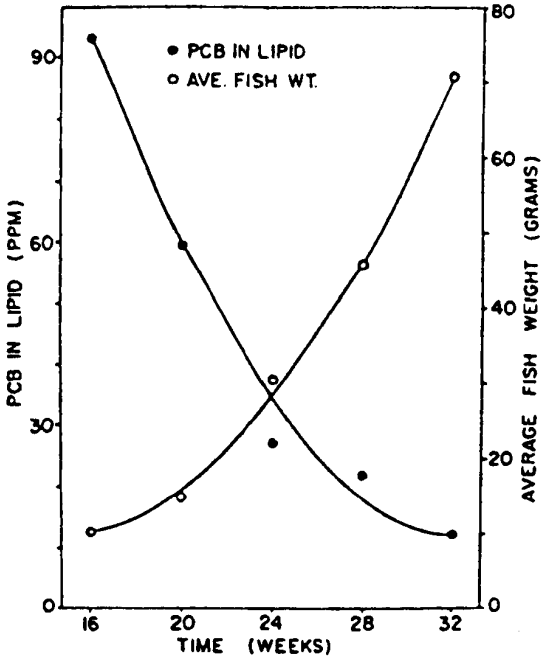


Figure 4. Dilution of the PCB concentration in lipid by the growth of rainbow trout after chronic dietary exposure to Aroclor 1254 was stopped. This figure was adapted from Lieb et al., 1974.

is extremely important in determining the persistence of various congeners in different biological systems (Kato et al., 1980).

BIOTRANSFORMATION AND PERSISTENCE

Only a limited amount of information is available concerning the biotransformation of specific PCB congeners in aquatic species, but it is clear from what is known that, as opposed

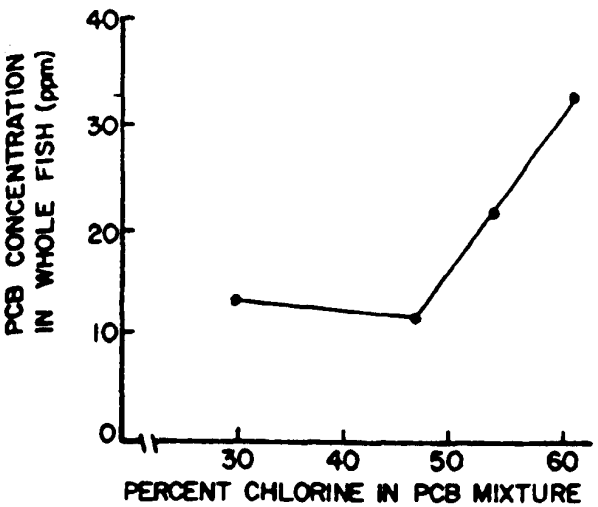


Figure 5. PCB concentration in channel catfish after chronic dietary exposure to PCB mixtures containing higher chlorinated congeners. All of the fish were continuously exposed to either Aroclor 1232, 1248, 1254, or 1260 at a concentration in the diet of 24 mg/kg for 193 days. This figure was adapted from Mayer et al., 1977.

to mammals, those species of fish studied have only a limited ability to metabolize PCBs containing a higher number of chlorine atoms (Hutzinger et al., 1972; Melancon and Lech, 1976; Hinz and Matsumura, 1977). For example, it has been found that when sunfish were exposed to three PCB congeners, they were able to efficiently metabolize 2,5,2'-trichlorobiphenyl to polar metabolites but not 2,5,2',5'-tetrachlorobiphenyl or 2,4,5,2',5'-pentachlorobiphenyl (Sanborn et al., 1975). In general, it would appear that while mono-, di-, and trichlorobiphenyl congeners can be metabolized by several species of fish, congeners with higher amounts of chlorination, regardless of chlorination position, are slowly metabolized. Although there is a variation among fish species in their ability to biotransform the lower chlorinated PCB congeners, there appears to be

general agreement that fish biotransform most PCB congeners at considerably slower rates than their mammalian counterparts. The overall result of this reduced capacity to biotransform many PCB congeners contributes to the persistence of PCB congeners in fish which are not persistent in mammals.

It is often observed that PCB residue patterns obtained from fish more closely resemble the patterns of congeners seen in the mixture to which the fish were exposed. In several studies in which Aroclors were fed to mammals, including the goat and the swine, the Aroclor residue pattern differed from the pattern of the Aroclors fed experimentally, particularly with respect to the lower chlorinated congeners (Hansen et al., 1977). This is illustrated in Figure 6 which shows an electron capture gas chromatographic analysis of a standard of Aroclor 1242 and extracts of channel catfish fat and liver after exposure to this PCB mixture (Hansen et al., 1976). It can be seen that the pattern in fat and liver closely resembled that of the standard. In comparable mammalian studies, the residue pattern from tissues is often different from that of the Aroclor fed to the animal. These experimental results agree with the observation that lower chlorinated congeners, such as 2,5,2',5'-tetrachlorobiphenyl tend to bioaccumulate and persist in fish but seem to be more transient in most mammalian species.

At present there is much information available concerning the metabolism of specific PCB congeners in mammals and its relationship to the propensity of a specific congener to be persistent in mammals (Kato et al., 1980) but information concerning biotransformation of specific PCB congeners in fish is sparse. Since in vitro and in vivo biotransformation studies indicated that 2,5,2',5'-tetrachlorobiphenyl (4-CB) is both slowly metabolized by fish and found in fish sampled from the wild, the disposition of 4-CB has been extensively studied in rainbow trout. Rainbow trout were exposed to ^{14}C-labeled 4-CB in a single exposure and subsequently were transferred to a raceway and were fed and maintained according to normal hatchery standards for over a year. After an initial equilibrium period in which some of the radioactive label was lost immediately after the transfer to freshwater, there was very little excretion of this compound by the experimental animals (Guiney et al., 1979). The data in Figure 7 dramatically illustrates the persistence of this compound. The calculated half-life from regression analysis of the elimination curve was approximately 1.76 yr. Note that the y axis in this curve represents the amount of 4-CB in tissues as a percent of total body burden and not concentration. It is obvious that over this period of time, the concentration would decrease because there was no input, and the animals grew to approximately three times their initial body weight. However, it should be noted that after the initial

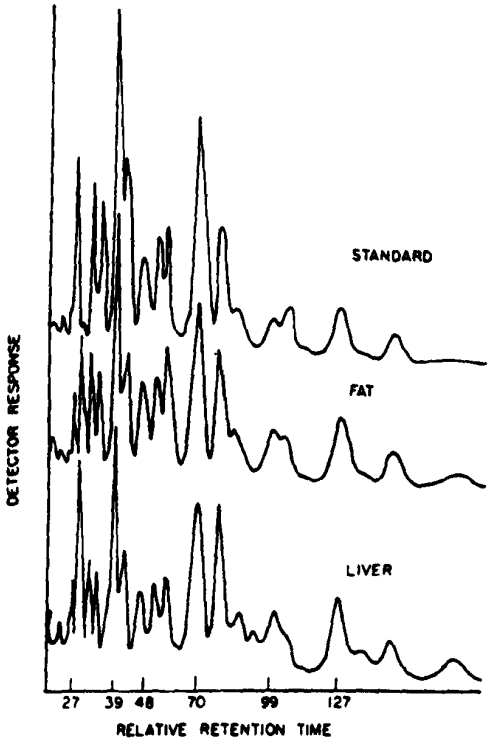


Figure 6. Electron capture gas-liquid chromatographs of an Aroclor 1242 standard and extracts of catfish fat and liver. The extracts were diluted to give a detector response comparable to the standard. This figure was adapted from Hansen et al., 1976.

equilibration period, very little of the total body burden was eliminated, even with this lower chlorinated PCB congener. In mammals, similar types of studies have indicated that the half-life of this lower molecular weight PCB congener is much

MONS 004971

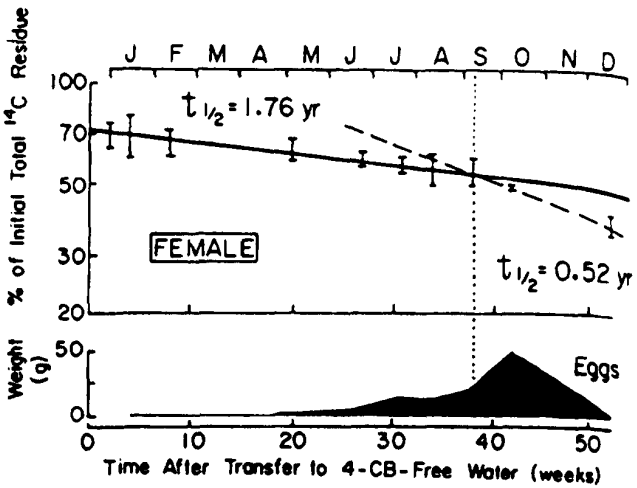


Figure 7. The enhancing effect of spawning on whole body elimination of 2,5,2',5'-tetrachlorobiphenyl (4-CB) residues from female rainbow trout. The top panel shows the rate of elimination of radioactive 4-CB residues from the whole fish. The bottom panel shows wet weight of the eggs in the fish. The months of the year after the fish were transferred to 4-CB free water are shown across the top of the figure. This figure was adapted from Guiney et al., 1979.

shorter. When this study was extended through the spawning season, the slope of the elimination curve increased sharply in both males and females at the time of spawning. Data shown in Figure 7 indicate that elimination of 4-CB was increased at the time of formation of eggs. In this figure, the y axis expresses the percent of the initial body burden of 4-CB. This change in slope which indicates an actual loss of 4-CB from the fish is in agreement with the observation that a corresponding amount of 4-CB was lost from fat and was recovered in the eggs expelled during spawning (Figure 8).

MONS 004972

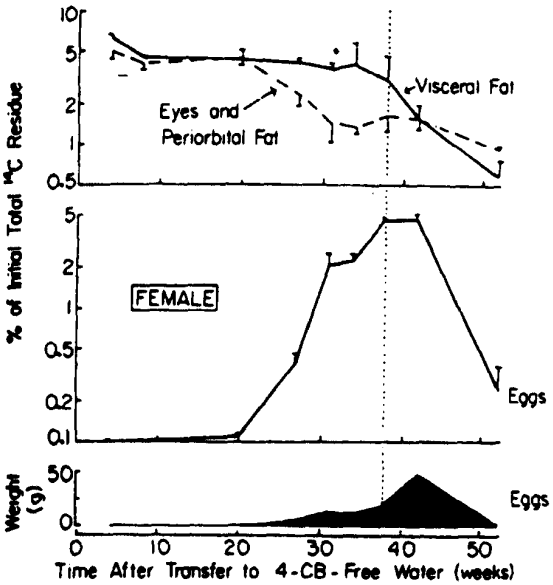


Figure 8. Illustration of the redistribution of 2,5,2',5'-tetrachlorobiphenyl (4-CB) residues that occurs between body fat depots and eggs during the spawning in female rainbow trout. This figure was adapted from Guiney et al., 1979.

The results of these latter experiments indicate that even some of the lower chlorinated PCB congeners may persist for a long period of time in a species such as trout which does not readily biotransform these congeners. These results also illustrate that the total body burden of such congeners may be reduced via the spawning mechanism; but under normal circumstances, elimination of this compound is slow when compared to mammals.

Most data indicate that 2,5,2',5'-tetrachlorobiphenyl (4-CB) as well as other PCB isomers may be extremely persistent in fish, and that dilution of residues by growth rather than

MONS 004973

actual elimination is the basis for the reduction of tissue concentrations over long periods of time. However, more recent work (Guiney et al., 1980) has demonstrated that actual eliminaton of 4-CB can occur during the fry-stage of rainbow trout development, but the mechanism concerned with the observed reduction in body burden at this time is poorly understood. When fertilized rainbow trout eggs were exposed to water-born ^{14}C-labeled 4-CB for 24 hr and transferred to an incubator supplied with flowing 4-CB free water, the burden of this isomer in the eggs and sac fry remained constant throughout these stages of development (Figure 9). This virtual cessation of elimination lasted for almost 2 months and the calculated half-life was 231 days. However, when the developing trout entered the fry stage, a rapid phase of 4-CB elimination was observed over the next 2 months. The calculated half-life of elimination during the fry stage was 14.6 days. This latter finding

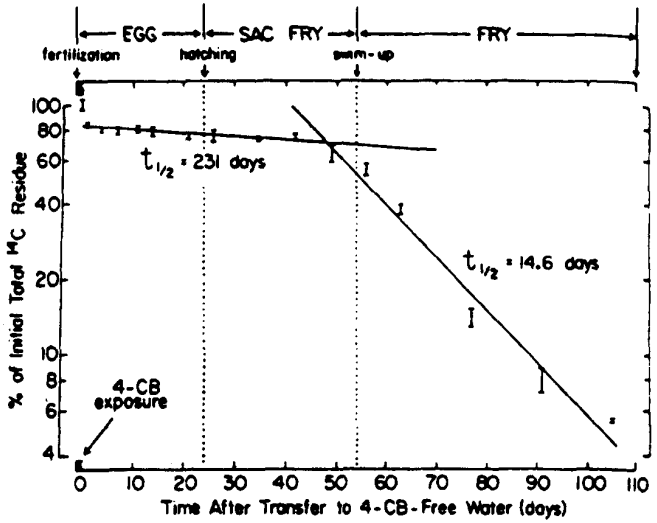


Figure 9. Elimination of 2,5,2',5'-tetrachlorobiphenyl (4-CB) residues during early development in rainbow trout. The time course of development is given at the top and the duration of 4-CB exposure at the lower left. This figure was adapted from Guiney et al., 1980.

MONS 004974

indicates that although 4-CB concentration in the fry was decreased because of dilution by growth, there was also actual, true elimination of the compound. More explicitly, the initial 4-CB body burden decreased from approximately 70 percent at the end of the sac fry stage to approximately 5 percent at the end of the fry stage (Figure 9). The underlying reason for this enhanced rate of elimination, that is uniquely confined to the fry stage of development, is not known. It is possible that it may be related to the low fat content of the fry as opposed to the adult or a high rate of biotransformation at this stage of the life cycle. Alternatively, it may be that lipids or lipoproteins absorbed from the yolk sac or synthesized in the liver bind 4-CB. The resulting 4-CB lipoprotein complex may then be more rapidly elimination in feces than the unbound form of 4-CB.

SUMMARY

Information gathered over the past several years in a variety of laboratories indicate that most fish species biotransform the lower chlorinated PCB congeners at slower rates than mammals. Although there is variation in this among fish species, it would appear that the overall residue patterns in fish resemble the patterns found in the exposure source, and there is less biotransformation and elimination of congeners which are readily excretable after metabolism in mammals. Current information also indicates that the degree of bioaccumulaton of PCBs in fish may be directly related to the fat content of the species in question and that the major mechanism for reducing PCB concentrations in fish is by dilution by growth, rather than by true elimination of a portion of the total body burden.

ACKNOWLEDGMENTS

Supported in part by NIH grant ES-01080 (JJL), ES-01332 (REP), and the Univeristy of Wisconsin Sea Grant Institute (REP and JJL). Some of the studies herein were carried out at the MCW NIEHS Aquatic Biomedical Research Center (ES-01985).

LITERATURE CITED

Fishbein, L. 1972. Chromatographic and Biological Aspects of Polychlorinated Biphenyls. J. Chromatog 68:345-426.

MONS 004975

Guiney, P.D., M.J. Melancon, J.J. Lech, and R.E. Peterson. 1979. Effects of Egg and Sperm Maturation and Spawning on the Distribution of a Polychlorinated Biphenyl in Rainbow Trout. Toxicol. Appl. Pharmacol. 47:261-272.

Guiney, P.D., J.J. Lech, and R.E. Peterson. 1980. Distribution and Elimination of a Polychlorinated Biphenyl During Early Life Stages of Rainbow Trout (Salmo gairdneri). Toxicol. Appl. Pharmacol. 53:521-529.

Hansen, L.G., W.B. Wiekhorst, and J. Simon. 1976. Effects of Dietary Aroclor 1242 on Channel Catfish (Ictalurus punctatus) and the Selective Accumulation of PCB Components. J. Fish. Res. Bd. Can. 33:1343-1352.

Hansen, L.G., M.E. Welborn, R.E. Borchard, R.H. Teske, and R.L. Metcalf. 1977. Tissue Distribution of PCB Components in Swine and Sheep Fed Three Different Rations Containing Aroclors 1242and 1254. Arch. Env. Cont. Toxicol. 5:257-278.

Hinz, R. and F. Matsumura. 1977. Comparative Metabolism of PCB Isomers by Three Species of Fish and the Rat. Bull. Env. Cont. Toxicol. 18:631-639.

Hutzinger, O., D.M. Nash, S. Safe, A.S.W. DeFreitus, R.J. Norstrom, D.J. Wildish, and V. Zitko. 1972. PCBs: Metabolic Behavior of Pure Isomers in Pigeons, Rats, and Brook Trout. Science 178:312-314.

Hutzinger, O., S. Safe, and V. Zitko. 1974. The Chemistry of PCB's. CRC Press, Inc., Cleveland, OH.

Kato, S., J.D. McKinney, and H.B. Matthews. 1980. Metabolism of Symmetrical Hexachlorobiphenyl Isomers in the Rat. Tox. Appl. Pharmacol. 53:389-398.

Lieb, A.J., D.D. Bills, and R.O. Sinnhuber. 1974. Accumulation of Dietary Polychlorinated Biphenyls (Aroclor 1254) by Rainbow Trout (Salmo gairdneri). J. Agr. Food Chem. 22:638-642.

Mayer, F.L., P.M. Mehrle, and H.O. Sanders. 1977. Residue Dynamics and Biological Effects of Polychlorinated Biphenyls in Aquatic Organisms. Arch. Env. Contam. Toxicol. 5:501-511.

Melancon, M.J. and J.J. Lech. 1976. Isolation and Identification of a Polar Metabolic of Tetrachlorobiphenyl From Bile of Rainbow Trou Exposed to ^{14}C-Tetrachlorobiphenyl. Bull. Env. Cont. Toxicol. 15:181-188.

MONS 004976

Norstrom, A.J., D.J. Hallett, and R.A. Sonstegard. 1978. Coho Salmon (Oncorhynchus kisutch) and Herring Guls (Larus argentatus) as Indicators of Organochlorine Contamination in Lake Ontario. J. Fish. Res. Bd. Can. 35:1401-1409.

Sanborn, J.R., W.F. Childers, and W.F. Metcalf. 1975. Uptake of Three Polychlorinated Biphenyls, DDT, and DDE by the Green Sunfish, Leponis cyanellus Raf. Bull. Env. Cont. Toxicol. 13:209-217.

MONS 004977

CHAPTER 15

METABOLISM OF PCBs IN MAMMALS: ROUTES OF ENTRY, STORAGE, AND EXCRETION

H. B. Matthews
National Institute of Environmental Health Sciences
National Toxicology Program
Research Triangle Park, North Carolina 27709

INTRODUCTION

The presence of toxic chemicals in the environment is not a recent occurrence. The presence of toxic chemicals pre-dates life itself and each class of chemicals has presented its own set of problems. The polychlorinated biphenyls (PCBs) are certainly no exception. Most of the effects of toxic chemicals can be tolerated if certain limits of exposure are not exceeded and exposure to most chemicals can be limited by removing the source. Because of their persistence in the environment and bioaccumultion in the food chain, removal of the source of exposure to PCBs has proved particularly difficult. Given the inevitability of past and future human exposure to PCBs, work in our laboratory has been directed to understanding the fate of these compounds in mammals. The following is a general overview of what we feel are the determining factors for the fate of PCBs in higher animals.

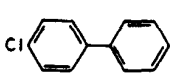
ADSORPTION AND DISTRIBUTION

With the exception of the laboratory situation, PCBs are always found as a mixture of many chlorinated biphenyls. Depending upon the degree and position of chlorination, there may be 209 different chlorinated biphenyls. Since it would be impractical to study the metabolism and disposition of all PCBs, we chose to study a series of carefully selected representative chlorinated biphenyls in an effort to learn the basic rules which determine why this group of chemicals tends to accumulate

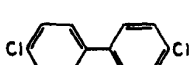
MONS 004978

in the bodies of higher animals. To facilitate the study, we used compounds which were labeled with carbon-14.

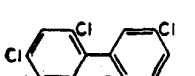
One of our first efforts was to study the absorption, tissue distribution, metabolism, and excretion of four chlorinated biphenyls. The chemicals studied were 4-chloro-(1-CB), 4,4'-dichloro-(2-CB), 2,4,5,2',5'-pentachloro-(5-CB), and 2,4,5,2',4',5'-hexachlorobiphenyl (6-CB)(Matthews and Anderson, 1975)(Figure 1). These biphenyls represent a range of chlorination from 10 to 60 percent. Our studies of the disposition of these biphenyls in the rat demonstrated that following ingestion each was readily absorbed from the gastrointestinal tract and distributed to all the tissues. The highest initial concentrations were observed in liver, but within a fews days the concentration in liver was reduced by 90 percent. The less chlorinated 1-CB and 2-CB were apparently cleared from the liver more rapidly than were the more highly chlorinated 5-CB and 6-CB. The rates of whole body clearance by excretion in urine and feces varied greatly. Greater than 90 percent of 1-CB was excreted in approximately two days, whereas approximately 4 to 10 days were required to excrete 90 percent of 2-CB and 5-CB, respectively. The 6-CB was excreted extremely slowly and the data indicated that the rat would never excrete 90 percent of the dose.



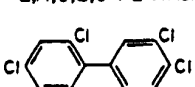
4-CHLOROBIPHENYL



4,4'-DICHLOROBIPHENYL



2,4,5,2',5'-PENTACHLOROBIPHENYL



2,4,5,2',4',5'-HEXACHLOROBIPHENYL

Figure 1. Structural formulas for four chlorobiphenyls.

MONS 004979

An examination of additional tissues made it obvious that 6-CB, and to a lesser extent 5-CB, was being cleared from liver and other lean tissues by redistribution to adipose tissue and skin. Once a PCB was sequestered in adipose tissue, the rate of clearance from the body by excretion in urine and feces was greatly reduced.

EFFECT OF POLARITY ON DISTRIBUTION

Investigations to determine the factors which account for clearance of PCBs from tissues showed that in each case the PCB derived radioactivity excreted was in the form of PCB metabolites. Very little parent compound was excreted. On the other hand, the material retained in the tissues was primarily unmetabolized PCB. Isolation and identification of PCB metabolites from several species in a number of laboratories have showed that the metabolites are always more polar than the parent compound (Gardner *et al.*, 1973; Goto *et al.*, 1974; Safe *et al.*, 1975; Hass *et al.*, 1977; Kato *et al.*, 1980). The polarity of PCB metabolites facilitates their excretion in the aqueous mediums of urine and bile. Unmetabolized PCBs are not soluble in water and, therefore, even when they are present in liver and kidney they have a greater affinity for the tissues than urine and bile and are not excreted. The net result is that those PCBs which can be readily metabolized are readily excreted, whereas those PCBs which are not readily metabolized are stored in lipid-rich tissues such as adipose tissue.

The effect of lipid solubility on the affinity of PCBs for various tissues as measured by the tissue/blood ratios is illustrated in Table 1. In this table, it is seen that as the number of chlorines on the biphenyl rings increase from one to six the tissue/blood ratio tends to increase. Furthermore, the increase is proportional to the amount of lipid in the tissue, so that the most highly chlorinated PCB studied, 6-CB, is 400 times as soluble in adipose tissue as in blood. On the other hand, the metabolites of these PCBs are approximately equally soluble in blood and tissues and the effect of chlorination is much less. Adipose tissue has little or no capacity to metabolize PCBs to more polar compounds. Enzymes responsible for PCB metabolism are located primarily in liver. Therefore, the lipid solubility of PCBs also acts to increase their persistence by isolating them from the enzymes which can convert them to metabolites which can be excreted.

MONS 004980

TABLE 1

Tissue/Blood Distribution Ratios for Selected PCBs and Respective Metabolites

	Parent PCB				PCB Metabolites			
Compartment	1-CB	2-CB	5-CB	6-CB	1-CB	2-CB	5-CB	6-CB
Blood	1	1	1	1	1	1	1	1
Gut Lumen	1	1	1	1	1	1	1	1
Muscle	1	2	1	4	0.14	0.40	0.10	0.30
Liver	3	6	12	2	5	2	4	
Skin	10	10	7	30	0.25	0.30	0.10	2
Adipose	30	50	70	400	0.40	0.60	0.40	2

PCB METABOLISM

An examination of the molecular structures of the four PCBs described above revealed two major differences between those which were readily metabolized and excreted and the one which was not. The most obvious difference was that 6-CB, the more persistant PCB, was more highly chlorinated than the others. However, 5-CB, which had almost as many chlorines as 6-CB, was metabolized and excreted much more rapidly. The second major difference between 6-CB and the other chlorinated biphenyls is that 6-CB does not have adjacent unsubstituted carbon atoms.

Work done in the fifties indicated that the presence of adjacent unsubstituted carbon atoms facilitates the metabolism of chlorinated benzenes (Jondorf et al., 1955; Jondorf et al., 1958). More recent studies of the metabolism of unchlorinated biphenyl indicate that the preferred route of biphenyl metabolism involves the formation of an arene oxide between the number 3 and 4 carbons of one biphenyl ring (Billings and McMahon, 1978). This arene oxide is degraded both spontaneously and enzymatically to yield a variety of hydroxylated metabolites. Hydroxylated metabolites of PCBs are much more polar than the parent compound; and possibly more important, they are readily conjugated with glucuronic acid to form water soluble conjugates which are readily excreted.

MONS 004981

We have studied the metabolism of a number of chlorinated biphenyls in our laboratory. A simplified metabolic scheme for 5-CB involving the arene oxide between the number 3 and 4 carbons of one ring is presented in Figure 2 (Chen et al., 1976). The arene oxide shown in Figure 1 is formed between the only two adjacent unsubstituted carbon atoms found in this PCB and all of the 5-CB metabolites detected were hydroxylated in the 3 or 4 positions.

In order to demonstrate that the reduced metabolism of 6-CB is due to the absence of adjacent unsubstituted carbon atoms and not simply a higher degree of chlorination, we studied the metabolism and disposition of three additional hexachlorobiphenyls (Kato et al., 1980; Matthews and Tuey, 1980). Two of these compounds, 2,4,6,2',4',6'-hexachlorobiphenyl and 2,3,5,2',3',5'-hexachlorobiphenyl, do not have adjacent unsubstituted carbon atoms. The third compound, 2,3,6,2',3',6'-hexachlorobiphenyl, is equally chlorinated but has adjacent unsubstituted carbon atoms in each ring (Figure 3). In this study, we observed that 2,3,6,2',3',6'-hexachlorobiphenyl was metabolised and excreted as rapidly as the dichlorobiphenyl described earlier. Approximately 90 percent of the dose of 2,3,6,2',

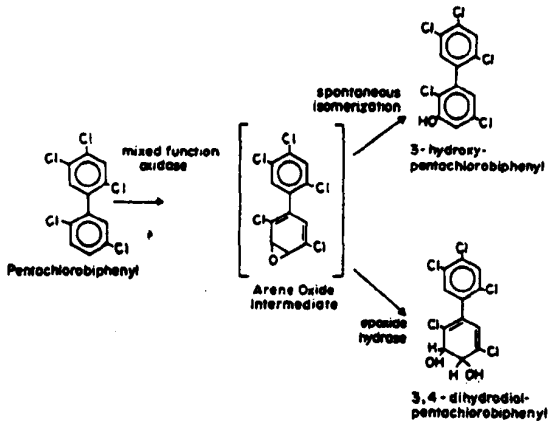


Figure 2. Metabolic scheme for 2,4,5,2',5'-pentachlorobiphenyl (5-CB).

MONS 004982

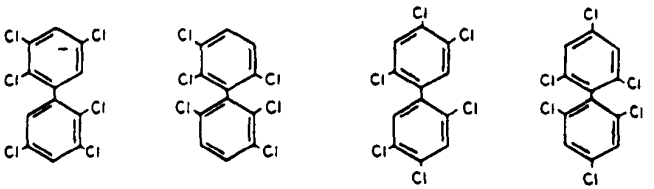


Figure 3. Structural formulas for four hexachlorobiphenyls.

3',6'-hexachlorobiphenyl was excreted in 4 to 6 days. On the other hand, those hexachlorobiphenyls which do not have adjacent unsubstituted carbon atoms were metabolized and excreted at a rate more comparable to that previously observed for 6-CB. A rat would not be expected to live long enough to excrete 90 percent of the dose of these compounds. Also, as observed with 6-CB, most of the dose of these PCBs were stored in adipose tissue.

The absence of adjacent unsubstituted carbon items is thought to inhibit the metabolism of PCBs in two ways. The presence of the relatively large chlorine atom sterically hinders the approach of the enzyme to the biphenyl molecule and chlorination deactivates the respective carbon atom and hinders the formation of an arene oxide involving that carbon atom. The net result is that the position of chlorination may be as important a determinant of PCB persistence as the degree of chlorination.

OTHER SPECIES

Most of the work discussed above describes metabolism and disposition of PCBs by laboratory rats. That is because rats have been most frequently used in toxicology studies because they are one of the most convenient and economical species to work with. However, the metabolism and disposition of PCBs have also been studied in a number of other species and some interesting species variations have been observed. Among the mammals studied, dogs appear to have the greatest capacity to metabolize PCBs (Sipes et al., 1979). Laboratory rats and mice are about equal and have an intermediate ability to metabolize PCBs (Tuey and Matthews, 1980) and monkeys metabolize and

excrete PCBs relatively slowly (Abdel-Hamid et al., 1981). PCB metabolism has also been studied in both birds (Hutzinger et al., 1972) and fish (Lech and Peterson, 1983) and each has some capacity to metabolize PCBs, but very limited capacity to metabolize those which are more slowly metabolized by mammals. In all species the mechanisms for PCB metabolism, as well as the distribution and excretion of the respective parent compounds and metabolites, appear to be similar. The net result being that those species which metabolize PCBs most slowly have the greatest potential to accumulate higher concentrations of these compounds in their tissues.

EQUILIBRATION OF PCBs AMONG TISSUES

It should be pointed out that even though PCBs and similar lipid soluble compounds are concentrated in adipose tissue they are not isolated there. Following exposure to PCBs, an equilibrium is reached in which the concentration in each tissue is dependent upon the concentration in all the other tissues. This equilibration among the tissues is illustrated by the model in Figure 4. As discussed earlier, PCBs are readily absorbed from the gastrointestinal tract. As shown in the model, these compounds are transported by blood to all tissues. Initial tissue distribution is proportional to the rate of blood flow to the tissue and tissue volume. Therefore, the highest initial concentrations are observed in highly perfused tissues such as liver and a significant portion of the dose is in muscle because it accounts for more than twice the volume of any other tissue. Within a few hours to a few days after exposure the PCB concentrations in each of the tissues reach an equilibrium. At equilibrium, the concentration in each tissue is determined primarily by the lipid content of that tissue. Thus, we see high concentrations of PCBs in adipose tissue and much lower concenrations in relatively lean tissues such as muscle, blood, and even liver.

The equilibrium between the tissues is maintained by their common intermediate, the blood. The tissue/blood ratio shown in Table 1 is determined by the partition of the respective PCB between the two mediums and is a constant for each PCB. Therefore, any change in the concentration of PCB in either blood or tissue will cause a net movement of PCB in the appropriate direction to reestablish the equilibrium (Lutz et al., 1977). Therefore, when the PCB concentration in liver is reduced by metabolism and excretion, more PCB will partition from blood to liver to reestablish the tissue/blood ratio. If the PCB concentration of blood is reduced by partition into liver, then additional PCB will partition from all other tissues into blood to reestablish the respective tissue/blood ratios.

MONS 004984

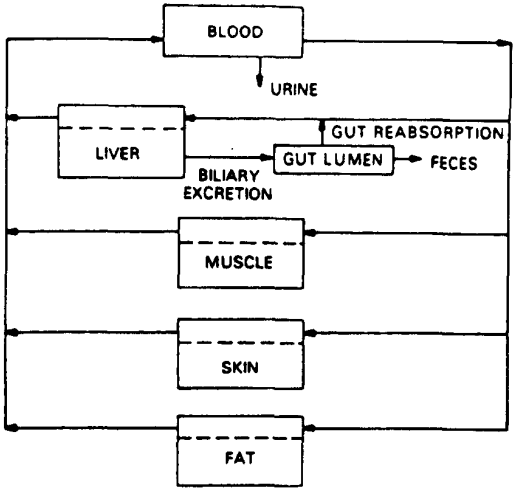


Figure 4. Schematic model of PCB absorption, equilibration in tissues, and excretion (Lutz et al., 1977).

It is in this way that those PCBs which can be cleared from the liver by metabolism and excretion are cleared from all the other tissues as well. Conversely, those PCBs which are not readily metabolized may be concentrated in adipose tissue, but all tissues are assured of a finite exposure by this same dynamic equilibrium. Therefore, even though adipose tissue is most probably not a site of toxic action for PCBs, a reservoir of PCB in adipose tissue assures chronic exposure of the site(s) of toxic action wherever they may be.

SUMMARY

The results presented here are a brief overview of a series of studies of carefully selected PCBs. The PCBs studied are selected as representatives of the 209 PCBs possible and were chosen to permit studies of the effect of degree and position of chlorination on PCB metabolism and disposition by mammals.

MONS 004985

The results of these studies indicate that PCBs are readily absorbed from the gastrointestinal tract. Following absorption, PCBs are transported by the blood primarily to those tissues having the greatest blood flow or tissue volume, such as liver and muscle. Those PCBs which can be readily metabolized are metabolized to more polar compounds and excreted. Those PCBs which are not metabolized are not readily excreted and tend to concentrate in lipid-rich tissues such as adipose tissue. Studies of PCB metabolism indicate that the presence of adjacent unsubstituted carbon atoms facilitate the metabolism of these compounds. PCBs which do not have adjacent unsubstituted carbon atoms are metabolized much more slowly than those which do and are consequently much more persistent in tissues.

The persistence of PCBs in the tissues of animals and man is of particular concern, because these compounds are not isolated in any one tissue but are carried throughout the body to all tissues by the blood. The persistence of PCBs in the environment and in the tissues of higher animals assures continued exposure for years to come, and to date there is no known method whereby PCBs may be safely removed from human tissues.

LITERATURE CITED

Abdel-Hamid, F.M., J.A. Moore, and H.B. Matthews. 1981. A Comparative Study of 3,4,3',4'-Tetrachlorobiphenyl in Male and Female Rats and Female Monkeys. J. Toxicol. Environ. Hlth. 7:181-191.

Billings, R.E. and R.E. McMahon. 1978. Microsomal Biphenyl Hydroxylation: The Formation of 3-Hydroxybiphenyl and Biphenyl Catecol. Mol. Pharmacol. 14:145-154.

Chem, P.R., J.D. McKinney, and H.B. Matthews. 1976. Metabolism of 2,4,5,2',5'-Pentachlorobipehnyl by the Rat. Drug Metab. Dispos. 4:362-367.

Gardners, A.M., J.T. Chen, J.A.G. Roach, and E.P. Ragelis. 1973. Polychlorinated Biphenyls: Hydroxylated Urinary Metabolites of 2,5,2',5'-Tetrachlorobiphenyl Identified in Rabbits. Biochem. Biophys. Res. Commun. 551377-1384.

Goto, M., K. Sugiura, M. Hattori, T. Miyaguwa, and M. Ikamura. 1974. Metabolism of 2,3,5,6-Tetrachlorobiphenyl-^{14}C and 2,3,4,5,6-Pentachlorobiphenyl-^{14}C in the Rat. Chemosphere 5:233-238.

MONS 004986

Hass, J.R., L.T. Jao, N.K. Wilson, and H.B. Matthews. 1977. Metabolism of 4-Chlorobiphenyl and 4,4'-Dichlorobiphenyl in the Rat:- Qualitative and Quantitative Aspects. J. Agric. Food Chem. 25:1330-1333.

Hutzinger, O., D.M. Nash, S. Safe, A.S.W. DeFreitas, R.J. Norstrom, D.J. Wildish, and V. Zitko. 1972. Polychlorinated Biphenyls: Metabolic Behavior of Pure Isomers in Pigeons, Rats, and Brook Trout. Science 178:312-313.

Jondorf, W.R., D.V. Parke, and R.T. Williams. 1955. Studies in Detoxication. 66. The Metabolism of Halogenobenzenes 1:2:3-, 1:2:4-, and 1:3:5-Trichlorobenzenes. Biochem. J. 61: 512-521.

Jondorf, W.R., D.V. Parke, and R.T. Williams. 1958. Studies in Detoxication. 76. The Metabolism of Halogenobenzenes 1:2:3:4-, 1:2:3:5-, and 1:2:4:5-Tetrachlorobenzenes. Biochem. J. 69: 181-189.

Kato, S., J.D. McKinney, and H.B. Matthews. 1980. Metabolism of Symmetrical Hexachlorobiphenyl Isomers in the Rat. Toxicol. Appl. Pharmacol. 53:389-398.

Lech, J.J. and R.E. Peterson. 1983. Biotransformation and Persistence of Polychlorinated Biphenyls (PCBs) in Fish. In: F.M. D'Itri and M.A. Kamrin (eds.), "PCBs: Human and Environmental Hazards," pp. 187-201, Ann Arbor Science Publishers, Inc., Ann Arbor, MI.

Lutz, R.J., R.L. Dedrick, H.B. Matthews, T.E. Eling, and M.W. Anderson. 1977. A Preliminary Pharmacokinetic Model for Several Chlorinated Biphenyls in the Rat. Drug Metab. Dispos. 5:386-396.

Matthews, H.B. and M.W. Anderson. 1975. Effect of Chlorination on the Distribution and Excretion of Polychlorinated Biphenyls. Drug Metab. Dispos. 3:371-380.

Matthews, H.B. and D.B. Tuey. 1980. The Effect of Chlorine Position on the Distribution and Excretion of Four Hexachlorobiphenyl Isomers. Toxicol. Appl. Pharmacol. 53:377-388.

Safe, S., N. Platonow, and O. Hutzinger. 1975. Metabolism of Chlorobiphenyls in the Goat and Cow. J. Agric. Food Chem. 23:259-261.

Sipes, I.G., D.H. McKelvie, and R. Collins. 1979. Excretion of Hexachlorobiphenyls and 2,4,5,2',4',5'-Hexabromobiphenyl in the Dog. Toxicol. Appl. Pharmacol. 48:A155.

MONS 004987

Tuey, D.B. and H.B. Matthews. 1980. Use of a Physiological Compartmental Model for the Rat to Describe the Pharmacokinetics of Several Chlorinated Biphenyls in the Mouse. Drug Metab. Dispos. 8:397-403.

CHAPTER 16

PATHOLOGIC EFFECTS OF PCBs IN MAMMALS

Stuart D. Sleight
Department of Pathology
Michigan State University
East Lansing, Michigan 48824-1316

INTRODUCTION

The toxicologic effects of polychlorinated biphenyls (PCBs) have been the subject of several reviews (Fishbein, 1974; Kimbrough, 1974; Kimbrough et al., 1978; Vos, 1972). Kimbrough (1976) described pathologic findings associated with long term administration of commercial mixtures of PCBs to rodents and primates. Her brief review stressed hepatotoxicity and described the lesions seen in the liver of rats and mice. She also described the tumorigenic response associated with the long term exposure of rodents to PCBs.

This review will describe major clinical signs associated with PCB toxicosis in mammals and emphasize the effects on the liver including hepatocarcinogenesis. It will also discuss typical lesions seen in the thyroid, skin, stomach, and lymphoid organs. Similarities with and differences between the effects seen with other polyhalogenated aromatic hydrocarbons will be pointed out as deemed appropriate.

CLINICAL SIGNS

Oral administration of high doses of Aroclor 1242 (4.25 g/kg) to rats resulted in a wasting disease characterized by diarrhea, chromodacryorrhea, loss of body weight, and terminal ataxia (Bruckner et al., 1973). In Vos review (1972) he cited several references in which death resulted after high doses of PCBs were given to rats, mice, and rabbits. Guinea pigs were killed by lower doses.

MONS 004989

Accidental exposure of a colony of rhesus monkeys to PCBs in a concrete sealant produced a disease characterized by slow and continuous weight loss, alopecia, acne, facial edema, and diarrhea (Altman et al., 1979). A high incidence of abortions and stillbirths was recorded. Allen (1975) described nearly identical signs in rhesus monkeys in experiments in which diets contained 100 or 300 mg/kg of Aroclor 1248. Long term administration of doses as low as 2.5 mg/kg caused periorbital edema, alopecia, erythema, and acneform lesions on the face and neck.

Miniats et al. (1978) reported that oral doses of 25 mg of Aroclor 1254/kg of body weight when given to germ free pigs caused inappetance, hemorrhagic diarrhea, retarded growth, incoordination, coma, and death.

Signs of a wasting disease have also been described after oral administration of commercial mixtures of polybrominated biphenyls (PBB) (Firemaster) to rats (Gupta and Moore, 1979). Guinea pigs react similarly but a lower dose of Firemaster (FM) is required to cause toxicosis (Sleight and Sanger, 1976). Collins et al. (1982) found that hamsters survived oral doses of 3.2 g/kg of FM; whereas, a single dose of 0.4 g/kg killed guinea pigs within 14 days. Generalized debilitation and weight loss are also seen after administration of chlorinated dibenzo-p-dioxins to rats (Gasiewicz et al., 1980) and mice (McConnell et al., 1978a). Again guinea pigs and rhesus monkeys are highly susceptible to the toxic effects of these compounds (McConnell et al., 1978a, 1978b).

Chemical structure of the PCB and PBB congeners affects toxicity. For example, 2,4,5,2',4',5'-hexachlorobiphenyl (HCB) and 2,4,5,2',4',5'-hexabromobiphenyl (HBB) are relatively nontoxic (Akoso et al., 1982a; Biocca et al., 1976; Moore et al., 1978). These congeners are classified as phenobarbital (PB)-type inducers of hepatic drug metabolizing enzymes. Congeners such as 3,4,5,3',4',5'-HCB and 3,4,5,3',4',5'-HBB are much more toxic and each is a 3-methylcholanthrene (MC)-type inducer. Poland and Glover (1977) stressed the structure/activity relationships for PCB congeners and emphasized that those which induce aryl hydrocarbon hydroxylase activity (MC-type) should be considered as toxic. Since the commercial mixtures of PCBs contain many congeners, the toxicity of a mixture will certainly be affected by the proportion of the various congeners in the mixture. Work with purified congeners of PBBs indicates that the major portion of the toxicity of FM is associated with 4 congeners, each of which is classified as a mixed-type inducer; that is, it can induce MC- and PB-type induction. Nearly 75 percent of the commercial mixture of PBB is comprised of congeners with only PB-type

MONS 004990

activity and these congeners are relatively nontoxic (Dannan et al., 1982).

LIVER

The gross lesions and histologic findings associated with administration of PCBs to animals were well summarized by Vos (1972) and by Kimbrough et al. (1972). Hepatomegaly is a commonly reported effect of PCB administration to animals. Hypertrophy of hepatocytes is seen and individual cells may appear foamy and contain sudanophilic vacuoles. Necrosis of hepatocytes can occur especially at high doses. Location of lesions may be discrete but often is centrilobular. Hyperplasia and increased mitotic activity is also seen in some animals. Kasza et al. (1978) compared the toxicity of PCBs and PBBs as to the effects on the rat liver. Similar lesions were caused by each of the mixtures. Fatty metamorphosis and necrosis was much more evident in mice given 3,4,5,3',4',5'-HCB than those given 2,4,5,2',4',5'-HCB (Biocca et al., 1976). Work with analogous PBB congeners in rats has also shown that hepatic lesions are much more severe with 3,4,5,3',4',5'-HBB than with 2,4,5,2',4',5'-HBB (Akoso et al., 1982a; Render et al., 1982).

Ultrastructural changes in hepatocytes of animals given commercial mixtures of PCBs have been described by several researchers (Kimbrough, 1974; Nishizume, 1970; Norback and Allen, 1972). Increases in smooth endoplasmic reticulum is a consistent feature and in part accounts for hypertrophy of hepatocytes. Mitochondria were described as atypical and concentric membrane arrays which sometimes surrounded lipid vacuoles were also reported. Kasza et al. (1978) compared the ultrastructural changes caused by PCBs or PBBs in rats. They found that changes were similar. They described decreased numbers of mitochondria, increased liposomes, and a decreased number of Golgi condensing vesicles in addition to the changes previously mentioned. Our work with congeners of PBB in rats indicates that MC-type inducers such as 3,4,5,3',4',5'-HBB produce many more concentric membrane arrays than seen with the PB-type inducers such as 2,4,5,2',4',5'-HBB. In addition, the rough endoplasmic reticulum is markedly disrupted by the MC-type inducer (Akoso et al., 1982a; Render et al., 1982).

The role of PCBs in hepatocarcinogenesis has attracted considerable public health and research interest. Commercial PCB mixtures have induced hepatic tumors in rats (Ito et al., 1974; Kimbrough et al., 1972, 1975; Kimura and Baba, 1973) and in mice (Ito et al., 1973; Kimbrough and Linder, 1974; Nagasaki, 1972). Hepatocellular carcinomas were described in each species; and in addition, what are classified as neoplastic

nodules and foci of cellular alteration were described (Squire and Levitt, 1975). More recent studies have been done to determine if PCBs serve as promoters of carcinogenesis. When the PCBs were given after a known tumor initiator such as diethylnitrosamine (Preston et al., 1981; Pereira et al., 1982), there was convincing evidence that they act as tumor promoters. An earlier study by Kimura et al. (1976) in which female rats were given PCB after they had been given 3'-methyl-4-dimethyl aminoazobenzene also indicated a tumor promoting effect in the liver.

PBBs apparently also may act as tumor promoters (Jensen et al., 1982; Trosko et al., 1981). A relatively nontoxic PBB congener, 2,4,5,2',4',5'-HBB, is apparently a relatively potent promoter of hepatocarcinogenesis in the rat (Jensen et al., 1982). Results of this study indicate that toxicity and carcinogenicity may not necessarily be related with compounds such as PBBs or PCBs. Although research is clearly demonstrating that PCBs and PBBs can act as promoters of hepatocarcinogenesis in animal test systems, it remains difficult to assess the potential hazard of these compounds as carcinogens in man.

Hepatic porphyria can be induced by PCBs in the female rat (Bruckner et al., 1974; Goldstein et al., 1974; Strik, 1973). Porphyria has also been seen in mice and 3,4,5,3',4',5'-HCB was much more potent than 2,4,5,2',4,'5'-HCB in causing porphyria (Biocca et al., 1976). Gupta et al. (1981) described porphyria in female rats and mice given FM, but they did not observe porphyria when rats or mice were given 2,4,5,2',4',5'-HBB. We have found that porphyria occurs when female rats are given FM or a combination of 2,4,5,2',4',5'-HBB and 3,4,5,3',4',5'-HBB. Porphyria is seen only rarely when either congener is given alone.

THYROID GLAND

There is considerable evidence that PCBs affect the metabolism of thyroid hormones. Bastomsky and co-workers reported that administration of PCBs to rats increased ^{131}I uptake by thyroid follicular cells, lowered serum thyroxine concentrations, and reduced protein-binding of thyroid hormones. Increased conjugation of thyroxine and increased excretion of thyroxine glucuronide in the bile were also found (Bastomsky, 1974; Bastomsky and Murthy, 1976; Bastomsky and Wyse, 1975; Bastomsky et al., 1976).

Collins et al. (1977) evaluated the histopathologic, histochemical, and ultrastructural changes in thyroid follicular cells after administration of 50 or 500 mg/kg of

MONS 004992

PCBs to rats for 4 to 12 weeks. They also attempted to correlate the structural changes in follicular cells to changes in serum thyroxine concentration. Hypertrophy and hyperplasia of follicular cells with projections into the lumen were prominent histologic features. Cells were more columnar than in controls. By 4 weeks, ultrastructural examination revealed that there was an accumulation of lysosomal bodies and colloid droplets and abnormalities of the luminal surface of follicular cells. Lesions became more pronounced by 12 weeks. Follicular cells were greatly distended and large lysosomal bodies with strong acid phosphatase activity were present. Mitochondria were vacuolated. The ultrastructural changes were associated with significant reductions of serum thyroxine at both doses of PCBs. Lesions persisted for 12 weeks after cessation of feeding PCBs, but by 35 weeks the thyroid follicular cells were similar to controls. Serum thyroxine levels had returned to normal by this time.

The PBBs apparently produce similar thyroidal alterations in rats (Akoso et al., 1982b). Feeding of FM or 3,4,5,3',4',5'-HBB to rats produced histologic and ultrastructural changes nearly identical to those described by Collins et al. (1977) with PCBs. However, ultrastructural changes were much less pronounced as a result of feeding diets containing 2,4,5,2',4',5'-HBB. Thyroxine concentrations were markedly reduced by FM and 3,4,5,3',4',5'-HBB, but were only slightly affected by 2,4,5,2',4',5'-HBB.

SKIN AND ASSOCIATED STRUCTURES

Persistent skin lesions such as increased pigmentation and chloracne are well documented as a result of human exposure to PCBs (Kuratsune et al., 1972). Similar if not identical changes occur in rhesus monkeys exposed to PCBs. Allen and co-workers have characterized the gross and histologic skin lesions associated with feeding PCBs (Allen, 1975; Allen and Norback, 1976). Grossly, hair loss from the face, head, and neck occurred within one month after exposure to diets containing 100 mg/kg of Aroclor 1248. The eyelids and the region around the mouth became edematous and there was a loss of eyelashes. Excessive lacrimation and congestion of the conjunctiva were apparent and small comedones were obvious around the face and neck. Excessive secretion of meibomian glands was a consistent feature. Histologically, large intrafollicular keratin cysts and epithelial hyperplasia of hair follicles were evident in the skin of the face. Tissues surrounding these cysts were edematous and contained inflammatory cells. Carstens et al. (1979) described hypertrophy, squamous metaplasia and keratinization of the meibomian glands and eyelids of infant

rhesus monkeys from dams given PCB. McConnell et al. (1979) described similar gross lesions and histologic appearance in rhesus monkeys accidentally exposed to PCBs. In addition, they described thickened and tortuous meibomian glands upon eversion of the eyelids. They also described onychogryphosis with rhexia in animals with severe alopecia. These lesions were more apparent in the nails of the feet.

Dermal applications of PCBs to the skin of rabbits caused hyperplasia and hyperkeratosis of the epidermal and follicular epithelium (Vos and Beems, 1971). Application of Aroclor 1260 caused earlier and more severe lesions than those caused by repeated applications of 2,4,5,2',4',5'-HCB (Vos and Notenboom-Ram, 1972).

STOMACH

Allen et al. (1974) described gastritis in adult rhesus monkeys fed diets containing PCBs. The gastric mucosa was greatly thickened and contained numerous cysts filled with mucin and lined by epithelium. The muscularis mucosa had penetrated into the underlying submucosa. Large cysts were abundant in the submucosa. Ulceration was also a feature. The gastric lesions were considered as highly debilitating and persisted for at least one year after exposure to PCBs. Carstens et al. (1979) described gastric mucosal hyperplasia in infant rhesus monkeys from dams given PCBs. Some of the glandular elements had penetrated the muscularis mucosa. Th submucosa was edematous and contained inflammatory cells. The PBBs apparently cause similar gastric lesions in rhesus monkeys (Lambrecht et al., 1978).

Morgan et al. (1981) recently reported an increased incidence of focal lesions in the glandular portions of the stomachs of male and female F344 rats fed diets containing 25, 50, or 100 mg/kg of Aroclor 1254 for two years. Histologically, the lesions were identified as intestinal metaplasia. Adenocarcinomas were diagnosed in the stomachs of 6 of 144 rats fed PCBs; whereas, no neoplasms were found in 47 control rats.

LYMPHOID ORGANS

Vos and Beems (1971) described cortical atrophy of the thymus, lymphopenia, and depletion of germinal centers of lymph nodes and spleen in rabbits given repeated applications of PCBs. Severely atrophied thymuses and small lymph nodes and spleens were seen in infant rhesus monkeys from dams fed PCBs (Aroclor

MONS 004994

1248) at a concentration of 2.5 mg/kg in the diet for 18 months (Carstens et al., 1979). Thymocytes were described as nonexistent and germinal centers were inapparent in the lymph nodes and spleen. Bone marrow was hypocellular.

Marked thymic involution and moderate depletion of lymphocytes in the spleen were described in mice fed diets containing 10 or 30 mg/kg 3,4,5,3',4',5'-HCB; whereas, 300 mg/kg of 2,4,5,2',4',5'-HCB caused only slight thymic involution and no splenic changes (Biocca, 1976). Studies with analogous PBB congeners in rats have given similar results (Akoso et al., 1982a; Render et al., 1982). Thymic atrophy typified by depletion of cortical lymphocytes was seen in rats fed diets containing 10 or 100 mg/kg of 3,4,5,3',4',5'-HBB for 10 and 30 days; whereas, rats given 100 mg/kg 2,4,5,2',4',5'-HBB had normal appearing thymuses. Lymphocytic depletion also occurred in the spleen and lymph nodes of rats given 3,4,5,3',4',5'-HBB.

Reproductive effects of PCBs including mutagenicity and teratology are not included in this review. Those interested in these areas are referred to the review of Kimbrough et al. (1978).

LITERATURE CITED

Akoso, B.T., S.D. Sleight, S.D. Aust, and H.D. Stowe. 1982a. Pathologic Effects of Purified Polybrominated Biphenyl Congeners in Rats. J. Amer. Col. Toxicol. 1(3):1-22.

Akoso, B.T., S.D. Sleight, R.F. Nachreiner, and S.D. Aust. 1982b. Effects of Purified Polybrominated Biphenyl Congeners on the Thyroid and Pituitary Glands in Rats. J. Amer. Col. Toxicol. 1(3):23-36.

Allen, J.R. 1975. Response of the Nonhuman Primate to Polychlorinated Biphenyl Exposure. Fed. Proc. 34:1675-1679.

Allen, J.R., L.A. Carstens, and D.A. Barsotti. 1974. Residual Effects of Short-Term, Low Level Exposure to Polychlorinated Biphenyls. Toxicol. Appl. Pharmacol. 30:440-451.

Allen, J.R. and D.H. Norback. 1976. Pathobiological Responses of Primates to Polychlorinated Biphenyl Exposure. Proceedings of the National Conference of PCBs, Environmental Protection Agency, Office of Toxic Substances, Washington, DC, pp. 43-49.

MONS 004995

Altman, N.H., A.E. New, E.E. McConnell, and T.L. Ferrell. 1979. A Spontaneous Outbreak of Polychlorinated Biphenyl Toxicity in Rhesus Monkeys (Macaca mulatta): Clinical Observations. Lab. Anim. Sci. 29:661-665.

Bastomsky, C.H. 1974. Effects of a Polychlorinated Biphenyl Mixture (Aroclor 1254) and DDT on Biliary Thyroxine Excretion in Rats. Endocrinology 95:1150-1155.

Bastomsky, C.H. and P.V. Murthy. 1976. Enhanced In Vitro Hepatic Glucuronidation of Thyroxine in Rats Following Cutaneous Application or Ingestion of Polychlorinated Biphenyls. Can. J. Physiol. Pharmacol. 54:23-26.

Bastomsky, C.H., P.V. Murthy, and K. Banovac. 1976. Alterations in Thyroxine Metabolism Produced by Cutaneous Application of Microscope Immersion Oil: Effects Due to Polychlorinated Biphenyls. Endocrinology 98:1309-1314.

Bastomsky, C.H. and J.M. Wyse. 1975. Enhanced Thyroxine Metabolism Following Cutaneous Application of Microscope Immersion Oil. Res. Commun. Chem. Pathol. Pharmacol. 10:725-733.

Biocca, M., J.A. Moore, B.N. Gupta, and J.D. McKinney. 1976. Toxicology of Selected Symmetrical Hexachlorobiphenyl Isomers. I. Biological Responses in Chicks and Mice. Proceedings of the National Conference on PCBs, Environmental Protection Agency, Office of Toxic Substances, Washington, DC, pp. 67-72.

Bruckner, J.V., K.L. Khanna, and H.H. Cornish. 1973. Biological Responses of the Rat to Polychlorinated Biphenyls. Toxicol. Appl. Pharmacol. 24:434-448.

Bruckner, J.V., K.L. Khanna, and H.H. Cornish. 1974. Effect of Prolonged Ingestion of Polychlorinated Biphenyls on the Rat. Food Cosmet. Toxicol. 12:323-330.

Carstens, L.A., D.A. Barsotti, and J.R. Allen. 1979. Exposure of Infant Rhesus Macaques (Macaca mulatta) to Polychlorinated Biphenyl (PCB). In: "Animals as Monitors of Environmental Pollutants," pp. 339-345. Nat. Acad. Sci., Washington, DC.

Collins, J.E., S.D. Sleight, and S.D. Aust. 1982. Acute Pathologic Effects of Polybrominated Biphenyls (PBB) in the Guinea Pig and Golden Hamster. The Pharmacologist 24:149.

MONS 004996

Collins, W.T., C.C. Capen, L. Kasza, C. Carter, and R.E. Dailey. 1977. Effect of Polychlorinated Biphenyl (PCB) on the Thyroid Gland of Rats. Am. J. Pathol. 89:119-130.

Dannan, G.A., S.D. Sleight, and S.D. Aust. Toxicity and Microsomal Enzyme Induction Effects of Several Polybrominated Biphenyls of Firemaster. Fund. Appl. Toxicol. (in press).

Fishbein, L. 1974. Toxicity of Chlorinated Biphenyls. Ann. Rev. Pharmacol. 14:139-156.

Gasiewicz, T.A., M.A. Holscher, and R.A. Neal. 1980. The Effect of Total Parenteral Nutrition on the Toxicity of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in the Rat. Toxicol. Appl. Pharmacol. 54:469-488.

Goldstein, J.A., P. Hickman, and D.L. Jue. 1974. Experimental Hepatic Porphyria Induced by Polychlorinated Biphenyls. Toxicol. Appl. Pharmacol. 27:437-448.

Gupta, B.N., E.E. McConnell, M.W. Harris, and J.A. Moore. 1981. Polybrominated Biphenyl Toxicosis in the Rat and Mouse. Toxicol. Appl. Pharmacol. 57:99-118.

Gupta, B.N. and J.A. Moore. 1979. Toxicologic Assessments of a Commercial Polybrominated Biphenyl Mixture in the Rat. Am. J. Vet. Res. 40:1458-1461.

Ito, N., H. Nagasaki, M. Arai, S. Makiura, S. Sugihara, and K. Hirao. 1973. Histopathologic Studies on Liver Tumorigenesis Induced in Mice by Technical Polychlorinated Biphenyls and Its Promoting Effect on Liver Tumors Induced by Benzene Hexachloride. J. Natl. Cancer Inst. 51:1637-1646.

Ito, N., H. Nagasaki, S. Makiura, and M. Arai. 1974. Histopathological Studies on Liver Tumorigenesis in Rats Treated With Polychlorinated Biphenyls. Gann 65:545-549.

Jensen, R.K., S.D. Sleight, J.I. Goodman, S.D. Aust, and J.E. Trosko. Polybrominated Biphenyls as Promoters in Experimental Hepatocarcinogenesis in Rats. Carcinogenesis 3(10):1183-1186.

Kasza, L., M.A. Weinberger, D.E. Hinton, B.F. Trump, C. Patel, L. Friedman, and L.H. Garthoff. 1978. Comparative Toxicity of Polychlorinated Biphenyl and Polybrominated Biphenyl in the Rat Liver: Light and Electron Microscopic Alterations After Subacute Dietary Exposure. J. Environ. Pathol. Toxicol. 1:241-257.

Kimbrough, R.D. 1974. The Toxicity of Polychlorinated Polycyclic Compounds and Related Chemicals. Crit. Revs. Toxicol. 2:445-498.

Kimbrough, R.D. 1976. Pathological Findings Associated With Chronic Exposure to PCBs. Proceedings of the National Conference on PCBs, Environmental Protection Agency, Office of Toxic Substances, Washington, DC, pp. 30-34.

Kimbrough, R., J. Buckley, L. Fishbein, G. Flamm, L. Kasza, W. Marcus, S. Shibko, and R. Teske. 1978. Animal Toxicology. Environ. Health Perspect. 24:173-185.

Kimbrough, R.D. and R.E. Linder. 1974. Induction of Adenofibrosis and Hepatomas of the Liver in Balb/cd Mice by Polychlorinated Biphenyls (Aroclor 1254). J. Nat. Canc. Inst. 53:547-552.

Kimbrough, R.D., R.E. Linder, and T.B. Gaines. 1972. Morphological Changes in Livers of Rats Fed Polychlorinated Biphenyls. Arch. Environ. Health 25:354-364.

Kimbrough, R.D., R.A. Squire, R.E. Linder, J.D. Strandberg, R.J. Montali, and V.W. Burse. 1975. Induction of Liver Tumors in Sherman Strain Female Rats by Polychlorinated Biphenyl Aroclor 1260. J. Nat. Cancer Inst. 55:1453-1459.

Kimura, N.T. and T. Baba. 1973. Neoplastic Changes in the Rat Liver Induced by Polychlorinated Biphenyl. Gann 64:105-106.

Kimura, N.T., T. Kanematsu, and T. Baba. 1976. Polychlorinated Biphenyl(s) as a Promoter in Experimental Hepatocarcinogenesis in Rats. Z. Krebsforsch. Klin. Onkol. 87:257-266.

Kuratsune, M., T. Yoshimura, J. Matsuzaka, and A. Yamaguchi. 1972. Epidemiologic Study of Yusho, A Poisoning Caused by Ingestion of Rice Oil Contaminated With a Commercial Brand of Polychlorinated Biphenyls. Environ. Health Perspect. 1:119-128.

Lambrecht, L.K., D.A. Barsotti, and J.R. Allen. 1978. Responses of Nonhuman Primates to a Polybrominated Biphenyl Mixture. Environ. Health Perspect. 23:139-145.

McConnell, E.E., J.R. Hass, N. Altman, and J.A. Moore. 1979. A Spontaneous Outbreak of Polychlorinated Biphenyl (PCB) Toxicity in Rhesus Monkeys (Macaca mulatta): Toxicopathology. Lab. Anim. Sci. 29:666-673.

MONS 004998

McConnell, E.E., J.A. Moore, J.K. Haseman, and M.W. Harris. 1978a. The Comparative Toxicity of Chlorinated Dibenzo-p-dioxins in Mice and Guinea Pigs. Toxicol. Appl. Pharmacol. 44:335-356.

McConnell, E.E., J.A. Moore, and D.W. Dalgar. 1978b. Toxicity of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Rhesus Monkeys (Macaca mulatta) Following a Single Oral Dose. Toxicol. Appl. Pharmacol. 43:175-187.

Miniats, O.P., N.S. Platonow, and H.D. Geissinger. 1978. Experimental Polychlorinated Biphenyl Toxicosis in Germfree Pigs. Canadian J. Comp. Med. 42:192-199.

Moore, R.W., S.D. Sleight, and S.D. Aust. 1978. Induction of Liver Microsomal Drug-Metabolizing Enzymes by 2,2',4,4',5,5'-Hexabromobiphenyl. Toxicol. Appl. Pharmacol. 44:309-321.

Morgan, R.W., J.M. Ward, and P.E. Hartman. 1981. Aroclor 1254-Induced Intestinal Metaplasia and Adenocarcinoma in the Glandular Stomach of F344 Rats. Cancer Res. 41:5052-5059.

Nagasaki, H., S. Tomii, T. Mega, M. Marugami, and N. Ito. 1972. Hepatocarcinogenicity of Polychlorinated Biphenyls in Mice. Gann 63:805.

Nishizumi, M. 1970. Light and Electron Microscope Study of Chlorobiphenyl Poisoning. Arch. Environ. Health 21:620-632.

Norback, D.H. and J.R. Allen. 1972. Chlorinated Aromatic Hydrocarbon Induced Modifications of the Hepatic Endoplasmic Reticulum: Concentric Membrane Arrays. Environ. Health Perspect. 1:137-143.

Pereira, M.A., S.L. Herren, A.L. Britt, and M.M. Khoury. 1982. Promotion by Polychlorinated Biphenyls of Enzyme Altered Foci in Rat Liver. Cancer Letters 15:185-190.

Poland, A. and E. Glover. 1977. Chlorinated Biphenyl Induction of Aryl Hydrocarbon Hydroxylase Activity: A Study of the Structure-Activity Relationship. Mol. Pharmacol. 13:924-938.

Preston, B.D., J.P. VanMiller, R.W. Moore, and J.R. Aller. 1981. Promoting Effects of Polychlorinated Biphenyls (Aroclor 1254) and Polychlorinated Dibenzofuran-Free Aroclor 1254 on Diethylnitrosamine-Induced Tumorigenesis in the Rat. J. Nat. Cano. Ins. 66:509-515.

Render, J.A., S.D. Aust, and S.D. Sleight. 1982. Acute Pathologic Effects of 3,3',4,4',5,5'-Hexabromobiphenyl in Rats: Comparison of Its Effects With Firemaster BP-6 and 2,2',4,4',5,5'-Hexabromobiphenyl. Toxicol. Appl. Pharmacol. 62:428-444.

Sleight, S.D. and V.L. Sanger. 1976. Pathologic Features of Polybrominated Biphenyl Toxicosis in the Rat and Guinea Pig. J. Amer. Vet. Med. Assoc. 169:1231-1235.

Squire, R.A. and M.H. Levitt. 1975. Report of a Workshop on Classification of Specific Hepatocellular Lesions in Rats. Cancer Res. 35:3214-3223.

Strik, J.J.T.W.A. 1973. Species Differences in Experimental Porphyria Caused by Polyhalogenated Aromatic Compounds. Enzyme 16:224-230.

Trosko, J.E., B. Dawson, and C.C. Chang. 1981. PBB Inhibits Metabolic Cooperation in Chinese Hamster Cells In Vitro: Its Potential as a Tumor Promoter. Environ. Health Perspect. 37:179-182.

Vos, J.G. 1972. Toxicology of PCBs for Mammals and for Birds. Environ. Health Perspect. 1:105-118.

Vos, J.G. and R.B. Beems. 1971. Dermal Toxicity Studies of Technical Polychlorinated Biphenyls and Fractions Thereof in Rabbits. Toxicol. Appl. Pharmacol. 19:617-633.

Vos, J.G. and E. Notenboom-Ram. 1972. Comparative Toxicity Study of 2,4,5,2',4',5'-Hexachlorobiphenyl and Polychlorinated Biphenyl Mixture in Rabbits. Toxicol. Appl. Pharmacol. 23:565-578.

MONS 005000

CHAPTER 17

TOXICOLOGY OF PCBs IN MINK AND FERRETS

Robert K. Ringer
Department of Animal Science
Center for Environmental Toxicology
Michigan State University
East Lansing, Michigan 48824-1206

INTRODUCTION

The first indication that the incorporation of Great Lakes fish into the diet of mink was creating reproductive problems was expressed by commercial ranchers in the early to mid 1960s (Hartsough, 1965). Ongoing investigations within our laboratory supported these contentions (Aulerich et al., 1970). In these studies, alewife-fed mink failed to produce any offspring. In 1968, Lake Michigan coho salmon were made available as mink food. Rations that contained these fish caused reproductive complications and mortality in mink that appeared to be dependent upon the percentage of coho salmon fed as well as the duration of feeding. Breeding and parturition were reported as normal or near normal, but newborn mortality was excessive and many still-born offspring were observed. Mortality of newborn was reported by the commercial ranchers to be as high as 80 percent. A direct relationship between the extent of reproductive failure by the mink and the chlorinated hydrocarbon pesticide content of the fish (DDT plus its metabolites and dieldrin) was demonstrated (Aulerich et al., 1971); however, no clinical signs of chlorinated hydrocarbon pesticide poisoning were evident. The feeding of these pesticides far in excess of the fish content of these pesticides prompted us to dismiss these compounds as being implicated (Aulerich and Ringer, 1970). Over the past 10 yrs (Ringer et al., 1981; Aulerich et al., 1973) we have clearly demonstrated that PCB residues within the Great Lakes fish were responsible for the reproductive complications of the mink and that mink were particularly sensitive to the polychlorinated biphenyl (PCB) mixtures used in capacitors, closed-system heat exchangers,

MONS 005001

hydraulic fluid, as plasticizers, and for many other uses. This paper discusses our current knowledge on this sensitivity in mink (Mustela vison) and relates it to another carnivore that is closely related, the ferret (Mustela putorius furo).

ACUTE AND CHRONIC TOXICITY

PCBs are not very toxic when given as a single dose to mammals or birds. The oral LD_{50} of Aroclor 1254 and 1260 in rats is in the range of 4 to 10 g/kg body weight (Kimbrough et al., 1978). The acute oral toxicity decreases in rats with increasing percentage of chlorine content (Kimbrough et al., 1978). In the mink, the acute oral toxicities of Aroclors 1221, 1242, and 1254 are approximately 1, 3, and 4 g/kg body weight, respectively (Aulerich and Ringer, 1977). Thus, as in the rat, the acute toxicity decreases with increased chlorine content and these PCBs would be classified as only slightly toxic based on acute oral toxicity.

In a series of experiments, Aroclor 1254 was fed to mink in graded dosages, for 4 or 9 months prior to whelping (parturition) and the chronic effects on reproduction were assessed (Table 1). The results clearly demonstrated that 2 mg/kg or more Aroclor 1254 fed continuously were detrimental to reproduction. Using the assumption that mink consume approximately 150 g of food per day, the total intake of PCB at 2 mg/kg and 9 months feeding prior to whelping would have been 81 mg. This level of intake is about the same as the intake on 5 mg/kg fed for 4 months (90 mg). Both treatments were equally detrimental to reproduction.

Not all Aroclors are as chronically toxic to reproduction as is Aroclor 1254. As can be seen by the data in Table 2, Aroclor 1016, 1221, and 1242 did not cause adverse reproductive effects when fed at 2 mg/kg in the diet for 9 months prior to whelping. However, as shown in Table 3, the feeding of 5 mg/kg of Aroclor 1242 is detrimental to reproduction. Aroclor 1016 at concentrations as high as 20 mg/kg does not lower the number of young (kits) born per female.

When concentrations higher than those that affect reproduction are chronically fed to mink, adult mortality results (Table 3). It can be readily seen from these data that for both Aroclor 1242 and 1254 feeding a level of between 5 and 10 mg/kg in the diet will kill 50 percent of the adult animals in about 9 months. An estimated LC_{50} (dietary concentration) calculated from these data yielded values of 6.65 mg/kg for Aroclor 1254 and 8.60 mg/kg for Aroclor 1242 (Ringer et al., 1981). Male mink survive longer than female mink when fed these

TABLE 1

Summary of the Effect of Aroclor 1254 on Mink Reproduction

Treatment Level	Period Fed	Reproduction Offspring/ Female
15 mg/kg	January-May	0
10 mg/kg	August-June	0
10 mg/kg + 10 mg/kg DDT	January-May	0
10 mg/kg + 0.5 mg/kg dieldrin	January-May	0
5 mg/kg	August-June	0
5 kg/mg	January-May	0.8
5 mg/kg + 6 mg/kg DDT	January-May	1.0[a]
5 mg/kg + 6 mg/kg DDT + 0.2 mg/kg dieldrin	January-May	2.0[a]
2 mg/kg	August-June	0.3
1 mg/kg	January-May	4.3
0 mg/kg		4.1
0 mg/kg		5.0
0 mg/kg		6.0

[a]All died before 4 weeks of age

lower levels of PCBs (Platonow and Karstad, 1973; Bleavins et al., 1980).

The question is often asked whether this sensitivity to PCBs by mink is an anomaly. However, our laboratory has demonstrated (Tables 4 and 5) that mink are sensitive to polybrominated biphenyl (PBB) toxicity (Aulerich and Ringer, 1979) and more recently, hexachlorobenzene (unpublished data). The estimated LC_{50} for PBBs is 3.95 mg/kg when fed for 313 days.

CLINICAL SIGNS AND LESIONS

Clinical signs and lesions in mink from PCB feeding and PBB feeding are fairly non-specific. These include anorexia, loss of weight, fatty infiltration of the liver, general unthrifty appearance, and lethargy. Often seen prior to death is the appearance of dark fecal stools indicative of the presence of blood from the upper intestinal tract. Necropsy reveals the presence of gastric ulcers of varying severity.

TABLE 2

Reproductive Performance and Mortality of Female Mink Fed a Control Ration or Experimental Diets Containing 2 mg/kg Supplemental PCB (August 8, 1972, to June 1, 1973, or Until the Kits Were 4 Weeks of Age)

	Adult Females			Kits				
Dietary Treatment	Percent Mortality	Number Mated	Number Whelped	Number Born Alive	Number Born Dead	Whelped/ Female Mated	Alive at 4 Weeks	Average Weight (g ± S.E.) at Birth
Control	0	8	8	28	5	4.1	18	9.9 ± 0.32
2 mg/kg PCB Aroclor 1016	0	8	8	28	8	4.5	16	9.2 ± 0.33
2 mg/kg PCB Aroclor 1221	12	7	7	43	1	6.3	37	9.6 ± 0.22
2 mg/kg PCB Aroclor 1242	12	7	7	35	4	5.6	32	9.3 ± 0.27
2 mg/kg PCB Aroclor 1254	17	7	2	1	1	0.3	0	5.4

MONS 005004

TABLE 3

Adult Breeder Mortality and Reproduction in Mink Fed Various Levels of Aroclors 1254, 1242, and 1016

Treatment Level (mg/kg)	Period Fed (days)	Adult Mortality Number Dead/ Number Total	Mortality (%)	Reproduction (Kits/ Female)
Aroclor 1254[a]				
0	280	1/ 7	14	5.0
0	297	0/ 8	0	4.1
0	297	1/ 8	12	0.3
5	280	2/ 7	29	0.0
10	280	5/ 7	71	0.0
Aroclor 1242[b]				
0	247	3/30	10	4.9
2[a]	297	1/ 8	12	5.6
5	247	1/15	7	0.0
10	247	10/15	67	0.0
20	192[c]	15/15	100	0.0
40	138[d]	15/15	100	0.0
Aroclor 1016[b]				
0	247	3/30	10	4.9
2[a]	297	0/ 8	0	4.5
20	247	3/15	20	6.3

[a]Data from Aulerich and Ringer, 1977
[b]Data from Bleavins et al., 1980
[c]All mink died within 192 days on diet
[d]All mink died within 138 days on diet

TABLE 4

Mortality and Reproduction in Mink Fed Various Levels of PBB

Treatment Level (mg/kg)	Period Fed (days)	Adult Mortality Number Dead/ Number Total	Reproduction Offspring/Female
PBB (FireMaster FF-1)[a]			
0	313	0/10	3.5
1.0	313	0/10	2.6
2.5	313	1/10	2.6
6.25	313	9/10	0.0
15.625	93[b]	10/10	-

[a]Data from Aulerich and Ringer, 1979
[b]All mink died by this period; no females survived to whelping

Liver weight and kidney weight relative to body weight are increased over that found in control animals.

COMPARISON TO THE FERRET

The European ferret, also a carnivore from the Mustelid family, shows reproductive complications when PCBs are fed at a slightly higher concentration in the diet. The feeding of 20 mg/kg of Aroclor 1242 for nearly 9 months prior to parturition is not lethal to the adult breeder (Table 6), yet results in total reproductive failure of these breeders (Ringer et al., 1981; Bleavins et al., 1980). As with the mink, 20 mg/kg of Aroclor 1016 does not alter the number of young born per breeding female. In our early studies, it was shown that the ferret was able to consume Great Lakes fish when fed at 30 percent of the diet without reproductive complications, whereas the same diet caused total failure in mink. The somewhat greater resistance of the ferret was what accounted for this difference.

PLACENTAL AND MAMMARY TRANSFER

Placental transfer of PCBs to the fetus from the mother has been demonstrated in rats (Takagi et al., 1976; Ando, 1978), mice (Masuda et al., 1979), rabbits (Grant et al., 1971), cattle

TABLE 5

Reproductive Performance of Mink Fed PBB Diets and the Weight and Survival of Their Offspring (Kits)

PBB Dietary Level (mg/kg)	Number Females Whelped/ Number Mated	Number Kits Whelped		Average Number Kits Whelped/Female		Percent Kit Mortality (Birth to 4 Weeks)	Average Kit Weight (g ± S.E.)	
		Alive	Dead	Whelped	Mated		At Birth	At 4 Weeks
0	5/8	22	6	5.6 ± 0.03	3.5 ± 1.07	23	9.1 ± 0.30	128 ± 7.0
1	5/8	17	4	4.2 ± 0.92	2.6 ± 0.95	47	7.5 ± 0.30[a]	87 ± 2.3[a]
2.5	6/8	15	6	3.5 ± 0.72	2.6 ± 0.78	47	8.6 ± 0.61	132 ± 16.0
6.25	0/1	--	--	--	--	--	--	--
15.625	0.0	--	--	--	--	--	--	--

[a]Significantly different from controls ($P < 0.01$) by t-test

TABLE 6

Adult Mortality of Mink and Ferrets Fed Aroclor 1242 or 1016 for 247 Days

Treatment Level and Aroclor Fed (mg/kg)	Adult Mortality	
	Died/Total	Percent
Mink		
0 PCB	3/30	10
5 Aroclor 1242	1/15	7
10 Aroclor 1242	10/15	67
20 Aroclor 1242	15/15	100
40 Aroclor 1242	15/15	100
20 Aroclor 1016	3/15	20
Ferret		
0 PCB	0/15	0
20 Aroclor 1242	0/15	0
20 Aroclor 1016	1/15	7[a]

[a]Died during whelping due to breech presentation

(Platonow and Chen, 1973), rhesus monkeys (Allen and Barsotti, 1976), and humans (Masuda et al., 1979). Our studies have shown that placental transfer of PCBs also occurs in the mink and ferret (Bleavins et al., 1981) and gives rise to the embryotoxicity demonstrated by these species. PCBs appear to cross the placenta more readily (Table 7) in the mink than in the ferret (Bleavins et al., 1981). The placenta in the two species differs in anatomical structure, with the mink having a greater area for diffusion. The greater placental surface area between the mother and fetus may contribute to the greater transplacental exchange and undoubtedly contributes to the greater PCB embryotoxicity in the mink than ferret.

In experiments using radiolabeled PCBs (Table 8), our laboratory has shown that a significantly greater quantity of PCBs entered the growing offspring through mammary transfer than through placental transfer (Bleavins et al., 1981). This greater transfer to the offspring by milk has been shown in

TABLE 7

Fetal Tissue Concentrations[1] of PCBs in Mink and Ferrets 2 Hours Following Maternal Intravenous Injection

		Whole Kit		Tissue				
Animal	n	Last Trimester	n	Adipose	Kidney	Liver	Brain	Intestine
Mink	4	0.019 ± 0.0017[a2]	2	0.037 ± 0.0181[a]	0.024 ± 0.0027[a]	0.095 ± 0.058][a]	0.011 ± 0.0007[a]	0.021 ± 0.0095[a]
Ferret	4	0.012 ± 0.0004[b]	4	0.020 ± 0.0019[a]	0.022 ± 0.0011[a]	0.018 ± 0.0023[a]	0.012 ± 0.0012[a]	0.013 ± 0.0021[a]

[1]Concentration is expressed as a percentage of the initial maternal dose per gram of tissue
[2]Means with the same superscript are not significantly different ($P > 0.05$) within columns

TABLE 8

PCB Concentrations[a] at Birth and 2 Weeks of Age in Kits Born to Female Mink Intraperitoneally Dosed With ^{14}C Aroclor 1242

Animal Number	Gestation (Days)	Time Between Dosing and Whelping (Days)	Biphenyl Concentration[b] Newborn Kits Per Gram	Newborn Kits Per Kit	2 Week Old Kits Per Gram	2 Week Old Kits Per Kit	Milk
B-2030	47	26	0.012	0.095	0.026	1.463	0.029
F-262[c]	54	28	0.009	0.079	--	--	--
F-754	56	30	0.008	0.083	0.014	0.795	0.023
F-1312[c]	60	35	0.015	0.125	--	--	--
F-1650	61	35	0.007	0.068	0.018	1.885	0.023
Mean ± S.E.[d]	56 ± 2.5	31 ± 1.8	0.010 ± 0.0015	0.089 ± 0.0102	0.019 ± 0.0035	1.231 ± 0.2831	0.025 ± 0.0020

[a]Concentration is expressed as a percentage of the initial maternal dose per gram of tissue
[b]Value is the average PCB concentration based on two kits per female
[c]No kits surviving to 2 weeks of age
[d]S.E. = standard error

MONS 005010

other mammals (Takagi et al., 1976; Masuda et al., 1979; Allen and Barsotti, 1976) and in man (Masuda et al., 1978). This PCB transfer by the lactating mink probably resulted in the high offspring mortality observed when Great Lakes fish were fed to commercial ranch mink in the late 1960s.

METABOLIZED PCBs

A recent study from our group has shown that considerably fewer PCBs are required to cause reproductive failure in mink, based on analysis, when metabolized by another species first and then fed to mink. Platonow and Karstad (1973) reported that levels of PCBs as low as 0.64 mg/kg caused reproductive complications in mink when fed meat from a cow that had been given Aroclor 1254. This level of effect is below that observed when the PCB mixture is added directly to the diet as discussed earlier. In our most recent study (Hornshaw, 1981), 30 percent Great Lakes fish were fed to mink and reproduction recorded (Table 9). Carp-fed mink failed to reproduce. Based on a calculated intake, over 250 days of feeding, and analyses of the fish against an Aroclor 1254 standard, these mink consumed approximately 56 mg of PCBs. Growth of the offspring was subnormal on several groups fed various fish at even lower levels of PCB intake. This toxicity, at dietary levels below Aroclor 1254 toxicity amounts, can probably be explained by the fact that tissues retain more of the highly chlorinated congeners of the PCB mixture once they have been metabolized. A similar response has been reported for meat taken from a cow fed PBB and then administered to mink (Aulerich and Ringer, 1979). Lethality of adults was somewhat greater on the metabolized form.

SUMMARY

Mink are among the more sensitive species or are the most sensitive mammalian species to PCB toxicity. Dietary administration of Aroclor 1254 at 2 mg/kg adversely affects reproduction. Meat containing PCB contamination when fed to this carnivore affects reproduction at even lower levels. PCBs are embryotoxic to the developing embryo. Spermatogenesis, oogenesis, and implantation are unaffected.

Placental transfer of PCB occurs but mammary transfer from the lactating dam is a more pronounced means of offspring contamination.

TABLE 9

Reproductive Performance and Calculated PCB Intake[a] of Mink Fed Great Lakes Fish Diets - 1981

Diet	Females Whelped/ Mated	Kits Born		Average Live Kits/ Female Mated	4 Weeks Kit Weight (g)	Calculated Total Intake, (mg)
		Alive	Dead			
Control (Marine Fish)	9/10	38	11	3.8	123	3.4
Carp	3/11	0	9	0	-	56.2
Sucker	9/10	25	14	2.5	111	23.6
Perch Scraps	9/11	33	12	3.0	98	25.9
Whitefish Necks	8/10	32	7	3.2	107	18.0
Alewife Fish Meal	10/12	53	9	4.2	124	7.9

[a]Based on an assumed food intake of 150 g/day

MONS 005012

LITERATURE CITED

Allen, J.R. and D.A. Barsotti. 1976. The Effects of Transplacental and Mammary Movement of PCBs on Infant Rhesus Monkeys. Toxicology 6:331-340.

Ando, M. 1978. Transfer of 2,4,5,2',4',5'-Hexachloro Biphenyl and 2,2-Bis-(p-chlorophenyl), 1,1,1-Trichloroethane (p,p'-DDT) From Maternal to Newborn and Suckling Rats. Arch. Environ. Contam. Toxicol. 41:179-186.

Aulerich, R.J. and R.K. Ringer. 1970. Some Effects of Chlorinated Hydrocarbon Pesticides on Mink. Amer. Fur Breeder 43(6):10-11.

Aulerich, R.J., R.K. Ringer, P.J. Schaible, and H.L. Seagran. 1970. An Evaluation of Processed Great Lakes Fishery Products for Feeding Mink. Feedstuffs 42(42):48-49.

Aulerich, R.J., R.K. Ringer, H.L. Seagren, and W.G. Youatt. 1971. Effects of Feeding Coho Salmon and Other Great Lakes Fish on Mink Reproduction. Can. J. Zoo. 49:611-616.

Aulerich, R.J., R.K. Ringer, and S. Iwamoto. 1973. Reproductive Failure and Mortality in Mink Fed on Great Lakes Fish. J. Reprod. Fert., Suppl. 19:365-376.

Aulerich, R.J. and R.K. Ringer. 1977. Current Status of PCB Toxicity to Mink and Effect on Their Reproduction. Arch. Environ. Contam. Toxicol. 6:279-292.

Aulerich, R.J. and R.K. Ringer. 1979. Toxic Effects of Dietary Polybrominated Biphenyl on Mink. Arch. Environ. Contam. Toxicol. 8:487-498.

Bleavins, M.R., R.J. Aulerich, and R.K. Ringer. 1980. Polychlorinated Biphenyls (Aroclors 1016 and 1242): Effects on Survival and Reproduction in Mink and Ferrets. Arch. Environ. Contam. Toxicol. 9:627-635.

Bleavins, M.R., R.J. Aulerich, and R.K. Ringer. 1981. Placental and Mammary Transfer of Polychlorinated and Polybrominated Biphenyl in the Mink and Ferret. In: D.W. Lamb and E.E. Kenaga (eds.), "Avian and Mammalian Wildlife Toxicology," pp. 121-131. Second Conference, ASTM STP 757. American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA.

Grant, D.L., D.C. Villeneuve, K.A. McCully, and W.E. Phillips. 1971. Placental Transfer of Polychlorinated Biphenyls in the Rabbit. Environ. Physiol. 1:61-66.

MONS 005013

Hartsough, G.R. 1965. Great Lakes Fish Now Suspect as Mink Food. Amer. Fur Breeder 38(10):25-27.

Hornshaw, T.C. 1981. Renewed Use of Underutilized Species of Great Lakes Fish for Animal Feed. M.S. Thesis, Michigan State University, East Lansing, MI. 45 pp.

Kimbrough, R., J. Buckley, L. Fishbein, G. Flamm, L. Kasza, W. Marcus, S. Shibko, and R. Teske. 1978. Animal Toxicology. Environ. Health Perspect. 24:173-185.

Masuda, Y., R.Kagawa, H. Kuroki, M. Kuratsune, T. Yoshimura, I. Taki, M. Kusuda, F. Yamashita, and M. Hayashi. 1978. Transfer of Polychlorinated Biphenyls From Mothers to Foetuses and Infants. Fd. Cosmet. Toxicol. 16:543-546.

Masuda, Y., R. Kagawa, H. Kuroki, S. Tokudome, and M. Kuratsune. 1979. Transfer of Various Polychlorinated Biphenyls to the Foetuses and Offspring of Mice. Fd. Cosmet. Toxicol. 17:623-627.

Platonow, N.S. and L.H. Karstad. 1973. Dietary Effects of Polychlorinated Biphenyls on Mink. Can. J. Comp. Med. 37:391-400.

Platonow, N.S. and N.Y. Chen. 1973. Transplacental Transfer of Polychlorinated Biphenyls (Aroclor 1254) in a Cow. Vet. Rec. 20:69-70.

Ringer, R.K., R.J. Aulerich, and M.R. Bleavins. 1981. Biological Effects of PCBs and PBBs on Mink and Ferrets - A Review. In: M.A.Q. Kahn (ed.), "Toxicology of Halogenated Hydrocarbons," pp. 329-343. Pergamon Press, Inc., NY.

Takagi, Y., T. Otake, M. Kataoka, Y. Murata, S. Aburada, S. Akasaka, K. Hashimoto, H. Uda, and T. Kitaura. 1976. Studies on the Transfer and Distribution of (^{14}C) Polychlorinated Biphenyls From Maternal to Fetal and Suckling Rats. Toxicol. Appl. Pharma. 38:549-588.

MONS 005014

CHAPTER 18

INHIBITION OF INTERCELLULAR COMMUNICATION BY VARIOUS CONGENERS OF POLYBROMINATED BIPHENYL AND POLYCHLORINATED BIPHENYL

Gen Tsushimoto[1]
Shoji Asano[1]
James E. Trosko
Chia-Cheng Chang
Department of Pediatrics and Human Development
College of Human Medicine
Michigan State University
East Lansing, Michigan 48824-1317

INTRODUCTION

The widespread use, distribution, and accidental contamination of polybrominated biphenyls (PBBs) and polychlorinated biphenyls (PCBs) have prompted a large variety of studies designed to ascertain if they might have biological consequences on human health.

Although there are no conclusive data indicating that either the PCBs (Green et al., 1975a, 1975b; Wyndham et al., 1976; Hoopingarner et al., 1972; Nilsson and Ramel, 1974) or PBBs (Wertz and Ficsor, 1978; Rubinstein et al., in preparation) are mutagenic, there have been reports on animals linking exposure to these chemicals to teratogenic consequences (Watanabe and Sugahara, 1981; Beaudoin, 1977; Beaudoin and Fisher, 1981) and to carcinogenesis (Nobuyuki et al., 1973; Kimbrough et al., 1975, 1981; Preston et al., 1981; Jensen et al., 1982). Recently, it has been postulated that certain chemicals which inhibit intercellular communication mechanisms might play a role in teratogenesis (Trosko et al., 1982a) and carcinogenesis (Trosko et al., 1982b).

---

[1]Present address: Otsuka Pharmaceutical Co., Ltd., 31, 463-10, Kagasuno, Kawauchi-cho, Tokushima 771-01, Japan.

MONS 005015

Based on the concept that carcinogenesis consists of initiation of a single cell, possibly by a mutagenic event (Trosko et al., 1981), and the subsequent promotion of that single cell into a clonal critical mass of dysfunctional cells, possibly by the inhibition of intercelluar communication (Trosko et al., 1980), several recent reports have implicated specific congeners of PBB with the tumor promotion process (Trosko et al., 1981; Tsushimoto et al., 1982). In addition, it is fairly well established that a variety of intercellular communication mechanisms play important roles in the developmental processes, as well as in the control of cellular proliferation and differentiation in multicellular organisms (Loewenstein, 1982; Gilula, 1980; Cline and Golde, 1979; Potter, 1980; Blumberg et al., 1982). Therefore, inhibition of these important intercellular communication mechanisms might be predicted to play a role in teratogenesis when occurring during organogenesis (Trosko et al., 1982a) and in tumor promotion of initiated differentiated tissue (Trosko et al., 1982b).

Recently, Yotti et al. (1979) and others (Murray and Fitzgerald, 1979; Fitzgerald and Murray, 1979; Umeda et al., 1980; Williams, 1981; Newbold and Amos, 1981; Kinsella et al., 1981; Warren et al., 1982) have shown that several known tumor promoters (and teratogens) have the ability to block one form of cell-cell communication i.e., metabolic cooperation, presumably by making gap junction mediated cell transfer non-functional (Enomoto et al., 1981; Yancey, 1982) . In addition, Trosko et al. (1981) and Tsushimoto et al. (1982) have shown 2,4,5,2',4',5'-hexabromobiphenyl (HBB), but not 3,4,5,3',4', 5'-HBB, inhibits intercellular communication at non-cytotoxic doses in Chinese hamster cells. Based on the assumption that inhibition of intercellular communication at non-cytotoxic doses could lead to tumor promotion, Jenson et al. (1982) have shown the 2,4,5,2',4',5'-HBB was a powerful liver tumor promoter in rats. Since it has already been shown that the PCBs are rat liver tumor promoters (Nobuyuki et al., 1973; Preston et al., 1981), we designed the following experiments to test if specific purified congeners of PCBs would inhibit intercellular communication in a manner similar to specific congeners of PBB.

METHODS

Cell Culture

A Chinese hamster cell line (V79), derived originally from lung tissue (Ford and Yerganian, 1958), was used for the assey. Cells were grown in modified Eagle's medium (Eagle, 1959) (Eagle's balanced salt sclution with 50% increase of vitamins and essential amino acids except glutamine), supplemented

with non-essential amino acids (100% increase), 1 mM sodium pyruvate and 5 percent fetal calf serum. Under the incubation condition with 5 percent CO_2 in humidified air at 37°C, cells not contact-inhibited have a generation time of about 12 hours.

Cytotoxicity

The effect of different concentrations of PBBs and PCBs on the colony-forming ability of Chinese hamster cells was tested. Initially, 300 to 2000 cells were plated in each of four 9 cm dishes. After about 4 hours when cells attached on the surface of the dish, the chemicals were added. 2,4,5,2',4',5'-HBB and 2,4,5,2',4',5'-hexachlorobiphenyl (HCB) were dissolved in dimethylsulfoxide (DMSO), while 3,4,5,3',4',5'-HBB and 3,4,5,3',4',5'-HCB were dissolved in a 1:1 acetone-DMSO mixture. The final concentration of the solution in the medium was kept lower than 1 percent. This concentration of DMSO had no effect on cell survival. The chemicals were removed from dishes after 3 days and growth was continued for 1 week, until colonies had grown to sufficient size to score. Colonies were rinsed with 0.85 percent saline, fixed with 95 percent ethanol, and stained with Giemsa. The resulting colonies were scored visually.

Tumor Promoter Assay

Inhibition of metabolic cooperation, which is one of the properties of tumor promoters (Yotti et al., 1979), was measured in Chinese hamster V79 cells. Initially, wild type Chinese hamster V79 cells ($6TG^S$, $HG\text{-}PRT^+$) were seeded in 6 cm dishes at a cell density of $4x10^5$ cells per dish. In each treatment group 12 dishes were used. Immediately after the plating of wild type cells, 100 6-thioguanine resistant ($6\text{-}TG^r$) cells (presumptive $HG\text{-}PRT^-$) were seeded in the same plate. After about 4 hours, the test chemical was added into a series of plates. As a positive control, 12-O-tetradecanoyl phorbol-13-acetate (TPA)(0.1 ug/ml) was added to another series of plates. Then, $6\text{-}TG^r$ (10 ug/ml) was added immediately after treatment with the chemicals. The cells were cultured with test chemicals and TPA for 3 days. After removal of the chemicals, cultures were grown in the selective medium for 4 additional days. The medium was decanted, survival colonies were fixed and stained. For each treatment group, there were 6 control dishes, each of which contained 100 $6TG^r$ cells to monitor the cytotoxicity of chemicals.

MONS 005017

Chemicals

Pure 2,4,5,2',4',5'-HCB and 3,4,5,3',4',5'-HCB were kindly given by Dr. James D. McKinney of the National Institute of Environmental Health Science (NIEHS) (NIEHS, Research Triangle Park, NC). Dr. Steven Aust (Michigan State University, East Lansing, MI) kindly provided purified samples of 2,4,5,2',4',5'-HBB and 3,4,5,3',4',5'-HBB. As a positive control from the promoter assay, TPA was obtained from Chemical Cancer Research Chemicals, Inc. (Brewster, NY), and dimethyl sulfoxide was obtained from Fischer Scientific Co. (Fairlawn, NY).

RESULTS AND DISCUSSION

The ability of different concentrations of two purified congeners of PBB and PCB to affect the colony-forming ability of Chinese hamster V79 cells and to inhibit metabolic cooperation was measured. In Figure 1, the data clearly indicate that 3,4,5,3',4',5'-HCB is far more cytotoxic than 2,4,5,2',4',5'-HCB. This is similar to the analogous congeners of HBB (Tsushimoto et al., 1982).

In Figure 2, it is obvious that the 2,4,5,2',4',5'-HCB is able to rescue 6-TG^r cells at non-cytotoxic levels; whereas, the 3,4,5,3',4',5'-HCB is unable to do so. Again, these results with the two purified PCB congeners are similar to the analogous PBB congeners (Tsushimoto et al., 1982). It is also important to note that there seems to be a real, "no effect" or threshold level below which the 2,4,5,2', 4',5'-HCB does not inhibit intercellular communication, and above which there seems to be a quantitative dose response over the dose range tested.

To test, under identical experimental conditions, the similar effects of the 2,4,5,2',4',5'-HBB and 2,4,5,2',4',5'-HCB congeners on metabolic cooperation, the experiment in Figure 3 was performed. It can be seen that the 2,4,5,2',4',5'-HCB congener is only slightly more cytotoxic than the 2,4,5,2',4',5'-HBB congener over the dose range tested (Panel A). In Panel B, it is clear that both 2,4,5,2',4',5'-HBB and 2,4,5,2',4',5'-HCB can rescue 6-TG^r cells by inhibiting intercellular communication, confirming earlier results. Although the relative recovery of 6-TG^r cells for the control, TPA-treated positive control and experimental treated cells differ from experiment to experiment (possibly due to physiological differences in cells and different growth factors found in serum from experiment to experiment), the pattern is reproducible.

MONS 005018

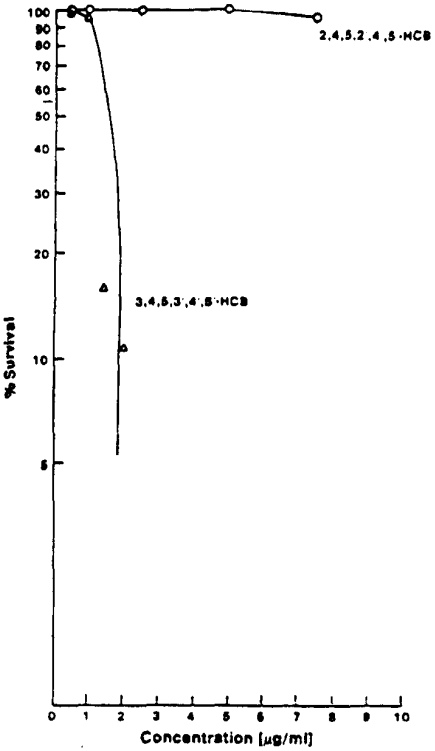


Figure 1. Dose-responsive curve for 2,4,5,2',4',5'-HCB and 3,4,5,3',4',5'-HCB on the colony-forming ability (percent survival) of Chinese hamster V79 cells.

These results, taken together with the reports in the literature, indicate that the ability of specific congeners of PCB, like those of PBB, to inhibit intercellular communication might be responsible, in part, for both their teratogenic and

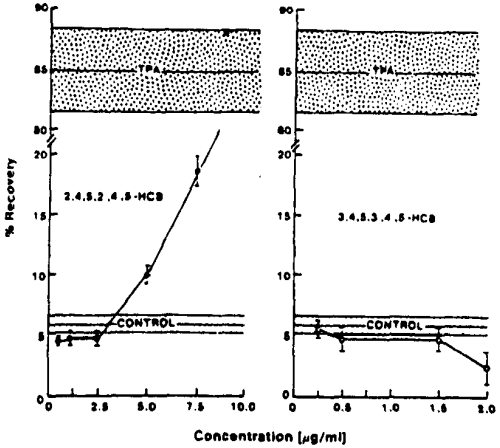


Figure 2. Dose-responsive curve for 2,4,5,2',4',5'-HCB (left panel) and 3,4,5,3',4',5'-HCB (right panel) on the inhibition of metabolic cooperation (rescue of 6-TG^r cells). Stipled area and striped areas represent negative and positive controls (solvent; TPA-treated, respectively) by their standard error of the mean (SEM).

tumor promoting activities. In the case of PCBs' ability to act as a tumor promoter, it can be speculated that by elimination of cell-cell communication at non-cytotoxic doses, the normalizing influence, suppressing the initiated cell's phenotype, is blocked. Consequently, the initiated cell might gain a selective growth advantage, allowing the clonal expansion of initiated cells, during which time additional genetic changes could occur (Yotti et al., 1979; Trosko and Chang, 1980). Once a stabilizing genetic change occurs, the cell might then be promoter-independent and have metastatic properties. The fact that certain congeners do not inhibit intercellular communication (i.e., 3,4,5,3',4',5'-HBB and 3,4,5,3',4',5'-HCB) does not necessarily rule out their potential as a tumor promoter or teratogen, since their cytotoxic natures might contribute to compensatory hyperplasia, which is correlated

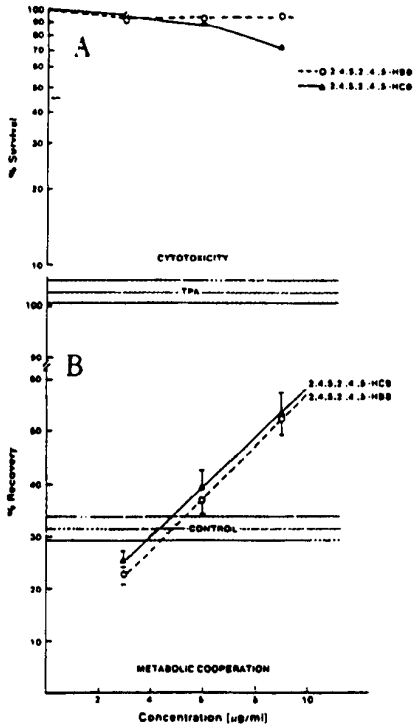


Figure 3. Dose-responsive curve for 2,4,5,2',4',5'-HBB and 2,4,5,2',4',5'-HCB on the inhibition of metabolic cooperation. Stipled area and striped areas are as described in Figure 2.

with tumor promoters (Frei, 1976; Trosko and Chang, 1980), and to the elimination of critical stem cells needed for development (Wilson, 1977), respectively.

ACKNOWLEDGMENT

The authors wish to thank Dr. Steven Aust of Michigan State University and Dr. James D. McKinney of NIEHS for kindly supplying the purified PCB and PBB samples. In addition, we acknowledge the critical review of the manuscript by Dr. Jay Goodman and Dr. Jerry Hook. Also, we thank Ms. Beth O'Malley for her technical assistance and Ms. Judy Copeman for her typing assistance. Research for this project was supported by grants from the Environmental Protection Agency (R808587010), NCI (CA21104), NCI (E502781), and Michigan State University Agricultural Experiment Station. Michigan Agriculture Experiment Station Journal No. 10405.

LITERATURE CITED

Beaudoin, A.R. 1977. Teratogenicity of Polybrominated Biphenyls in Rat. Environ. Res. 14:81-86.

Beaudoin, A.R. and D.L. Fisher. 1981. An In Vivo/In Vitro Evaluation of Teratogenic Action. Teratology 23:57-61.

Blumberg, D.D., J.P. Margolskee, E. Barkles, S.N. Chung, and H.F. Lodish. 1982. Specific Cell-Cell Contacts Are Essential for Induction of Gene Expression During Differentiation of Dictyostelium Discoideum. Proc. Natl. Acad. Sci. U. S. 79:127-131.

Cline, M.J. and D.W. Golde. 1979. Cellular Interactions in Haematopoiesis. Nature 277:177-181.

Eagle, H. 1959. Amino Acid Metabolism in Mammalian Cell Cultures. Science 130:432-437.

Enomoto, T., Y. Sasaki, Y. Kanho, and H. Yamasaki. 1981. Tumor Promoters Cause a Rapid and Reversible Inhibition of the Formation and Maintenance of Electrical Cell Coupling in Culture. Proc. Natl. Acad. Sci. U. S. 78:5628-5632.

Fitzgerald, D.J. and A.W. Murray. 1979. Inhibition of Intercellular Communication by Tumor Promoting Phorbol Esters. Cancer Res. 40:2935-2937.

Ford, D.K. and G. Yerganian. 1958. Observation on the Chromosomes of Chinese Hamster Cells in Tissue Cultures. J. Natl. Cancer Inst. 21:393-425.

MONS 005022

Frei, J.V. 1976. Some Mechanisms Operative in Carcinogenesis: A Review. Chem. Biol. Interact. 12:1-25.

Gilula, N.B. 1980. Cell-to-Cell Communication and Development. In: S. Subtelny and N.K. Wessels (eds.), "Cell Surface," pp. 23-42. Academic Press, New York, NY.

Green, S., J.V. Carr, K.A. Palmer, and E.J. Oswald. 1975a. Lack of Cytogenetic Effects in Bone Marrow and Spermatogonial Cells in Rats Treated With Polychlorinated Biphenyls (Aroclors 1242 and 1254). Bull. Environ. Contam. Toxicol. 13:14-22.

Green, S., F.M. Sauro, and L. Friedman. 1975b. Lack of Dominant Lethality in Rats Treated With Polychlorinated Biphenyls (Aroclors 1242 and 1254). Food Cosmet. Toxicol. 13:507-510.

Hoopingarner, R., A. Samuel, and D. Krause. 1972. Polychlorinated Biphenyl Interactions With Tissue Outline Cells. Environ. Health Perspect. 1:155-158.

Jensen, R.K., S.D. Sleight, J.I. Goodman, S.D. Aust, and J.E. Trosko. 1982. Assessment of the Capacity of Polybrominated Biphenyls to Serve as Promoters of Hepatocarcinogenesis (Abst.). The Toxicologist 2:99.

Kimbrough, R.D., R.A. Squire, R.E. Linder, J.D. Strandberg, R.J. Montali, and V.N. Burse. 1975. Induction of Liver Tumors in Sherman Strain Female Rats by Polychlorinated Biphenyl Aroclor 1260. J. Natl. Cancer Inst. 5:1453-1459.

Kimbrough, R.D., D.F. Groce, M.P. Korver, and V.W. Burse. 1981. Induction of Liver Tumors in Female Sherman Strain Rats by Polybrominated Biphenyls. J. Natl. Cancer Inst. 66:535-542.

Kinsella, A.R. 1981. Investigation of the Effects of the Phorbol Ester TPA on Carcinogen-Induced Forward Mutagenesis to 6-Thioguanine-Resistance in V79 Chinese Hamster Cells. Carcinogenesis 2:43-48.

Loewenstein, W.R. 1981. Junctional Intercellular Communication: The Cell-to-Cell Membrane Channel. Physiol. Reviews 61: 829-913.

Murray, A.W. and D.J. Fitzgerald. 1979. Tumor Promoters Inhibit Metabolic Cooperation in Co-Cultures of Epidermal and 3T3 Cells. Biochem. Biophys. Res. Commun. 91:395-401.

MONS 005023

Newbold, R.F. and J. Amos. 1981. Inhibition of Metabolic Cooperation Between Cells in Culture by Tumor Promoters. Carcinogenesis 2:243-249.

Nilsson, B. and C. Ramel. 1974. Genetic Tests on Drosophila Melanogaster With Polychlorinated Biphenyls (PCB). Hereditas 77:319-322.

Nobuyaki, I., H. Nagasaki, M. Arai, S. Makiura, S. Sugihara, and K. Hirao. 1973. Histopathologic Studies on Liver Tumorigenesis Induced in Mice by Technical Polychlorinated Biphenyls and Its Promoting Effect on Liver Tumors Induced by Benzene Hexachloride. J. Natl. Cancer Inst. 51:1537-1646.

Potter, V.R. 1980. Initiation and Promotion in Cancer Formation: The Importance of Studies on Intercellular Communication. Yale J. Biol. Med. 53:367-384.

Preston, B.D., J.P. VanMiller, R.W. Moore, and J.R. Allen. 1981. Promoting Effects of Polychlorinated Biphenyls (Aroclor 1254) and Polychlorinated Dibenzofuran-Free Aroclor 1254 on Diethylnitrosamine-Induced Tumorigenesis in the Rat. J. Natl. Cancer Inst. 66:509-515.

Rubinstein, C., C.C. Chang, P.L. Liu, and J.E. Trosko. Failure to Induce 6-Thioguanine and Ouabain-Resistant Mutations by Two Congeners of Polybrominated Biphenyls in Chinese Hamster Cells (in preparation).

Trosko, J.E. and Chang, C.C. 1980. An Integrative Hypothesis Linking Cancer, Diabetes, and Atherosclerosis: The Role of Mutations and Epigenetic Changes. Med. Hypothesis 6:455-468.

Trosko, J.E. and Chang, C.C. 1981. The Role of Radiation and Chemicals in the Induction of Mutations and Epigenetic Changes During Carcinogenesis. In: J. Lott and H. Adler (eds.), "Advances in Radiation Biology," pp. 1-36, Vol. 9. Academic Press, NY.

Trosko, J.E., B. Dawson, and C.C. Chang. 1981. PBB Inhibits Metabolic Cooperation in Chinese Hamster Cells In Vitro: Its Potential as a Tumor Promoter. Environ. Health Persp. 37:179-182.

Trosko, J.E., B. Dawson, L.P. Yotti, and C.C. Chang. 1980. Saccharin May Act as a Tumor Promoter by Inhibiting Metabolic Cooperation Between Cells. Nature 285:109-110.

MONS 005024

Trosko, J.E., C.C. Chang, and M. Netzloff. 1982a. The Role of Inhibited Cell-Cell Communication in Teratogenesis. Teratogenesis, Carcinogenesis, and Mutagenesis 2:31-45.

Trosko, J.E., L.P. Yotti, S.T. Warren, G. Tsushimoto, and C.C. Chang. 1982b. Inhibition of Cell-Cell Communication by Tumor Promoters. In: E. Hecker (ed.), "Carcinogenesis," pp. 565-585, Vol. 7. Raven Press, NY.

Tsushimoto, G., J.E. Trosko, C.C. Chang, and S.D. Aust. 1982. Inhibition of Metabolic Cooperation in Chinese Hamster V79 Cells in Culture by Various Polybrominated Biphenyl (PBB) Congeners. Carcinogenesis 3:181-185.

Umeda, M., K. Noda, and T. Ono. 1980. Inhibition of Metabolic Cooperation in Chinese Hamster Cells by Various Chemicals Including Tumor Promoters. Gann 71:614-620.

Warren, S.T., D.J. Doolittle, C.C. Chang, J.I. Goodman, and J.E. Trosko. 1982. Evaluation of the Carcinogenic Potential of 2,4-Dinitrofluorobenzene and Its Implications Regarding Mutagenicity Testing. Carcinogenesis 3:139-145.

Watanabe, M. and T. Sugahara. 1981. Experimental Formation of Cleft Palate in Mice With Polychlorinated Biphenyls. Toxicology 19:49-53.

Wertz, G.F. and G. Ficsor. 1978. Cytogenetic and Teratogenic Test of Polybrominated Biphenyls in Rodents. Environ. Health Persp. 23:129-132.

Williams, G.M., S. Telang, and C. Tong. 1981. Inhibition of Intercellular Communication Between Liver Cells by the Liver Tumor Promoter 1,1,1-Trichloro-2,2-Bis(P-Chlorophenyl) Ethane. Cancer Letters 11:239-244.

Wilson, J.G. 1977. Current Status of Teratology. In: J.G. Wilson and F.C. Fraser (eds.), "Handbook of Teratology," pp. 47-74. Plenum Press, NY.

Wyndham, C., J. Devenish, and S. Safe. 1976. The In Vitro Metabolism, Macromolecular Binding and Bacterial Mutagenicity of 4-Chlorobiphenyl, A Model PCB Substrate. Res. Commun. Chem. Pathol. Pharmacol. 15:563-570.

Yancey, S.B., J.E. Edens, J.E. Trosko, C.C. Chang, and J.P. Revel. 1982. Decreased Incidence of Gap-Junctions Between Chinese Hamster V79 Cells Upon Exposure to the Tumor Promoter 12-O-Tetradecanoyl-Phorbol-13-Acetate. Exp. Cell Res. 139:329-340.

MONS 005025

Yotti, L.P., C.C. Chang, and J.E. Trosko. 1979. Elimination of Metabolic Cooperation in Chinese Hamster Cells by a Tumor Promoter. Science 206:1089-1091.

MONS 005026

CHAPTER 19

EFFECTS OF POLYCHLORINATED BIPHENYLS ON THE EXPRESSION OF EMBRYOTOXICITY CAUSED BY MODEL TERATOGENS

Frank Welsch[1]
Department of Pharmacology and Toxicology
and Center for Environmental Toxicology
Michigan State University
East Lansing, Michigan 48824-1317

INTRODUCTION

Although polychlorinated biphenyls (PCBs) were produced in large quantities ever since the 1930s, it was not until a major accident of human poisoning occurred in Japan in 1968 (Yusho disease) that substantial interest in their toxicity was aroused. There were a number of accidental food contaminations discovered and reported in the United States in 1971. Thus, PCBs also became very much a national concern. The rapid generation of new information concerning the chemistry and toxicology of these compounds is witnessed by the large number of scientific publications and comprehensive review articles published during the 1970s (see, for example, Fishbein, 1974; Kimbrough et al., 1978; Matthews et al., 1978; Report, 1976).

In spite of the total production ban in this country, the persistence of PCBs in the environment and their concentration in the biological food chain has caused much concern and indeed is the stimulus for this gathering and scientific discussion on the issue of PCBs in the Great Lakes Region of North America and the toxicological importance of the contamination.

The acute mammalian toxicity of PCBs can be classified as slightly toxic to practically nontoxic (Kimbrough et al., 1978).

---

[1]New address: Chemical Industry Institute of Toxicology (CIIT), P.O. Box 12137, Research Triangle Park, North Carolina 27709.

MONS 005027

Remarkable species differences are well documented. Much more important than the acute effects are the subacute and chronic toxicities of PCBs. In this mode of exposure, the species sensitivities differ drastically. Notable are the high susceptibilities of mink (Aulerich et al., 1973) and of subhuman primates (Barsotti et al., 1976; McConnell et al., 1979). The visible symptoms in monkeys corresponded to the typical signs of PCB intoxication which have also been reported in accidental human exposure such as the Yusho incident or mishaps in industrial production plants. However, the issue of high primate sensitivity is confounded by the fact that Aroclor 1248 and 1254 were involved, and that PCBs with lower degrees of chlorination have different and higher toxicity than those with higher degrees of chlorination.

The PCBs have been investigated thoroughly in a variety of species in order to assess their reproductive and prenatal toxicology. Many of these studies used the commercial PCB mixtures which cause our environmental contamination problems. Most prominently the chromatographic pattern of samples collected from man and his environment resembles closest the chromatograms obtained with authentic Aroclor 1254 (Report, 1976). Typically, embryotoxicity studies followed the standard protocols for teratology screening. Most of these evaluations led to the conclusion that PCBs have low potential to cause gross deviation in morphologic development (=terata), yet dysmorphogenesis has been reported (e.g., Watanabe and Sugahara, 1981) with mixtures and pure congeners (Lucier et al., 1978; Marks et al., 1981). In the modern terminology of research in prenatal toxicology, teratogenicity is only one very obvious form of the manifestation of embryotoxicity. Experimental designs to unmask much more subtle effects brought about by prenatal exposure to PCBs have already revealed definitive subtle neurotoxic sequelae which were unmasked by behavioral testing (Tilson et al., 1979). Furthermore, immunotoxic consequences have been reported (Loose et al., 1979).

The intent of the experiments which will be described in this contribution to the symposium was not to reassess the teratogenicity of PCBs. Rather the concept to be tested in the first phase of a study that is much more comprehensive was that of embryotoxic interactions between PCBs as the primary chemical insult to embryonal tissues followed by a well established model teratogen as the secondary chemical insult. The measurements pursue the hypothesis advanced by a number of investigators that in the large category (65-70%) of human embryopathies of unknown etiology many cases may eventually become explainable as being due to interactions and combinations of two or more factors. There is considerable concern over the potential relationship between chemical exposure at low levels from multiple

MONS 005028

sources and the effects that this may have on the manifestation of embryotoxicity.

Among the objectives of the experimental design was to deliberately select PCB exposure levels which were or were not expected to be sufficient to induce the metabolism of endogenous and exogenous chemicals. The induction or lack thereof was then to be correlated with the outcome of a second embryotoxic insult inflicted by either one of two model teratogens which differ fundamentally in their need for and mode of bioactivation to unfold their embryotoxic effects.

MATERIALS AND METHODS

We selected 1, 10, and 100 mg/kg[1] of Aroclor 1254 as an additive to ground mouse chow fed ad libitum to female ICR Swiss mice HAP: Swiss (ICR) Br; Harlan Industries, Indianapolis, Indiana . The batch of Aroclor 1254 had been thoroughly analyzed in the Pesticide Research Center of Michigan State University by GC/MS and was found to be free of contaminants such as dibenzofurans and dibenzo-p-dioxins which have often confounded previous PCB related research. Compared to other studies involving laboratory rodents, the exposure levels chosen may be considered low to moderate. When calculated on the basis of estimated daily food consumption, the dosage would be no higher than 15 to 20 mg PCB/kg at the highest 100 mg/kg diet level.

The treatment scheme differentiated between acute PCB ingestion which was started on day 6 of gestation (vaginal plug day = day 0) and chronic PCB intake. In the latter design, 30 day old female mice were put on the PCB diets for 90 days prior to mating. The PCB exposure was maintained throughout gestation in both situations. The two modes of PCB treatment were chosen with the desire to separate the effects of enzyme induction and the resultant metabolic consequences from more direct effects that PCBs might have on rapidly differentiating embryonal tissues. In the acutely exposed pregnant mice, significant liver enzyme induction by 1 and 10 mg/kg PCB was not expected after 5 days of ingestion when the exposure to the second chemical insult occurred. Common to both acute and chronic PCB ingestion was that on day 11 of gestation (260-265 hr after successful mating) the animals received a single intraperitoneal injection of the model teratogen. One of the drugs is

---

[1]mg/kg in the animal's diet is not equivalent to mg/kg in the animal.

cyclophosphamide (CPA) and the other 5-fluorodeoxyuridine (FUdR). These compounds were chosen because CPA in mice and other typical laboratory animal models relies exclusively on bioactivation in the maternal liver by a cytochrome P-450 mediated reaction to 4-hydroxycylophosphamide (4-OH-CPA). Further conversion occurs to a stable alkylating phosphoramide mustard (Mirkes et al., 1981). This metabolite is stable enough that it can be transferred across the placenta and exert its effect on the embryo, which cannot perform cytochrome P-450 dependent drug oxidation reactions. By contrast, FUdR can be readily activated in the embryo. These distinctive features of the model drugs are witnessed by the fact that CPA is inactive in vitro in both whole embryo (Fantel et al., 1979) as well as limb bud cultures (Manson and Smith, 1977; Barrach et al., 1978), but causes teratogenic effects similar to those induced at comparable stages of development in vivo when a bioactivation system is added to the culture (Fantel et al., 1979; Mirkes et al., 1981) or when 4-OH-CPA is used directly in limb bud cultures (Barrach et al., 1978). The pyrimidine analogue FUdR, on the other hand, is converted by embryonal tissues to 5-fluorodeoxyuridine monophosphate (FdUMP) which blocks thymidilate synthetase and thus DNA synthesis (Myers, 1981). A characteristic of both drugs is also that many of the teratogenic effects are expressed in deviant development of the limbs and the paw (Gibson and Becker, 1968a; Knudsen and Kochhar, 1981). This appeared to be advantageous as regards the ease of evaluation of the drug's effects and for later in vitro correlations with cultured limb buds. Since both enhancement or attenuation of teratogenicity were among the possible interactions between PCBs and the model compounds, we had to first define two doses of each drug that would cause (a) an effect clearly distinguishable from background events in untreated controls and (b) a teratogenic response in most of the positive control animals with a minimum degree of embryotoxicity or embryolethality.

The data obtained during the course of the investigation were analyzed by Dunnett's t-test and by one-way analysis of variance.

RESULTS AND DISCUSSION

First, the observations with CPA will be discussed. In teratogenesis research this compound has received considerable attention over the past two decades, but only recently has a clearer picture emerged linking CPA bioactivation to teratogenesis (see above citations) and mutagenesis as well as teratogenesis (Hales, 1981a, 1981b). Throughout the course of this

study repeat blocks of control animals were used concomitantly with the particular single drug or drug combination group. At different times the various control group fetuses had differing weights on day 18. In order not to complicate the comprehensive tabular presentation of the results, these differences were not reported in the tables, but they were accounted for only in the statistical evaluations. While none of the PCBs alone either in the acute or in the chronic exposure mode caused any signs of dysmorphogenesis compared to control fetuses (Table 1), 10 mg CPA/kg caused visible malformations in 21.6 percent of the live fetuses. There was no increase in embryonal losses at this dose and only a modest reduction in body weights on day 18 of fetal development. The second and higher dose of 16 mg CPA/kg did not increase embryolethality, but drastically raised the percentage of malformed surviving fetuses to 93.4 percent, while at the same time reducing the fetal weights significantly. This was a clear sign of general embryotoxicity for which fetal weight is a very sensitive indicator.

The emphasis in the morphologic evaluation was put on an assessment of limb and paw development. Bone length measurements were performed on about two-thirds of the live fetuses since bone development has previously been shown to be very sensitive to the effects of CPA (Gibson and Becker, 1968a). Combination of PCBs with CPA brought about a variety of alterations in the expression of embryotoxicity. The fetal weights were reduced by all combinations of 10 mg CPA with PCBs compared to either chemical alone. However, the percentage of malformed live fetuses was attenuated at 1 and 10 mg/kg PCBs, while it remained unchanged at 20.6 percent with 100 mg/kg (Table 1). When paw development was assessed in particular, a strikingly similar effect was observed (Table 2). At both 10 mg CPA/1 mg/kg PCBs and 10 mg CPA/10 mg/kg PCBs, the incidence of paw malformations was reduced, while there was no sigificant change at 10 mg CPA/100 mg/kg PCBs with 16.5 percent occurrence compared to 21.6 percent observed at 10 mg CPA/10 mg/kg PCBs.

In the higher CPA dose group of the acutely PCBs exposed animals, there was a peculiar effect in the combination of 16 mg CPA/10 mg/kg PCBs which was also encountered with the higher FUdR dose (see below). This combination led to the most severe weight reductions among the day 18 fetuses. Coincident with this expression of embryotoxicity was that the 16 mg CPA/10 mg/kg PCBs acute fetuses were almost all malformed (94.8%; Table 1) just as in the positive control of 16 mg CPA where the incidence frequency was 93.4 percent. By contrast, fetal weights of 16 mg CPA/1 mg/kg PCBs and 16 mg CPA/100 mg/kg PCBs under the acute PCB ingestion design were indistinguishable from each other and somewhat higher than those observed after

TABLE 1

Effects of Acute PCB Ingestion on the Response of Mouse Embryos Treated on Day 11 With Cyclophosphamide (CPA)

Treatment			Dead or Resorbed		Malformed		
CPA (mg/kg)	PCBs (mg/kg)	Number of Litters	Total Number	Percent	Total Number	Percent	Fetal Wt. (g) Mean±S.E.M.
0	0	14	5/173	2.9	0/168	0	1.31±0.02
0	1	4	0/41	0	0/41	0	1.19±0.03
0	10	3	1/33	3.0	0/32	0	1.17±0.03
0	100	4	1/40	2.5	0/39	0	1.19±0.03
10	0	11	6/140	4.3	29/134	21.6	1.15±0.01
10	1	10	9/116	7.8	6/107	5.6	1.11±0.01
10	10	6	10/84	11.9	6/74	8.1	1.02±0.02
10	100	9	2/100	2.0	20/97	20.6	1.05±0.02
16	0	19	12/223	5.4	197/211	93.4	0.89±0.02
16	1	8	11/98	11.2	37/87	42.5	0.93±0.02
16	10	6	8/85	9.4	73/77	94.8	0.85±0.01
16	100	10	3/115	2.6	64/112	57.1	0.97±0.01

Pregnant animals consumed a diet containing the amount of PCBs indicated beginning from day 6 of gestation. On day 11 the mice received an intraperitoneal injection of CPA. Fetuses were obtained on day 18.

MONS 005032

TABLE 2

Effects of Acute PCB Ingestion on Paw Development of House Embryos Treated on Day 11 With Cyclophosphamide (CPA)

Treatment				Percent of Fetuses Affected						
				Malformed	Paw Development		Syndactyly		Ectrodactyly	
CPA (mg/kg)	PCBs (mg/kg)	Number of Litters	Live	Percent	Total Number	Percent	Fore	Hind	Fore	Hind
0	0	14	168	0	0/168	0	0	0	0	0
10	0	11	134	21.6	29/134	21.6	9.7	6.0	3.7	9.7
10	1	10	107	5.6	3/107	2.8	0	0.9	0	0
10	10	6	74	8.1	5/74	6.8	1.4	0	0	0
10	100	9	97	20.6	16/97	16.5	8.2	9.3	1.0	2.1
16	0	19	211	87.2	192/211	91.0	64.9	50.7	2.8	16.1
16	1	8	87	42.5	37/87	42.5	10.3	11.5	20.7	16.1
16	10	6	77	98.8	76/77	98.7	23.4	46.8	15.6	66.2
16	100	10	112	57.1	64/112	57.1	8.0	28.6	25.0	39.3

Pregnant animals consumed a diet containing the amount of PCBs indicated beginning from day 6 of gestation. On day 11 the mice received a single intraperitoneal injection of CPA. Fetuses were obtained on day 18.

MONS 005033

16 mg CPA alone. This trend was particularly noticeable at 16 mg CPA/100 mg/kg PCBs (0.97 g vs. 0.89 g; Table 1). At the same time, the CPA combination with both 1 and 100 mg/kg PCBs reduced the percentage of malformed fetuses (Table 1) and the rate of incidence of paw malformations (Table 2).

Upon closer analysis of the paws, there were numerous alterations detectable in the manifestation of teratogenic effects brought about by CPA/acute PCBs. For example, the frequency of occurrence of syndactyly of the forelimb was reduced at 10 mg CPA/1 mg/kg PCBs as well as 10 mg/kg PCBs and at all three PCB levels at 16 mg CPA (Table 2). Ectrodactyly of the forelimb and hindlimb were markedly increased at 16 mg CPA and all PCB levels in the forelimbs as well as at 10 and 100 mg/kg PCBs in the hindlimbs.

In the chronic PCB animals, the percentage of malformed fetuses was lower at all three PCB exposure levels when 10 mg CPA/kg was given. However, at 16 mg/kg there was attenuation by PCBs only at the 100 mg/kg dose (Table 3). This effect was also reflected in the significantly higher mean fetal body weight determined among the 16 mg CPA/100 mg/kg PCB fetuses.

The examination of paw development reflected these interactions very clearly (Table 4). Syndactyly incidence was reduced in both forepaws and hindpaws at 10 mg CPA and all PCB levels. Notable was again the interaction between the higher CPA dose of 16 mg/kg and 10 mg/kg PCBs which enhanced the frequency of syndactyly and ectrodactyly in forelimbs (Table 4).

As regards the measurements of bone lengths, some of the results could be anticipated on the basis of fetal weights. Thus, while 10 mg CPA alone caused little decrease in the fetal weights (Table 1) and was without significant effect on humerus, radius, ulna, femur, tibia, and fibula length, the higher dose of 16 mg CPA caused a substantial fetal weight reduction and concomitantly a significant reduction in length of all those long bones in the forelimbs and hindlimbs (Figure 1). Upon combination with various PCB levels, the 10 mg CPA dose both in acute (data not shown) and chronic animals (Figures 2 and 3) brought about bone length reductions in all long bones at all PCB levels. However, in the combined exposure the correlation of fetal weights to bone lengths was not as obvious as with CPA alone (compare Table 1 and Figure 1). In the forelimbs of acute PCB animals, the combination of 16 mg CPA with 10 mg/kg PCBs caused the largest reductions in all long bones of both forelimbs and hindlimbs, while this effect was attenuated at 100 mg/kg PCBs. Very similar observations were made in the off-spring of mice that were on the chronic PCB regimen (Figures 2 and 3). Overall, there appeared to be a

MONS 005034

TABLE 3

Effects of Chronic PCB Ingestion on the Response of Mouse Embryos Treated on Day 11 With Cyclophosphamide (CPA)

Treatment			Dead or Resorbed		Malformed		
CPA (mg/kg)	PCBs (mg/kg)	Number of Litters	Total Number	Percent	Total Number	Percent	Fetal Wt. (g) Mean±S.E.M.
0	0	13	8/153	5.2	0/145	0	1.29±0.02
0	1	4	0/41	0	0/41	0	1.19±0.01
0	10	3	1/33	3.0	0/32	0	1.17±0.03
0	100	4	1/40	2.5	0/39	0	1.19±0.03
10	0	11	6/140	4.3	29/134	21.6	1.15±0.01
10	1	8	11/94	11.7	7/83	8.4	1.07±0.10
10	10	8	4/91	4.3	9/87	10.3	1.06±0.13
10	100	11	8/120	6.6	10/112	8.9	0.99±0.14
16	0	19	12/223	5.4	197/211	93.4	0.89±0.02
16	1	9	10/90	11.1	79/80	98.8	0.83±0.14
16	10	8	15/99	15.1	84/84	100.0	0.84±0.10
16	100	9	6/98	6.1	49/92	53.3	0.97±0.13

Mice had consumed 0, 1, 10, and 100 mg/kg PCBs in their diet for at least 90 days prior to breeding and continuing throughout gestation. On day 11 of pregnancy, CPA was injected intraperitoneally and fetuses were obtained on day 18.

TABLE 4

Effects of Chronic PCB Ingestion on Paw Development of Mouse Embryos Treated on Day 11 With Cyclophosphamide (CPA)

Treatment				Percent of Fetuses Affected						
				Malformed	Paw Development		Syndactyly		Ectrodactyly	
CPA (mg/kg)	PCBs (mg/kg)	Number of Litters	Live	Percent	Total Number	Percent	Fore	Hind	Fore	Hind
0	0	13	145	0	0/145	0	0	0	0	0
10	0	11	138	21.6	29/138	21.6	9.7	6.0	3.7	9.7
10	1	19	83	7.1	192/211	91.0	1.2	0	0	0
10	10	8	87	10.3	7/83	8.4	3.4	3.4	1.1	1.1
10	100	8	112	8.9	6/87	6.9	3.6	0.9	0	0
16	0	11	211	87.2	8/112	7.1	64.9	50.7	2.8	16.1
16	1	9	80	98.8	79/80	98.8	11.3	45.0	36.3	80.0
16	10	6	84	100.0	84/84	100.0	49.2	56.0	72.6	90.5
16	100	9	92	53.3	48/92	52.2	16.3	25.0	22.8	22.8

Mice had consumed a diet containing the amounts of PCBs specified for 90 days prior to breeding and continuing throughout gestation. On day 11 of pregnancy, the animals received a single intraperitoneal injection of CPA. Fetuses were obtained on day 18.

MONS 005036

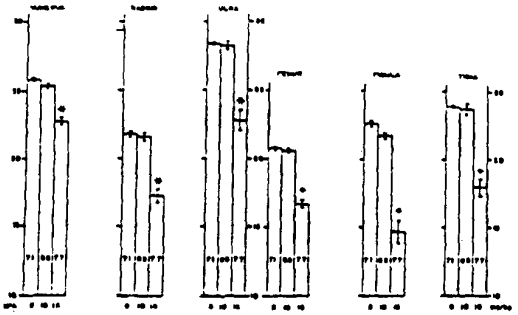


Figure 1. Effects of cyclophosphamide (CPA) on bone length of fetal limbs in mice. On day 11 of gestation, animals received a single intraperitoneal injection of CPA at the dose specified. Fetuses were obtained on day 18. The results on the ordinate are recorded in reticle units, and one unit corresponds to 0.1 mm. Values shown represent mean ± S.E. derived from examining the number of fetuses indicated in the bars. Asterisks denote significant differences from control ($p < 0.05$).

tendency that chronic PCB exposure caused slightly more bone length reduction than the acute PCB intake did.

The results obtained in our present experiments have some resemblance to those obtained by Gibson and Becker (1968b) in the Swiss-Webster strain of mice. They used phenobarbital as a pure inducer of cytochrome P-450 and enzyme reactions coupled to this hemoprotein although the effects of the drug were not quantitated. We have correlated our observations to measurements of cytochrome P-450 content and selected xenobiotic metabolizing enzymes in microsomes prepared from livers of the pregnant mice. The cytochrome content was significantly elevated only at the 100 mg/kg PCB exposure level, both acute and chronic. Aminopyrine demethylation was used as a prototype reaction coupled to P-450 as the terminal oxidase. The reaction was significantly enhanced at 10 mg/kg PCB chronic as well as at 100 mg/kg acute and chronic. Arylhydrocarbon hydroxylase

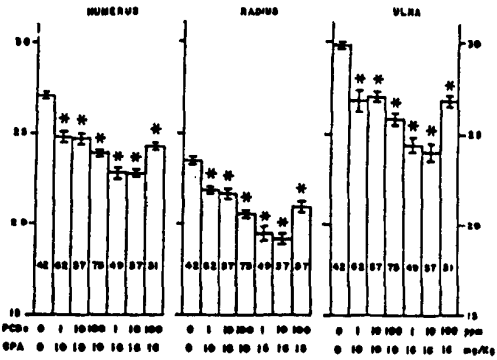


Figure 2. Effects of chronic PCBs in combination with cyclophosphamide (CPA) on bone length of fetal forelimbs in mice. Animals had consumed the doses of PCBs indicated on the abscissa in their diet for at least 90 days prior to breeding and continuing throughout gestation. On day 11 of pregnancy, mice received a single intraperitoneal injection of CPA. Other details as in Figure 1.

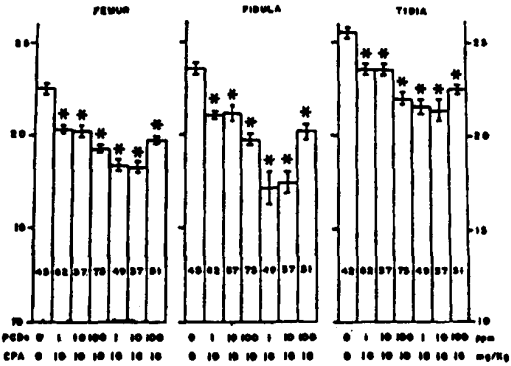


Figure 3. Effects of chronic PCBs in combination with cyclophosphamide (CPA) on bone length of fetal hindlimbs in mice. Experimental details are as in Figures 1 and 2.

MONS 005038

and ethoxyresorufin-o-desethylase activity were also measured. Although both reactions are coupled to cytochrome P-448 and thus probably not relevant to CPA bioactivation, these enzyme activities were measured to obtain a more complete picture of the induction pattern brought about by the PCBs. At 100 mg/kg PCB which caused significant induction of aminopyrine demethylation after acute and chronic ingestion, the teratogenicity of the 16 mg CPA dose was markedly reduced in the present observations. This conclusion agrees with the findings of Gibson and Becker (1968b), who described reduced teratogenicity caused by 20 mg CPA/kg after induction of the pregnant mice with phenobarbital. These investigators correlated their measurements with the appearance of alkylating activity in the plasma of mice which was elevated as judged by more alkylation of the indicator dye nitrobenzyl pyridine. The outcome of experiments similar in design performed in the rat were entirely different as the recent publications by Hales (1981a, 1981b) have shown. In that species it was demonstrated quite convincingly that phenobarbital pretreatment led to enhanced activation of CPA to mutagenic molecular forms and that the *in vivo* teratogenic effect of CPA was markedly increased. If more alkylating metabolites are formed by the stimulation of P-450 coupled monooxygenase activity which hydroxylates CPA to 4-OH-CPA, and if the accumulated evidence unequivocally shows that this reaction is the prerequisite for biological activity (Mirkes *et al.*, 1981), then it is not unreasonable to anticipate that teratogenicity should be increased. The observations revealing that the opposite was happening in the mouse led Becker and his associates about a decade ago (when much less was known about CPA metabolism than now) to study the binding of radioactive CPA and its then still unidentified metabolites to macromolecules of the maternal liver and of the mouse embryo (Murthy *et al.*, 1973). It was found that pretreatment with phenobarbital decreased binding to embryonal DNA without affecting RNA or embryonal protein binding. On the other hand, more radioactivity derived from CPA was associated with maternal liver proteins.

In the meantime, the bioactivation of CPA has been elucidated in much more detail. We have initiated experiments which are aimed at defining the basis for the interactions between PCBs and CPA regarding embryotoxicity of CPA. The approach involves an examination of the pharmacokinetics of ^{14}C-CPA, binding to maternal and embryonal macromolecules as well as an *in vivo-in vitro* correlation. For the latter experiments, limb buds from embryos exposed to PCBs *in utero* will be used in organ culture. The activated metabolite 4-OH-CPA at accurately defined concentrations can then be added for very specific exposure times to the explants.

MONS 005039

The second model teratogen, FUdR, whose interactions with PCBs were examined has not attracted anywhere as much attention by investigators in teratogenesis as it has in carcinogenesis. The malformations caused by this important therapeutic agent which is used as an antimetabolite in cancer chemotherapy (Myers, 1981) are also clearly reflected in deviant paw and limb development (Knudsen and Kochhar, 1981). After a dose of 7.5 mg FUdR/kg 49 percent of the live fetuses had visible malformations, while this dose caused no embryolethality or significant fetal weight reduction on day 18 of gestation (Table 5). The higher dose of 20 mg FUdR/kg increased the percentage of live, malformed fetuses to 99 percent, while at the same time producing only a very modest increase in embryolethality (Table 5). Combination of 7.5 mg FUdR with each of the 3 PCB acute dietary exposure levels almost doubled the percentage of malformed fetuses, but had no such clear-cut effect in chronic PCB mice (data not shown). This increase was reflected almost exclusively by a rise in the frequency of paw malformations (Table 6). When the development of the phalanges was examined more closely, a number of changes was noted in the expression of malformations by FUdR alone or in combination with the PCBs. Examples are that syndactyly in hindlimbs of all live fetuses was increased from 7.7 percent at 7.5 mg FUdR alone to 44.4 percent at 7.5 mg FUdR/100 mg/kg PCBs acute, but not chronic (data not shown). Also, ectrodactyly occurrence in forelimbs of acute PCBs fetuses was markedly increased from the positive control level where it was 6.2 percent at the 7.5 mg FUdR/kg dose. At both doses of FUdR, polydactyly in the hindlimb occurred more frequently among those embryos/fetuses that had been acutely exposed to PCBs.

TABLE 5

The measurements of bone length revealed a number of interactive effects with PCBs and showed the most noteworthy differences between acute and chronic PCB ingestion that were observed in the entire study of bone development. The model teratogen alone caused small, but significant, reductions at both 7.5 and 20 mg FUdR/kg in the length of humerus, radius, and ulna, while in the hindlimb only the higher dose led to shortened long bones including femur, fibula, and tibia (Figure 4). The magnitude of this effect in the hindlimb appeared to be unrelated to the rather modest weight reduction observed in the fetuses of this dose group (Table 5). When the pregnant mice were acutely exposed to PCBs, then the most conspicuous effect was noted in the combination of 20 mg FUdR with 10 mg/kg PCBs (Figure 5). It was pointed out during the description of the effects of CPA that there was a particularly pronounced effect by combining 16 mg CPA with 10 mg/kg PCBs on an acute basis. Here a similar phenomenon occurred with FUdR. The fetal weights in this group were reduced further than those measured

TABLE 5

Effects of Acute PCB Ingestion on the Response of Fetuses Treated on Day 11 With 5-Fluorodeoxyuridine (FUdR)

Treatment			Dead or Resorbed		Malformed		
FUdR (mg/kg)	PCBs (mg/kg)	Number of Litters	Total Number	Percent	Total Number	Percent	Fetal Wt. (g) Mean±S.E.M.
0	0	9	3/104	2.9	0/104	0	1.21±0.03
0	1	4	0/41	0	0/41	0	1.19±0.03
0	10	3	1/32	3.1	0/32	0	1.17±0.03
0	100	4	1/39	2.6	0/39	0	1.19±0.03
7.5	0	5	1/65	1.5	31/64	49.2	1.16±0.03
7.5	1	5	4/52	7.7	43/48	89.6	1.14±0.02
7.5	10	5	8/65	12.3	51/59	86.4	1.08±0.02
7.5	100	5	3/57	5.3	45/54	83.3	1.12±0.03
20.0	0	6	5/72	6.9	66/67	98.6	1.15±0.03
20.0	1	6	5/77	6.5	71/72	98.6	0.99±0.01
20.0	10	6	5/84	6.0	75/79	94.9	0.86±0.01
20.0	100	8	12/83	14.5	69/71	97.2	0.99±0.02

Pregnant animals consumed a diet containing the amount of PCB indicated beginning from day 6 of gestation. On day 11 the mice received an intraperitoneal injection of FUdR. Fetuses were obtained onday 18.

MONS 005041

TABLE 6

Effects of 5-Fluorodeoxyuridine (FUdR) Alone and of FUdR Plus Acute PCBs on Paw Development in Mouse Fetuses

Treatment				Percent of Fetuses Affected								
				Malformed	Paw Development		Syndactyly		Ectrodactyly		Polydactyly	
FUdR (mg/kg)	PCBs (mg/kg)	Number of Litters	Live	Percent	Total Number	Percent	Fore	Hind	Fore	Hind	Fore	Hind
0	0	9	33	0	0/104	0	0	0	0	0	0	0
7.5	0	5	65	49.2	32/65	49.2	12.3	7.7	6.2	33.8	1.5	1.5
7.5	1	5	73	98.6	71/72	98.6	18.0	13.1	82.0	34.4	1.6	6.6
7.5	10	5	48	89.6	42/48	87.5	37.2	16.3	39.5	58.1	0	14.0
7.5	100	5	54	83.3	51/59	86.4	26.7	44.4	53.3	42.2	4.4	11.1
20.0	0	6	67	98.5	45/54	83.3	48.6	38.9	29.2	61.1	1.3	18.1
20.0	1	6	72	98.6	71/72	98.6	40.8	46.5	57.8	47.9	1.4	39.4
20.0	10	6	79	94.6	75/79	94.6	50.7	40.0	48.0	3.3	1.3	44.0
20.0	100	8	71	97.2	69/71	97.2	44.9	47.8	31.9	49.3	1.5	36.2

Pregnant animals consumed a diet containing the amount of PCBs indicated beginning from day 6 of gestation. On day 11 the mice received a single intraperitoneal injection of FUdR. Fetuses were obtained on day 18.

MONS 005042

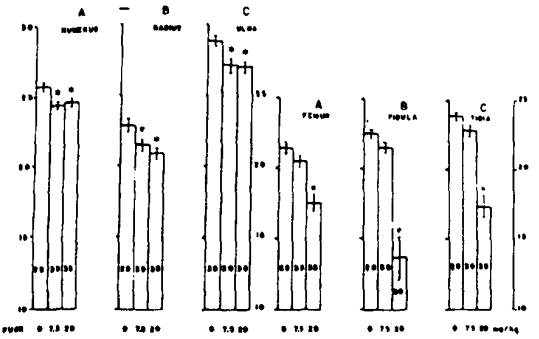


Figure 4. Effects of 5-fluorodeoxyuridine (FUdR) on bone length of fetal limbs in mice. All details are as in Figure 1, except that pregnant mice received a single intraperitoneal injection of FUdR.

in 1 or 100 mg/kg PCB exposed fetuses (Table 5). This observation was reflected in the reduction of bone length not only in the forelimb but also in hindlimbs (Figure 6). Furthermore, in hindlimbs of acutely PCB exposed fetuses, the reduction of femur, fibula, and tibia length resulting from 7.5 mg FUdR/kg became significant when PCBs were ingested acutely at 10 and 100 mg/kg (Figure 6).

In striking contrast were the observations made when PCB intake was chronic. The effects of both 7.5 and 20 mg FUdR on radius and ulna were completely reversed while they persisted in the humerus (Figure 7). Similar results were obtained in hindlimbs (Figure 8). The drastic reductions in length caused by 20 mg FUdR in femur, fibula, and tibia were attenuated to control fetus length by the combination with chronic PCBs at each of the 3 dietary intake levels (Figure 8). Thus, the differences between acute and chronic PCBs in the results obtained with the two model teratogens regarding bone development is remarkable. Among the CPA treated mouse fetuses, chronic PCBs did not affect the bone length reductions, while many of the effects of FUdR were completely eliminated by PCBs.

MONS 005043

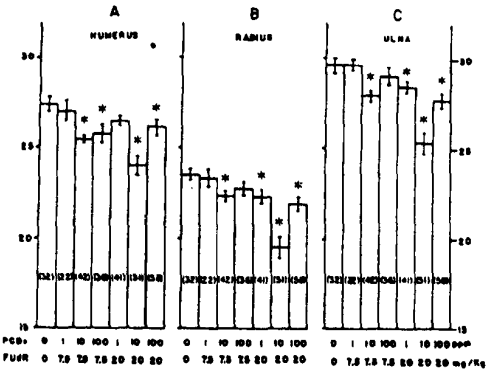


Figure 5. Effects of acute PCBs in combination with 5-fluorodeoxyuridine (FUdR) on bone length of fetal forelimbs in mice. Animals consumed a diet containing the amount of PCBs indicated on the abscissa beginning from day 6 of gestation. On day 11, the mice received a single intraperitoneal injecton of FUdR. Fetus procurement and examination details are as in Figure 1.

There is no plausible explanation yet for the multitude of interactions described in this communication between CPA or FUdR and PCBs. We have established that CPA as the prototype of a drug dependent exclusively on maternal liver activation in the mouse by a cytochrome P-450 dependent monooxygenase reaction shows markedly altered teratogenicity when combined with PCBs. However, it appears that bioactivation cannot be the only explanation for the observations presented. This conclusion is based on the fact that the bioactivation of FUdR by thymidine kinase to FdUMP is not coupled to cytochrome P-450 or P-448. We have just embarked on experiments to study the pharmacokinetics and placental transfer of ^{3}H-FUdR in control and PCB exposed mice. Part of these measurements will include ion exchange chromatography to differentiate between ^{3}H-FUdR and ^{3}H-FdUMP in mouse embryos. One may then become able to estimate whether PCBs alter the distribution ratio between parent compound FUdR and the bioactive inhibitor of thymidilate synthetase. Another approach in the desire to elucidate the basis for the alteration in expression of teratogenicity of FUdR by

MONS 005044

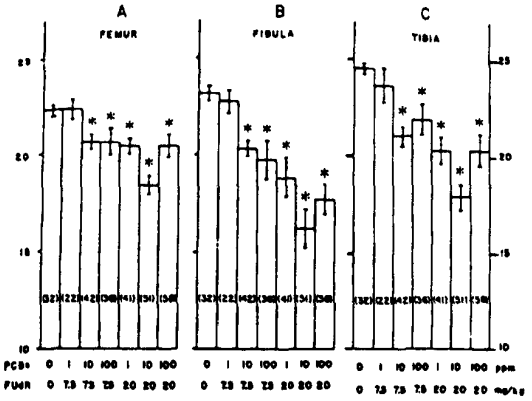


Figure 6. Effects of acute PCBs in combination with 5-fluorodeoxyuridine (FUdR) on bone length of fetal hindlimbs in mice. Other details as in Figure 5.

the PCBs will involve limb bud culture. Limb buds from PCB exposed embryos are to be exposed to FUdR *in vitro* in order to measure whether PCBs have altered the embryonal tissue responsiveness to FUdR. We hope that by a combination of the *in vivo* results described here with the *in vitro* studies to be performed on isolated, PCB pretreated embryonal tissues a better understanding will be obtained for why the observed *in vivo* changes occurred.

ACKNOWLEDGMENTS

The author is grateful to Miss Karen Hardyniec for her skillful assistance during the conduct of this research project. The patience and efficiency of Miss Diane Hummel in preparing this manuscript is gratefully acknowledged. The work described was supported by grant no. ES02461 from the National Institute of Environmental Health Sciences.

MONS 005045

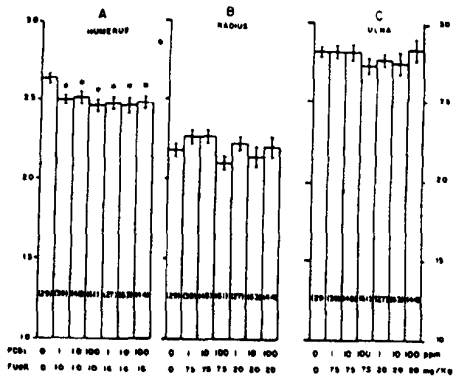


Figure 7. Effects of chronic PCBs in combination with 5-fluorodeoxyuridine on bone length of fetal forelimbs in mice. Other details as in Figures 1 and 2.

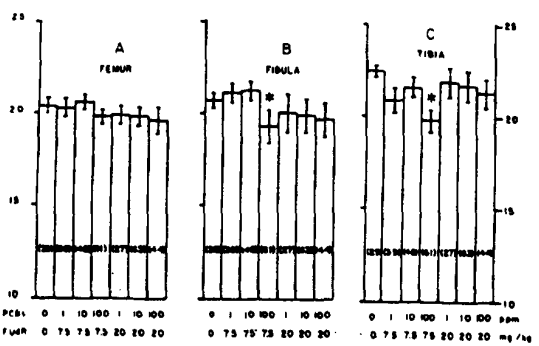


Figure 8. Effects of chronic PCBs in combination with 5-fluorodeoxyuridine on bone length of fetal hindlimbs of mice. Other details as in Figures 1 and 2.

MONS 005046

LITERATURE CITED

Aulerich, R.J., R.K. Ringer, and S. Iwamoto. 1973. Reproductive Failure and Mortality in Mink Fed on Great Lakes Fish. J. Reprod. Fert. (Suppl.) 19:365-376.

Barrach, H.J., I. Baumann, and D. Neubert. 1978. The Applicability of In Vitro Systems for the Evaluation of the Significance of Pharmacokinetic Parameters for the Induction of an Embryotoxic Effect. In: D. Neubert, H.-J. Merker, H. Nau, and J. Langman (eds.), "Role of Pharmacokinetics in Prenatal and Perinatal Toxicology," pp. 323-336. Georg Thieme Publishers, Stuttgart.

Baraotti, D.A., R.J. Marlar, and J.R. Allen. 1976. Reproductive Dysfunction in Rhesus Monkeys Exposed to Low Levels of Polychlorinated Biphenyls (Aroclor 1254). Fd. Cosmet. Toxicol. 14:99-103.

Fantel, A.G., J.C. Greenaway, M.R. Juchau, and T.H. Shepard. 1979. Teratogenic Bioactivation of Cyclophosphamide In Vitro. Life Sci. 25:67-72.

Fishbein, L. 1974. Toxicity of Chlorinated Biphenyls. Ann. Rev. Pharmacol. 14:139-156.

Gibson, J.E. and B.A. Becker. 1968a. The Teratogenicity of Cyclophosphamide in Mice. Cancer Res. 28:475-480.

Gibson, J.E. and B.A. Becker. 1968b. Effect of Phenobarbital and SKF 525A on the Teratogenicity of Cyclophosphamide in Mice. Teratology 1:393-398.

Hales, B.F. 1981a. Modification of the Teratogenicity and Mutagenicity of Cyclophosphamide With Thiol Compounds. Teratology 23:373-381.

Hales, B.F. 1981b. Modification of the Mutagenicity and Teratogenicity of Cyclophosphamide in Rats With Inducers of Cytochrome P-450. Teratology 24:1-11.

Kimbrough, R., J. Buckley, L. Fishbein, G. Flamm, L. Kasza, W. Marcus, S. Shibko, and R. Teske. 1978. Animal Toxicology. Environ. Hlth. Persp. 24:173-184.

Knudsen, T.B. and D.M. Kochhar. 1981. Limb Development in Mouse Embryos. III. Cellular Events Underlying the Determination of Altered Skeletal Patterns Following Treatment With 5'-Fluoro-2-Deoxyuridine. Teratology 23:241-251.

MONS 005047

Loose, L.D., J.B. Silkworth, S.P. Mudzinski, K.A. Pittman, K.F. Benitz, and W. Mueller. 1979. Modification of the Immune Response by Organochlorine Xenobiotics. Drug Chem. Toxicol. 2:111-132.

Lucier, G.W., G.J. Davis, and J.A. McLachlan. 1978. Transplacental Toxicology of the Polychlorinated and Polybrominated Biphenyls. In: D.D. Mahlum, M.R. Sikov, P.L. Hackett, and F.D. Andrew (eds.), "Developmental Toxicology of Energy-Related Pollutants," pp. 188-203. Technical Information Center, U.S. Department of Energy CONF-771017. Richland, WA, October 17-19, 1977.

Marks, T.A., G.L. Kimmel, and R.E. Staples. 1981. Influence of Symmetrical Polychlorinated Biphenyl Isomers on Embryo and Fetal Development in Mice. I. Teratogenicity of 3,3',4,4',5,5'-Hexachlorobiphenyl. Toxicol. Appl. Pharmacol. 61:269-276.

McConnell, E.M., J.R. Hass, N. Altman, and J.A. Moore. 1979. A Spontaneous Outbreak of Polychlorinated Biphenyl (PCB) Toxicity in Rhesus Monkeys (Macaca mulatta): Toxicopathology. Lab. Anim. Sci. 29:666-673.

Manson, J.M. and C.C. Smith. 1977. Influence of Cyclophosphamide and 4-Ketocyclophosphamide on Mouse Limb Development. Teratology 15:291-299.

Matthews, H., G. Fries, A. Gardner, L. Garthoff, J. Goldstein, Y. Ku, and J. Moore. 1978. Metabolism and Biochemical Toxicity of PCBs and PBBs. Environ. Hlth. Persp. 24:147-155.

Mirkes, P.E., A.G. Fantel, J.C. Greenaway, and T.H. Shepard. 1981. Teratogenicity of Cyclophosphamide Metabolites: Phosphoramide Mustard, Acrolein, and 4-Ketocyclophosphamide in Rat Embryos Cultured In Vitro. Toxicol. Appl. Pharmacol. 58:322-330.

Murthy, V.V., B.A. Becker, and W.J. Steele. 1973. Effects of Dosage, Phenobarbital, and 2-Diethylaminoethyl-2,2-Di-Phenylvalerate on the Binding of Cyclophosphamide and/or its Metabolites to the DNA, RNA, and Protein of the Embryo and Liver in Pregnant Mice. Cancer Res. 33:664-670.

Myers, C.E. 1981. The Pharmacology of the Fluoropyrimidines. Pharmacol. Rev. 33:1-15.

Report. 1976. Final Report of the Subcommittee on the Health Effects of Polychlorinated Biphenyls and Polybrominated Biphenyls. Department of Health, Education, and Welfare, Washington, DC.

MONS 005048

Tilson, H.A., G.J. Davis, J.A. McLachlan, and G.W. Lucier. 1979. The Effects of Polychlorinated Biphenyls Given Prenatally on the Neurobehavioral Development of Mice. Environ. Res. 18:466-474.

Watanabe, M. and Sugahara, T. 1981. Experimental Formation of Cleft Palate in Mice With Polychlorinated Biphenyls (PCB). Toxicology 19:49-53.

MONS 005049

PART IV

THE EFFECTS OF PCBs ON HUMAN HEALTH

CHAPTER 20

THE EPIDEMIOLOGY OF PCBs

William R. Gaffey
Monsanto Company
St. Louis, Missouri 63167

INTRODUCTION

This is a review and evaluation of the epidemiologic evidence concerning the health effects of exposure to polychlorinated biphenyls (PCBs), particularly at levels that do not cause acute toxic effects. A study is considered "epidemiologic evidence" if it measures, directly or indirectly, the differences in the risk of ill health among populations with different exposures to PCBs.

In the past several decades there have been many clinical studies of the effects of heavy exposures to PCBs (e.g., Von Wedel et al., 1943; Schwartz, 1936). Such studies are extremely useful in identifying the kinds of effects that should be investigated. However, they do not address the question of the risk of incurring such effects and are, therefore, not included in this review.

The studies reviewed here fall into three categories. First, there are studies of accidental heavy exposures and the resulting acute and chronic effects. In each case the study was prompted by an outbreak of illness or the occurrence of a death in an exposed population, after which the population was studied.

Second, there are studies of the relationship between exposure to PCBs and the resulting body burden of PCBs in serum or adipose tissue. Strictly speaking, these are not epidemiologic studies since they do not deal with health effects. However, if a relationship between level of exposure and body burden cannot be verified, the interpretation of epidemiologic studies becomes difficult if not impossible.

MONS 005051

The third category is studies that were done because the populations in question were known or suspected to be exposed to PCBs, rather than because some untoward health outcome had been observed first.

Many published reports combine some or all of these types of investigations. In the sections that follow, we consider first the studies of accidental over exposure; second, the studies of PCB exposure versus body burden; and third, the epidemiologic studies of exposed populations. In the latter section, the discussion will be organized with respect to the health effects that were investigated. These are:

(1) dermatologic symptoms,
(2) biochemical alterations,
(3) other symptoms and illnesses,
(4) carcinogenicity.

ACCIDENTAL HEAVY EXPOSURE

Two epidemiologic studies of accidental exposure have been reported. The first (Meigs et al., 1954) described an outbreak of chloracne in a plant in which a process change had introduced an unspecified PCB compound into the work environment. Breathing zone levels of PCB were stated to be 0.1 mg/m^3. Seven of 14 exposed workers developed chloracne, but liver function tests were normal in six of these, with some borderline abnormalities in the seventh. The chloracne disappeared after treatment, and the single borderline liver function abnormality improved, but did not disappear after 13 months. Improved process control prevented any recurrence.

Although the estimated PCB level must be accepted with reservation because of the state of the art at that time, it is clear that the chloracne resulted from the PCB exposure. Given the lack of controls and the small rate of abnormal liver function, it is unlikely that the PCB exposure had any connection with the liver function findings.

The second incident is the now famous Yusho incident in 1968 which has been documented in many reports (Kuratsune et al., 1972; Urabe et al., 1979) in which some thousand Japanese became ill after eating cooking oil which had been contaminated with Kanechlor 400, a PCB compound of Japanese manufacture.

The most common acute symptoms observed were hyperpigmentation and acne-like lesions, discharge from the eyes, central nervous system symptoms, and vomiting and diarrhea. There was a dose-response relationship between the amount of oil ingested

MONS 005052

and the proportion of persons reporting symptoms. Three years later about half the patients had improved, but still had symptoms. Six years later many patients still reported such symptoms as headache, stomach pain, numbness of the extremities, joint pain, and respiratory symptoms.

Out of ten live births to women affected by Yusho, nine showed hyperpigmentation and most had increased eye discharges. These symptoms later disappeared. Although there have been reports of premature eruption of teeth (2 children out of a series of 13) and unusally wide fontanelles and sagittal sutures (3 out of 13), it is not at all clear that these findings represent any more than the normal variation to be expected, since no control observations were made (Funatsu et al., 1972).

In general, laboratory tests of the Yusho victims showed elevated serum triglyceride levels, low serum cholesterol in serious cases, and elevated serum glutamic-oxaloacetic transaminase (SGOT) and serum glatamic-pyruvic transaminase (SGPT) levels in serious cases (Higuchi, 1976).

As of the end of 1977, fifty-one deaths among Yusho patients had been identified. The percentage of cancer deaths (35.4) exceeded that of the prefecture in which the deaths occurred (21.1). However, the figures do not appear to be very useful for several reasons. First, after the original incident, the criteria for diagnosis of Yusho had been changed, so that it is impossible to determine the denominator which produced this number. The completeness of ascertainment of the deaths is unknown. In addition, no adjustment for age appeared to have been made in the above comparison. Finally, the average elapsed time from exposure to death was less than ten years, and cannot be calculated precisely because the dates of death are not provided. This may well be too short a period for cancers resulting from the exposure to show up.

Although the Yusho incident represented a massive ingestion of PCBs, recent reanalysis of the cooking oil and of the estimated intake by the patients shows that the exposure to polychlorinated dibenzofurans (PCDFs) and polychlorinated quaterphenyls (PCQs) was about equal to the exposure to PCBs, and current determinations of PCQs in blood and other tissues of Yusho patients have shown levels similar to that of PCBs (Kimbrough, 1980). It is, therefore, doubtful whether any generalization can be made from this incident to lower level environmental or occupational exposures to PCBs.

ENVIRONMENTAL LEVELS AND BODY BURDENS

Two studies of the relationship between ingestion of PCBs and blood levels of PCBs have been reported (MDPH, 1975; Kreiss et al., 1981). In each case the study was concerned with ingestion of fish known to contain relatively high levels of PCBs. In the first, an association was found between blood PCBs and exposure level as estimated by the amount of Lake Michigan sport fish consumed. In the second, the relationship between blood PCBs and a complex of factors was examined in a population in an area with high levels of environmental contamination. Age, sex, and fish consumption, in that order of importance, were associated with blood levels of PCBs. To the extent that fish consumption measures ingestion of PCBs, these studies confirm that blood PCBs are a function of ingestion of PCBs as well as of age and sex. Other associated variables were examined in Kreiss et al. (1981) but will be discussed in the following section.

A number of studies of blood PCBs and exposure to PCBs have been made, most of them in conjunction with studies of health effects. The portions of the studies relevant to this section are reviewed here.

There are three types of studies. The first compares groups which have had different exposure levels as estimated from process considerations or environmental measurements. For convenience, such a study design will be called Type A. The second, which we will designate Type B, measures the change over time in a single group after PCBs have been removed from the environment (or after the group has left the environment). The third, Type C, compares groups that have had different durations of exposure. Often the same report will contain more than one type of study. For example, an exposed group may be compared with an unexposed group (Type A) and within the exposed group long-term exposed workers may be compared with short-term workers (Type C).

The measure of body burden has in most cases been a single number representing, depending on the study, blood PCBs, plasma PCBs, serum PCBs (all of which are called "blood" PCBs in this review), or level of PCBs in adipose tissue. Analytic methods have varied over time and among investigators. More recently, measures of body burden have sought to determine separately the levels of higher chlorinated biphenyls (5 or more chlorine atoms per molecule) and lower chlorinated biphenyls.

Table 1 lists the studies considered in this section, with the type of design and whether or not separate determinations of higher and lower chlorinated biphenyls were made. All of the studies except Baker et al. (1980) are occupational.

MONS 005054

TABLE 1

Studies of Environmental Levels and Body Burden of PCBs by Type of Body Burden Measure

Study	Study Type[a]	High and Low Chlorinated PCBs	Adipose PCBs
Baker et al., 1980	A	No	No
Bumgarner et al., 1973	C	No	No
Chase et al., 1982	A,C	No	Yes
Hara et al., 1974, 1975	B,C	No	No
Hasegawa et al., 1972	A,B,C	No	No
Inoue et al., 1975	A,C	No	No
Karppanen and Kolho, 1973	A	No	Yes
Kitamura et al., 1973	B	No	No
Maroni et al., 1981a	A,C	Yes	No
Ouw et al., 1976	A,B	Yes	No
Smith et al., 1982	A,C	Yes	No

[a]A = Comparisons of groups with different exposure levels
B = Evaluation of results of decreasing or removing exposure
C = Comparisons of groups with different durations of exposure

All of the Type A studies agree in showing a higher body burden of PCBs in populations with higher environmental exposure, except for one anomaly in Baker et al. (1980). There, persons exposed to sludge containing PCBs had slightly lower blood levels than the controls, on the average. However, the sludge-exposed persons and the controls were not matched for age, which Kreiss et al. (1981) showed to be the most important factor associated with blood PCB level. It, therefore, appears unequivocal that higher exposure to PCBs means a higher body burden, all other things being equal.

The Type B studies appear at first glance to be more equivocal (Table 2). Two studies show a decrease when exposure ceased or decreased and two do not. However, the studies showing no decrease remeasured their study groups within a month or two after exposure changed. The ones showing a decrease remeasured after three months and one year.

The fact that Ouw et al. (1976) found no decrease after two months while Kitamura et al. (1973) found over a 50 percent

TABLE 2

Studies of Blood PCB Levels Before and After Exposure Levels Changed, and Interval From Exposure Change to Remeasurement

Study	Exposure Change	Interval to Remeasurement (months)	Decrease in Blood PCB Level (percent)
Hara et al., 1974, 1975	Ceased	12	ca75
Hasegawa et al., 1972	Ceased	1	None
Kitamura et al., 1973	Ceased	3	>50
Ouw et al., 1976	Decreased	2	None

decrease after three months gives rise to some uneasiness. However, in the former study exposure was decreased but still present, while in the latter study PCB use had ceased. Ouw et al. (1976) also suggest that after exposures in their study plant had decreased, workers did not wear gloves as recommended, so that the blood PCB levels may have resulted from skin contact.

Table 3 shows the findings for the Type C studies other than Maroni et al. (1981a) and Smith et al. (1982) that is, for those that compared duration of exposure with a single measurement of blood PCB level. The results are not consistent. The study of Bumgarner et al. (1973) found very low levels (average 4 ug/kg) in exposed workers, which may have accounted for their failure to find a relationship with duration. On the other hand, the exposed workers in Hasegawa et al. (1977) had an average level of 370 ug/kg and still showed no relationship with duration.

The studies of Maroni et al. (1981a) and Smith et al. (1982) suggest a possible explanation. Maroni et al. (1981a) made separate comparisons of high chlorinated PCBs and low chlorinated PCBs between workers with present and past exposures. They found differences in the low chlorinated PCBs but not in the high chlorinated compounds. Even though their analysis did not adjust for age, it suggests that the relationship between blood PCB levels and duration and recency of exposure may be a function of the level of chlorination of the PCBs. Smith et al. (1982), however, in an elaborate analysis

TABLE 3

Studies of PCB Levels by Duration of Exposure

Study	Relationship of Blood PCB to		
	Duration of Exposure	Age	Race
Bumgarner et al., 1973	No	No	No
Chase et al., 1982	Yes	Yes	--
Hara et al., 1974, 1975	Yes	--	--
Hasegawa et al., 1972	No	--	--
Inoue et al., 1975	Yes	--	--

of high and low chlorinated blood PCBs versus present and past exposure, found no "evidence either to support or refute different accumulation kinetics in humans for the lower and higher chlorinated biphenyls". Nevertheless, they found a significant correlation between current personal air PCB levels and low chlorinated blood PCBs, but no significant correlation with high chlorinated blood PCBs.

In summary, body burdens of PCBs are clearly related to the level of exposure to environmental PCBs. Observations of a decrease in the burden of PCBs after exposure is eliminated or decreased are not consistent. The lack of consistency may be due to the short periods of observation of some of the studies, or possibly to differences in the average chlorination of the PCBs involved. Studies of the relationship of PCB burden to duration of exposure again are not consistent. There is a suggestion that this may be due to the confounding effects of age and sex, or to differences in the metabolism of high and low chlorinated PCBs, with the higher PCBs being more likely to accumulate in adipose tissue.

EPIDEMIOLOGIC STUDIES OF PCBs AND HEALTH

Excluding mortality studies, there are 18 epidemiologic studies of health effects related to PCB exposure. The accident report of Meigs et al. (1954) is included since it did not

differ in design from many of the studies that were not motivated by accident reports.

These studies are listed in Table 4 with a summary of the findings by major category. Five of the reports are in Japanese (Hara et al., 1974, 1975; Hasegawa et al., 1972; Inoue et al., 1975; Kitamura et al., 1973). The details of those studies are taken from the NIOSH criteria document for PCBs (NIOSH, 1977).

Two of the studies (Kaappanen and Kolho, 1973; SCDH, 1978) are not specific as to health effects. The first of these is a comparison of groups with different work exposures and different blood PCB levels (74-1900 ug/kg in the 12 persons with the greatest exposure) in which the authors simply state that all persons studied were in good health. The second is a study of 32 workers in a capacitor plant, 10 of whom were exposed regularly to PCBs. The authors state that there is "no evidence of physical harm resulting from working with PCBs".

The remaining 16 studies in Table 4 are reviewed below with respect to their findings in each major category of health effects. The studies are considered in the order of their population.

Dermatologic Effects

There are 12 studies of dermatologic effects associated with PCB exposure. The first is Meigs et al. (1954) described in the above section on accidental heavy exposure, who found that 7 of 14 exposed workers got chloracne where the PCB concentration in their breathing zones averaged 0.1 mg/m^3. Hasegawa et al. (1972) reported an unstated number of cases of hyperpigmentation of the hands, and acne-like lesions of the jaw, back, and thighs in exposed workers. The average blood PCBs in the workers was 370 ug/kg. However, the authors state that skin complaints were unrelated to blood PCB levels and appeared to be due to skin contact. Kitamura et al. (1973) reported a range of skin disorders in 10 of 13 exposed workers with an average blood level of 820 ug/kg. The disorders occurred on parts of the body not normally in direct contact with PCBs. Hara et al. (1974, 1975) reported that about 45 percent of 118 capacitor workers complained of blackheads and other acne-like symptoms while working with PCBs. The complaints were not related to blood levels of PCBs, and virtually disappeared within a year after exposure had ceased.

Inoue et al. (1975) reported one case of chloracne in an exposed worked whose blood PCBs were in the 190 to 210 ug/kg range, but no symptoms in the rest of a small work force whose

MONS 005058

TABLE 4

PCB Epidemiology Studies (Other Than Mortality) and Summary of Findings[a]

Study	Dermatologic Findings	Physiological Parameters	Symptoms and Illness	Other
Alvarez et al., 1977	--	Y	--	--
Baker et al., 1980	N	Y	N	--
Bumgarner et al., 1973	--	N	--	--
Chase et al., 1982	Y	Y	Y	--
Fischbein et al., 1979	Y	N	Y	--
Hara et al., 1974, 1975	Y	Y	--	--
Hasegawa et al., 1972	Y	Y	--	--
Inoue et al., 1975	Y	--	--	--
Kaappanen and Kolho, 1973	--	--	--	N
Kitamura et al., 1973	Y	N	--	--
Kreiss et al., 1981	--	Y	N	N
Maroni et al., 1981b	Y	Y	Y	--
Meigs et al., 1954	Y	Y	Y	--
MDPH, 1975	N	--	N	--
Ouw et al., 1976	Y	N	--	--
Smith et al., 1982	Y	Y	Y	--
SCDH, 1978	--	--	--	N
Warshaw et al., 1979	--	Y	Y	Y

[a]Y = Findings associated with exposure
N = No findings associated with exposure
No entry = No data presented

MONS 005059

blood PCBs ranged from 130 to 520 ug/kg. The Michigan Department of Public Health (1975) reported no relationship of any Yusho symptoms to consumption of fish with high levels of PCBs. Ouw et al. (1976) reported 14 cases of dermatitis, eye irritation, or burning sensations on the skin out of 34 exposed workers, where air levels of PCBs ranged from 0.32 to 2.22 mg/m^3. The complaints appeared to occur more often in those with higher blood PCB levels. Fischbein et al. (1979) reported that about 50 percent of 326 capacitor manufacturing workers reported a history of dermatological symptoms, the most common symptom being a rash. Those with symptoms had higher blood levels of high chlorinated PCBs. Baker et al. (1980) reported no chloracne in 18 exposed workers (average blood PCBs 75.1 ug/kg) or 19 members of their families (average blood PCBs 33.6 ug/kg). Maroni et al. (1981b) reported 10 cases of dermatitis (5 diagnosed as active or past chloracne) out of 80 exposed workers. The average blood PCB level in the study was 342 ug/kg. Chase et al. (1982) observed chloracne and an increase in other dermatological findings in 86 exposed male railroad workers, but the findings were not significantly associated with blood or fat PCB levels. Smith et al. (1982) found no chloracne in a study population of 324 exposed workers in capacitor manufacturing and transformer repair, whose average blood PCBs ranged from 38 to 546 ug/kg. However, there was a significant association of skin rash or dermatitis with blood levels of high chlorinated PCBs.

Interpretation of this mass of data is complicated by the difficulty of diagnosing chloracne, the uncertainties of blood PCB determinations, and the changing technology for making such determinations. Nevertheless, the data suggest strongly that when PCB blood levels exceed about 150 to 200 ug/kg, chloracne can occur. However, most studies have shown that the occurrence of chloracne is not further associated with blood PCB levels. This suggests that (a) personal idiosyncratic factors may be involved and/or (b) that the high blood levels are an indicator of the existence of environmental contamination which actually produces chloracne by skin contact.

The reports of dermatitis other than chloracne suffer from an additional complication. According to the National Health Survey, about one-third of all Americans of working age have at least one current skin condition serious enough to warrant evaluation by a physician (NCHS, 1979). Clearly, substantially more than one-third must have either a current condition or a history of such a condition in the past. The prevalence figures reported by Maroni et al. (1981b) and Fischbein et al. (1979) are, therefore, not in themselves remarkable, but the agreement of Fischbein et al. (1979) and Smith et al. (1982) on the relationship between dermatitis and

high chlorinated blood PCBs suggests that this association may be real.

Liver Function -

Ten studies examined liver function. Meigs et al. (1954) found one borderline abnormal liver function in 14 exposed workers. Hasegawa et al. (1972) found mild disturbances in exposed workers (increased SGOT, SGPT, SAP, decreased serum cholinesterase) which they did not consider to be clinically significant. Kitamura et al. (1973), Ouw et al. (1976), Fischbein et al. (1979), and Baker et al. (1980)(a non-occupational study) found no abnormalities associated with exposure, except that Ouw et al. (1976) found a high BSP retention in four out of seven workers with blood levels above 500 ug/kg.

Maroni et al. (1981b) found 16 out of 80 workers with abnormalities in GGT, OCT, and transaminases. Their blood PCB levels were higher than those in the workers with normal liver function. Kreiss et al. (1981)(non-occupational study) found no relation between liver function and blood PCBs when age and alcohol consumption were taken into account. Chase et al. (1982) found among exposed railroad workers a statistically significant correlation between blood PCBs and SGOT after adjusting for age. Smith et al. (1982) found elevated SGOT and GGT levels in persons with higher blood PCB levels.

In summary, six studies of the ten found some mild liver function abnormalities, none of which were associated with any measurable adverse health effects. The two non-occupational studies, Baker et al. (1980) and Kreiss et al. (1981), found no abnormalities associated with blood PCB leve. Fischbein et al. (1979) in their study of capacitor manufacturing workers, noted that "there was a paucity of abnormal results in the biochemical studies."

Finally, Alvares et al. (1977) reported that in five workers occupationally exposed to PCBs, the rate of drug metabolism was significantly higher than in a group of controls matched for age, sex, and smoking and drinking habits.

Fat Metabolism

Six studies considered cholesterol levels. One (Bumgarner et al., 1973) found no relationship between cholesterol level and blood PCB level. One of the remaining five (Hasegawa et al., 1972) found a decrease in cholesterol, glycerides,

phospholipids, and beta-lipoprotein in exposed workers. Three of the other four studies found no relationship of cholesterol to blood PCBs (Baker et al., 1980; Chase et al., 1982; Smith et al., 1982) while one found increased cholesterol at higher blood levels of PCBs (Kreiss et al., 1981). Kreiss et al.)1981) and Smith et al. (1982) also present contradictory findings with respect to HDL cholesterol levels; the former found no relationship to blood PCBs, but the latter found an inverse relationship.

Five studies examined triglyceride levels. Four found an increase with increased blood PCBs (Hara et al., 1974, 1975; Baker et al., 1980; Chase et al., 1982; Smith et al., 1982) while one found no relationship when cholesterol level was taken into account (Kreiss et al., 1981).

In summary, most studies, including one non-occupational study, have associated increased triglycerides with PCB exposure. The data on cholesterol show no relationship in three studies, and an increase and decrease in one study each. HDL cholesterol either decreased or was unchanged (one study each). Even if PCB exposure has some effect on fat metabolism, it appears to be without any apparent clinical significance.

Blood and Blood Pressure

There are five studies of blood chemistry: Bumgarner et al. (1973), Kitamura et al. (1973), Fischbein et al. (1979), Baker et al. (1980), and Maroni et al. (1981b). None of them report any relationship of blood chemistry to PCB levels.

Bumgarner et al. (1973) and Kreiss et al. (1981) measured blood pressure in exposed persons. Bumgarner et al. (1973) found no association with PCBs, but Kreiss et al. (1981) found a statistically significant association between diastolic blood pressure and blood PCBs. Since there was no control group and since Kreiss et al. (1981) are the only investigators to report this finding, its significance is not clear at this time.

Symptoms, Illness, and Other Conditions

Eight studies investigated symptoms, illness, and other conditions in persons exposed to PCBs. None of the three non-occupational studies reported any abnormalities. The first of these (MDPH, 1975) compared the incidence of 18 conditions, most of which were reported in Yusho disease, in consumers of sports fish containing PCBs and in controls. The second (Baker et al., 1980) found none of the following conditions were associated with blood PCB levels in a community study; fever,

weight loss, anorexia, fatigue, headache, eye irritation, cough, shortness of breath, nausea, vomiting, diarrhea, abdominal pain, arthralgia, and persistent rash. The third study (Kreiss et al., 1981) reported the same thing for prevalence of illness or weight loss in the preceding year, use of medication, use of medical care, history of heart disease, and percentage of pregnancies ending in miscarriage, stillbirth, or infant death.

Of the occupational studies, Chase et al. (1982) reported no evidence of organ toxicity from the medical histories or physical examinations of 86 exposed railroad workers. Three studies reported various symptoms. Fischbein et al. (1979) reported a history of gastrointestinal symptoms in 18 percent of 326 capacitor manufacturing workers, a prevalence of from 3.0 to 15.2 percent of various musculoskeletal symptoms, and a prevalence of from 4.8 to 27.8 of various neurological symptoms. These were, however, unrelated to duration of employment or to level of blood PCBs. Maroni et al. (1981b) reported eight cases of gastrointestinal complaints in 80 exposed workers, with no indication of whether there was a relationship to duration of employment. They also reported two bleeding haemangiomas and one case of chronic myelocytic leukemia. These findings do not appear to have any significance, since they apparently are unrelated to the circumstances of exposure.

Smith et al. (1982) reported an increased prevalence of general malaise and possibly altered peripheral sensation with increased blood PCB levels among occupationally exposed workers, but found no clinical abnormalities on physical examination.

Finally, one study of pulmonary function (Warshaw et al., 1979) reported decreased vital capacity in 243 capacitor workers. However, the pulmonary function values in the study population, most of whom were current or ex-smokers, were compared with a standard population of non-smokers, so that the effect of smoking was not taken into account.

The weight of evidence, as Smith et al. (1982) conclude, is that no studies to date "have shown that occupational exposure to PCBs is associated with any adverse health outcome, to be distinguished from demonstrable subclinical biochemical alterations."

There appear to be no significant clinical effects associated with the occupational or environmental exposures studied in these reports.

Carcinogenicity

It is generally agreed that epidemiologic evidence for carcinogenicity should fulfill certain requirements in order to be acceptable. These requirements, presented below, deal with the study design, the logic of the observed pattern, and the repeatability of the results (Doll, 1981).

(1) Positive associations in groups of individuals with known exposure (case-control or cohort studies).

(2) That are not explained by bias in recording or detection.

(3) That are not explained by confounding.

(4) That are not explained by chance.

(5) That vary appropriately with dose.

(6) That vary appropriately with period of exposure.

(7) That are observed repeatedly in different circumstances.

There are four studies directed solely or primarily to the question of the carcinogenicity of PCBs. Table 5 lists the studies and their findings. They are reviewed here keeping in mind Doll's requirements.

The most obvious feature in Table 5 is that no study agrees with any other. That is, the requirement of repeatability is not met.

The first study by Bahn et al. (1976, 1977) observed three melanomas in a group of 92 research and development and refinery workers. These workers had an unknown exposure to other possible carcinogens, so that there could have been confounding. In any case, the study was withdrawn for revision in the definition of the exposed population, and has not yet been released (NIOSH, 1977).

Zack and Musch (1982) studied 89 Monsanto workers exposed for at least six months between 1945 and 1965 inclusive. There were no deaths from cancer of the liver or cirrhosis. The excess in respiratory cancer was based on four deaths and was not statistically significant. As with Bahn et al. (1976, 1977), there was confounding because of other chemical exposure at the plant and, in this case, possibly cigarette smoking.

TABLE 5

Inconsistencies in Studies of Cancer in PCB Exposed Populations With Findings

Study	Number Studied	Findings
Bahn et al., 1976; 1977	92	Melanoma[a]
Zack and Musch, 1982	89	Lung
Brown and Jones, 1981	2,567	Liver Rectum
Bertazzi et al., 1981	1,310	Digestive[b], Lymphatic, and hematopoietic

[a]Significant at 1 percent level
[b]Significant at 5 percent level

Brown and Jones (1981) studies 2,567 workers in a capacitor plant. About half the cohort had a latency period of 20 yrs or more. Although there was an excess of liver cancer deaths, it was inversely related to duration and latency of exposure, which does not support an occupational explanation. There was also an excess of rectal cancer. However, the two plants studied are located in an area whose mortality from rectal cancer is greater than the U.S. average (Mason et al., 1975). Since U.S. population rates were used as a basis for comparison, the rectal cancer excess is at least partly an artifact.

Bertazzi et al. (1981) studied 1,310 workers with at least six months employment in capacitor manufacturing between 1946 and 1970. Although excess digestive cancer was observed, there were no liver cancer deaths. The total number of deaths was small (27) and the excess cancer observed was based on two or three deaths for each of the two major sites involved. There is no indication of the duration or latency of exposure for the cancer deaths. The authors state that there were no other major exposures at the plant, and propose to continue the study with a larger cohort. In spite of the statistical significance of the excesses from all cancers, this study must be considered a preliminary report, particularly since it shares with the other studies a failure to agree on any particular pattern of mortality.

The existing mortality studies of occupational exposure do not show the agreement that would lead one to infer an excess risk of cancer. Much of the conflicting findings can be attributed to the possible effect of confounding exposures, and to the "noise level" of sporadic excesses which would be expected in the absence of any occupational hazard.

SUMMARY AND CONCLUSIONS

The epidemiologic studies of exposure to PCBs show that the body burden in exposed persons, whether the exposure is by ingestion, inhalation, or skin contact, is related to the environmental levels and distribution of PCB. The relation of body burden to duration of exposure is less clear, and appears to differ depending on the degree of chlorination of the PCBs. Nevertheless, the evidence is clear that higher exposures mean higher blood PCB levels, and that persons with occupational exposures have blood PCB levels that may be an order of magnitude greater than that of environmentally (that is, non-occupationally) exposed persons.

Occupational exposure to PCBs at high levels has been associated with the occurrence of chloracne, but the relationship is not straightforward, suggesting that the actual risk of chloracne is also a function of individual susceptibility and personal work habits, as well as possible exposure to other contaminants.

Dermatologic problems other than chloracne are associated with occupational exposure, and may be related to exposure to high chlorinated PCBs.

Alterations of liver function and fat metabolism associated with PCB exposure have been observed in several studies, but are characterized by investigators as mild and of no clinical significance.

The one fact on which all occupational studies of health effects agree is that there has been no clinical illness associated with PCB exposure other than dermatitis. Studies of non-occupationally exposed populations have found neither dermatitis nor other clinical evidence of exposure-related effects, with the exception of a single study which suggests that diastolic blood pressure may be related to blood level of PCBs.

Mortality studies concerned primarily with cancer present problems of interpretation due to the small sample size of some of the studies, and to the confounding effect of other

exposures. However, they do exhibit a pattern, which is that none of the studies agree on the cancer sites at which an excess mortality was found, and the excesses that were found are in general not statistically significant. One must conclude that the findings of the mortality studies reflect a sporadic pattern of excess mortality at different sites which is not consistent with a carcinogenic effect of PCBs. In addition, where an examination of duration and latency of exposure was possible, no association with these variables was found (Brown et al., 1981).

Taken as a whole, the epidemiologic studies find that high occupational exposures to PCBs may cause dermatitis of various kinds, but that there are no other clinically observable effects, including the occurrence of cancer.

LITERATURE CITED

Alvares, A.P., A. Fischbein, K.E. Anderson, and A. Kappas. 1977. Alterations in Drug Metabolism in Workers Exposed to Polychlorinated Biphenyls. Clin. Pharmacol. Ther. 22:140-146.

Bahn, A.K., P. Grover, I. Rosenwaike, K. O'Leary,and J. Stellman. 1977. PCB? and Melanoma. N. Engl. J. Med. 296:108.

Bahn, A.K., I. Rosenwaike, N. Herrman, P. Grover, J. Stellman, and K. O'Leary. 1976. Melanoma After Exposure to PCBs. N. Engl. J. Med. 295:450.

Baker, E.L., P.J. Landrigan, C.L. Glueck, M.M. Zack, J.A. Liddle, V.W. Burse, W.J. Houseworth, and L.L. Needham. 1980. Metabolic Consequences of Exposure to Polychlorinated Biphenyls (PCB) in Sewage Sludge. Amer. J. Epidemiol. 112:553-563.

Bertazzi, P.A., C. Zocchetti, S. Guercilena, M.D. Foglia, A. Pesatori, and L. Riboldi. 1981. Mortality Study of Male and Female Workers Exposed to PCBs. International Symposium on Prevention of Occupational Cancer, April, 1981, Helsinki, Finland, pp. 1-15.

Brown, D.P. and M. Jones. 1981. Mortality and Industrial Hygiene Study of Workers Exposed to Polychlorinated Biphenyls. Arch. Environ. Health 36:120-129.

Bumgarner, J.E., D.I. Hammer, A.V. Colucci, J.P. Creason, and J.F. Finklea. 1973. Polychlorinated Biphenyl Residues in Refuse Workers. Research Triangle Park, North Carolina, USDHEW, PHS, NIEHS, 10 pp. (as reported in NIOSH criteria document).

Chase, K.H., O. Wong, D. Thomas, P.W. Berney, and R.K. Simon. 1982. Clinical and Metabolic Abnormalities Associated With Occupational Exposure to Polychlorinated Biphenyls (PCBs). J. Occup. Med. 24:109-114.

Doll, R. 1981. Relevance of Epidemiology to Policies for the Prevention of Cancer. J. Occup. Med. 23:601-609.

Fischbein, A., M.S. Wolff, R. Lilis, J. Thornton, and I.J. Selikoff. 1979. Clinical Findings Among PCB Exposed Capacitor Manufacturing Workers. Ann. N. Y. Acad. Sci. 320:703-714.

Funatsu, I., F. Yamashita, Y. Ito, S. Tsugawa, T. Funatsu, T. Yoshikane, M. Hayashi, T. Kato, M. Yakushiji, G. Okamoto, S. Yamasaki, T. Arima, T. Kuno, H. Ide, and I. Ide. 1972. Polychlorobiphenyls (PCB) Induced Fetopathy I. Clinical Observation (Abstract No. 72-2360) Kurume Med. J. 19:43-51.

Hara, I., A. Harada, S. Kimura, T. Endo, and K. Kawano. 1974. Follow-Up Study of Condenser Factory After Use of PCB Discontinued. Part I. Jpn. J. Ind. Health 16:365-366.

Hara, I., A. Harada, S. Kimura, T. Endo, and K. Kawano. 1975. Follow-Up Study of Condenser Factory After Use of PCB Discontinued. Part III. Jpn. J. Ind. Health 17:371-372.

Hasegawa, H., M. Sato, and H. Tsuruta. 1972. Report on Survey of Work Area Environment Where PCB is Handled and of the Health of Workers Handling PCB. Special Report on Prevention of Environmental Pollution by PCB-Like Substances. Japan, Research Coordination Bureau, Science and Technology Agency, pp. 141-199.

Higuchi, K. (ed.). 1976. PCB Poisoning and Pollution. Academic Press, NY, p. 5.

Inoue, Y. 1975. Discovery of PCB Pollution in a Textile Factory I. PCB in Blood Serum of Laborers and Results of Physical Examination. Jpn. J. Pub. Health 22:461-463.

Kaappanen, E. and L. Kolho. 1973. The Concentration of PCB in Human Blood and Adipose Tissue in Three Different Research Groups: PCB Conference II. Stockholm, Sweden. National Swedish Envionmental Protection Board (Pub. 1973; 4E), pp. 124-128.

Kimbrough, R. (ed.). 1980. Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products. Chapter 9, 21, Elsevier/North Holland Biomedical Press, Amsterdam.

MONS 005068

Kitamura, T., T. Tsukamoto, K. Sumino, K. Hayakawa, T. Shibata, and I. Hirano. 1973. PCB in Blood of Workers Employed in an Electrical Parts Manufacturing Plant. Jpn. J. Ind. Health 15:539.

Kreiss, K., M.W. Zack, R.D. Kimbrough, L.L. Needham, A.L. Smrek, and B.T. Jones. 1981. Association of Blood Pressure and Polychlorinated Biphenyl Levels. JAMA 245: 2505-2509.

Kuratsune, M., M. Takesumi, J. Matsuzaka, and A. Yamaguchi. 1972. Epidemiology Study on Yusho. Environ. Health Perspect. 1:119-128.

Maroni, M., A. Colombi, S. Cantoni, E. Ferioli, and V. Foa. 1981a. Occupational Exposure to Polychlorinated Biphenyls in Electrical Workers. I. Environmental and Blood Polychlorinated Biphenyls Concentrations. Br. J. Ind. Med. 38:49-54.

Maroni, M., A. Colombi, G. Arbosti, S. Cantoni, and V. Foa. 1981b. Occupational Exposure to Polychlorinated Biphenyls. II. Health Effects. Br. J. Ind. Med. 38:55-60.

Mason, T.J., F.W. McKay, R. Hoover, W.J. Blot, and J.F. Fraumeni. 1950-1969. Atlas of Cancer Mortality for U.S. Counties. DHEW Pub. No. (NIH) 75-780, Department of Health, Education, and Welfare, Washington, DC.

Meigs, J.W 1954. Chloracne From an Unusual Exposure to Arochlor. JAMA 154:1417-1418.

MDPH. 1975. Final Report on FDA Contract 223-73-2209. Evaluation of Changes in the Level of Polychlorinated Biphenyls (PCBs) in Human Tissue. Michigan Department of Public Health, Lansing, MI.

NCHS. 1971-1974. Skin Conditions and Related Need for Medical Care Among Persons 1-74 Years. USDHEW Pub. No. (PHS) 79-1660, National Center for Health Statistics, Department of Health, Education, and Welfare, Washington, DC.

NIOSH. 1977. Criteria for a Recommended Standard - Occupational Exposure to Polychlorinated Biphenyls (PCBs). USDHEW, NIOSH Pub. No. 77-225.

Ouw, H.K., G.R. Simpson, and D.S. Siyali. 1976. Use and Health Effects of Arochlor 1242, a Polychlorinated Biphenyl, in an Electrical Industry. Arch. Environ. Health 31:189-194.

Schwartz, L. 1936. Dermatitis From Synthetic Resins and Waxes. Amer. J. Public Health 26:586-592.

MONS 005069

Smith, A.B., J. Schloemer, L.K. Lowry, A.W. Smallwood, R.N. Ligo, S. Tanaka, W. Stringer, M. Jones, R. Hervin, and C.J. Glueck. 1982. Metabolic and Health Consequences of Occupational Exposure to Polychlorinated Biphenyls. Br. J. Ind. Med. 39:361-369.

SCDH. 1978. Study of Pickins, SC Plant of Sangamo Capacitor Division (News Report). South Carolina Department of Health and Environmental Control, Columbia, South Carolina.

Urabe, H., H. Koda, and M. Asahi. 1979. Present State of Yusho Patients. Ann. N. Y. Acad. Sci. 320:273-276.

Von Wedel, H., W.A. Holla, and J. Denton. 1943. Observations on the Toxic Effects Resulting From Exposures to Chlorinated Naphthalene and Chlorinated Phenyls With Suggestions for Prevention. Rubber Age 54:419-426.

Warshaw, R., A. Fischbein, J. Thornton, A. Miller, and I.J. Selikoff. 1979. Decrease in Vital Capacity in PCB-Exposed Workers in a Capacitor Manufacturing Facility. Ann. N. Y. Acad. Sci. 320:277-283.

Zack, J.A. and D.C. Musch. 1982. Mortality of PCB Workers at the Monsanto Plant in Sauget, Illinois. In preparation.

CHAPTER 21

POPULATION STUDIES OF PCBs IN MICHIGAN RESIDENTS

Harold E.B. Humphrey
Center for Environmental Health Sciences
Michigan Department of Public Health
Lansing, Michigan

INTRODUCTION

Between 1929 and 1977, about 1.4 billion pounds of polychlorinated biphenyls (PCBs) were produced in this country. Although U.S. production of the chemical has ceased, it is estimated that 750 million pounds are still in service (Miller, 1982). The rest has been exported, destroyed, buried, or lost to the environment. Acknowledgment that PCB is a worldwide pollutant serves as proof that past and potential future losses to the environment are not insignificant.

The Great Lakes present a unique situation for long lived contaminants which can bioaccumulate in living organisms. Our lakes act as reservoirs for atmospheric and terrestrial pollutants such as PCB. The relatively slow turnover and removal of contaminants plus biomagnification in the food chain make the aquatic environment of the Great Lakes a potential source for significant human exposure.

PCB has been shown to be toxic in animals, has a long half-life in mammals, and is present in our environment. Most humans are unavoidably exposed to small quantities of this chemical during their lives. It is not certain whether or not contact with additional sources constitutes an increase in exposure which will produce disease or degraded human health. It is of scientific and public interest to define whether such exposure in the Great Lakes basin has the potential for impact on the population using this resource.

At the Michigan Department of Public Health, we are conducting several cohort studies which examine the extent of

MONS 005071

human-exposure to chemical contaminants. We are attempting to define whether or not possible negative health effects have occurred or may appear as a result of such exposure. In this presentation, I will draw on data collected from our long-term polybrominated biphenyl (PBB) study of farmers from Michigan and Iowa (Landrigan et al., 1979), a long-term study of families exposed to farm products contaminated by PCB's from silos, the 1974 evaluation of Great Lakes fishermen (Humphrey, 1976), and our on-going study of persons who consume Great Lakes fish. Human specimens tested in these studies will demonstrate levels of exposure, and evaluation of interview and medical data collected from participants will document the occurrence of health events in these cohorts.

HUMAN EXPOSURE ASSESSMENT

Human breast milk has been reported to be a good predictor of exposure to fat soluble chemicals (Brilliant et al., 1978). The data shown in Table 1 indicate that PCBs are frequently found in women nationally and always found in women residing

TABLE 1

PCB in Mothers Milk

Study	Number of Women	PCB (Fat Basis) Concentration (mg/kg) Detectable (percent)	Median	Range
1975 National	1,038	69	--	--
1977-78 Serv. Testing	1,057	100	1.35	0.3 - 5.1
1976 Random Survey	95	100	0.82	0.1 - 3.3
1980-81 HDET Study	120	100	0.96[a]	0.2 - 3.0
1974 Fish Eater 12.73 kg/yr	1	--	4.0	--
Silo Daughter	1	--	13.0	--

[a]Mean

MONS 005072

in Michigan. Monitoring of the general population indicates that most people receive a background exposure to this ubiquitous chemical contaminant. It is of interest to note that persons exposed to additional known sources of PCB receive significantly greater exposures. The consumption of contaminated fish from the Great Lakes or food from a farm with a PCB coated silo appear to significantly increase contaminant levels in breast milk.

The extent of PCB exposure can also be demonstrated by evaluation of serum specimens from population groups. The lower fat content of blood makes this a less sensitive specimen than breast milk for detecting small exposures to fat soluble chemicals. However, if exposure has been sufficient or long standing as in the case of PCB, circulating levels provide a convenient method for establishing exposure in cohorts. In addition, detection of PCB in blood gives an indication of the level at which the internal organs of the body are exposed to the circulating contaminant. Table 2 shows the range and median levels of PCB found in sera from the four cohorts which we have under evaluation. The data again demonstrate that PCB is commonly found in American citizens at low levels (Michigan and Iowa farmers with median values of between 5 and 6 ug/kg), and at significantly greater levels in persons who consume food which has been shown to be contaminated with PCBs (fish eaters and silo farm families with median values of 56 and 28 ug/kg, respectively). It can be concluded that consumption of Great Lakes fish represents a convenient and substantial way to increase human exposure to PCB.

TABLE 2

PCB Levels Found in Humans

Group	Sample	Number of People	Range (ug/kg)	Median (ug/kg)
Iowa Farmers	Sera	803	5-50	5
Michigan Farmers	Sera	1,631	ND-57	6
Silo Farmers	Sera	149	5-300	28
Fish Eaters	Sera	90	25-366	56

ND = Detection limit of <5 ug/kg

Contaminants from environmental sources would be less of a problem if the chemical was quickly excreted from the body and did not accumulate in fat stores. However, for fat soluble chemicals, this is not the case. Because of its long half-life, many small exposures to PCB result in a gradual increase in body burden. The long-term study of over 4,000 Michigan farmers who have had no extraordinary exposure to sources of PCB has shown that serum PCB levels gradually rise with age (Kreiss et al., 1982). This indicates that unavoidable background exposure results in small but significant increases in human body burden over a lifetime. Additional sources of exposure will add to this background body burden, and such additions will also be retained for long periods of time.

EVALUATION OF PERSONS EATING GREAT LAKES FISH

In his talk earlier today, Dr. Swain indicated that cooked Great Lakes fish provide a significantly greater potential dose of PCB than that provided from water and atmospheric sources combined. Table 3 presents these estimates and shows that habitual fish consumption could provide a dose 4,300 times that estimated from background environmental sources.

Our interest in evaluating the significance of this source of human exposure to PCB led to our 1974 study of 178 persons who consume Great Lakes fish (Humphrey, 1976). This investigation showed that persons from four communities who ate greater than 10.91 kg of fish per year had serum PCB levels which were significantly greater than people from the same communities who rarely ate such fish (Table 4). The contrast in serum PCB levels between groups who never eat fish, rarely

TABLE 3

Comparison of Non-Occupational Sources of PCB Exposure

Estimated Human Exposure	Exposure Source
7.8 ug/yr	Ambient air at 1.9 ng/m^3 air level PCB
2.9 ug/yr	Drinking water at 4 ng/l raw water PCB
46.5 mg/yr	Cooked Lake Michigan fish at 0.4 to 5.4 mg/kg PCB

MONS 005074

TABLE 4

Median Serum PCB Values for Persons From Michigan Communities in 1973

City	Median Serum PCB (ug/kg)	
	Comparison (0-2.73 kg/yr)	Exposed (>10.91 kg/yr)
Traverse City	13	41
Manistee	23	105
Ludington	15	62
South Haven	22	48

TABLE 5

Relationship Between Fish Consumption by Geographical Location and Human Serum PCB Levels

Source of Fish	Consumption (kg)	Number of People	Serum PCB (ug/kg)		
			Range	Mean	Median
--	0	29	ND-41	17.3	15
Lake Michigan	0-2.73	39	ND-41	18.5	20
Lake Michigan	10.91-118	90	25-366	72.7	56
Lake St. Clair	5-66.8	15	ND-38	19.4	17

ND = Detection limit of <5 ug/kg

eat fish, eat more than 10.91 kg/yr of contaminated Lake Michigan fish, and eat uncontaminated fish from Lake St. Clair is shown in Table 5. The study documented a direct relationship between consumption of contaminated fish and elevated serum PCB levels. Individual serum PCB levels varied as a function of the quantity of fish eaten, type of fish eaten, and history of

fish consumption. Consumption for the "exposed" group ranged from 10.91 kg/yr (an average of about one fish meal per week) to as much as 118 kg/yr. Human blood levels correspondingly ranged from the limit of detection (< 5 ug/kg) to a high of 366 ug/kg. When the exposed group was sorted according to the length of time participants had actively been catching and eating Great Lakes fish, it was found that those who habitually ate fish over the longest period of time had greater serum PCB levels than those who had eaten fish for shorter periods (Table 6).

The 1974 study confirmed that contaminated Great Lakes fish are a source of exposure which contributes to elevated human PCB levels which are significantly greater than background. In addition, the absence of a reduction in PCB levels in the exposed group between fishing seasons when no fish were consumed, and the correlation between the number of years of fish consumption and PCB levels supports the contention that PCB exposure from this source, if sustained, may result in a continuing accumulation of PCB which is retained over time.

The evaluation of human exposure to Great Lakes fish is continuing through a follow-up study currently in progress. In addition to re-evaluation of the participants in the 1974 study, the current work has expanded the cohort to include over 600 persons from 12 communities who eat 10.91 or more kg of Lake Michigan fish per year. An equal number of persons who do not consume fish are being randomly selected and matched for

TABLE 6

Relationship Between Serum PCB Levels and Number of Years of Fish Consumption

Number of Years Fish Eaten	Number of People	Serum PCB (ug/kg)		
		Range	Mean	Median
1-3	9	ND-90	48.9	48
4-6	33	ND-164	56.1	45
7-17	9	15-261	79.8	61
≥ 20	41	12-366	87.1	64

ND = Detection limit of <5 ug/kg

MONS 005076

comparison. This study when finished will provide data on human levels of PCB and 10 other contaminants, 1980-82 fish consumption patterns, regional differences in serum and cooked fish contaminant levels, and comparison to findings from the earlier study. Preliminary data from 1980 on part of the original 1974 cohort show that these people ate less fish in 1980 than they did in 1974 (Table 7). The decline in number of meals and pounds of fish eaten in combination with the general reduction in contaminant levels in Lake Michigan fish reported earlier in this conference appear to have contributed to a decline in serum PCB levels (median of 56 ug/kg in 1974 versus median of 48 ug/kg in 1980). Although these results are encouraging, it should be noted that the range of serum values remains similar to that observed in 1974; many individuals continue to eat large quantities of fish (up to 84 kg/yr in 1980), and the association between consumption of fish and significantly elevated serum PCB levels remains unchanged. Further analysis of the species of fish eaten is also necessary before the data in Table 7 can be confirmed as a real trend or artifact. This evaluation is underway.

EVALUATION OF PCB SILO FARM FAMILIES

Tables 1 and 2 show that persons from farms with silos coated on the interior with a sealant containing PCB are a second group who have received significant non-occupational exposure to PCB. We have had the opportunity to include some of these farm families in our long-term study of PBB exposure. Blood collected from 183 people (60 families) indicated a PCB concentration range nearly equal to that of the fish eater group

TABLE 7

Comparison of Fish Consumption and Serum PCB Levels, 1974 Versus 1980

Persons Consuming >10.91 kg of Fish/Yr	Median Values for Study Year	
	1974	1980
Number of Meals/Yr	60	39
Kilograms of Fish/Yr	14.55	9.55
Serum PCB (ug/kg)	56	48

MONS 005077

and a median serum PCB value (28 ug/kg) which is nearly five times that expected in the general population. Farm family exposure to PCB occurred when the sealant peeled off the silo walls over the years and contaminated the silage eaten by the farm animals. Those families who regularly ate dairy products and beef directly from their own farm unknowingly consumed PCB contaminated food. Because of the relatively small number of farms involved, the domestic food supply for the general public is not believed to have been adversely affected. For the farm families, this situation represents a continuous daily exposure of long duration which contrasts with exposure from fish which is intermittent in nature. Contamination of farm food is presumed to have occurred over many years, possibly greater than twenty since some of the silos which were constructed in the 1940s and 1950s were still in use in the mid-1970s when these families were enrolled. A current survey by the Michigan Department of Agriculture is expected to identify all of the farms in Michigan which have silos contamined by PCBs. Evaluation of persons exposed in this manner is of interest because it provides the opportunity to learn more about the human impact of long-term exposure to PCBs.

HUMAN HEALTH IMPLICATIONS

The cohorts established in Michigan to study persons exposed to halogenated biphenyls constitute the largest such investigation in the country and provide an opportunity to investigate the meaning and significance of such exposure. Specimens from these cohorts have documented the extent of PCB exposure from potential sources of concern. Interview and medical record data which record actual human experiences have been evaluated in an attempt to determine whether or not there is a relationship between symptoms and diseases of toxicological importance and body burden. The difficulty in such an evaluation lies in quantifying subtle or delayed physiological changes in humans which would indicate the presence of a toxic reaction or disease attributable to exposure as predicted from animal experiments. Environmental exposures are seldom extensive enough to produce easily observable toxic effects. Yet, the long half-life of the halogenated biphenyls results in a continuing internal exposure, the outcome of which has not been fully defined in humans.

The medical histories of study participants were obtained by interview and screened for acute, neurological, dermatological, skeletal, and metabolic disorders or diseases characteristic of those presumed to be caused by chlorinated biphenyl exposure. Those exposed to Great Lakes fish did not in 1974 report health problems or medical conditions which could be

correlated with serum PCB levels or fish consumption. The type and frequency of various medical complaints were similar for exposed and comparison persons. Evaluation of data collected during the current investigation is incomplete at this time. Whether or not the lack of symptomatology is due to insufficient exposure, insufficient time since initiation of exposure, or the lack of sensitivity in detecting slowly emerging toxic effects is undecided at this time. Follow-up studies will help clarify this as time passes and diagnostic techniques improve. It should also be noted that this cohort study was not designed to seek out former fishermen who may no longer be up to the rigors of sport fishing because of medical problems or chronic illness. Instead, it was designed to assess exposure in those currently practicing sport fishing on the Great Lakes.

The silo farm family cohort provides an opportunity to evaluate the outcome of long-term continuous PCB exposure. Medical histories for farmers with PCB contaminated silos were reviewed and compared to those of Iowa farmers and Michigan farmers recently exposed to PBBs.

Comparison of reported symptoms (Table 8) showed that the PCB exposed silo farmers had a greater frequency of joint problems and numbness. To a lesser extent, this was also found among the PBB exposed farmers. These symptoms were found to have weak but positive correlation with serum PCB levels when adjusted for age. Such a correlation was not seen for PBB

TABLE 8

Percent Persons Reporting Health Symptoms

Symptom	Percent of Silo Farmers	Percent of Iowa Farmers	Percent of PBB Farmers
Tiredness	14	3	17
Headaches	10	3	10
Rashes	7	<1	4
Skin Problems	4	1	4
Numbness	19	5	10
Joint Problems	20	6	13
Nausea	5	3	11
Number of People	183	1,636	2,150

levels. Although the subjectivity of reported symptoms makes a firm conclusion difficult, the correlation with PCB exposure is interesting because central nervous system and connective tissue defects are possible outcomes of prolonged PCB exposure.

The occurrence of diseases which have been confirmed by medical records were also compared for the three cohorts and are shown in Table 9. Among the diseases evaluated, the 3.3 percent frequency of cancer in the silo farm family cohort was significantly greater than the occurrence of this disease in the other two farm groups and was greater than the 0.3 percent rate predicted by the national Surveillance, Epidemiology, and End Results Program (SEER) cancer morbidity rates. The cancers found in the silo group were located in a variety of sites and occurred more frequently in females, 6.1 percent than males 1.8 percent. This observation is interesting because PCB is considered to be a promoter (Nobuyuki, 1973), a carcinogen (Kimbrough, 1974, 1975, 1979), and is regarded as a human carcinogen (IARC, 1978). The silo families have possibly received a chronic repeated exposure from their diet on a regular basis for over twenty years. It has been speculated that prolonged exposure to a potential carcinogen with a long half-life could produce continuous target organ exposure which would result in tumor production. The occurrence of disease events in the silo farm group also serves an indication of health events which could possibly occur in fish eaters in the future. However, this data should be treated cautiously at this time. The PCB silo cohort is too small to provide appropriate statistical

TABLE 9

Percent Persons Reporting Disease Conditions

Symptom	Percent of Silo Farmers	Percent of Iowa Farmers	Percent of PBB Farmers
Heart	6	4	4
Hepatitis	1	1	1
Diabetes	3	1	2
Thyroid	2	1	2
Tumor (benign)	6	3	4
Cancer	3.3	0.8	0.4
Number of People	183	1,636	2,150

evaluation of events which are occurring and needs to be enlarged to properly evaluate the PCB/cancer hypothesis. The findings to date do demonstrate a lead which should be pursued with continued and expanded surveillance of persons exposed to PCB in this manner.

In conclusion, our cohort studies have provided data which demonstrates a clear relationship between environmental sources of PCB and increased human exposure. Consumption of contaminated fish or farm products results in elevated PCB levels in humans. No acute disease has been identified in exposed individuals, but the long-term outcome of this added body burden remains to be determined. The data generated to date provide viable leads which should be pursued. The cohorts which we have established in Michigan provide an excellent opportunity to continue evaluation of the significance of halogenated biphenyl exposure in humans.

LITERATURE CITED

Brilliant, L.B., K. Wilcox, G. Van Amburg, J. Eyster, J. Isbister, A.W. Bloomer, H.E.B. Humphrey, and H. Prince. 1978. Breast Milk Monitoring to Measure Michigan Contamination With Polybrominated Biphenyls. Lancet 2:643-646.

Humphrey, H.E.B. 1976. Evaluation of Changes of the Level of Polychlorinated Biphenyls in Human Tissues. Final report to the FDA, Michigan Department of Public Health, Lansing, MI, 86 pp.

IARC. 1978. Evaluation of the Carcinogenic Risk of Chemicals to Humans. International Agency for Research on Cancer, IARC Monograph 18:43-103.

Kimbrough, R.D. and R.E. Linder. 1974. Induction of Adenofibrosis and Hepatomas of the Liver of Balb/cd Mice by Polychlorinated Biphenyl (Aroclor 1254). J. Natl. Cancer Inst. 53:547-552.

Kimbrough, R.D., R.A. Squire, R.E. Linder, J.D. Strandberg, R.J. Montali, and V.W. Burse. 1975. Induction of Liver Tumors in Sherman Strain Female Rats by Polychlorinated Biphenyl Aroclor 1260. J. Natl. Cancer Inst. 55:1453-1459.

Kimbrough, R.D. 1979. The Carcinogenic and Other Chronic Effects of Persistent Halogenated Compounds. Ann. N. Y. Acad. Sci. 320:415-418.

Kreiss, K., C. Roberts, and H.E.B. Humphrey. 1982. Serial PBB Levels, PCB Levels and Clinical Chemistries in Michigan's PBB Cohort. Arch. Environ. Hlth. 37:141-147.

Landrigan, P.J., K.R. Wilcox, J. Silva, H.E.B. Humphrey, C. Kauffman, and C.W. Heath. 1979. Cohort Study of Michigan Residents Exposed to Polybrominated Biphenyls: Epidemiological and Immunological Findings. Ann. N. Y. Acad. Sci. 320:284-294.

Miller, S. 1982. The Persistent PCB Problem. Environ. Sci. Technol. 16:98-99A.

Nobuyuki, I., H. Nagaski, M. Arai, S. Makiuri, S. Sugihara, and K. Hirao. 1973. Histopathologic Studies on Liver Tumorigenesis Induced in Mice by Technical Polychlorinated Biphenyls and Its Promoting Effect on Liver Tumors Induced by Benzene Hexachloride. J. Natl. Cancer Inst. 51:1637-1646.

MONS 005082

CHAPTER 22

INTRAUTERINE EXPOSURE OF HUMAN NEWBORNS TO PCBs: MEASURES OF EXPOSURE

Sandra W. Jacobson
Department of Psychology
Wayne State University
Detroit, Michigan 48202

Joseph L. Jacobson
Department of Psychology
Wayne State University
Detroit, Michigan 48202

Pamela M. Schwartz
School of Public Health
University of Michigan
Ann Arbor, Michigan 48109

Greta G. Fein
College of Education
University of Maryland
College Park, Maryland 20742

INTRODUCTION

Behavioral assessment is becoming an important tool for evaluating the consequences of intrauterine exposure to chemical agents routinely encountered in the environment (Fein et al., 1983b; Spyker, 1975). However, studies of the effects of these agents on human infants pose several special problems for research design and for the assessment of behavioral outcomes. The purpose of the present paper is two-fold:

(1) to summarize what is known about the pre- and postnatal effects of an especially ubiquitous chemical compound, polychlorinated biphenyls (PCBs); and

MONS 005083

(2) to examine empirically some of the linkages proposed in an analytic model of PCB exposure in human infants. The linkages of interest are those between the source of contamination and the exposure of mother and infant.

Evidence from several sources indicates that PCBs cross the placenta and are teratogenic in human infants exposed at high levels. PCBs are found in umbilical cord serum at birth when exposure results from ordinary dietary sources, and maternal serum levels are moderately related to fetal serum levels (Kodama and Ota, 1980; Masuda et al., 1978; Polishuk et al., 1977). In separate incidents in Japan and Taiwan, infants of pregnant women who consumed rice oil accidentally contaminated with sizable amounts of PCBs showed elevated PCB serum levels and a set of physical characteristics (e.g., chloracne, brown pigmentation of the skin, swollen eyelids) known in the literature as Yusho (rice oil) disease (Harada, 1976; Higuchi, 1976; Wong and Hwang, 1981). Infants exposed in utero were small-for-gestational age and tended to be born prematurely (Funatsu et al., 1972). Follow-up studies of exposed infants reported an average IQ of 70; sluggish, clumsy, and jerky movement; apathy and hypotonia; autonomic disturbances; and growth impairment (Harada, 1976). These disturbances in responsiveness and neuromuscular organization are consistent with reports of slowed sensory and motor nerve conductance in exposed adults (Chia et al., 1981; Harada, 1976). Although PCB blood levels diminish once exposure ceases, infants born several years after the exposure of their mothers showed elevated PCB blood levels, reduced birth weight, and brown pigmentation of the skin (Abe et al., 1975; Harada, 1976).

Placental passage and fetopathy have also been demonstrated in experimental studies with mammals such as rabbits, mice, rats, and rhesus monkeys (Allen et al., 1980; Bowman et al., 1978; Chou et al., 1979; Masuda et al., 1979; Grant et al., 1971; Tilson et al., 1979). PCBs may cross the placenta more freely as gestation progresses. In mice, higher concentrations are found in the fetus, placenta, and amniotic fluid as parturition approaches (Torok and Weber, 1981).

In rhesus monkeys, prenatally exposed infants weighed less at birth than controls and by 2 months of age developed Yusho-like symptomatology. Behavioral tests given between 6 and 24 months of age revealed hyperlocomotor activity and learning retardation (Bowman et al., 1978); but when tested at 44 months of age, these animals were hypoactive relative to controls (Bowman and Heironimus, 1981). In a follow-up study, adult female monkeys were removed from their PCB diet for a 1 yr period prior to conception (Allen et al., 1980). Although the

physical condition of these animals improved and PCB levels in maternal adipose tissue declined markedly, 4 of the 15 offspring were stillborn. The birth weight of the liveborn infants was reduced relative to nonexposed infants, and four infants died after weaning at 4 months of age. In these studies, animals were fed diets containing only 2.5 or 5.0 mg/kg of PCBs, levels thought at the time to be low. In rhesus monkeys, as in humans (Harada, 1976), teratogenic effects appear in infants whose mothers had consumed PCB prior to, but not during, pregnancy.

When mice were fed relatively low levels of PCBs during pregnancy (32 mg/kg on days 10-16 post-conception), some pups subsequently developed the "spinning syndrome" (Chou et al., 1979; Tilson et al., 1979). More subtle signs of neurobehavioral dysfunctioning appeared in prenatally PCB-exposed mice which did not develop obvious clinical signs of neurotoxicity. Assessments of subtle behavioral functions indicate that exposed but apparently asymptomatic mice have learning deficits and depressed neuromuscular reflexes even though PCBs are no longer detectable in their body tissues (Tilson et al., 1979). A sluggish response to a novel situation and less pronounced habituation have been observed in asymptomatic mice exposed perinatally to PCB doses below those associated with obvious neuromotor disorders (Storm et al., 1981).

Table 1 summarizes the major assessment categories used in teratogenic assessment (Spyker, 1975) and the results of the studies reviewed above. While to date no morphological anomalies have been found to result from fetal exposure to PCBs, such exposure has been associated with clinical symptoms, maturational and growth retardation, and a variety of subtle behavioral deficits.

Consumption of PCB-contaminated fish caught in Lake Michigan constitutes a major source of human exposure to PCBs, with PCB body burden directly related to amount of fish consumed ($r = 0.51$; Humphrey, 1976). Although epidemiological studies of acutely exposed humans and experimental studies of chronically exposed animals indicate that PCBs are injurious, there are problems in extrapolating from studies of humans acutely exposed at high levels to those exposed chronically at low to moderate levels. Even at relatively high levels of consumption of PCB-contaminated fish, chronic exposure is considerably less than that experienced in the rice oil incidents. In contaminated fish eaters, obvious and distinctive Yusho symptoms have not been noted, and infants born to mothers who consume contaminated fish are likely to be clinically asymptomatic. Analyses of the consequences are complicated because the effects of low level chronic exposure are likely to be subtle and may occur in the absence of symptoms typically associated with acute

MONS 005085

TABLE 1

Assessment Categories in the Evaluation of Teratogenic Effects

Assessment Category	Illustration
Morphological characteristics	Anomalies not found in PCB studies
Physical characteristics	Chloracne; brown pigmentation of skin, lips, gums; parchment-like skin; swollen eyelids, face; premature eruption of teeth
Maturational landmarks	Preterm birth (neuromuscular and physical immaturity)
Growth	Small birth size; depressed postnatal growth
Reflexes	"Spinning syndrome" in mice
Activity levels	Hypo- and hyper-activity in an open-field; clinical assessment of apathy
Neuromuscular and sensory motor capacities	Tests of coordination (swimming in mice)
Sensory and attentional functions	Deficits in visual, auditory, olfactory, or attentional functions not found; numbness reported in humans exposed in adulthood
Learning ability	Alteration and reversal learning deficits in monkeys
Autonomic regulation	Inappropriate response to stress; deficits in temperature control; tremulousness
Sexual development	Reproductive failure; menstrual irregularities

MONS 005086

exposure. Although subtle behavioral effects appear in animals exposed to low doses of PCBs, extrapolation from animals to humans is also risky. For example, species differ in their ability to eliminate PCBs, and as a result, the dose required to produce an effect will vary among species. Animal models are an essential aspect of teratogenic testing; however, the findings of this type of research must be corroborated in studies of humans.

The present study involves two groups of humans who are particularly at risk: the pregnant woman and her newborn offspring. The study, which utilizes a prospective longitudinal design, investigates the model shown in Figure 1. In this model, consumption of contaminated lake fish, assumed to be a major source of PCB exposure, results in elevated maternal PCB levels. Elevated maternal body burden has both direct and indirect implications for the developing fetus. Since PCBs cross the placenta, the developing fetus is exposed directly to some part of the mother's body burden. Maternal body burden may also affect maternal health and reproductive capacity, which in turn may influence fetal development. PCBs are also transferred from maternal tissue to breast milk, which provides an additional source of direct exposure for breast-fed infants. In order to evaluate the contribution of these sources of exposure, infant behavioral and medical assessments are administered at birth and again at 5, 7, and 13 months.[1] The longitudinal design is necessary because the effects of low levels of exposure may not appear at birth. Further, subtle behavioral effects may appear in the absence of gross structural anomalies or obvious functional deficits long before classical symptoms of pathology become apparent (Spyker, 1975; Weiss and Spyker, 1974).

Several available measures of PCB contamination are examined. Each of these presents its own set of problems. Since maternal and cord blood are low in lipids, PCBs are difficult to recover. Breast milk, which contains higher lipid levels, can be assessed more reliably but is biologically more removed from the infant, obtained postpartum, and only available for a limited number of women. Maternal reports of fish consumption provide an alternative measure of exposure. They summarize the history of the respondent's exposure in contrast to biological measures, which are limited to a single point in

---

[1]Since the fish consumption interviews were not conducted by the same persons who subsequently collected medical and behavioral data, those engaged in assessment activities were blind with respect to the mother's pattern of fish consumption and infant's potential exposure levels.

MONS 005087

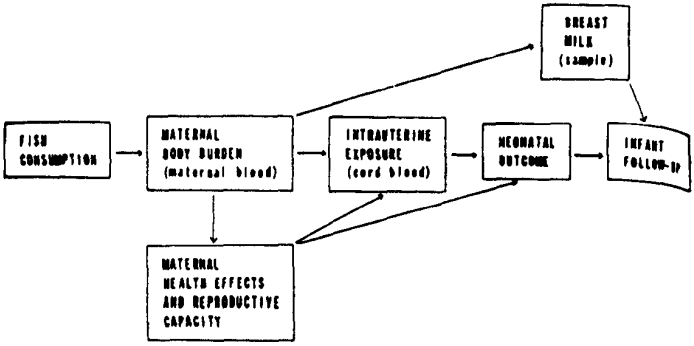


Figure 1. Model of pre- and post-natal exposure to polychlorinated biphenyls via ingestion of contaminated fish.

susceptible to short-term fluctuations. However, maternal recall may be inaccurate, and attempts to adjust for the contaminant levels of the particular species of fish consumed yield at best only rough approximations of exposure. In this report, relations among these various measures of exposure are used to validate critical linkages in the model described above.

METHOD

Subjects

The sample, comprised of 313 infants and their mothers, was drawn from three hospitals in Grand Rapids and one in Muskegon.[2] All mothers delivering at these hospitals were considered eligible to participate with the following exceptions:

---

[2]Results of a state-wide survey of breast milk found PCB levels exceeding 2 mg/kg (fat basis) in 27 percent of the counties in the western part of the lower peninsula, in contrast to only 5 percent of the eastern counties (Wickizer et al., 1981). Grand Rapids is the largest metropolitan area located near Lake Michigan. The Grand River connects it to the lake and a fish ladder has made Grand Rapids a popular location for lake trout and spawning salmon. Muskegon is located directly on Lake Michigan.

MONS 005088

mothers had to be at least 18 years of age and have completed 10th grade in high school.

The infant sample consisted of 164 males and 149 females. The proportion of males (52%) did not differ significantly from expected (51%). All infants were white, with the exception of two black infants. Forty-three percent were firstborns. Six were the larger members of twin pairs, none of whom died during infancy. Anthropometric measures are presented in Table 2. Only one infant was below the tenth percentile on weight-for-gestational age (Lubchenco *et al.*, 1963). One severely premature newborn (GA = 26.9 weeks, birth weight = 909 g) died. When the health status of the sample was evaluated on the Postnatal Complications Scale, the mean score was 94.1 percent optimal (Littman and Parmelee, 1978).[3] Only five infants (2.1%) had a 5-minute Apgar score below 7.

Socioeconomic status (SES) of the study sample, based on a weighted sum of father's education and occupational status (Hollingshead, n.d.),[4] was predominantly middle-middle class. Most of the fathers' occupations ranged from semi-skilled laborers to middle-level management, with only 4.5 percent classified as menial or unskilled. Almost all of the women were married and living with the father of their newborn infant.

The sample was also homogeneous in terms of maternal education and age. Only 7.7 percent of the mothers failed to complete high school, while 18.2 percent completed college. Eighty-one percent were between 18 and 30 yr of age and only 3.2 percent over 35. Fifty-seven percent attended prenatal birth classes; 95.8 percent began prenatal medical care by the fourth month of pregnancy, and the remaining 13 women by the sixth month. Their scores on the Obstetrical Complications

---

[3]Data from the infant medical records were used to assign infants at-risk scores based on questions from the Postnatal Complications Scale (PCS)(Littman and Parmelee, 1978). The PCS is based on 10 items considered to reflect increased risk of mortality and morbidity to newborns, such as respiratory distress, infection, hyperbilirubinemia, and metabolic and temperature disturbances. The PCS uses an optimal scoring technique, such that high scores indicate few complications.

[4]If the father was a student, his father's education and occupation were used to estimate the family's socioeconomic status. In those cases in which the mother was unmarried, socioeconomic status was based on the occupation and education of the individual from whom the family was receiving most of its financial support.

MONS 005089

Scale (OCS)(Littman and Parmelee, 1978)[5] ranged from a minimum of 63 percent to a maximum of 98 percent optimal, with a median of 85 percent optimal, suggesting little variability in obstetrical history.

The sample was selected to over-represent women who had consumed Lake Michigan fish during some time in their lives. The majority (77%) reported consuming moderate to large quantities of Lake Michigan fish, while the rest (23%) reported consuming none of these fish. This design permits two types of analyses. First, adverse effects can be identified by comparing women who consume Lake Michigan fish with those who do not. Additional analyses can be performed to determine the statistical magnitude of the toxic effects and the particular dose-response relationships.

Procedure

Preliminary Screening

To ensure participation of infants likely to have been exposed *in utero* to a broad range of PCB levels, women were screened for past and present consumption of Lake Michigan fish on the morning following delivery. A questionnaire was used to ascertain the source,[6] amount, and kind of fish consumed in the year prior to the infant's birth, and the number of years of fish consumption at that rate. Women were also asked if there was a time in the past (dating back to 1966) when they ate greater amounts of Lake Michigan fish (e.g., the woman grew up in a family in which the father was a sports fisherman). If so, the amount and kind of fish consumed in the past, as well as the number of years of consumption at that rate, were recorded.

---

[5]Data from the maternal interview and medical records are used to assign mothers at-risk scores based on 41 questions in the OCS (Littman and Parmelee, 1978). The OCS score is derived from data relating to pregnancy, such as maternal infection, bleeding, parity, age; the reproductive history, such as previous premature births or stillbirths; and the delivery, such as obstetric medication, duration of labor, type of delivery, and birth weight. Like the PCS, the OCS is based on optimal scoring with high scores reflecting few complications.

[6]Lake Michigan was the primary source of fish. In addition, coho and chinook salmon and lake trout from rivers and lakes connected to Lake Michigan were included since these fish are normal inhabitants of the lake populations.

MONS 005090

TABLE 2

Characteristics of the Sample at Birth (N = 313)

Assessment Parameter	Mean (SD)	Range
Infant characteristics		
Birth weight (g)	3502.7 (560.3)	909.1 - 5028.9
Crown-heel length (cm)	51.1 (2.5)	28.5 - 56.0
Head circumference (cm)	35.1 (1.4)	30.5 - 41.3
Ponderal index[a]	2.7 (0.3)	1.9 - 5.6
Gestational age (weeks)[b]	39.9 (2.3)	26.9 - 45.9
Apgar scores		
1-minute	7.9 (1.3)	1.0 - 9.0
5-minute	8.9 (0.8)	2.0 - 10.0
Postnatal complications score[c]	0.9 (0.1)	0.2 - 1.0
Family characteristics		
Socioeconomic status (SES)[d]	39.3 (13.5)	14.0 - 66.0
Maternal age	26.1 (4.6)	18.0 - 42.0
Maternal education (years)	13.3 (1.9)	10.0 - 19.0
Marital status (married)[e]	283.0 (90.4)	--
Obstetrical complications score[f]	84.0 (0.1)	0.6 - 1.0

[a]Based on equation (Miller and Hassanein, 1971):
$$\frac{\text{birth weight (g)} \times 100}{\text{crown-heel length (cm)}^3}$$
[b]Based on obstetrician's estimated date of confinement
[c]Based on PCS (Littman and Parmelee, 1978)
[d]Based on Hollingshead index (n.d.)
[e]N is presented rather than mean; percent of women married in parentheses
[f]Based on OCS (Littman and Parmelee, 1978)

Sampling for contaminants in Lake Michigan fish has shown that most species tested contain detectable levels of PCBs, with especially high levels in fatty species, such as salmon and lake trout (IJC, 1978; Swain, 1981; Willford *et al.*, 1976). These fish, although high in PCB contamination, may be eaten in small quantities, while other less contaminated fish, such as perch or smelt, may be eaten in large quantities. To obtain a more accurate measure of contaminated fish consumption, a weighted value was assigned to each fish species based on

MONS 005091

average contaminant levels for the species (Table 3). The range of values was normalized to lake trout, salmon, carp, and catfish, species containing the highest concentrations of PCBs (e.g., a fish having half the average PCB level of salmon or lake trout would be weighted 0.5).

The following equation was used to estimate the mother's annual rate of consumption for each type of fish:

Relative PCB Fish Weight		Number of Fish Meals/Year		0.23 kg (1 Fish Meal)	=	PCB-kg Per Year
	X		X			

This measure is summed across species for each individual to determine a woman's annual fish consumption rate. To estimate

TABLE 3

Relative PCB Values of Lake Michigan Fish[a]

Type of Fish	PCB Weighted Value
Chinook salmon	1.0
Coho salmon	1.0
Lake trout	1.0
Carp	1.0
Catfish	1.0
Bullhead	0.6
Pike or pickerel	0.6
German brown trout	0.4
Perch	0.4
Walleye	0.4
White sucker	0.4
Alewife	0.3
Burbot	0.2
Steelhead or rainbow trout	0.2
Brook trout	0.2
Menominee (round whitefish)	0.1
Smelts	0.1
Whitefish and chubbs (herring)	0.1

[a]Derived from data supplied by the Large Lakes Research Station,

MONS 005092

cumulative exposure, annual PCB fish consumption rate was multiplied by the number of years the mother reported eating contaminated fish at that rate. If she reported eating contaminated fish at a higher rate in the past, the number of years at the current and past rates were determined separately and then multiplied by their respective consumption rates to yield a measure of cumulative exposure as follows:

Present PCB kg/ Year	X	Number of Years at Present Rate	+	Past PCB kg/ Year	X	Number of Years at Past Rate	=	Cumulative Consumption (PCB-kg)

Sampling Criteria: Exposed and Unexposed

Two criteria were used to determine inclusion of women in the study:

(1) If cumulative exposure within a 6 yr period reported by the mother was equal to 11.8 kg (26 pounds) or more of contaminated fish, the mother qualified for inclusion in the study. This criterion was based on evidence that PCBs are retained in body tissues over relatively long periods of time (Humphrey, 1976).

(2) In addition, a control group was selected comprised of newly-delivered mothers who reported consuming no Lake Michigan fish in the past or during pregnancy.

Of the 8,482 women screened (i.e., 96% of all maternity patients in the four participating hospitals), about 4 percent or 343 ate PCB-contaminated fish in sufficient quantities to qualify for inclusion in the exposed group.[7] About 29.3 percent of the women screened reported eating no Lake Michigan fish; 4.6 percent or 114 of these women were invited to serve as controls. As a check on whether women invited to participate in the study, either as fish eaters or as controls, were similar demographically to women who were not asked to participate, a demographic comparison group was selected by matching each potential participant with the next woman whose screening

[7]The qualification rate of 4 percent of the population screened, coupled with demographic data on the 18 county areas adjacent to Lake Michigan, suggests that almost 100,000 women in this region might qualify as high-fish eaters. These figures do not include women in nearby Wisconsin, considered the salmon capital of the world, or those from the Chicago area.

interview followed her own. This procedure assured a comparison group matched for hospital and approximate date of delivery with the potential sample of exposed and nonexposed mothers. Women invited to participate did not differ significantly from others in their community in socioeconomic status, maternal age, education, marital status, or sex of infant (Table 4). Among those women invited to participate, fish eaters did not differ from control women on these variables (Table 5).

TABLE 4

Characteristics of Qualifier and Demographic Comparison Groups (N=914)

	Qualifiers: Exposed and Control Groups (N=457)		Demographic Comparison Group (N=457)		
Assessment Parameter	Mean	(SD)	Mean	(SD)	t
Socioeconomic status (SES)[a]	38.5	(13.1)	37.6	(12.9)	1.10
Maternal age	25.9	(4.5)	25.9	(4.8)	0.05
Maternal education (yr)	13.2	(1.9)	12.9	(2.0)	1.88
	N	(%)	N	(%)	χ^2
Marital status (married)	419	(91.7)	413	(90.4)	0.18
Sex of infant (male)	224	(49.6)	241	(53.9)	1.71

[a]Based on Hollingshead index (n.d.)

Note: Data on SES, maternal age, and sex of infant were unavailable as follows: SES was unavailable for eight qualifiers and ten comparison women; sex of infant for five qualifiers and ten comparison women; maternal age for one

TABLE 5

Comparison of Qualifying Exposed and Control Groups (N=457)

Assessment Parameter	Qualifying Exposed Group (N=345) Mean	(SD)	Qualifying Control Group (N=112) Mean	(SD)	t
Socioeconomic status (SES)[a]	38.3	(13.1)	39.4	(13.2)	-0.76
Maternal age	26.0	(4.6)	25.4	(4.3)	1.33
Maternal education (yr)	13.1	(1.9)	13.2	(1.9)	-0.44
	N	(%)	N	(%)	x^2
Marital status (married)	319	(92.5)	100	(89.3)	1.12
Sex of infant (male)	167	(49.4)	54	(49.5)	0.00

[a]Based on Hollingshead index (n.d.)

Note: Data were unavailable on SES for six exposed and two control women; sex for seven exposed and three control infants.

Of the 457 women invited to participate, 144 (32%) refused. Mothers who consented to participate were more educated than refusers, suggesting that greater education may be associated with greater interest in research. Among women who agreed to participate, exposed and non-exposed control groups did not differ in socioeconomic status, maternal age or education, number of offspring (parity), or sex of infant (Table 6). While slightly more of the exposed women were married, this difference was not statistically significant ($p > 0.05$).

MONS 005095

TABLE 6

Study Sample: Exposure and Control Groups (N=313)

Assessment Parameter	Exposure Group (N=242) Mean	(SD)	Control Group (N=71) Mean	(SD)	t
Socioeconomic status (SES)[a]	39.3	(13.6)	39.5	(13.4)	-0.14
Maternal age	26.2	(4.7)	25.7	(4.5)	0.81
Maternal education (yr)	13.3	(1.9)	13.3	(2.0)	0.15
	N	(%)	N	(%)	χ^2
Marital status (married)	223	(92.1)	60	(84.5)	3.70
Sex of infant (male)	124	(51.2)	40	(56.3)	0.39
Parity (first-borns)	100	(42.2)	32	(45.1)	0.18

[a]SES, based on Hollingshead index (n.d.), was unavailable for three exposed women

Measures of Exposure

PCB-Fish Consumption. The principal measures of contaminated-fish consumption were:

(1) highest annual rate of PCB-fish consumption;
(2) cumulative PCB-fish consumption; and
(3) rate of PCB-fish consumption during pregnancy.

These measures were weighted for the contaminant levels of the species reported by the mothers. The first measure (highest annual rate) reflects findings from previous studies that the highest level of contaminated fish consumption predicts

subsequent PCB serum levels (Humphrey, 1976), findings consistent with the tendency of PCBs to be poorly metabolized. But PCBs tend to accumulate in body tissues over time, and prediction might be improved when reported values and years at these levels are taken into account. The measure of cumulative PCB-fish consumption, which sums rates over years after normalizing each component of the measure to z scores, was constructed to assess this possibility. The third measure, rate of PCB-fish consumption during pregnancy, was used to assess a somewhat different possibility (i.e., that the impact on the infant is especially pronounced when the mother consumes contaminated fish during pregnancy). PCB-kg refers to a fish consumption score weighted by the contaminant levels of the species reported by the mother. Mean annual rate of PCB-fish consumption at the highest levels reported by the exposed mothers was 6.7 PCB-kg (14.7 PCB-pounds) per yr (SD = 5.8 PCB-kg, range = 1.2 to 41.7 kg/yr). This rate is equivalent to about 0.6 PCB-kg per month or 2 to 3 salmon or lake trout meals (at 0.2 kg/meal). The women reported eating Lake Michigan fish for an average of 16.1 yr (SD = 9.0, range = 1.0 to 40.0 yr). In the year preceding the infant's birth, mean level of fish consumption was 4.4 PCB-kg (9.7 PCB-pounds; SD = 4.4 PCB-kg, range = 0.0 to 26.5 PCB-kg). Therefore, the selection procedure described earlier yielded a range of exposure levels with specific values depending on the particular measure of maternal fish consumption used. The fish consumption variables were positively skewed and were normalized by means of log transformations. One outlier, a women who reported ingesting 54.5 kg of contaminated fish in one year, was eliminated from the analyses.

Laboratory Analyses

Hospital personnel collected samples of umbilical cord blood for every infant born in the participating hospitals at the time of delivery. Cord blood specimens for newborns in the sample were available, therefore, for laboratory analysis, while those of non-participants were discarded shortly thereafter. Samples of maternal blood were collected on the second day following delivery as part of routine blood tests. Sixty-one percent of the infants in the sample were breast fed; and of those, 70.3 percent of the mothers provided breast milk samples between 1 and 16 weeks after delivery. A second sample of breast milk was collected from 45 women who continued breast feeding at 5 months.

Analyses of cord serum, maternal serum, and breast milk samples for PCBs were performed at the Michigan Department of Public Health by means of packed column gas chromatography

MONS 005097

(Burse et al., 1980; Needham et al., 1981). A 4 ml sample of serum was mixed with 2 ml methanol. This mixture was extracted with 5 ml hexane/diethyl ether (1:1, v/v) three times by agitating on a rotary mixer 15 to 20 minutes at 50 to 55 rpm. The extracts were combined in a Kontes concentrator tube, reduced to a small volume (about 0.5 ml), and transferred quantitatively to a miniature Florisil cleanup column from which PBBs, PCBs, and chlorinated hydrocarbon pesticides were eluted with 6 percent diethyl ether/petroleum ether mixture (v/v). The eluate was concentrated to a small volume (1.0 ml), transferred with three x 1.0 ml rinsings of hexane to a column of Silica Gel 60, and eluted with hexane to separate PCBs from the chlorinated hydrocarbon pesticide group (Picer and Ahel, 1978). The fraction containing PCBs, PBBs, and DDE was concentrated to 2 ml and analyzed by electron-capture gas chromatography with a 3 percent SE-30 column. Injector, initial column, final column, and detector temperatures were 240°C, 160°C, 210°C, and 320°C, respectively. Quantification was provided by adapting the Webb-McCall method (Sawyer, 1978; Webb and McCall, 1973) to a computer data system with Aroclors 1016 and 1260 used as calibration standards. Estimation of PCB levels in sample extracts was based on comparison of peaks on the chromatogram with respective peaks of known concentrations in the reference standards. The Aroclor 1016 portion of the chromatogram was used to estimate the quantity of lower chlorinated congeners, while the 1260 portion was applied to measure levels of more highly chlorinated congeners and isomers. Limits of detection were 5 ng/ml for Aroclor 1016 and 3 ng/ml for Aroclor 1260 in the sample extracts. Quality control over time was ensured by addition of a spiked sample of bovine serum with every batch of 10 samples, as well as the use of a glassware blank and a reagent blank. Serum lipids were determined colorimetrically using the Dade Total Standard for plotting the calibration curve of concentration vs. absorbence (Fringe et al., 1972).

A similar procedure was used in analyzing breast milk samples. A 5 g sample of breast milk in a screw-capped (teflon-lined) culture tube was mixed with 0.1 g of potassium oxalate and 5 ml methanol. This mixture was extracted in the same manner as serum samples. Extracts were combined in a micro distilling assembly and concentrated to a small volume. Evaporation of solvent from the concentrated extract was conducted in a small preweighed aluminum dish and the residue dried under vacuum in a desiccator. In contrast to serum analysis, wherein lipid levels were estimated, lipid content of the breast milk sample was determined gravimetrically. The lipid residue was then redissolved in a small amount of petroleum ether and transferred quantitatively to a miniature Florisil cleanup column. Subsequent procedures for serum were

MONS 005098

then applied to the breast milk analyses.[8] (For a review of technical problems associated with these analytical procedures, see IARC Monograph, 1978; Mullin et al., 1983; Humphrey, 1976.)

All serum samples containing lipid levels below 200 mg/dl were omitted from the data analyses, since measurement techniques were judged to be insufficiently sensitive to detect PCB levels at lipid values of this magnitude. The removal of three maternal serum and 43 cord serum samples for this reason did not alter the fundamental nature of the PCB distribution. Twenty-seven additional cord blood samples could not be analyzed because insufficient quantities had been collected, the hospital had mistakenly discarded them, or because of equipment failures in the laboratory. Included in the following analyses were 198 cord serum and 196 maternal serum samples, and 138 neonatal and 45 five-month breast milk samples.

RESULTS

Laboratory results for cord serum, maternal serum, and breast milk samples are presented in Table 7. The column labeled "nondetectable" refers to PCB values of 0.1 ng/ml to five times the noise level on the chromatogram; the right hand column refers to PCB levels that are detectable, but still below the laboratory's quantification limits. The majority of the PCB levels matched to the 1016 standard were below quantification limits. This was particularly true for the cord and maternal sera analyses. Among these samples, only one of 195 and five of 190 cases, respectively, were quantifiable. Since comparisons with the 1260 standard yielded considerably fewer values below the quantification limit, 1260 values may provide a more reliable measure of PCB body burden. Arithmetic means for the more highly chlorinated isomers exceeded the lower chlorinated isomers by a ratio of 2.7 to 1 for the cord samples and as much as 5.5 to 1 for the neonatal breast milk samples. This differential presumably results from the tendency of lower chlorinated isomers to be less stable, more susceptible to degradation in the environment, and metabolized more rapidly in the organism (Matthews, 1983).

PCB levels for a large proportion of the cord serum samples were not quantifiable, even when the 1260 standard was used. A pair-wise comparison of PCB 1260 serum levels on a whole basis indicates that mean PCB levels in maternal serum were

---

[8]The summary of the laboratory techniques used to analyze the serum and breast milk samples was written in conjunction with Dr. Harold A. Price of the Michigan Department of Public Health.

TABLE 7

Polychlorinated Biphenyls in Cord Serum, Maternal Serum, and Maternal Breast Milk (Whole Basis)

Assessment Parameters	N	Mean (SD)	Median	Nondetectable[a] N (%)	Detectable But Nonquantifiable[b] N (%)
Cord serum (ng/ml)					
1016 standard	195	0.9 (0.9)	0.6	23 (11.8)	171 (87.7)
1260 standard	198	2.5 (1.9)	2.0	4 (2.0)	130 (65.7)
Maternal serum (ng/ml)					
1016 standard	190	1.6 (4.5)	0.8	16 (8.4)	169 (88.9)
1260 standard	196	5.5 (3.7)	4.6	0 (0.0)	44 (22.4)
Breast milk - neonatal (ng/g)					
1016 standard	138	4.1 (4.5)	2.9	11 (8.0)	85 (61.6)
1260 standard	138	22.5 (12.3)	20.4	0 (0.0)	2 (1.4)
Breast milk - 5 months (ng/g)					
1016 standard	45	3.7 (3.4)	2.8	3 (6.7)	30 (66.7)
1260 standard	45	17.4 (12.1)	14.1	0 (0.0)	4 (8.9)

[a]Nondetectable refers to values of 0.1 ng/ml to five times the noise level of the chromatogram

[b]Nonquantifiable refers to detectable levels below the quantifiable limits of 5 ng/ml for Aroclor 1016 and ng/ml for Aroclor 1260

substantially higher than in cord serum (Table 8), confirming previous findings (Akiyama et al., 1975; Kodama and Ota, 1977). Masuda et al. (1978) found a similar differential in a recent Japanese sample and concluded that the placenta may act as a partial barrier to PCBs. However, in the present sample lipid levels in maternal serum are twice those in cord serum. When PCB concentrations are calculated on a fat basis, the mean PCB values are similar for the cord and maternal sera (Table 8), and the differential is no longer significant. Thus, four studies provide evidence that PCBs cross the placenta, thereby exposing the fetus.

PCB values were also obtained for two samples of breast milk, one during the first few weeks after birth and a more limited sample when the infant was 5 months old. Matched pair t-tests indicate that PCB levels on a whole basis were substantially higher in breast milk than cord and maternal sera samples. Again, when samples were compared on a fat basis, differences were no longer significant. Kodama and Ota (1980) suggested that breast feeding may decrease PCB body burden in the mother. Although PCB concentrations in the breast milk of nursing mothers in our sample tended to decline over time, this decline was not significant.

Correlations among PCB levels in the four biological specimens are shown in Table 9. The highly significant correlation of cord with maternal serum levels provides further evidence for the transplacental passage of the PCB molecule and corroborates a similar relation reported by Masuda et al. (1978) and Kodama and Ota (1977), using smaller samples of women. The significant correlation between PCBs in maternal serum and breast milk indicates that PCBs are moderately stable in the mother, an inference further supported by the significant correlations between breast milk samples obtained shortly after the baby's birth and those obtained at 5 months.

Correlations between maternal and cord sera were similar in magnitude, whether calculated on a whole serum or fat basis, $r = 0.41$ and 0.43, respectively (Table 9). While the whole and fat basis findings were also similar for correlations between maternal serum and breast milk, the two approaches yielded different results for the neonatal to 5-month breast milk correlation.

Consistency between analyses derived on a whole and fat basis was also indicated by the pattern of the intercorrelations shown in Table 10. PCB levels in the cord and maternal sera on a whole serum basis were highly correlated with levels calculated on a fat basis ($r = 0.93$). Thus, for serum, it seems to make little difference whether measures are derived on a

MONS 005101

TABLE 8

Pairwise Comparisons of PCBs and Lipids in Cord Serum, Maternal Serum, and Maternal Breast Milk (1260 Standard)

Assessment Parameters	N	Whole Basis (ng/ml or ng/g)[a] Mean (SD)	t	Fat Basis (ng/g) Mean (SD)	t	Lipids Percent	t
Cord serum	148	2.4 (1.9)	-10.18[b]	788.1 (696.5)	-0.82	0.32	-25.69[b]
Maternal serum		5.3 (3.7)		835.3 (557.1)		0.64	
Cord serum	95	2.4 (1.8)	-15.45[b]	824.2 (714.2)	0.13	0.31	-20.45[b]
Breast milk - neonatal		22.8 (13.0)		813.9 (377.9)		2.89	
Maternal serum	91	5.6 (3.2)	-13.36[b]	932.2 (579.1)	1.55	0.63	-17.06[b]
Breast milk - neonatal		22.7 (12.3)		827.8 (380.4)		2.85	
Breast milk - neonatal	42	20.0 (9.3)	1.31	750.5 (408.8)	-0.19	2.96	0.51
Breast milk - 5 month		18.0 (12.2)		772.3 (671.2)		2.82	

[a]Cord and maternal sera values on a whole basis are given in ng/ml and breast milk values in ng/g

[b]$p < 0.0001$

MONS 005102

TABLE 9

Intercorrelations of Log PCBs (1260 Standard) in Cord Serum, Maternal Serum, and Maternal Breast Milk

Assessment Parameter	Cord Serum	Maternal Serum	Breast Milk Neonatal	Breast Milk 5 Month
Cord serum	--	0.41[a] (148)	0.09 (95)	-0.06 (25)
Maternal serum	0.43[a] (145)	--	0.23[b] (91)	0.01 (30)
Breast milk - neonatal	0.16 (93)	0.28[c] (91)	--	0.61[a] (42)
Breast milk - 5 month	-0.01 (24)	-0.10 (30)	.30[b] (42)	--

[a] $p < 0.0001$
[b] $p < 0.05$
[c] $p < 0.01$

Note: Rs above the main diagonal are values calculated on a whole basis, while those below are on a fat basis. N appears in parentheses. Lipid values were missing for three cord serum samples, two neonatal breast milk samples, and one 5-month breast milk sample.

whole or fat basis. Although cord and maternal sera are low in lipids, lipid levels tend to be relatively stable. Because breast milk lipids fluctuate considerably, the same consistency does not appear for breast milk values derived by the two methods. This apparent instability suggests that in the analyses of breast milk, measures that take lipid fluctuation into account are likely to be more reliable.

These findings were further supported by an analysis of the degree to which PCB levels could be predicted from lipid levels in serum or breast milk. While the PCB levels in the cord and maternal sera were unrelated to corresponding cord and maternal lipid levels, there was a significant association between PCB and lipid levels in the neonatal and 5 month breast

MONS 005103

TABLE 10

Intercorrelations of Log PCBs (1260 Standard) in Cord Serum, Maternal Serum, and Maternal Breast Milk

	Whole Basis			
Assessment Parameter	Cord Serum	Maternal Serum	Breast Milk Neonatal	Breast Milk 5 Month
Fat basis				
Cord serum	0.93[a] (194)	0.37[a] (145)	0.07 (93)	0.05 (24)
Maternal serum	0.43[a] (148)	0.93[a] (196)	0.20[b] (91)	0.01 (30)
Breast milk - neonatal	0.16 (95)	0.35[a] (91)	0.62[a] (138)	0.30[c] (42)
Breast milk - 5 month	-0.06 (25)	-0.08 (30)	0.08 (42)	0.39[d] (45)

[a] $p < 0.001$
[b] $p < 0.10$
[c] $p < 0.05$
[d] $p < 0.01$

Note: N appears in parentheses.

milk ($r = 0.58$, $p < 0.0001$; and $r = 0.63$, $p < 0.0001$, respectively).

Women and their offspring were selected for the study on the basis of reported fish consumption patterns. Levels of fish consumption reported by the exposed and control mothers for whom the different biological measures were available are shown in Table 11. When women who breast fed were compared with those who did not, no difference was found for highest annual rate or cumulative consumption measures. While their rate during pregnancy was slightly lower than the rest of the sample ($M = 2.9$ vs. 3.8 PCB-kg/yr), the difference failed to

MONS 005104

TABLE 11

Levels of Reported Contaminated Fish Consumption (PCB-kg) of Women Providing Blood and Breast Milk Samples

Assessment Parameters	N	Mean (SD)	Median	Range
Cord serum analyses				
Consumption at highest rate	198	4.3 (5.5)	3.0	ND - 41.7
Consumption during pregnancy	189	2.8 (3.9)	1.9	ND - 22.4
Cumulative consumption	198	61.3 (97.8)	27.8	ND - 716.6
Maternal serum analyses				
Consumption at highest rate	196	4.4 (5.5)	3.2	ND - 41.7
Consumption during pregnancy	190	2.8 (3.6)	2.2	ND - 22.4
Cumulative consumption	196	62.4 (97.5)	28.6	ND - 716.6
Breast milk - neonatal				
Consumption at highest rate	138	4.7 (5.3)	3.3	ND - 41.7
Consumption during pregnancy	135	2.9 (3.5)	2.2	ND - 20.0
Cumulative consumption	138	62.9 (90.9)	38.4	ND - 716.6
Breast milk - 5 month				
Consumption at highest rate	45	5.5 (8.0)	3.8	ND - 41.7
Consumption during pregnancy	45	2.8 (2.9)	2.2	ND - 9.5

MONS 005105

Table 11 (continued)

Assessment Parameters	N	Mean (SD)	Median	Range
Cumulative consumption	45	82.5 (135.3)	43.4	ND - 716.6

Note: Consumption levels include data on exposed and control women.

reach conventional levels of statistical significance ($t = 1.90$, $p < 0.10$).

Correlations between maternal reports of contaminated fish consumption and the four biological measures of PCB body burden are presented in Table 12. No relationship was found between cord serum PCB levels and maternal fish consumption, possibly because of the detection problems in cord serum analysis described earlier. In contrast, a positive correlation was found between PCB levels in maternal serum and all three reported fish consumption measures. Mean PCB level in maternal serum was 6.1 ng/ml ($SD = 3.7$) among women who ate contaminated fish, as contrasted to 4.1 ng/ml ($SD = 2.7$) among those who abstained ($t = 3.83$, $p < 0.0001$). These data replicate in a sample of women of child-bearing age Humphrey's (1976) finding that Lake Michigan fish consumption predicts PCB body burden in Michigan residents. The data extend this finding by showing a significant correlation between fish consumption and PCB levels in neonatal breast milk. Mean PCB residues were higher in breast milk samples of exposed than in samples of nonexposed women ($M = 865.6$ vs. 622.2 ng/g on a fat basis, $t = 3.21$, $p < 0.005$). The lack of a consistent relationship between maternal report of prenatal fish consumption and breast milk levels at 5 months may be due in part to postpartum ingestion of contaminated fish, which will be examined in future analyses. Figure 2 shows a scatterplot demonstrating the linear relationships between maternal serum 1260 and fish consumption at the highest annual rate. For every pound of contaminated fish ingested by the mother, the PCBs in her serum increase by about 0.15 ng/ml on a whole basis or 23.6 ng/g on a fat basis.

MONS 005106

TABLE 12

Correlations Between Log Contaminated Fish Consumption and Log PCBs in Cord Serum, Maternal Serum, and Breast Milk (1260 Standard)

Assessment Parameters	N	r	Regression Equation
Fish consumption at highest annual rate with			
Cord (whole serum basis)	198	0.09	y = 1.05 + 0.04x
Maternal (whole serum basis)	196	0.38[a]	y = 1.47 + 0.15x
Breast milk - neonatal (fat basis)	138	0.30[a]	y = 6.36 + 0.12x
Breast milk - 5 month (fat basis)	45	0.24	y = 6.24 + 0.11x
Fish consumption during pregnancy with			
Cord (whole serum basis)	189	0.13	y = 1.05 + 0.05x
Maternal (whole serum basis)	190	0.31[a]	y = 1.57 + 0.13x
Breast milk - neonatal (fat basis)	135	0.24[b]	y = 6.47 + 0.10x
Breast milk - 5 month (fat basis)	45	0.36[c]	y = 6.19 + 0.18x
Cumulative fish consumption (normalized) with			
Cord (whole serum basis)	198	0.08	y = 1.05 + 0.02x
Maternal (whole serum basis)	196	0.29[a]	y = 1.52 + 0.07x
Breast milk - neonatal (fat basis)	138	0.21[b]	y = 6.38 + 0.06x

MONS 005107

Table 12 (continued)

Assessment Parameters	N	r	Regression Equation
Breast milk - 5 month (fat basis)	45	0.10	$y = 6.31 + 0.04x$

[a] $p < 0.001$
[b] $p < 0.01$
[c] $p < 0.05$

DISCUSSION

Despite their widespread distribution in our environment and concern about human accumulation, few studies are currently available on the serum PCB levels of individuals chronically exposed to PCBs via their diet. Moreover, the toxicology of PCBs is little understood in comparison with that of other xenobiotic chemicals, such as DDT and BHC (Hirayama, 1976; Yoshimura and Yoshimura, 1976). The present longitudinal study was designed to investigate effects of PCB exposure from contaminated fish consumption on two potential at-risk groups, pregnant women and their newborn offspring. While several reports have appeared on the transfer of PCBs from mother to child via breast milk (e.g., Kodama and Ota, 1980; Kuwabara et al., 1979), only a few studies examined the transfer of PCBs in utero (Akiyama et al., 1975; Kodama and Ota, 1980; Masuda et al., 1978). These studies used either relatively small unexposed samples or women and infants exposed during the Yusho incident. No study to date has examined the pattern of transfer from mothers to offspring exposed via the food chain.

The data in this report provide empirical support for linkages between source of contamination and body burden shown in the analytic model (Figure 1). They also provide evidence of the preponderance of more heavily chlorinated isomers in the serum and breast milk of women whose exposure to PCBs is due in part to the ingestion of contaminated fish. The small amounts of 1016 present in the biological specimens and the poor reliability of their measurement indicate that values matched to the 1260 standard are more likely to yield meaningful findings.

The present study evaluated the linkages from fish consumption to maternal body burden and subsequently to the

MONS 005108

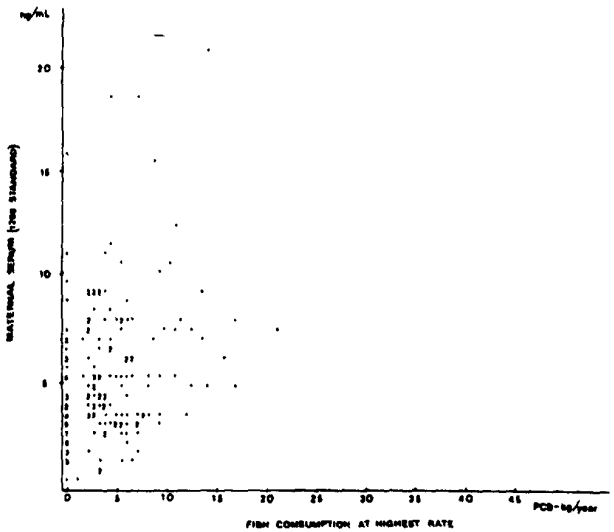


Figure 2. Scatterplot of maternal serum (1260 standard) by fish consumption at the highest annual rate.

developing fetus and breast milk. Even though exposure levels were only moderate in the women studied, reported contaminated fish consumption predicted PCB residues in two measures of body burden, maternal serum and breast milk. These results confirm prior studies which found an association between fish consumption and PCB residues in serum specimens (Kreiss et al., 1981; Kuwabara et al., 1979; Humphrey, 1976), while also demonstrating that the relationship holds for younger women, an age group not previously studied. The particular significance of this finding is that PCBs in the environment may pose a risk to the fetus and newborn, since the women in this age group are in the middle of their childbearing years.

Transplacental passage by the PCB molecule was indicated by the significant positive correlation between maternal and

cord sera (r = 0.41, p < 0.0001), confirming two prior studies which yielded similar findings (r = 0.24, Masuda *et al.*, 1978; r = 0.45, Kodama and Ota, 1977). The transfer of PCBs to breast milk was confirmed by a similar positive correlation (r = 0.27, p < 0.01, for maternal serum on a whole basis to neonatal breast milk on a fat basis), confirming the 1978 finding of Masuda *et al.* (r = 0.29). While cord and maternal sera yield similar results regardless of whether the analysis is performed on a whole serum or fat basis, breast milk residues yield varying results due presumably to fluctuations in lipid levels in breast milk.

The present data are consistent with the notion that PCBs move through the environment and the human body into systems which may potentially threaten the infant both before and after birth (Swain, 1981). At this time it is not clear which of these exposures--prenatal (intrauterine) or postnatal (via breast milk)--has the greater impact on infant development. While the absolute quantity of PCB residues is substantially lower in cord serum than in breast milk, the fetal organism is particularly vulnerable during the prenatal period. One factor that has been overlooked in this debate (e.g., Masuda *et al.*, 1978) is the size of the fetus. When PCB exposure is calculated on the basis of body weight, the infant's prenatal exposure is substantial. In addition, the values for PCBs in cord serum may underestimate actual levels of exposure for reasons discussed earlier. Moreover, different biological systems in the fetus and newborn may be affected depending on the developmental period during which exposure occurs.

The long-term implications for human health of the association between contaminated food ingested at chronic low levels and PCB body burden have only begun to be studied. Unlike findings from studies of persons exposed occupationally to PCBs, preliminary reports suggest possible increases in elevated blood pressure levels (Kreiss *et al.*, 1981) and a greater frequency of reported cancers (Humphrey, 1983) in persons exposed to PCBs through the ingestion of contaminated food. Preliminary analyses of the effect of intrauterine exposure on neonatal behavior indicate a number of subtle behavioral deficits, which may have implications for subsequent development (Fein *et al.*, 1983a). The present study provides empirical support for the use of maternal reports of fish consumption as reliable indicators of PCB exposure, while also predicting transfer of PCBs *in utero* and in the breast milk.

MONS 005110

ACKNOWLEDGMENTS

This research was funded under grant number CR808520010 from the U.S. Environmental Protection Agency (EPA). We wish to thank Wayland R. Swain and Nelson A. Thomas of the EPA Large Lakes Research Station and Harold E.B. Humphrey of the Michigan Department of Public Health for their generous assistance in the development of this project. We also wish to thank Harold A. Price, Michael D. Mullin, and Janet Eyster for their many helpful suggestions regarding the analysis of biological data. We greatly appreciate the assistance of Carol Alexander, Gail A. Brumitt, Gwen Hendrickse, and Patricia Yaros in the collection of the data; Jeffrey K. Dowler and Gregory A. Proulx in data analysis; and Carol Stanik and Maria Petkoff in preparation of this manuscript. Finally, without the cooperation of physicians, hospital personnel, and parents in Grand Rapids and Muskegon, this study would not have been possible.

LITERATURE CITED

Abe, S., Y. Inoue, and M. Takamatsu. 1975. Polychlorinated Biphenyl Residues in Plasma of Yusho Children Born to Mothers Who Had Consumed Oil Contaminated by PCB. Acta Medica Fukuoka 66:605-609.

Akiyama, K., K. Fujitani, G. Ohi, and H. Yagyu. 1975. Polychlorinated Biphenyl Residues in Maternal and Cord Blood in Tokyo Metropolitan Area. Bull. Environ. Contam. Toxicol. 14:588-592.

Allen, J.R., D.A. Barsotti, and L.A. Carstens. 1980. Residual Effects of Polychlorinated Biphenyls on Adult Nonhuman Primates and Their Offspring. J. Toxicol. Environ. Health 6:55-66.

Bowman, R.E. and M.P. Heironimus. 1981. Hypoactivity in Adolescent Monkeys Perinatally Exposed to PCBs and Hyperactive as Juveniles. Neurobehav. Toxicol. Teratol. 3:15-18.

Bowman, R.E., M.P. Heironimus, and J.R. Allen. 1978. Correlation of PCB Body Burden With Behavioral Toxicology in Monkeys. Pharmacol., Biochem., Behav. 9:49-56.

Burse, V.W., L.L. Needham, J.A. Liddle, D.O. Bayse, and H.A. Price. 1980. Interlaboratory Comparison for Results of Analyses for Polybrominated Biphenyls in Human Serum. J. Anal. Toxicol. 4:22-26.

MONS 005111

Chia, L., M. Su, R. Chen, Z. Wu, and F. Chu. 1981. Neurological Manifestations in Polychlorinated Biphenyls (PCB) Poisoning. Clinical Medicine (Taipai) 7:45-61.

Chou, S.M., T. Miike, W.M. Payne, and G.J. Davis. 1979. Neuropathology of "Spinning Syndrome" Induced by Prenatal Intoxication With a PCB in Mice. Ann. N. Y. Acad. Sci. 320:373-395.

Fein, G.G., S.W. Jacobson, P.M. Schwartz, and J.L. Jacobson. 1983a. Intrauterine Exposure to Environmental Toxins: Behavioral Effects in the Human Newborn. Child Development (in press).

Fein, G.G., P.M. Schwartz, S.W. Jacobson, and J.L. Jacobson. 1983b. Behavioral Teratology: A New Role for Psychological Research. American Psychologist (in press).

Fringe, C.S., T.W. Fendley, R.T. Dunn, and C.A. Queen. 1972. Improved Determination of Total Serum Lipids by the Sulfo-Phospho-Vanillin Reaction. Clin. Chem. 18:673-674.

Funatsu, I., F. Yamashita, Y. Ito, S. Tsugama, T. Funatsu, T. Yoshikane, M. Hayashi, T. Kato, M. Yakushiji, G. Okamoto, S. Yamasaki, T. Arima, T. Kuno, H. Ide, and I. Ibe. 1972. Polychlorobiphenyls (PCB)-Induced Fetopathy. Kurume Med. J. 19:43-51.

Grant, D.L., D.C. Villeneuve, K.A. McCully, and W. Phillips. 1971. Placental Transfer of Polychlorinated Biphenyls in the Rabbit. Environ. Physiol. 1:61-66.

Harada, M. 1976. Intrauterine Poisoning. Clinical and Epidemiological Studies and Significance of the Problem. Bulletin of the Institute of Constitutional Medicine, Kumamoto University 25 (Suppl.):1-69.

Higuchi, K. (ed.) 1976. PCB Poisoning and Pollution. Academic Press, New York, NY, 184 pages.

Hirayama, C. 1976. Clinical Aspects of PCB Poisoning. In: K. Higuchi (ed.), "PCB Poisoning and Pollution," pp. 87-104. Academic Press, New York, NY.

Hollingshead, A.B. n.d. Four Factor Index of Social Status. Unpublished manuscript, Yale University, New Haven, CT, 30 pages.

MONS 005112

Humphrey, H.E.B. 1976. Evaluation of Changes of the Level of Polychlorinated Biphenyls (PCB) in Human Tissue. Unpublished manuscript, Michigan Department of Public Health, Lansing, MI, 86 pages.

Humphrey, H.E.B. 1983. Population Studies of PCBs in Michigan Residents. In: F.M. D'Itri and M.A. Kamrin (eds.), "PCBs: Human and Environmental Hazards," pp. 299-310. Ann Arbor Science Publishers, Ann Arbor, MI.

IARC. 1978. Polychlorinated Biphenyls and Polybrominated Biphenyls. International Agency for Research on Cancer, IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans 18:1-140.

IJC. 1978. Status Report on Organic and Heavy Metal Contaminants in the Lake Erie, Michigan, Huron, and Superior Basins. Appendix E, International Joint Commission, Great Lakes Water Quality Board, pp. 1-373.

Kodama, H. and H. Ota. 1977. Studies on the Transfer of PCB to Infants From Their Mothers. Jap. J. Hyg. 32:567-573.

Kodama, H. and H. Ota. 1980. Transfer of Polychlorinated Biphenyls to Infants From Their Mothers. Arch. Environ. Health 35:95-100.

Kreiss, K., M.M. Zack, R.D. Kimbrough, L.L. Needham, A.L. Smrek, and B.T. Jones. 1981. Association of Blood Pressure and Polychlorinated Biphenyl Levels. J. Amer. Med. Assoc. 245:2505-2509.

Kuwabara, K., T. Yakushiji, I. Watanabe, S. Yoshida, K. Koyama, and N. Kunita. 1979. Levels of Polychlorinated Biphenyls in Blood of Breast-Fed Children Whose Mothers are Non-Occupationally Exposed to PCBs. Bull. Environ. Contam. Toxicol. 21:458-462.

Littman, B. and A.H. Parmelee, Jr. 1978. Medical Correlates of Infant Development. Pediatrics 61:470-474.

Lubchenco, L.O., C. Hansman, M. Dressler, and E. Boyd. 1963. Intrauterine Growth as Estimated From Live-Born Birthweight Data at 24 to 42 Weeks of Gestation. Pediatrics 32:793-800.

Masuda, Y., R. Kagawa, H. Kuroki, M. Kuratsune, T. Yoshimura, I. Taki, M. Kusuda, F. Yamashita, and M. Hayashi. 1978. Transfer of Polychlorinated Biphenyls From Mothers to Foetuses and Infants. Bull. Environ. Contam. Toxicol. 16:543-546.

MONS 005113

Masuda, Y., R. Kagawa, B. Kuroki, S. Tokudome, and M. Kuratsune. 1979. Transfer of Various Polychlorinated Biphenyls to the Foetuses and Offspring of Mice. Fd. and Cosmetic Toxicol. 17:623-627.

Matthews, H.B. 1983. The Metabolism of PCBs in Mammals. In: F.M. D'Itri and M.A. Kamrin (eds.), "PCBs: Human and Environmental Hazards," pp. 203-213. Ann Arbor Science Publishers, Ann Arbor, MI.

Mullin, M., S. Safe, L. Safe, C. Pochini, S. McCrindle, and M. Romkes. 1983. Analysis of PCBs Using Specific Isomer High Resolution Capillary Gas Chromatography. In: F.M. D'Itri and M.A. Kamrin (eds.), "PCBs: Human and Environmental Hazards," pp. 165-176. Ann Arbor Science Publishers, Ann Arbor, MI.

Needham, L.L., V.W. Burse, and H.A. Price. 1981. Temperature-Programmed Gas Chromatographic Determinations of Polychlorinated and Polybrominated Biphenyls in Serum. J. Assoc. Off. Anal. Chem. 64:1131-1137.

Picer, M. and M. Ahel. 1978. Separation of Polychlorinated Biphenyls From DDT and Its Analogues on a Miniature Silica Gel Column. J. Chromatog. 150:119-127.

Polishuk, Z.W., D. Wasserman, M. Wasserman, S. Cucos, and M. Ron. 1977. Organochlorine Compounds in Mother and Fetus During Labor. Environ. Res. 13:278-284.

Sawyer, L.D. 1978. Quantitation of Polychlorinated Biphenyl Residues by Electron Capture Gas-Liquid Chromatography. J. Assoc. Off. Anal. Chem. 61:272-291.

Spyker, J.M. 1975. Assessing the Impact of Low-Level Chemicals on Development: Behavioral and Latent Effects. Fed. Proc. 34:1835-1844.

Storm, J.E., J.L. Hart, and R.F. Smith. 1981. Behavior of Mice After Pre- and Post-Natal Exposure to Arochlor 1254. Neurobehav. Toxicol. Teratol. 3:5-9.

Swain, W.R. 1981. An Ecosystem Approach to the Toxicology of Residue Forming Xenobiotic Organic Substances in the Great Lakes. In: "Ecotoxicology Working Papers: Testing for the Effects of Chemicals on Ecosystems," pp. 194-257. National Research Council, National Academy of Sciences.

MONS 005114

Tilson, H.A., G.J. Davis, J.A. McLachlan, and G.W. Lucier. 1979. The Effects of Polychlorinated Biphenyls Given Prenatally on the Neurobehavioral Development of Mice. Environ. Res. 18:466-474.

Torok, P. and L.W. Weber. 1981. Distribution of Polychlorobiphenyls in Pregnant Mice and Fetuses on Various Days of Gestation. Arch. Environ. Contam. Toxicol. 10:289-296.

Webb, R.G. and A.C. McCall. 1973. Quantitative PCB Standards for Electron Capture Gas Chromatography. J. Chromatog. Sci. 11:366-373.

Weiss, B. and J.M. Spyker. 1974. Behavioral Implications of Prenatal and Early Postnatal Exposure to Chemical Pollutants. Pediatrics 53:851-859.

Wickizer, T.M., L.B. Brilliant, R. Copeland, and R. Tilden. 1981. Polychlorinated Biphenyl Contamination of Nursing Mothers' Milk in Michigan. Amer. J. Pub. Health 71:132-137.

Willford, W.A., R.J. Hesselburg, and L.W. Nicholson. 1976. Trends in Polychlorinated Biphenyls in Three Lake Michigan Fishes. In: "Proceedings of the National Conference on Polychlorinated Biphenyls," pp. 177-181. U.S. Environmental Protection Agency, Washington, DC.

Wong, K.C. and M.Y. Hwang. 1981. Children Born to PCB Poisoned Mothers. Clinical Medicine (Taipei) 7:83-87.

Yoshimura, H. and S. Yoshimura. 1976. Toxicological Aspects II: The Metabolic Fate of PCBs and Their Toxicological Evaluation. In: K. Higuchi (ed.), "PCB Poisoning and Pollution," pp. 41-67. Academic Press, New York, NY.

MONS 005115

PART V

REGULATION OF PCBs

MONS 005116

CHAPTER 23

REGULATION OF PCBs IN MICHIGAN

Howard A. Tanner
Director
Michigan Department of Natural Resources
Lansing, Michigan 48909

Everyone who speaks should make some effort to identify his credentials and, in that regard, I am not sure just what I should say. I come here not having heard what you listened to yesterday, nor will I be able to listen to what may follow. I am sort of hit-and-run and that is not really fair; it is not fair to you and it is not fair to me, but that is the way it is. I guess what I'll tell you is how I view myself. I view myself as a regulator. I think I once qualified as a scientist. I don't think I do anymore; however, some people still tend to be confused as to whether I am a regulator or a scientist. I am responsible to a policy-making citizen board of seven people. I welcome the advice that I hope this conference will provide. I should tell you, however, that I receive a lot of advice. As near as I can count, there are about thirteen commissions that make up a part of state government that, in one way or another, are intended for citizen input into advising the Department or having an even more direct impact on Department of Natural Resources (DNR) programs. In addition to those 13 "core" commissions, give or take one or two, as near as we can tell there are about 200 advisory committees that provide advice to the agency I direct. I spend a lot of time taking advice and I appreciate it; I do the best I can with it. Today I have a semi-prepared set of comments and a few from my cuff. First of all, I hope it is obvious that I am pleased that this conference is taking place. I genuinely expect that your product will be helpful to the DNR and to the State of Michigan regarding fishes of the Great Lakes. It should go without saying we are dealing with a highly controversial area and I hope that you will provide help with regulatory decisions. We've already seen some of the background that may be useful to a number of us to more formally appraise our choices. And I

MONS 005117

hope that regulators will better understood the scientific dilemmas and I hope that scientists will better understand our regulatory dilemmas. I think there is enough for both of us. Now, it is probably not known to most of you, but for the sake of completeness, remember that the DNR deals with a number of issues, a number of responsibilities that relate to the question of polychlorinated biphenyls (PCBs) in fish. First of all, we are charged with controlling air and water pollution in Michigan, the two major sources of PCBs in the Great Lakes. We are charged with regulating sport and commercial fishing in the Great Lakes and we provide and promote sport fishing opportunities. Most trout and salmon in the Great Lakes are paid for by Michigan sportsmen and are released from our hatcheries. They wouldn't be out there, and people wouldn't be eating them, if we--as an agency channeling sportmen's dollars--weren't busily putting them out there. That is a very significant responsibility. I would thus categorize us as both a promoter and regulator in several areas affected by the PCB question, which likens us to the old Atomic Energy Commission--in the position of both promoting and regulating atomic energy. I suggest that this is not a comfortable place for anyone to be, nor is it the kind of structure that I think is ideal. But to some degree, that is how it is. I believe that this presents a dilemma to us that few others face. We are constantly on the defense to justify our position by those who do not believe we should allow fish to be taken that contain any PCBs and, to the other extreme, by those who think that PCBs are not dangerous. Of course, it should be understood that we are not burdened with setting food standards nor are we burdened with inspecting food for compliance. I am glad to share those responsibilities with the appropriate agencies.

But where do we go for realistic advice? I guess the only response to that is to the scientific community. Unfortunately, from our determination prior to this meeting, and I suspect maybe after this meeting, we will find that there is some disagreement on facts and some disagreement on interpretation among the scientific community. I hope that what we would describe as a large gray area will be seen as a somewhat smaller area, and one not quite so gray. I think most scientists and most all of us agree that the less PCBs in food, the better. Most responsible scientists also agree that PCB concentrations in fish in the Great Lakes at least have decreased considerably in recent years. Ripe for discussion, however, are questions regarding acceptable concentration, sampling the fish with the skin on or off, and how to discourage people from eating fish which are over the limit. These are the kinds of questions that produce varying responses.

MONS 005118

One of my staff members was very helpful to me recently when he defined a regulatory decision as something like this: "Regulation by its nature is a pass-fail situation. Either it is or it isn't." In effect, our task is to draw a line across a large gray area, making one side of it black and one side of it white.

Now, perhaps we can realistically expect additional research funding, additional research results. We will improve our scientific base, our data base, regarding the question of PCBs as a human health hazard. Speaking realistically, however, if I read correctly, the opportunities, the funding sources for such scientific investigations, those budgets are shrinking along with everybody else's.

Well, what are we to do and what have we done and what are we doing? Very briefly, I would point out: The record will show that Michigan has led the nation with the PCB Control Act of 1976. Michigan's DNR was an early and strong supporter of this bill. I understand you have been told that we were prodded into it, but I will let you make your own decisions on that. Subsequent national legislation to stop production and usage of PCBs should ultimately pay off in reduced atmospheric inputs of PCBs to the Great Lakes. Within the state of Michigan we have vigorously pursued the removal of PCBs from any use, anywhere. Incidently, we are also oftentimes responsible for disposal, and as of the moment we have no authorized disposal site, incineration, or entombment facility for PCBs within the state of Michigan. The State Department of Agriculture regulates PCB content in food. Of course, you are aware of the debate over whether Michigan should unilaterally reduce the allowable PCB content of fish from 5 to 2 mg/kg. As you examine that question, with or without responsiblity to take action, I ask that you present yourself another question. If PCB content were up to 2 mg/kg in Michigan commercial fish, what would we achieve in reduced exposure and at what cost? I would have to point out that in the quick review of the knowledge that I have of consumption of fish and PCB-tainted fish in Michigan, one species that has consistently shown the higher level of PCB is the lake trout. Under commercial fishing, the only legally caught lake trout in Michigan currently are taken by the Indian fishery. Many of those lake trout go directly to restaurants without Inspection of any kind. Many of those trout also are sent outside the state. It is the DNR's position that commercial fishing in Michigan should be regulated no differently than in other states, and that the best scientific information should be used to decide the national standards. I personally would have no difficulty in going to 2 mg/kg if it were part of a national standard. I see enormous difficulties in attempting to do it unilaterally.

MONS 005119

Obviously, the greatest number of fish, the greatest risk, the greatest exposure, whatever that may be, comes to sport anglers. That is the way that most of the fish are taken, the way most of the fish enter the food chain. We, in conjunction with and guided by the Michigan Department of Public Health, have warned sport anglers of the dangers of eating contaminated fish. We show on the Michigan Fishing Guide, which every person receives upon purchasing a fishing license, just what waters have been found to contain contaminated fish. The fishing guide also tells how to prepare and cook fish to reduce contaminants to maximum extent, and gives a special warning to pregnant women or women who expect to bear children at a later date.

I would say our general philosophy is to respond to the threat of contaminants in what we view should be a balanced manner. We realize that this will not satisfy certain elements of the public who have certain philosophical viewpoints or single-issue interests. However, we feel it is the only way we can fulfill our multiple statutory charges as a regulatory department. I want to preface my next remark very, very carefully, but I would ask you to look at it as an alternative which I definitely would not propose, nor would I support; but if you wanted to go to maximum lengths to limit exposure of people to fish, I think the thing you would do would be to discontinue stocking of trout and salmon. Those fish are not naturally reproduced generally but are there because we as an agency put them there. That ends my prepared remarks. I would just ask you to think about the things I think about, that we think about, as an agency as we view our multitude of roles in this subject. We have to recognize the value of the tourist industry that is supported by the sport fishery. I suspect you are going to get more details about that a little bit later on. It is a very, very large, several hundred million dollar, annual industry. As I said before, obviously most of the fish that are eaten from the Great Lakes are taken by sport fishermen. I am going to use the word "most" a number of times here. Most are taken by sport fishermen. Most trout and salmon would pass the standard of 2 mg/kg most of the time. Most trout and salmon are cooked for eating with the skin off. Fishermen have been advised for years to skin and trim body fat. Most of the PCB exposure is behind us. These are not necessarily in order. Canada, as you are aware, does have a 2 mg/kg standard. It is my understanding that they established that on the basis of "dorsal plug of muscle". This is a very conservative way of sampling; and I would say that based on what we know of our fish, our fish will consistently pass 2 mg/kg if sampled in that manner. It is also my understanding, maybe I should brand it as hearsay, that fish from Canada that will not pass the 2 mg/kg standard are customarily exported. PCB concentrations in

Michigan fish are declining and nearly all salmon will pass the standard of 2 mg/kg any time in 1982 either on the Great Lakes themselves and in the stream harvest in the fall. As we examine the question of going to 2 mg/kg, I think if we looked at the costs in terms of reduced risk that is one of the elements on the board. If the State Department of Agriculture is asked to enforce a 2 mg/kg standard on PCBs in fish, and to do it unilaterally, I think they have every right to ask what other programs, also erected as defenders of risk, do you want them to drop. How much net reduction of risk will be achieved by that?

In closing, I am reminded of something of the PCB situation as I view the question of whether it is appropriate to go to two mg/kg or not, something like a question that was asked of Will Rogers during World War I. Reportedly, Will Rogers was asked, "What should we do about the German submarine mess?" Very quickly he said, "Drain the Atlantic Ocean." The reporter immediately said, "Well, how are you going to do that?" Rogers said, "That wasn't the question you asked me. That is for somebody else to worry about." So don't leave asking the position of Will Rogers. It is harder to drain the Atlantic Ocean than it is to decide how to do it.

CHAPTER 24

THE SCIENCE-POLICY INTERFACE IN REGULATORY DECISION-MAKING

Eileen O. van Ravenswaay
Department of Agricultural Economics
Michigan State University
East Lansing, MI 48824-1039

INTRODUCTION

Several speakers have noted that decisions to regulate environmental contaminants proceed on uncertain grounds. Scientific data are equivocal. Public demands are in conflict. We are here in hopes of improving our understanding of what should be done to resolve these issues.

If issues are to be resolved, they must be stated clearly. Hopefully, this paper will serve that purpose. My objective is to identify issues that arise because of scientific uncertainty in decisions to regulate environmental contaminants and to examine how social policy is or may be used to resolve these issues.

The following section describes the major types of tasks involved in decisions to regulate environmental contaminants. I use this description to illustrate the science-policy interface that occurs in regulatory decision-making. The next section continues this theme by examining how scientific uncertainty arises and creates a need for resolution of issues by means of policy. How policy is or may be used to resolve issues associated with scientific uncertainty is described in two more sections of the paper. One section examines procedural mechanisms and the second describes sources of policy guidelines for resolving issues in regulatory proceedings. Before concluding, I very briefly examine the implications for scientific uncertainty and how it is resolved that are present in proposals that have been recently made for reforming the regulatory process.

MONS 005122

THE SCIENCE-POLICY INTERFACE

In a very general sense, decisions to regulate environmental contaminants involve balancing risks and benefits. This is not to say that risks to human health are not the primary concern of regulators. Rather, this statement reflects the fact that the act of reducing risks means foregoing some things we value. For example, in order to reduce the risks to health associated with polychlorinated biphenyls (PCBs) we reduce consumption of fish from the Great Lakes and reduce the fire resistance of dielectric fluids used in capacitors and transformers. We give up something and gain something by regulating environmental contaminants. Collective choices would be made irresponsibly if they did not include some consideration of what must be foregone in benefits in order to achieve a reduction of involuntary health risks.

The process of balancing risks and benefits involves many tasks which may be summarized as follows:

(1) identify risks and benefits to be considered;
(2) gather data to be used in assessing risks and benefits;
(3) assess the magnitude of risks and benefits;
(4) weigh and judge the risks and benefits associated with different regulatory options;
(5) choose a performance standard from the list of options.

These tasks do not necessarily proceed in the order I have listed them. Moreover, the extent to which any one of them is carried out depends on a number of factors. Among these are the time available for making a decision, the amount of data that exists, and the policy area (e.g., environmental contamination in food, air, water, or land) that is involved. Despite variation among different decisions, however, there is always an interface where science gives way to policy choice.

The task of determining what risks and benefits are to be included in decision-making (task 1) is a matter of policy. For example, risk consideration may be limited to human health risks or it may encompass a wide range of environmental risks. Benefits might be limited to issues of food supply or they might be expanded to include secondary and tertiary impacts of regulations. The job of making these policy choices belongs in legislatures. Although legislatures are sometimes less than explicit, they do indicate the major categories of risks and benefits to be examined. The extent of consideration is indicated by legislative provisions concerning decisions which must be made rapidly and those that should proceed in a more

MONS 005123

deliberative fashion. Scientific findings inform the specific selection of what risks and benefits are to be included, but choices are guided primarily by policy, not science.

The task of collecting data (task 2) would appear to be a matter of science, but it also involves policy choices. Existing scientific knowledge and ability do determine the extent to which this task can be carried out. But the degree of factual accuracy required of regulators will influence the actual extent to which it is carried out. Requirements about factual accuracy in regulatory decision-making are determined by policy. For some decisions which must be made quickly, accuracy requirements are usually reduced. Regardless of the time frame involved, requirements on factual accuracy may differ greatly from those relied on by the scientific community.

The task of assessing the magnitude of risks and benefits (task 3) is also a matter of science and of policy. Science provides both data and theoretical guidelines for interpretation and inference. Nonetheless, scientists' data may be incomplete, their interpretations of the data may vary, and their inferences may disagree. Despite scientific disputes, regulators must decide. How they choose among different interpretations and inferences amounts to a policy on science.

The fourth and fifth tasks, weighing risks and benefits and choosing a performance level, are policy dominated. In all statutes pertaining to environmental contaminants, the direction of policy is toward reducing risks (McGarity, 1979). However, the amount of reduction of risks that is indicated will depend on the relative weights or values assigned to risks and benefits by policy and policy makers. One may disagree with these relative weights or values, but this disagreement is based on policy preference, not scientific grounds.

To state that weights or values are assigned to risks and benefits is somewhat misleading. I do not mean to imply that the regulatory decision process involves taking a unique set of numbers, assigning them weights, and then performing a kind of linear combination to arrive at an answer. The process is far more subtle. It is subtle because there are few, if any, unique numbers in regulatory decision-making. The task of weighing risks and benefits is not separate from the tasks which precede it. The weights which are assigned to risks and benefits implicitly determine how policy is applied in the tasks of collecting data, interpreting data, and drawing inferences about the magnitude of risks and benefits. Policy weights are not simply applied to numbers, they are used to determine numbers. To understand why this is so, we need to examine the

MONS 005124

nature of scientific uncertainty in more detail, for it is this uncertainty that defines the science-policy interface.

SCIENTIFIC UNCERTAINTY

Some observers contend that risk and benefit assessment is entirely a scientific process, whereas deciding what to do about risk is a question of pure social policy. However, three types of situations diminish our ability to settle questions about the magnitude of risks and benefits on purely scientific grounds (McGarity, 1979). These are:

(1) insufficient data;
(2) disagreements over data interpretations;
(3) disagreements over inferences from data.

The scientific uncertainty created by insufficient data is especially problematic for regulators dealing with environmental contaminants. By definition, these substances are not intentionally added to food, air, water, or land. Therefore, the extent of contamination is initially unknown. Since exposure is unanticipated, little information may exist about the health risks posed by exposure, let alone the economic impacts of regulations designed to reduce risks.

Since existing data is extremely limited in this situation, regulators must decide what data should be collected beyond what currently exists. But additional time spent collecting data means prolonged exposure. Thus, regulators are faced with a choice between resolving issues raised by insufficient data by means of science or by policy conclusions that quick regulatory action is needed. Resolution of issues raised in this situation is based on policy, not science.

Generally speaking, regulators will act on insufficient data when harms due to human exposure are suspected to be irreversible (McGarity, 1979). An added impetus for responding quickly exists if the amount of time and resources required to obtain the needed scientific data would be relatively large. Needed time and resources can be expected to be large when exposure is of the chronic, low-dose variety and where conditions of exposure are not stable. Furthermore, if regulatory action is not expected to result in substantial economic impacts, quick action is more likely to be taken (McGarity, 1979). Where these conditons do not hold, regulators are more likely to await further data. If they did not delay, the likelihood of reversal on appeal in the courts would increase, thus making the possiblity of quick action moot.

MONS 005125

A second situation which creates uncertainty is the problem of scientific disagreement over data interpretation. Even when data is relatively complete, scientists may not agree about the validity of the data or its meaning. This problem occurs frequently in diagnoses of lesions by pathologists, interpretations of epidemiological data, and reviews of test methodologies employed in experiments (McGarity, 1979).

To a certain extent, substantive issues which arise over data interpretation can be resolved by further scientific judgment. Through years of experience in interpreting data and the meaning of the physical world, scientists may develop different outlooks and, thus, judge differently. These differences in scientific judgment are unlikely to be changed by lengthy regulatory proceedings. The crux of the problem for regulation is separating differences in scientific judgments from the public policy preferences of scientists (McGarity, 1979). This matter cannot be settled simply on the basis of a scientist's reputation since highly respected scientsts are not immune to having opinions. Rather, the problem calls for a thorough understanding of and distinction between those issues that require scientific judgment and those that require policy judgment.

A third situation that creates scientific uncertainty is disagreement over inferences about unobserved events to be drawn from observed data. For a variety of practical or moral reasons, some questions posed in scientific terms simply cannot be answered by science. Alvin Weinberg has labeled these types of questions as being "trans-scientific" issues (McGarity, 1979).

One example of a trans-scientific issue is the extrapolation from high dose to low dose. One can give arguments in support of one or another dose response at a very low dose (Weinberg, 1978). The value of a particular set of arguments to regulators depends, of course, on the validity of the assumptions used, a matter which science has yet to settle. Another example of a trans-scientific issue is the problem of using data on other species to arrive at estimates of dose response for humans. Even at the high dose level, uncertainties will persist over this method of inference.

The existence of trans-scientific issues does not mean that regulatory decisions should be postponed until the scientific community resolves them. Indeed, it is precisely because the scientific community is unlikely to provide answers to these questions in the foreseeable future, if ever, that regulatory decisions should not be postponed (McGarity, 1979). Superficially, trans-scientific issues appear to be questions of

MONS 005126

fact. They are not. They are questions that can only be resolved by law and policy.

In order for regulators to resolve uncertainties about appropriate inferences, they must know the type of result intended by policy. For example, if a scientist informs a regulator that a certain assumption will tend to overstate risks or benefits, the regulator must decide whether this result is desirable. If the regulator knows what result is desired by policy, he can resolve the issue on policy grounds. The phrase "erring on the side of safety" reflects this result-oriented approach to resolving issues of scientific uncertainty (McGarity, 1979).

Similarly, regulatory policy may not require the same level of certainty that scientists do in drawing inferences from data (McGarity, 1979). It is routine for scientists to use the 95 percent confidence level for determining statistical signficance. Regulatory decisions may require something less than this. Again, it is a matter of policy, not science, to decide the direction in which one wants to err and how much.

Not all scientific facts involve uncertainty. When this is the case, or when consensus exists among scientists, principles of scientific proof are followed in regulatory decision-making (Ricci and Molton, 1981). But there are many regulatory decisions in which scientific certainty does not exist and disagreement prevails. Policy judgment enters where scientific uncertainty begins. Therefore, assessments of risks and benefits are not uniquely determined by facts, but reflect the weights assigned to them by policy.

The conclusion that regulators must exercise policy judgment in assessing the magnitude of risks and benefits, as well as in balancing risks and benefits, is important. It aids understanding of the respective roles of science and policy in regulatory decision-making. However, while it tells us that policy values may be substituted for facts, it does not tell us to what degree this may be done or what policy guidelines are used. The next two sections explore these questions.

PROCEDURAL MECHANISMS

The degree to which regulators can substitute policy for scientific facts depends on the procedural requirements contained in organic statutes and related laws on administrative procedure. This legislation indicates the degree of factual accuracy required of regulators by the extent to which

MONS 005127

trial-type hearings rather than more informal procedures are required of agencies.

Trial-type hearings are designed to increase the factual accuracy of agency decision-making (McGarity, 1979). These proceedings do not assume pure objectivity of all parties. Rather, through an adversarial process, each party has the opportunity to reveal defects in the reasoning of others (Majone, 1979). Thus, factual accuracy improves as implicit assumptions and biases that color testimony are revealed.

However, trial-type hearings have several drawbacks. They are lengthy. They are costly. And they can only resolve issues of fact (McGarity, 1979). Because a speedy response to health risks is desirable, and because many issues of scientific uncertainty cannot be resolved through trial-type hearings, legislators have made provisions for the use of less formal procedures. As we shall see, however, these procedures may lead to decreased factual accuracy.

One of the less formal alternatives is the "notice and comment" procedures for informal rulemaking (Majone, 1979). In this procedure, regulators publish a rationale for a proposed action and public comments are invited. The agency then publishes its final decision along with a response to written comments. The Food and Drug Administration (FDA) uses a variant of this procedure in regulating environmental contaminants in food (Merrill and Schewel, 1980).

The advantage of the notice and comment procedure is that it permits relatively quick response to situations in which regulators believe postponement may lead to undue harm to exposed populations. It is also useful when conditions, such as scientific evidence or rates of exposure, are changing rapidly. The drawback, however, is that this method provides little incentive to regulators to fully investigate available or soon to be developed scientific information.

Another procedural reform is the use of advisory panels or special commissions comprised of scientists and experts (Majone, 1979). These panels not only provide peer review of scientific findinga, but can be helpful in sorting out questions of scientific fact from issues of science policy. They can help improve regulatory proceedings by helping to build consensus and by advising when trial-type hearings would be productive. Too much consensus, however, can result in a retreat from, rather than a confrontation with, important political issues. As a result, scientific advisory groups have been accused of undue enhancement of the extent to which regulatory

MONS 005128

decisions are based on scientific fact rather than policy (Nelkin and Pollak, 1979).

There are other alternatives, such as "paper-hearings" and science courts, but the two alternatives just presented illustrate an important point. While the "notice and comment" procedure minimizes incentives for increased factual accuracy, the scientific advisory panel maximizes incentives to obscure issues while over-emphasizing the objectivity of decision-making. Neither of these alternatives offers sufficient incentives for clarifying where science ends and policy begins. Responsiblity for recognizing the science-policy interface thus depends on the awareness and insight of the individuals involved. In contrast, trial-type hearings focus strictly on factual issues and do not depend solely on the abilities of those who testify.

The extent to which regulators may substitute policy for facts depends on the degree of factual accuracy required of them. This varies from one decision to another, but a trend has developed toward increased use of informal procedures. Some of these (e.g., paper-hearings) seek to remedy the limitations of informal procedures (Majone, 1979). Continued improvement is still needed. Agencies now use a variety of informal procedures, and, for the reasons I have pointed out, each one may be expected to produce different performance outcomes.

POLICY GUIDELINES

Despite the type of procedure followed, all regulatory decisions involve degrees of uncertainty. Policy must be applied to resolve issues that cannot or will not be resolved by scientific fact. In order for regulators to resolve issues, they must know the type of results intended by policy.

Regulators determine desired results by examining their legislative mandate, court decisions, and the political environment (McGarity, 1979). The legislative mandate indicates the direction of desired results, though finding legislative intent is hardly a straightforward affair. Key phases of mandates are important.

For example, the FDA has characterized environmental contaminants as "added" substances that are "unavoidable" in the production of food. This interpretation triggers the "may render injurious" standard of the Food, Drug, and Cosmetic Act. This standard means that the FDA must demonstrate a significant possiblity of harm created by food containing an environmental contaminant. Conclusive proof of injury is not required

MONS 005129

(Merrill and Schewel, 1980). Thus, the FDA's mandate indicates the desired result, providing the agency policy grounds on which to resolve issues caused by uncertainty.

For a variety of reasons, legislatures are sometimes less than clear on the results they desire from legislation. Thus, the courts play an important role in interpreting regulatory mandates. In the area of environmental contaminants, the courts have been especially important in testing agency interpretations of their mandates. Numerous court decisions have been instrumental in distinguishing the regulator's responsibility to resolve trans-scientific issues on policy grounds and the degree of factual accuracy required in regulatory decisions (McGarity, 1979; Ricci and Molton, 1981).

While one should expect that agency interpretations of their mandates and subsequent court decisions are important in determining how they resolve issues by means of policy, it is also true that politics is an important policy referrent as well. Agencies that misinterpret the political climate will quickly find themselves subject to scrutiny by legislators. This is most likely when the intent of legislative mandates are blurred, leaving wide discretion to regulators in construing that intent (Noll, 1971). Inasmuch as an agency must rely on the political environment for policy signals, they should make sure that all affected parties have the opportunity to be heard (McGarity, 1979; Nelkin and Pollack, 1979). But, political winds are fickle. If we desire consistent policy choices of reglators, they should be given more stable policy referrents than the political climate.

A CRITIQUE OF PROPOSALS FOR CHANGE

Critics of regulatory decision-making have charged that current procedures result in irrational decisions and poor social choices. They have proposed a number of analytical frameworks which, they contend, will improve the regulatory decision calculus. Of these frameworks, four apply to environmental contaminants and will be examined here briefly. They are:

(1) risk-benefit analysis;
(2) cost-effectiveness analysis;
(3) regulatory budgeting; and
(4) cost-benefit analysis.

Risk-benefit analysis is a shorthand way of saying that the types of risks and benefits now included in decision-making should be expanded. The steps involved are similar to those I

MONS 005130

described earlier in this paper. The difference is that the consideration of different types of risks and benefits would be encyclopedic rather than delimited by policy. Accordingly, data collection and assessment would be enlarged. Presumably, risks and benefits would be weighed equally. No guidance would be provided as to how issues of scientific uncertainty would be resolved. Greater factual accuracy would be required, thus increasing the response time to contamination problems, but decreasing the substitution of policy for scientific fact.

Cost-effectiveness analysis involves divising an "effectiveness index" based on the goals of regulation. In the case of environmental contaminants, the index might be number of lives saved, years of longevity produced, number of cancers averted, or person-days of illness prevented. Regulatory options would be rated in terms of their output using the effectiveness index as a measure. Each level of effectiveness would be associated with the cost of administering the regulatory option. The ratio of cost to effectiveness for each option would then become an added piece of information to decision-makers, although the most cost-effective option would not necessarily have been chosen.

Many difficulties are presented by this framework. Different results are achieved with different effectiveness indices (Schwing, 1979). Important costs, such as reductions in food supply, are omitted. Scientific uncertainty remains, but with no policy guidance as to its resolution in index measurement.

Regulatory budgeting is similar to cost-effectiveness analysis, except that the notion of costs is expanded to include costs of regulation to society beyond purely administrative costs (Lave, 1981). Agencies would be limited in the total costs they could annually produce. In addition to the problems enumerated for cost-effectiveness, this framework would involve uncertain cost estimations and give greater weight to costs than is now the case. It also adds a new political dimension to regulation through the annual development of the regulatory budget constraint by Congress.

Cost-benefit analysis involves enumerating all the costs and benefits of a regulatory option in terms of dollars, where possible. Under this framework, decision-makers receive the added piece of information of whether or not an option's benefits exceed its costs. In practice, however, techniques for valuing benefits and costs in dollars are unreliable (Baram, 1980). This framework does not resolve problems of inadequate data, disagreement over data interpretation, or disagreement over inferences. In fact, these difficulties are confounded by

MONS 005131

the expansion of the number and types of costs and benefits to be considered. This in turn raises the problem of appropriate procedural means for enhancing factual accuracy while preserving regulators' flexibility for responding quickly to contamination problems. This framework would also give greater weight to economic efficiency goals than is now the case.

Despite their weaknesses, the proposed frameworks do contain a number of valuable suggestions. They would focus increased attention on implicit policy choices and the establishment of consistent grounds for balancing competing objectives. They would also provide a mechanism for comparing different regulatory actions which seek to achieve the same goal—risk reduction—thus enhancing our ability to establish priorities for allocating our limited resources. Finally, they give more attention to what must be given up in order to achieve risk reduction.

Adopting any one of these frameworks would result in a subtle shifting of policy goals. Perhaps we as a society desire such changes. But if that is the case, the appropriate forum for deciding is legislative not regulatory. Before legislators decide, more attention should be given to the consequences of change. In particular, the fact that these frameworks will produce assessments of risk and benefits that are not unique, but are outcomes of both policy and science, needs greater recognition. These frameworks would not simply change the range of numbers used and how they weighed in reaching decisions. They would also change the policies used to resolve the scientific uncertainty encountered in producing estimates of risks and benefits.

CONCLUSIONS

I have attempted to clarify the interface at which science and policy meet and to show how procedural means and policy are used to resolve issues of scientific uncertainty in regulatory decision-making. I have argued that the weights given to risks and benefits by policy not only determine how regulators balance them in choosing a performance level, but determine as well how the magnitude of risks and benefits is assessed.

When scientific uncertainty arises because of questions that transcend science, there is little we can do to improve decision-making except to devise clear policy referrents. Scientists have a role here, I think, in investigating the relative magnitude of risks and benefits that accompany various collective and personal choices. Beyond this, we should expect better decisions by regulators as more and better data are

MONS 005132

collected on questions of fact that do not transcend science. However, we should become more aware of those issues that must be settled on policy grounds. Better procedures can be designed if things that are not issues are resolved in appropriate forums and given policy guidance by legislatures and courts.

We should not be quick to adopt new frameworks for decision-making whose policy consequences have not been thought out. Many of the problems of interpretation of legislative intent are now being resolved in the courts. We should expect that as they are resolved and agency procedures are reformed that the lengthiness, if not the complexity, of regulatory proceedings will be reduced. Scientists can help by carefully examining where their contributions can be made most valuably at the science-policy interface.

LITERATURE CITED

Baram, M.S. 1980. Cost-Benefit Analysis: An Inadequate Basis for Health, Safety, and Environmental Regulatory Decision-Making. Ecology Law Quarterly 8:473-529.

Lave, L.B. 1981. The Strategy of Social Regulation. The Brookings Institution, Washington, DC. 166 pp.

Majone, G. 1979. Process and Outcome in Regulatory Decision-Making. In: C.H. Weiss and A.H. Barton (eds.), "Making Bureaucracy Work," pp. 235-258. Sage Publications, Beverly Hills, CA.

McCarity, T.O. 1979. Substantive and Procedural Discretion in Administrative Resolution of Science Policy Questions: Regulating Carcinogens in EPA nd OSHA. The Georgetown Law Journal 67:729-811.

Merrill, R.A. and M. Schewel. 1980. FDA Regulation of Environmental Contaminants of Food. Virginia Law Review 66:1357-1441.

Nelkin, D. and M. Pollak. 1979. Problems and Procedures in the Regulation of Technological Risk. In: C.H. Weiss and A.H. Barton (eds.), "Making Bureaucracy Work," pp. 259-280. Sage Publicatons, Beverly Hills, CA.

Noll, R.G. 1971. Reforming Regulation. The Brookings Institution, Washington, DC. 116 pp.

Ricci, P.F. and L.S. Molton. 1981. Risk and Benefit in Environmental Law. Science 214(4):1096-1100.

MONS 005133

Schwing, R.C. 1979. Longevity Benefits and Costs of Reducing Various Risks. Technological Forecasting and Social Change 13:333-345.

Weinberg, A.M. 1978. On-Dose Response and Standard Setting. Environment International 1:285-287.

GENERAL REFERENCES

Coyer, B.W. and D.S. Schwerin. 1981. Performance and Institutions in the Regulation of Toxic Chemicals: A Comparative Analysis of Ontario and Michigan. Canadian-American Studies Conference, Michigan State University, East Lansing, MI. 50 pp.

Hanke, S.H. 1981. On the Feasibility of Benefit-Cost Analysis. Public Policy 29:147-157.

National Research Council. 1975. Decision Making for Regulating Chemicals in the Environment. National Academy of Science, Washington, DC. 232 pp.

Page, T. 1978. A Generic View of Toxic Chemicals and Similar Risks. Ecology Law Quarterly 7:207-242.

U.S. Congress, Office of Technology Assessment. 1979. Environmental Contaminants in Food. U.S. Government Printing Office, Washington, DC. 229 pp.

MONS 005134

CHAPTER 25

DEALING WITH MULTI-AGENCY AND MULTI-STATE REGULATION OF POLYCHLORINATED BIPHENYLS

Karl E. Bremer
Toxic Materials Branch
U.S. Environmental Protection Agency
Region V
Chicago, Illinois 60604

INTRODUCTION

During the early 1960s, interest increased concerning the biological effects of environmental levels of chlorinated pesticide residues such as DDT and chlordane. Measurement of low levels of these compounds in biological samples required the development of sensitive analytical procedures that could both separate the pesticides from each other and from similar compounds and measure the amount of each compound present. The technique that was developed to perform this analysis was gas chromatography. Gas chromatography proved to be a very useful method for determining the concentrations of low levels of pesticides in environmental samples, but the detector often recorded the presence of a number of chemicals that could not be identified by comparison with known pesticide chemicals.

In 1966, Soren Jensen attempted to identify the unknown compounds that were being recorded during routine pesticide analyses. In order to determine when the unknown compounds first appeared in biological samples, he analyzed feathers from eagles that had been taken from museum collections. He found the unknown materials in feathers collected as early as 1944, before the widespread use of chlorinated pesticides, and so concluded that the unknown materials were not pesticides or degradation products of pesticides. By testing chlorinated materials that were in wide use before 1944, he eventually identified commercial polychlorinated biphenyls (PCBs) as the source of the unknown compounds, and published this finding in late 1966 (Jensen, 1966).

MONS 005135

A full discussion of the presence of PCBs in pesticide analyses was published by Widmark (1967), and this set off a number of investigations to determine the extent of environmental contamination by PCBs. The discovery that PCBs were common in the environment in sufficient concentrations to affect the reproduction of wild birds was published by Risebrough et al. (1968). This article was picked up in the press and initiated the widespread concern about possible human health effects from PCBs in the environment.

The Yusho incident that occurred in Japan during the summer of 1968 added to the public concern over the toxicity of PCBs. This was a case of widespread PCB poisoning caused by contamination of cooking oil. The resulting concern over PCBs led to regulatory activity and increased research throughout the world. In July of 1971, a similar incident in the United States contaminated a considerable quantity of chicken feed as the result of leakage of PCB heat transfer fluid. The U.S. Food and Drug Administration (FDA) eventually destroyed thousands of chickens and eggs that were fed this contaminated feed. Starting in 1971, Monsanto voluntarily limited sales of PCBs to closed electrical equipment applications and recommended that existing PCB-filled heat transfer systems be drained and refilled with non-PCB fluid.

PCB USE RESTRICTIONS AND FEDERAL GOVERNMENT REGULATIONS

The Yusho incident created considerable concern in the United States over possible contamination of food by PCBs. The FDA started routine sampling of foods for PCBs in 1969, and soon found that PCBs were present in fish from the Great Lakes, that there was PCB contamination of milk caused by use of PCBs as a solvent in pesticide sprays and as a component of sealants used in farm silos, and that there was contamination of chickens resulting from PCBs introduced into the feed as a component of ground bread cartons and wrappers. It has since become apparent that the presence of PCBs in fish is a problem that has existed since at least 1968, although PCBs were not identified as the cause of the problem until 1971.

From 1969 through 1971, the FDA established temporary tolerance levels for PCBs at 0.2 mg/l in milk, 5 mg/kg in edible flesh of fish, 5 mg/kg in poultry, and 0.5 mg/kg in eggs. In 1970, the FDA prepared a summary of the available information on the chemistry and toxicity of PCBs, and in 1972 published a notice of proposed rulemaking. The U.S. Department of Agriculture (USDA) also prepared a report on ways that it could act to limit PCB contamination of food (USDA, 1972). In 1973,

the FDA formally established limits for PCBs in food and animal feed and proposed a revision of these limits in 1977.

During 1970, the Council on Environmental Quality (CEQ) studied regulatory approaches to the problem of toxic chemicals in the environment. In its report, "Toxic Substances," published in 1971, CEQ identified PCBs as a major problem. The initial response of the responsible agencies was to establish a task force to review the available information on PCBs and recommend regulatory alternatives.

During 1973 and 1974, the U.S. Environmental Protection Agency (EPA) proposed the establishment of water quality criteria for PCBs in industrial discharges as part of a program for establishing such criteria for a larger group of pesticides. However, PCBs were not covered in the effluent standards until 1977.

The Occupational Safety and Health Administration (OSHA) adopted the standards for PCB exposure in industrial air that had previously been established by the American Industrial Hygiene Association. The National Institute of Occupational Safety and Health (NIOSH) conducted a major review of available data and an extensive program of industry assessment in the mid-1970s, and the final report published in 1977 recommended that the allowable concentration of PCBs in the workplace be reduced.

Government actions restricting the use of PCBs were not limited to the United States. Japan banned the manufacture and use of PCBs in the early 1970s because of public pressure following the Yusho incident. Sweden banned the use of PCBs at about the same time. International actions, particularly in the European community, were also taken to reduce the risk of food contamination by PCBs during the early 1970s. United States and Canadian activity to regulate manufacture, use, transport, and disposal followed during 1975 and 1976.

PCB LEGISLATION UNDER THE TOXIC SUBSTANCES CONTROL ACT

Senator Gaylord Nelson introduced a bill to amend the pending proposed Toxic Substances Control Act (TSCA) on March 26, 1976. This bill required the EPA to establish labeling and disposal requirements for PCBs and mandated an eventual ban on the manufacture and processing of PCBs. This provision was incorporated into TSCA as Section 6(e) and became a legislated requirement when TSCA was signed into law on October 11, 1976. The effective date of TSCA was January 1, 1977.

MONS 005137

Section 6(e) of TSCA required the EPA to establish rules to: (1) govern the disposal and marking of PCBs; and (2) prohibit, with certain exceptions, the manufacture, processing, distribution in commerce, and non-totally enclosed use of PCBs.

Final marking and disposal rules appeared in the Federal Register on February 17, 1978 (clarifying amendments to this rule appeared in the August 2, 1978, Federal Register).

On June 7, 1978, the proposed PCB ban rule was published in the Federal Register. The final PCB ban rule appeared in the Federal Register on May 31, 1979; this rule took effect on July 2, 1979.

The May 31, 1979, PCB ban rule specifically:

(1) prohibits the manufacturing, processing, distribution in commerce, and use of PCBs, except in a totally enclosed manner (with certain exemptions), after July 2, 1979;

(2) provides authorizations for certain processing, distribution in commerce, and use of PCBs in a non-totally enclosed manner;

(3) prohibits, unless exempted by EPA, all manufacturing of PCBs after July 2, 1979; and

(4) prohibits, unless exempted by EPA, all processing and distribution in commerce of PCBs after July 1, 1979.

Since the February 17, 1978, PCB disposal and marking rule requirements are integrated into this PCB ban rule, the rule now supersedes all earlier PCB regulations.

STATE LEGISLATION REGULATING PCBs

During the period between 1975 and 1977, significant activity, particularly among the Great Lakes states, occurred with respect to PCB regulation. The following states passed PCB regulations.

Michigan

Michigan Act 60, Public Acts of 1976, was passed by the legislature and signed by the Governor on March 25, 1976. The Act took effect April 1, 1977, and banned the use, manufacture,

mg/kg PCB, except as a dielectric fluid in electrical transformers and capacitors. Act 60 also provided for labeling, reporting, and proper disposal of PCBs.

Indiana

In February, 1976, the State of Indiana passed PCB legislation similar in scope and intent to Michigan Act 60. The law became effective May 1, 1976, because it was stated that an emergency existed with respect to PCBs in Indiana. The law mandated that the Environmental Management Board promulgate rules required by the law, including rules regarding the disposal of PCBs. In Indiana, however, the law was not applied, nor were rules promulgated because of the pre-emption aspect of the Federal Toxic Substances Control Act.

Wisconsin

The Wisconsin Statute 144.79 (The Manufacture and Purchase of PCBs) was passed on July 1, 1977. This legislation required the Wisconsin Department of Natural Resources to adopt rules prescribing methods and designating sites and facilities for disposal of PCBs and products containing PCBs. The rule required reporting and the use of a manifest for PCB disposal. The rule also granted exemptions for sludge produced by waste water treatment effluents and the manufacture and sale of recycled paper products containing PCBs.

Minnesota

During 1977, the State of Minnesota passed the PCB Prohibited Use Act. This Act required that the Minnesota Pollution Control Agency develop regulations on labeling, use, sale, purchase, handling, and disposal of PCBs. These regulations became effective in October, 1977. Response to PCB spills and PCB disposal has been regulated through more current state waste disposal and regulations.

THE INTEGRATED APPROACH TO LEGISLATION

The primary agencies regulating PCBs at the federal level include the FDA, NIOSH, OSHA, and EPA; and at the state level, include the State Pollution Control Agencies (those in particular having existing regulations) and State Departments of Health. During the past six years, there has been a unified

MONS 005139

effort among these agencies to restrict further PCB contamination caused by this widely used substance.

A recent example of this unified effort may be illustrated by a recent case involving PCB contamination at a scrap yard facility. A state pollution control agency was recently investigating general disposal practices at a scrap yard in the Chicago area. The state inspector noted that PCB-containing transformers were being reclaimed and disposed of indiscriminantly. The inspector called EPA and indicated that violations of the federal PCB regulation were occurring at the facility. EPA performed a follow-up inspection immediately; and while correcting the disposal violations related to the PCB transformers, interviewed a number of workers at the site. A crane operator at this facility complained of skin irritations and recurrent headaches from his particular job of removing copper cores from the PCB transformers. The EPA inspector required the assistance of the State Health Department and the Cook County Hospital Department of Occupational Health in examining and reviewing the case of the crane operator. OSHA and EPA are completing enforcement work on violations of their respective regulations related to the workers' health and work practices and illegal disposal practices at the facility.

Other integrated approaches to PCB regulation often include discovery of PCB-contaminated fish in interstate transport by FDA. Such contamination incidents are generally reported to State Health Departments and State Pollution or Conservation Departments. These departments inform the EPA and a coordinated effort may then be initiated to track environmental and possibly industrial contamination in a particular area.

During the interim period, state warnings are often placed on a watershed advising against the consumption of sport-caught fish or toward limiting consumption. If an industrial facility is isolated as a possible contributor to the PCB contamination incident (from federal and state information), a complete facility inspection is conducted. This inspection may be conducted jointly by state and federal officials provided confidentiality is not requested under TSCA by the facility to be inspected. Enforcement action may then be taken if violations of the PCB regulation are documented.

Other integrated multi-agency approaches to the regulation of PCBs include the establishment of enforcement cooperative agreements with the states of Michigan and Ohio. These recent pilot grant programs (established between EPA and the state pollution control agencies) include the inspection of approximately 300 facilities using or disposing of PCBs. Inspections

MONS 005140

will determine compliance with the TSCA regulations and appropriate follow-up actions such as letters of compliance, notices of violation, or other enforcement proceedings. In cases where the state agency is not to conduct the enforcement activities, the case will be referred to EPA. State personnel are being delegated federal authority to do this work.

CONCLUSION

Multi-agency regulatory approaches to PCB contamination incidents during the past five years have proved to be effective. Both state and federal agencies have observed improved compliance during the period; and proper disposal, labeling, and industrial awareness of the PCB problem seem to be the strongest contributing factors. The joint regulatory approaches to PCB control will continue and will provide a strong base for control of other chemicals of concern to human health and the environment.

LITERATURE CITED

Jensen, S. 1966. Report of a New Chemical Hazard. New Scientist 32:612.

Risebrough, R.W., P. Reiche, D.B. Peakall, S.G. Herman, and M.N. Kirven. 1968. Polychlorinated Biphenyls in the Global Ecosystem. Nature (London) 220:1098-1102.

USDA. 1972. Ad Hoc Group on PCBs. Agriculturist's Responsibility Concerning Polychlorinated Biphenyls (PCBs). Office of Science and Education, U.S. Department of Agriculture, Washington, DC.

Widmark, G. 1967. Possible Interference by Chlorinated Biphenyls. J. Assoc. Off. Anal. Chem. 50:1069.

MONS 005141

CHAPTER 26

THE ROLE OF THE LEGISLATURE IN THE REGULATION OF TOXIC MATERIALS

Thomas Anderson
Michigan State Representative
1965-1982
(Chair, Committee on Conservation
and Environment, 1969-1982)

Legislatures must take action on a number of issues that affect the lives of everyone although legislators are often ignorant of the technical aspects of these issues. Only a very small percentage of the people in any legislature are competent in some technical discipline. You may find in the average legislature, similar in size to Michigan's (148 members), at the most 6, 7, or 8 people who have technical competence in some scientific discipline. To deal with this problem, states, with the help of the National Science Foundation (NSF), have established technical advisory mechanisms first for the governors of the several states around the country and then, in recent years, for the special needs of the several legislatures. Michigan is one of about twenty states that now have advisory mechanisms for their legislatures.

The legislature and the legislative process have a definite role in the kinds of issues we are discussing in this conference. In Michigan, the role is clearly stated in the state Constitution and let me take a moment to quote Section 51 of Article 4. It states:

> The public health and general welfare of the people of the state are hereby declared to be matters of primary public concern. The legislature shall pass suitable laws for the protection and promotion of the public health . . . Conservation and development of the natural resources of the state are hereby declared to be of paramount concern in the interest of the health, safety, and general welfare of the people.

MONS 005142

> The legislature shall provide for the protection of the air, water, and other natural resources of the state from pollution, impairment, and destruction.

I am proud to tell you that the Michigan legislature leads the nation in what they have done about these kinds of problems. It has responded by enacting a great number of environmental protection statutes, some of them dating back 20 to 25 yrs, but most dating back to the late 1960s and early 1970s. At that time, there was a rash of legislative action providing for environmental control. I can only give you a sample of the wide variety of those controls. I'm quite well aware of these because I was the sponsor, or one of the sponsors, of many of them. The legislature started out with what is considered to be the most important Michigan act: The Environmental Protection Act of 1970. It allows any citizen of the state to sue any entity or any other citizen of the state (citizen has a broad definition) in behalf of the public trust in the environment. Anybody can sue anybody because of a possible threat to the environment; no proof is needed that something has already happened. The class action opening has been used many, many times since the Act's passage. Twenty-eight other states have tried to pass such a law and 11 have actually passed one. It was even tried several times in the U.S Congress, but unsuccessfully. It was a landmark piece of legislation.

Several important amendments to the Water Resources Commission Act, which dates all the way back to 1929, were made in 1970 and 1973. The Air Pollution Control Act of 1965 was amended several times. The Phosphate Control Act was passed. The Inland Lakes and Streams Act, which dealt with the quality of the water in our inland lakes and streams, was enacted. Other environmental legislation of this period included: The Shoreland Protection Act, The Soil Erosion and Sedimentation Control Act, The Pesticide Control Act, and The Recreational Land Trust Fund Act. I would like to comment on this last one. Senator Kammer, from Pontiac, had the idea that we ought to set aside the oil and gas revenues from the Pigeon River Country State Forest, a second growth area but nevertheless a unique environmental area in which we have great pride. He said we should use this money for the benefit of posterity by buying lands that are sensitive in nature, but which Michigan doesn't now own. The revenues have been set aside for that purpose and, in the last several years, a great many excellent purchases of sensitive, environmentally important land have been made.

In addition, the legislature passed The Sand Dune Protection Act, The PCB Control Act, several acts on PBBs (polybrominated biphenyls), and an act creating The Toxic Substance Control

Commission. This Commission, which is taking part in this conference, has been bringing to the forefront some important information on the problems that toxic materials and substances are posing for the people of Michigan. The Wetlands Protection Act, which I'll allude to later, was also enacted as was The Land Resource Inventory Act. The Public Health Code was completely revised with many of the revisions dealing with environmental concerns.

A Solid Waste Management Act and a Hazardous Waste Management Act were passed, although with great difficulty. There were many meetings drawing up the language of these acts and interested parties were brought in from all over the country. They were necessary to provide legislators with answers to many of the technical questions. Just yesterday, the House passed three bills which prohibit drilling and exploration for hydrocarbons in the Great Lakes waters. These bills went back to the Senate, will be dealt with this morning, and sent on to the Governor.

We have a long record of trying to deal with the questions you are grappling with here and other questions like them. Many of these Michigan acts preceded federal acts on the same subjects. One of the problems we have in trying to deal with federal acts, and several of the speakers have alluded to it, is the extensive delay often experienced in federal control. The previous speaker talked about all the work that was done in the 1960s on PCBs, the subject of this conference. In 1973, the Food and Drug Administration (FDA) set some limits on how many parts per million could be let into the food chain. In 1975, Congressional action was begun. In 1976, Congress passed The Toxic Substances Control Act and it was 1979 before the final rules were published in the Federal Register. Meanwhile, several of the states found it necessary to take control in hand on their own and they did.

I want to touch briefly on some other things the legislature does besides enacting laws. After a law is enacted, it is fleshed out. The law is pretty generic in nature and doesn't contain many details. A system of rules has to be established. These are also known as administrative procedures or regulations or by other names in different states. In Canada, they are called guidelines. After a bill is passed and becomes an act, the responsible agency works up a series of rules which provide the intimate details. In Michigan, this process requires public hearings, review by the Attorney General for legality, review by the Legislative Service Bureau to see that the words are right, and so on. Then the rules come to a joint legislative committee for review and approval or rejection. The committee

MONS 005144

cannot modify the rules because they are not the legislature's rules, they are the agency's rules. The legislative committee does, however, have a veto power if it doesn't think that the rules agree with the statute. If it thinks that the statute has been circumvented or otherwise distorted, or if it appears that the questions that were raised at public hearings have not been properly dealt with, the agency can be asked to take the rules back and amend them to deal with these concerns. Michigan is the only state of the 50 that has such complete veto power at the legislative level over administrative rules. To get that power, a gubernatorial veto of the bill allowing it had to be overriden several years ago--a very significant gain for the legislative process.

These administrative rules are very, very important and sometimes are extremely difficult to establish (as an example, it took over two years of diligent work to get the rules finally passed for both The Solid Waste Management Act and The Hazardous Waste Management Act, after the acts were passed). The agency had dozens of meetings trying to work out difficulties that people throughout the state had brought up with respect to these rules. They were finally passed, however, and are now under review to see if the rules, or the act itself, need to be changed in any respect.

Once administrative rules have been adopted, another legislative process comes into play--called funding. Funding doesn't seem to be a big word, but it is a very big word when an agency is trying to get it. In the legislative process, funding is set up by the appropriations committees of the two houses. The rules are taken to the appropriations committees and the amount needed to carry them out is requested from the committees through the annual budget review process. More than likely, the committee will say that there isn't any money for that or will ask the agency to see what can be done with less money. A struggle then ensues to get the job done as well as possible with the funding that is available.

Probably no one in this room is unaware of the fiscal trouble besetting Michigan. Such trouble translates into everyone's budget being cut. Michigan State University has been told, for example, that it is going to have to cut back a percentage of its budget and that then results in tuition increases or cutbacks in programs, or perhaps elimination of whole departments. Other agencies of government have been told that they must cut back, or that a particular program must be dropped, or there will be no funding for a particular operation. Funding is an activity that comes into play after all the other activities have been completed and, notwithstanding the

completion of prior steps, can virtually eliminate a program by its absence or diminution.

I am not going to deal in any significant detail with what has happened at the state level with federal funding except to tell you that the federal funding has been a very real problem for state and local governments throughout the country. One good example is that Michigan had been led to expect a grant of $308,000 to develop a pilot state enforcement program for PCB regulation under TSCA, and it was expected that the money would be available on January 1, 1982. Well, it is now past this date and the funds have not arrived (and probably won't), because this is the way the federal government agencies have been treating people lately. They lead a state to expect a grant and then they change their minds or their policy of payment as a means of control.

Another problem is that the federal administration's budget further proposes to freeze the absolute dollar amounts. For example, if there were $3 million to do a job last year, the same amount is available this year notwithstanding that there are some built-in incremental cost increases in the program. The idea apparently is that the states will find a way to pick up the difference. Well, I don't know how we are going to find a way in Michigan.

The Governor appeared on television the other night saying that, just to keep things at the present level, even allowing some cutbacks in very significant and important areas, we are going to have to consider an income tax increase. I have been in politics for 33 yrs now and I have yet to receive a letter from a constituent saying "please raise my taxes." A letter came in early the next morning after the Governor spoke from a fellow who must have run to the post office to mail it after the Governor's appearance. He said, "Whatever you do, don't vote for Governor Milliken's crazy scheme to raise taxes or you are a dead man at election time." I know that; he didn't have to tell me. I know what gets one elected and what gets one defeated, and voting for taxes is what gets an office holder defeated. For that reason, the programs we are talking about here will probably be cut back more and more severely because it does not seem likely that we will pass the Governor's income tax increase however necessary it appears to many of us, myself included.

Now I want to mention another responsibility of the legislative process, and that is oversight. For example, a special committee was just convened under House Resolution 406 for the purpose of looking at The Hazardous Waste Management Act and

The Solid Waste Management Act to see if these acts are serving the purposes for which they are intended. If they are not, because of certain loopholes or problems, the committee must decide what must be done to change them. So a final legislative responsibility is to see that, once everything is in place, everything is working all right. Oversight is an area of serious legislative concern, but not enough of it is done because of the limitations of time and staff. More ought to be done, and is being done in the legislative process in several states. I hope Michigan can join these ranks.

I want to touch briefly on one aspect of the environmental control situation that some of you may not be aware of. In the early 1970s and late 1960s, there was a worldwide crescendo of environmental movements which originated in America. The aim was to improve the quality of the environment, to remove contaminants from the environment, and to protect the health of the people from pollution and contamination sources of all kinds. As a consequence of this atmosphere, we were able to pass The Environmental Protection Act of 1970, were able to pass PCB controls, PBB controls, and to ban DDT from use in Michigan, as well as other states and other countries in the world. All this resulted from the growth of the feeling that something had to be done to turn around the dangerous condition that had begun to exist in the environment.

Things got tougher, however, around the middle of the decade and it began to be more and more difficult to collect the votes to pass environmental issues. The name of the game in the legislative process is votes. You couldn't pass a bill authorizing motherhood without votes, which have "magic" numbers, varying from state to state. The "magic" numbers of votes in Michigan are 56, 20, and 1: 56 votes in the House, 20 in the Senate, and 1 in the Governor's chair. If you don't have 56 votes in the House, you don't have a bill. If you don't have 20 votes in the Senate, you don't have a bill. If you don't have one in the Governor's chair, you don't have a bill. Regarding environmental issues, those "magic" numbers became harder and harder to reach in the last years of the decade. The Wetlands Protection Act, of which I was one of the sponsors, took 6 yrs of hard, diligent effort to pass. It has gotten tougher and tougher to get any sort of environmental control through the legislative process.

What has happened now in the 1980s? It has become even tougher. What is being experienced is that some of the environmental controls that we passed, some of the prohibitions, some of the regulatory measures from those easier years, are now under attack. Last year, for example, in order to stave off

MONS 005147

an even worse situation, we had to eliminate the air and water pollution surveillance fees which we have been charging industry for the inspections and control processes on their smoke stacks and other outfalls, since about 1969 or 1970. The legislature finally agreed recently to a 5 yr phase out plan in order to avoid an immediate cut off. During this 5 yr phase out, the cost of surveillance will be gradually absorbed by the general fund of the state, and industry, which caused the problem requiring the surveillance operations, won't have to pay special fees for it.

There is now a bill before the state Senate which seeks to amend The Phosphate Control Act which was designed to limit phosphorus compounds reaching surface waters. Actually, the new bill seeks to set the phosphorus level so high that we may as well not have the act. The Sand Dunes Protection Act is under two court suit attacks right now and is also the focus of legislative efforts for repeal. Some other acts are also under this kind of pressure.

We have another problem. The federal government has begun to shift its gears. The present administration has taken a decided posture of trying to eliminate environmental and regulatory control. The Environmental Protection Agency (EPA), for example, is now in the business of eliminating the EPA and it is in the business, moreover, of getting rid of the controls for the benefits of the people that EPA has represented all these years. I consider that to be a dismal occurrence. I am sorry to see it happen but I don't know what to do about it since the President, of course, has more control than I. As long as he is in control, it's going to get worse instead of better, it would seem. The philosophies of the present administration are to minimize the controls and to turn them back to the states, which have demonstrated over time in some areas, that they did not have the capabilities or the interest to deal with them. We are thus scrapping the gains of the past several years.

There is a misshapen notion of how things are done in the legislative process. The notion has to be changed. First, you have to remember that the legislative process takes votes. No matter what you are trying to do, you have to have the votes; again, 56, 20, and 1. You have to have people in the legislative process who have an understanding of and sympathy for the kinds of interests that you have. If you don't, your interests are not going to be reflected in the outcome of the process.

Then, once they get there, it is important that the right people serve on the appropriate committees: appropriations

MONS 005148

committees, the conservation committees, or on the administrative rules committee. One of the reasons so many conservation-oriented acts were passed in the past decade or decade and a half in our legislature is that I was given by the speaker good, competent people who agreed with me on many of the things that I thought were important to change. Had those kinds of persons not been on my committee, many good bills would still all be resting in the file.

So it is important who gets elected, important who gets appointed to committees, and important who does the appointing. Thus, each person in our society must go out and express himself or herself at the ballot box so that the candidates he or she thinks will do the kind of thing that is important to him or to her get elected.

MONS 005149

CHAPTER 27

REGULATION OF PCBs IN CANADA

Donald L. Grant
Toxicological Evaluation Division
Health Protection Branch
Health and Welfare Canada
Ottawa, Ontario
Canada K1A 0L2

REGULATION OF USE

Although polychlorinated biphenyls (PCBs) were never manufactured in Canada, they received widespread industrial use for at least 40 yrs. Since 1977 their use has been regulated under the Environmental Contaminants Act. Section 3 of Chlorobiphenyls Regulation No. 1 states:

> For the purpose of subsection 8(2) of the Act, the following commercial, manufacturing and processing uses are hereby prescribed effective September 1, 1977, as uses in respect of which chlorobiphenyls may not be used.
>
> (a) use in the operation, servicing or maintenance of any product, machinery or equipment other than
>
> > i) electrical capacitors, electrical transformers and associated switchgear and machinery or equipment used to manufacture electrical capacitors, electrical transformers and associated switchgear;
> >
> > ii) heat transfer equipment, hydraulic equipment and vapour diffusion pumps that were designed to use chlorobiphenyls and were in use in Canada before March 1, 1977; and

MONS 005150

iii) machinery or equipment, the operation of which is intended to destroy the chemical structure of chlorobiphenyls, and

(b) use as a constituent of any machinery, equipment or product manufactured in or imported into Canada after September 1, 1977, other than electrical capacitors, electrical transformers and associated switchgear. Chlorobiphenyls is defined as "those chlorobiphenyls that have the molecular formula $C_{12}H_{10-n}Cl_n$ in which 'n' is greater than 2." (Canada Gazette Part II, Vol. III, No. 18, 28/9/77)

In 1980, Section 3 of the Chlorobiphenyl Regulations No. 1 was revoked and the following substituted therefore:

3. For the purpose of subsection 8(2) of the Act, the following commercial, manufacturing or processing uses are hereby prescribed as uses in respect of which chlorobiphenyls may not be used:

(a) use in the operation of any product, machinery or equipment other than

i) electrical capacitors, electrical transformers and associated electrical equipment;

ii) heat transfer equipment, hydraulic equipment, electromagnets, and vapour diffusion pumps that were designed to use chlorobiphenyls and were in use in Canada before September 1, 1977; and

iii) machinery or equipment, the operation of which is intended to destroy the chemical structure of chlorobiphenyls;

(b) use in the operation of electromagnets that are used to handle food, animal feed or anything intended to be added to food or animal feed for any purpose whatsoever;

(c) use as a constituent of any product, machinery or equipment manufactured in or imported into Canada after September 1, 1977, other than electrical capacitors, electrical transformers and associated electrical equipment;

(d) use as a constituent of electrical capacitors, electrical transformers and associated electrical

equipment manufactured in or imported into Canada after July 1, 1980;

(e) use in the servicing or maintenance of any product, machinery or equipment, other than electromagnets, electrical transformers and associated electrical equipment; and

(f) use as new filling or as make-up fluid in the servicing or maintenance of any electromagnet, electrical transformer or associated electrical equipment. (Canada Gazette Part II, Vol. 114, No. 13, 9/7/80)

In addition, regulations will soon be promulgated respecting the release of PCBs into the environment and prohibiting the importation or sale of equipment containing PCBs in a concentration of greater than 50 mg/kg.

The Environmental Protection Service (EPS) of Environment Canada developed a labelling system (Figure 1) to alert people to the presence of PCBs in equipment and to allow preparation of an inventory of PCBs contained in equipment and in storage awaiting disposal. A "Handbook on PCBs in Electrical Equipment" was prepared by EPS to help insure the success of this voluntary labelling program, and to provide guidelines for the management of electrical equipment and wastes containing PCBs.

As an extension of this program, a federal interdepartmental committee was given the task of assessing the hazard potential from equipment containing PCBs in use in the food, feed, and grain industries. Officials from Agriculture Canada, Environment Canada, Health and Welfare Canada, and Fisheries and Oceans developed a joint training program for their inspectors which are located across Canada. To accommodate the various federal inspection agencies, EPS organized and conducted 36 seminars to train the inspectors on the procedures for:

(1) conducting inspections of equipment containing PCBs;
(2) monitoring and evaluating the condition of the equipment; and
(3) assessing the potential hazard of PCB-filled equipment in use in or around food processing areas.

After attending a "PCB inspection training session", the inspectors then integrated this "PCB inspection" into their department's regular inspection program. To obtain uniformity in inspection, a guide "PCBs Inspection Procedures and Guidelines for Completing the Plant Evaluation Form" was prepared by EPS.

MONS 005152

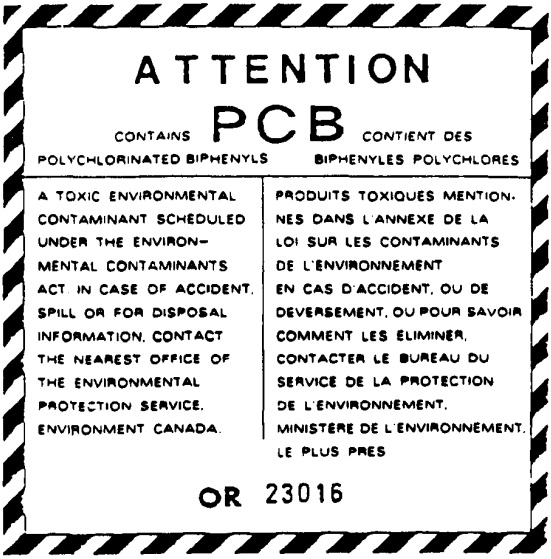


Figure 1. Environmental Protection Services labels for equipment containing PCBs.

A Communique is jointly being prepared by these four federal departments for mailing to the various food, feed, and grain industries. This Communique briefly outlines the reason for our concern and the scope of our inspection program.

The inspection program and the Communique are aimed at making the industrial sector aware of our concern. It is anticipated that industry will volunteer to initiate any remedial action that may be necessary to correct potential problems.

MONS 005153

REGULATING RESIDUES IN FOODS

In 1975, the Health Protection Branch (HPB) announced a guideline of 2 mg/kg for PCB residues in the edible portion of commercial fish. This guideline is administered through the cancellation of commercial fishing licenses for those fish in those waters likely to contain PCB residues greater than 2 mg/kg. This program requires the cooperative participation of the Federal Department of Fisheries and Oceans and the appropriate provincial department which has jurisidiction over commercial fishing.

In Canada, the great majority of the chemical residue analyses of commercial fish are carried out by Fisheries and Oceans. Since the potential for PCB residues is greatest in fish from the Great Lakes, a monitoring program to measure residue trends is conducted in this area. In this program, the samples are collected by the Ontario Ministry of Natural Resources and analyzed by Fisheries and Oceans. The results are used to determine which areas will be closed to commercial fishing. Fisheries and Oceans also sample Great Lakes commercial fish in their compliance program.

Sport fishing comes under the jurisdiction of the provinces. The Province of Ontario publishes, on a yearly basis, 3 booklets entitled "Guide to Eating Ontario Sports Fish -Northern Ontario, -Southern Ontario, -Great Lakes".

Although residues of PCBs are not frequently detected in foods other than freshwater fish, administrative guidelines have also been established for PCB residues in dairy products (0.2 mg/kg, fat basis), poultry (0.5 mg/kg, fat basis), eggs (0.1 mg/kg, whole weight less shell), and beef (0.2 mg/kg, fat basis). These administrative guidelines, as well as the 2 mg/kg guidelines for commercial fish, would be enforced under Part 1, Section 4(a) of the Food and Drug Regulations. This regulation states, "No person shall sell an article of food that has in or upon it any poisonous or harmful substance."

Results of analyses of human tissues for chemical residues are frequently used to provide a basis for measuring exposure to persistent chemicals. Nationwide surveys of adipose tissue in 1972, and of breast milk in 1975, indicated that 100% and 98%, respectively, of the samples contained detectable levels of PCB residues. The mean and range for the adipose tissues were 0.907 and 0.106 to 6.603 mg/kg, respectively. The mean and range for the breast milk were 12 and 0 to 68 ug/kg, respectively.

MONS 005154

In an advisory capacity, the HPB has frequently been asked to comment on the health significance of chemical residues in human milk. To meet these requests, in January, 1978, the Minister of Health and Welfare Canada convened a committee to "consider whether there are any problems related to the presence of PCBs in human milk" (HWC, 1978). In part, the committee concluded:

> The major sources of human exposure to PCBs are occupational exposure and consumption of game fish (such as coho salmon, eelr, lake trout, catfish, smelts, and sturgeon) from water contaminated with PCBs. One such area of contamination is the Great Lakes Basin. Women from this area and those women who may have had exposure to PCBs from industrial sources and who intend to breast-feed their babies, should contact their physicians. The physician should carefully consider the woman's lifetime history of exposure to PCBs to determine the advisability of having the breast milk analyzed.
>
> A Health Protection Branch (HPB) national survey indicated that the PCB level of mother's milk ranges between one and sixty-eight micrograms per kilogram (ug/kg) of whole milk. At the present time there are insufficient toxicological data to define precisely the level of PCBs in human milk that could cause health problems in the suckling infant. However, on the basis of available toxicological data in animals, where levels are above 50 ug/kg, the physician should pay particular attention to the mother's history, the child's birth weight, general conditions and subsequent growth and development in advising the mother concerning breast-feeding. In the light of currently available information it was the Committee's opinion that, in view of the benefits of breast feeding in most instances, it would be advisable to continue nursing. In the 1975-76 HPB survey of one hundred samples from across Canada, 98% of the breast milk samples tested were below 50 ug/kg whole milk. Detailed dietary and occupational histories should eliminate the need to have breast milk analyzed in the great majority of cases.

REGULATING RESIDUES IN FEEDS

In 1981, Agriculture Canada published a Trade Memorandum entitled "Polychlorinated Biphenyls (PCBs) in Marine Oils". In part, this memorandum states:

MONS 005155

Agriculture Canada is concerned about the use of fish oils containing PCBs in the manufacture of livestock feeds inasmuch as the quality of feeds and feed ingredients are subject to the standards as set out in Section 16(1)(i and j) of the Feeds Regulations. Feed manufacturers are reminded of their legal responsibility under the Feeds Act and Regulations to produce feeds which are safe for all classes of livestock and which do not result in a residue in animal products.

In consultation with toxicologists from Health and Welfare Canada and Agriculture Canada an actionable level of 2.0 mg/kg PCBs in fish oil has been established.

TOXICOLOGICAL EVALUATION

As indicated by the breadth of the papers presented earlier in the symposium, the scope of the scientific literature on the toxicity of PCBs to laboratory animals is very broad.

In our first evaluation of PCB (Aroclors 1242, 1254, and 1260) toxicity, the lowest no-observed effect level (NOEL) in 2 yr rat, 2 yr dog, and 3 generation rat reproduction studies was 10 mg/kg. For the rat and dog, a 10 mg/kg dietary level is considered equivalent to a dose of 0.5 and 0.25 mg/kg/day, respectively. The application of a 100-fold safety factor to the NOEL gave a 2.5 to 5 ug/kg/day "tolerable" exposure. We tended to lean towards the 5 ug level since 2 (Aroclor 1242 and 1254 studies) of the 3 dog studies resulted in a no-observed effect level of 2.5 mg/kg/day.

The "Yusho" incident has provided most of the information on the toxic effects of PCB to humans. Analysis of the rice oil for PCBs and collection of oil consumption data has allowed the estimation of the level of PCB exposure to the Japanese "Yusho" patients. This estimation gave a no-observed effect level of 200 mg/person. One approach to safety evaluation is to use this 200 mg/60 kg person no-observed effect level along with a 1000 day exposure period to estimate a "tolerable" exposure level of 3 ug/kg/day (Kolbye, 1976). This level agrees very well with the 2.5 to 5 ug/kg/day level estimated from laboratory animal data.

However, further analysis of the rice oil (Hayabuchi et al., 1979) indicated the presence of polychlorinated dibenzofurans (PCDFs) at 5 mg/kg, polychlorinated quaterphenyls (PCQs) at 866 mg/kg, and PCBs at 920 mg/kg. This PCB level (920 mg/kg)

is approximately one-half that which the first analysis indicated. Estimates of exposure from this data gave the patients total mean (geometric) exposure at 1232 mg (633 mg PCBs, 3.4 mg PCDFs, and 596 mg PCQs) compared to the previously estimated mean (arithmetic) of 2000 mg PCBs. Furthermore, the estimated minimum effect level for the sum of PCBs, PCDFs, and PCQs was 56 ug/kg/day. The presence of this cocktail of contaminants in the rice oil makes it impossible to estimate a "tolerable" level of exposure to any one of the contaminants.

Then, in the late 1970s, a number of publications from Dr. Jim Allen's laboratory indicated that the rhesus monkey was more sensitive to the toxic effects of PCBs than was the rat (Allen, 1975; Allen and Barsotti, 1976; Allen et al., 1974; 1980; Barsotti et al., 1976; Bowman et al., 1978). In particular, the reproductive system was very vulnerable. Dietary levels of 2.5 and 5 mg/kg Aroclor 1248 (equivalent to 100 and 200 ug/ kg/day) resulted in reproductive dysfunction in the female rhesus monkey. The findings of hyperpigmentation, chloracne, etc., in the PCB-treated monkeys were also observed in the "Yusho" patients.

These results indicated a need to reconsider our previously estimated 5 ug/kg/day "tolerable" exposure level. After evaluation, it was considered necessary to apply at least a 100-fold safety factor to the lowest level (100 ug/kg/day) in Dr. Allen's monkey reproduction study. The resulting 1 ug/kg/day "tolerable" exposure level should be considered temporary, pending further research. In addition to the regular uncertainties in using animal laboratory data to estimate an "acceptable" exposure level to humans, there is the additional problem that the PCBs which were tested may be somewhat different to those which are present in foods.

ESTIMATION OF EXPOSURE

The estimation of exposure to PCBs derived from the consumption of commercial foods by the average Canadian was made by multiplying the maximum residue limits (MRLs) for the various foods by the quantity of the particular foods consumed by the average Canadian (Table 1). The consumption figures are actually Statistics Canada figures for disappearance of foods and are thus over-estimates of actual consumption. With the exception of the MRL for fish, MRLs were obtained by compiling all available Canadian residue data for the various foods and then choosing a MRL which covers the great majority of the food samples. The choice of the 2 mg/kg MRL for fish took into consideration such factors as: available residue data; "remaining tolerable PCB exposure" (e.g., approximately 40

TABLE 1

Estimation of Maximum Exposure to PCBs from the Consumption of Commercial Foods

Food		Maximum Residue Limit (MRL)	PCBs
Type	Intake (g/person/day)	(ug/g)	Intake (ug/person/day)
Fish	20	2[a]	40
Dairy Products[b]	32.8	0.2[c]	6.6
Meat, Beef	48	0.2[c]	9.6
Poultry	3.6	0.5[c]	1.8
Eggs	34	0.1[d]	3.4

[a]Edible portion
[b]Milk, cheese, butter
[c]Fat basis
[d]Whole weight less shell

ug/person/day); and economic impact on the fishing industry and potential decrease of food source to the consumer.

FURTHER RESEARCH

Since the lowest level of PCBs administered to rhesus monkeys resulted in reproductive dysfunction, and because of the uncertainty in relating exposure to the infant monkey through suckling to effects observed, a monkey reproductive study is being planned. This study will have a control and four treatment groups. A major effort will be made to relate the level of PCB exposure to the dam:to the blood PCB level:to the PCB level in the milk:to the effects observed in the suckling monkey. This is extremely important since the question most often raised by the public is: "What is the health significance of a certain PCB residue level in human milk."

MONS 005158

ACKNOWLEDGMENT

The author is grateful to C. MacDonald, Environment Canada; J. Standish, Agriculture Canada; and B. Williams, Health and Welfare Canada for review of this manuscript.

LITERATURE CITED

Allen, J.R. 1975. Response of the Nonhuman Primate to Polychlorinated Biphenyl Exposure. Fed. Proc. 34:1675-1679.

Allen, J.R. and D.A. Barsotti. 1976. The Effects of Transplacental and Mammary Movement of PCBs on Infant Rhesus Monkeys. Toxicology 6:331-340.

Allen, J.R., L.A. Carstens, and D.A. Barsotti. 1974. Residual Effects of Short-Term, Low-Level Exposure of Nonhuman Primates to Polychlorinated Biphenyls. Toxicol. Appl. Pharmacol. 30:440-451.

Allen, J.R., D.A. Barsotti, and L.A. Carstens. 1980. Residual Effects of Polychlorinated Biphenyls on Adult Nonhuman Primates and Their Offspring. J. Toxicol. Environ. Health 6:55-66.

Barsotti, D.A., R.J. Marlar, and J.R. Allen. 1976. Reproductive Dysfunction in Rhesus Monkeys Exposed to Low Levels of Polychlorinated Biphenyls (Aroclor 1248). Fd. Cosmet. Toxicol. 14:99-103.

Bowman, R.E., M.P. Heironimus, and J.R. Allen. 1978. Correlation of PCB Body Burden With Behavioral Toxicology in Monkeys. Pharmacol. Biochem. Behavior 9:49-56.

HWC. 1978. Polychlorinated Biphenyls: Department of National Health and Welfare - Committee Report. Information Letter DD-24, Health Protection Branch, Health and Welfare Canada (HWC), Ottawa, pp. 2-3.

Hayabuchi, H., T. Yoshimura, and M. Kuratsune. 1979. Consumption of Toxic Rice Oil by "Yusho" Patients and Its Relation to the Clinical Response and Latent Period. Fd. Cosmet. Toxicol. 17:455-461.

Kolbye, A.C. 1976. Biomedical Considerations of PCBs. In: "PCBs in Mother's Milk," pp. 20-41. Proceedings of September 23, 1976, meeting convened by Department of Health, Education and Welfare at Bethesda, MD.

MONS 005159

CHAPTER 28

FDA REGULATION OF PCB IN FOOD

Alan L. Hoeting
U.S. Food and Drug Administration
Detroit, Michigan 48207

INTRODUCTION

Industrial chemicals such as polychlorinated biphenyl (PCB) become contaminants in food from three main sources:

(1) as a result of an industrial chemical accident (e.g., a spill);
(2) from discharges during manufacturing of the chemical; and
(3) from use or disposal of the chemical and eventual reintroduction from the environment into the food chain (FDA, 1979).

FEDERAL AUTHORITIES

The U.S. Environmental Protection Agency (EPA) has authority under the Toxic Substance Control Act to regulate industrial chemicals per se and the effects of chemicals on humans and the environment. However, the authority for controlling food contaminated with these chemicals is assigned exclusively to the Secretary of the Department of Health and Human Services under the provisions of the Federal Food, Drug, and Cosmetic Act (FFDCA) (FFDCA, 1979). The authority vested in the Secretary under the FFDCA for regulation of chemical contaminants in foods has been redelegated to the Commissioner of Food and Druga (CFR, 1981a, see Part 5.1).

The provisions of the FFDCA prohibit the introduction into interstate commerce, receipt in interstate commerce, and holding for sale after receipt in interstate commerce any foods and drugs which are adulterated or misbranded (FFDCA, 1979).

MONS 005160

Section 402(a)(1) of the Act deems a food to be adulterated:

> if it bears or contains any poisonous or deleterious substance which may render it injurious to health; but in case the substance is not an added substance, such food shall not be considered adulterated under this clause if the quantity of such substance in such food does not ordinarily render it injurious to health (FFDCA, 1979).

Section 402(1)(2) deems a food to be adulterated:

> if it bears or contains any added poisonous or added deleterious substance other than one which is a pesticide chemical, a food additive, a color additive, or a new animal drug which is approved for such purposes and controlled by tolerance and regulations (FFDCA, 1979).

Section 406 deems any added poisonous or deleterious substance to be unsafe unless its presence in food is required in the production thereof or cannot be avoided by good manufacturing practice. Section 406 also authorized the agency to promulgate regulations limiting the quantity of such a required or unavoidable substance that can be present legally in foods (FFDCA, 1979).

In the administration of these statutory provisions, the U.S. Food and Drug Administration (FDA) distinguishes between "avoidable" and "unavoidable" sources of contamination for determining the level of contamination at which enforcement action will be as follows.

Avoidable Contamination

Adulteration of food caused by failure to follow good manufacturing practice constitutes "avoidable" contamination of food if the cause of contamination could have been prevented (e.g., by not storing containers of a toxic chemical next to food with subsequent leakage and contamination of food). Contamination due to some known or very apparent episode (e.g., an explosion), with subsequent marketing of an adulterated product in interstate commerce is also considered "avoidable". In such cases, FDA's policy is to set, for uniform enforcement purposes, a limit for the avoidable contaminant that is no higher than the level provided by available residue analytical methodology for detecting, measuring, and confirming the identity of the contaminant (FDA, 1979).

MONS 005161

Unavoidable Contamination

Unavoidable contamination occurs when, in spite of strict adherence to good manufacturing practice, the presence of the added substance in food cannot be completely prevented. Such is the case when an industrial chemical persists in the environment and causes indirect "unavoidable" contamination of food. Because no amount of intervention by man can completely remove the contaminant from food, agency policy is to follow Section 406 of the FFDCA, viz., limit the amount of the contaminant that can be present to the extent necessary to safeguard consumer health while taking into account the extent to which the contaminant is unavoidable. This is accomplished by establishing either an action level or tolerance as the standard for determining whether food containing some specific amount of the substance can legally be marketed (FDA, 1979).

Action Levels

"Action levels" are sometimes used by FDA to determine the legal status of an industrial chemical residue in food or feed. Although any amount of an industrial chemical in the absence of a tolerance may render food adulterated within Section 402, Section 306 of the FFDCA permits FDA to refrain from taking regulatory action for minor violations (e.g., when the residue level poses little or no risk to the public health). This enforcement discretion is often applied when no tolerance for a residue has been established, but the presence of the residue cannot be avoided by good manufacturing practices. Such a situation would be the persistence of an industrial chemical in the environment and the chemical's subsequent "unavoidable" contamination of food. An action level defines this discretionary authority in terms of a specific limit that is used to determine whether FDA will, when the limit is exceeded, take regulatory action. An action level neither condones nor permits the intentional addition of a contaminant to food. In setting an action level, the criteria of Section 406 of the FFDCA are followed; that is, the level must be sufficient to protect the public health, while also taking into account the extent to which the contaminant is unavoidable. FDA is responsible for determining when an action level is to be applied in a particular situation and for enforcing an action level (FDA, 1979).

Tolerances

A "tolerance" may also be established for unavoidable industrial chemical residues under Section 406 and in accordance with the formal rulemaking procedures of the FFDCA. Table 1

MONS 005162

presents the tolerances which have been established for only one such substance, PCBs, on a variety of food and feed commodities. A tolerance for another environmental, but nonindustrial chemical food contaminant, aflatoxin, is pending. When

TABLE 1

Tolerances for Unavoidable Poisonous or Deleterious Substances for PCBs, April 1, 1981[a]

	Type of Food	Tolerance (mg/kg)
1.	Milk (fat basis)	1.5
2.	Manufactured dairy products (fat basis)	1.5
3.	Poultry (fat basis)	3.0
4.	Eggs	0.3
5.	Finished animal feed for food-producing animals, except feed concentrates, feed supplements, and feed pre-mixes	0.2
6.	Animal feed components, including fish meal and other by-products of marine origin and finished feed concentrates, supplements, and pre-mixes	2.0
7.	Fish and shellfish (edible portion) excluding head, scales, viscera, and inedible bones	2.0[b]
8.	Infant and junior foods	0.2
9.	Paper food packaging material intended for use in contact with human food and finished animal feed	10

[a]CFR, 1981b, Part 109.30

[b]The effective date of the 2 mg/kg tolerance for PCB in fish and shellfish was stayed until further notice by a document published in the Federal Register (FR, 1979a). The previous tolerance of 5 mg/kg in the edible portion of fish and shellfish remains in effect until further notice (FR, 1973).

MONS 005163

FDA establishes an action level, the agency publishes a notice in the Federal Register stating that an action level has been established and inserts in the public record documentation describing the scientific and related factors considered by the agency in arriving at the action level. Action levels are particularly useful when available toxicity data are incomplete, or the causes or levels of contamination are not clearly established or are in a state of flux. This explains why tolerances for such contaminants are infrequently used by FDA. The main disadvantage in the informal process for setting action levels for food contaminated by a nonpesticide chemical is that FDA must defend such an action level in court. For a tolerance, FDA only has the legal burden of proving that the tolerance was exceeded (FDA, 1979).

USDA/FSIS and most state regulatory agencies rely on FDA's recommended action levels or established tolerances for unavoidable industrial chemical residues in meat, poultry, and other foods.

ENFORCEMENT AUTHORITY

The FFDCA authorizes FDA to initiate seizure of an interstate shipment of food, seek an injunction against further shipment of adulterated food, and/or criminal penalties against the firm and/or persons responsible for the violation of the law. Food means articles used for food or drink for man or other animals, chewing gum, and components of such articles. Also, FDA may refuse entry into the country of any imported food found adulterated or misbranded (FFDCA, 1979, see Sections 304, 302, 303, 801).

FDA investigators are authorized to sample and analyze food to determine if chemical contaminants are present. FDA investigators also have the authority to conduct investigations and to enter and inspect firms engaged in the manufacture, production, processing, or distribution of food to determine whether such foods are adulterated or misbranded (FFDCA, 1979, see Sections 702, 704).

CURRENT PESTICIDE AND INDUSTRIAL CHEMICAL RESIDUE PROGRAMS

FDA field operations are managed under a complex program planning and management system involving some 36 major project areas which are currently subdivided under 123 compliance programs.

MONS 005164

During Fiscal Year (FY) 82, FDA will spend about 168 operating person years of effort on its chemical contaminants programs which represents about 12 percent of its available field resources. About 50 percent of this person power (85 person years) will enable the agency to analyze 6900 samples of domestic foods and 4900 samples of imported foods for chemical contaminants under 17 different specific programs (FDA, 1982).

The largest program, Pesticides and Industrial Chemicals in Domestic Food, is designed to determine the levels of pesticides and industrial chemicals in selected samples of raw agricultural products, milk, cheese, eggs, grain, and fish (FDA, 1982).

The selection of the products to be sampled and the numbers of samples of each product to be analyzed with the available resources are generally left to the discretion of each FDA district. Districts generally sample and analyze locally produced commodities having dietary significance and where local experience, inspectional information, or other intelligence make it aware of potential food contamination problems (FDA, 1981a).

During FY82, Detroit District is authorized to collect and analyze only 294 samples of foods produced in the states of Michigan and Indiana (FDA, 1982). Detroit District plans to analyze 46 domestic and 20 import samples of fish under this program. In addition, Detroit District plans to analyze a limited number of samples of fish for dioxin residues under a cooperative program with EPA and cooperating officials in seven Great Lakes states (Hoeting, 1981).

The results of the analysis of samples of fish analyzed for PCB in FY79, FY80, and FY81 are shown in Tables 2, 3, and 4, respectively.

When a major problem is identified, FDA field managers are free to use a part or all of the available person power in the home district and other districts as may be needed, for the detection and removal of contaminated products from the market place (FDA, 1981a).

FDA "official samples" must be representative of the shipment and generally consist of 12 fish (or a minimum of 12 one-pound portions) collected at random (IOM, 1978). Samples of fish may be collected from commercial fishermen, fish processing plants, in transit (e.g., from a truck), and from wholesale and retail establishments (FDA, 1981a).

MONS 005165

TABLE 2

Domestic Fish Samples Analyzed for PCB by Detroit District from Known Locations, Fiscal Year 1979

Species	Lake	Number of Samples	Range (mg/kg)	Average (mg/kg)	Samples Over 2 mg/kg PCB
Carp	Huron	5	2.0 - 7.4	3.59	4
Carp	Erie	1	3.16	3.16	1
Perch	Huron	3	0.32 - 0.65	0.45	0
Catfish	Huron	12	0.8 - 7.5	3.2	9
Catfish	Erie	4	3.1 - 5.6	4.3	4
Whitefish	Huron	3	ND - 3	1.5	1
Lake Trout	Huron	6	0.94 - 4.33	2.75	4
Lake Trout	Michigan	4	ND - 4.6	2.85	3
Walleye	Erie	6	Trace - 1.1	0.5	0
Chubs	Michigan	3	0.47 - 1.21	0.9	0
TOTAL		47			26

ND = Not Detected

TABLE 3

Domestic Fish Samples Analyzed for PCB by Detroit District, Fiscal Year 1980

Spe	Number of Samples	Samples With PCB	Range (mg/kg)	Average (mg/kg)	Samples Over 2 mg/kg PCB
Coho Salmon	1	1	--	2.49	1
Chinook Salmon	5	5	0.72 - 5.29	3.27	4
Whitefish	22	9	0.5 - 1.11 (5 with trace)	0.82 (0.4)	0
Lake Trout	12	4	0.31 - 21.7	4.72	3
Chubs	5	1	--	1.41	0
Lake Herring	1	0	--	--	0
King Salmon Eggs	1	1	--	1.48	0
Coho Salmon Eggs	1	1	--	1.35	0
TOTAL	48	22			8

MONS 005167

TABLE 4

Domestic Fish Samples Analyzed for PCB by Detroit District, Fiscal Year 1981

Species	Number of Samples	Samples With PCB	Range (mg/kg)	Average (mg/kg)	Samples Over 2 mg/kg PCB
Coho Salmon	1	1	--	1.67	0
Chinook Salmon	2	2	1.19, 2.62	1.90	1
Whitefish	24	4	--	All Trace	0
Lake Trout	6	1	--	4.87	1
Lake Herring	1	0	--	--	0
Smelt	1	0	--	--	0
Sucker	1	0	--	--	0
Chinook Eggs	2	2	4.32, 5.8	5.06	2
Coho Eggs	1	1	--	1.68	0
TOTAL	39	11			4

MONS 005168

The fish in the sample will be cleaned, scaled, and eviscerated to prepare an edible portion for analysis. Inedible portions such as bones and catfish skin are discarded. Fillets, including all flesh and edible skin, are removed from head to tail and from top of back to belly on both sides of fish. Where extremely large fish are analyzed, three cross-sectional slices from each fish may be taken and combined for analysis (PAM, 1977).

Fish samples are analyzed with the methods specified in the Pesticide Analytical Manual (PAM) I (PAM, 1978) or the method of Luke et al. (PAM, 1980), and the Laboratory Information Bulletin (LIB, 1980; FDA, 1981b).

TOTAL DIET STUDIES

FDA also surveys the total United States diet, in a program designed to obtain information about levels of chemical contaminants to which consumers are exposed. The study is based on 30 "market basket" samples each year, collected from representative areas of the United States, and purchased in retail stores. Since FY75, 20 samples are collected under the adult program and 10 under the infant and toddlers program (FDA, 1981b). Each sample represents the entire 14 day diet. For the adult, the sample represents the diet (approximately 117 individual food items) of a typical 15 to 20 yr old American male in the region of collection. All foods are prepared for table-ready consumption (meats are cooked, vegetables boiled if so eaten, etc.). The prepared foods are then divided into different food class composites (dairy products, meat-fish-poultry, root vegetables, grain and cereal products, etc.) and each composite is analyzed for residue content. The results are used to determine:

(1) the total daily intake of each residue;
(2) which food classes contribute the greatest residues to the diet; and
(3) seasonal and regional trends (Kennedy, 1978).

The FDA initiated the market basket study in 1965 as a supplement to the coverage of individual foods by other compliance programs. It provided the first means for determining the level of residue in the diet as consumed. Originally, only chlorinated hydrocarbon, organophosphorus, and arsenical pesticides were included. Through the years, the program has expanded and now includes analysis for organochlorine and organophosphorus residues, chlorphenoxy acids (herbicides), carbaryl and orthophenylphenol, and six heavy metals (mercury, cadmium, arsenic, lead, selenium, and zinc)(Kennedy, 1978).

Although most of our activities are directed at ensuring that unsafe residues do not occur in foods, we also have surveillance programs for pesticide residues in animal feeds. Illegal levels of pesticides may result in the adulteration of animal feed, with subsequent deposition of harmful residues in meat, poultry, eggs, fish, and dairy products (Kennedy, 1978).

We have also used special purpose surveys, designed to attack geographically isolated problems. They provide information that compliments the regular data gathering activity described above (Kennedy, 1978; FDA, 1981c, 1981d).

In the past, these Total Diet Studies discovered that PCBs from food packaging materials were contaminating the diet. This source of PCB has been eliminated after the establishment of a tolerance of 10 mg/kg for PCB in food packaging materials (FDA, 1978; CFR, 1981b, see Part 109.3).

After finding no PCB in the Total Diet Samples for FY75 and FY76, the samples for FY77 and FY78 show total relative daily intakes of 0.0164 and 0.0269 mg/kg of body weight per day. During FY78, PCB was found in 6 composite samples of meat, fish, and poultry; 2 composite samples of legume vegetables; and 2 composite samples of oils, fats, and shortening at levels ranging from 0.006 to 0.050 mg/kg (FDA, 1978).

Jelinek and Corneliussen (1975) compiled data on the concentration of PCB obtained in different foods from 1969 through mid 1975. These data show that there has been a significant decrease in PCB levels in all foods with the exception of fish. PCBs were found in 1973 in samples of milk (2.2% of samples contained PCB), eggs (1.1%), cheese (0.9%), feed components (12.7%), animal feeds (2.2%), processed fruits (4.5%), and infant and junior food (1.1%). Most samples of fish containing more than 5 mg/kg PCB originated from the Great Lakes area.

FEDERAL STATE PARTNERSHIP

Thus far, the food chemical contaminant programs at the federal level have been discussed. Collectively, the states analyze about 60,000 samples for a wide variety of pesticides and industrial chemicals each year. FDA has long recognized the significant role of the states in this area and has actively exchanged information and provided assistance as may be needed (Kennedy, 1978). FDA provides state officials:

(1) Copies of analytical results on samples containing pesticides, warning letters, and other information.

(2) Action levels for chemical contaminants in food when no such levels have been established.

(3) Inspectional information and intelligence about possible sources of food contamination for other states.

(4) Training, methods manuals, and assistance with methodology.

(5) Check samples for verification and uniformity of results.

(6) Analytical assistance when needed.

(7) Analytical reference standards.

By the same token, the Michigan Department of Agriculture and other state agencies have provided FDA with inspectional information, analytical findings on samples, alerts to possible food contamination problems, check samples, analytical methodology, and immediate embargo/seizure of contaminated foods. We share common goals with the Michigan Department of Agriculture and enjoy a close federal-state relationship.

Most states formally adopt or follow the federal action levels and tolerances for contaminants in food. However, FDA has no objection to the adoption by a state of more restrictive standards, such as was done by Michigan with PBB.

TOLERANCES FOR PCB

The original tolerances for PCB, including the 5 mg/kg in fish, were published in 1973. A new tolerance of 2 mg/kg in fish was published in the Federal Register (FR, 1979b). This new tolerance was based upon:

(1) new toxicity data which show the toxic effects of PCB are serious and irreversible;

(2) the declining levels of PCB in the environment permit a reduction of the tolerance (thereby effecting a meaningful risk to consumers) while excluding from commerce only a small amount of food (about $5.7 million landed value in 1974 dollars)(FR, 1979b).

The effective date of this 2 mg/kg tolerance was stayed on October 5, 1979, after written objections concerning the economic impact of the regulations were filed by the National Fisheries Institute and others with the FDA Hearing Clerk (CFR,

MONS 005171

1981b, see Part 109.30; FR 1979a). On February 8, 1982, FDA Administrative Law Judge Daniel J. Davidson determined that a 2 mg/kg tolerance for PCB would bar the sale for human food of fish and shellfish with a retail value of $86.7 million in 1980 dollars. The National Fisheries Institute has estimated the total loss at over $500 million when the fish are cleaned, canned, distributed, and sold at retail (Grigg, 1982). Judge Davidson agreed that the retail value is an appropriate measure of the economic impact of the PCB tolerance and that a multiplier of six should be used to oonvert landed value to retail value (FCN, 1982).

Judge Davidson found the retail losses of fish in 1980 from other tolerances would be $44.9 million at 2.5 mg/kg, $10.6 million at 3 mg/kg, $3.9 million at 3.5 mg/kg, $1.4 million at 4 mg/kg, and $366,000 at 5 mg/kg (Grigg, 1982). In 1979, FDA estimated that a 1 mg/kg tolerance for PCB would result in the loss of food with a 1974 landed value of $16 million (FR, 1979).

FDA Commissioner Arthur Hull Hayes will make the final decision on the tolerance for PCB in fish after exceptions are filed to Judge Davidson's ruling on the economic impact of the proposed tolerance.

FDA has consistently supported the public health warnings and advisories issued by state agencies to sports fishermen and others who consume large quantities of fish from waters contaminated with PCB and other industrial chemicals. These warnings about restriction or non-consumption of PCB contaminated fish are especially significant for young women, and pregnant and nursing mothers because PCBs have been linked in test animals to reproductive problems and toxic effects in young animals exposed to PCB in mothers milk (Kennedy, 1979; FR, 1979b).

PESTICIDE AND INDUSTRIAL CHEMICAL RESEARCH CENTER

A four person Pesticide and Industrial Chemical Research Center (PICRC) was established as a new branch in the Detroit District Laboratory during FY81. This laboratory is responsible for researching new analytical methods in order to improve our ability to detect, quantitate, and confirm the presence of pesticides and industrial chemicals in foods. The laboratory is also responsible for attempting to identify unknown peaks found during analyses of samples for chemical residues.

MONS 005172

CONCLUSION

The FDA works in close cooperation with many federal and state agencies to monitor the food supply to insure that it is free of unsafe chemical residues. Unfortunately, fish from the Great Lakes are more highly contaminated with PCB than are most fish caught in other waters. Since sports fishermen generally consume larger quantities of fish than do average consumers who buy their fish in commercial channels, sportsmen generally consume greater quantities of PCB and other contaminants.

I suggest that the time has come for all interested persons to join together in a cooperative atmosphere in an effort to reduce the exposure of consumers of both commercial and sports fish to toxic PCB residues.

LITERATURE CITED

CFR. 1981a. Code of Federal Regulations (CFR), Title 21, Parts 1 to 99.

CFR. 1981b. Code of Federal Regulations (CFR), Title 21, Parts 100 to 169.

FCN. 1982. FDA Law Judge Rules on Loss Resulting from Lowering PCB-In-Fish Tolerance. Food Chemical News:37-38, February 5, 1982.

FDA. 1978. FY78 Total Diet Studies - Adult (7305.003). FDA Compliance Program Report of Findings.

FDA. 1979. Monitoring Programs for Pesticide and Industrial Chemical Residues in Food. FDA Programs, June 1979.

FDA. 1981a. Pesticides and Industrial Chemicals in Domestic Foods Program (FY82). FDA Compliance Program Guidance Manual, Section 7304.004.

FDA. 1981b. Total Diet Studies - Adult, Infant, and Toddlers (FY82). FDA Compliance Program Guidance Manual, Section 7304.002.

FDA. 1981c. Pesticides in Mexican Produce (FY82). FDA Compliance Program Guidance Manual, Section 7304.008.

FDA. 1981d. Import Foods - General Program (FY82). FDA Compliance Program Guidance Manual, Section 7303.819.

MONS 005173

FDA. 1982. Edro Workplan, FY82. Food and Drug Administration. Rockville, MD.

FFDCA. 1979. Federal Food, Drug, and Cosmetic Act (as amended). FFDCA, January.

FR. 1973. Federal Register 38:18102, July 6, 1973.

FR. 1979a. Federal Register 44:57389, October 5, 1979.

FR. 1979b. Federal Register 44:38330-38340, June 29, 1979.

Grigg, B. 1982. Low PCB Tolerance for Fish Would Cost $86.7 Million. FDA Talk Paper, February 2, 1982.

Hoeting, A.L. 1981. Letter to Vadas Adamkus, EPA Region V Administrator, October 21, 1981.

IOM. 1978. Inspection Operations Manual. Food and Drug Administration.

Jelinek, C.F. and P.E. Corneliussen. 1975. Levels of PCBs in the U.S. Food Supply. National Conference on Polychlorinated Biphenyls, Chicago, IL.

Kennedy, D. 1978. Statement before the Subcommittee on Oversight and Investigations, Committee on Interstate and Foreign Commerce, House of Representatives.

Kennedy, D. 1979. Letter to Governor William G. Milliken, June 27, 1979.

LIB. 1980. Laboratory Information Bulletin, Section 2434.

PAM. 1977. Pesticide Analytical Manual, Section 141.12.

PAM. 1978. Pesticide Analytical Manual, Sections 211.1 and 212.1.

PAM. 1980. Pesticide Analytical Manual, Sections 212.2, 232.4, and 242.1.

MONS 005174

CHAPTER 29

ECONOMIC IMPACTS OF PCB REGULATION IN FOOD FISH

Daniel R. Talhelm
Fisheries and Wildlife Economics
Department of Fisheries and Wildlife
Michigan State University
East Lansing, Michigan 48824-1222

On June 29, 1979, the U.S. Food and Drug Administration (FDA) issued its final regulations lowering the allowable polychlorinated biphenyl (PCB) level from 5 to 2 mg/kg in the edible portion of fish and shellfish (Federal Register, June 29, 1979). Twenty objections were filed with the FDA. One objection, filed by the National Fisheries Institute (NFI), requested a formal hearing on the issue of the economic value of the food loss. They contended that the value of the food loss would be $7-10 million per year rather than the FDA's estimated $5.7 million. As a result, the change in PCB tolerance levels was delayed until after a formal evidentiary hearing could be held on the question: What would be the value of the human food loss caused by lowering the PCB standard from 5 to 2 mg/kg?

The hearing was stricly limited to that question--the value of the food lost due to the change in regulations--not whether the regulation was a "good" or "bad" choice. The hearing concluded recently and the hearing examiner has made his recommendations. The FDA Commissioner is now in the process of hearing both the recommendations and any exceptions to the recommendations that may be filed. Then the Commissioner can decide whether or not to execute the rules.

I was only peripherially aware of this proposed rule until last summer when Al Hoeting of the FDA, Detroit, Michigan office, called asking if there were such a thing as a fisheries economist working on Great Lakes fisheries and, if so, could I name some. He wanted some names of independent people who could

MONS 005175

serve as expert witnesses to examine this issue. I agreed, along with Dr. Richard Bishop (University of Wisconsin) and Dr. Gary Johnson (University of Illinois). We testified last fall.

This paper reflects my perspective, after having examined the issues, and drawing whatever conclusions I could from them on "what is the value of the food loss that would be caused by this proposed change in regulations".

This paper will show (1) how a fairly simple issue became complicated quickly, (2) how these values were estimated using greatly-simplifying assumptions, and (3) the findings of the hearing examiner. The paper also briefly contrasts the legal issues and the real social issues. Carlos Fetterolf, in the opening session, summarized the real social issue when he asked, "What is the right tolerance level?" That is a question I can't answer. However, we will examine the issue to see what we can say.

INITIAL ESTIMATE OF LOSSES

Table 1 will summarize the original argument as well as some subsequent data. The species in question were several freshwater species found in the Mississippi River system (catfish and buffalo) and the Great Lakes (whitefish, chubs, trout, catfish, and carp). Two saltwater species (striped bass and bluefish) were included. Alewives and lobsters were later added as more information became available. Losses were estimated by first finding the total landings in pounds and the value of those landings. Next the percentage of landed fish that would exceed the 2 mg/kg tolerance level was estimated based upon FDA sampling. For example, the initial loss percentage estimated for whitefish and chubs was 10.5 percent, and for lake trout was 33.3 percent. Finally, the dollar losses were calculated assuming every contaminated fish was excluded.

TABLE 1

It was decided for this hearing that all values would be converted to 1974 dollars to correct for inflation, but not all documents did that, particularly earlier documents. The FDA, in its proposal regulations, estimated that the value lost would be $5.7 million per year (1974 dollars)(Federal Register, June 29, 1979, p. 38333). The NFI then said that if 1978 landings and value data were used and alewives were added, a loss of about $7.3 million would occur (1978 dollars)(FDA, 1982, Document N-1). Furthermore, NFI argued that adding lost imports and unexploited fisheries, $10.1 million would be lost. Later, PCBs were discovered in lobsters, so lobster losses were also included by FDA and NFI. The value of all lobster landings was about $37 million in 1974 and $64.8 million in 1978. Twenty

TABLE 1

Comparison of 1974 and 1978 Fish Landing Data and Economic Loss
(Thousands of Dollars and Metric Tons)

Species	Landings 1974	Landings 1978	Landings in Current Dollars 1974	Landings in Current Dollars 1978	Percentage Exceeding 2 mg/kg PCB'S 1978	Percentage Exceeding 2 mg/kg PCB'S 1978-80	Expected Loss in Current Dollars 1974	Expected Loss in Current Dollars 1978
	----Metric Tons----		-----$ x 10^3-----		-----Percent-----		-Current $ x 10^3-	
Whitefish	4,492	2,138	6,266	4,703	10.5	32.5	683	494
Cisco		618		1,700	10.5	34.9		179
Trout	166	159	207	279	33.3	18.2	69	93
Carp	11,158	8,926	1,455	1,963	14.8	16.9	215	291
Catfish	15,935	12,747	11,779	12,339	25.8	33.2	3,039	3,184
Buffalo	11,548	9,238	5,246	6,706	2.8	5.7	147	188
Stripped Bass	5,023	2,044	3,351	4,664	44.9	3.5	1,448	2,094
Blue Fish	4,791	5,256	1,143	1,613	4.3	3.1	49	69
SUBTOTAL	53,114	41,126	29,407	33,967			5,650	6,590
Alewives	31,978	19,218	1,493	702	100.0	(100)	1,493	702
Lobster	12,974	15,645	37,134	64,813	--	22.5	--	14,583
TOTAL	98,066	75,989	37,034	99,482	--	--	7,143	21,875

Source: National Marine Fisheries Service (landings data); FDA (PCB levels data)

MONS 005177

two and half percent were calculated as being over the 2 mg/kg tolerance level in 1979 and 1980 data, resulting in an estimated loss of over $14 million in 1978 dollars (FDA, 1982, Testimony of National Marine Fisheries Service). That is about twice the combined loss from all other species.

ALEWIVES

The FDA regulation included only food for human consumption. Alewives harvested from the Great Lakes are used in pet food, not human food, so the FDA dismissed the industry's argument that alewife values should be used.

LOSS PERCENTAGES

The estimated percentage of a species' catch that would be taken off the market was assumed to be the same as the percentage of samples in which the fish were found to exceed the corresponding PCB level (Table 1). Table 2 illustrates the sketchy nature of this data base in 1978. Later figures expanded the data base by up to several fold, but samples for some species were expanded only slightly. For carp, for example, 54 samples were taken, 8 of which exceeded the 2 mg/kg level. For catfish, 295 samples were taken, 76 of which exceeded 2 mg/kg. The total number of samples was not very great. Lobster loss estimates were based on only 40 samples. Losses were estimated in this manner for tolerance levels of 1, 2, 2.5, 3, 3.5, 4, 4.5, and 5 mg/kg, all based on the same samples.

MORE RECENT DATA

The National Marine Fisheries Service (NMFS) argued in support of the industry, against lowering the tolerance level, but I found their figures to be most reliable. The NMFS calculated the value of losses from 1978, 1979, and 1980 catches, using 1978-1980 FDA fish sampling results, converted back to 1974 dollars for each of these tolerance levels except 1 mg/kg. Table 3 presents the 1980 results at 2 mg/kg. The American lobster is the largest component at $10 million. The total loss was about $14 million. This study did not include alewives. At various levels of PCB regulations (Figure 1), the value of the economic loss goes up quite rapidly after 3 mg/kg.

INDUSTRY'S ANALYSIS

The fishing industry (National Fisheries Institute) presented a different argument. Their updated analysis by Dr.

TABLE 2

1978 Pesticides and Metals in Fish Program - PCB Levels Data

Species	Number of Samples Violative at 2 mg/kg	Percent	Lost Value $x103	Number of Samples Violative at 5 mg/kg
Carp	8/54	14.8	215	2/54
Catfish	76/295	25.8	3,039	14/295
Buffalo	1/36	2.8	147	0/36
Lake Trout	29/87	33.3	69	2/87
Whitefish/Chub	2/19	10.5	685	0/19
TOTAL		16.7	4,155	
Sea Trout	0/10	0	--	0/10
Bluefish	1/23	4.3	49	0/23
Scap (Porgy)	0/10	0	--	0/10
Drum	0/12	0	--	0/12
Mackerel	0/21	0	--	0/21
Stripped Bass	4/9	44.4	1,488	0/9

Source: FDA, 1982, Document G-2 (1979)

Ivar Strand confused the issues greatly by (1) using 1980 dollars and 1974 landings even though all parties had previously agreed to use 1974 dollars and 1980 landings, and (2) including Great Lakes alewives which are not used as human food and therefore not even under FDA jurisdiction. Furthermore, East Coast alewives, which are used as food, were apparently not sampled for PCB. In 1980 dollars and including alewives, the value lost, according to the industry, was about $24 million--almost twice as high as the NMFS estimate (Table 4).

The industry also said that there were a number of other values that needed to be considered in calculating this loss (Table 5). First, they reconsidered the assumption that the value of the food taken off the market would be equal to the percent found violative in the FDA samples. That is a questionable assumption because fish shipments are rarely sampled. Many fish could go to market without being sampled; and sampling is slow and expensive, so regulatory agencies may simply remove all fish from the market. An example of this was found in

TABLE 4

Estimated Annual Economic Impact at Various PCB Tolerance Levels

Species	PCB Tolerance Level (mg/kg) 2.0	2.5	3.5	4.0	4.5	5.0
	(000's $)					
Freshwater						
Alewives	2,813	---	---	---	---	0
Buffelofish	128	128	0	0	0	0
Carp	295	137	118	79	79	73
Catfish	4,740	2,917	1,458	1,094	911	856
Trout	86	47	13	8	6	6
Whitefish and Chubs	1,161	1,161	0	0	0	0
Marine						
Bluefish	68	0	0	0	0	0
Lobster	11,673	11,673	8,735	8,735	5,796	2,898
Stripped Bass	2,984	2,210	0	0	0	0
TOTAL	23,948	18,273	10,324	9,916	6,792	3,833

Source: Testimony of Ivar Strand (FDA, 1982, Document M-21); PCB levels based on 1978-1980 FDA sampling; Dollar values are in 1980 dollars; landings data are from 1974

TABLE 5

MONS 005180

TABLE 5

Potential Losses (in $ thousands) Associated With Various PCB Tolerance Levels[1]

Source of Loss	Tolerance Level (mg/kg) 2.0	2.5	3.5	4.0	4.5	5.0
Loss based on % of violative samples	167,636	127,911	72,268	69,412	47,548	26,831
Loss to "recreational" fishermen	257	196	0	0	0	0
Loss based on unviable fisheries	361,200	204,570	0	0	0	0
Loss based on other related species	10,409	---	---	---	---	---
Loss to imported products	31,410	31,056	22,302	14,790	14,774	7,414
Loss due to bad publicity	(32,011)[2]	---	---	---	---	---
TOTAL ECONOMIC LOSS (1980 dollars)	570,912	363,733	94,570	84,202	62,318	34,345
TOTAL ECONOMIC LOSS (1974 dollars)	303,965	217,680	56,596	50,392	37,295	20,554
FDA ESTIMATES (1974 dollars)	56,000	---	---	---	---	---

[1]Includes the seven-fold increase from harvest level to processor
[2]Not included in total because unviable fisheries would already include the loss
SOURCE: Testimony of Ivar Strand (FDA, 1982, Document M-21)

MONS 005181

TABLE 3

Summary of Projected Economic Losses Due to PCBs in 1980 at 2.0 mg/kg (Deflated 1974 Dollars in Thousands)

Species	Losses at 2.0 mg/kg (1980)
Chub	$ 286
Whitefish	707
Lake Trout	54
Buffalofish	229
Carp	199
Bluefish	45
Catfish	2,181
Striped Bass	103
American Lobster	10,130
Total Economic Loss	$13,933
Percent Loss of Total Value of Catch	21.7

Source: National Marine Fisheries Service Testimony (FDA, 1982)

Michigan where chubs were in effect taken off the market when about 50 percent of them were found to be contaminated with dieldrin. The State of Michigan simply eliminated chub harvesting. Thus, 100 percent was lost instead of 50 percent. Furthermore, fishers would find it too risky to harvest fish if shipments were likely to be confiscated. The industry argued that anytime over 25 percent were found violative in FDA's samples, the whole fishery should be assumed to be taken off the market. They attributed a large loss to such "unviable" fisheries (Table 5). However, one could also argue that if less than something like 25 percent are violative, all would go to market because of inefficient sampling. Second, they estimated some loss due to "recreational" fishermen. These are sales of bluefish (saltwater fish) caught by anglers and, therefore, not appearing in commercial fishery statistics and FDA estimates. Third, they contended that, since fisheries for some species might stop, the whole fishing industry in some cases might shut down, so there would be some losses due to other related species as well. Fourth, they estimated that applying the same standards to imported fish would result in

MONS 005182

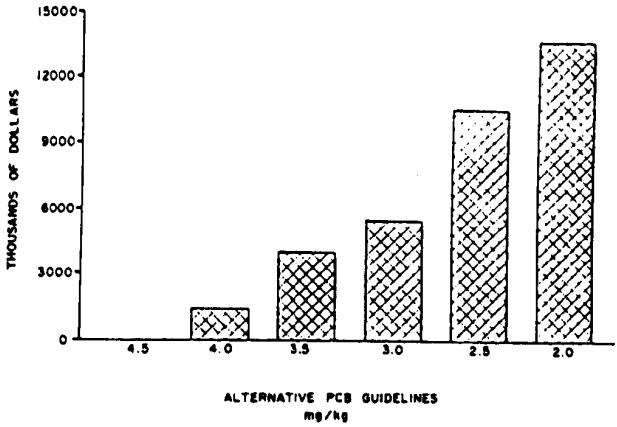


Figure 1. Total economic loss at alternative guidelines - 1980 (deflated 1974 dollars).

an impact of $31 million, apparently assuming that those losses would not be made up by additional imports. Finally, they suggested that the value of fish not taken off the market would also be reduced because of bad publicity.

Ultimately, the hearing examiner found that these four arguments on behalf of industry were irrelevant. They were outside the scope of the problem as it had been narrowly defined.

LOBSTER LOSSES: UNREPRESENTATIVE SAMPLING

In estimating the food loss, the FDA assumed that the percent found violative in the various samples would be the percentage removed from the market. That was accepted as one of the ground rules for the hearing. However, there was one exception: the lobster data. In this case, only those samples from the New Bedford, Massachusetts, area were found to be over the limit. FDA samples fish to spot violations, not to establish national percentages found in violation. When they found

MONS 005183

contaminated lobsters, they naturally intensified their sampling in New Bedford to get a handle on this "hot lobster population". About 22.5 percent of the total samples (1979-80 sampling period) of lobsters from all over the country were shown to be violative at 2 mg/kg, but the only ones shown over the limit were from the New Bedford area. There happens to be a source of PCB contamination in the New Bedford/Hartford area. If we simply removed all the lobsters from New Bedford from the market, and none of the others, the value lost would not be $14.5 million (1978 dollars) but more likely be $.25 million dollars (1974 dollars) because they represent only 1/2 of 1 percent of total U.S. lobster landings (FDA, 1982, Testimony of Dr. John Gates). Or, calculated in a slightly different way based on fishing effort, the loss would be slightly over $1 million ($1.3 million). These later figures are much more representative of the actual prospective impact than the $14.5 million estimate.

PRESENT ESTIMATES

What is the current estimate of losses, considering all of these arguments? Table 3, entered as evidence on behalf of the industry by the U.S. Department of Commerce, National Marine Fisheries Service, is based on the latest PCB data and fish landings. Changing the lobster losses from $10,130 million (Table 3) to $.25 or $1.3 million, the estimate becomes $4.053 million or $5.103 million. At most, the loss as I estimate it has dropped from the original $5.7 million to about $5 million, using 1980 catch and new PCB data, but continuing with 1974 dollars. One additional factor, price elasticity, still remains to be considered.

MULTIPLIER EFFECT

Before we allow for price elasticity, let us consider another issue--the multiplier. If the above is the landed value of the fish lost, what is the total impact on the U.S. economy? Fish are processed, transported, and marketed (wholesale and retail) so the final food value of those fish reflects these costs. The value added in the process of wholesaling, retailing, transporting, and processing fish is only a factor of about three according to recent national studies (Centaur, 1977). In other words, the final sales value of the fish is about three times higher than the initial landed value. After the fish are sold, the income is respent in the community, adding another component of economic impact. This is the multiplier effect. The total of both the multiplier and value added effects is about seven.

In its 1979 regulations statement, the FDA incorrectly multiplied the landed values by a factor of six to convert them to food values. The more correct way of finding the total value of the food lost is to convert the landed values to final sales values by multiplying the landed values by three, the average value added. The hearing examiner, in his findings, recommended a value of six even though all three Great Lakes economists that considered this thought the multiplier should be three instead of six or seven. He used six primarily because that is the multiplier the FDA chemist used to originally estimate the losses officially adopted by FDA.

PRICE ELASTICITY

Another factor that Gary Johnson and I recognized was price elasticity. The price elasticity of fish is low. That means that if fish are taken off the market, the prices of the remaining fish of the same species go up, but in smaller proportion than the amount of fish taken off the market. For example, the price elasticity of whitefish is -0.3 (Ghanbari, 1977), which means that if the quantity of whitefish were reduced by 10 percent, the price of whitefish would increase 3 percent. Fish price elasticities are low because each kind of fish has many substitutes in the market. If new regulations remove fish from the market, the values of the remaining fish will increase. Therefore, the prices of the fish removed from the market will be slightly higher than existing prices. The values of the losses will not be much higher than $4.053 million or $5.103 million because the elasticities are low and the prices will increase only gradually. I testified that the total loss would still be less than $6 million (1974 dollars). Apparently, the hearing examiner misinterpreted what I said; he added another $6 million for the elasticity effect, referring to my testimony.

HEARING EXAMINER'S FINDINGS

The hearing examiner found that the landed value lost would be $13.5 million in 1980 dollars, or $8 million in 1974 dollars. Multiplying $13.5 million by six and adding the $6 million for elasticity, he estimated the total food loss at $86 million. In my opinion, this includes at least five mistakes in addition to the big assumption that the percent violative in FDA samples equals the percent lost. We have discussed the multiplier of six mistake and the elasticity mistake. Two other mistakes were (1) that 10 percent of lobsters would be lost (because he felt a consistent approach to estimating losses should be taken even if we know better), and (2) that 30 percent of alewives

would be lost (because those caught outside of the Great Lakes are used as food and comprise 30 percent of the U.S. catch, even though I believe all the violative samples came from Great Lakes fish). He estimated lobster and alewife losses at almost $5 million (combined) in 1980 dollars, or about $3 million in 1974 dollars. His final mistake was that he used different percentage losses than I believe he intended to. He used the percentage found violative in 1980 samples only, rather than the 1978-1980 samples combined, yet he referred to the fact that the parties agreed to a set of losses based on 1978-80 samples. This resulted in significantly higher loss estimates for stripped bass. Other than these errors, the total loss figures are about the same as the original losses estimated by FDA.

CURRENT STATUS

Some groups will soon be filing exceptions to the ruling based on some of those issues. When the period for exceptions expires later this spring, the findings and the exceptions will be presented to the Commissioner of the FDA. He will then decide whether or not to change the PCB tolerance levels.

BROADER ISSUES

This hearing did not consider two broader social issues that have not been addressed by the FDA in the hearing or in any other document I have seen on this issue. I think it is particularly unfortunate that a benefit-cost analysis was not attempted because that would focus on the advantages and disadvantages; whereas the economic impact analysis the hearing focused on would only be one part of that analysis. For example, although the losses in landed and food values were estimated, any associated reduction in the costs of landing and otherwise handling the fish were ignored.

Some of the real issues--the social questions--that should be examined in this case are as follows:

(1) What are the equity considerations? We know that much of the Great Lakes fishing industry would be devasted. Most of the projected losses are species that comprise the bulk of the commercial fishery in Lakes Superior, Huron, and Michigan. If those were taken off the market, the already depressed fishing industry there would be seriously hurt. Is it worth penalizing those particular people when we are not sure there would be any corresponding benefits? On

the other hand, is it fair to expose fish consumers to risks they are not aware of?

(2) What are the benefits and costs? The benefits would be the value of reducing the health risk, increasing life spans, and increasing the security available to fish consumers. The cost would be (1) the final sales value of the fish lost minus the costs that would have been incurred to produce, process, and otherwise handle the fish; plus (2) the cost of regulation. Dr. Van Ravenswaay discussed this issue much more thoroughly than I can here. Much more information would be needed to assess the benefits accurately, and that kind of information is not presently available. However, at least it is the right question, even if we don't have good answers yet.

ANGLING VALUES

Dr. Howard Tanner, Michigan DNR, suggested that I would mention how the sport fishing values would be affected. I have not evaluated that carefully, but I do know the upper limit of sport fishing impacts and values. If sport fishing were discontinued in the Great Lakes, the economic impact would be over $1 billion per year (Talhelm et al., 1979). Anglers spend about $500 million, and the multiplier effect is 2 to 2.5 times that amount. In addition, anglers would lose a fishery they value at about $600 million per year. In other words, not only do anglers spend $500 million for Great Lakes angling, but they would be willing to pay up to $600 million beyond those expenditures in an effort to prevent the loss of the fishery (Talhelm et al., 1979). These values are much greater than the commercial fishery losses.

LITERATURE CITED

Centaur Management Consultants, Inc. 1977. Economic Activity Associated with Marine Recreational Fishing. National Marine Fisheries Service, U.S. Department of Commerce, Washington, DC, pp. 206 plus xii.

Ghanbari, M.R. 1977. Optimum Allocation of a Renewable Resource: A Bioeconomic Model of the Great Lakes Whitefish Fishery. Unpublished Ph.D. Dissertation, Michigan State University, Department of Agricultural Economics, East Lansing, MI, pp. 180 plus xiii.

MONS 005187

FDA. 1982. Docket No. 77N-0080 in the Matter of: Polychlorinated Biphenyls (PCB's) in Fish and Shellfish; Reduction of Tolerance; Initial Decision. U.S. Department of Health and Human Services, Food and Drug Administration, Washington, DC.

Talhelm, D.R., R.C. Bishop, K.W. Cox, N.W. Smith, D.N. Steinnes, A.L.W. Tuomi. 1979. Current Estimates of Great Lakes Fisheries Values: 1979 Status Report. Great Lakes Fishery Commission, Ann Arbor, MI, pp. 18.

MONS 005188

CHAPTER 30

PROBLEMS IN LEGISLATING AND REGULATING TOXIC MATERIALS: PANEL DISCUSSION

William E. Cooper, Moderator
Department of Zoology
Michigan State University
East Lansing, MI 48824-1115

COOPER[1]: Over the last few days you have heard the discussion about many aspects of polychlorinated biphenyls (PCBs): the sampling, analyses, health effects, etc. There has probably been more research done on PCBs than on any other single compound in the last five or ten years. Based on all of this, what would you provide Governor Milliken as a consensus recommendation? What I would like you to do is to try to address three questions that need to be answered if you are going to come to such a consensus. First of all, what do action levels mean in terms of the humans that we say we are going to try to protect? The concept of action levels is embedded in federal law and is the primary mode of regulating interstate commerce. The levels are based on nationwide statistics (e.g., on a typical 18 year old from Des Moines, Iowa, who eats 19.2 grams of fish a day). How appropriate is this for people who live on the shores of the Great Lakes and eat much more fish containing higher levels of PCBs?

A second question is whether or not there should be uniformity among the state governments, the federal government, and provincial governments, all of whom have the same regulatory mandates. There is both an economic and an exposure argument in that question. If we are convinced that Michigan consumers are really consuming a

[1]Members of the audience contributing to the Panel Discussion are identified at the end of the chapter. The other speakers are identified in the front matter in the List of Participants.

MONS 005189

much greater percentage of the fish out of the Great Lakes, maybe Michigan should have a lower standard than what is acceptable for the average consumer served by the Food and Drug Administration (FDA).

One other problem is that the population with the greatest exposure is sports fishermen, not the average consumer; and the only way we are dealing with this group is with warnings stamped on the back of fishing licenses and some education programs describing how to clean fish properly. The third question is whether or not these steps are really adequate. Before we focus on these questions, I would like to give panel members an opportunity to make some general comments.

AUST: I would like to make the point that much of the action prior to this meeting relative to a consensus PCB action level in fish has been due to the Toxic Substance Control Commission (TSCC). The TSCC was established to examine state programs and regulations relating to toxic substances in Michigan. The TSCC has been dealing with many subjects; but the one that has been persistent has been the PCBs, probably because they, too, are persistent. The Commission was made aware of a letter to Governor Milliken a number of years ago from the Director of the FDA saying that Michigan was unique in that PCBs in Great Lakes fish were another source of contamination of the people of Michigan and suggesting that the state should consider its own action level. Nothing was really done until the Commission took up the subject with the FDA. Taylor Quinn, from the Bureau of Foods at FDA, wrote back that: "The FDA would have to leave it up to the state and local officials to determine whether additional steps are necessary to reduce PCB exposure in situations atypical of the general population and, further, what types of steps should be taken."

That was in January of 1981. Needless to say, no action has been taken; therefore, the Commission decided that we should seriously consider this subject. We argued for many hours as to what the recommendation should be. Should it be an action level? A standard? At what point should it be imposed? I, personally, feel that 2 mg/kg is not low enough. A think many other people at this conference voiced the same opinion. However, the 2 mg/kg action level is at least somewhat similar to what Ontario is proposing. If we do not have a 2 mg/kg standard, I am certain that the Commission could live with some other level as long as it is below the 5 mg/kg federal level. However, the Commission is going to be quite insistent that something

McCRACKEN: I have a few statements that I think partly represent what Dr. Tanner said this morning and partly represent what I think based on what I have heard in the past few days. Together my remarks represent, in effect, a Department of Natural Resources (DNR) position on the issue of PCBs in the Great Lakes.

First of all, because of our combination of regulatory and promotional activities, we feel that the DNR must take a balanced viewpoint on PCBs. In our role as a pollution control agency, we will continue to work diligently to reduce the discharges of PCBs through the National Pollution Discharge Effluent Standards (NPDES) program and otherwise.

We are pleased that PCB control legislation is having a more rapid effect in reducing PCB residues in fish than had been predicted by scientists. By PCB control legislation I mean state and federal laws which ban manufacturing and uses other than in closed systems. We are pleased that most fish now fall below 5 and 2 mg/kg, depending on what portion of the fish is sampled.

We share the concern of the Michigan Department of Public Health (MDPH), and many people here at this conference, that many people eat large amounts of contaminated fish which they or friends catch, especially because this is the primary source of PCB to humans and the FDA risk assessments indicate that even a 2 mg/kg tolerance may not properly protect sport anglers.

We do not believe that unilaterally lowering the PCB tolerance for commercial fish is a particularly useful approach to help sport anglers. We feel that Michigan commercial fish should be regulated just like other states; and we would not object to lowering the tolerance from 5 to 2 if the scientific information led the FDA to make that judgment. We do believe that a better approach is to improve our information and explanations to the people of the state about the concern over PCBs and about how to reduce their intake of PCBs; and I think a good example of that is in the latest DNR magazine. It contains a wonderful article on how to take out the fat which contains most of the PCBs before the fish are cooked. We need to carry out a fish contaminant monitoring program to obtain better data for doing this informational program. As Representative Anderson said, that depends on funds. We can't do it without funds.

At present, we do not believe there is enough hard evidence on the dangers of PCBs to humans to stop the salmon planting program. The program provides many benefits to the state that have not been discussed in detail at this conference and which must be considered before such a decision is made. I say "at present" because Dr. Greta Fein's study may provide more information on health effects, and it is certainly possible that we might want to change our minds about that.

Last, we think standardization is needed, at least on the type of sample of the edible portion to be taken; and we will propose that to the FDA, the International Joint Commission, and other jurisdictions.

HUMPHREY: The basic issue here is how to reduce exposure to this kind of chemical. I believe the information brought forward at this conference reinforces the literature saying that PCB is not a biologically inert compound. Depending on whose viewpoint you take, you accept or reject certain degrees of how harmful this chemical could be. We do know that it is present in the Great Lakes where the basin and its drainage patterns are unique. More importantly, PCB bioaccumulates and stores in biological tissue. Thus, with our understanding of the nature of the compound and its potential to do harm, we have to consider how we can reduce exposure and the potential for disease.

COOPER: There are two types of exposure: voluntary and involuntary. Involuntary is when you go to the market to buy fish that have no labels to tell you that it is from the Great Lakes. Action levels and tolerances are designed to protect people from this type of exposure. Voluntary exposure is when you put a warning on fishing licenses and people choose whether or not to eat what they catch. The two types of exposure have different societal levels of acceptability. People perceive risks differently if they are chosen or imposed. I've heard that the U.S. federal government recommended lowering action levels to 2 mg/kg because if it did not, every batch of fish landed in Canadian ports by American fishermen would have to be chemically analyzed before it would be allowed in. To what degree is the U.S. government suggesting 2 mg/kg purely in terms of economic stability between the U.S. and Canada and the international fishing agreements with no consideration of toxicology at all?

GRANT: That's news to me at Health and Welfare.

MONS 005192

COOPER: From the FDA's point of view, is there a constraint if Canada and the U.S. have different levels?

HOETING: I am not aware of any problems with marine fish whether they are caught off the coast of the U.S. or of Canada. I do not believe freshwater fish from the Great Lakes are caught by American fishermen and sold in Canada. The reverse is true.

COOPER: Are you saying that the major issues between 2 and 5 mg/kg are biochemistry, risk assessment, exposure rates, and toxicology?

McCRACKEN: The differences between 2 mg/kg in Canada and 5 mg/kg in the U.S. reflect the fact that in Canada they are taking different kinds of samples. The plug of lean muscle used in Ontario is the portion least likely to show high contaminant levels, while the American samples show higher levels. We don't think that there is a lot of difference in which fish pass or fail inspection in the U.S. or Ontario because of the differences in sample type.

GRANT: Dorsal muscle is Ontario's interpretation of the edible portion. Our interpretation of an edible portion is not necessarily the dorsal muscle. The samples which we identify are collected by the Federal Fisheries and Oceans as they would flow into the marketplace.

COOPER: Are you saying that you don't sample at the Federal level in Canada the same way as you do in the Province of Ontario?

GRANT: Not necessarily. If you only eat the dorsal muscle, it is the same.

COOPER: I'd like to ask Dr. Cardwell a question about 2 versus 5 mg/kg. Is the only difference the way you analyze your fish so that if you analyze them all the same way everyone gets the same level? Also, is there any reason that there can't be standardized analytical techniques?

CARDWELL: Because the level of fat in the filet is greater than in the dorsal muscle, I would expect a higher level from our way of making the measurement. I see very little problem in reaching some type of agreement with regard to general standardization.

COOPER: Is that one thing we could pass on to the Governor as a strong recommendation--a standard set of sampling and analytical techniques? Anyone disagree?

AUST: My stand is that the best available technology be used on the most appropriate samples. We went through these arguments with the polybrominated biphenyls (PBBs), and it was decided that a fat sample was to be used. I don't know if you could use, say, a rendered sample of fish to do a fat analysis. So far I have heard no discussion of the PCBs in the fat or PCBs in fish on a fat basis. We have been talking about a whole fish or a filet where PCBs are present in the ppm range; whereas when the PBBs issue arose, we set a standard of 20 ug/kg in the fat of cattle. Variability was removed by always sampling the fat and reporting the data on a fat basis. Now we are talking about using some other portion and not using the fat basis; and, also, we are discussing a level which is considerably higher than 20 ug/kg on a fat basis. It would appear that there is a large difference here without there being a significant difference in chemicals.

COOPER: One thing I would recommend in considering environmental legislation is to have scientists give not just the means but also the 95 percent confidence intervals around their estimates. If you put in the bimodality of the population you are sampling, the 20 fish the FDA has homogenized from which you take a uniform sample, the analytical variation from lab to lab and sample to sample, and multiply these variations together, I'll bet you couldn't tell 2 from 5 statistically. I think we have to be honest as to where we have precision and where we don't.

What about the concept of uniformity? Is it essential or non-essential from anyone's point of view?

CARDWELL: I would agree to that because at least then we are attempting to compare like situations and like circumstances. At the present time, we are not doing that.

COOPER: Might it be that the one place you would not want to do that is if you had sub-populations in Michigan that had higher exposure rates because of their occupation or sports? With a unique population that has a much higher than average exposure, uniformity might not be the best way to protect health. How are you going to balance the economics of uniformity versus the public health concern to control exposure when you know populations differ?

McCRACKEN: What we have now is uniformity within jurisdictions. We aren't, in every case, using the worst case or series of cases representing all of the various ways fish could be consumed. We have a standard in Ontario, one in Michigan, and so on. These are not based on ethnic food

eating habits. They are based on regulatory policy. What we are saying is why not require the same regulatory policy in all jurisdictions? That's a different question from whether or not we should use the worst case.

Should we protect the person who eats the portion of the fish that has the most fat? Ontario handles this problem by using a lean plug of muscle and saying that if you eat a portion with more fat, beware because these are not serious enough warnings for you. Perhaps that's the way to handle somebody who eats an unusually high fat portion.

COOPER: Dr. Hoeting, you deal mostly with national averages because that is your mandate. How do you handle high-risk or high-exposure sub-populations?

HOETING: We face that problem with many regulatory situations. We have the same problem with saccharin, cyclamates, and sensitivity to anti-perspirants. A certain segment of the population, in fact, is far more sensitive to or consumes much greater quantities of the compound than others. The rational process is to attempt to determine what the no-effect levels are, extrapolate from them, and base a decision on that group which typically represents the greatest majority of the people.

The average consumer of fish eats somewhere in the range of 10 to 15 pounds a year. Humphrey's data show that a sports fisherman in Michigan consumes between 20 and 28 pounds a year. Out of that group of between 400 and 500 subjects, one or two people consume upwards of between 100 and 200 pounds a year. The existing regulation does not provide adequate protection for the person who consumes 200 pounds of fish a year.

COOPER: Dr. Talhelm, from an economist's point of view, is there any great argument for or against uniformity between states or between Canada and the U.S.?

TALHELM: If Michigan adopted its own standard, it would probably put Michigan's industry at some disadvantage; but most of the fish caught would find markets outside the state, assuming that they kept their levels at 5 mg/kg. Good markets for Michigan fish are found in Chicago and New York. The main people who would be put at a disadvantage would be the processors. Consumers would substitute either other kinds of fish or other kinds of food, but the people who processed and handled fish in Michigan would have to find something else to do.

MONS 005195

GRANT: If you want to decrease exposure, do you really help the situation that much by having the same level for the fish that is eaten rarely as opposed to that which is eaten more often? We do not necessarily have the same pesticide tolerance for insecticides on apples and pears, but we have the same level for fish. On the basis of exposure, is there any reason not to have different levels?

COOPER: You could argue that it depends on the distribution of the chemical in the environment and the distribution of access to the resource. Dr. Tanner said he would be willing to support 2 mg/kg as long as it is uniform. Does anyone disagree with that or have any problem with that position?

AUST: The Commission's question is: Does that mean that we simply wait until there is a federal standard?

COOPER: Not at all. All we are saying is the data should be proven to be accurate before we commit ourselves. Let's see that we all agree that if there was a uniform set of standards, 2 mg/kg would be acceptable in terms of the public, the economics, risk assessment, public health concerns, FDA's problems, etc.

ANDERSON: The question of uniformity is very important. I recall that when we were dealing with PBBs, we were passing legislation on the level of containment (i.e., how much would the reading be before you must dispose of the animal). The question came up several times in the midst of arguments from technical people as to how, when, and in what manner to measure PBBs. The question wasn't what level should be set, but what sampling and analysis methods should be used in setting the levels. A standard of uniformity is most important. Another feature of this is that the Governor has to make a determination. He also has to have some sort of a uniform advice mechanism. The broad spectrum of populace deserves, and I think rightly so, some degree of uniformity in its reporting.

COOPER. Let's look at the last issue: Voluntary exposure to sports fishermen. Do you feel that the public notice on the fishing license and the educational program have worked and are sufficient with our current knowledge of PCB risks?

ANDERSON: I can touch on that because I travel the state looking at these kinds of things a lot. I came across a man in Ludington not long ago who told me they canned 30 qts of salmon so far this season and that they were almost out of the salmon that they had canned the previous season. I asked him how he trimmed the fish. He said: "I use the

recommended method of trimming. I take off all the fat, take off the fat along the side, along the backbone, cut off the belly flap." So he had an awareness. I talked to others who had also done the same thing when they trimmed their fish. In our home, we, as a routine practice, cut off the fat. My experience has been that more people than not are aware and are being cautious.

HUMPHREY: Yesterday, I presented some statistics which address this question. We interviewed some people who consumed a considerable amount of fish in 1974 and then we interviewed them again last year. For whatever reason, the quantity they were consuming, numbers of meals per year, as well as pounds, had gone down. I don't know exactly why. One possibility is that they have been hearing the message concerning consumption. It could also simply be that they are not as lucky at catching fish as they were a few years ago.

COOPER: You could say the reflexes slowed up in eight years.

HUMPHREY: No, the fish aren't there.

COOPER: Does anyone in the audience have questions for the panel members?

CHARLES CUBBAGE: I am not sure that you can answer the questions I have been troubled by during the conference. The objective in setting any standard is whether or not man is going to benefit from it, but you can't just limit it to those people who just happen to be in the population right now. Are Homo sapiens going to be impacted by PCBs 20,000 years from now, assuming we will be here for that length of time? We have to consider the health of our life support systems as well as the health of man.

COOPER: There is a legislative mandate to stop the prduction of this PCB except in closed systems. The PCBs are being tied up in the sediments, and the amount in water and fish has been dropping systematically over the past eight years. It looks as if it is working its way through the ecosystem. I think the question is whether or not The Toxic Substances Control Act will keep we from making these same mistakes in the future. Any comments from the panel?

AUST: I want to address another issue. We saw Dr. Ringer's data that 2 mg/kg PCBs in fish that make up 30 percent of a mink's diet led to a reproductive problem. I have been alarmed at the number of individuals who come to the TSCC and say there are human reproductive problems. I don't

know what the relationship might be between PCBs and reproductive problems in humans. It is impossible to compare humans to minks, but what kind of a safety factor are we adding to the mink food level of 2 mg/kg? Another problem is carcinogenesis. I haven't had a chance to really analyze Dr. Humphrey's latest data on "PCB silo farmers", but it may be alarming. We are not going to find the exact risk of PCB to human beings published in some journal because PCBs are unique substances. They are promoters of carcinogenesis and so should always be studied in conjunction with another chemical. This type of data is impossible to obtain for humans. Therefore, we will not have data for risk analysis.

COOPER: We have to put what we know and don't know in balance. There are many chemicals which have been in the environment since World War II, and we are just finding out that they are there. When you look back at the history of environmental episodes, you see that when the ion detector became available for heavy metal analysis we discovered mercury. When the gas chromatograph came into use, you found organic chemicals. To a degree, environmental awareness has come about with the ability to monitor various chemicals. The compounds have been out there for a long time.

AUST: Would you rather discover them with an epidemiological study?

BREMER: I have something I want to add for clarification and maybe ask you a favor. The federal money for PCB enforcement has been available for just about a year now; and the legislature has failed to approve the authority for the DNR to spend those funds. They are in limbo right now; and if the legislature doesn't come along and approve them, they will probably be lost by this time next year.

ANDERSON: I'll check that within the hour.

COOPER: That's one constructive thing to come out of this morning's session.

CARDWELL: The Michigan Department of Agriculture (MDA) is very much interested in anything that will ultimately lower the exposure of the people of Michigan. However, we feel that a uniform process must be utilized. If you are going to lower the allowable level for the commercial fishermen, you must also consider lowering the total exposure for the sports fishermen. The Director of the MDA has indicated that he will go along with the recommendations of the

Hazardous Materials Cabinet, which was formed by the Governor and which met for the first time in December.

GISELA KING: After hearing testimony at this conference, I am very angered and frustrated at the prospect of not being able to nurse a baby, to fulfill this basic need a mother has to nurture and protect her baby. As a consumer, I think what would be important to me to protect myself is a labeling system. As a part-time farmer, for example, I would like to know if any of the equipment I may be purchasing contains PCBs. I would also like to see labels on different food items that are purchased; and on fish, the actual chemical content, and not just the point of origin.

COOPER: One of your questions concerns the degree to which laws that restrict PCBs to closed systems are being enforced. It is true that currently the only PCBs manufactured and sold are in closed transformers and similar equipment.

HUMPHREY: It is my understanding that PCBs are no longer being manufactured and sold in this country. An article that I cited yesterday says that about half of the PCBs ever made are still in use, but in closed systems.

COOPER: But, if she went out and bought a new piece of equipment, would the hydraulic fluids, lubricating fluids, and cutting oils all be PCB-free?

HUMPHREY: I belive they should be.

COOPER: The other question was to what degree you can label a food product as to its PCB concentration. There you have a problem because of the period of time it takes to get food analyzed. With kepone in Chesapeake Bay, it took about two weeks and the fish were either rotten or sold by then. I don't know of any way that you could actually monitor fast enough and label products soon enough so that actual levels would show up in the market place for a fresh item.

KING: Do I understand that there are certain levels of PCBs in milk, eggs, meat, and various other consumer products?

CARDWELL: To the best of my knowledge, based on data from the USDA, that has not been borne out.

HUMPHREY: Mrs. King was disturbed as a mother because she could not breast feed her child. The point we were trying to make is that a woman in Michigan, who is not a consumer

of large quantities of sports fish or does not live on a farm with a particular type of silo, does not have particularly high levels of PCBs; and there has never been any advice that she should not breast feed her child.

AUDIENCE MEMBERS CONTRIBUTING TO THE PANEL DISCUSSION: Charles Cubbage, Water Quality Investigators, 826 Squire Lane, Milford, Michigan 48042; and Gisela King, 9601 Fish Lake Road, Holly, Michigan 48442.

MONS 005200

Action levels (U.S.) 395, 397, 423-424, 426, 429-430
Acute exposure 280-281
Acute toxicity 143, 228
Administrative guidelines (Canada) 387
Agriculture Canada 385, 388-389
Analysis of PCBs
  capillary gas chromatography 165-176, 195
  electron capture detector 168-169, 195
  gas-liquid chromatography 141, 143
  mass spectrometry 168-169
  proton magnetic resonance 169
  UV spectra 144-145, 147-151
Arylhydrocarbon hydroxylase 166-167
Atlantic Ocean 50

Behavior 311-315, 338
Benzene 106, 165
Bioaccumulation 188-192, 194
Biomagnification 16, 187
Biotransformation 192-195
Blood composition 170-171, 281, 290
Blood levels
  adult 31-32, 279, 282, 284-285, 288-290, 294, 301-307, 312, 315, 325-338
  cord 312, 315-316, 325-336, 338
  fetal 312
  infant 312
Blood pressure 290, 338
Body burden 105, 282-285, 302, 309, 313, 315
Breast milk 31-32, 105, 235-237, 300, 315-316, 325-338

Canadian Environmental Protection Service 385-386
Capillary gas chromatography 165-176, 195
Carcinogenicity
  humans 89, 281, 292-295, 308-309, 338
  laboratory animal and cell cultures 217-218, 241
  theory 83-87, 179-184
Chlorinated benzenes 106, 165
Chlorinated dibenzofurans 78, 106, 281
Chlorinated dioxins 106, 165, 216
Chlorinated naphthalenes 78
Chlorinated quaterphenyls 78, 281
Cholesterol levels 289-290, 294
Clinical signs 215-216, 229
Clinical studies 279, 287, 290-291, 294, 306-308, 312-313
Commercial fishing 109-112, 405, 409-422
Council on Environmental Quality 369
Cyclophosphamide (CPA) 256-266, 269-270
Cytochrome P-448 166, 270
Cytochrome P-450 263, 265, 270

DDT 6-7, 69-70, 77, 106, 112,

MONS 005201

133, 227, 336, 380
Diabetes 308
Dibenzofurans 78, 106, 281
Dieldrin 109
Dioxins 106, 166, 216
Drinking water 33-34, 302

Economics of PCBs
commercial fishing 109-112, 405, 409-422
production of PCBs 41, 299
risk-benefit analysis 354-356, 358, 361-363, 420-421
sports fishing in Michigan 103
uses of PCBs 142
Edible portion 118, 123, 126-137
Electron capture detector 168-169, 195
Embryotoxicity 253-275
Environment Canada 385
Environmental distribution 11-48, 51-76, 141
Environmental Protection Agency (U.S.) 126-128, 137, 369-373, 381, 393
Environmental Protection Agency (Canada) 385-386
Enzyme induction 166-167, 216, 255
Epidemiology 279-310
Erie (PA) County Health Department 128
Ethoxyresorufin-o-diethylase 265
Excretion 203, 205, 209-211

Farmers 300-302, 305-309
Fate of PCBs in humans
excretion 203, 205, 209-211
metabolism 143-145, 205-211
storage 32, 236, 279, 283
tissue distribution 204-206, 209-211, 235
transplacental passage 31, 82, 216, 232, 234, 311-313, 336, 338

Fish
bioaccumulation in 188-192, 194
biomagnification in 16, 187
biotransformation in 192-195
edible portion 118, 123, 126-137
human consumption of 31, 105, 301-307, 313, 315-316, 318, 321-322, 324-325, 332-338, 429
persistence of PCBs in 194-199
PCB levels in 12-29, 34-43, 50, 63, 69-70, 93, 104-106, 110, 117-120, 170, 173, 188-201, 302-304, 319-320
Fish and Wildlife Service (U.S.) 37, 106, 124
Fisheries and Oceans (Canada) 385, 387, 407
5-Fluorodeoxyuridine 256-257, 266-272
Food and Drug Administration (U.S.) 29-30, 32, 36, 77-78, 80-81, 105, 110-111, 123-124, 126, 129-132, 137, 360-361, 368-369, 371, 377, 393-406, 409-420, 424, 428

Gas-liquid chromatography 141, 143
Great Lakes
monitoring 37, 116-122, 124, 127-129, 398-401
physical characteristics 60
PCB burden 60-64
sediments 50, 53, 56-63
sources and sinks of PCBs 62-70
water 14, 37, 49-50, 53-56, 60-61, 63

Health and Welfare Canada 385, 387-389, 426
Heart 308

MONS 005202

Hepatitis 308
Human consumption 31, 105, 301-307, 313, 315-316, 318, 321-322, 324-325, 332-338, 429
Human exposure to PCBs
  farmers 300-302, 305-309
  occupational 280, 282-295
  sports fishermen 31, 36, 81, 94, 103-104, 117, 288, 290, 300-304, 307, 313-315
  Yusho incident 78-79, 82, 280-281, 368, 389

Illinois Department of Conservation 126
Immunotoxicity 254
Indiana Department of Natural Resources 126
Indiana State Board of Health 126
Infants 312-315
Intercellular communication 241-252
International Joint Commission 106, 117, 121, 137, 426

Joints 307

Liver 217, 280, 289, 294
Lymphoid organs 220-221
Legislation
  Canadian Environmental Contaminants Act 383-385
  Michigan PCB Control Act 349, 370-371, 376
  United States Food, Drug, and Cosmetics Act 393-397
  United States Toxic Substance Control Act 369-370, 372-373, 377, 379, 393, 431

Mass spectrometry 168-169
Mercury 106
Metabolism 205-211, 143-145
Michigan constitution 375
Michigan Department of Agriculture 123-124, 349, 404, 432
Michigan Department of Natural Resources 102, 104, 124, 347-349, 421, 425, 432
Michigan Department of Public Health 3-4, 37, 96, 104, 106, 124, 288, 299, 325, 350, 425
Michigan environmental legislation
  Air Pollution Control Act 376
  Environmental Protection Act of 1970 376, 380
  Hazardous Waste Management Act 378-379
  Inland Lakes and Streams Act 376
  Pesticide Control Act 376
  Phosphate Control Act 376, 381
  Recreational Land Trust Fund Act 376
  Sand Dune Protection Act 376, 381
  Shoreland Protection Act 376
  Solid Waste Management Act 378, 380
  Toxic Substance Control Commission Act 376-377
Michigan Fish Contaminants Advisory Committee 111, 124-125, 132-133, 137
Michigan Fishing Guide 350
Michigan Hazardous Materials Cabinet 433
Michigan Legislature 375-382
Michigan Toxic Substances Control Commission 107, 424, 431
Michigan United Conservation Clubs 101-103
Minks and ferrets 227-240
Minnesota Department of Natural Resources 126
Minnesota Department of

MONS 005203

Public Health 126
Minnesota Pollution Control Agency 126
Monitoring of PCBs 115-122
Great Lakes Environmental Contamination Survey 124
Great Lakes International Surveillance Plan 127-128
Illinois 126, 130
Indiana 126, 130
Michigan 123-125
Minnesota 126-127, 130
New York 127, 130-131
Ohio 127, 130-131
Ontario 105, 127
Pennsylvania 128, 130-131
Surveillance, Epidemiology and End Results Program 308
United States EPA Basic Water Monitoring Program 126, 128, 130-131
United States FDA (Detroit) 129-131, 398-402
United States FWS Contaminant Monitoring Program 37
Wisconsin 128, 130-131
Monsanto Chemical Company 49, 368
Mrak Commission 77
Mutagenicity 241

Naphthalenes 78
National Academy of Sciences 50
National Conservation Council 110
National Fisheries Institute 110, 404-405, 409-412
National Health Survey 288
National Institute of Occupational Safety and Health 282, 369, 371
National Marine Fisheries Service 110, 412-414, 418
National Science Foundation 375
New York Department of Environmental Conservation 127
Occupational exposure 280, 282-295
Occupational Safety and Health Administration 369, 371
Ohio Department of Natural Resources 127
Ontario Ministry of the Environment 127
Ontario Ministry of Labor 127
Ontario Ministry of Natural Resources 127, 387

Pennsylvania Department of Environmental Resources 128
Persistence 194-199
Phenobarbital 263, 265
Phosphorescence 152-153, 157
Photochemistry 141-163
Photolysis 144-158
Physical characteristics of the Great Lakes 60
Polybrominated biphenyls (PBBs) 7, 96-97, 217-220, 229, 232-233, 242-247, 300, 305, 307, 326, 376, 380, 428, 430
Polychlorinated biphenyls (PCBs)
analysis of
capillary gas chromatography 165-176, 195
electron capture detector 168-169, 195
gas-liquid chromatography 141, 143
mass spectrometry 168-169
proton magnetic resonance 169
UV spectra 144-145, 147-151
congeners of 142-143, 165-167, 169, 170-171, 187, 190
economics of
commercial fishing 109-112, 405, 409-422
production of PCBs 49,

299
risk-benefit analysis 354-356, 358, 361-363, 420-421
sports fishing in Michigan 103
uses of PCBs 142
fate in humans
excretion 203, 205, 209-211
metabolism 205-211, 143-145
storage 32, 236, 279, 283
tissue distribution 204-206, 209-211, 235
transplacental passage 31, 82, 216, 232, 234, 311-313, 336, 338
human exposure to
farmers 300-302, 305-309
occupational 280, 282-295
sports fisherman 31, 36, 81, 94, 103-104, 117, 288, 290, 300-304, 307, 313-315
Yusho incident 78-79, 82, 280-281, 368, 389
in environmental samples
environmental distribution 11-48, 51-76, 141
Great Lakes burden 60-64
in Atlantic Ocean 50
in atmosphere 34, 50-54, 60-61, 63, 302
in Great Lakes water 14, 37, 49-50, 53-55, 60-61, 63
in lithosphere 50
in rain 53, 170, 172
in rivers 55
in sediments 50, 53, 56-63
in Shiawassee River 102
in silos 300-301, 305-308
sources and sinks in the Great Lakes 62-70
in fish
bioaccumulation 188-192, 194
biomagnification 16, 187
biotransformation 192-195
edible portion 118, 123, 126-137
human consumption 31, 105, 301-307, 313, 315-316, 318, 321-322, 324-325, 332-338, 429
levels 16-29, 34-43, 50, 63, 69-70, 93, 104-106, 110, 117-120, 170, 173, 188-201, 302-304, 319-320
persistence 194-199
in food and water
human consumption 31, 105, 301-307, 313, 315-316, 318, 321-322, 324-325, 332-338, 429
in drinking water 33-34, 302
in fish 16-29, 34-43, 50, 63, 69-70, 93, 104-106, 110, 117-120, 170, 173, 188-201, 302-304, 319-320
in non-fish food 80
in rice oil 78
reducing level in food 106, 431
total diet studies 402-403
legislation
Canadian Environment Contaminants Act 383-385
Michigan PCB Control Act 349-370, 371, 376
United States Food, Drug and Cosmetic Act 393-397
United States Toxic Substance Control Act

MONS 005205

369-370, 372-373, 377, 379, 393, 431
levels in humans
body burdens 105, 282-285, 302, 309, 313, 315
blood 31-32, 279, 282, 284-285, 288-290, 294, 301-307, 312, 315, 325-338
breast milk 31-32, 105, 235-237, 300, 315-316, 325-338
cord blood 312, 315-316, 325-336, 338
fetal blood 312
infant blood 312
storage in the body 32, 236, 279, 283
tissue distribution 204-206, 209-211, 235
Michigan public health advisory 37, 102-104
monitoring 115-122
Great Lakes Environmental Contamination Survey 124
Great Lakes International Surveillance Plan 127-128
Illinois 126, 130
Indiana 126, 130
Michigan 123-125
Minnesota 126-127, 130
New York 127, 130-131
Ohio 127, 130-131
Ontario 105, 127
Pennsylvania 128, 130-131
Surveillance, Epidemiology and End Results Program 308
United States EPA Basic Water Monitoring Program 126, 128, 130-131
United States FDA (Detroit) 129-131, 398-402
United States FWS Contaminant Monitoring Program 37
Wisconsin 128, 130-131
physical properties of
phosphorescence 152-153, 157
photochemistry 141-163
photolysis 144-158
production 49, 299
public concern 90-99
regulation of
Canada 383-392, 424, 427, 429
Ontario 127, 387
Japan 369
Sweden 369
United States 3-4, 29-30, 77-89, 110-111, 347-351, 353-365, 367-373, 393-407, 423, 427, 429
Illinois 126, 372
Indiana 126, 371
Michigan 349-370, 376
Minnesota 126, 371
New York 127
Ohio 127, 372
Pennsylvania 128
Wisconsin 128
standards
Canadian administrative guidelines 387
Canadian maximum residue limit 390-391
Canadian standard 34
United States action levels 395, 397, 423-424, 426, 429-430
United States tolerance levels 29, 111, 349, 351, 368, 395-396, 404, 409-420, 425-430
toxicology in humans
acute toxicity 280-281
behavioral effects 311, 314-315, 321, 338
carcinogenicity 89, 281, 292-295, 308-309, 338

MONS 005206

clinical studies 279, 287, 290-291, 294, 306-308, 312-313
diabetes 308
effects on
blood composition 170-171, 281, 290
blood pressure 290, 338
cholesterol levels 289-290, 294
heart 308
infants 312-315
joints 307
liver 280, 289, 294
skin 280-281, 286-287, 294, 306-307
sperm 33
thyroid 308
epidemiology 279-310
hepatitis 308
tumors (benign) 308
toxicology in laboratory animals and cell cultures
acute toxicity 143, 228
behavioral effects 313-315
carcinogenicity 217-218, 241
clinical signs 215-216, 229
effects on
intercellular communication 214-252
liver 215, 217
lymphoid organs 220-221
reproduction 82, 227-232, 237, 241, 368, 389-390
skin 219-220
stomach 220
thyroid gland 218-219
embryotoxicity 253-275
enzyme induction 166-167, 216, 255
immunotoxicity 254
minks and ferrets 227-240
mutagenicity 241
teratogenicity 254, 312-314
tumor promotion 88, 243, 246-247
Proton magnetic resonance 169
Public policy 5-10

Quaterphenyls 78, 281

Regulations of PCBs
national
Canada 383-392, 424, 427, 429
Japan 369
Sweden 369
United States 3-4, 29-30, 77-89, 110-111, 347-351, 353-365, 367-373, 393-407, 423, 427, 429
state and provincial
Illinois 126, 372
Indiana 126, 371
Michigan 349-371, 376
Minnesota 126, 371
New York 127
Ohio 127, 372
Ontario 127, 387
Pennsylvania 128
Wisconsin 128
Reproductive effects 82, 227-232, 237, 241, 368, 389-390
Rice oil 78
Risk-benefit analysis 354-356, 358, 361-363, 420-421

Shiawassee River 102
Silos 300-301, 305-308
Skin 219-220, 280-281, 286-287, 294, 306-307
Sperm 33
Sports fishermen 31, 36, 81, 94, 103-104, 117, 228, 290,

MONS 005207

300-304, 307, 313-315
Standards
Canadian administrative guidelines 387
Canadian maximum residue limit 390-391
Canadian standard 34
United States action levels 395, 397, 423-424, 426, 429-430
United States Tolerance Levels 29, 111, 349-351, 368, 395-396, 404, 409-420, 425-430
Statistics Canada 390
Stomach 220
Storage in the body 32, 236, 279, 283

Teratogenicity 254, 312-314
Thyroid 218-219, 308
Tissue distribution 204-206, 209-211, 235
Tolerance levels 29, 111, 349-351, 368, 395-396, 404, 409-420, 425-430
Total diet studies 402-403
Toxicology of PCBs in humans
acute toxicity 280-281
behavioral effects 311-312, 314-315, 338
carcinogenicity 89, 289, 292-295, 308-309, 338
clinical studies 279, 287, 290-291, 294, 306-308, 312-313
diabetes 208
effects on
blood composition 170-171, 281, 290
blood pressure 290, 338
cholesterol levels 289-290, 294
heart 308
infants 312-315
joints 307
liver 280, 289, 294
skin 280-281, 286-287, 294, 306-307
sperm 33
thyroid 308
epidemiology 279-310
hepatitis 308
tumors (benign) 308
Toxicology of PCBs in laboratory animals and cell cultures
acute toxicity 143, 228
behavioral effects 313-315
carcinogenicity 217-218, 241
clinical signs 215-216, 229
effects on
intercellular communication 241-252
liver 215, 217
lymphoid organs 220-221
reproduction 82, 227-232, 237, 241, 368, 389-390
skin 219-220
stomach 220
thyroid gland 218-219
embryotoxicity 253-275
enzyme induction 166-167, 216, 255
immunotoxicity 254
minks and ferrets 227-240
mutagenicity 241
teratogenicity 254, 312-314
tumor promotion 88, 243, 246-247
Toxicology, principles of 180, 183
Transplacental passage 31, 82, 216, 232-234, 311-313, 336, 338
Tumor promotion 88, 243, 246-247
Tumors (benign) 308

United States Council on Environmental Quality 369
United States Department of Agriculture 368, 397
United States Department of

MONS 005208

Commerce
National Marine Fisheries Service 110, 412-414, 418
United States Department of Health and Human Services
Food and Drug Administration 29-30, 32, 36, 77-78, 80-81, 105, 110-111, 123-124, 126, 129-132, 137, 360-361, 368-369, 371, 377, 393-406, 409-420, 424, 428
National Institute of Occupational Safety and Health 282, 369, 371
United States Department of the Interior
Fish and Wildlife Service 37, 106, 124
United States Department of Labor
Occupational Safety and Health Administration 369, 371
United States Environmental Protection Agency 126-128, 137, 369-373, 381, 393
Uses of PCBs 142
UV spectra 144-145, 147-151

Wisconsin Department of Agriculture and Consumer Protection 128
Wisconsin Department of Natural Resources 128

Yusho incident 78-79, 82, 280-281, 368, 389

MONS 005209

ANALYTICAL CHEMISTRY OF PCBs

Mitchell D. Erickson

BUTTERWORTH PUBLISHERS
Boston • London
Sydney • Wellington • Durban • Toronto
An Ann Arbor Science Book

MONS 005210

To my sister, Beverly J. Erickson, who was most interested in my progress with this book, but did not live to see it completed.

MONS 005211

ABOUT THE AUTHOR

Mitchell D. Erickson is a Principal Chemist with Midwest Research Institute in Kansas City, Missouri. He has conducted research in all major areas of trace organic analysis in air, water, soil, sediment, biota, tissue, sludge, and hazardous waste; has developed methods for determination of PCBs in a variety of matrices; provided technical assistance to the U.S. EPA in permitting PCB destruction processess; has investigated the formation of chlorinated dibenzofurans and other toxic products from PCBs and other transformer fluids under fire conditions. He has also studied halogenated hydrocarbon levels in the environment and human tissues and fluids, and developed methods for the analysis of organic materials in diesel exhaust. He has worked extensively in developing analytical techniques using GC, FTIR and GC/FTIR.

Dr. Erickson has published 40 government reports, 36 papers in peer review journals and presented 36 papers at scientific meetings. He is a member of the American Chemical Society, the American Society for Mass Spectrometry, the Society for Applied Spectroscopy, Sigma Xi (Scientific Research Society of North America), and the Coblentz Society. He received the A.B. in Chemistry (1972) from Grinnell College and the Ph.D. in Analytical Chemistry (1976) from the University of Iowa.

MONS 005212

CONTENTS

List of Figures	**xii**
Preface	**xvii**
Acknowledgments	**xix**
1. Introduction	1
2. Physical, Chemical, Commercial, Environmental, and Biological Properties	5
I. Introduction	5
II. PCB Nomenclature	5
III. Physical Properties	9
A. Molecular Weights	9
B. Physical Constants	10
C. Electrochemical Properties	13
D. Ultraviolet and Fluorescence Spectra	13
E. Infrared Spectra	13
F. Nuclear Magnetic Resonance (NMR) Spectra	14
IV. Synthesis and Standards	14
V. Production and Use	15
A. Aroclor and Related Mixtures	15
B. Impurities in Commercial Mixtures	17
C. Monochlorobiphenyls	22
D. Decachlorobiphenyl	22
E. PCBs as By-products	22
F. PCB Formation During Water Chlorination	23
G. PCB Formation from Thermal Degradation of Other Chlorinated Organics	23
VI. Environmental Occurrence	24
A. General Levels and Distribution	24
B. Major Environmental Contamination	24
VII. Environmental Transport and Fate	34
VIII. Destruction, Degradation, and Metabolism	36
A. Intentional Destruction	36
B. Environmental Degradation	37
C. Microbial Degradation	37
D. Metabolism by Higher Animals	39
E. Degradation During Use and Analysis	39
F. Degradation in Fires	40

MONS 005213

IX. Toxicology 45
X. Occupational Exposure and Its Effects 51

3. Analytical Procedures 55
I. ANSI and ASTM Procedures 56
II. EPA Procedure for Oils 61
III. EPA Procedure for Spills and Incinerators 61
IV. Procedures for Food 62
V. Procedures for By-product Analysis 62

4. Sample Collection and Storage 63
I. Water 63
A. Grab Sampling 64
B. Automatic Composite Samplers 64
C. Solid Adsorbent Sampling 65
D. Liquid-Liquid Extraction Sampling 67
E. Rainwater Sampling 68
F. Water Sample Storage 68
II. Air 71
A. Ambient Air 71
B. Source Sampling 78
III. Natural Gas in Pipelines 84
IV. Solids 85
V. Surfaces 85
VI. Oil, Dielectric Fluids, Etc. 86

5. Extraction 87
I. General Considerations 87
II. Water 88
A. Liquid-Liquid Extraction 88
B. Continuous Liquid-Liquid Extraction (CLE) 89
C. Sorbent Column Extraction 90
D. Purge and Trap 90
E. Comparison of Extraction and Techniques 91
III. Sewage and Sludge 91
IV. Sediment and Soil 92
A. Solvent Extraction 92
B. Collaborative Studies 93
C. Thermal Desorption 93
D. Comparison of Sediment and Soil Extraction Techniques 94
V. Air 95
A. Polyurethane Foam 96
B. Florisil 96
C. XAD-2 97
D. Dry Deposition Samples 97
VI. Blood 97
A. Environmental Protection Agency 98
B. Centers for Disease Control 99
C. Comparison of Blood Extraction Techniques 100
VII. Animal and Plant Tissues 100
A. Adipose Tissue 100

MONS 005214

B. Fish 103
C. Milk 106
D. Eggs 107
E. Other Animal Organs 108
F. Plant Tissue 108
G. Discussion of Tissue Extraction 109
VIII. Paper Products 110
IX. Oils 111
A. Transformer and Related Oils 111
B. Vegetable Oils 113
X. Ancillary Considerations 114
A. Solvent Evaporation 114
B. Sorption onto Glassware 114
C. Sources of Contamination 115

6. Cleanup 117
I. Adsorbent Column Chromatography 118
A. General Practices 118
B. Florisil 119
C. Silica Gel 123
D. Alumina 130
E. Carbon 134
II. High Performance Liquid Chromatography 141
A. Characteristics 141
B. Applications 143
C. Detailed Procedure 147
III. Thin-Layer Chromatography 147
IV. Adsorbent Slurry Techniques 148
V. Gel Permeation Chromatography 149
A. Properties 149
B. Eluting Solvents 149
C. Calibration 150
D. Comparison to Other Cleanup Techniques 153
E. Automation 153
F. Applications 154
G. Detailed Procedure 154
VI. Liquid-Liquid Partitioning 154
VII. Chemical Degradation 156
A. Specific Reactions 156
B. Sulfuric Acid 156
C. Chromium Trioxide 158
D. Base 161
VIII. Cleanup of Oil Samples 162
IX. Sulfur Removal 164
X. Criteria for Choice of a Cleanup Technique 166
A. Lipids 167
B. Macromolecules 168
C. Organochlorine Pesticides 168
XI. Validation of Cleanup Techniques 168

7. Determination 171
I. Criteria for Choice of Techniques 171

MONS 005215

II. Gas Chromatography 173
A. Separation 175
B. Injection 196
C. Detection 197
D. Perchlorination 240
E. Carbon Skeleton Chromatography 242
III. Thin-Layer Chromatography 242
A. Historical Perspective 243
B. Comparison to Other Techniques 247
C. Current and Potential Applications 247
IV. High Performance Liquid Chromatography 247
A. Literature Citations 248
B. Current and Potential Applications 254
V. Nonchromatographic Methods 254
A. Nuclear Magnetic Resonance (NMR) Spectrometry 255
B. Infrared (IR) Spectrometry 255
C. Radioimmunoassay 256
D. Other Techniques 257
VI. Confirmation 257
A. Literature Citations 257
B. Current and Potential Applications 258
VII. Screening 259
A. Screening for PCBs 259
B. Screening for Interferences 264
VIII. Summary 264

8. Data Reduction 267
I. Qualitative 267
A. The Importance of Proper Qualitative Data Interpretation 267
B. Interpretation of Retention Data 269
C. Interpretation of Mass Spectrometric Data 275
II. Quantitative 278
A. Calibration 279
B. Quantitation Techniques 281
III. Data Reporting 302

9. Quality Assurance 305
I. General Considerations 305
II. Special Considerations in PCB Analyses 310
A. Reference Materials 310
B. QA in Multiple Laboratory Networks 310
III. Previous QC Measures 314
IV. Recommended QA/QC Measures 315
A. Transformer Oil 315
B. Transformer Fluids and Waste Oils 317
C. By-product PCBs 318

10. Collaborative Studies 319
I. Wildlife 320
II. Chicken Fat and Fish 320

MONS 005216

III. Paperboard 320
IV. Marine Sediments 324
V. Quantitation Techniques and Milk 324
A. Quantitation Techniques 324
B. Milk 325
VI. Paper Mill Effluent 325
VII. Wet Lake Sediment 327
VIII. Naturally Contaminated Dry Sediments 329
IX. Ambient Air 329
X. Dry Pigments 330
XI. Insulating Oils 330
XII. By-products from Industrial Processes 331
XIII. By-products in a Chlorinated Aromatic Waste 333
XIV. Herring 336
XV. Bovine Serum 336
XVI. Lubricating Oils 337

Bibliography 339

Appendix A - Nomenclature and Physical Constants of Polychlorinated Biphenyls 461

Appendix B - Composition of Some Commercial PCB Mixtures 469

Appendix C - Mass Spectral Characteristics of PCBs 477

Appendix D - PGC/ECD Chromatograms of Aroclor Mixtures 483

Appendix E - Terms and Abbreviations 489

Index 501

MONS 005217

LIST OF FIGURES

2-1	Distribution of Chlorine Atoms in the Two Rings of Biphenyl	8
2-2	Bioaccumulation of PCBs in the Lake Ontario Ecosystem	26
2-3	Environmental Persistence of Selected Chlorinated Biphenyl Isomers	38
2-4	Common *In Vivo* PCB Metabolites	40
2-5	Polychlorinated Dibenzofurans Formed from Thermal Degradation of 2,2',4,5,5'-Pentachlorobiphenyl	43
2-6	Tetrachlorodibenzofurans Formed from Thermal Combustion of PCBs and a Trichlorobenzene Mixture	44
2-7	Summary of PCB Isomers Which Induce Cytochrome P-450	51
4-1	Passive Water Sampling Device	66
4-2	Effect of Storage Conditions on Recovery of Aroclor 1016 from River Water	70
4-3	Modified Method 5 Train for Organics Sampling of Stack Gas	79
5-1	Exhaustive Steam-Distillation and Solvent-Extraction Apparatus	105
6-1	Separation of *p,p'*-DDE from Aroclor 1254 by Column Chromatography with Different Activities of Silica Gel	125
6-2	Apparatus for Pressure-Assisted Silica Gel Microcolumn Chromatographic Separation of Organochlorine Pesticides from PCBs Following Florisil Cleanup	128
6-3	Aroclor Elution Patterns from Silica Gel Microcolumn with Hexane as Eluting Solvent	129
6-4	PGC/ECD Chromatograms (A) Before and (B) After Alumina Column Chromatographic Cleanup	132
6-5	Flow Chart of Extraction and Cleanup Using Florisil and Carbon/Foam Column Chromatography to Separate PCBs from Other Organochlorine Compounds in Sediment Samples	135
6-6	Chromatograms of PCBs Fractionated According to Number of *Ortho* Chlorines Using a Charcoal Column	137

MONS 005218

6-7 Elution Order of PCBs from Carbon Column, Illustrating Dependance on Number of *ortho* Chlorines 139

6-8 Enrichment and Fractionation of PCBs, PCNs, PCDDs, and PCDFs from Tissue Samples Using Carbon Column 142

6-9 Preparative Reversed-Phase HPLC Cleanup of Paperboard Extract 144

6-10 Preparative-Scale HPLC Fractionation of Oil 146

6-11 GPC Elution Profiles of Selected Biogenic Compounds and Environmental Contaminants 151

6-12 GPC Chromatograms of Fat Sample Showing the Separation of Low Molecular Weight Organic Chemicals (LMWO) from Lipids (Top) and Fractionation of LMWOs (Bottom) 152

6-13 PGC/ECD Chromatograms of Fish Extract (A) Before and (B) After Treatment with KOH and Chromium Trioxide to Degrade the *p,p'*-DDE (Peak 1) and *p,p'*-DDt (Peak 2) 160

6-14 HRGC/ECD Chromatograms Illustrating Interference by Sulfur in the Early Portion of Chromatogram A 165

7-1 Temperature-Programmed PGC/ECD Chromatogram of Arocior 1254 181

7-2 PGC/FID Chromatogram of PCBs and PCTs Using a Bonded Liquid Phase 183

7-3 HRGC/ECD Chromatogram of Arocior 1016, 1254, and 1260 (5:3:2, w/w/w) 184

7-4 HRGC/EIMS Reconstructed Full Scan Ion Chromatogram of PCBs and d_{10}-Anthracene (Internal Standard) 185

7-5 Retention Times of 77 PCB Congeners Relative to d_6-3, 3', 4, 4'-Tetrachlorobiphenyl (RRT of 1.00) 187

7-6 HRGC/ECD Chromatograms of Arociors 1242, 1254, and 1260 on a 0.29 mm ID × 20-m Apiezon L Column 189

7-7 Plot of HRGC Relative Retention Time Versus Congener Number for all 209 PCBs 193

7-8 Comparison of PGC/ECD (Top) and HRGC/ECD (Bottom) Chromatograms of 29 PCB Congeners 195

7-9 HRGC/ECD Chromatogram of Arocior 1260 Short Capillary Illustrating Rapid Separation 196

7-10 Detection Limits and Dynamic Range for Several Instrumental Methods 199

7-11 PGC/ECD Chromatograms of Arocior 1260 (921 pg, Solid Line) and Nine Common Pesticides (38 pg Each, Dashed Line) Illustrating the Potential for Interference 203

7-12 HRGC/ECD Chromatogram of Process Intermediate (Bottom) and Arocior 1248 (Top) 204

7-13	Plot of HRGC/ECD Relative Response Factor Versus Congener Number for All 209 PCBs	208
7-14	Reconstructed Ion Current Chromatogram of HRGC/EIMS Analysis of a Fish Sample from Chesapeake Bay	213
7-15	Extracted Ion Current Profiles for Tetra-Through Heptachlorobiphenyls in Fish Sample from Chesapeake Bay	214
7-16	Mass Spectrum of Hexachlorobiphenyl in Fish Sample from Chesapeake Bay	215
7-17	HRGC/EIMS Data for a Chlorinated Aromatic Waste Showing Presence of Octachlorobiphenyls as By-products	220
7-18	Plot of Average Response Factors Versus PCB Homolog	229
7-19	Comparison of HRGC/NCIMS and HRGC/EIMS (Bottom) Total Ion Current Profiles for a Fish Sample	235
7-20	HREIMS Spectrum of Fish Sample After Sulfuric Acid and Alumina Column Chromatographic Cleanups	237
7-21	PGC/ECD Chromatograms of Aroclor 1254 Before (Top) and After Perchlorination (Bottom)	241
7-22	TLC of Aroclors 1221 Through 1268 in Three Systems	245
7-23	Two Dimensional TLC of Aroclor 1254 and DDT Analogs on a Silver Nitrate-Impregnated Silica Gel Plate	246
7-24	HPLC Chromatogram of PCBs with UV Detection at Two Wavelengths (205 nm and 254 nm)	250
7-25	Reverse Phase HPLC/UV Separation of Aroclors 1221, 1016, and 1254 (1:1:1, w/w/w) in Tetrahydrofuran on a μBondapak C_{18} Column Monitored at 254 nm	251
7-26	High Resolution Reversed-Phase HPLC/UV Chromatogram of PCB Mixture Containing 48% Chlorine	252
7-27	Total Organic Halide (TOX) Analysis Using a Short Column PGC/HECD	261
7-28	TOCl Measurements of Aroclor 1248 Using Electrolytic Conductivity	262
8-1	Principal Components Plot of PCB Data	274
8-2	PGC/ECD Chromatogram of Aroclor 1254	285
8-3	Flow Chart for Division of PGC/ECD Chromatograms Into Retention Time Regions for Quantitation of Samples With Mixed Aroclor Patterns	286
9-1	Quality Control Chart for HRGC/ECD Analysis of PCBs and Other Organochlorine Compounds in Human Milk	316

List of Figures xv

10-1	Paired Sample (Youden) Plot for Two Wet Sediment Samples	328
10-2	Histogram of Error Contribution by Homologs for Sample A from CMA Study	332
10-3	Analysis Flow Scheme for By-product Collaborative Study, Showing Sample Entry Points	334
10-4	Plot of Error in By-product Collaborative Study by Sample Type, Showing Contributions of the Analysis Steps	335

MONS 005221

PREFACE

This book is a comprehensive review of the analytical chemistry of polychlorinated biphenyls (PCBs). It is part history, part annotated bibliography, part comparison and part guidance. It is *not*, however, a cookbook for the neophyte. There are no written step-by-step procedures for the analysis of given matrices for PCBs; the field is much too complex to recommend a finite set of analytical procedures. Chemists with no experience in PCB analysis should benefit greatly from this book by gaining an appreciation for the analytical complexity and reviewing possible approaches to analytical problem. Experienced analysts may find some guidance on possible improvements to their current practices.

This project grew out of a literature review that I conducted along with a colleague, John Stanley, in 1982 for the Office of Toxic Substances of the U.S. Environmental Protection Agency (Erickson and Stanley, 1982). All of the material from that review has been substantially revised, updated, and augmented. In addition the size of the bibliography has more than doubled.

The references in the bibliography were obtained by multiple computer and manual searches of the published literature and from personal contacts. Every effort has been made to be comprehensive and current in the coverage of articles pertaining to analysis. Nevertheless, I am quite sure that there are some omissions. I apologize in advance to those authors whose work may have been slighted and request that they send a reprint so that any subsequent editions can be properly updated. No attempt was made to be comprehensive on the ancillary subjects (environmental occurrence, toxicology, etc.) presented in Chapter 2.

The book contains ten chapters. Following an introductory chapter, Chapter 2 reviews the physical, chemical, commercial, environmental, and biological properties of PCBs. While these areas are not all central to analytical concerns, they provide relevant data and a perspective on the properties of PCBs which make them of such great interest to analysts. Chapter 3 discusses the available written procedures (standard methods, etc.) which may be used directly by analysts. For those desiring more detail or where no written procedure exists, the next six chapters discuss the discrete steps of analysis: sampling, extraction, cleanup, determination, data reduction, and quality assurance. Chapter 10 discusses collaborative testing, which is the ultimate step in a method validation.

MONS 005222

A bibliography is presented. All references in the text are in the bibliography; however, not all entries in the bibliography are discussed in the text. The sheer volume of data overwhelms any attempt to adequately discuss all of the references. In addition, many references are redundant or outdated. The additional references in the bibliography may help those who need details in a specific area. Where appropriate, secondary citations to *Chemical Abstract* have been included to assist those interested in obtaining the reference. The reference callouts in the text use the date of the original citation, not that of the secondary citation. Five appendices present ancillary material on PCB nomenclature and physical properties, composition of commercial mixtures, mass spectra characteristics, and PGC/ECD chromatograms. The final appendix (E) is a glossary of the specialized terms and abbreviations used throughout this book.

As noted repeatedly throughout this book, the analytical chemistry of PCBs is an evolving science or, in some cases, an evolving art. Much research still needs to be done to supply methods for the routine analysis of all of the sample matrices in which PCBs may occur. Many of the current methods suffer from lack of precision or accuracy, or they do not provide the proper qualitative information. This book should bring the discipline into better focus and permit analysts to move forward with development of need methods.

Mitchell D. Erickson
Midwest Research Institute
Kansas City, Missouri

MONS 005223

ACKNOWLEDGMENTS

I wish to thank many colleagues who provided encouragement and reviewed the book during its gestation. They devoted a great deal of time and thought to their reviews and supplied several references to augment certain sections and tables. I also received reviews of individual chapters from John Craddock, John Going, Daniel Heggem, John Hosenfeld, and John Stanley.

I have received encouragement on this project from Midwest Research Institute's management, particularly John Going. The editorial staff at Butterworths, has been most helpful in providing assistance and encouragement. Some of the data were tabulated and proofread by Leslie Moody, Jon Onstot, Audrey Sanford, Steve Turner, and P. J. Boone. Technical assistance was provided by the Midwest Research Institute Office Services Department, notably the Word Processing Center consisting of Kathy Funk, Cindy Melenson, Lanora Moore, Susie Powell, Carol Shaw, and especially Gloria Sultanik.

I would like to thank my family and friends, especially my wife Colleen and my son Adam, for their forbearance over the past two years. They lost many weekends to this project.

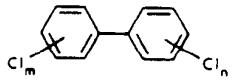
To all of you who helped me make this book a reality, thanks!

MONS 005224

1

INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of 209 discrete chemical compounds, called congeners, in which one to ten chlorine atoms are attached to biphenyl.



m + n = 1 to 10

Polychlorinated biphenyls (PCBs) were commercially produced as complex mixtures for a variety of uses, including dielectric fluids in capacitors and transformers. The major producer, Monsanto Corporation, marketed PCBs under the trade name Aroclor® from 1930 to 1977. Aroclors® were marketed for use in transformers, capacitors, printing inks, paints, dedusting agents, pesticides, and many other applications (Durfee et al., 1976). Their chemical and physical stability and their electrical insulating properites led to the commercial utility of PCBs. The production and use of PCBs is discussed in detail in Chapter 2.

Their chemical and physical stability has also been responsible for the PCB environmental contamination problem. Since PCBs do not readily degrade in the environment after disposal or dissemination and are lipophilic, they are persistent and tend to bioaccumulate. In 1966, Jensen (Anon., 1966; Jensen et al., 1969; Jensen, 1972; Hutzinger et al., 1974a) reported PCBs in eagles, herring, and other Swedish environmental samples. Since then, PCBs have been shown to be nearly ubiquitous environmental pollutants, occurring in most human and animal adipose samples, milk, sediment, and numerous other matrices.

MONS 005225

As early as 1936, occupational exposure was reported to cause toxic effects and workplace threshold limit values were subsequently set. Animal studies with both commercial mixtures and individual congeners have shown a variety of chronic toxic effects (National Research Council, 1979). PCB-contaminated cooking oil caused a total of 1,291 "Yusho" patients in 1968 in western Japan. The clinical manifestations include various somatic complaints, low birth weights, chloracne, and pigmentation (Kuratsune, 1972; Higuchi, 1976). The animal toxicological data have tended to indicate that PCBs are toxic. However, contamination of the commercial PCB mixtures with more toxic compounds such as polychlorinated dibenzofurans (PCDFs) confounds the toxicological data. For example, it is unclear whether the PCBs or other contaminants in the Yusho oil are responsible for the observed health effects. In addition, it has been shown that the toxicity of PCBs varies with both homolog and isomer (Safe et al., 1983e). Thus, the toxicology of PCBs remains an area of controversy and continued research.

The discovery of the widespread environmental occurrence, the increased general environmental concern, and the apparent link to carcinogenesis prompted a public outcry which culminated in the United States in 1976 with the regulation of PCBs by the Toxic Substances Control Act (TSCA), PL 94-469 (U.S. Congress, 1976). Section 6(e) of TSCA specifically regulates manufacture, processing, distribution in commerce, or use of PCBs. The U.S. Environmental Protection Agency (EPA) was charged with rule promulgation and enforcement. The EPA was also given latitude to grant exemptions to the ban if the manufacture, processing, distribution in commerce, or use is totally enclosed or will not present an unreasonable risk of injury to health or the environment. The EPA subsequently promulgated a series of rules on the various aspects of the law.

Several EPA rules are of concern to analytical chemists, since they require determination of PCBs in various matrices. A rule promulgated on May 31, 1979 (EPA, 1979d; Velie and Kuntz, 1982; EPA, 1983d) categorized the use, concentration, and type (liquid or nonliquid) of PCBs. Portions of this rule were declared invalid by a U.S. Court of Appeals and several rules have since been issued to satisfy the court-ordered changes. Certain totally enclosed electrical uses of PCBs are allowed for the remainder of the useful life of existing equipment (EPA, 1982f; Department of Transportation, 1984). In 1982, a rule on use in closed and controlled manufacturing processes was promulgated (EPA, 1982c; Velie and Kuntz, 1982; EPA, 1983d). The rule excludes PCBs in products or wastes below the practical limit of quantitation

MONS 005226

(LOQ) from the TSCA ban on manufacture, processing, distribution in commerce, and use; i.e., PCBs below the LOQ are not regulated. The practical LOQ was defined as 10 µg/m³ per resolvable gas chromatographic peak for air, 100 µg/L per resolvable gas chromatographic peak for water, and 2 µg/g per resolvable gas chromatographic peak for any product or waste. It should be noted that these defined LOQs are much higher than those obtainable with state-of-the-art instrumentation and with low levels of interferences. In this rule, the EPA recommended high resolution (capillary) gas chromatography/electron impact mass spectrometry (HRGC/ EIMS) as the analytical technique and supplied suggested methods for the three matrices (Erickson et al., 1982). The EPA also recognized that the PCB composition as by-products would not resemble that of commercial products such as Aroclors and cautioned against the use of classic Aroclor-based analyses methods. TSCA and the PCB rules promulgated under it were reviewed recently (Dyer, 1981; Trench, 1981; Cairns and Siegmund, 1981b, Velie and Kuntz, 1982; Department of Transportation, 1984).

Disposal has been a major area of concern since the restriction of PCB use in the United States and other countries. Large quantities of PCB-containing products such as transformer oils and capacitors are being removed from service and must be disposed of properly. In the United States (EPA, 1979d), the allowed methods of disposal are keyed both to concentration and to the matrix. If the PCB concentration is 500 ppm or greater, disposal in a high efficiency incinerator is stipulated. If the concentration is 50 to 500 ppm and the PCBs are in a liquid matrix such as a mineral oil dielectric fluid, then incinerators, landfills, or high efficiency boilers can be used. In addition, alternate methods of disposal are allowed if they can be shown to be equivalent. To demonstrate compliance, incinerators must pass an initial test which, among other things, requires that air emissions be ≤ 1 mg PCB/kg PCB introduced for nonliquid PCBs. A full listing of current U.S. EPA rules on PCBs may be obtained in the current annual edition of the Code of Federal Regulations, 40 CFR 761 (EPA 1983d or current update).

While PCB regulations and disposal requirements differ from country to country, there is a common analytical interest in determining their presence in the environment and in potential sources to the environment. Regardless of the laws and rules, the analytical needs are similar: reliable, practical, sensitive methods which can determine PCBs--commercial mixtures, by-products, and destruction residues--in a variety of matrices.

MONS 005227

This book reviews the publications related to PCB analysis. Some of the older methods may be merely of historical interest, but are included for completeness and to provide the reader with a record of what techniques have been used for specific applications. In addition and more importantly, state-of-the-art methods are discussed and their relevance to various applications presented. The analyst moving into PCB analysis for the first time or encountering a new PCB-related problem will find the discussions helpful in choosing or designing appropriate methods.

MONS 005228

2

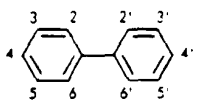
PHYSICAL, CHEMICAL, COMMERCIAL, ENVIRONMENTAL, AND BIOLOGICAL PROPERTIES

I. INTRODUCTION

This chapter presents brief overviews of PCB nomenclature, physical and chemical properties, synthesis, commercial production and use, toxicology, metabolism, degradation and destruction, environmental occurrence, environmental fate and transport, and occupational exposure of PCBs. The treatment of these subjects is not intended to be comprehensive but rather to provide sufficient information to give the reader a perspective of the PCB problems which have lead to the analysis of various samples. Where possible, monographs and review articles have been cited to guide the reader with more than a casual interest in a topical area.

II. PCB NOMENCLATURE

For the purposes of this book, a PCB is one of 209 compounds having the formula $C_{12}H_{(10-n)}Cl_n$, where n = 1-10; i.e., monochlorobiphenyl through decachlorobiphenyl (Table A-1, see Appendix A), with the general structure:



The term "PCB" is used to refer to the entire class or any subset of one or more compounds. I recognize that, strictly speaking, "mono" is not "poly;" however, the three monochlorobiphenyls have been included in this book since they are members of the chemical class, colloquial usage usually includes them, and U.S. court rulings (Perlman, 1980; McCallum, 1982) have declared them to be PCBs for EPA enforcement purposes. Biphenyl is not counted as a PCB, although some investigators have used it as a degenerate member of the set

MONS 005229

for chromatographic retention behavior and other studies (see, for example, Albro et al., 1977). Biphenyl is included in some physical and chemical property tables in this work for completeness.

PCBs are listed in Chemical Abstracts under "1,1'-biphenyl, chloro derivs." with a generic CAS registry number of 1336-36-3. However, this CAS number does not yield many citations in a computerized literature search. Apparently it is not widely used. CAS No. 12767-79-2 is assigned to "Aroclor" and may be useful in generic PCB literature searches. The synonyms listed by Chemical Abstracts are biphenyl, chlorinated; chlorinated diphenyl; and diphenyl, chlorinated.

The entire set of 209 PCBs forms a set of congeners (Table 2-I). When PCBs are subdivided by degree of chlorination, the term homolog is used; e.g., the trichlorobiphenyl homolog. PCBs of a given homolog with different chlorine substitution position are called isomers (Table 2-II, Figure 2-1). 2,3,4-Trichlorobiphenyl and 3,3',5-trichlorobiphenyl are two of the twelve trichlorobiphenyl isomers.

Many researchers have found the full chemical names unwieldy and have adopted various shorthand nomenclatures. For instance, 3,3',4,4',5,5'-hexachlorobiphenyl has been referred to as 3,3',4,4',5,5'-hexa or simply 3,3'4,4',5,5'. Recently Ballschmiter and Zell (1980) arranged the 209 congeners in ascending numeric order and assigned what are commonly termed "Ballschmiter" or "IUPAC" numbers from 1 to 209, as shown in Table A-I. A minor discrepancy was corrected by Schulte and Malisch (1983) and has been incorporated into Table A-1. This shorthand nomenclature has become increasingly popular and is convenient for many uses such as labeling chromatograms. An alternate shorthand numbering system, using base 16, can designate each PCB congener by a three digit number (Zitko, 1983).

Table 2-I. PCB Nomenclature Categories

Category	Number of Individual Compounds[a]
Congener	209
Homolog	10
Isomers/Homolog	1-46

a Natural isotopic abundance only.

MUNS 005230

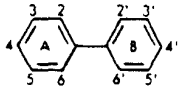
Table 2-II. Composition of Chlorinated Biphenyls by Homolog

Empirical Formula Chloro-biphenyls	Molecular Weight[a]	Average Molecular Weight[b]	Percent Chlorine	No. of Isomers
$C_{12}H_{10}$	154.1	154.2	0	1
$C_{12}H_9Cl$	188.0	188.7	19	3
$C_{12}H_8Cl_2$	222.0	223.1	32	12
$C_{12}H_7Cl_3$	256.0	257.6	41	24
$C_{12}H_6Cl_4$	289.9	292.0	49	42
$C_{12}H_5Cl_5$	323.9	326.4	54	46
$C_{12}H_4Cl_6$	357.8	360.9		42
$C_{12}H_3Cl_7$	391.8	395.3	63	24
$C_{12}H_2Cl_8$	425.8	429.8	66	12
$C_{12}HCl_9$	459.7	464.2	69	3
$C_{12}Cl_{10}$	493.7	498.7	71	1

a Based on ^{35}Cl (atomic weight 34.969) and ^{12}C (atomic weight 12.000) and ^{1}H (atomic weight 1.0079). Corresponds to the lowest mass in the molecular cluster of the mass spectrum.

b "Average" molecular weight; based on natural abundance chlorine (atomic weight 35.453), carbon (atomic weight 12.011) and hydrogen (atomic weight 1.0088).

MONS 005231

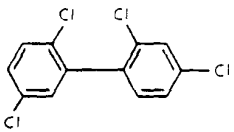


Chlorine Atoms on Ring B	Chlorine Atoms on Ring A: 0	1	2	3	4	5
0	1	3	6	6	3	1
1		6	18	18	9	3
2			21	36	18	6
3				21	18	6
4					6	3
5						1

Figure 2-1. Distribution of Chlorine Atoms in the Two Rings of Biphenyl

Reprinted with permission from Hutzinger et al. (1974a), copyright 1974, CRC Press, Inc., Boca Raton, Florida.

As with any complex, symmetric molecule, several nomenclatures may be employed for the same structure. The molecule shown here would be correctly identified as the



2,2',4,5' congener, with alternate but less correct designations of 2,4,2',5'; 2,2',4',5; 2,3',4,6'; 2',3,4',6; etc. Another example is Ballschmiter congener No. 98, designated 2,2',3',4,6; which is listed by Chemical Abstracts as 2,2',3,4',6' The reader should convince himself that these are in fact the same compound and be wary of these types of redundancies.

The complex commercial mixtures marketed as PCBs (see "Commercial Production," below) have often been treated as a single chemical entity. Repeatedly, authors have used the term "PCB" to refer specifically to the commercial mixtures (e.g., Aroclors) rather than the entire compound class. The reader must develop an awareness of the difference and an appreciation of the significance. For instance, many PCB analytical methods focus on only one or more of the commercial PCB mixtures and could neither detect nor quantitate all PCBs.

III. PHYSICAL PROPERTIES

The physical properties of PCBs are important to an understanding their analytical properties as well as their physiological and environmental properties. The interactions of the various physical properties and their relevance to specific applications can be extremely complex and are not well defined. Many of the references cited in the sections below use physical properties to derive bioconcentration factors (Mackay, 1982b), environmental transport and data (Mackay, 1982a), aqueous movement (Yalkowsky et al., 1980), and environmental persistence (Neely, 1983).

A. Molecular Weights

Table 2-II lists the molecular weight, and percent chlorine for the PCB homologs. Two values of the molecular

weight are presented based on the atomic weight of the most common isotopes (^{12}C, ^{35}Cl, and ^{1}H) and on the average atomic weight of the natural abundance ratios of the different isotopes. The former corresponds to the lowest mass in the molecular cluster of the mass spectrum. The latter is the average molecular weight. The exact masses and relative abundances of the major components of the molecular cluster are listed in Table C-1.

8. Physical Constants

Table A-I in Appendix A presents the CAS registry number for all 209 PCB congeners, and the available melting point, and aqueous solubility data. The physical and electrical properties of the commercial mixtures are discussed in the "Production and Use" section below. There is growing evidence that the subcooled liquid properties of organic chemicals control some environmental partitioning processes (Mackay, 1982b; Mackay et al., 1982). Thus, melting point data are important in calculating various environmental properties of PCBs. Table 2-III presents the boiling points, vapor pressures and octanol-water partition coefficients (log K_{ow}) for several PCBs. The boiling point and vapor pressure data from Neely (1983), Weast and Selby (1967), Cook (1972), Leifer et al. (1983), Bidleman et al. (1983), and Bidleman (1984) may not be comparable since different experimental techniques were used in the determinations. Bidleman et al (1983), for example, compared vapor pressures determined by gas saturation, gas chromatography, and from the literature. While most values were in reasonable agreement, some of their determinations differ by more than a factor of two. As can be seen in Table 2-III, the boiling points and vapor pressures vary not only with the degree of chlorination, but also with the position of substitution. This is manifested in the gas chromatographic elution orders, as discussed in Chapter 7. The vapor pressures of Aroclor 1232, 1242, 1248, and 1254 were discussed by Bopp (1983). Additional data on vapor pressures (Westcott and Bidleman, 1981) and boiling points (Augood et al., 1953) of individual PCB congeners has been published.

The log K_{ow} and water solubility data (Table A-I) are useful in estimating transport and fate through the environment (Mackay, 1982b), as well as analytical properties. Mackay (1982b) has published the octanol-water partition coefficients for Aroclor 1016, 1248, 1254, and 1260. Additional work on aqueous solubility (Mackay et al., 1980, Stolzenburg and Andren, 1983; Leifer et al., 1983; Yalkowsky et al., 1983) and partitioning (Voice et al., 1983; Shaw and

Table 2-III. Boiling Points, Vapor Pressures, and Octanol-Water Partition Coefficients (K_{ow}), of Selected PCB Congeners

IUPAC No.	Compound	Boiling Point (°C) (mm Hg)[a,b]	Vapor Pressure (mm Hg, 25°C)[a]	Log K_{ow}[c]
-	Biphenyl	255	9.5×10^{-3}	4.10
1	2	274	8.4×10^{-3}	4.56
2	3	284-5[d]	1.5×10^{-3}[e]	4.72
3	4	291	4.6×10^{-3}	4.69
4	2,2'		1×10^{-3}	5.02
5	2,3	172 (30)[f]		
7	2,4		1.8×10^{-3}[e]	5.15
8	2,4'			< 5.32[g]
9	2,5	171 (15)[f]	1.4×10^{-3}[e]	5.18
11	3,3'	322-4[f]	6.8×10^{-4}[e]	5.34
12	3,4	195-200 (15)[f]		
14	3,5	166 (10)[f]		
15	4,4'	315-9[d]	1.9×10^{-5}	5.28
18	2,2',5		9×10^{-6}	5.64
33	2',3,4		7.7×10^{-5}[h]	6.1[g]
28	2,4,4'			5.74
29	2,4,5		3.3×10^{-4}[e]	5.77
30	2,4,6		8.8×10^{-4}[e]	
31	2,4',5		3.0×10^{-4}[e]	5.77
37	3,4,4'			5.90
40	2,2',3,3'		7.3×10^{-5}[e]	6.67[g]
44	2,2',3,5'			6.67[g]
47	2,2',4,4'		8.6×10^{-5}	6.44[g]
52	2,2',5,5'		3.7×10^{-5}	6.26
53	2,2',5,6'		2.1×10^{-4}[e]	
54	2,2',6,6'			5.94
61	2,3,4,5			6.39
66	2,3',4,4'		4.6×10^{-5}[e]	6.67[g]
70	2,3',4',5		4.4×10^{-6}[e]	6.39
77	3,3',4,4'		2.3×10^{-6}[i]	6.52
80	3,3',5,5'			6.58
86	2,2',3,4,5		5.8×10^{-7}[i]	6.38[g]
87	2,2',3,4,5'		1.6×10^{-5}[e]	6.85
88	2,2',3,4,6			7.51[g]
99	2,2',4,4',5		2.1×10^{-5}[e]	
101	2,2',4,5,5'		9.0×10^{-6}	6.85
105	2,3,3',4,4'		6.8×10^{-6}[e]	
116	2,3,4,5,6			6.85

MONS 005235

Table 2-III (continued)

IUPAC No.	Compound	Boiling Point (°C) (mm Hg)[a,b]	Vapor Pressure (mm Hg, 25°C)[a]	Log K_{ow}[c]
118	2,3',4,4',5	195-220 (10)[f]	9.0×10^{-6}[e]	
128	2,2',3,3',4,4'		2.6×10^{-6}[e]	7.44
129	2,2',3,3',4,5			9.26[g]
134	2,2',3,3',5,6			9.18[g]
138	2,2',3,4,4',5'		4.0×10^{-6}[e]	
149	2,2',3,4',5',6		1.1×10^{-5}[e]	
153	2,2',4,4',5,5'		5.2×10^{-6}[e]	7.44
155	2,2',4,4',6,6'		1.3×10^{-5}	7.12
156	2,3,3',4,4',5		1.6×10^{-6}[e]	
170	2,2',3,3',4,4',5		6.3×10^{-7}[e]	
171	2,2',3,3',4,4',6		1.8×10^{-6}[e]	
180	2,2',3,4,4',5,5'	240-280 (20)[f]	9.7×10^{-7}	
185	2,2',3,4,5,5',6			7.93
187	2,2',3,4',5,5',6		2.3×10^{-6}[e]	
194	2,2',3,3',4,4',5,5'			8.68
202	2,2',3,3',5,5',6,6'			8.42
206	2,2',3,3',4,4',5,5',6			9.14
209	Decachlorobiphenyl			9.60

a Neely (1983), unless otherwise noted.
b Values in parentheses indicate pressure of measurement if different from 760 mm Hg.
c All log K_{ow} values from Bruggenman et al. (1982), unless otherwise noted.
d Weast and Selby, 1967.
e Bidleman, 1984. Values presented here are averages of two experimental values in original publication.
f Cook, 1972.
g Yalkowsky et al., 1983.
h Bidleman et al., 1983.
i Calculated by Neely (1983).

MONS 005236

Connell, 1984; Rapaport and Eisenreich, 1984; Leifer et al., 1983; Yalkowsky et al., 1983; NTIS, 1984a) has been reported.

Considerable work has been done on measuring and calculating the gas-phase physical constants, especially the Henry's Law constants and fugacities (Mackay et al., 1980, 1983; Mackay, 1982a, 1982b; Murphy et al., 1983; Leifer et al., 1983; Bapp, 1983; Mackay and Hughes, 1984). The Henry's Law constant is a measure of the equilibrium distribution coefficient between air and water (or other gas and liquid). Fugacity is a quantitative measure of the escaping tendancy of a substance and is the driving force that causes diffusion and partitioning between phases (environmental compartments). The fugacity in the gas phase is simply the vapor pressure. In the liquid phase, fugacity is the product of the Henry's Law constant and the concentration in solution.

C. Electrochemical Properties

The electrochemical properties of PCBs have not been well studied. Since PCBs are very stable molecules, determining their oxidation/reduction potential is difficult. However, many of the commercial destruction methods, some metabolic pathways and other routes of degradation, occur via free radical mechanisms. Thus, their electrochemical properties can be important. A limited study gave the standard potentials and electron transfer routes of four PCB congeners (Conners et al., 1985).

D. Ultraviolet and Fluorescence Spectra

The UV spectral properties of PCBs are of use not only for HPLC analysis with UV detection, but also for identification of synthetic products. The UV spectral properties of PCBs were reviewed by Hutzinger et al. (1974a). More recently, additional data on individual congeners (IARC, 1978; Appleby, 1976; Brinkman et al., 1976b) and Aroclor mixtures (Brinkman et al., 1976a) have been published.

The excitaton, fluorescence, and room temperature phosphorescence maxima for six congeners have been reported (Weinberger et al., 1983). The fluorescence spectra of seven congeners in cyclodextrin have been reported (Femia et al., 1985).

E. Infrared Spectra

The IR spectral properties of PCBs were reviewed (Hutzinger et al., 1974a). A major component of that review was based on the work of Webb and McCall (1972). Recently,

the diffuse reflectance IR spectra of 16 PCB congeners were published (Nyquist et al., 1983). In addition to the spectra, the group frequencies were assigned and correlations presented which should be of use in the identification of other PCB congeners.

F. Nuclear Magnetic Resonance (NMR) Spectra

Hutzinger et al. (1974a) presented an extensive review with 22 references of the proton NMR data on PCBs. Data on 17 synthetic congeners, the major components of Aroclor 1254, and other data were tabulated. Both the ^{13}C and ^{1}H NMR spectra of 10 symmetric PCB congeners were investigated by Wilson and Anderson (1973). The relationship of structure to shielding and coupling constants were discussed. As part of a program to synthesize all 209 congeners, the proton NMR spectral features were reported for all tetra-, penta-, hexa-, and heptachlorobiphenyls (Mullin et al., 1984) and for all octa- and nonachlorobiphenyls (Mullin et al., 1981).

IV. SYNTHESIS AND STANDARDS

The commercial PCB mixtures were synthesized by chlorination of biphenyl with chlorine gas (NRC, 1979; Durfee et al., 1976). Commercial production is discussed in the following section. Small quantities (10 to 1,000 mg or dilute solutions) of Aroclors are available for use in scientific studies from Analabs, North Haven, Connecticut; Ultra Scientific, Hope, Rhode Island; and other suppliers.

Routes for synthesis of specific congeners have been reviewed (Hutzinger et al., 1974a; Roth et al., 1982; Mullin et al., 1981, 1984). Recently, 3,3',4,4'-tetrachlorobiphenyl was synthesized in gram quantities (Nakatsu et al., 1982). Although all 209 congeners have been synthesized recently (Mullin et al., 1984), only about 80 are commercially available from Ultra Scientific, Hope, Rhode Island, and Analabs, North Haven, Connecticut, in small quantities (5 to 50 mg or 100-ppm solutions).

Various isotopically labeled PCBs have been synthesized. ^{36}Cl-Labeled (β-emitter) Aroclors 1248 and 1254 were prepared by neutron irradiation of the natural abundance materials (Stalling and Huckins, 1971). A universally-^{14}C-labeled PCB mixture with 54% chlorine (i.e., Aroclor 1254) has been available from New England Nuclear (Kohli et al., 1979a). Chlorination of ^{14}C-labeled biphenyl to 54% chlorine content was reported by Albro et al. (1984). Tritiation of Aroclor 1254 to yield an Aroclor 1248-like mixture was also

reported by Albro et al. (1984). Several ^{14}C-labeled individual congeners have been used in PCB studies. For instance, ^{14}C-2,2',5,5'-tetrachlorobiphenyl and ^{14}C-2,2',4,4',5,5'-hexachlorobiphenyl were used in determining the tissue distribution in trout and mice (Vodicnik, 1983). ^{14}C-2,2',4,4',5,5'-hexachlorobiphenyl has also been used to study sorption from water to glass surfaces (Pepe and Byrne, 1980; Muldrew et al., 1981) and was obtained from California Bionuclear Corp. d_6-3,3',4,4'-Tetrachlorobiphenyl has been available from ICN-KOR Isotopes, Cambridge, Massachusetts, and MSD Isotopes, Pointe Claire-Dorval, Quebec, Canada. $^{13}C_6$-4-Chlorobiphenyl, $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl, $^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl, and $^{13}C_{12}$-decachlorobiphenyl were synthesized by Roth et al. (1982) and are available as a mixed solution from Quality Assurance Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, and also from Chemsyn Science Laboratories, Lenexa, Kansas.

Standard reference materials, usually a solution of an Aroclor, are available. These SRMs are discussed in Chapter 9 (see Table 9-III).

V. PRODUCTION AND USE

A. Aroclor and Related Mixtures

PCBs were commercially produced as complex mixtures beginning in 1929. They are not known to occur naturally. Most producers throughout the world reduced or stopped production in the 1970s (Brinkman and DeKok, 1980), although some production continued through at least 1983 (personal communication, G. Kuntz, USEPA, Washington, DC, December 1983). Production by Monsanto, the major world manufacturer, ceased in 1977. All of the commercial mixtures were synthesized by direct chlorination of biphenyl with chlorine gas. The average degree of chlorination was controlled by the reaction conditions to yield the desired physical and chemical properties. The total worldwide production through 1976 is estimated at about 6.1×10^{11} g (1.3 billion pounds; Durfee et al., 1976), of which about 5.7×10^{11} g (93%, 1.25 billion pounds) were produced by Monsanto in the United States. The total production of PCBs through 1980 is estimated to be about 1.1×10^{12} g (2.4 billion lb; unpublished OECD estimate, J. D. Bletchly, PCB Seminar, The Hague, Netherlands, September 1983). The Monsanto PCB mixtures were sold under the registered trade-mark of Aroclor®. The Aroclor (the trademark designation is not used throughout this book) trade-name designated a variety of polychlorinated aromatic

MONS 005239

mixtures, not just PCBs. For instance, Aroclor 5460 is a complex mixture of polychlorinated terphenyls. Additional information has been presented in a review by Brinkman and deKok (1980).

Commercial PCB mixtures were used in a wide variety of applications, including dielectric fluids in capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating and cutting oils, and as additives in pesticides, paints, copying paper, carbonless copy ("NCR") paper, adhesives, sealants, and plastics. In 1974, capacitor manufacture (10×10^9 g) and transformer manufacture (5×10^9 g) accounted for all of the PCBs sold by Monsanto. An additional 1.8×10^8 g used in investment casting and 2.2×10^7 g used in specialized heat transfer systems (totaling 1% of U.S. sales) were imported. The PCB used in investment casting, unlike the other commercial PCBs, was decachlorobiphenyl (Durfee et al., 1976).

As reviewed by WHO (1976), an Organization for Economic Cooperation and Development report (1973) divided PCB use into three categories:

> Controllable closed systems. PCBs used as dielectrics in transformers and large capacitors have a life equal to that of the equipment, and with proper design leakage does not occur. When the equipment is scrapped the quantity of dielectric is sufficiently large to justify regeneration.
>
> Uncontrollable closed systems. PCBs are used in heat transfer and hydraulic systems which, although technically closed, permit leakage. The need for frequent replacement of small quantities makes recovery impractical. PCBs are very widely dispersed in small capacitors, and there are great difficulties in collecting these items for disposal.
>
> Dissipative uses. PCBs have been used in the formulation of lubricating and cutting oils, in pesticides, and as plasticizers in paints, copying paper, adhesives, sealants, and plastics. In these applications, the PCBs are in direct contact with the environment, and there is no way of recovering them when the product is scrapped. (OECD, 1973; WHO, 1976)

It should be noted that one uncontrollable closed system, old fluorescent light ballasts, continues to put PCBs in close contact with humans. When they fail, high indoor air concentration have been observed (MacLeod, 1979).

MONS 005240

Since the vast majority of PCBs of concern to analytical chemists are derived from the commercial sources, the general composition and characteristics of these mixtures are relevant. Table 2-IV presents a comparison of the commercial PCBs. The approximate compositions of Aroclors by homolog are presented in Table 2-V. The composition has been shown to vary from batch to batch and according to the analytical procedure. As can be seen in Table 2-IV, with the exception of 1016, the last two digits of the Aroclor series number correspond to the percent chlorine. A more detailed list of physicochemical properties of the Aroclor mixtures is presented in Table 2-VI (Brinkman and DeKok, 1980). Similar tables are in the literature (Hubbard, 1964; Hutzinger et al., 1974a; Durfee et al., 1976; NIOSH, 1977c; NRC, 1979; Hutzinger and Roof, 1980a). Some of these contain other properties of the commercial mixtures.

A common PCB-containing product class used in transformers and capacitors is askarel. The capacitor askarels include neat Aroclor 1242, 1254, and 1016 and a mixture of 75% Aroclor 1254 and 25% trichlorobenzene. The most common transformer askarels were 60% Aroclor 1260/40% trichlorobenzene (Type A) and 70% Aroclor 1254/30% trichlorobenzene (Type O). The transformer askarels contain other minor components used as free radical scavengers. The ASTM (1978a,b) published standard specifications for askarels.

PCB production and use has been thoroughly reviewed by several authors (Sarofim, 1972; OECD, 1973; Hutzinger et al., 1974a; Durfee et al., 1976; WHO, 1976; IARC, 1978; NRC, 1979; OECD, 1979; Brinkman and DeKok, 1980; Miller, 1982).

B. Impurities in Commercial Mixtures

The impurities in the commercial PCBs are reportedly < 0.01% (NRC, 1979), although Table 2-V indicates that, in some cases, biphenyl can be present at well over 1% levels. The presence of polychlorodibenzofurans (PCDFs) has been documented (Table 2-VII) at the microgram per gram level and may account for some of the toxicological properties attributed to the commercial PCB mixtures (NRC, 1979). PCDFs, polymeric adducts such as polychloroquaterphenyls (PCQs), and other impurities may form during use and handling. The presence and levels of impurities are thought to vary widely from batch to batch. The subject of impurities in the commercial PCBs is presented in more detail (Zitko and Choi, 1971; Anon., 1972; Nagayama et al., 1975; Bowes et al., 1975a, 1975b; Miyata and Kashimoto, 1976; NIOSH, 1977c; Morita et al., 1977; Buser, 1978; Kamps et al., 1978; Buser et al., 1978a; IARC, 1978; OECD, 1979; NRC, 1979; Brinkman and DeKok, 1980; Vuceta et al., 1983; Cull and Dobbs, 1984).

MONS 005241

Table 2-IV Comparison of Commercial PCB Mixtures

Trade Names								
Aroclor[a]	Clophen[b]	Phenoclor[c]	Pyralene[c]	Kanechlor[d]	Fenclor[e]	Av. No. Cl/ Molecule	Approx. Wt.% Cl	Approx. "Mol. Wt."
1221						1.15	21	193.7
1232			2,000	200		2	32-33	223.0
			1,500			2.5	38	240.3
1242, 1016	A30	DP1	3,000	300	42	3	40-42	257.5
1248	A40	DP4		400		4	48	291.9
1254	A50	DP5		500	54	5	52-54	326.4
1260	A60	DP6		600	64[f]	6-6.3	60	366.0
1262						6.8	62	388.4
					70[f]	7.7	65	419.4
1268						8.7	68	453.8
1270						9.5	70	481.4
					DK	10	71	498.6

a Monsanto Industrial Chemicals Company, USA.
b Bayer, GFR.
c Caffaro, Italy
d Kanegafuchi Chemical Company, Japan.
e Prodelec, France
f The two-digit number should indicate the wt.% Cl; however, this does not fit in with the manufacturer's specifications

Source: Brinkman and DeRok, 1980. Reproduced with permission, copyright 1980, Elsevier Biomedical Press BV

MONS 005242

Table 2-V. Average Molecular Composition (wt.%) of Some Aroclors

Homolog (Chlorines)	Aroclor						
	1221	1232[a]	1016	1242	1248	1254	1260
0	10						
1	50	26	2	1			
2	35	29	19	13	1		
3	4	24	57	45	2	1	
4	1	15	22	31	49	15	
5				10	27	53	12
6					2	26	42
7						4	38
8							7
9							1

a Five percent unidentified (biphenyl?).
Source: Brinkman and DeKok, 1980. Reproduced with permission, copyright 1980, Elsevier Biomedical Press BV.

MONS 005243

Table 7.VI Characteristics of Aromatic Mixtures

Aromatic	Density (g/cm³) at 20°C	Viscosity (Centipoise) (Abso lute) at 40 °C	n_D^{20}	Flash Point (°C)	Fire Point (°C)	Pour Point (°C)	Distillation Range (°C)	Vapour pressure mm Hg (g/cm² Pa) x 10^{-2} at 25°C	Dielectric Const at 20°C	Dielectric Const at 100°C	Solubility in water at 25°C (ppm)	CAS Registry No.[b]
1771	1.16	10.11	1.518	153-158	176	5	275-278	1.74n				11144-78-2
1772	1.26	11.17	1.521	152-154	230	15	278-325	n/a	5.7	4.6		51151-36-5
1816	1.17		1.521	170	nib		321-356					12674-11-2
1747	1.18	14.15	1.628	176-184	nib	-19	325-366	118	5.8	4.9	240	51069-21-9
1748	1.55	16.16	1.618	191-196	nib	-7	340-375	152	5.6	4.6	52	12672-29-6
1750	1.58	44.58	1.648	nib[a]	nib	10	365-398	53	5.0	4.3	12	11097-69-1
1766	1.62	72.78	1.648	nib	nib	31	385-420	23	4.3	3.7	1	61088-93-5
1767	1.64	96.100	1.651	nib	nib	35-38	390-425	9				37324-23-5
1768	1.81			nib	nib		435-450		2.5			61088-14-0
1770	1.95			nib	nib		450-460					

a nib none to boiling
b The registry number for "Aromatic" (mixture unspecified) is 12767-79-2
Source Drinkmann and Rehse, 1980 Reproduced with permission, copyright 1980, Elsevier Biomedical Press BV

MONS 005244

Table 2-VII. Levels (ug/g) of PCDFs in Commercial PCBs

Mixture	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Total
Aroclor 1248 (1969)	-	0.5	1.2	0.3	-	2.0
Aroclor 1242	-	0.07	0.03	0.003 [a]	-	0.15
Aroclor 1242	-	2.3	2.2	N.D. [a]	-	4.5
Aroclor 1243	0.1	0.25	0.7	0.81	-	1.9
Aroclor 1254 (1969)	-	0.1	0.2	1.4	-	1.7
Aroclor 1254 (1970)	-	0.2	0.4	0.9	-	1.5
Aroclor 1254	-	0.02	0.2	0.4-0.6	-	0.8
Aroclor 1254 (KK 602)	-	0.05	0.1	0.02	-	0.2
Aroclor 1254	-	0.1	3.6	1.9	-	5.6
Aroclor 1260	0.06	0.3	1.0	1.10	1.35	3.8
Aroclor 1260 (1969)	-	0.1	0.4	0.5	-	1.0
Aroclor 1260	-	0.8	0.9	0.5	-	2.2
Aroclor 1260 (AK 3)	-	0.2	0.3	0.3	-	0.8
Aroclor 1016 (972)	-	N.D.	N.D.	N.D.	-	-
Clophen A60	-	1.4	5.0	2.2	-	8.4
Clophen T64	0.1	0.3	1.73	2.45	0.82	5.4
Phenaclor DP-6	-	0.7	10.0	2.9	-	13.6
Prodelec 3010	0.41	1.08 [b]	0.35	0.07	-	2.0
Kanechlor 400	-	-	-	-	- ca	20.0
Mitsubishi (used)	2.13	4.00	3.30	0.53	-	10.0

a N.D. = None detected.
b Major isomer 2,3,7,8-tetra-CDF.
Source: Vuceta et al., 1983. Reproduced with permission, copyright 1983, Electric Power Research Institute.

MONS 005245

C. Monochlorobiphenyls

Monochlorobiphenyl (isomer unspecified) was a low concentration component of several products manufactured by Dow Chemical Company. Dowtherm G, a heat transfer fluid designed to replace the Aroclor-type fluids, is primarily biphenyl phenyl ether but contains up to 1,000 ppm monochlorobiphenyl. Manufacture of Dowtherm G was estimated to produce up to 1.8×10^6 g (4,000 lb) of monochlorobiphenyl (Copeland, 1979; Perlman, 1980; McCallum, 1982). Current production levels are assumed to be negligible. No other instances of monochlorobiphenyl manufacture in commerce are known.

D. Decachlorobiphenyl

As can be seen in Table 2-IV, Fenclor DK is technical grade decachlorobiphenyl. It was imported to the United States and used in investment casting waxes in the middle 1970's (Durfee et al., 1976; Brinkman and DeKok, 1980). Presumably applications in other countries were similar.

E. PCBs as By-products

PCBs can be unintentionally produced as by-products in a wide variety of chemical processes. These by-product PCBs are also referred to as incidental PCBs, inadvertently generated PCBs, or unintentionally generated PCBs. Primary concern about these contaminants came about in the United States when the EPA published a rule to implement the TSCA ban on these PCBs (EPA, 1979d; Velie and Kuntz, 1982). A rule amendment for PCB processes which are not closed or controlled set an annual average upper limit of 25 ppm for products (EPA, 1984b). Closed manufacturing processes and controlled waste manufacturing processes are excluded from the TSCA ban if the PCBs are not quantifiable; with practical limits of quantitation defined as 10 $\mu g/m^3$/resolvable chromatographic peak for air; 100 µg/L/resolvable chromatographic peak for water; and 2 µg/g/resolvable chromatographic peak for products and wastes (EPA, 1982c).

Thus, current U.S. rules not only control the use of dilute commercial mixtures such as "contaminated" transformer oils, but also impinge on any manufacturing process which could manufacture PCBs as a by-product. These processes include, but are not limited to, manufacture of chlorinated benzenes, chlorinated solvents (e.g., chloroform), chlorinated alkanes, chlorophenylsiloxane adhesives, organosilicone drugs, organic intermediates (e.g., 3,3'-dichlorobenzidine salts), and pigments (e.g., phthalocyanine green). The PCB composition in these products or their wastes has

MONS 005246

been shown to range from a single congener (e.g., 3,3'-dichlorobiphenyl in a pigment; DCMA, 1982) to complex mixtures (e.g., over 80 congeners representing all 10 homologs in a chlorinated aromatic production waste; Hanneman, 1982; Hodges et al., 1983).

Since by-product PCBs are not generally looked for in routine production QC analyses, and no organized production records are kept or reported, estimates of by-product PCB production are crude at best. The (U.S.) Chemical Manufacturers Association (CMA) surveyed its members on the subject of by-product PCB manufacture, processing, distribution, and use (Pittaway et al., 1981; Zoll et al., 1982). The production of by-product PCBs has also been estimated by EPA (1982b) and Versar, 1982). Based on these surveys, along with data from the Dry Color Manufacturers Association, the total annual by-product PCB production in the United States is estimated at about 4.5×10^7 g (100,000 lb), of which $< 5 \times 10^6$ g (11,000 lb) is found in products and $< 4.5 \times 10^5$ g (1,000 lb) enters the free environment [personal communication, R. J. Fensterheim, E. Warren, and T. Hardy, Kirkland and Ellis, Washington, D.C., February 15, 1983].

F. PCB Formation During Water Chlorination

A laboratory study (Gaffney, 1977) demonstrated the formation of mono- and dichlorobiphenyls under municipal water chlorination conditions. The lack of other studies in this area and the paucity of data on PCB formation in municipal water systems would indicate that the incidence of PCBs from this source is small, relative to the commercial mixtures already in the environment.

G. PCB Formation from Thermal Degradation of Other Chlorinated Organics

Mono- through tetrachlorobiphenyls have been found in the pyrolysis (helium atmosphere) and combustion (air atmosphere) products of chloroalkanes (Bergman et al., 1984b). Polychlorododecanes (59% chlorine and 70% chlorine) were combusted for 10 to 1,200 sec at temperatures from 300 to 700°C. Several hundred micrograms of the PCB isomers were found under most conditions. Many other compounds were detected, including other chlorinated organics, and many nonchlorinated organics. It may be speculated that combustion of other chlorinated organics may lead to formation of PCBs.

MONS 005247

VI. ENVIRONMENTAL OCCURRENCE

A. General Levels and Distribution

PCBs may be considered ubiquitous pollutants. They have been found in nearly all marine plant and animal specimens, fish, mammals, birds (especially fish-eating birds), bird eggs, and, of course, humans. All U.S. residents have measurable PCBs in their adipose tissue (Lucas et al., 1983). The occurrence in animals was thoroughly reviewed by Wassermann et al. (1979) and is summarized in Table 2-VIII. Generally, the PCB levels increase through the food chain, as depicted in Figure 2-2 and reviewed by EPA (1980d).

Selected levels in air, water, soil, sediment, and food are summarized in Tables 2-IX through 2-XII. Note that the units are not the same for all matrices. This is a reflection of the general levels of parts per billion in soil, sediment and food, and sub-parts per trillion in water. The concentrations in all matrices generally span a large range since everything from highly polluted to pristine environments has been monitored. Differences in analytical methodology and elimination of interferences make direct comparison of the data difficult. In addition, some matrices are poorly defined in the literature. For example, the high value reported for birds (14,000 ppm) may in fact be selected tissue since the value was reported for an eagle, which is not easily analyzed in toto.

Dietary exposure to PCBs was reviewed by Cordle et al. (1978). The environmental occurrence of PCBs has been reviewed in numerous articles and monographs (Yobs, 1972; Finklea et al., 1972; Nisbet, 1972a; Holden, 1973; Harvey et al., 1974; Kutz and Strassman, 1975; Fuller et al., 1976; Risebrough et al., 1976; DeNardi and Desmarais, 1976; Finlay et al., 1976; WHO, 1976; NIOSH, 1977c; Cordle et al., 1978, IARC, 1978; Wasserman et al., 1979; National Research Council, 1979; EPA, 1980d; Landrigan, 1980b; Kimbrough, 1980b; Pavlou, 1980; Hutzinger and Roof, 1980b; Baker et al., 1980; Eisenreich et al., 1981a; Murphy et al., 1981; Miller, 1982; Mackay, 1982; Vodicnik, 1983; Hunter, 1983; Eisenreich et al., 1983a, 1983b; Kauss et al., 1983; Cone et al., 1983; Farrington et al., 1983; Leifer et al., 1983; Tanabe et al., 1983; NTIS, 1982, 1983a, 1983b, 1984a, 1984b).

B. Major Environmental Contamination

Two major contaminations by localized discharge are of note since they have received so much attention and have stimulated analytical research: Yusho and the Hudson River

Table 2-VIII. Occurrence of PCBs in Animals

Organism	Concentration Range (μg/g)
Marine Organisms	
Zooplankton	< 0.003 - 1.055
Shellfish	< 0.003 - 7
Seals	3 - 212
Whales and Dolphins	0.012 - 147
Fish	
Fresh Water (USA)	0.1 - 15
Marine	0.03 - 190
Birds	
North America	0.1 - 14,000
Europe	0.5 - 9,570
Eggs	0.1 - 434
Terrestrial Animals	0.01 - 45
Humans	
Adipose (general population)	0.3 - 10.0
Plasma (general population)	0.001 - 0.029
Plasma (occupational exposure)	0.036 - 1.9
Adipose (Yusho)	0.7 - 75.5
Plasma (Yusho)	0.002 - 0.015
Milk	0.01 - 0.39
Milk-extracted Lipids	0.01 - 18.6

Adapted from Wassermann et al., 1979. Reproduced with permission, copyright 1979, New York Academy of Sciences.

MONS 005249

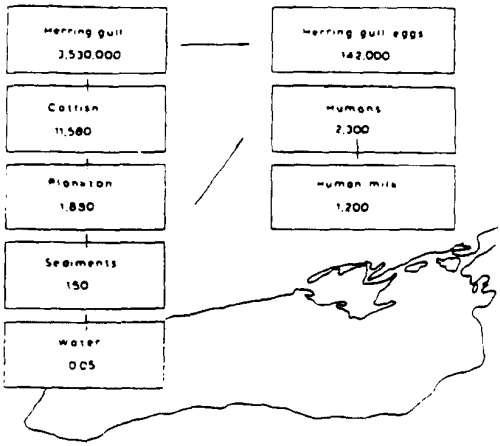


Figure 2-2. Bioaccumulation of PCBs in the Lake Ontario Ecosystem

All values are in parts per billion (ng/g).

Reprinted, with permission, from Safe (1980); copyright 1980 by Elsevier Biomedical Press B.V.

MONS 005250

Table 2-IX. Occurrence of PCBs in Air

Matrix	Location	Concentration (ng/m³)	Source
Ambient Air	Antarctic Coast	0.06 - 0.2	Tanabe et al., 1983
	Remote	0.02 - 0.5	Eisenreich et al., 1983b
	Great Lakes	0.1 - 5	Eisenreich et al., 1983b
	Rural	0.1 - 2	Eisenreich et al., 1983b
	Urban	0.5 - 30	Eisenreich et al., 1983b
	Various USA Locations	0.02 - 36	NRC, 1979
	Marine Air	0.05 - 2.0	NRC, 1979
	Atlantic Ocean	0.05	WHO, 1976
	Gulf of Mexico	0.2 - 0.9	Giam et al., 1976
	North Pacific Ocean	0.54	Atlas and Giam, 1980
	North Atlantic Ocean	1.84	Tanabe et al., 1982
	west Pacific Ocean	0.06 - 1.2	Tanabe et al., 1982
	North Atlantic Ocean	0.05 - 0.2	Bidleman et al., 1976
	North Atlantic Ocean	0.05 - 1.6	Bidleman et al., 1981b
	Tokyo, Japan	20	Kimbrough, 1980b
	Matsuyama, Japan	2 - 5	Kimbrough, 1980b
	Sweden	0.8 - 3.9	WHO, 1976

MONS 005251

Table 2-IX (continued)

Matrix	Location	Concentration (ng/m³)	Source
	USA	5	WHO, 1976
	USA, Indoor Contaminated by Light Ballast Burnout	5,860	MacLeod, 1979
	USA, Indoor	39 - 620	MacLeod, 1979
	USA, Indoor Near Spill Site	< 10 - 190	MacLeod, 1979
	USA, Landfills	2 - 18	MacLeod, 1979
	USA, Electrical Substations	1 - 47	MacLeod, 1979
	USA, Transformer Manufacturer	17 - 5,900	MacLeod, 1979
	USA, Spill Site	10 - 10,800	MacLeod, 1979
Stack Gas	ENSCO, El Dorado, Arkansas	12,000 - 58,000	Erickson et al., 1984a
	Rollins, Deer Park, Texas	9.8	Erickson et al., 1984a
Occupational	Massachusetts, PCB User Plants	$0.1\text{-}5.8 \times 10^6$	NIOSH, 1977c
	Capacitor Factory	$5\text{-}7 \times 10^6$	NIOSH, 1977c
	Various Occupational Environments	$0.01\text{-}10 \times 10^6$	Kimbrough, 1980c

MONS 005252

Table 2-K. Occurrence of PCBs in Water

Matrix	Location	Concentration (ng/L)	Source
Water	Antarctic, Marine	0.03 - 0.07	Tanabe et al., 1983
	Antarctic, Snow	0.3 - 1.0	Tanabe, et al., 1983
	Ocean Water	0.3 - 4,200[a]	Bidleman et al., 1976
	North Pacific Ocean	0.2 - 1.1	Tanabe & Tatsukawa, 1980
	West Pacific Ocean	0.04 - 0.25	Tanabe et al., 1982
	Deep Ocean[b]	0.03 - 0.6	Tanabe et al., 1983
	Atlantic	0.3 - 8	Harvey & Steinhauer, 1976
	Mediterranean Coast	13	Elder, 1976
	Sweden, River	0.5	WHO, 1976
	Sweden, Tap	0.33	WHO, 1976
	USA/Canada, Great Lakes	0.8 - 31	NRC, 1979
	Japan, Tap	1 - 100	WHO, 1976
	USA, Lake Michigan, Spill Site	100 - 450	WHO, 1976
	General Unpolluted Rivers	< 0.5	WHO, 1976
	USA/Canada, Great Lakes	< 5	WHO, 1976
	General, Moderately Polluted Rivers	< 50	WHO, 1976
	General, Highly Polluted Rivers	< 500	WHO, 1976
Rain	Remote	0.1 - 10	Eisenreich et al., 1983b

MONS 005253

TABLE 2-K (continued)

Matrix	Location	Concentration (ng/L)	Source
	Marine	0.5 - 10	Eisenreich et al., 1983b; Atlas & Giam, 1980
	Rural	1 - 50	Eisenreich et al., 1983b
	Great Lakes	10 - 150	Eisenreich et al., 1983b
	Urban	10 - 250	Eisenreich et al., 1983b

a Review of several studies at coastal and open ocean sites.
b No significant concentration differences were observed at depths from 0 to 4,500 m.

MONS 005254

Table 2-X1. Occurrence of PCBs in Soil and Sediment

Matrix	Location	Concentration (µg/g)	Source
Soil	Sweden	15	WHO, 1976
	Japan - Agricultural	< 1,000	WHO, 1976
	Japan - Near Electrical Component Factory	510,000	WHO, 1976
	USA - 1972	(99.9% < LOD)	Kimbrough, 1980b
	USA - Urban	(27% < LOD)	Kimbrough, 1980b
	USA - Transformer Manufacturer	17 - 17,800	MacLeod, 1979
Sediment	Spill Site	1,400 - 61,000	WHO, 1976
	16 km Downstream	600	WHO, 1976
	Sweden - Atmospheric Deposition Only	8 - 20	NRC, 1979
	Sweden - Potential Industrial Contamination	4 - 170	NRC, 1979
	USA	20 - 300[a]	NRC, 1979
	USA/Canada - Great Lakes	tr - 250	NRC, 1979
	Japan (1,445 sites)	< 1,000	Kimbrough, 1980b
	Japan - Polluted Site	up to 2,700	Kimbrough, 1980b

a Median values by state for 10 to 293 samples/state in nine states.

MONS 005255

Table 2-XII. Occurrence of PCBs in Food

Matrix	Location	Concentration (µg/kg)
Food		
Fish	USA	1,870
Fish By-products	USA	1,170
Cheese	USA	250
Milk	USA	2,270
Shell Eggs	USA	550

Source: Finlay et al., 1976.

The contamination of other ecosystems, including New Bedford, MA, Waukegan, IL, and Bloomington, IN has been reviewed (Weaver, 1984).

1. Yusho: "Yusho" was a mass food poisoning caused by the ingestion of a commercial brand of rice oil contaminated with PCBs, polychlorinated dibenzofurans (PCDFs), and polychlorinated quaterphenyls (PCQs). The poisoning occurred in Western Japan in 1968, involving more than 1,600 people. The clinical criteria for the Yusho patient included fatigue, headache, joint swelling and pain, bursitis, inhibition of growth and tooth formation in children, anemia, unusual PCB patterns in the blood, reduced neural conduction velocity, acneform eruptions, increased skin pigmentation, and swelling of the eyes. PCB concentrations in blood averaged about 7 ppb (range 1-32) for Yusho patients (Kuratsune, 1980), while a control population of normal persons had a mean of 3 ppb (range 1-7) and a group of PCB production workers showing only minor clinical signs had a mean of 364 ppb (range 60-920). This, plus other evidence, indicated that the PCBs in the rice oil were not solely responsible for the clinical manifestations. Other, more toxic, chlorinated aromatics have been found in the Yusho oil, including PCDFs and polychlorinated quaterphenyls but not polychlorinated dibenzodioxins (PCDDs). Table 2-XIII summarizes the PCDF concentrations (Kuratsune, 1980). Polychlorinated quaterphenyls, along with minor amounts of polychlorinated terphenyls and polychloroquaterphenyl ethers, were found at concentrations equal to or up to four times that of PCBs in Yusho oil, although saponification during cleanup may have created these compounds as artifacts (Miyata et al., 1977; NRC, 1979). Many of the Yusho patients have died and epidemiological studies continue. Yusho was the subject of a

MONS 005256

Table 2-XIII. Concentrations of PCBs and PCDFs and Their Ratios in Yusho-Related Materials

Materials	PCBs (ppm[b])	PCDFs (ppm[b])	PCBs/PCDFs
Kanechlor-400 (unused)	1,000,000	ca. 20	50,000
Yusho oils[a]	ca. 1,000	5	200
Yusho patients[c]			
Adipose tissue	1.3	0.009	144
Liver	0.05	0.013	4

a Produced on February 5 or 6, 1968.
b On whole base.
c Two patients who died in 1969 and one patient who died in 1972 were included.
Source: Kuratsune, 1980; reproduced with permission, copyright 1980 by Elsevier Biomedical Press BV.

book (Higuchi, 1976) and was more recently reviewed (Kuratsune, 1980). Other reviews and key articles include Kuratsune (1972); Kuratsune et al. (1972); Nagayama et al. (1975); Miyata and Kashimoto (1976); Miyata et al. (1977); Morita et al. (1977); Bowes et al. (1978); Cordle et al. (1978); Kamps et al. (1978); Urabe et al. (1979); Rappe et al. (1979); Kashimoto et al. (1981a, 1981b); and Masuda et al. (1982).

A similar outbreak in Taiwan affected about 2,000 people between 1979 and 1981. This so-called Taiwanese Yusho incident was reported by Chen et al. (1980, 1981, 1982); Kashimoto et al. (1982); Masuda et al. (1982); and Chen and Hites (1983).

2. Hudson River: General Electric manufactured PCB-containing capacitors in two plants at Hudson Falls and Ft. Edward, New York. Both plants are located immediately adjacent to the Hudson River about 5 km apart and about 320 km (200 miles) from the river mouth. PCB discharges from these plants have led to massive contamination of the Hudson basin estimated at a total of 6×10^8 g. The problem has been reviewed by Horn et al. (1979) and Carcich and Tofflemire (1982). Average sediment levels ranged as high as 150 µg/g in some of the river reaches, with occasional samples exceeding 1,000 µg/g. It has been estimated that 2.6×10^6 g/year of PCBs flow over the dam 67 km (42 miles) downstream of Ft. Edward and into the estuarian portion of the river.

MONS 005257

Thus, not only is the ecosystem contaminated, but the PCBs are not controlled and the contamination is spreading.

The contamination of the Hudson River Basin exceeds, in level and scope, any other area found to date in the United States. River sediment concentrations are at least an order of magnitude higher than other contaminated systems (e.g., Lake Ontario; Lake Michigan; Escambia Bay, Florida; and soils from the Monsanto plant). The PCB levels at a few other sites (e.g., Waukegan River, Illinois and Housatonic River, Connecticut) are comparable, but the size of the areas contaminated do not appear to be as great as the Hudson River. Estimates of the quantity of PCBs in the sediments of the Great Lakes (e.g., Lake Ontario, 9×10^6 g; Lake Erie, 3.6×10^7 g; and Lake Michigan, 7×10^6 g) are considerably lower than those for the Hudson River (6×10^8 g; Horn et al., 1979; Carcich and Tofflemire, 1982). Between 1966 and 1974, General Electric's Ft. Edward and Hudson Falls facilities purchased 3.5×10^{10} g of PCBs or approximately 15% of Monsanto's domestic sales during that time. This suggests that General Electric's discharges to the Hudson River Basin might represent close to 15% of the nationwide total discharges to the environment (Horn et al., 1979).

VII. ENVIRONMENTAL TRANSPORT AND FATE

Of the 5.7×10^{11} g (1.25 billion lb) of PCBs estimated to have been produced in the United States (NRC, 1979; see Section V, above, for more details) about 5.5×10^{11} g are thought to be in service, destroyed, or otherwise unavailable, leaving 0.11×10^{11} g (24 million lb) in the mobile environmental reservoir. Table 2-XIV presents an estimate of the PCB distribution (Mackay, 1982a). In 1979, the NRC estimated that 50-80% of the PCBs in the environment had been deposited in the North Atlantic Ocean and that the major continental sink for PCBs is freshwater sediment.

The environmental transport of PCBs is complex and global. PCBs are transported by air, water, fish, birds, and other routes. They are deposited from air by rain, snow, dry fall-out, and vapor-phase deposition. As noted in Tables 2-IX and 2-X, environmental transport has resulted in fairly uniform global background of PCBs.

By virtue of their high lipid-water partition ratio (see octanol-water partition coefficients in Table 2-III), PCBs tend to accumulate in fatty tissues. The long-term distribution in tissue is adipose > skin > liver > muscle > blood (Safe, 1980). As with the well-publicized case of DDT (Carson, 1962), PCBs biomagnify through the food chain (see

Table 2-XIV. Estimated Distribution of PCBs in 1981

	Mass of PCB ($g \times 10^6$)	Concentration (g/m^3)
Atmosphere	18	1.2×10^{-9}
Water	20	1.7×10^{-6}
Fresh water sediments	4,000	9.3×10^{-2}
Fresh water biota	15	3.0
Soil - natural	1,000	1.1×10^{-2}
Soil - sewage sludge	4,800	?
Vegetation	1,000	1.7×10^{-3}
Wildlife	0.3	0.48
Livestock	0.6	9.3×10^{-3}
Humans	5	0.36
TOTAL ACCESSIBLE	10,859	
Oceanic water and biota	6,000	
Oceanic sediments	1,000	
Total near oceanic	7,000	
Landfill and storage	175,000	
Other industry	75,000	
Electric utilities	74,000	
TOTAL INACCESSIBLE	324,000	
TOTAL DEGRADED AND ADVECTED	228,000	
GRAND TOTAL (equals amount produced)	570,000	

Source: Mackay, 1982a. Reproduced with permission from author and Edison Electric Institute.

Table 2-VIII). A concentration factor of nearly 10^8 was reported from Lake Ontario water to herring gulls (International Joint Commission, 1977).

The environmental transport and fate is of great importance since use and disposal practices of existing PCBs must be controlled based on sound predictions of their environmental impact. The subject has been reviewed (Nisbet and Sarofim, 1972a, 1972b; Nisbet, 1972b; Durfee et al., 1976; Bidleman et al., 1976; Risebrough et al., 1976; Fuller et al., 1976; Finlay et al., 1976; WHO, 1976; NIOSH, 1977c; Pomerantz et al., 1978; NRC, 1979; Hutzinger and Roof, 1980b; Pavlou, 1980; Miller, 1982; Mackay, 1982a, 1982b; Neely,

MONS 005259

1983; Vodicnik, 1983; Moolenaar, 1983; Eisenreich and Johnson, 1983; Hunter, 1983; James, 1983; Leifer et al., 1983; NTIS, 1984a, 194b; Mackay and Hughes, 1984). A recent monograph, Physical Behavior of PCBs in the Great Lakes (Mackay et al., 1983b), contains 13 chapters which discuss various aspects of environmental transport and fate.

VIII. DESTRUCTION, DEGRADATION, AND METABOLISM

PCBs are very stable compounds and do not degrade easily. However, under certain conditions, they may be destroyed by chemical, thermal, and biochemical processes. These may occur intentionally (e.g., incineration), unintentionally, or metabolically. Because of their high thermodynamic stability, all degradation mechanisms are difficult. Intentional degradation generally requires high heat or catalysis. Environmental and metabolic degradation generally proceeds quite slowly relative to most other compounds.

A. Intentional Destruction

Destruction has generally been limited to incineration, although some chemical degradation processes (e.g., dechlorination with metallic sodium) are permitted in the United States and other countries. PCB destruction is of particular analytical interest since the determination of destruction efficiency requires the analysis of feed stocks, stack gases, and other effluents.

In the United States, incinerators are strictly regulated to assure that PCBs are effectively destroyed. The rules specify for nonliquid PCBs (i.e., solids containing PCBs, such as capacitors) that < 0.001 g/kg of the PCB introduced may be emitted to air. This 99.9999% ("six-9's") destruction efficiency has generally been the overall target in the United States for all emissions from all PCB categories. Most incinerators employ a combination of high heat (ca. 1200°C), a long residence time (> 2 sec), an agitation mechanism such as a rotary kiln to mix and move solids through the heated zone, and various pollution control systems (filters, precipitators or scrubbers). PCBs may also be effectively and legally destroyed in the high efficiency boilers used by utilities to generate electricity (EPA, 1983d; Hunt et al., 1984).

Several nonthermal processes for PCB destruction are being used, investigated, or developed. The chemical techniques include adsorption, chlorinolysis, catalytic dehydrochlorination, microwave plasma, ozonation, photolytic, wet air oxidation, reaction with sodium naphthalide, reaction

MONS 005260

with molten sodium, and reaction with a sodium salt in an amine solvent. The biological processes include activated sludge, trickling filters, and special bacterial methods. The subject of nonthermal PCB destruction has been reviewed (Ackerman et al., 1981; Ackerman et al., 1983a; Fradkin and Barisas, 1982; Addis and Komai, 1984).

Reviews by Erickson and Shah (1983) and Neulicht et al. (1985) contain annotated bibliographies of major books, articles, rules, and documents on PCB destruction. A book on detoxication of hazardous waste (Exner, 1982a) contains two reviews of PCB destruction technology (Exner, 1982b; Weitzman, 1982), a chapter summarizing the U.S. PCB regulations (Velie and Kuntz, 1982), and four chapters on research into novel destruction technologies (Barton and Arsenault, 1982; Brown et al., 1982; Kitchens et al., 1982; Miller and Fox, 1982).

B. Environmental Degradation

In the environment, photolysis is the only significant chemical degradation process (Hutzinger et al., 1972b; WHO, 1976; NRC, 1979). Several recent publications also discuss photochemical degradation (Kalmaz et al., 1982; Parlar and Mansour, 1982; West et al., 1983; Dilling et al., 1983; Zabik, 1983). The atmospheric half-lives for photodegradation are dependent on the degree of chlorination. Half-lives of the monochlorobiphenyls range from 0.62 to 1.4 days, while pentachlorobiphenyl had a half-life of 67 days (Dilling et al., 1983). Acid- or base-catalyzed reactions are not likely to degrade PCBs under environmental conditions. It should be noted that volatilization and other transport mechanisms can result in significant removal of PCBs from an environmental compartment without any net loss of PCBs from the environment. Once volatilized, however, the chances of photolytic degradation are increased. The environmental degradation of PCBs has been reviewed (Zell and Ballschmiter, 1980; Neely, 1983; Leifer et al., 1983).

C. Microbial Degradation

Microbial degradation of PCBs depends on the degree of chlorination and the position of the chlorine atom on the biphenyl molecule. Lower chlorinated biphenyls are readily transformed by bacteria, but the higher chlorinated compounds are not, as illustrated in Figure 2-3 (Moolenaar, 1983). In addition, the position of chlorine substitution affects biodegradation; ortho substitution decreases the rate. The major products are conjugated and/or free hydroxychlorobiphenyls. A further degradation product of 4-chlorobiphenyl is 4-chlorobenzoic acid (Messier et al., 1983).

MONS 005261

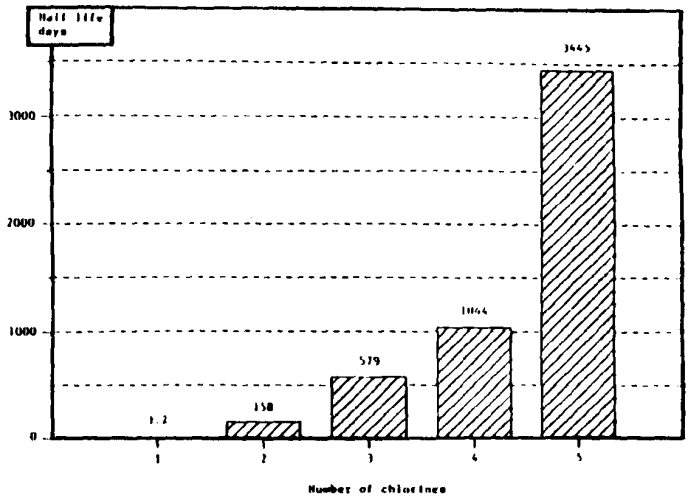


Figure 2-3. Environmental Persistence of Selected Chlorinated Biphenyl Isomers

Reprinted from Moolenaar (1983).

MONS 005262

The half-lives of the three monochlorobiphenyls were reported to be 2 to 3 days in river water (Bailey et al., 1983). Wong and Kaiser (1975) showed complete metabolic breakdown of Aroclor 1221 by lake water bacteria after 1 month incubation. The products were identified only as "several low molecular weight compounds." Furukawa et al. (1978) studied the microbial degradation of 31 PCB congeners from mono- through pentachlorodiphenyls. They concluded that degree of chlorination and extent of ortho substitution affected degradability, as discussed in the previous paragraph. In addition, they found that PCBs with a nonchlorinated ring degraded faster, with preferential fission of the unsubstituted benzene rings. Microbial degradation has been reviewed (Menzie, 1978, 1980; NRC, 1979; Leifer et al., 1983; Peyton, 1984).

D. Metabolism by Higher Animals

The major PCB metabolites in higher animals are mono- and dihydroxychlorobiphenyls and their conjugates. These compounds are then excreted in the urine. Figure 2-4 summarizes the in vivo metabolites (Safe, 1980). Methylthio- and methylsulfone PCB derivatives have also been identified in tissues from Yusho victims (Haraguchi et al., 1984) and other environmental matrices, as reviewed by Bergman et al. (1980). Bergman et al (1980) synthesized and characterized 25 of the methylthio- and 28 of the methylsulfone PCB derivatives.

The metabolic rates are both isomer- and homolog-dependent. The higher the homolog, the slower the metabolism (Safe, 1980). Most of the studies reported have used rats, rabbits, and other high level species. It is assumed that hydroxylation is also the major degradation route in other species. Biological degradation does not significantly reduce the total environmental burden, although it does have a marked influence on the relative concentrations of PCBs (i.e., chromtographic patterns) passing through the food chain (WHO, 1976). The metabolism of PCBs has been reviewed (Hammond, 1972; Hutzinger et al., 1974a; NIOSH, 1977; Menzie, 1978, 1980; IARC, 1978; Matthews et al., 1975; Matthews and Kato, 1979; Safe, 1980; Safe et al., 1980; Hutzinger and Roof, 1980b; Safe et al., 1983b; Hutzinger, 1983a, 1983b; Matthews, 1983; NTIS, 1984b).

E. Degradation During Use and Analysis

Some PCB uses generate sufficient heat to degrade commercial PCB mixtures, forming PCDFs (Buser et al., 1978a, 1978b) and polymeric products (Zitko and Choi, 1971; NRC, 1979). These findings are of interest, expecially to the

MONS 005263

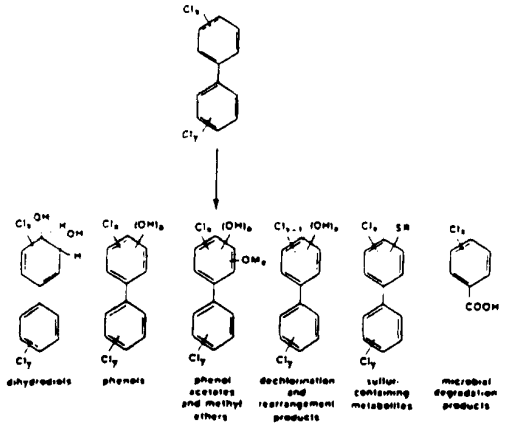


Figure 2-4. Common In Vivo PCB Metabolites

Reprinted, with permission, from Safe (1980); copyright 1980 by Elsevier Biomedical Press B.V.

toxicologists and epidemiologists studying the health effects of PCBs, since toxic contaminants can confound research results. The classic case of toxic effects caused by PCB contaminants is the Yusho incident discussed in Section VI.B.1, above.

A variety of hostile conditions can degrade PCBs by oxidation, hydrolysis, alcoholysis, and photochemistry (Pomerantz et al., 1978). These conditions are of particular interest to those investigating nonthermal PCB destruction methods. In addition, the analyst must be aware that certain harsh cleanup techniques can destroy PCBs, especially the lower chlorinated congeners. This topic is addressed more thoroughly in the acid and base cleanup sections of Chapter 6 (Cleanup).

F. Degradation in Fires

An extreme case of degradation while in use occurs when PCB-containing electrical equipment is involved in a

fire. Not only are PCBs degraded but they are also dispersed. Such an event occurred in 1981 in Binghamton, New York, where the 18-story State Office Building was damaged by fire (Vuceta et al., 1983; EPA, 1984a). Leakage from a PCB transformer was dispersed throughout the building. The average PCB concentration on exposed horizontal surfaces was 162 µg Aroclor 1254/m^2. Samples of the soot were found to contain PCDDs (20 µg/g), PCDFs (700-2,200 µg/g), and polychlorinated biphenylenes (54 µg/g). Hilker et al. (1983) analyzed samples from the same fire and found 200 ppm of 2,3,7,8-TCDF and 2.8 ppm of 2,3,7,8-TCDD. Similar results at several other PCB fire sites were reported by Williams et al. (1983a, 1983b, 1985). The contaminants from Binghamton and other "accident" sites were recently reviewed (Vuceta et al., 1983). Table 2-XV presents a summary of the compounds found at these sites.

Some research has been conducted to identify the products, especially the PCDFs, of incomplete PCB combustion (Buser et al., 1978a,b; Buser and Rappe, 1979; Rappe et al., 1983; Buser and Rappe, 1984; Rappe, 1984; Erickson et al., 1984b, 1984c, 1984e, 1985a, 1985b; Swanson et al., 1985). PCDFs were observed to form on heating in sealed ampules containing PCBs (Aroclors or individual congeners) and oxygen (Buser and Rappe, 1979). Even at temperatures as low as 300°C, increased levels of PCDFs were observed after 1 week (Morita et al., 1978). Figure 2-5 shows the reaction products of 2,2',4,5,5'-pentachlorobiphenyl. The trichlorodibenzofuran was the major product, with smaller amounts of the four tetra- and a single pentachloro dibenzofuran (Buser and Rappe, 1979).

Using a bench-scale thermal combustion system, Erickson et al. (1984b, 1984c, 1984e, 1985a, 1985b; Swanson et al., 1985) found that the optimum conditions for PCDF formation from PCBs are near 675°C for 0.9 sec or longer, with 8% excess oxygen. Under these conditions, percent levels of PCDFs are formed from mineral oil or silicone oil contaminated with PCBs at 5 ppm or greater. The amount of PCDFs formed from the PCB-containing materials was directly dependent on the amount of PCBs fed into the system. As illustrated in Figure 2-6, the composition of the PCDF mixtures formed was independent of the feed concentration or matrix. PCDFs and PCDDs are formed at much lower levels from a trichlorobenzene dielectric fluid used in askarels which contained no detectable PCBs. As illustrated in Figure 2-6, the composition of the PCDF mixture formed from the trichlorobenzene mixture is different from that formed from the PCB feed.

MONS 005265

Table 2-XV. Summary of Chlorinated Aromatic Hydrocarbons Detected During Different PCB Accidents[a]

Accident	PCDDs	PCDFs	PCQs	PCQEs	PCTs	PCBPs	PCPYs	PCCYs
Toronto		5 ppm						
Norrtalje, Sweden		45-107 µg/g						
Binghamton, NY	2.8-19.9 ppm	124-2,163 ppm			b	b	b	b
Stockholm (1981)		43-104 µg/g			b	b	b	b
Skovde, Sweden		0.01-0.773 µg/m²				b	b	b
Yusho, Japan		1-18 ppm	b	b	b			
Yusho, Taiwan		0.18-1.68 ppm	b		b			

a PCQs = polychlorinated quaterphenyls
PCQEs = polychlorinated quaterphenyl ethers
PCTs = polychlorinated terphenyls
PCBPs = polychlorinated biphenylenes
PCPYs = polychlorinated pyrenes
PCCYs = polychlorinated chrysenes.

b Quantification and confirmation not possible due to lack of standards.

Source: Vuceta et al., 1983. Reproduced with permission, copyright 1983, Electric Power Research Institute.

MONS 005266

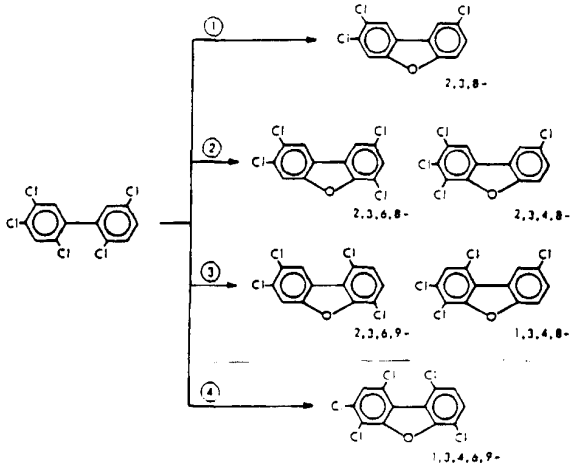


Figure 2-5. Polychlorinated Dibenzofurans Formed from Thermal Degradation of 2,2',4,5,5'-Pentachlorobiphenyl

Mechanism 1 involves loss of two ortho chlorines; Mechanism 2 involves loss of HCl and a 2,3 chloride shift; Mechanism 3 involves loss of HCl, and Mechanism 4 involves loss of H_2. The sample (100 µg) was heated in the presence of air in a sealed ampule at 600°C for 60 sec.

Reprinted, with permission, from Buser and Rappe (1979); copyright 1979 by Pergamon Press.

MONS 005267

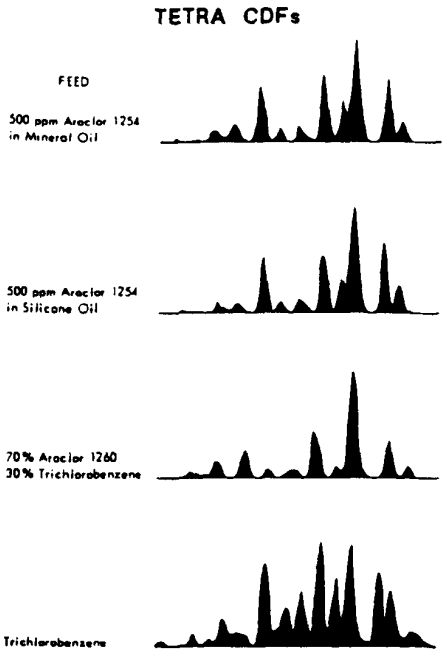


Figure 2-6. Tetrachlorodibenzofurans Formed from Thermal Combustion of PCBs and a Trichlorobenzene Mixture

All mixtures were combusted at 675°C for 0.8 sec with 8% excess oxygen. The products were trapped on XAD-2, extracted, cleaned up, and analyzed by HRGC/EIMS. The samples were analyzed under slightly different conditions, accounting for the minor variations in the chlormatographic patterns.

Reprinted from Erickson et al. (1984b).

MONS 005268

The formation of PCDFs and other compounds from thermal degradation of PCBs has been reviewed (Choudhry and Hutzinger, 1983; Addis and Komai, 1984; Rappe, 1984; Erickson et al., 1984b).

IX. TOXICOLOGY

The public, legal, and scientific concerns about PCBs arose from the findings that PCBs were toxic and therefore undesirable as commercial products or environmental contaminants. The evidence for this toxicity was sufficient for special citation by the U.S. Congress in the Toxic Substances Control Act (see Chapter 1) as well as similar actions by other governments. However, the degree of toxicity and the nature of the effects on man and other organisms has been and continues to be highly debatable. The U.S. National Research Council (1979) concluded,

> "An analysis of PCB data... leads to the conclusion that PCBs are persistent, and are likely to accumulate. PCBs do not appear particularly toxic for short-term exposure, but results are subject to interpretation (Roberts et al. 1978)."

Table 2-XVI presents the NRC's survey of the chronic effects of PCBs. Table 2-XVII presents a summary of PCB effects from Reggiani (1982) and Table 2-XVIII presents a summary of the pathologic findings from McConnell (1980). Many studies of both occupational or environmental exposure and laboratory exposure are subject to question because of the type and purity of PCB used. All of the occupational and environmental studies and many other laboratory studies have been conducted with commercial mixtures. Not only are the effects of up to 70 different PCB congeners being studied simultaneously, but the possible presence of contaminants such as polychlorinated terphenyls and quaterphenyls and the much more toxic PCDDs and PCDFs make assignment of the observed effects to PCBs subject to criticism.

Some studies, however, have been conducted on individual pure congeners. These studies indicate that PCB toxicity is dependent not only on the degree of chlorination but also on the isomer. For instance, those PCBs which have no ortho-substitution and are heavily substituted at the meta and para positions are capable of assuming a planar conformation which can interact with the same receptor as TCDD. Examples include 3,3',4,4'-tetrachlorobiphenyl (I), 3,3',4,4',5-pentachlorobiphenyl (II), and 3,3',4,4',5,5'-hexachlorobiphenyl (III).

MONS 005269

Table 2-XVI. Summary of Chronic Toxic Effects of PCBs

Test	Effects
Chronic feeding	
Aquatic species	Threshold effects in egg hatchability of vertebrates and invertebrates at levels of 2-5 µg/L
	Embryo toxicity evident at 50 µg/L
Terrestrial species	Mouse - some liver change with exposure to high chlorine containing products, 300-500 µg/g
	Rat - some liver changes, minimal reproductive effects, 100-500 µg/g
	Monkey - Yusho symptoms, altered reproduction cycles, hyperplastic gastritis and ulceration, 2.5-5 µg/g
	Chicken - some morphologic deformity, reproduction decline, subcutaneous edema, 20-50 µg/g
	Mink - dose response relationship in growth and reproduction, 10 µg/g
	Pelican - some hepatocelluiar changes, 100 µg
	Dogs - reduced growth, some liver changes, 100 µg
	Wildfowl - some reproduction changes, varies with species, 50-200 µg/g

MONS 005270

TABLE 2-XVI (continued)

Test	Effects
Teratogenicity	Effects seen in avian species, 50-200 µg/g
Mutagenicity	Chromosomal abnormalities - negative results
	Dominant lethal mutations - negative results
	Ames test - 1221, 4 chlorobiphenyl significantly mutagenic
Oncogenicity	High chlorinated compounds produced tumors in rats and mice, relationship with PCB not always clear

Source: National Research Council (1979); reprinted with permission from the National Academy of Science.

MONS 005271

Table 2-XVII Clinical Features Following Exposure to PCBs

Signs and Symptoms	Rat	Mice	Monkey	Yusho Cases	Kanechlor Workers Japan (n = 32)	Prior Workers USA (n = 341)
Blood Levels in ppb				22-34	60-920	105-351
1. Dermatological						
Chloracne			+		Chloracne, 2 cases	+
Hyperpigmentation			+	+		+
Hair Loss				+		
2. Ocular						+
Cyst formation of Distal Ducts			+	+		
Swelling and Pigmentation of Eyelid and Conjunctive				+		
3. Hematological						
Pigmentation of Oral Mucosa				+		
Anemia as of Teeth Growth and Number				+		
4. Liver						+
Enlargement						+
Serum Enzymes						+
Enzymes Induction						+
Parenchymal Lesions						+
5. Respiratory Tract						
Chronic Bronchitis				+		
Reduction of Vital Capacity				+	+	+
6. Neurological						
Polyneuropathies				+		
Sensorial Impairment				+		
Reduced Conduction Velocity				+		
7. Endocrinological						
Female Sterility			+	+		
8. Metabolism						
Overweight						
Carbohydrates						
Fat Metabolism			+			
9. Mortality			+	+		
10. Tumors						
Specific Hybrid Rat		+	+	+		
Liver		+	+	+		

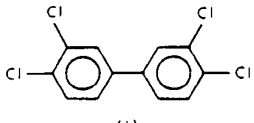
Source: Modified, reprinted with permission, Copyright 1981, Pergamon Press

MONS 005272

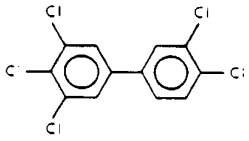
Table 2-XVIII. Summary of Pathologic Findings Due to the Toxicity of PCBs

Pathologic Finding	Rat	Mouse	Guinea Pig	Chicken	Monkey	Human
Decreased Body Weight	+	+	+	+	+	+
Acne/Alopecia	(-)	(-)	(-)	(-)	+	+
Edema	(-)	+	(-)	+	+	+
Lymphoid Atrophy						
Thymus	+	+	+	+	+	n.r.
Spleen	+	+	+	+	+	n.r.
Hepatomegaly	+	+	+	+	+	+
Hepatomegalocytosis	+	+	(-)	(-)	+	+
Multinucleated Giant Cell	+	(-)	(-)	(-)	(-)	(-)
Necrosis, Degeneration	+	+	+	+	+	+
Fat	+	+	+	+	+	+
Bile Duct Hypertrophy	+	(-)	(-)	(-)	(-)	(-)
Porphyria	+	+	(-)	+	(-)	+
Urinary Bladder Hypertrophy	(-)	(-)	+	(-)	(-)	(-)
Gastropathy	(-)	(-)	(-)	+	+	(-)
Tumor Induction	+	+	(-)	(-)	(-)	(-)

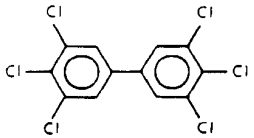
Source: McConnell, 1980. Reprinted with permission, copyright 1980, Elsevier Biomedical Press, BV.



(I)



(II)



(III)

These are known as cytochrome P-448 inducers or 3-MC inducers (Goldstein, 1980) or aryl hydrocarbon hydroxylate (AHH) inducers (Safe et al., 1981, 1982). These congeners are not major components (generally much less than 1%) of the Aroclor mixtures (Albro and Parker, 1979; Huckins et al., 1980; Albro et al., 1981; Safe et al., 1981, 1982, 1983d; see Appendix B).

The other active group of congeners is the phenobarbital-type or "PB-type" inducers or cytochrome P-450 inducers, as shown in Figure 2-7 (Goldstein, 1980). Many congeners exhibit mixed responses or no observable response.

Other reviews are available (Hammond, 1972; Kimbrough, 1974; Fishbein, 1974; Calandra, 1976; Durfee et al., 1976; NIOSH, 1977; Matthews et al., 1978; Kimbrough et al., 1978; IARC, 1978; Department of Health, Education and Welfare, 1978a, 1978b, 1978c; Wassermann et al., 1979; EPA, 1980d; Strik et al., 1980; Goldstein, 1980; McConnell, 1980; Baker et al., 1980; Vos et al., 1980; Brown et al., 1981a; Ecology and Environment, 1982; Gaffey, 1983a,b; Friess et al., 1983; Safe et al., 1982, 1983a, 1983b, 1983d, 1983e; and James, 1983; Goodman, 1983; Sleight, 1983; Ringer, 1983; Safe, 1984).

MONS 005274

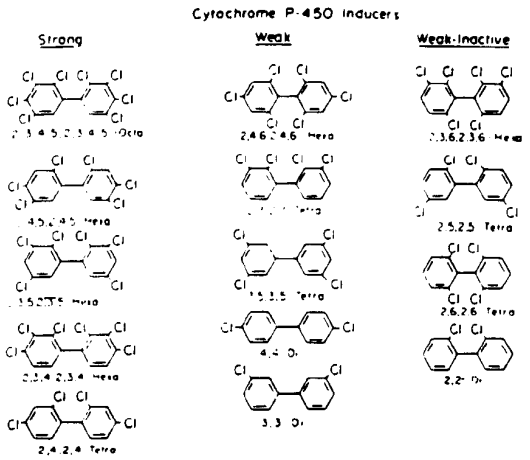


Figure 2-7. Summary of PCB Isomers Which Induce Cytochrome P-450

Reprinted, with permission, from Goldstein (1980); copyright 1980 by Elsevier Biomedical Press B.V.

X. OCCUPATIONAL EXPOSURE AND ITS EFFECTS

Workers in PCB production and use occupations were exposed to high levels of commercial mixtures of PCBs through both dermal contact and inhalation of vapors (Table 2-IX). Capacitor plants provided the highest reported exposure potential (Kimbrough, 1980c). The first report of any effects of occupational exposure was in 1936 (Jones and Alden, 1936), when chloracne was associated with PCBs. Symptoms of high PCB exposure include burning of eyes, face, and skin. Several clinical symptoms are indicative of PCB-related liver injury, including elevated serum triglycerides and induction of mixed function oxidases. Although there has been some evidence of increased incidences of cancer, it is inconclusive (Kimbrough, 1980c).

The occupational air levels were quite high relative to ambient (see Table 2-XII). Table 2-XIX lists a summary of some of the PCB levels in workplace air along with blood levels and duration of exposure and clinical effects (Kimbrough, 1980c). Several other studies have reported PCB concentrations in workplace air in the 1-10 mg/m^3 range (about 1 million times ambient; NIOSH, 1977c). These exposures generally involved the handling of PCB-containing capacitors which were heated as part of the manufacturing process.

Table 2-XIX. PCB Concentrations in the Occupational Environment and in Blood of Workers Exposed to PCBs

Druation of PCB Exposure	PCB Levels: Environmental (mg/m^3)	PCB Levels: Blood (ppb)	Effects Reported
Not known	10	-	Unbearable irritation
4-8 months	5-7	-	Chloracne
< 1-20 years	0.2-1.6	370, ave.	Chloracne, hyperpigmentation, liver injury
2.5 year ave.	Not reported	820, ave.	Chloracne
2.5-18 years	0.013-0.27	36-286	Irritation, liver injury
14 months	0.1	-	Chloracne, liver injury
2-23 years	0.32-1.44	> 200	Chloracne, liver injury
Up to 15 years	Not reported	7-300	Chloracne, elevated triglycerides
	< 1	74-1,900	No effect

Source: Kimbrough (1980c). Reprinted with permission, copyright 1980, Elsevier Biomedical Press, BV.

As noted in the WHO document (1976), occupational exposure may be widespread among workers handling PCBs in use: mechanics handling lubricating and hydraulic oils, office workers handling carbonless copy paper, analytical laboratory workers, and electrical component handlers.

MONS 005276

Occupational exposure was thoroughly reviewed (NIOSH, 1977c; Kimbrough, 1980c). Other reviews include Hubbard (1964), WHO (1976), IARC (1978), and Cordle et al. (1978).

Reviews specifically concentrating on the epidemiological aspects of PCB exposure, both occupational and accidental (Yusho) include WHO (1976), NIOSH (1977), and IARC (1978). The seven epidemiologic and three cohort mortality studies reported since 1978 were reviewed by Gaffey (1983a, 1983b).

MONS 005277

3

ANALYTICAL PROCEDURES

This chapter focuses on the written analytical procedures for the analysis of PCBs in various matrices. These procedures have been written in sufficient detail that the analyst can implement them in the laboratory with little or no modifications or development. Most also contain detailed descriptions of the apparatus, instrumentation, supplies and reagents necessary for use of the procedure. Table 3-I and the sections below describe the techniques and methods which comprise some of the procedures, the applicable matrices, and the limits of detection, where available. Subsequent chapters are devoted to the specific techniques for PCB analysis and present these techniques in more detail.

The methodology definitions of Taylor (1983), given below in increasing heirarchical order, have generally been followed throughout this book.

Technique: Scientific principle or specific operation (e.g., GC/ECD, Florisil column cleanup, or Webb and McCall quantitation).

Method: A distinct adaptation of a technique for a selected measurement purpose (e.g., a specific GC/ECD operating mode for analysis of PCBs, including column specifications and sample preparation.

Procedure: The written directions necessary to use a method or series of methods and techniques.

Protocol: A set of definitive directions that must be followed without deviation to yield acceptable analytical results. A true analytical protocol is rare, possibly nonexistent, in PCB analysis.

MONS 005278

Table 3-I lists the analytical procedures available for PCBs. Several are general organic pollutant or chlorinated hydrocarbon procedures which include PCBs along with many other analytes. These include Devenish, EPA (Halocarbon), EPA (Priority Pollutant), EPA (soil and sediment), EPA (304h), EPA (B100), EPA (5,A,[1]), EPA (5,A,[3]), EPA (608), EPA (625), EPA (8080), EPA (8250), EPA (8270), and FDA-PAM. The procedures in Table 3-I address a variety of materials including water, wastewater, soil, sediment, sludge, air, combustion and incinerator emissions, capacitor askarels, transformer fluid, waste oil, mixtures of chlorinated benzenes, pigments, food, milk, blood, and adipose tissue.

Extraction and cleanup techniques are presented in Table 3-I in terms of the materials and reagents required for analysis. Less than half of the procedures comment on the criteria required to make qualitative determinations for the presence of PCBs in sample extracts. The quantitation technique for each of the analysis schemes is presented along with the limit of detection (LOD), if specified. More than half of the procedures mention quality control (QC). The quality control steps presented include analysis of blanks, replicates, control samples, spiked additions, and criteria for accuracy, precision, and instrumental performance.

Not all of the procedures listed are sanctioned by a sponsoring organization at this point. Many have interim status and some have been proposed but never endorsed by an organization.

I. ANSI AND ASTM PROCEDURES

The ANSI procedures for the isolation and determination of PCBs in air, water, soil, sediment, and biological materials are based on techniques that were used by the Monsanto Industrial Chemical Company. Packed column gas chromatography with electron capture detection (PGC/ECD) is the designated method for quantitation of PCBs as Aroclors in the ANSI procedures. The PCBs are quantitated against an Aroclor standard using the largest peak, or a secondary peak if the largest peak appears to be interfered with. If the PCB profile is altered with respect to the standard, all major peaks are summed. Mass spectrometry is recommended for confirmation. The cleanup techniques are required only if interferences are noted for the PGC/ECD determination. The quality control measure in the ANSI procedures emphasize the number of theoretical plates and tailing factor for the packed gas chromatography column. The LOD for the procedure is 2 ppb in air, based on an instrumental LOD of 0.5 ng. The calculation

Table 3.1 Standard Procedures of Analysis for PCBs

Procedure Designation	Matrix	Extraction	Cleanup[1]	Determination Method	Qual	Quantitation Method	LOD	QC	Reference
DI/H O 4M	Water	Hexane/ether (1:1)	(florisil) (silica gel)	PGC/ECD[4]	No	Total area or peak height	0.1 µg/l	No	AWWA 1981a
GHD	Water	(1:1)	(florisil) (S removal)	PGC/ECD	No	Area	0.04 to 0.15 µg/l	Yes	EPA 1984a, Longbottom and Lichtenberg, 1982
GCS	Water	(1:1),	None	PGC/ECMS (CGC)	Yes	Area	10 to 40 ug/l	Yes	EPA 1984f, Longbottom and Lichtenberg, 1982
3650	Water	Hexane/ (CH_2Cl_2), (85/15),	(florisil/ silica gel (CH_2Cl_2) (S removal)	PGC/ECD or HECD	Yes	Summed areas or peak height	0.5	Yes	EPA 1978
EPA 1Dy product(s)	Water	Several	Several	HRGC/ECMS	Yes	Ind. peaks	0.5	Yes	Erickson et al 1982, 1983d, EPA 1984a
8081	Water	Hexane	(H_2SO_4) (Saponification) Alumina	PGC/ECD	No	Single peak or summed peaks	2 ppm	Yes	AOAC, 1975
Monsanto	Water	Hexane	Alumina	PGC/ECD	No	Individual or total peak heights	2 ppm	No	Mowrer 1976
EPA 1000	Water	Hexane	silica gel	PGC/ECD	No	0.5	100 ng/l	No	40 CFR 1979 Beranek and Haring Bowen 1980
Method 70	Air, Water, soil, sediment	Hexane or D (CH_2Cl_2)	(H_2SO_4) (saponification) (Alumina)	PGC/ECD	No	Total area	0.5	Yes	AOAC 1981b
EPA (Sediments)	solids and liquids	Several	Several	HRGC/ECMS	Yes	Ind. peaks	0.5	Yes	Erickson et al 1983c
EPA 625 S	Sludge	(1:1)	Several, silica gel, or GPC	HRGC/ECMS or PGC/ECD	Yes	Area	0.5	Yes	Harris and Lopez-Avila 1984

MONS 005280

Table 3-1 (Continued)

Procedure Designation	Matrix	Extraction	Cleanup[c]	Determination Method	Qual.	Quantitation Method	LOD	QC	References
EPA (Petrocarbon)	Sludge	Hexane/ CH_2Cl_2/ acetone (80/15/2)	GPC 5 removal	PGC/ECD	Yes	Peak area or peak height	MS	Yes	Boettinger et al., 1980
Priority Pollutant	Sludge	CH_2Cl_2 (base/ neutral and acid fractions)	GPC	PGC/EIMS	Yes	MS	MS	Yes	EPA, 1979a
8100	Sludge	CH_2Cl_2 (3 fractions)	GPC Silica gel	HRGC/EIMS or PGC/EIMS	Yes	MS	MS	Yes	Boettinger, 1978
8080	Solid waste	CH_2Cl_2	(Florisil)	PGC/ECD	No	Area	3 ng/g	Yes	EPA, 1982a
8250	Solid waste	CH_2Cl_2	Hexane	PGC/EIMS	No	MS	1 ng/g	Yes	EPA, 1982a
8270	Solid waste	$CHCl_3$	Hexane	HRGC/EIMS	MD	MS	1 ng/g	Yes	EPA, 1982a
EPA (spills)	Unspecified	Hexane/ acetone	(CH_2CH) (Florisil) (Silica gel) (Mercury)	PGC/ECD	No	Total area or Wood-McCall	MS	No	Beard and Schoen, 1979
EPA	Soil and Sediment	Acetone/ Hexane	Florisil Silica gel (S removal)	PGC/ECD	No	Computer	MS	Yes	EPA, 1982a
Monsanto	Sediment	CH_2CH	Saponification H_2SO_4 Alumina	PGC/ECD	No	Individual or total peak heights	2 ppm	No	Monin, 1976
ANSI	Sediment, soil	CH_2CH	Saponification H_2SO_4 Alumina	PGC/ECD	No	Single peak or summed peaks	2 ppm	Yes	ANSI, 1976
EPA (by-products)	Air collected on Florisil or XAD-2	Hexane	(H_2SO_4) (Florisil)	HRGC/EIMS	Yes	Ind. peaks	MS	Yes	Erickson et al 1980, 1980a, Erickson, 1984
EPA (ambient air)	Air near hazardous waste sites collected on PUF	Hexane/ ether	Alumina	PGC/ECD	No	Total area or peak height	10 50 ng/m³	No	Lewis, 1982

MONS 005281

Table 1.1 (Continued)

Procedure Designation	Matrix	Interferences	Clean-up	Determination Method	Qual	Quantitation Method	LOD	OK	Reference
EPA (stack)	Incinerator emissions and ambient air collected on filters	Hexane	[illegible]	Perchlorination; then PGC/ECD	Yes	Area	10 ng	No	Wolfe and Bufalo 1977; Beard and Schaum 1978
EPA	Combustion source collected on filters	Pentane or DMSO	Liquid-liquid (silica gel)	PGC/MS	Yes	Area/homolog	0.1 ng/m³	No	Irving et al 1979
EPA (micro orifice)	Stack gas	Pentane/methanol		PGC/MS	Yes	Simple peak	NA	Yes	Beard and Schaum 1978
ANSI	Air (Ambient impinger)		[illegible] (Quantitation: Attorney)	PGC/ECD	No	Simple peak	7 ppb	Yes	ANSI 1978
NIOSH (P&CAM 244)	Air collected on filters	Hexane	None	PGC/ECD	Yes	Peak height or area from standard curve or Webb McCall	0.01 mg/m³	No	NIOSH 1977b
NIOSH (P&CAM 253)	Air collected on filters	Hexane	None	PGC/ECD Perchlorination	No	Peak height or area from standard curve	0.01 mg/m³	No	NIOSH 1977b
EPA (gas)	Natural gas sampled with Tedlar	Hexane	None	PGC/ECD		Total area, peak height or Webb McCall (Perchlorination)	0.1 / ng-m³	No	Harris et al 1981
EPA (S.A.(1))	Blood	Hexane	Liquid-liquid	PGC/ECD	No	NS	NS	No	Watts 1980
EPA (S.A.(1))	Adipose	Pet ether/CH₂Cl₂	Florisil	PGC/ECD	No	NS	NS	Yes	Watts 1980
EPA (9.0)	Adipose	Pet ether/CH₂Cl₂	Sulfonation; Florisil	TLC	No	Semiquant	10 ppm	No	Watts 1980
EPA (9.0)	Milk	Acetone/hexane	CH₂Cl₂ Florisil Silica gel	PGC/ECD	Yes	End peaks	50 ppb	Yes	Watts 1980 Sherma 1980

MONS 005282

Table 3-1 (Continued)

Procedure Designation	Matrix	Extraction	Cleanup[c]	Determination Method	Qual	Quantitative Method	LOD	QC	Reference
AOAC (29)	Food	CH_2Cl_2/Pet. ether	Florisil MgO/Celite Saponification	PGC/ECD	No	Total area or ind. peaks	NS[d]	No	AOAC, 1980a
Tyson	Food	Pet. ether/$(CH_3)_2CO$	Silica gel Saponification (Florisil)	PGC/ECD	Yes	Summed areas perchlorination	NS	No	Tyson, 1976
FDA	Food	Pet. ether/$(CH_3)_2CO$	Silicic acid (Saponification) (Oxidation) (Florisil)	PGC/ECD (PGC/MECD) (DEP-TLC) (DEP-TLC)	No	Area	NS	No	FDA 1977
AOAC (29)	Paper and paperboard	Saponification	Florisil MgO/Celite Saponification	PGC/ECD	No	Total area or ind. peaks	NS[b]	No	AOAC, 1980b
03303-76	Capacitor asbestos	Oil[b]	None	SCOT HRGC/FID	No	Total area	2.8 x 10^{-4} cm³/l	No	ASTM, 1980a
04059-83	Mineral oil	Dilute with hexane or isooctane	Florisil slurry (H_2SO_4) (Florisil column)	PGC/ECD (PGC/MECD)	Yes	Ind. peaks or Webb-McCall	50 ppb	No	ASTM, 1983
EPA (oil)	Transformer fluids or waste oils	Oil	(H_2SO_4) (Florisil) (Alumina) (Silica gel) (GPC), (CH_2Cl_2)	PGC/MECD or /ECD or /ELCD (HRGC)	No	Total area or Webb-McCall	1 ng/kg	Yes	EPA, 1983 Dolfer and Eichenberg 1984
EPA (By-products)	Products or wastes	Several	Several	HRGC/ELCD	Yes	Ind. peaks	NS	Yes	Erickson et al 1982, 1983a Erickson 1984a
OCMA	3 pigment types	A Hexane/H_2SO_4 B CH_2Cl_2	None Florisil	PGC/ECD	No	10 isomers	~ 1 ppb/homolog	Yes	OCMA 1982
OSHA	Chlorinated benzenes	Oil	None	PGC/ELCD	Yes	Total peak height/homolog	NS	Yes	Shen, 1981
EPA (isomer groups)	Unspecified	Not addressed	Not addressed	HRGC/ELCD	Yes	Ind. peaks	NS	Yes	EPA, 1980d

a No specific details
b Direct injection or dilute and inject
c Techniques in parentheses are described as optional in the procedure.
d Or PGC with electrolytic conductivity.

MONS 005283

procedure is not specified. No validation data are given, although general discussions of the applicability of the techniques are presented. The ASTM procedure for water is similar.

The ASTM (1983) procedure for mineral insulating oils utilizes solvent dilution and a Florisil slurry cleanup prior to PGC/ECD determination. The procedure assumes that the composition of the PCBs present in transformer or capacitor oils closely resembles that of the Aroclor standards. It notes that the sensitivity of the ECD is reduced by mineral oil and instructs the analyst to make the amount of oil in the standard and sample equivalent to minimize the effects of the oil interference on the quantitative results.

II. EPA PROCEDURE FOR OILS

The EPA procedure for analysis of PCBs in transformer oils and waste oils (EPA, 1981a; Bellar and Lichtenberg, 1981) provides a generalized approach with respect to sample preparation, and instrumental analysis. Several cleanup techniques are provided as optional approaches in this procedure (see Chapter 6). For the instrumental analysis, GC with halogen specific, electron capture, or mass spectrometry detectors are all allowed, provided appropriate limits of detection can be achieved. A strong quality control program including control samples, daily quality control check samples, blanks, standard additions, accuracy and precision records, and instrumental and chromatographic performance criteria is required to support all data generated by the method.

III. EPA PROCEDURES FOR SPILLS AND INCINERATORS

The EPA procedures for PCB spills and incinerators (Beard and Schaum, 1978) are part of a manual for PCB disposal, primarily focusing on incineration methods. Although this interim report is badly flawed and incomplete, it has been widely used as the guidance document by the EPA Regional Administrators for testing incinerators.

The stack gas is sampled using the modified EPA Method 5 technique developed by Haile and Baladi (1977). PCBs are extracted from the sorbent material in a Soxhlet extractor using both pentane and methanol. The GC/MS analysis is taken from a tentative procedure for PCBs in water (Dudenbostel, 1978). Samples may be chromatographed on columns packed with 3% Dexsil 300, OV-1, or OV-101 and may be detected using either electron impact or chemical ionization mass spectrometry.

MONS 005284

The "Tentative Method for Testing of Polychlorinated Biphenyls (PCBs) in Spilled Material" (Attachment A, Beard and Schaum, 1978) directs the analyst to air-dry the sample (matrix is not further specified), grind it, and then extract a 100-g subsample in a Soxhlet extractor with hexane-acetone (1:1). The procedure then patches into an unreferenced industrial effluent method, which first specifies a PGC/ECD screen. If necessary, various cleanup techniques are specified. An acetonitrile partition is used to remove fats and oils. A Florisil column cleanup fractionates out some pesticides using 6%, 15%, and 50% ethyl ether/petroleum ether eluates. Two alternate silica gel microcolumn cleanups are presented, one of which provides for sulfur removal with mercury.

IV. PROCEDURES FOR FOOD

The FDA (1977), AOAC (1980a), and Japanese (Tanabe, 1976) procedures for food are similar. Samples of food are ground, extracted with petroleum ether, and the lipids removed by an acetonitrile partition. Various cleanup techniques are utilized prior to determination by PGC/ECD.

V. PROCEDURES FOR BY-PRODUCT ANALYSIS

The procedures for by-product analysis (Dow, 1981; OCMA, 1982; Erickson et al., 1982, 1983d; Erickson, 1984a, 1984b, 1984c) all require strong QC programs. The EPA procedures (Erickson et al., 1982, 1983d; Erickson, 1984a, 1984b, 1984c) allow a maximum of flexibility in the extraction and cleanups to accomodate the wide range of matrices (the product and product waste procedure is applicable to liquids, gases, or solids of virtually any composition). In lieu of method control, the procedures rely on the QC, notably the measurement of the recovery of four ^{13}C-labeled PCBs spiked into each sample as recovery surrogates.

MONS 005285

4

SAMPLE COLLECTION AND STORAGE

The first step in any successful analysis is the collection of a sample. The selection of sampling sites, frequency of sampling, number of samples, measurement of physical and chemical parameters of the sample, and the overall statistical design of sampling methods have been provided in extensive detail (see for example, Moser and Huibregtse, 1976; EPA, 1976; Mason, 1982; Kelso et al., 1985). The sampling design in most cases is directly related to the objectives of a specific research program or a regulatory action.

PCBs are an inert, non-polar class of semivolatile organic compounds. As such, they are reasonably well-behaved during sample collection and storage. Consequently, with the exceptions of the air and water sampling techniques which concentrate the PCBs from the matrix onto an adsorbent, most PCB sample collections have utilized the standard or customary methods for semivolatile organics in the subject matrix. For example, the ASTM procedure (1981b) references general methods for water sampling, sediment and soil sampling, and air sampling. The reader is referred to general sampling and storage procedures in the absence of a PCB-specific method. Sampling for chemical analysis has been reviewed (Kratochvil et al., 1984).

I. WATER

Water samples may be collected by grab or integration techniques. Grab sampling has been much more common. The integration techniques include automatic composite samplers, adsorption onto a solid (XAD resin, polyurethane foam, etc.), and liquid-liquid extraction. Since water sampling for PCB analysis may be readily adapted from general water sampling procedures for semivolatile organics, the reader is referred to these procedures for specific guidance. These include EPA's Priority Pollutant Methods 608 and 625 (EPA, 1979a, 1979b, 1984e, 1984f; Longbottom and Lichtenberg,

MONS 005286

1982), ASTM's (1981b) Method D 3304; the EPA Handbook for Sampling and Sample Preparation of Water and Wastewater (Moser and Huibregtse, 1976) and an EPA document on Procedures for Handling and Chemical Analysis of Sediment and Water Samples (Plumb, 1981).

A. Grab Sampling

Most water procedures and methods have used simple grab sampling. For example, EPA's Method 608 for organochlorine pesticides and PCBs in wastewater (EPA, 1979a) stipulates that grab samples be collected in glass containers. A rigorous glassware cleaning method is described in the procedure. Samples must be iced or refrigerated from the time of collection until extraction. If samples will be stored for more than 48 hours, the pH is to be adjusted to between 6.0 and 8.0.

The Bodman bottle can collect up to 90 L (Palmork et al., 1982; Harvey and Steinhauer, 1976). As the sample is lowered, water flows through a weighted aluminum cylinder. At the desired depth, plates at either end are closed and the sample is retrieved. The sample is transfered to steel drums under nitrogen for storage. A glass sphere which collects a 10-L sample has the advantage of direct hexane extraction in the sample vessel (Palmork et al., 1982). Extraction in the sampling vessel not only reduces the volume of sample to be stored, but also minimizes adsorptive losses to the container walls. The use and specifications of two large-volume grab samplers were described for sampling seawater (Pavlou et al., 1980). The samplers were designed to be used in conjunction with a filtering system (also described) to collect large volumes of particulate.

A gaslift system can collect unlimited water volumes (Palmork et al., 1982). Water is aspirated through a 3/4 in. stainless steel pipe by injecting nitrogen near the base of the pipe. Marine water can be collected at 8 to 10 L/min at a depth of 10 m and transferred directly to stainless steel drums to prevent contamination by the shipboard environment.

B. Automatic Composite Samplers

An automatic composite sampler generally consists of a pump, tubing, a timer, and a collection vessel. Typically, the timer cycles the pump on for a fraction of every hour, during which water is pumped into the collection vessel. This permits collection of an integrated sample from a flowing water stream over a 1-day period or longer. The EPA

MONS 005287

(1979a,b) stipulates that automatic samplers use refrigerated glass containers for the water-sample and that the equipment be as free as possible of Tygon tubing and other potential sources of contamination.

C. Solid Adsorbent Sampling

A wide variety of solid adsorbent materials have been investigated for use in water sampling. The objective has been to preconcentrate PCBs from a large volume of water onto a small volume of solid adsorbent which may be easily transported, stored, and extracted. In addition to its convenience, preconcentration can enhance the method detection limit.

As discussed below, investigators have reported mixed results with adsorbent columns. Background from the sorbent, poor precision, and non-quantitative recovery have all been reported. Thus, investigators must demonstrate that results obtained with these sampling techniques are valid. Risebrough et al. (1976) reviewed early uses of solid adsorbents to sample seawater.

1. Polyurethane foam: The use of polyurethane foam (PUF) to adsorb PCBs from water samples was reported by Gesser et al. (1971). They reported 91 to 98% recovery from 1-L samples passed through a PUF plug in a glass column. The PCBs were recovered from the sorbent with 20 mL acetone, followed by 100 mL hexane. Bellar and Lichtenberg (1975), however, noted that this technique was not applicable to river water samples, since the suspended solids plugged the column. Uthe et al. (1974), reported success with PUF coated with DC-200 silicone grease. They used their plugs as indwelling monitors; the plug is submerged in a water system to collect PCBs as they come in contact with the sampler as shown in Figure 4-1. While the simplicity and low cost of this system make it appealing, the authors did not validate the PCB concentrations against an accepted method. Bellar and Lichtenberg (1975) noted that this method led to poorer precision and accuracy with dosed river water than with distilled water.

An active in situ seawater sampler using PUF plugs permits collection of PCBs from large water volumes (Risebrough et al., 1976). The sampler contains five PUF plugs in a 975-cm^3 tube. The sample is lowered to depth and water pumped at 500 mL/min by a vacuum hose connected to the ship. The PCBs are subsequently extracted by successive elution with 500 mL each acetone and hexane. The PCB concentrations obtained from 26 to 79 L samples by this sample compared

MONS 005288

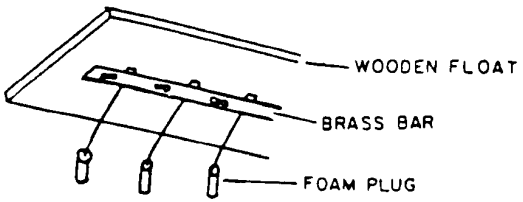


Figure 4-1. Passive Water Sampling Device

Polyurethane foam plugs are held just beneath the water surface.

Reprinted, with permission, from Uthe et al. (1974); copyright 1974 by Marcel Dekker, Inc.

---

favorably with those obtained by methylene chloride extraction and were about twice those obtained with hexane extraction.

Ahling and Jensen (1970) used PUF coated with n-undecane and Carbowax 4000 monostearate to effect a "reverse phase liquid-liquid partitioning." Water samples (up to 200 L) were concentrated onto 3 g of sorbent and then desorbed with 5 mL petroleum ether. Recoveries of 93 to 100% were observed for 10 µg of Clophen A50 added to 5-L water samples.

2. Macroreticular resins: The use of macroreticular resins (specifically the Amberlite XAD series) has been reported by several groups (Musty and Nickless, 1974a; Lawrence and Tosine, 1976; Harvey and Steinhauer, 1976; Osterroht, 1977; Coburn et al., 1977; Picer and Picer, 1980; Palmork et al., 1982; and Eisenreich et al., 1983a). Musty and Nickless (1974a) reported an overall recovery of 76% after one liter of tap water spiked at the ppb level was adsorbed onto XAD-4 (a styrene-divinylbenzene copolymer), and then eluted with diethyl ether-hexane mixture. Coburn et al. (1977) reported 78 to 86% recovery of an Aroclor mixture from 2-L natural water samples collected on XAD-2 (also a styrene-divinylbenzene copolymer), and then eluted with ether.

Recovery of chlorinated hydrocarbons, including PCBs, was reported to be low and variable by Picer and Picer (1980). In fact, they noted that the results of a collaborative study produced results varying by over two orders of magnitude from replicate XAD-2 resin cartridges which had been prepared by one laboratory.

A column containing 50 mL XAD-2 was used to extract PCBs from 50 to 200 L of seawater which had been collected in a 65-L sampler (Harvey and Steinhauer, 1976). The water was pumped through the column at a rate of 5 bed volumes/min. The authors noted that the flow rate was critical to selective adsorption of the organochlorines relative to other organic matter. PCBs were eluted from the column with acetonitrile. The precision, based on replicate analyses, was within ± 20%. The accuracy based on comparison to solvent extraction of 50-L aliquots of the same sample was also within ± 20%.

Eisenreich et al. (1983a) used XAD-2 to concentrate PCBs from Lake Superior water. The 40-L sample size permitted the authors to quantitate PCBs with average concentrations around 1 ng/L (parts per trillion). The resin was extracted in a Soxhlet extractor using a 1:1 mixture of hexane and acetone. No validation data were given.

3. Tenax GC: Leoni et al. (1976b) reported essentially quantitative recovery of 1.6 ppb of PCBs spiked into 10 L of seacoast water which were concentrated without filtration onto a column packed with a mixture of Celite (diatomaceous earth), and Tenax GC [poly(2,6-diphenyl-p-phenylene oxide)]. The PCBs were eluted with diethyl ether. They noted that it was often necessary to filter water samples, but did not measure PCB recovery under these conditions. Picer and Picer (1980) reported considerable background from Tenax columns using a variety of cleanup and desorption solvents.

D. Liquid-Liquid Extraction Sampling

Ahnoff and Josefsson (1973, 1974, 1976) reported the use of a continuous liquid-liquid extractor which concentrated PCBs from hundreds of liters of river water into 100 to 300 mL of lighter-than-water solvent. The sampler mixed the water and solvent with a stirring bar. Water entered from the top and exited from the bottom. Pumping rates were variable up to about 5 L/hr. Recoveries of chlorinated pesticides were > 80%. PCB concentrations in river water were measured as low as 0.1 ng/L.

MONS 005290

E. Rainwater Sampling

Rainwater sampling can employ simple apparatus. For example, stations for continuous collection of rain plus dry deposition (Bidleman et al., 1981a) consisted of 22-cm diameter stainless-steel funnels which emptied into 3 8-L brown-glass jugs. The funnels were placed about 2 m above a marsh surface and were surrounded with wire spikes to discourage perching birds. These "continuous" stations were tended at 2 to 3 week intervals. Event rain samples were collected by exposing stainless-steel bowls during rainstorms.

More elaborate apparatus designed to either concentrate the water sample as it is collected or to prevent dry deposition of particulate is used more often. For example, Murphy et al. (1981) used a sampler which concentrated PCBs onto a sorbent for their studies of PCB deposition in the Great Lakes. Rain fell on a 1.5 m^2 surface, was filtered through glass fiber, and then the PCBs sorbed onto polyurethane foam. This approach, however, was subsequently abandoned in favor of an integrated wet/dry sampler, which simply collected the rainwater in buckets. The sampler had a roof which automatically uncovered a bucket at the start of a rainfall.

Two samplers have been described which automatically collect rainwater and concentrate it onto a resin cartridge (Strachan and Huneault, 1984; Pankow et al., 1984). Both systems sense rainfall and automatically open a cover for the collection period. The rain then falls on a clean surface and flows toward the sorbent cartridge. Strachan and Huneault used XAD-2 or XAD-7 resin. Recoveries from the XAD-2 were higher than from the XAD-7 (86% versus 68% for several pesticides). Pankow et al. (1984) used Tenax-GC as the adsorbent.

F. Water Sample Storage

Most general procedures (e.g., the EPA priority pollutant methods) merely specify cold storage, sometimes in the dark or in amber bottles. No special precautions are stipulated for PCBs.

The adsorption of PCBs from water onto the container wall has been reported (Pepe and Byrne, 1980; Muldrew et al., 1981; Sutcliffe and Nielsen, 1983). If precautions are not made to prevent these adsorptive losses during sampling and storage, then the extraction technique should include extraction of the interior of the sample container.

MONS 005291

The use of formaldehyde has been shown to preserve water samples for PCB analysis as shown in Figure 4-2 (Bellar and Lichtenberg, 1975). Aroclor spiked in river water at 1 µg/L decreased steadily over a 15-day study in unpreserved samples, while no losses were observed when an unspecified amount of formaldehyde had been added. The temperature and light conditions were not specified. The authors noted greater losses with the congeners containing ≤ 3 chlorine atoms. Other preservation techniques were less effective: over the range of 2.7 to 10.5, pH had no effect on storage losses. Both refrigeration and the absence of light retarded PCB loss relative to storage at ambient temperature in the light, but still showed significant losses, as shown in Figure 4-2. The authors noted that the rate of loss appeared to be affected by the physical, chemical, and biological characteristics of the samples. They also documented a faster rate of loss with Teflon than with aluminum cap liners; although no PCBs could be recovered by extraction of the Teflon liners.

Storage temperature (4°C versus 24°C), pH (2, 7, and 10), and chlorine (0 or 2 ppm NaOCl) did not markedly affect the recoveries of seven different Aroclors from clean water after storage for 7 days (Millar et al., 1981, 1982). Most of the samples exhibited greater than 90% recovery.

Sorption of PCBs to glass and plastic surfaces has been shown to cause significant losses (Pepe and Byrne, 1980; Muldrew et al., 1981; Sutcliffe and Nielsen, 1983), although the first two studies are flawed in that the concentration of the ^{14}C-2,2',4,4',5,5'-hexachlorobiphenyl was well in excess of either the water solubility or environmentally significant levels. Nevertheless, sorption onto the sample container (and the cap) should be considered as a potential source of loss from a sample.

Under most storage conditions, photochemical, chemical or biological degradation of PCBs in water samples appear unlikely. However, as noted in the two preceeding paragrapns, losses due to physical removal have been observed and can be significant. The sorption of PCBs onto glass, particulate, and other surfaces is only to be expected, given their low water solubility and high octanol-water partition coefficients. It may be that the preservation effects of formaldehyde noted by Bellar and Lichtenberg (1975) above, may have been simply the effect of increasing the solubility of the PCBs in the sample by the addition of a water-miscible organic "solvent."

Analysts can generally counteract sorptive losses by treating the entire interior of the sample vessel (water,

MONS 005292

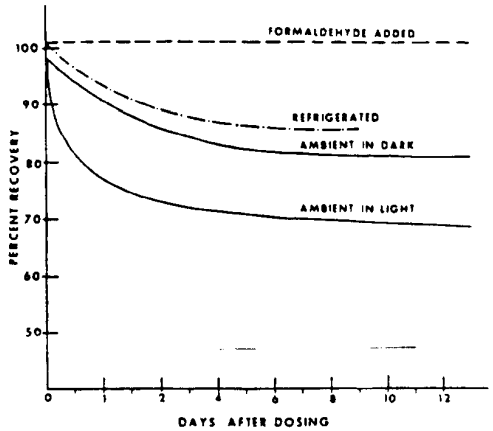


Figure 4-2. Effect of Storage Conditions on Recovery of Aroclor 1016 from River Water

Samples were dosed at 1 µg/sample, stored at ambient temperature (in light and the dark) under refrigeration, and preserved with formaldehyde.

Reprinted, with permission, from Bellar and Lichtenberg, 1975; copyright 1975 by American Society for Testing and Materials.

MONS 005293

surface, and cap liner) as part of the "sample." If the sample container is extracted and combined with the water extract, the adsorbed PCBs should be recovered. In addition, the use of spiked field controls and/or samples which are spiked (standard addition) in the field as part of the overall QC (see Chapter 9) should aid the analyst in assessing any losses during storage.

II. AIR

The general category of air sampling encompasses a wide variety of objectives and techniques. Ambient (i.e., breathable) air includes both indoor and outdoor sites, and may be sampled using personal, fixed, and atmospheric deposition sampling techniques. The non-ambient air which has been sampled is stack gas from incinerators, power plants, etc. Regardless of the air type or sampling objective, nearly all reported procedures involve some technique of concentrating the PCBs from the air to a much smaller volume of solid or liquid sorbent; usually with an active pumping mechanism to draw the air through the sorbent medium. The only exceptions to active sampling are the techniques designed to monitor atmospheric deposition.

Air sampling techniques must quantitatively concentrate the PCBs from the air. In addition, the PCBs must be recoverable, the sorbent medium must not generate interferences, and the entire process must be shown to accurately reflect the true concentration in air. This section presents the techniques used for air sampling and also discusses the validation and utility of the techniques.

A. Ambient Air

1. Solid sorbents: Several of the common solid sorbents have been used for collection of PCBs from air--porous polyurethane foam (PUF), Florisil, and XAD-2. With all of these sorbents, the PCBs are rather loosely bound and migrate slowly through the medium with the air flow, just as they do through a gas chromatography column. Thus, a major task in characterizing a sorbent is assessing the breakthrough volume. The more volatile, lower-chlorinated PCBs break through first, so many of the recovery studies show poorer recoveries for these compounds than for the heavier homologs.

a. Polyurethane foam: PUF plugs have been extensively studied by Bidleman and coworkers (Bidleman and Olney, 1974; Simon and Bidleman, 1979; Burdick and Bidleman, 1981; Bidleman and Leonard, 1982; Billings and Bidleman,

MONS 005294

1980, 1983; Bidleman et al., 1981b, 1983, 1984). Commercially available PUF is cut into cylindrical plugs (e.g., 7.6 cm diameter x 7.6 cm thick). The plugs are then extracted in a Soxhlet (Billings and Bidleman, 1983), or by repeated manual compression (Erickson et al., 1980a) with organic solvents. The plugs are then dried in a vacuum desiccator at 40 to 45°C (temperature is not critical). The movement of 3,3'-dichlorobiphenyl and 2,4',5-trichlorobiphenyl through PUF has been studied (Burdick and Bidleman, 1981; Bidleman et al., 1983). They found that the penetration depths of the PCBs depended on the ambient temperature and volatility of the compound and were linearly related to the total air volume, i.e., the system behaves like a gas-solid chromatograph. Even for these lighter PCBs, breakthrough volumes for a 15-cm PUF plug at 20°C were over 1,000 m^3. Thus, PUF may be used for high-volume air sampling. Bidleman's group has typically collected 600 to 1,500 m^3 of air with PCB concentrations ranging from 0.08 to 100 ng/m^3, measured as Aroclor 1016 and 1254. The blank values for the PUF plugs were in the 5 to 10 ng/plug range for freshly cleaned plugs and 10 to 20 ng/plug range for plugs used after 3 months of storage.

Lewis et al. (1977a,b) reported collection efficiencies in the 70 to 85% range for different Aroclors when 200 to 325 m^3 of air containing 19 to 153 ng/m^3 PCBs were sampled through 5-cm diameter x 7.6 cm PUF plugs. The collection efficiency correlated with the degree of chlorination. Using PGC/ECD, they calculated a theoretical detection limit of 0.1 ng/m^3. Lewis and Jackson (1982) reported improved collection efficiencies with a dual sorbent cartridge consisting of a 25 cm^3 bed of granular sorbent sandwiched between two PUF plugs (5 cm thick upstream and 2.5 cm thick downstream). The granular sorbents tested were Chromosorb 102, Porapak R, XAD-2, Tenax GC, and Florisil. No specific sorbent was recommended. The sampling cartridge was Soxhlet-extracted without disassembly. The results, shown in Table 4-1, indicate improved collection for the lighter PCBs (di- and trichlorobiphenyls) over PUF alone. Lewis and MacLeod (1982) reduced the size of the cartridge to 2.2 cm diameter x 6 cm for use in personal sampling. At flow rates of 3.8 L/min and a total sampling volume of 900 L, recoveries of Aroclor 1242, 1254, and 1260 were 96%, 95%, and 109%, respectively. An analytical procedure has been prepared, which summarizes the method (Lewis, 1982).

Oehme and Stray (1982) and Oehme and Ottar (1983) used PUF plugs to sample arctic air for extremely low levels of PCBs. They reported a sampling efficiency of 80 to 100% for the first 11-cm diameter x 5 cm plug. The levels

MONS 005295

Table 4-1. Collection Efficiencies of Sorbents

Chlorobiphenyl	Calcd Air Concn (ng/m³)	PUF Alone	% Collected[a] After 24 hr at 225 l/min PUF / Chromosorb 102	PUF / Porapak R	PUF / XAD-2	PUF / Tenax GC	PUF / Florisil PR
4,4'-DB	2.0-20	67	87	82	96	85	111
2,4,5-Tri	0.2-2.0	16	80	87	91		92
2,4',5-Tri	0.2-2.0	86	81	89	93	80	88
2,2',5,5'-Tetra	0.2-2.0	94	81	88	88	81	92
2,2',4,5,5'-Penta	0.2-2.0	92	79	92	96	84	97
2,2',4,4',5,5'-Hexa	0.2-2.0	86	84	92	95	85	93

a Average of 6 to 12 determinations
Source: Lewis and Jackson, 1982 Reprinted with permission, copyright 1982, American Chemical Society

MONS 005296

found in arctic air using HRGC/EIMS ranged from 0.2 to 4.0 pg/m³ measured as Cl_6 and Cl_7 homologs and from 0.6 to 5.0 pg/m³ measured as Phenochlor DP6. Other investigators reporting successful use of PUF plugs include Erickson et al. (1980a), and Stratton et al. (1978). Although PCBs were not studied, Adams and Caro (1980) published an extensive study of the utility of PUF as a sorbent for pesticides from air. In a review of available methods for ambient air, Margeson (1977) recommended the use of PUF for sample collection.

b. Florisil: Florisil, a magnesium silicate salt, has been widely used for stack sampling applications, but its application to sampling PCBs from ambient air has been rather limited. Small sampling cartridges containing 0.3 g of deactivated Florisil (3% water w/w) and 1 g of anhydrous sodium sulfate were used to sample for up to 60 hr at 2 to 4 L/min air flow (Giam et al., 1975). PCB concentrations were in the 35 to 90 ng/m³ range. Losses during sampling were negligible, even after 5 days of sampling at 2 to 3 L/min air flow.

The NIOSH (1977 a,b,c) methods for PCBs in air utilize Florisil tubes which are sampled with a personal sampling pump at 50 to 200 mL/min. The glass tubes are 4 mm ID x 7 cm long with two sections of 30/48 mesh deactivated Florisil containing 100 mg and 50 mg (backup). Glass wool preceeds the first section; PUF separates the sections and follows the backup Florisil. PCBs are solvent-desorbed and determined by PGC/ECD. A collection efficiency of 100% is reported for a 50-L air sample with PCB concentrations of up to 10 mg/m³. This method was recently used to sample for 2,2',4,4'-tetrachlorobiphenyl as a by-product in 2,4-dichlorobenzoyl peroxide manufacture (Rubenstein, 1983). The PCB concentrations were in the 100 to 200 ng/m³ range.

The Ontario Ministry of the Environment uses Florisil cartridges to sample air in their ambient air surveys (Singer et al., 1983). The cartridge blanks average less than 0.3 ng/m³ PCBs/m³ air.

c. XAD-2: The macroreticular resin XAD-2 is a styrene-divinylbenzene copolymer with a surface area of 300 to 350 m²/g. The successful use of XAD-2 with a high volume sampler has been reported (Doskey and Andren, 1979). The XAD-2 was held in a resin capsule with 60-mesh screens. Two 70-g portions of the resin were sampled in tandem. The resin was cleaned up by first drying at 60°C overnight, then Soxhlet-extracting with petroleum ether for 72 hr, then drying as before. At a flow rate of 0.5 to 0.7 m³/min (total air volume of 700 to 3,100 m³), 90% collection efficiencies were reported for a tetrachlorobiphenyl and Arocior 1221.

MONS 005297

Under similar conditions, 90 to 95% recoveries of Aroclors 1221, 1242, and 1254 have been reported (Hollod and Eisenreich, 1981; Eisenreich et al. 1983b). Only 100-400 m^3 of air could be sampled before breakthrough occured.

d. Comparison of sorbents. PUF, silicone oil coated on PUF, Florisil, and XAD-2 were evaluated (Doskey and Andren, 1979) using ^{14}C-labeled 2,2',5,5'-tetrachlorobiphenyl. The retention of the PCB spiked (300 ng) onto the top of the sorbent was tested with flow rates of 3 to 7 L/min and total sample volumes of 7 to 26 m^3. XAD-2 and Florisil exhibited essentially quantitative retention of the PCB, while the PUF exhibited 80% retention and the silicone oil coated PUF exhibited 58% retention. The collection efficiency was then measured. The radiolabeled PCB (150 ng) was also vaporized into the air stream and then collected by the sorbents. The coated PUF was not evaluated due to its poor performance in the previous experiment. At flow rates of 5 to 16 L/min and total sample volumes of 5 to 17 m^3, the XAD-2 and Florisil collected the PCB at 99 and 100%, respectively. The efficiency of the PUF was measured at 50%. XAD-2 was selected over Florisil as the sorbent of choice because it was coarser, had a lower pressure drop, and thus permitted higher air sampling rates.

Billings and Bidleman (1983) compared PUF, Tenax GC, and XAD-2 in field studies. All three effectively collected Aroclor 1254 on a 10 to 20-g trap with negligible penetration to a backup trap. In a 24-hr sampling period (500 to 700 m^3 air) at 20°C, about 15% of Aroclor 1016 broke through the backup trap with PUF. The breakthrough was less for the other two sorbents. The ambient concentrations found with the three sorbents agreed well; generally within 10 to 15%.

2. Liquid sorbents: In methods involving liquid adsorbents, the air is bubbled through the liquid trapping medium. As reviewed by Margeson (1977), a wide variety of glassware geometries and liquids, ranging in volatility from hexane to ethylene glycol, have been used. The latter is used in an EPA (Watts, 1980) method for pesticides and PCBs. Air is bubbled through two impingers in series containing 100 mL of ethylene glycol each, with a glass fiber filter in front to trap particulate matter.

The ANSI (1974) procedure for PCBs in air uses toluene. An unspecified volume of air is drawn through one or more gas scrubbers containing toluene. The procedure notes that neither the capacity nor the collection efficiency has been evaluated. It further cautions the user to make only comparative measurements with samples collected under equivalent conditions.

MONS 005298

1. Sampling apparatus: The sampling apparatus for PCBs is no different from that used for other semivolatile organics. A typical sampling train includes a filter, sorbent, pump, and a volume or flow-rate measurement device. A filter (e.g., glass fiber) often preceeds the collection medium to filter out particulate matter, insects, etc. The filter generally contains only a small fraction of the PCBs at normal temperatures. In cold climates, this may not be true and analysis of the filter should be considered.

Air is drawn through the filter and sorbent assembly by a pump. The size and type of pump depend on the desired detection limit and portability required. Collection of sufficient sample to detect PCBs at low concentrations requires either a high sampling rate (i.e., big pump), or long sampling periods. Personal sampling requires small, battery-powered pumps. In addition to the pump, most samplers include a volume or rate measurement device. This may be a dry gas meter or simply a pump cycle counter. Regardless, the system must be calibrated before use. It is important that the exhaust air be vented away from the intake to prevent recycling of the same air.

a. High volume samplers: A number of investigators have modified the classic "Hi-Vol" for PCB sampling by inserting sorbent cartridges in the throat between the 8 x 10 in. (20 x 25 cm) filter holder and the motor. These samplers generally operate at flow rates of about 1,000 L/min. Among those using these samplers are Eisenreich et al. (1983b), Bidleman and Olney (1974), Billings and Bidleman (1983), and Lewis et al. (1977a). A sampler based on the designs of Lewis and Jackson (1982) is commercially available (Model PS-1, General Metals Works Company).

b. Medium volume samplers: Erickson et al. (1980a) reported the use of a sampler which collected air at rates up to 250 L/min.

c. Personal samplers: A personal sampler, capable of sampling up to 4 L/min for at least 12 hr was developed by the EPA (MacLeod, 1979; Lewis and MacLeod, 1982). The air was pumped by a DuPont P-4000 constant flow sampling pump. PCBs were collected on a small PUF cartridge. Concentrations from < 10 to 10,000 ng/m^3 were reported.

4. Atmospheric deposition: The measurement of atmospheric deposition is an important link in environmental fate studies involving aerial transport of PCBs. Atmospheric deposition may be divided into rainfall (discussed above in the water section) and dry deposition. Dry deposition is generally measured by passively sampling on a flat surface.

MONS 005299

the surface may be dry or wetted with mineral oil (McClure, 1976; Heesen et al., 1979), glycerin (Christensen et al., 1979), a mixture of diols and water (Murphy et al., 1981a) or other liquids. Bidleman et al. (1981a) and Christensen et al. (1979) collected PCBs on large aluminum baking pans. They compared the collection efficiency of dry, water-filled, and water/glycerin-coated (50:50) pans. The wet surfaces collected 1.5 to 3 times more than the dry pans. The use of coated horizontal surfaces appears to be the only common dry deposition collection technique (Andren, 1983), although its validity has not been established and is, in fact, open to considerable question (Andren, 1983). An exchange of comments by Murphy et al. (1981b) underscores both the theoretical and practical differences in the collection mechanisms of wet versus dry surfaces. They also note that the polarity of the wetting agent can affect the collection efficiency. It is possible that wet surfaces collect PCBs not only by deposition but also by adsorptive scavenging of vapor-phase components which would not normally settle out.

An innovative approach to obtaining realistic atmospheric deposition samples is ice coring (Murphy and Schinsky, 1983). Multiple cores (7.6 cm dia. x 10 to 80 cm in length) were composited to get representative samples of sufficient volume for detection. A net deposition rate of 2.0 g/km^2/mo was measured for Saginaw Bay in Lake Huron.

5. Direct sampling: Direct introduction of an air sample into a mobile mass spectrometer system has been reported (Thomson et al., 1980; Thomson and Roberts, 1980, 1982). The system allows a 2-min average concentration to be measured at 3- to 4-min intervals. The detection limit was estimated to be in the nanogram per cubic meter range.

6. Discussion of ambient air sampling techniques: There is no clear mandate for one particular sampling technique. The use of solid sorbents is preferable to liquid sorbents for several reasons. Higher air volumes may be sampled. The solid sorbent is more portable and more adaptable to personal monitoring. The apparatus is simpler.

Regardless of the sorbent or the apparatus used, background contamination, breakthrough losses, and sample recovery must all be monitored by careful validation and quality control. Before sampling, the volume or flow rate device must be calibrated and the system checked for leaks.

An interesting observation by Billings and Bidleman (1983) may serve as a good rule of thumb: "Because vapor pressures of pesticides and PCB isomers increase rapidly with temperature, a 5°C rise in temperature has nearly the same

effect on sample penetration [into the sorbent] as doubling the air volume."

B. Source Sampling

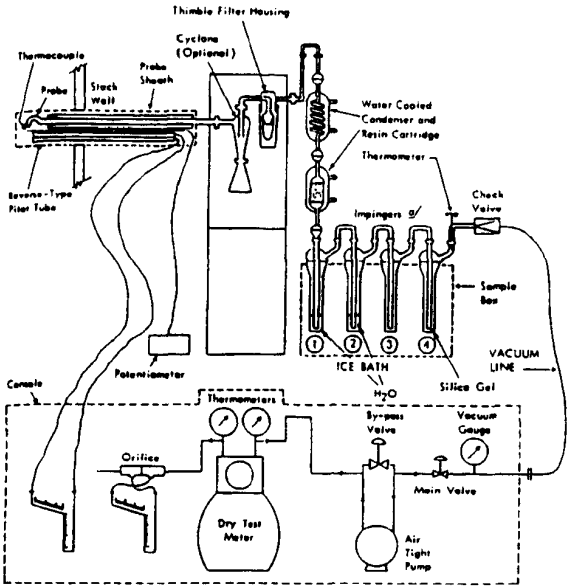
Stationary source emissions (stack or flue gas) represent the point of entry into the environment for many pollutants, including PCBs which may be in stack gas as a result of incomplete combustion during PCB incineration, or may be passed through from contaminated fuel. Since stack emissions of PCBs are controllable, measurement of PCBs and stack gases is important. In addition, the measurement of PCBs in the stack gas during trial burns of PCB incinerators is required in the United States to assess the destruction efficiency (EPA, 1979d; EPA, 1983a; Erickson and Shah, 1983; Ackerman et al., 1983).

Stack gas differs from ambient air in several respects. The gas is generally hot (70°C to 500°C), flowing rapidly (5 to 20 m/sec), and hostile. The gas can contain large amounts of particulate, is often corrosive, and is nearly always laden with water. All of these properties must be considered when collecting stack gas samples.

1. Sampling techniques: Sampling methods for PCBs have been adapted from the general stack sampling methods used to measure particulate, acids, and other stack effluents. The sampling train used most often in the U.S. is the modified EPA Method 5, shown in Figure 4-3. The stack gas is drawn in through a probe. The sampling rate is adjusted so that the flow into the probe matches that in the stack (isokinetic sampling) to minimize the flow disturbances which would discriminate the gas sampled according to particle size. The filter collects particulate at the same temperature as the stack. The resin cartridge (generally XAD-2) is designed to collect PCBs and other semivolatile organics. The impingers collect water and vapors (e.g., HCl). The geometry and sequence of the resin cartridge and impingers differ among investigators. Different impinger styles and sequences have been employed to deal with specific stack situations (high temperature, high particulate loading, etc.). The modified Method 5 train is generally operated at 1 cfm (28 Lpm) to collect a 2 to 10 m^3 sample. The modified Method 5 uses all glass or glass-lined tubing, so corrosion is not generally a problem.

The filter for the Modified Method 5 should not be used to obtain the Method 5 total particulate emissions from the stack in addition to measuring the PCBs. The particulates are measured gravimetrically after the filter has been dried to a constant weight. This drying process can vaporize the PCBs off the filter, resulting in low PCB recoveries.

MONS 005301



a/ Impingers 1, 3 and 4 are of the Modified Greenburg-Smith Type
Impinger 2 Is of the Greenburg-Smith Design
Impingers 1 and 2 Contain 100 ml Water
Impinger 3 Empty
Impinger 4 Contains 200-300 Grams Silica Gel

Figure 4-3. Modified Method 5 Train for Organics Sampling of Stack Gas

Reprinted from Haile et al. (1983a).

Another sampling train used in the United States, the Source Assessment Sampling System (SASS) train (Fearheller et al., 1976; Lentzen et al., 1978) has not been widely used for PCB sampling. Quantitative collection and recovery of PCBs may not be possible with this system. In addition, the SASS train has many stainless steel parts, notably the sorbent module. Corrosion of these components has been noted to be a serious problem, especially with high concentrations of HCl, such as during PCB incineration (Ackerman et al., 1983b). A side-by-side comparison of the MM5 train with Florisil sorbent and the SASS train with XAD-2 sorbent at a utility oil-fired boiler was inconclusive (Hunt et al., 1984). No PCBs were detected in the samples from either train. The SASS train demonstrated a higher PCB destruction efficiency solely on the basis of the larger stack gas sample volume.

A simple sampling device, consisting of a filter, one condensate trap, and an XAD-2 cartridge was reported by Junk and Richard (1984). Mono- through hexachlorobiphenyls were quantitatively collected from 200°C air by the system at the 10 ng/m^3 level with a collection volume of 5 m^3. The PCB concentrations in a power plant stack were comparable when collected by either this simple sampling train or SASS.

Lovett et al. (1983) reported a direct sampling/analysis system. Stack gas from an incinerator is pumped from an incinerator stack through a 10 μm filter and through a heated transfer line to an atmospheric pressure chemical ionization mass spectrometer (see Chapter 7) mounted in a van. Using this system, the concentration of PCBs in the stack gas could be measured every 3 min with a method detection limit of 8 μg/m^3.

More detailed discussions of sampling trains and their use are presented elsewhere (Ackerman et al., 1983b; Stanley et al., 1982; Erickson et al., 1982, 1983d; Erickson, 1984b; Haile and Baladi, 1977; Beard and Schaum, 1978; EPA, 1977; Johnson and Merrill, 1983).

2. Solid sorbents: The sorbent cartridge of the modified Method 5 and, presumably, other trains can accomodate any granular sorbent.

Adams et al. (1977) studied the breakthrough of Aroclor 1242 on XAD-2 in a study of sorbents for use in SASS and modified Method 5 trains. They found no breakthrough under experimental conditions and projected that XAD-2 would quantitatively trap PCBs under stack sampling conditions.

MONS 005303

Haile and Baladi (1977) recommended Florisil over Tenax GC and XAD-2 for PCB sampling in a modified Method 5 train because of its lower background and high trapping efficiency. In laboratory studies, they found sampling efficiencies of 86 to 92% for Aroclors with Florisil. At flow rates of 17 to 20 L/min and ambient temperatures, Florisil and Tenax-GC exhibited much better recovery from an adsorption/desorption experiment as shown in Table 4-II. Subsequent adsorption/desorption experiments at 120°C found only 50 to 70% recoveries for Florisil while interferences prevented quantitation of the dichlorobiphenyl from the Tenax. Thus, they recommended cooling the gas before the sorbent to improve adsorption efficiency. The combined sampling efficiency and method recovery of the Florisil in the field sampling train is shown in Table 4-III. A recovery of 88% for Aroclor 1221 from XAD-2 in the sampling train was also reported.

Hanneman (personal communication, 1982) reported that PCBs were not retained at acceptable levels on common solid adsorbents when the flue gas temperature was greater than 150°C or in cases where the air contained an aerosol of a nonpolar material in which PCBs are very soluble. Hanneman reported successful collection of PCBs in these instances using PUF plugs coated with liquid polydimethylsiloxane. Several plugs of the coated polyurethane were placed in a water-cooled jacket to sample the air at elevated temperatures. A PCB congener was added to the surface of the foam plugs as a surrogate prior to sampling. A second PCB congener was added to the foam plugs after sampling to monitor surrogate recovery and collection efficiency.

More recently, Haile et al. (1983a) examined the PCB collection recovery efficiency for a modified Method 5 train with XAD-2 as the sorbent. Aroclor 1254 was spiked at two levels (110 and 1,100 µg total) into a simulated flue gas during an 8-hr laboratory test. The recovery was measured by GC/MS as total tri-, tetra-, penta-, and hexachlorobiphenyls. The total recoveries from both the probe rinse and train extract ranged from 68 to 99%. While there was no notable trend with homolog in the total recovery, the distribution between the probe rinse and train extract was most illuminating. Only the trichlorobiphenyls were volatile enough to collect appreciably in the train (~ 30%). The rest of the PCBs apparently adsorbed to the first cooled surface they encountered--the probe. These data suggest that the type of sorbent is not nearly as important as the provision of a cool surface for the PCBs to condense onto. Thus, sample collection apparatus geometry and temperature may be of much greater importance than is commonly realized.

TABLE 4-II

COMPARISON OF ADSORPTION AND RECOVERY EFFICIENCY OF THREE SORBENTS

	Adsorbent[a]		
	Florisil	Tenax	XAD-2
Sampling rate (L/min)	17[b]	20	20
Recovery (%)			
2,2'-Dichlorobiphenyl	71.4	82.7	34.0
2,2',4,5'-Tetrachlorobiphenyl	90.5	92.8	59.2
2,2',3,3',4,4'-Hexachlorobiphenyl	80.6	91.0	57.0
Mean	80.8	88.8	50.1

a Similar volumes of sorbent in a 22-mm ID tube sampled at ambient temperatures. PCBs vaporized in air upstream of sorbent.
b Maximum flow rate obtainable.
Source: Haile and Baladi (1977).

TABLE 4-III

SAMPLING EFFICIENCY OF FLORISIL SAMPLING TRAIN

PCB Mixture	Total Spike (μg)	Recovery[a] (%)
Aroclor 1221	23.8	86 ± 9
Aroclor 1242	18.2	88 ± 10
Aroclor 1254	11.6	92 ± 3

a Average and standard deviation for six tests.
Source: Haile and Baladi (1977).

MONS 005305

Based on the work by Haile and Baladi (1977) which was recommended by EPA's interim manual (Beard and Schaum, 1978), Florisil has often been used to trap PCBs from stack gas. For example, it was used in the first (October 1979) trial burn at the ENSCO incinerator in El Dorado, AR (EPA, 1981b), and at two industrial boiler tests (Hall et al., 1982; Polcyn et al., 1983). One disadvantage is its relatively fine mesh which results in a high pressure drop and lower flow rates during sampling. Another disadvantage is its intolerance of water. In high humidity, Florisil will hydrate, cake up, and block the air flow. The use of Florisil in four PCB incineration trial burns was reviewed by Ackerman et al. (1983a).

A dual trap system with Florisil followed by XAD-2 was employed at the Rollins Environmental, Deer Park, TX (EPA, 1981), second ENSCO, El Dorado, AR (EPA, 1981b), and Vulcanus MT trial burns (Ackerman et al., 1983b). The lack of a consensus on sorbents has apparently led some sampling teams to use both XAD-2 and Florisil to ensure the acceptability of the data.

A number of studies have employed XAD-2 in the sorbent cartridge in a modified Method 5 train (Stanley et al., 1982; Haile et al., 1983a,b, 1984). Its use in PCB incineration trial burns has been reviewed by Ackerman et al. (1983b). XAD-2 was recommended by the EPA for sampling during PCB trial burns (Beard and Schaum, 1978) and also by a standards working group (ASME, 1984).

3. Liquid sorbents: Despite some early use, liquid sorbents have not been extensively used for sampling stack gas. The primary liquid sorbent has been ethylene glycol. Liberti et al. (1980) used toluene in two tandem impingers to sample organochlorine compounds, including PCBs, from an urban incinerator. The subject has been reviewed (Margeson, 1977; Ackerman et al., 1983a).

4. Sampling design: The sampling design must meet the objectives of the study. The sample volume, number of samples, waste feed rates, etc., must all be carefully considered beforehand. It is particularly important to understand all of the related variables which impact on the measurable destruction efficiency. This subject has been presented in more detail (Erickson et al., 1984a). Another aspect of the study design is distinguishing between PCB emissions and background. A background or baseline run may be an appropriate part of the QC program. Haile et al. (1983b) found that the PCBs emitted from seven coal-fired utility boilers were higher than the levels in background

air, but that the two levels were generally within one standard deviation. Furthermore, the homolog distributions were similar. These two facts indicate that the PCB emissions from these plants may have just passed through the plant with the combustion air.

5. Discussion: Stack sampling for PCBs is generally done using a complex sampling apparatus designed to sample isokinetically and to collect several fractions for a variety of analytes. In the U.S., the apparatus of choice is the modified Method 5 train. The exact geometry of the modified sampling train and the choice of sorbent (XAD-2 or Florisil) differ among sampling groups although XAD-2 appears to have been more preferred in recent years. It appears that the chemical properties of the sorbent may be less important than the physical presence of a cool surface for condensation of the PCBs. Since it has been shown that substantial amounts of PCBs are collected in the probe and other parts of the train plumbing (Haile et al., 1983a) it is particularly important to validate the collection and recovery efficiency with the full train under realistic conditions. Better validation techniques are needed to fully assess the collection and recovery efficiency of a sampling system under a given set of sampling conditions.

Unless further method validation studies indicate an acceptable alternative, source sampling should utilize a modified Method 5 train with XAD-2 as the sorbent. The contents of the entire train (probe, rinse, filter, any upstream impingers, and the sorbent cartridge) must be analyzed for PCBs. As noted above, the modified Method 5 filter should not be used to measure the Method 5 total particulate. Proper experimental design and QC are necessary to discriminate between unreacted PCBs from the incinerator and PCBs collected from background air.

III. NATURAL GAS IN PIPELINES

A procedure (Harris et al., 1981) for the sampling and analysis of natural gas for PCBs utilizes the NIOSH Florisil tubes (NIOSH, 1977a,b,c). The Florisil tube is connected to a valved port in the line through appropriate fittings. A Magnahelic, rotometer or dry gas meter downstream monitors the flow rates or volume.

IV. SOLIDS

Soil, sediment, biota, and tissue sampling for PCBs all utilize general trace organic sampling techniques. Sampling equipment and containers must be glass, steel, TFE, or other non-contaminating materials. The samples collected must be representative of the system, and the sample volume must be sufficient for the analyst's needs. Documents on sampling hazardous waste streams (deVera et al., 1980), soil (Mason, 1982), and PCB spill sites (Kelso et al., 1985) give additional guidance.

Using a mobile atmospheric pressure chemical ionization mass spectrometer, Lovett et al. (1983) demonstrated a real-time sampling/analysis technique for soil and other solids. Air from the surface of a spill, or soil core was pumped through a heated transfer line, "surface sniffing," to the spectrometer. A detection limit of 500 µg/g was reported.

V. SURFACES

Solid surfaces may need to be sampled to assess either PCB contamination or the effectiveness of cleanup after a PCB spill. These solid surfaces may be smooth and impervious, such as a drum interior, or rough and porous, such as an asphalt driveway. No standard surface sampling technique has been issued by an organization.

In an EPA guidance document on PCB spill cleanup, Kelso et al. (1985) recommended that nonporous surfaces be sampled by wiping. Surface wipes are taken with a moistened piece of filter paper with toluene, isooctane, or other appropriate solvent. The filter paper is held with a pair of stainless steel forceps and used to thoroughly swab a 10 cm x 10 cm area of the surface to be sampled. A template should be used to define the area. The wipe technique should be performed reproducibly. The wipe sample is stored at approximately 4°C in a precleaned glass jar.

Wipe samples are not appropriate for porous surfaces which may absorb the PCBs. These surfaces such as wood, asphalt, and concrete should be sampled by physical removal of a representative portion (Kelso et al., 1985). The sample can be collected by chipping, drilling, coring, chiseling, etc.

MONS 005308

VI. OIL, DIELECTRIC FLUIDS, ETC.

A large number of PCB analyses involve transformer oil, hydraulic fluid, askarels, and other similar oils which may be contaminated with PCBs. Since these oils are generally contained in a transformer, drum, tank, etc., obtaining a sample may be as simple as opening a drain valve. The only consideration in sampling is representativeness. Especially where the oil is highly contaminated, the PCB content may not be homogeneous. For example, a drum of waste oil may contain several phases--a sludge, a water layer, and an oil layer. The PCB content of the three layers would differ markedly. Thus, the sampler must attempt to obtain a representative sample. Small containers may be mixed. With larger containers, subsamples from various depths may need to be taken.

MONS 005309

5

EXTRACTION

Reliable trace organic analysis begins with the quantitative extraction or the analytes from the sample matrix. The general objective of an extraction technique is to separate the analyte (e.g., PCBs) from the sample into a matrix which is more compatible with the rest of the analytical procedure. The exact separation process is dependent on the complexity of the physical and chemical nature of the matrix. The general principles and techniques of extraction for trace organic analysis have been reviewed (Poole and Schuette, 1983). PCBs are readily extracted from matrices such as water, but are difficult to extract from oil and other matrices in which they are readily soluble.

This chapter reviews the literature and discusses applicable extraction techniques by matrix. After a discussion of general physical and chemical considerations, extraction techniques for water, sewage and sludge, sediment and soil, air, blood, animal and plant tissue, paper products, and oils are presented. A section at the end of the chapter discusses solvent evaporation, losses of PCBs through sorption onto glass containers, and sources of contamination.

Many of the extraction techniques discussed in the literature are derived from traditional pesticide analytical methods, and their adaptation to PCB analysis was made with little or no reported research or validation. Thus, most of the PCB extraction techiques discussed in this chapter may be best described as "workable" but not "optimized."

I. GENERAL CONSIDERATIONS

As noted in Chapter 2, PCBs are nonpolar, semivolatile organics. Thus, they are highly soluble in nonpolar solvents such as hexane and only slightly soluble in polar solvents such as water and acetonitrile. This property is advantageous for extraction from water samples, since the PCBs will readily partition from the water to most nonpolar (i.e., immiscible) organic solvents. However, when the PCBs are

MONS 005310

dissolved in a nonpolar matrix such as oil, the extraction process becomes much more difficult, if not impossible.

The physical mechanism of the extraction can also be important. The extraction solvent must come into contact with the entire sample to reliably extract the PCBs. With soil, tissue, and other solids, physical mixing or maceration is necessary to assure effective contact. Even more harsh techniques such as ultrasonic disruption or chemical degradation (e.g., saponification with base) may be required to break up cells, macromolecules, or other matrix components which could entrain PCBs. The rigor of the technique must be balanced between efficient extraction and degradation or loss of the analyte.

As with any partition scheme between two phases, PCB extraction relies on a favorable partition of the PCBs from the sample matrix into the extraction matrix. The more favorable the partition coefficient, the higher the extraction efficiency. Efficiency is also improved by repetitious extractions. If, for example, the partition coefficient, K, is 9, then 90% of the PCBs will extract from the sample to the solvent in the first extraction (at equilibrium). The second extraction will also yield 90% of the remaining PCBs for a total extraction of 99%. After three extractions, the combined extracts should contain 99.9% of the sample. With a lower partition coefficient, more repetitions are required for a similar total extraction. For most matrices, K has been presumed to be high and the traditional number of repetitions is 3.

II. WATER

Extraction of PCBs from water is generally straightforward, since the solubility is so low. A simple liquid-liquid extraction with any water-immiscible solvent should yield adequate results. As shown in Table 3-1, the standard procedures prescribe hexane, methylene chloride, or mixed solvents for water extraction. The sections below describe considerations for liquid-liquid extractions and also present some of the other extraction techniques reported in the literature. A steam distillation technique has been used for extraction of water samples, but was validated primarily for fish samples and is discussed in Section VII.B.3, below.

A. Liquid-Liquid Extraction

The classic liquid-liquid extraction techniques involve a simple shaking of the water and solvent in a separatory funnel. Continuous liquid-liquid extraction is simply

an "automation" of the separatory funnel shakeout. More esoteric extraction techniques include steam distillation and sorbent column extraction. The latter is particularly appealing for on-site extraction of large volume water samples to achieve very low detection limits. On-site water extraction was covered under "sampling" (Chapter 4).

A study of water extraction solvents and conditions by Millar et al. (1981; 1982) found no distinctly advantageous combination of solvent and pH for all PCBs. In the study, Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260 were spiked into unchlorinated well water. The spiked samples were then adjusted to pH 2, 7, and 10 and extracted with either dichloromethane/hexane (15:85) or pure dichloromethane. The results were analyzed by analysis of variance (ANOVA). For some PCB mixtures either one or the other solvent was preferable. The effect of pH was similarly confounding; neutral, basic, and "no preference" were statistically shown to be the best conditions for various Aroclors. It appears from these data that there is no significant difference in these conditions for all PCBs.

A liquid-liquid extraction followed by a KOH saponification technique has been developed for paper mill effluents (Easty and Wabers, 1978; Delfino and Easty, 1979). Water samples are extracted three times with hexane and then cleaned up on a Florisil column prior to PGC/ECD determination. After the hexane extraction, the water sample is filtered and the isolated paper fibers are refluxed in alcoholic KOH to remove any PCBs. Without the KOH saponification, about 10% of the PCBs remained on the fibers after the hexane extraction.

B. Continuous Liquid-Liquid Extraction (CLE)

Continuous liquid-liquid extraction (CLE) is a labor-saving technique to replace the common separatory funnel. In addition CLE is less likely to cause emulsion problems with very dirty matrices. A wide variety of apparatus have been described to effect CLE. Most involve refluxing solvent from a flask, which then drips through a water sample and returns to the flask.

Godefroot et al. (1982a,b) demonstrated the applicability of a combined steam distillation/solvent extractor for PCBs. The technique, a micro version of the Nickerson and Likens (1966) apparatus, simultaneously steam distills and gas-phase extracts PCBs and similar organics from 50 mL water into 1-mL pentane. The recovery for Aroclor 1260 averaged 95%.

MONS 005312

C. Sorbent Column Extraction

With this technique, a water sample is passed through a sorbent column where the PCBs and other organics are "extracted" onto the sorbent. The adsorbed organics are then eluted from the column with an organic solvent. The distinct advantage of sorbent column extraction is the ability to extract large water volumes to enhance the method detection limit. The sorbent column extraction of large water volumes (over two liters) has been employed in the field, as discussed under "Sampling" (Chapter 4).

Coburn et al. (1977) reported an XAD-2 column technique for extraction of 2-L samples with subsequent elution with ethyl ether. At the 250-ppt level, 78-86% recoveries were observed for a mixture of Aroclors. A polyurethane foam column technique gave 91-98% recovery at the 20-ppb level from 1-L water samples (Gesser et al., 1971). The PCBs were eluted with acetone and then hexane. Similar results have been shown using XAD-2 or XAD-4 for sea water (Osterroht, 1974) and tap water (Musty and Nickless, 1974a). Picer and Picer (1980) compared XAD-2, XAD-4, and Tenax for extraction of PCBs from sea and tap water. The Tenax yielded many more peaks at larger intensity, which more closely resembled an Aroclor mixture than the other resins. However, severe PGC/ECD interferences were noted with all of the sorbents. Leoni et al. (1976b) achieved 100% recovery of PCBs at 1.6 ppb in 10-L samples of surface water. The PCBs were collected on a column containing Tenax and Celite and then eluted with three 10-mL portions of ethyl ether.

A C-18 reversed phase partitioning cartridge (Sep-Pak, Waters Associates) was used by Gallis et al. (1983) to adsorb PCBs from water samples. The cartridges were preconditioned with methanol.

D. Purge and Trap

A purge and trap technique was demonstrated to yield greater than 90% recoveries for Aroclor 1221, 1248, and 1254 (Colenutt and Thorburn, 1980). Water samples (2.0 L) were purged at room temperature for 4 hr at 1 L/min. The PCBs and other compounds were trapped on 5-25 mg activated carbon. The carbon trap was subsequently desorbed with 50-1,000 µL of pentane, carbon disulfide, carbon tetrachloride, or diethyl ether. This extract could then be analyzed by PGC/ECD.

MONS 005313

E. Comparison of Extraction Techniques

Solvent extraction gave better results than XAD-4, a "partition system" (Carbowax 4000 monostearate and n-undecane coated on Chromosorb W) or polyurethane foam (Musty and Nickless, 1976). Recovery of PCBs at the 10-20 ppb level from water with the partition system ranged from 97% to 48%, decreasing with increasing chlorine content of the PCBs. The concentration of PCBs, measured as Aroclor 1260, in a water sample with the solvent extraction (diethyl ether/hexane, 15:85) technique was over twice that found with any of the three sorbent column techniques.

Bellar and Lichtenberg (1975) found separatory funnel liquid-liquid extraction to be the most efficient extraction technique for recovery of PCBs from natural waters. The use of polyurethane foam plugs--both in a column-elution mode and where the plug is soaked in the water sample--gave good recoveries with distilled water. With natural waters, however, the particulate matter stopped flow through the column. With natural waters, the recoveries from the soaking technique had poor precision. In addition, the PUF contributed significant background interferences to the GC/ECD analysis. A vortex extractor gave lower and less reproducible results, although it was not thoroughly evaluated.

III. SEWAGE AND SLUDGE

These ill-defined matrices range from "dirty water" to high-organic solids. Thus, many different extraction techniques have been employed. For raw municipal sewage with relatively low organic content, the sample can be extracted using a water technique, such as solvent extraction in a separatory funnel. More viscous samples can also be treated this way by simply diluting the matrix to the desired consistency--at a sacrifice of the method detection limit.

The effects of the high levels of organics on extraction efficiency were illustrated with a sorbent-column technique. Only 23 or 60% of the PCBs spiked into raw sewage were extracted with XAD-2 or XAD-4, respectively (Lawrence and Tosine, 1976). Apparently, the sorbent overloaded with this high organic-content matrix. Surprisingly, a column of polyvinyl chloride chips gave the best (73%) adsorption of PCBs and was recommended by the authors.

Four extraction techniques were compared by Rodriguez et al. (1980) in the development of a method for analysis of municipal sewage sludge for PCBs and chlorinated pesticides. The extraction techniques evaluated were:

MONS 005314

(1) Centrifuge. Acetone/dichloromethane/hexane (2:15:83) mixture and then centrifuged to separate the emulsified mixture. The upper solvent layer is removed and the process repeated twice more.

(2) Column Elution. The sludge (20 g) is mixed with 80 g annydrous sodium sulfate and then packed into a liquid chromatographic column. The PCBs are then eluted with 150 mL of acetone/hexane (20:80).

(3) Soxhlet Extraction. The sludge (20 g) is mixed with 180 g anhydrous sodium sulfate and then Soxhlet-extracted with dichloromethane/hexane (15:85) for about 40 cycles.

(4) Continuous Liquid-Liquid Extraction. The sludge (20 g), diluted with 10 mL water during transfer, was extracted overnight with dichloromethane in a modified Soxhlet extractor.

The latter technique gave poor (< 50%) recovery, presumably because of poor solvent-sample contact. The first three techniques gave high (> 80%) recoveries. A variety of reasons, including potential interferences, cost, and ease of use, led the authors to recommend the centrifuge technique, which gave 98% recovery of Aroclor 1260 from primary sludge and 80% recovery from digested sludge.

IV. SEDIMENT AND SOIL

Sediment and soil differ from sewage sludge in their generally lower organic content. As with sewage sludge, the critical component of an extraction technique for either sediment or soil is the contact between the solvent and the matrix. This has generally been accomplished by physical mixing (e.g., manual shaking) and use of a "wetting" solvent mixture (e.g., hexane and acetone). With soil samples, especially, thorough mixing and pulverizing of chunks is an important preextraction step.

A. Solvent Extraction

The classic work on extraction of chlorinated insecticides (PCBs were "co-extractives" which could be removed in the chromatographic cleanup) from sediment is by Goerlitz and Law (1974). The sediment (50 g) is centrifuged to remove excess water, wetted with 40 mL acetone, extracted with 80 mL hexane, re-wetted with 20 mL acetone, and extracted again

with hexane. Between each solvent addition, the sample is shaken 20 min on a wrist-action shaker. The extraction should be repeated until at least 75% of the added solvent is recovered. PCB recoveries were 100% after 3 extractions.

This basic approach has been utilized in many other studies, with modifications in the solvent ratio, volume, agitation time, etc. (Eder, 1976a; Jensen et al., 1977; Chau et al., 1979). Other "wetting" solvents have also been used, such as acetonitrile (ANSI, 1974) or water/acetonitrile (ASTM, 1981b).

Wetting the soil prior to solvent extraction appears to increase the extraction efficiency. A Soxhlet extraction of dry soil with hexane for 10 hr gave 30% recovery of radiolabeled Chlophen A-30 (Seidl and Ballschmiter, 1976a), while 85% recovery was measured using the same techniques from wet soil. The soil was wetted with 1 g water per 15 g soil.

B. Collaborative Studies

Lee and Chau (1981a) conducted an interlaboratory validation for PCBs in wet sediments. Both native and spiked (about 1 ppm) samples were analyzed. The participants were permitted to use analytical methods of their choice for the analysis of the materials. Of the methods used in the extraction of PCBs from sediment, which included ultrasonic, Soxhlet, blender and shaker methods, the ultrasonic was the most popular. In this study, Soxhlet extraction did not seem to provide higher recoveries of PCBs in comparison with other extraction techniques. Most participants used a mixture of polar and nonpolar solvents, such as 1:1 acetone and hexene, as the extracting solvent, while others used a single polar solvent such as acetonitrile or acetone. No obvious relationship was observed between the recoveries and the extraction procedure. This suggested to the authors that all the extraction methods used in this study were equally efficient for the recovery of PCBs in spiked sediment samples. A second collaberative study (Lee and Chau, 1981b) of PCBs in naturally contaminated dry sediments exhibited too much variability for the authors to make inferences on the differences in analytical techniques. The study is described in more detail in Chapter 10.

C. Thermal Desorption

Thermal desorption is commonly used for volatile compounds, such as chloroform, but only rarely employed for semivolatiles such as PCBs. The higher desorption temperatures and possibly lower desorption efficiencies probably

MONS 005316

contribute to this lack of popularity. On the other hand, thermal desorption can yield fewer interferences and has the distinct advantage of introducing the entire sample to the instrument. This provides potentially much better method detection limits than with solvent extraction where only 1/1000 of the sample is typically injected onto the gas chromatograph.

Lovett et al. (1983) reported the use of both a surface-sniffing and thermal desorption techniques for rapid analysis of PCBs at spill sites. Samples were volatilized and then directly introduced into a mobile atmospheric pressure chemical ionization mass spectrometer (see Chapter 7). The surface sniffing technique had a detection limit of 500 µg/g, while thermal desorption could detect 10 µg/g. The thermal desorption technique used mini-core soil samples and had a total analysis time of 3 min. No details or validation was reported.

Thermal desorption has also been used to introduce PCBs to a conventional PGC/EIMS (McMurtrey et al., 1983). Samples were desorbed under a helium stream for 10 sec at 1000°C. The desorbed materials were trapped at the head of the cool GC column. PCBs were detectable at the 10 ppm level, although the MDL was not determined, nor was the quantitative reliability of the method presented. The authors mistakenly termed the PCB desorption technique "pyrolysis." Thermal desorption of PCBs from hazardous waste samples into a triple quadrupole MS/MS system has also been described (Hunt et al., 1985).

The above results indicate that thermal desorption may well be a viable technique for rapid screening analyses. Until validation data are presented, the technique cannot be recommended for quantitative analysis.

O. Comparison of Sediment and Soil Extraction Techniques

Three techniques were compared for the extraction of PCBs from bottom materials (Bellar et al., 1980); they were:

(1) Soxhlet extraction: The Soxhlet extraction was conducted overnight with acetone/hexane (10:90) and the extract concentrated with a Kuderna-Danish evaporator, cleaned up on Florisil, and then treated with mercury to remove sulfur.

(2) Sonication: The sonication technique involved a single 5-min sonication at a power of 150 watts with 150 mL acetone over a 60-90 g sample. The acetone was then decanted, diluted with water, and the organics extracted with hexane/dichloromethane (85:15). The extract was concentrated and cleaned up as with the Soxhlet extraction.

(3) Steam distillation: The steam distillation technique employed the Nielson-Kryger apparatus for simultaneous distillation and extraction with hexane.

Prior to extraction with all three techniques, samples were air-dried, debris (stones, leaves, twigs, etc.) was removed, the sample was mixed, ground in a mortar and pestle and then subsampled. All three extractions gave quantitative recoveries of Aroclor 1254 spiked onto lake bottom samples; however, the Soxhlet extraction gave 25-40% higher results than the other two techniqeus for environmentally contaminated samples. These results emphasize the importance of validating methods with real samples, where the PCBs have been thoroughly incorporated into the matrix.

Bellar and Lichtenberg (1975) found that Soxhlet extraction of air-dried, 10% water-added bottom materials (muck and sandy muck) with a mixture of acetone/hexane (10:90) was the most efficient method for extracting PCBs. The less-efficient techniques included shaking with acetone and then hexane, shaking with an isopropanol/hexane mixture, blending with an acetonitrile/acetone mixture, preparation of a column by mixing with sodium sulfate and then eluting with either hexane or hexane-acetone, and high frequency dispersion with acetone. All of the techniques tested were taken from the literature.

Water/methanol/hexane (10:40:50) gave the best recovery of Aroclor 1242 from dry sediment (Spittler, 1983, 1984) in a single extraction of the sediment for screening purposes. The other solvent systems, which gave poorer recoveries were hexane, water/hexane (50:50), water/ethyl ether/hexane (33:33:33), water/ethyl ether (50:50), water/methanol/ethyl ether (33:33:33), and methanol/hexane (50:50).

V. AIR

PCBs should be readily extracted from the sorbent materials used in air sampling. As discussed in Chapter 4, PCBs are generally "extracted" from the air sample onto a

sorbent material during the sampling. This sorbent is then returned to the laboratory for analysis, the first step of which is a solvent extraction. Chapter 4 presents a detailed discussion of the various sorbents used in air sampling. These include polyurethane foam (PUF), Florisil, XAD-2 and other macroreticular resins.

PCBs are extracted from these sorbent matrices by repeated extraction with a nonpolar solvent such as hexane, benzene, or methylene chloride. Often a continuous extractor, such as the Soxhlet extractor, is used to effect the repeated extractions. An important consideration of the extraction technique is contact between the solvent and all of the sorbent. Column elution or other techniques which may develop channeling of the solvent and thus do not ensure complete contact must be scrutinized carefully to assure quantitative extraction of the PCBs.

A. Polyurethane Foam

PCBs are extractable from PUF plugs using nonpolar or semi-polar solvents. Petroleum ether (a mixture of pentanes and hexanes, now generally replaced with pesticide residue grade n-hexane) has been used to Soxhlet-extract PUF plugs (Bidleman and Olney, 1974; Bidleman, 1981; Bidleman et al., 1981a; Bidleman and Leonard, 1982). MacLeod (1979) used ethyl ether/hexane (5:95) in a Soxhlet. Erickson et al. (1980a) used toluene, which had been shown to be the most efficient for extraction of polychlorinated naphthalenes (Erickson et al., 1978). Mechanical squeezing was used instead of Soxhlet extraction to improve the efficiency of extraction from the middle of the plug.

One study (Adams and Caro, 1980) has compared the mechanical extraction techniques for PUF, although PCBs were not tested, similar organochlorine pesticides make the data relevant to this discussion. Soxhlet extraction (5 cycles) squeezing (5 times with a metal plunger) and column elution, all using acetone/hexane (50:50) were compared. The three techniques gave 96 to 101% recoveries with 11 to 18% RSD. Thus, for a series of 11 organochlorine pesticides, these three mechanical extraction techniques appear to be equivalent.

B. Florisil

Florisil (trademark, Floridin Company) is a synthetic magnesium silicate. Most of the authors using Florisil for air sampling have extracted the PCBs with hexane, although one early report (Glam et al., 1975) used petroleum ether followed by ethyl ether to elute PCBs from a column

MONS 005319

prepared with the air sampling Florisil. Column elution has been reported when the amount of Florisil is small (Giam et al., 1975; Harris et al., 1981; Williams et al., 1980). The NIOSH method (1977a,b,c) directs the analyst to simply mix the hexane and Florisil for at least 10 min and then inject an aliquot of the supernatant hexane on the PGC/ECD. Haile and Baladi (1977) used a Soxhlet-extraction with hexane to desorb PCBs from a 7.5 g Florisil stack sampling cartridge.

C. XAD-2

The extraction of XAD-2 is generally done with a nonpolar solvent such as hexane, benzene (Stanley et al., 1982) or petroleum ether (Eisenreich et al., 1981a) in a Soxhlet extractor. The amount of XAD-2 used (typically 75 g of low-density polymeric resin) makes sample handling more difficult than with the small amounts of Florisil, so the Soxhlet technique has been more popular.

D. Dry Deposition Samples

Sample collectors (aluminum pans or glycerin-coated pans) are rinsed with solvent to remove the particulate and PCBs. Bidleman et al. (1981a) rinsed their pans with distilled water and acetone or dichloromethane and then scraped the surface repeatedly with a piece of Teflon® to ensure removal of adhered material. The combined rinses were then extracted with dichloromethane. Eisenreich et al. (1981a,b) washed the PCBs from dry deposition pans with PCB-free water only, which was subsequently extracted by steam distillation into toluene. It is surprising that only a water wash was employed, given the poor solubility of PCBs in water (see Chapter 2).

VI. BLOOD

The extraction of blood samples generally entails a simple liquid-liquid partition of whole blood, plasma, or serum with solvent. The techniques differ from those for other aqueous liquids in how the cells and proteins are handled to assure complete extraction and avoid emulsions. In addition, blood samples are generally small (e.g., 10 mL) relative to water and many other samples, so the mechanical techniques of agitation, etc., are different.

Whole blood is essentially the same matrix as obtained from the body, except for the possible addition of an anticoagulant, such as heparin, to retard clot formation. Plasma is the liquid portion of the blood obtained after

MONS 005320

physical removal of the cells from whole blood by centrifugation. Serum is the fluid remaining after the cells and platelets are allowed to coagulate. PCB analyses have been conducted on all three "blood" matrices. The results may not be comparable, since an unknown portion of the PCBs in whole blood can be removed with the cells or clot.

Blood extraction procedures have been issued by two organizations: the U.S. Environmental Protection Agency and the U.S. Centers for Disease Control. Most of the references in the primary literature involve one or the other of these procedures. Thus, this section has been divided into subsections describing these two procedures and their validation.

A. Environmental Protection Agency

The EPA manual for pesticide residue analysis (Section 5,A,(3),(a), Watts, 1980) describes a hexane extraction for serum:

> "A 2-mL aliquot of serum is extracted with 6 milliliters of hexane in a round-bottom tube. The extraction is conducted for 2 hours on a slow-speed rotating mixer. The formation of emulsion is unlikely, but if it should occur, centrifugation may be used to effect separation of the layers. A 5-mL aliquot of the hexane layer is quantitatively transferred to an evaporative concentrator tube to which is affixed a modified micro-Snyder column. The extract is concentrated in a water or steam bath, and the final volume is adjusted to correspond to the expected concentration of the pesticide residue. A suitable aliquot is analyzed by electron capture gas chromatography."

The method was developed for organochlorine pesticides (Dale et al., 1966) and PCBs are not listed as potential analytes in the method (Watts, 1980). Nevertheless, the technique has been adapted for the determination of PCBs (Curley et al., 1971) and has been routinely used for PCB analysis (Erickson et al., 1983e). In the original form (Dale et al., 1966), the extraction entails a vigorous mixing for 3 min on a mini-mixer, yielding an emulsion which is then broken by centrifugation. The EPA modification (Watts, 1980) recommends a gentle mixing for 2 hr on a rack which gently rotates the tubes end-for-end. This technique, while much slower, avoids emulsions in most cases and thus saves an additional step.

The EPA extraction involves only a single partition. In addition, although 6 mL hexane are added, only 5 mL are recovered, since the hexane-serum interface is indistinct

MONS 005321

due to a layer of protein. The lack of full solvent recovery is compensated in the calculations by multiplying the PGC/ECD results by 6/5.

B. Centers for Disease Control

Researchers at the Centers for Disease Control (CDC) have developed methods for determination of PCBs in serum which utilize a triple extraction with ethyl ether/hexane (50:50) (Needham et al., 1981; Burse et al., 1983a). Specifically, 4 mL serum and 2 mL methanol are mixed to denature the protein. The specimen is then extracted with 3 x 5 mL ethyl ether/hexane (50:50). Each extraction is conducted for 15 min on a rotary mixer at 50 rpm. The organic and serum layers are separated by centrifugation at 1800 rpm. The combined extracts are concentrated to 0.5 mL, cleaned on silica gel, and determined by PGC/ECD. No recovery data were presented; however, the precision of the entire method was ± 33% RSD at 2 ppb Aroclor 1254 and ± 12% RSD at 46 ppb. Using a similar extraction, McKinney et al. (1984) quantitatively (90-100%) recovered Aroclor 1254 except near the detection limit (10 ppb), where the recoveries were 77%. The precision was less than ±10% RSD.

An earlier publication (Needham et al., 1980) employed a similar extraction technique, except the extraction solvent was hexane alone. A recovery of 94 ± 5% for Aroclor 1260 spiked into serum at 41 ppb was measured for the entire method. Yet another version employed the ethyl ether/hexane extractions, but added a saponification step (Baker et al., 1980; Stratton and Geiszler, 1977). The concentrated organic extract was saponified by addition of 2 mL of a 2% KOH in methanol solution. The mixture was refluxed and concentrated to about 0.3 mL, taken up in 2 mL water/methanol (50:50), and then extracted three times with 2 mL hexane. The combined hexane extracts were then submitted to silica gel chromatography. Recoveries of 99 ± 1% and 108 ± 7% were reported by two laboratories (Stratton and Geiszler, 1977). Based on these limited results, the choice of hexane or ethyl ether/hexane does not appear to have a marked effect on the extraction.

Hexane was the favored extraction solvent in a collaborative study of PCBs in blood serum (Burse et al., 1983b). Of the 25 participants, 12 used hexane; 8 used ethyl ether/hexane; 2 extracted with acetonitrile and then partitioned into hexane or petroleum ether (see section on extraction of adipose tissue, above); 1 used a mixture of isopropanol/petroleum ether, and 1 adsorbed the blood on a Florisil column. Nine of the participants denatured the protein with methanol, while 15 did not. The scatter of the data did not

permit comparison of the efficiency of the extraction techniques. This study is discussed further in Chapter 10.

C. Comparison of Blood Extraction Techniques

The extraction of whole blood with hexane-saturated acetonitrile was found to be quantitative (97%), while extraction with hexane alone achieved about 40% recovery (Welborn et al., 1974). In addition, the hexane extraction was selective, with higher recoveries for early-eluting PCB peaks on the PGC/ECD. The hexane extraction involved vigorous shaking with three aliquots. The combined extracts were dried with sodium sulfate, concentrated, cleaned on alumina, and determined by PGC/ECD. The more efficient technique entailed vigorous shaking three times with hexane-saturated acetonitrile. The combined extracts were dried with sodium sulfate, diluted with water, and extracted with three portions of hexane. The combined hexane extracts were concentrated, cleaned on alumina and determined by PGC/ECD. The publication does not explain why both techniques were conducted on a macro scale. The solvent volumes were 50 mL/extraction--the volume often used for extraction of 1-L water samples.

VII. ANIMAL AND PLANT TISSUES

This broad sample matrix category spans a continuum of polarity and extractability. At the one extreme, adipose tissue can be almost entirely extracted into the organic solvent, leaving only a small residue of non-extractable matrix. In this case, the matrix has simply been dissolved in the solvent and the PCBs must still be extracted from the lipids. At the other extreme, many plant tissues (food) can be easily extracted with organic solvents, yielding a relatively clean extract.

A. Adipose Tissue

Adipose tissue, from either humans or animals, consists of both lipids ("fat") and connective tissue. Spearman (1982) has published a detailed review of the properties and biochemistry of adipose tissue. Most extraction techniques first separate the PCBs along with the lipids and any other soluble organics from the connective tissue. The PCBs and other compounds of similar polarity are then separated from the lipids.

Most procedures also contain provisions for determining "percent fat" by evaporating the solvent from an aliquot of the original extract and then weighing the residue.

MONS 005323

Knowledge of the fraction of the sample which is extractable is important in comparing the PCB content of different samples.

1. Acetonitrile back-partition: A classic adipose and food extraction procedure developed by Mills et al. (1963) involves first extraction of the lipids from the connective tissue with petroleum ether and then extraction of the PCBs and pesticides from the petroleum ether into acetonitrile. Like many other techniques, it was originally developed for organochlorine pesticides and subsequently adapted for PCBs. This Mills-Onley-Gaither ("MOG") procedure has formed the basis of many techniques subsequently reported. For example, the EPA method (Watts, 1980) for pesticides in adipose involves:

> "A 5 g. sample is dry macerated with sand and Na_2SO_4 and the fat is isolated by repetitive extractions with petroleum ether. Pesticide residues are extracted from the fat with acetonitrile and then partitioned back into petroleum ether by aqueous dilution of the acetonitrile extract. Petroleum ether extract is concentrated to 5 mL by Kuderna-Danish evaporation and transferred to a Florisil column for successive elutions with 6% and 15% ethyl ether/ petroleum ether. The respective eluates are both concentrated to suitable volumes in Kuderna-Danish evaporators and the final extracts are examined by electron capture gas-liquid chromatography."

The PCBs and pesticides are separated in the Florisil step. PCBs are resolved from some co-eluting pesticides by silicic acid chromatography (see Chapter 6). Many users of this method now substitute pesticide residue grade n-hexane for the petroleum ether stipulated in the above procedure.

The acetonitrile-hexane (or petroleum ether) partitioning step is reported to be time-consuming (Smrek and Needham, 1982). PCBs may also be lost during this step, since the partition ratio between the two solvents is probably relatively low.

2. Acid digestion: An alternative approach was presented by Murphy (1972) in which the biological substances were removed from the hexane extract of adipose tissue by shaking the extract with concentrated sulfuric acid. The acid presumably degraded the lipids and other molecules, while leaving the relatively stable PCBs and chlorinated pesticides intact.

MONS 005324

3. Column chromatography: Several groups have investigated the use of a column chromatographic step to "extract" PCBs from the lipids. Ernst et al. (1974) ground frozen tissue samples with sand and sodium sulfate to form a powder which was poured into a glass column. The PCBs were then eluted from the column with acetone/n-hexane (33:67) while the entire system was kept cold. PCB recoveries for the entire procedure, including an alumina cleanup, were 96-98%. A similar elution of a mixture of animal tissue and sodium sulfate with hexane was judged better than other techniques (Bowes and Lewis, 1974). Specifically, lower recoveries were obtained for elution of the column with a methanol/chloroform mixture (33:67), digestion with a hot perchloric/glacial acetic acid mixture (40:60), and extraction with acetone followed by refluxing with hot isopropanol.

Smrek and Needham (1982) used a column of 10% silver nitrate on silica gel to retain the lipids, DDT, and DDT metabolites, while eluting the PCBs with hexane. Recoveries were greater than 90% with standard deviations of less than 3%. Prior to the column chromatography, adipose samples were ground with sodium sulfate to macerate the tissue and adsorb water. The samples were then extracted with petroleum ether three times. Porter and Burke (1973) mixed 8 g fat with 25 g unactivated Florisil, placed the mixture in a column, and eluted with 150 mL water/acetonitrile (10:90). The eluate was diluted with water and the PCBs partitioned into petroleum ether, which was further cleaned up with a Florisil column and determined by PGC/ECD. Eighty-five percent of Aroclor 1254 was recovered from corn oil spiked at 100 ppb. Similarly, Swift and Settle (1976) isolated PCBs by distributing the fat sample on the top of a column of unactivated Florisil and eluting with water/acetonitrile (10:90).

4. Distillation: Sweep codistillation from animal fat gave extracts which had PGC/ECD detection limits of 10 μg Aroclor/g fat (Neidert and Saschenbrecker, 1984). With silanized distillation tubes to prevent adsorptive losses, 98-99% recoveries of Aroclors 1248-1268 were observed.

5. Low temperature precipitation: Low temperature precipitation has also been used to remove lipids (McLeod and Wales, 1972). Samples were extracted by refluxing in acetone/ benzene (95:5) for 1 hr. The extract was then cooled in a dry ice bath for 30 min with a nitrogen stream bubbling through the solution. This caused lipids, waxes, water, and other compounds to precipitate. The supernatant was then separated from the precipitate by vacuum filtration on cellulose. Although not validated for use with PCBs in the original publication, the technique has been applied to PCB analysis of tissue and milk samples (Mes and Campbell, 1976; Mes et al., 1977; Mes and Davies, 1978, 1979).

MONS 005325

6. Comparison of lipid removal techniques: Several mechanical techniques and extraction solvents were compared in a study by Mes and Campbell (1976). A Silverson mixer was found to be slightly more effective at lipid extraction and easier to use than a Waring Blender or a Virtis Model 23. They also evaluated nine solvents and found a acetone/benzene (95:5) mixture to give the highest PCB concentrations in unspiked human adipose samples. The other solvents were hexane, acetone/hexane (33:67), methanol/dichloromethane (67:33 and 50:50), dichloromethane, benzene, water-saturated butanol, and diethyl ether/petroleum ether (50:50).

B. Fish

Fish samples can often be extracted by techniques similar to those used for adipose tissue, since fish can contain several percent lipids. Fish are of interest because of their human consumption, indication of PCB movement through aquatic and marine tropnic levels, and the ability to study PCB transport by comparison of migratory and nonmigratory species.

1. Solvent extraction: Soxhlet extraction has been used extensively for extraction of fish samples (Zitko, 1971a; Zitko et al., 1974b; Frank et al., 1978; Kuehl et al., 1980a) and shallfish (Kilikidis et al., 1981). Average recoveries of 85-90% for PCBs (Frank et al., 1978), including cleanup and all other analytical steps, indicate that the extraction is generally adequate. Nevertheless, the lack of mixing cannot assure complete contact of the solvent with the fish tissue.

Extraction with hot solvents in a Soxhlet extractor was demonstrated to be more efficient for fish extraction than use of cold solvents in a glass column extraction (Hattula, 1974a). The study involved comparison of four solvent systems with three different fish (pike, perch and bream). The solvent systems were diethyl ether, diethyl ether/n-pentane (50:50), acetone/diethyl ether/n-hexane/petroleum ether (31:6:14:50), and methanol/chloroform (50:50). In the column extraction technique, 50 mL of the solvent was added to a glass column containing 5 g of loosely packed, ground fish tissue. After 2 hr of unagitated extraction, the solvent was drawn off and the tissue rinsed. Thus, only a single partition was effected. The Soxhlet extractions were carried out for 6 hr. The amount of native PCBs extracted from the fish were consistently higher with the Soxhlet extractor. The efficiencies of the different solvents were comparable. The author noted that the ±10 to ±20% RSD in the amounts extracted was high and cautioned that the extraction step is critical to the overall analytical precision.

MONS 005326

Blending of the solvent and fish assures good contact. This technique is employed in the AOAC (1980a) procedure for extraction of fish (Method 29.012(e)). In this procedure, 25-50 g of fish are ground with Na_2SO_4 in a high speed blender to disintegrate the sample and bind any water. The sample is then extracted three times with petroleum ether. The supernatant solvent is filtered, combined, dried with Na_2SO_4, and concentrated in a K-D evaporator. A portion of the sample is removed for percent fat determination. The AOAC method is widely used, sometimes with minor modifications, such as substitution of n-hexane for petroleum ether. The collaborative validation was published by Sawyer (1973).

2. Column chromatography: The use of extraction columns has been reported for extraction of PCBs from fish (Stalling, 1971; Erney, 1974b; Hattula, 1974a). Fish samples are ground with sodium sulfate and sand to yield a dry powder and loosely packed into a column. The PCBs are then eluted with solvent. A minor variation reported by Stalling (1971) used dry ice during the grinding step to keep the tissue solid and therefore more amenable to pulverization. Although quantitative recoveries (97 ± 3%) have been reported by Stalling (1971), the lack of agitation and possible channeling of the column may lead to poor or irreproducible recoveries.

3. Distillation: A modification of the Nielsen-Kryger steam distillation apparatus was used for extraction of PCBs and other chemicals from fish, water and sediment (Veith and Kiwus, 1977; Dougherty et al., 1980). The apparatus (Figure 5-1) permits simultaneous steam distillation and solvent extraction. The final extract is amenable to analysis without further cleanup. A recovery of 92% from 10 g Ohio River catfish diluted with 2.5 L of water was reported for a 7-hr extraction. Kuehl et al. (1980b) reported success with a micro version of the extractor for analysis of 0.5 g of tissue. In contrast to the work by Veith and Kiwus, Kuehl et al. added 10% H_2SO_4 to the distillation flask, presumably to "digest" the matrix.

4. Saponification with base: Saponification has also been used to prepare samples of fish, shellfish, and other marine organisms (Castelli et al., 1983). The samples were homogenized with water, refluxed with ethanolic KOH and extracted twice with n-hexane. The hexane was washed with water, dried and concentrated samples were cleaned on Florisil and analyzed by HRGC/EIMS-SIM. The precision of the entire method was measured with Aroclor-spiked biological samples and found to be between 1.6-19%, depending on the homolog. The injection precision was similar, indicating that the instrumental determination contributed most of the measurement error.

MONS 005327

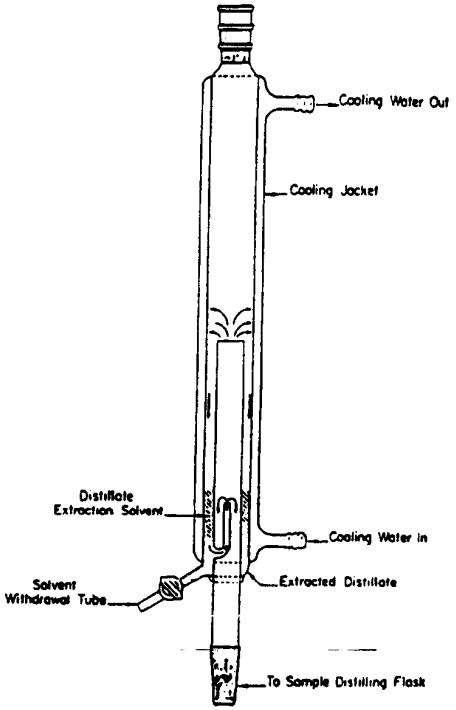


Figure 5-1. Exhaustive Steam-Distillation and Solvent-Extraction Apparatus

Reprinted, with permission, from Veith and Kiwas (1977); copyright 1977 by Springer-Verlag.

C. Milk

Milk is a fatty sample, which can retain PCBs and other pollutants. Cow's milk is of interest as a possible source of human consumption. Similarly, human milk is of concern with respect to consumption by infants. In addition, milk can be studied as a non-invasive sample collection procedure to measure body burden (Erickson et al., 1980b).

1. Acetonitrile back-partition: The AOAC (1980a) method for extraction of milk samples (Method 29.012(c)) uses 100 mL of milk. Ethenol (100 mL) and 1 g of sodium oxalate are added. The mixture is extracted three times with ethyl ether/petroleum ether (50:50), separating the layers by centrifugation. The combined organic layers are then washed with water three times, dried with sodium sulfate, and concentrated by evaporation. The PCBs and related compounds are separated from the fat by acetonitrile partitioning.

McKinney et al. (1984) validated a slight modification of the AOAC method, substituting hexane for petroleum ether. Five other solvent systems (all mixtures of a polar, water-miscible and nonpolar solvent) were investigated in lieu of the hexane-ether-ethanol combination. The latter yielded the highest lipid extraction and best reproducibility. At 20 and 40 ppb, PCB recoveries of about 102% with RSDs of ± 14 to ± 24% were reported. The method was applied to both human milk and infant formula samples.

EPA has utilized two methods for PCBs in human milk (Watts, 1980). The macro method employs an extraction with acetone, followed by hexane. The micro method uses an acetonitrile extraction, followed by a hexane partition. In the macro method, up to 25 g of milk are extracted three times with acetone and then twice with hexane. The combined extracts are washed with water twice to remove water-soluble materials, including the acetone. The extract is then dried and concentrated. The extract is then partitioned with acetonitrile as described for adipose tissue, above, and analyzed by PGC/ECD.

2. Saponification with base: A milk extraction technique similar to the AOAC method was published by Yakushiji et al. (1978). However, instead of the acetonitrile partition, they employed a reflux in ethanolic KOH to saponify the lipids. The resulting digestate was diluted with water and extracted with hexane. Saponification of milk samples has been reported by Tuinstra et al. (1980, 1981) and Tuinstra and Traag (1979a, 1979b).

MONS 005329

3. Acid digestion: A single extraction of acidified milk with petroleum ether gave 90-95% recovery for PCBs (Veierov and Aharonson, 1980). The milk was acidified by slowly adding conc. H_2SO_4. The sample was then mixed until the curds redissolved before the extraction. The extract was then cleaned up by addition of sulfuric acid, three times the quantity needed for decoloration. The organic layer was then concentrated and analyzed by PGC/ECD.

4. Column chromatography: Savage et al. (1973a,b) published procedures similar to those in Watts (1980) except a Florisil column cleanup was used instead of the acetonitrile partition. In the micro method, 500 mg of milk are extracted three times with acetonitrile. The extraction is performed in a tissue grinder to effect mixing and the resulting emulsion is broken by centrifugation. The combined extracts are diluted with water and extracted three times with hexane. The PCB-containing hexane extracts are concentrated, cleaned on a Florisil column, fractionated with a silicic acid column and analyzed by PGC/ECD.

A combination extraction/cleanup technique for milk and dairy products used silica gel (Steinwandter, 1982a). Milk was slurried with silica gel and added to a chromatography column on top of 10% water-deactivated silica gel. The column was then eluted with dichloromethane/petroleum ether (20:80), which extracted the PCBs from the milk and cleaned up the eluate on the lower portion of the column. Samples were then analyzed by HRGC/ECD or HRGC/EIMS.

5. Extraction of freeze-dried samples: Freeze-dried milk samples have been Soxhlet-extracted with hexane (Bush et al., 1983). Recoveries from the entire method, which included a Florisil column cleanup and HRGC/ECD determination, were generally 60 to 80% for most congeners. However, recoveries in the 26 to 50% range were observed for mono-, di-, and trichlorobiphenyls, presumably because of volatilization losses in the freeze-drying step. The precision of the method was ± 5% or better for the major individual congeners. Bush et al. (1983) noted the poor recovery of the lighter PCB congeners, but judged that the simplicity of the technique made it worth using.

D. Eggs

Eggs from various species of birds have been extracted with hexane after grinding with sodium sulfate. The lipids were removed by chromatography on alumina (Zitko, 1976).

A column elution technique (Wardall, 1977) combined the extraction and lipid removal steps. Eggs were ground with sodium sulfate and then mixed with Celite 545. This mixture was added to a glass chromatography column on top of a 5-g bed of alumina. The PCBs were then eluted with hexane. The eluate was analyzed by GC/ECD without further cleanup. Recoveries from 60-80% were observed for four PCB congeners.

E. Other Animal Organs

The above sections have described the extraction techniques for fatty organs and samples which generally contain the highest PCB concentrations and are therefore of the most interest. Other organs also contain PCBs (see Chapter 2) and are extracted by similar techniques. The lower lipid content of these samples often allows the analyst to use less stringent PCB/lipid extraction techniques.

Quail brains have been extracted using a column technique after homogenization with Florisil and sodium sulfate. The eluent was dichloromethane/petroleum ether (30:70). Whole bald eagle carcasses were homogenized and 20-g aliquots Soxhlet extracted to determine the PCB concentration in the entire bird (Begley et al., 1970).

Tarradellas et al. (1982) describe an analytical method for earthworms and their gut contents. The earthworms were digested with a mixture of perchloric acid/glacial acetic acid (40:60) for 24 hr over a steam bath. The digestate was then extracted three times with hexane. Sulfuric acid, mercury, and Florisil cleanup steps prepared the samples for HRGC/ECD analysis. The analysis of earthworms was promoted as a sensitive indicator of the concentration of PCBs in soil, since the earthworms exhibited five to eight times the concentration of the soil. Furthermore, the earthworms appeared to "average" the PCBs as they migrated through the soil, since the RSD of earthworm samples was much smaller than the RSD of the PCB concentrations of soil samples taken from different areas of a plot.

F. Plant Tissue

Plants, feed, grain, etc., must be ground and thoroughly mixed before extraction. This preparation step may be combined with addition of sodium sulfate to bind water, as with many other matrices. Corn silage has been extracted in a blender with isopropanol/hexane (33:67), followed by a second extraction with benzene (Ernst et al., 1974). The extracts were filtered, combined, concentrated, cleaned by Florisil chromatography, and analyzed by PGC/ECD.

MONS 005331

1. Acetonitrile back-partition: A classic procedure for organochlorine pesticides in nonfatty foods employs an acetonitrile extraction of the chopped sample, followed by a petroleum ether back extraction of the acetonitrile after dilution with water (Mills et al., 1963; FDA, 1977-Section 212). After blending or chopping, the 100-g sample is blended with 200-mL acetonitrile and 10 g Celite in a blender. The acetonitrile is separated from the solids by filtration. The filtrate is diluted with 600 mL water, 10 mL saturated NaCl, and extracted with 100 mL petroleum ether. The organic layer is washed with 2 x 100 mL water and dried with sodium sulfate. The extract is then cleaned with Florisil column chromatography and analyzed by gas chromatography. The procedure has not been validated for PCBs, but quantitative recoveries of several organochlorine pesticides from green vegetables, soups, fruits, and other foods (Mills et al., 1963) indicate that it would be suitable for PCBs.

2. Column chromatography/acid digestion: A column extraction with a bed of sulfuric acid/silica gel (40:60, v/v) yielded an extract which was sufficiently clean for silica gel cleanup and then PGC/ECD analysis, without the need for acetonitrile partition, GPC, or other cleanup (Schwartz and Lehmann, 1982). The plant tissue was ground with sodium sulfate and then added to a glass chromatography column on top of the acid/silica gel mixture with a layer of sodium sulfate in between. The PCBs were eluted with hexane. The recoveries of Aroclor 1242 and 1254 were about 75 ± 6% at 10 ppb fortification level and about 90 ± 1% at 250 ppb fortification. This extraction presumably combines matrix degradation by the sulfuric acid with chromatographic separation in the column elution.

G. Discussion of Tissue Extraction

Proper extraction of PCBs from animal and plant tissue samples presents a challenge. The matrix must be disrupted, the PCBs must be removed, and finally the lipids and other co-extractive material must be separated. The tissue can be macerated with a mechanical mixer, as long as the size is appropriate, sufficient maceration is achieved, and no contaminants are introduced from gaskets or other sources. Sodium sulfate and/or sand are often added during this step to adsorb any water and for "grit" to aid in the grinding. The extraction solvent--often added prior to maceration--must not only be a good solvent for PCBs but should also assist in cell disruption. Acetone and alcohols are good solvents for cell lysis. A mixed polar/nonpolar solvent such as acetone/benzene, ether/hexane, or methanol/chloroform appears to be the best extractant for PCBs.

The separation of the lipid materials has been achieved by many techniques, as discussed above. If PCBs are the sole analyte, a chemical destruction of the lipids may be the most straightforward. Sulfuric acid will destroy many biological (aliphatic) interferents, although losses of the lower-chlorinated PCBs have been reported (see Chapter 6). Saponification with base is also a useful technique for destroying triglycerides and other esters.

If additional analytes, such as the chlorinated pesticides, must be preserved, sulfuric acid digestion may not be advisable. The silver nitrate column of Smrek and Needham (1982) appears to be an elegant separation technique. The "classic" acetonitrile-hexane partition (Mills-Onley-Gaither) may be used, but recoveries from this step must be well-documented through validation and appropriate QC measures.

VIII. PAPER PRODUCTS

By virtue of their use in carbonless copy paper and other paper products and the extensive recycling of paper products, analysis for PCBs in paper products has been of considerable interest. A number of simple solvent extractions with hexane (Giacin and Gilbert, 1973; Serum et al., 1973; DeVoogt et al., 1984), petroleum ether (Shahied et al., 1973), and acetone (Kuratsune and Masuda, 1972) have been reported. Recoveries of 80-102% were reported by DeVoogt et al. (1984) from a variety of paper products ranging from toilet paper to paperboard.

An alcoholic KOH reflux was recommended as the technique for use with routine paper samples (Young et al., 1973) and ultimately adopted as an official method (AOAC, 1980b). While both the KOH saponification and a sulfuric acid digestion gave 96-97% recoveries from fortified paper samples, the latter technique was more tedious. In the KOH procedure, the samples (10 g) are cut up, mixed, and refluxed with 60 mL 2% KOH in ethanol or methanol for 30 min. The sample is diluted with water and repeatedly extracted with petroleum ether. The combined extracts are then washed with water, dried with sodium sulfate, concentrated in a Kuderna-Danish evaporator, cleaned on a Florisil column, and determined by PGC/ECD. Similar methods have been used by others (Stanovick et al., 1973; Easty, 1973; Becker and Schulte, 1976; Easty and Wabers, 1977).

MONS 005333

IX. OILS

The determination of PCBs in oils has been of interest because of the high frequency of contamination of certain types of oils. PCBs have many similar chemical, physical, and use properties of mineral oil, silicone oil, and other oils. Mixing PCBs with these oils and cross-contamination has led to broad-scale contamination of non-PCB fluids with PCBs at low concentrations. For example, many askarel transformers have been retrofilled with mineral oil or other dielectric fluid to declassify the transformer from "PCB" status. The resulting transformers generally have trace (50-500 ppm) quantities of residual PCBs and are classified as "PCB-contaminated." In addition, many electrical components were contaminated from residual PCBs at the manufacturing site. As discussed in Chapter 2, the PCB contamination of these oils determines their classification, and thus use and disposal rules, in the U.S.

PCBs have also contaminated other oils which enter the animal or human food sources. A notable, classic example is the Yusho incident (see Chapter 2 for a more detailed discussion), in which cooking oil which had been contaminated with PCBs, was distributed in Japan. Many people were contaminated by the PCBs in this oil. As noted above, PCBs and many oils have similar properties. For this reason, extraction techniques used for polar matrices, such as water, are not appropriate for extraction of oils. Often, the "extraction" is simply a dilution of the matrix to lower the viscosity to make an injection on a GC. Some "extractions" are conducted under cleanup steps, as described in Chapter 6.

A. Transformer and Related Oils

1. Organic oils: Liquid-liquid partition of PCBs from oils is difficult. The similar polarity of the PCBs and the matrix make unfavorable partition ratios. In addition, the lack of chemical reactivity of the matrix generally prevents the use of any chemical degradation techniques to convert the oil to an extractable matrix. Therefore, the most common "extraction" technique for these matrices has been simple dilution.

Hexane dilution has been successfully used in the preparation of common PCB-containing oils for analysis by PGC/ECD or PGC/HECD (Sonchik et al., 1984; Levine et al., 1983). Samples were diluted either 1:25 or 1:100. Hexane dilution is also recommended for analysis of transformer fluid and waste oils by the U.S. EPA (1981a; Bellar and Lichtanberg, 1981). The procedure specifies 1:100 or 1:1000

dilution of the oil with pesticide grade hexane. The procedure recommends screening the sample to determine the approximate concentration by X-ray fluorescence, microcoulometry, density measurement, or GC screening of a very dilute (1:10,000) sample. Samples are then analyzed by PGC/HECD, PGC/ECD, or PGC/EIMS. Several optional cleanup techniques are presented. Several types of matrices are covered by the simple dilution approach:

a. Transformer oils: The most common transformer oil which might be contaminated with PCBs is mineral oil, which contains 20-30% aromatics and the balance hydrocarbons. Polydimethylsiloxane (silicone) fluids, discussed below, are the next most common. Other transformer dielectrics which are used to retrofill PCB transformers are paraffinic hydrocarbons, high temperature esters, tetrachloroethylene (Perc, Wecosol®), and non-PCB askarels (chlorinated benzenes). The properties and uses of these matrices are discussed more thoroughly in a review (PEDCo, 1984). In addition to these non-PCB dielectric fluids, old transformer oil samples can be PCB askarels, containing up to 70% PCBs, as discussed in Chapter 2.

b. Capacitor fluids: Capacitor askarels contain high levels of PCBs such as Aroclor 1016, as described in Chapter 2. Substitutes which may be contaminated with PCBs include alkyl phthalate esters, 1,1-phenylxylylethane, isopropylbiphenyl, and butylated monochlorodiphenyl ether.

c. Hydraulic fluids: Hydraulic fluids may be petroleum based oils, phosphate esters, water glycols, and invert emulsions. These matrices are most often contaminated with Aroclor 1242 in the U.S. (Sonchik et al., 1984).

d. Waste oils: Waste oils can come from many sources and have various compositions, including road oil, automotive crank case oil, and recycled fuel oil.

e. Other oils: Water glycol and invert emulsion hydraulic fluids were immiscible with hexane. These matrices were extracted three times with hexane (Sonchik et al., 1984).

A liquid-liquid partition of transformer oil with acetonitrile/hexane (90:10) has been described (Gordon et al., 1982). Specifically, 1.0 mL of the transformer oil is shaken with 15 mL of the acetonitrile/hexane mixture, centrifuged, and the oil layer discarded. The acetonitrile is then diluted with 10 mL water and the PCBs extracted into 10 mL hexane. The hexane is concentrated to 1.0 mL and cleaned up with a silica gel cartridge (Sep-Pak®) and then determined

MONS 005335

by HRGC/ECD. Recoveries for the total method were 70 to 100% for Aroclors 1254 and 1260 but only 40 to 75% for Aroclor 1242 over a concentration range of 5 to 500 ppm. Volatility of the lighter Aroclor 1242 was blamed by the study authors for the low recoveries, although different partition ratios of the lower PCB congeners must also be considered.

2. Silicone oils: Two extraction techniques have been used for silicone fluids: an acetonitrile partition for subsequent HPLC determination, and a carbon column extraction for PGC/ECD determination (Klimisch and Ingebrigtson, 1980). The acetonitrile partion was deemed necessary, since direct injection of the silicone fluid degraded the HPLC column efficiency. A 0.1 g sample was diluted with 2.9 g of clean silicone fluid and extracted with 3 mL of dry (< 0.5% water) acetonitrile. The acetonitrile was then diluted with water to the same composition as the HPLC mobile phase (62% acetonitrile). The authors noted that PCBs are only slightly soluble (0-2%) in acetonitrile and that low recoveries would be observed if the PCB concentration in the oil exceeded that concentration.

A charcoal extraction technique was used for samples in the 25 ppb to 5 ppm range (Klimisch and Ingebrigtson, 1980). A 1-2 g sample was dissolved in acetone/diethyl ether (25:75) and applied to a 1 x 15 cm column of 50-200 mesh activated coconut charcoal. A 75-mL portion of the acetone/diethyl ether mixture was eluted through the column. The PCBs were then eluted from the column with 75 mL toluene, which was concentrated, and then determined by PGC/ECD. Aroclor 1248 was quantitatively recovered (91-106%) from the column in the 1-20 µg range.

8. Vegetable Oils

Vegetable oil and related products have been analyzed by dilution with ethyl acetate/toluene (75:25), filtration if necessary, gel permeation chromatography, Florisil chromatography, and determination by PGC/ECD (Young and Kamps, 1982). The method was applied to crude soybean oil and its refinery by-products (soapstock, deoderizer distillate, and clabber stock). Specifically, 5.0 g of sample was diluted to 50 mL with ethyl acetate/hexane (75:25). Viscous or solid samples were liquified by gentle heating. The sample preparation technique was not specifically validated, although a recovery of 98% for Aroclor 1254 at 3 ppm was measured for the entire method.

The rice oils implicated in the Yusho incidents (both in Japan and in Taiwan) were prepared for analysis by saponification (Nagayama et al., 1975, 1976; Chen et al.,

1981). The oil was heated in ethanolic sodium hydroxide and extracted with n-hexane. Saponification is described in more detail in Section VII.C.2 in this Chapter.

X. ANCILLARY CONSIDERATIONS

A. Solvent Evaporation

Concentration of the sample extract by solvent evaporation is common to many of the extraction techniques discussed above for the various matrices. Common evaporative techniques involve either boiling of the solvent or blowing a dry gas stream (usually nitrogen) across the solvent surface. The former technique is often accomplished with a reflux column to reduce the chance of solute loss through vaporization or spattering. The most common evaporative apparatus is the Kuderna-Danish (KD) evaporator. Numerous studies have investigated the efficacy of the various concentration techniques with a common conclusion that the most important factor in preventing loss of analyte during this step is operator skill and attention. In short, solvent evaporation techniques are an "art."

Caragay and Levins (1979) reported significant losses of Aroclor 1254 during KD concentration of dichloromethane/hexane (15:85). They noted that with proper attention to a rapid evaporation, "good recoveries" were obtained.

B. Sorption onto Glassware

As noted in Chapter 4, significant adsorptive losses onto both glass and plastic surfaces have been documented in water (Pepe and Byrne, 1980; Muldrew et al., 1981; Sutcliffe and Nielsen, 1983). Silanization appears to retard the losses (Muldrew et al., 1981; Neidert and Saschenbrecker, 1984). While data are available for water and adipose samples only, sorptive losses from any matrix or solvent is possible. For example, during an evaporative concentration in hexane, it is entirely possible that significant amounts of PCBs (and other organic analytes) could be deposited on the glass surface as the volume is reduced. Even with hexane and other "good" solvents, the low concentrations of PCBs could easily favor partition to the glass surface.

Analysts can guard against sorptive losses through good analytical technique. The entire interior of a sample container (contents, glass surface, and cap liner) should be treated as the "sample." An extract of the container can easily be combined with the sample extract. Furthermore, all sample transfers should be accompanied by a quantitative

MONS 005337

rinse--including pipets. During the sample concentration steps, the sides of the container should be rinsed where possible and care should be taken to avoid spattering. If losses are observed or suspected, silanization may improve recovery. Finally, proper QC practices will monitor the recovery, so that any PCB losses will be detected (see Chapter 9).

C. Sources of Contamination

Contamination of samples by PCBs, interfering compounds, or non-specific interferences can lead to erroneous results and require repetition of the analysis, if the problem is detected. Interferences may come from solvents, reagents, glassware, the laboratory environment (contaminated air or work areas), or anything else that comes into contact with the sample. Generally, the analysis of laboratory reagent blank is sufficient to demonstrate that the samples are free from contaminants.

Preventing contamination of samples requires good general laboratory practice. Glassware must be scrupulously cleaned. It should be rinsed as soon as possible after use to remove gross contaminants from the sample and then subjected to a strict cleaning protocol. Many standard methods (see Chapter 3) give guidance on glassware cleaning. A good glassware cleanup protocol should reduce carryover from previous samples by at least 10^4 (i.e., only 0.01% of the previous sample should remain on the glassware). Nevertheless, a laboratory should segregate glassware and space for low and high level samples to prevent cross contamination of samples at the nanogram-per-gram level by samples at the percent level.

High purity solvents and reagents (e.g., pesticide residue grade) are generally free from interferences. Nevertheless, many standard procedures and many laboratories stipulate that each new lot of a reagent be checked for purity. In addition, most adsorbents used for sampling, extraction, or cleanup are purified prior to use by solvent extraction or thermal desorption. Some of the adsorbents commonly used for sample cleanup have been found to contain interferences, as discussed in Chapter 6.

Contamination of final extracts can also be a problem. Contaminants can leach from the vial cap, cap liner, or the glue that holds the two together. PCB contamination can occur if the syringe used to inject onto a GC is not scrupulously cleaned between injections. Syringes should be segregated for high and low level work, since cleanup to trace levels is extremely difficult once a syringe has been contaminated.

MONS 005338

MONS 005339

6

CLEANUP

The cleanup step in an analytical procedure removes other compounds which may interfere with the determination of specific analytes such as PCBs. A cleanup takes advantage of the difference in physical or chemical properties of PCBs and interferences to remove the unwanted constituents. The cleanup process may be expressed in terms of enrichment, where the ratio of PCBs to interferents is increased. Ideally, a cleanup reproducibly achieves 100% recovery of PCBs in one fraction, with the interfering compounds relegated to other fractions.

The extent of cleanup required is dependent on the requirements of the determination step (see Chapter 7). With a highly selective detector such as mass spectrometry, less cleanup to remove other chlorinated organics would be required than for electron capture detection. On the other hand, low resolution electron impact mass spectrometry requires extensive cleanup to remove the oil matrix components prior to determination of trace levels of PCBs, while ECD is virtually blind to the components of a transformer oil matrix and little cleanup is required.

This chapter discusses the cleanup techniques available for PCBs, including adsorption column chromatography; high performance liquid chromatography (HPLC); thin layer chromatography (TLC); gel permeation chromatography; and chemical degradation with acid or base. When appropriate, adsorption column chromatographic fractionation techniques which isolate PCBs into different groups are also presented in this chapter. Partition techniques to remove bulk matrix interferences were presented in Chapter 5 (Extraction), since these techniques are highly matrix-dependent. Some of these techniques combine extraction and cleanup in one step.

MONS 005340

I. ADSORBENT COLUMN CHROMATOGRAPHY

Adsorption column chromatography is the most common sample cleanup. In this technique, a solvent eluted a sample extract through a column containing at least one adsorbent. The differences in polarity, solubility and partition cause the PCBs and other compounds to move at different rates. Thus, the PCBs can be isolated in an appropriate fraction. Common adsorbents include Florisil, silica gel, alumina, and carbon. In addition, a combination of adsorbent materials in one column, a column cleanup after liquid-liquid partition, or a column cleanup after matrix destruction by sulfuric acid or saponification have all been reported.

Adsorption chromatography separates compounds by liquid-solid partitioning. The affinity of the PCBs and other components of the sample for the adsorbent depends on their polarity and the surface activity of the adsorbent. The adsorbent can be activated by heat (e.g., 130°C) or other treatment, which makes more binding sites available. Conversely, adsorbents can be deactivated by tying up the sites. A common deactivation for many of the adsorbents is adding water to hydrate some of the binding sites, thereby making them unavailable for PCBs or other organic sample constituents. The other aspect of liquid-solid partition is the solubility of the sample components in the solvent. The solvent polarity can be precisely controlled to either enhance or retard the elution of the organic components from the column.

A. General Practices

An adsorption column is generally prepared by either a slurry-packing or dry-packing technique. The sample is then applied to the top of the column in a small volume. The PCBs and other components are eluted through the column with an appropriate solvent. Air or nitrogen pressure can be applied to accelerate the elution. The separation is often enhanced by changing the polarity of the solvent during the elution. The PCBs are eluted in a given, predetermined fraction. This fraction may include many other organics or may include only a specific subset of the PCBs.

Because of the differences in adsorbent activity and packing efficiency, each batch of adsorbent should be tested for the PCB elution volume. This is usually done by passing a PCB mixture through the column and collecting the eluent in small (e.g., 10 mL) fractions. The individual fractions are then analyzed to determine where the PCBs elute. This permits the analyst to define a routine collection fraction which will contain all PCBs. Azulene, a blue-colored

MONS 005341

aromatic compound which is not detected by GC/ECD, has been found to be a useful visual indicator to monitor the elution of each individual Florisil, silica gel, or alumina column (Nowicki, 1981; Erickson et al., 1983e). This technique appears to greatly reduce the uncertainties in the appropriate volume of the PCB fraction. The position of the blue azulene band serves to mark the location of the end of the first fraction. The cut between fractions is made by the analyst when the azulene band reaches a prescribed point, not when a specified volume of solvent has eluted. Griffin et al. (1980) measured the movement of the azulene down a silica gel column as the fraction of the total column length, R_f. They found that the best cut point to separate PCBs from p,p'-DDE ranged only from an R_f of 0.32 to 0.38, while the absolute volume ranged from 90 to 150 mL. Clearly, the azulene indicator provides a more precise measure of the appropriate elution volume. The authors noted that azulene eluted from a packed OV-101 column well ahead of the earliest peaks in Aroclor 1221 or any other Aroclors and also exhibited a response of 3×10^{-4} relative to aldrin. Therefore, azulene should not interfere with PCB determination by GC/ECD.

B. Florisil

1. Properties: Florisil (trademark, Floridin Co.) is a synthetic magnesium silicate. The Florisil generally used in PCB analyses is 60/100 mesh pesticide residue ("PR") grade. It has typically been activated by heating to 650°C by the manufacturer. Although cleanup of the reagent with solvent may improve the blank values, most of the standard procedures simply prescribe heating the Florisil, as received, at 130°C until it is to be used (FDA, 1977; AOAC, 1980a; Watts, 1980). The U.S. EPA (Watts, 1980) specifically recommends storing pre-packed Florisil columns in a 130°C oven at least overnight to ensure column uniformity. It also recommends that the oven used to store sorbents should be restricted from general use to prevent contamination.

While fully activated Florisil has been most widely used, the use of deactivated Florisil has been reported. A 2% deactivated Florisil column cleanup has been used by Bush et al. (1983, 1984) for cleanup of milk and blood samples, and by Bush and Barnard (1982) for cleanup of fish eggs, rat brain, and aquatic macroinvertebrates. Specifically, Florisil was activated at 450°C, deactivated by addition of 2% water (v/w), and equilibrated by shaking for at least 0.5 hr. Columns (1 cm I.D.) were dry-packed with 10 g sorbent and the PCBs eluted with 40 mL hexane. Mirex, photomirex, p,p'-DDE, o,p'-DDE, hexachlorobenzene, and octachlorostyrene eluted with the PCBs. Other pesticides were eluted with ethyl ether/hexane (10:90).

MONS 005342

2. Evaluation of activity: As with other sorbents, the adsorption characteristics of Florisil can vary significantly from lot to lot. Thus, it has often been recommended that each lot be evaluated. An evaluation of the quality of Florisil has been described in detail in Section 3,D of EPA's pesticide residue analysis manual (Watts, 1980). A representative sample of Florisil is thoroughly mixed and packed into columns. A standard solution of pesticides (PCBs could also be added if they are to be an analyte) is then eluted through the column and the appropriate fractions collected. The elution pattern is then measured and the acceptability of the batch determined. Acceptable total recovery of organochlorine pesticides from all fractions is 90 to 105% (Watts, 1980; Sherma, 1981). No provision is made by Watts (1980) for adjusting the volume or composition of the elution solvents to optimize recovery. However, FDA (1977) permits the analyst to adjust the amount of sorbent in the column from the normal 4-in. depth to compensate for "over-retentive" or "under-retentive" Florisil.

A lauric acid adsorption technique has also been widely used to estimate the adsorptive capacity of Florisil (Mills, 1968; FDA, 1977). An excess of lauric acid in hexane is added to a weighed amount of Florisil and the amount not adsorbed is measured by titration with sodium hydroxide. A "lauric acid value" is then calculated as the milligrams lauric acid adsorbed per gram Florisil. From this lauric acid value, the amount of Florisil in the column is adjusted from the normal 20-g column. The elution characteristics of the batch are then verified by elution of a standard mixture of pesticides (FDA, 1977), similar to that described for the EPA procedure in the previous paragraph.

The elution of each column can also be visually monitored with azulene. This technique is discussed in Section I.A, above.

3. Mills-Onley-Gaither technique: The Florisil column cleanup in a classic pesticide analysis method (Mills et al., 1963) was the basis for many of the standard PCB procedures presented in Chapter 3. These include food (FDA, 1977; AOAC, 1980a); adipose (Watts, 1980); soil and bottom sediment (EPA, 1982d); and paper and paperboard (AOAC, 1980b). Specifically, the "Mills-Onley-Gaither" (MOG) method used a large column (10 x 2.5 cm) of activated Florisil to clean up extracts of 100-g samples of fruits and vegetables. The elution solvents were ethyl ether/petroleum ether (6:94; Fraction I), ethyl ether/petroleum ether (15:85; Fraction II), and ethyl ether/petroleum ether (50:50; Fraction III). The method was adopted for PCB analysis. Seven Aroclor mixtures (1221 through 1262) were shown to elute in Fraction I,

MONS 005343

"the 6% fraction" (McMahon and Burke, 1978; Watts, 1980; Millar et al., 1981, 1982). This fraction is often submitted to further cleanup, as discussed in the section on silica gel (Section I.C, below), since many organochlorine pesticides (e.g., DDE, DDT, heptachlor) also elute in this fraction and interfere with PGC/ECD determination.

The MOG Florisil cleanup has been widely used to clean up fish (Erney, 1974; Sawyer, 1973), animal and human adipose (Sawyer, 1973; Erickson et al., 1983e); wastewater (Millar et al., 1981, 1982) and other matrices in addition to the food matrices for which it was originally validated.

4. Eluting solvent: It has been noted (Watts, 1980, Section 3, D, VIII, 2) that the polarity of the solvent dramatically affects the elution characteristics of many pesticides on a Florisil column. The standard elution characteristics have been obtained with ethanol/diethyl ether (2:98). The solvent composition should be tightly controlled to ensure reproducible results.

Ethyl ether/petroleum ether (6:94) or ethyl ether/hexane (6:94) is the classic solvent mixture used to elute PCBs and many organochlorine pesticides from Florisil (Mills et al., 1963; see Section I.B.3, above). A substitution of dichloromethane/hexane (20:80 to elute PCBs) has also been shown to be effective (Seidl and Ballschmiter, 1976b). PCB recoveries of > 90% from up to 1 g fat were observed. Methanol/hexane (2:98) has also been found effective for elution of PCBs and DDE from Florisil columns (McKinney et al., 1984).

Hexane has been found to be a satisfactory eluent for PCBs, in a cleanup of adipose (Erickson et al., 1983e), fish and shellfish (Castelli et al., 1983), milk and blood (Bush et al., 1984, 1984), and eggs, brain, and aquatic invertebrates (Bush and Barnard, 1982). Dichloromethane was used to elute PCBs from a Florisil column to clean up phthalocyanine blue, phthalocyanine green, and diarylide yellow pigments (DCMA, 1982).

5. Cartridges: A rapid cleanup using commercially prepared Florisil cartridges (Sep-Pak®, Waters Associates, Milford, MA) was demonstrated to yield quantitative PCB recoveries from fish samples (McKone and Daub, 1983). In addition, the Sep-Pak and conventional column Florisil cleanups were compared using eight fish samples with Aroclor 1260 concentration ranging from 2 to 178 ppm. The results from the two techniques compared within 10%. In the Sep-Pak cleanup a 5-mL petroleum ether extract of fish was flushed through the cartridge. The eluate, plus an additional 2-mL of petroleum

ether, was collected, diluted to a known volume and analyzed by PGC/ECD. Repetition with a second cartridge was required to effectively remove the lipids from samples containing more than 4% fat. The use of the cartridges gave equivalent performance and was much faster and easier to perform.

6. Applications: In addition to the applications noted above, Florisil has been used to remove gross interferences from sample extracts from air, water, wastewater, tissue, dairy products, oil pigments, paper, paperboard, and paper mill effluent (AOAC, 1980; Adams et al., 1979; Delfino and Easty, 1979; Easty, 1973; EPA, 1979a; EPA, 1979b; EPA, 1978; EPA, 1980; Sonchik et al., 1984; Kamps et al., 1979; Kuehl et al., 1980; Modi et al., 1976; Price and Welch, 1972; Reynolds, 1969, 1971; Robbins and Willhite, 1979; Rodriguez et al., 1980; Stijve et al., 1974; Swift and Settle, 1976; Tessari and Savage, 1980; Yakushiji et al., 1978; Bagley et al., 1970; Bagley and Cromartie, 1973; Bellar and Lichtenberg, 1975; Chau and Babjak, 1979).

Florisil has also been used to provide additional separation of sample extracts following initial cleanup of matrices by low temperature precipitation, acetonitrile partitioning, oxidation, sulfuric acid digestion, alumina chromatography, or gel permeation chromatography (Eder, 1976a; Ernst et al., 1974; Kohli et al., 1979; Mes et al., 1977a, Mes et al., 1977b; Mulhern et al., 1972; Stanovick et al., 1973; Swift and Settle, 1976; Tessari and Savage, 1980; Trotter, 1974; Uk et al., 1972; Bagley et al., 1970; Bagley and Cromartie, 1973; Copeland and Gohmann, 1982).

7. Detailed procedure: As an example of the Florisil column cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Variations among batches of Florisil (PR grade or equivalent) may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all PCBs must be verified by the analyst. The weight of Florisil can then be adjusted accordingly.

2. Place a 20-g charge of Florisil, activated overnight at 130°C, into a Chromaflex column. Settle the Florisil by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the Florisil. Pre-elute the column with 70 to 80 mL of hexane. Just before the exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

MONS 005345

3. Add the sample extract to the column.

4. Carefully wash down the inner wall of the column with 5 mL of hexane.

5. Add 200 mL of ethyl ether/hexane (6:94) and set the flow to about 5 mL/min.

6. Collect 200 mL of eluate in a Kuderna-Danish flask. All the PCBs should be in this fraction. Concentrate to an appropriate volume.

7. Analyze the sample.

C. Silica Gel

1. Properties: Silica gel is a granular form of silicic acid (H_2SiO_3). It is widely used as an adsorbent for organic molecules in both gas and liquid phases. It has been used both for primary sample cleanup and for fractionation of PCBs from similar organics after another cleanup.

2. Contaminants: Contaminated silica gel can present blank problems. Up to 160 ng PCBs/g silica gel were found in liquid-chromatographic grade silica gels from several manufacturers (Bergman et al., 1984a). The authors attributed the contamination to either the final cleanup or adsorption of PCBs from ambient air during storage. The PCBs were extracted from the silica gel by eluting a column with dichloromethane. This cleanup step was recommended by the authors as a satisfactory cleanup technique. Huckins et al. (1976) also reported contaminants, including bis-2-ethylhexyl phthalate, and PCBs. The occasional presence of H_2SO_4 in the sorbent may have produced other contaminants which interfered with PGC/ECD analysis. A purification of the silica gel by extraction with acetonitrile/dichloromethane (40:60) and then drying at 160°C for at least 48 hr was recommended.

3. Eluting solvent: The composition of the elution solvent can have marked effects on the elution of PCBs (and other organics) through silica gel. Zitko (1971b) demonstrated that the benzene content of different pesticide grade hexanes could markedly affect the elution of Aroclor 1254. Only 18% of the PCBs eluted with 10 mL of hexane containing 210 ppm benzene, while 56% of the PCBs eluted when the hexane contained 800 ppm benzene. Even higher recoveries were observed when more benzene was intentionally added. The benzene content of hexane has also been shown to decrease the resolution of PCBs from p,p'-DDE on silica gel (Griffin et al., 1980).

MONS 005346

4. Elution characteristics

a. Activated silica gel: The source and activity of the silica gel are important factors in the elution of PCBs and other compounds. Griffin et al. (1980) compared several batches of silica gel and demonstrated a wide variation in their activity. The best cut point to separate Aroclor 1254 and p,p'-DDE ranged from 20 to 150 mL of hexane for different brands of fully activated silica gel. Mallinckrodt No. 2847 (100 mesh, re-sieved to 100 mesh), which had the highest cut point, was judged best since it gave the best resolution of the PCBs from the p,p'-DDE. Davidson No. 923 was also judged acceptable; Davidson No. 950, fair; Davidson No. 50, poor; and Merck Silica Gel 60, poor. The latter two adsorbents exhibited very low adsorbent activity. With the Mallinckrodt No. 2847, lot-to-lot variation did not affect the cut point, relative to an azulene visual indicator, although the absolute elution volumes did vary.

b. Deactivated silica gel: Intentional deactivation with distilled water is a common practice to speed up the elution of PCBs through a silica gel column. As illustrated in Figure 6-1, a less active sorbent (i.e., more water) will exhibit a shorter PCB retention, but will have poorer resolution (Griffin et al., 1980). Similar results were obtained by Armour and Burke (1970). The choice of the activity depends on the objective of the cleanup. If a gross cleanup of polar materials such as lipids is desired, a deactivated adsorbent may be practical, while a fractionation of PCBs from p,p'-DDE and other pesticides would be most effectively done with a fully activated adsorbent.

The elution volumes of PCBs and 50 pesticides on silica gel have been tabulated (Leoni, 1971). PCBs and several nonpolar pesticides such as hexachlorobenzene, aldrin, heptachlor, and several DDT analogs were eluted with n-hexane. The more polar pesticides required correspondingly more polar solvents. Davison 950 silica gel was activated for 2 hr at 130°C and then deactivated with 5% water.

c. Modified silica gel: An early application of silica gel to clean up samples for PCB analysis utilized an 80:20 mixture of 3%-activated silica gel/celite (Armour and Burke, 1970). A 25-g portion of the mixture was slurry-packed into a chromatographic column. PCBs were eluted with 250-mL petroleum ether, using air pressure to accelerate the elution. Fish extracts were first cleaned up on a Florisil column and the PCB fraction further cleaned up with the silica gel. The recoveries for Aroclor 1254 and 1260 were 95 to 100% at the 40-µg level in solvent. Recoveries of 100% and 76% were observed for the same PCB mixtures at a similar column loading when spiked into trout extract.

MONS 005347

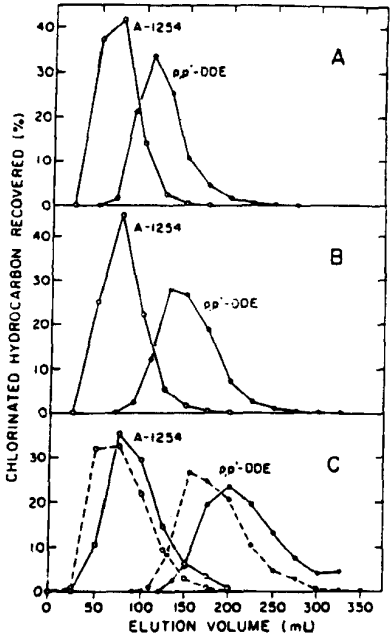


Figure 6-1. Separation of p,p'-DDE from Aroclor 1254 by Column Chromatography With Different Activities of Silica Gel

A - 1% Water-deactivated; B - 0.5% water-deactivated; and C - 0% water-deactivated, either activated in column (___) or bulk-deactivated and then cooled before packing (---). Columns were eluted with UV-grade hexane with 100 µg Aroclor 1254 or 10 µg p,p'-DDE.

Reprinted, with permission, from Griffin et al. (1980); copyright 1980 by Association of Official Analytical Chemists, Inc.

Silver nitrate has been used to alter the properties of a silica gel column (Needham et al., 1980; Trevisani, 1980). The $AgNO_3$ (10%) acts as a "trap" for ODE and related compounds, according to the authors who originated the technique for cleanup of fish samples for TCDD analysis (Lamparski et al., 1979).

d. Alumina and silica gel in series: Silica gel columns were used to separate PCBs and pesticides into groups after an initial cleanup with alumina (Holden and Marsden, 1969; Musial et al., 1974; Zitko, 1971a). PCBs, ODE, ODT and several other pesticides eluted with 10-mL hexane, while the BHCs, dieldrin, endrin, and heptachlor epoxide eluted with 10-mL ethyl ether/hexane (10:90) (Holden and Marsden, 1969). A careful cut of the hexane eluent could separate the PCBs and ODE (6-8 mL hexane) from the p,p'-ODT (14-16 mL hexane) (Musial et al., 1974). A similar separation scheme, using alumina and silica gel columns in series was used to separate phthalate esters, PCBs, pesticides and other compounds into appropriate fractions for analysis (Russell and McDuffie, 1983). The phthalate esters must be determined separately because they interfere with the GC/ECD detection of the PCBs and other chlorinated organics.

5. Column size: The size of the silica gel column should be scaled to the amount of material in the sample to be cleaned up. Steinwandter (1983) demonstrated that micro silica gel columns could effectively remove fat, while providing quantitative recovery of PCBs and pesticides when eluted with dichloromethane/petroleum ether (20:80). Columns containing 2, 3, and 4 g of silica gel retained 90, 140 and 190 mg fat with elution volumes of 20, 25, and 30 mL, respectively. The adsorbent was prepared by activating the silica gel at 450°C for 3 hr and then deactivating with 10% distilled water. Similarly, Erney (1974a) demonstrated quantitative elution of Aroclor mixtures from a 5-g silica gel column with 35 mL of petroleum ether. p,p'-ODE coeluted with the PCBs, while other common pesticides (e.g., ODT) eluted in a more polar fraction. Silica gel "as received" (i.e., no activation) was used for the validation studies after it was found that the "as received" material gave separations equal to or better than activated silica gel. This cleanup, following a Florisil cleanup, was used in a procedure for fish analysis (Erney, 1974b). The procedure gave comparable results, was faster, and used smaller amount of reagents than those in FDA's (1977) Pesticide Analytical Manual (PAM) standard procedure.

6. Applications: The ASTM (1981a) standard procedure for PCBs in water utilizes the silica gel microcolumn cleanup technique shown in Figure 6-2 after an initial

MONS 005349

cleanup using Florisil. The PCBs in the 6% fraction (ethyl ether/petroleum ether; 6:94) from the Florisil column are separated from the other organochlorine compounds by elution with n-hexane. The pesticides can be eluted with ethyl ether/benzene (0.5:99.5). The amount of solvent needed to elute the PCBs is determined by collecting 1-mL fractions of the eluate of standard solutions of PCBs and pesticides. Figure 6-3 presents the Aroclor elution patterns given by ASTM. It is interesting to note that the more highly chlorinated mixtures (e.g., Aroclor 1260) elute before the less chlorinated mixtures (e.g., Aroclor 1242).

Silica gel column cleanup has been applied to the determination of PCBs in a variety of matrices, including fish (Armour and Burke, 1970; Erney, 1974b; Stalling, 1971; Huckins et al., 1976), adipose (Sawyer, 1973; Swift and Settle, 1976; Mes and Campbell, 1977), blood (Needham et al., 1980; Stratton and Geiszler, 1977), milk (Watts, 1980; Musial, 1974; Steinwandter, 1982a), food (Tanabe, 1976; FDA, 1977; Leoni et al., 1973; Nose, 1973; Vannuchi et al., 1976; Trevisani, 1980), biological matrices (Kveseth and Brevik, 1979), sewage sludge (Erickson and Pellizzari, 1977, 1979; Ballinger, 1978), soils (EPA, 1982d; Nose, 1973), sediment (Bellar and Lichtenberg, 1975), air and stack gas (Bidleman et al., 1978; Levins et al., 1979; MacLeod, 1979), water (EPA, 1978; ASTM, 1981a; Erickson et al., 1982, 1983d; Nose, 1973; United Kingdom Department of Environment, 1979; Derenish and Harling-Bowman, 1980), paper (Serum et al., 1973), transformer oils (Bellar and Lichtenberg, 1981; Gordon et al., 1982; Ogata et al., 1980; Steichen et al., 1982; Balya and Farrah, 1980) and industrial products and wastes (Erickson et al., 1982, 1983d, 1984d).

7. Detailed procedure: As an example of the silica gel cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Activate silica gel (Davison Grade 950 or equivalent) at 135°C overnight.

2. Variations between batches of silica gel may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completed elute all of the PCBs must be verified by the analyst. The weight of silica gel can then be adjusted accordingly.

MONS 005350

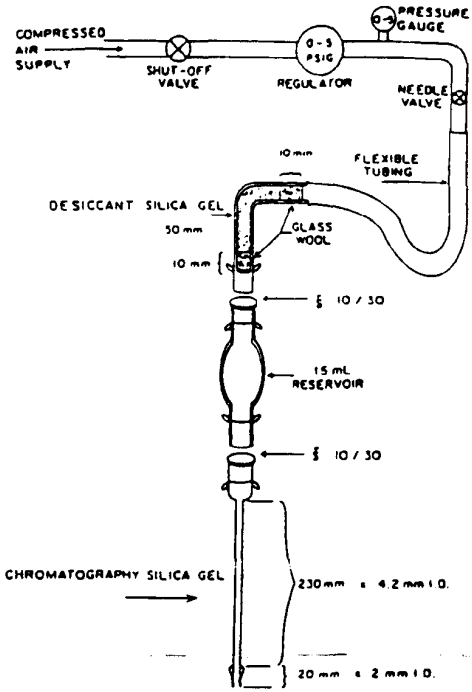


Figure 6-2. Apparatus for Pressure-Assisted Silica Gel Microcolumn Chromatographic Separation of Organochlorine Pesticides from PCBs Following Florisil Cleanup

The sample is added to the top of the column and the 15 mL reservoir filled with sufficient hexane to elute the PCBs. The flow is adjusted to 1 mL/min using the air pressure.

Reprinted, with permission, from ASTM (1981a); copyright 1981 by American Society for Testing and Materials.

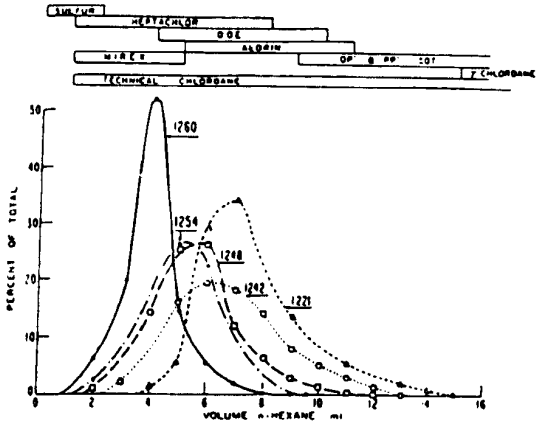


Figure 6-3. Aroclor Elution Patterns from Silica Gel Microcolumn with Hexane as Eluting Solvent

See Figure 6-2 for column specifications.

Reprinted, with permission, from ASTM (1981a); copyright 1981 by American Society for Testing and Materials.

---

3. Place a 25-g charge of activated silica gel into a Chromaflex column. Settle the silica gel by tapping the column. Add about 1 cm of anhydrous sodium sulfate to the top of the silica gel.

4. Pre-elute the column with 70 to 80 mL of hexane. Discard the eluate. Just before exposing the sodium sulfate layer to air, stop the flow.

5. Add the sample extract to the column.

6. Wash down the inner wall of the column with 5 mL of hexane.

7. Elute the PCBs with 195 mL of diethyl ether/hexane (10:90; v:v).

8. Collect 200-mL of the eluate in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

9. Analyze the sample.

D. Alumina

1. Properties: Alumina (Al_2O_3) is a common inorganic sorbent with a typical surface area of 100 to 400 m^2/g (Stahl, 1969). It is typically activated by heating to remove water (anywhere from 120°C to 800°C has been reported). The activated material is then often deactivated with water to varying degrees, sometimes referred to as Brockmann Activity I through V. Activity I is most active (i.e., 0% water) and Activity V (15% water) is least active (p. 203 in Stahl, 1969). Intermediate activities are II (3% water), III (6% water) and IV (10% water).

2. Lipid removal: A classic alumina cleanup, developed for organochlorine pesticides, (Holden and Marsden, 1969), has been successfully used to remove lipids from fish (Zitko, 1971a) and milk (Musial et al., 1979) for PCB analysis. Columns were prepared by dry packing 2 g of 5% water-deactivated alumina. PCBs, as well as many organochlorine pesticides, eluted in 20 mL hexane. The sample was then chromatographed on a silica gel column of the same size to separate the pesticides and PCBs into groups. A 2-g column of alumina has a capacity for 50 mg lipid (Hutzinger et al., 1974a), while at least 100 mg of fat are removed with both the silica and alumina columns (Holden and Marsden, 1969). A combination of alumina and silica gel in one column was used to simultaneously clean up fat and egg samples and concurrently separate PCBs p,p'-DDE from (Kveseth and Brevik, 1979). Hexane was used to elute the analytes from the columns which were packed with 2 g alumina on top and 4 g of fully activated silica gel on the bottom. Quantitative recoveries were observed.

PCBs were quantitatively recovered in the first fraction of hexane eluted from a column of 5%-deactivated neutral alumina (Teichman et al., 1978). Many pesticides such as DDE, DDT, aldrin, and heptachlor were also recovered in this fraction. The technique was used for the cleanup of soil, sediment, and oyster samples.

MONS 005353

Telling et al. (1977) used two alumina columns for the cleanup of oily extracts from fish and fatty foods. The smaller column, 4 g alumina (activity II), had a capacity for at least 200 mg oil, with 100% recovery of PCBs in 5 mL hexane. A larger column with 22 g activity IV alumina could quantitatively elute PCBs in 10 mL hexane with 500 mg oil present. Some fractionation from the pesticides was achieved. The major co-eluting pesticides were p,p'-DDE and o,p'-DDT. Millar et al. (1981, 1982) demonstrated that the larger column gave quantitative recoveries for seven common Aroclor mixtures from wastewater (Millar et al., 1981, 1982). This and a Florisil cleanup (Mills et al., 1963) gave similar results, except the alumina column spread chlordane, toxaphene, and some other pesticides over a broad band, often in two or three fractions. The PCBs eluted quantitatively in the first 40 mL hexane.

3. Cleanup of air samples: Alumina column chromatography has been used to clean up extracts of air samples collected on polyurethane foam (Lewis et al., 1977; MacLeod, 1979; Lewis, 1982). The cleanup reduced interferences to < 1 pg/m^3 air (Lewis et al., 1977). A 1-mL concentrated extract was applied to a column of basic alumina (Brockman Activity IV) and eluted with 15 mL hexane. Recoveries of 88 to 107% were observed for five individual di- through hexachlorobiphenyls. Figure 6-4 illustrates the extent of the cleanup achieved. Clearly, the cleanup removes many ECD-active interferences.

4. Separation of PCDFs and PCDDs from PCBs: Column chromatography using alumina has been used to separate PCDFs and PCDDs from commercial PCBs and Yusho oil (Nagayama et al., 1975, 1976). After saponification of the Yusho oil (see Chapter 2) and an initial cleanup on silica gel, an alumina fractionation was performed. The alumina column was eluted with four solvents: (a) 20 mL n-hexane, (b) 120 mL carbon tetrachloride/n-hexane (20:80), (c) 10 mL n-hexane, and (d) dichloromethane/n-hexane (20:80). The PCDFs and PCDDs were recovered in the final fraction. A second fractionation was required in some cases to adequately remove the PCBs. A smaller column and smaller solvent volumes were used for the repetition of the alumina fractionation. A recovery of 90% was obtained for an unspecified PCDF.

5. Other applications: Alumina has been used for column chromatographic cleanup of a wide variety of matrices, including fish (Zitko, 1971a; Ofstad et al., 1978), human and animal adipose (Donkin et al., 1977); eggs (Wardall, 1977; Zitko, 1976), blood (Welborn et al., 1974), milk (Musial et al., 1972; Siyali, 1973; Tuinstra and Traag, 1919a), biological matrices (Keveseth and Brevik, 1979; Tuinstra and

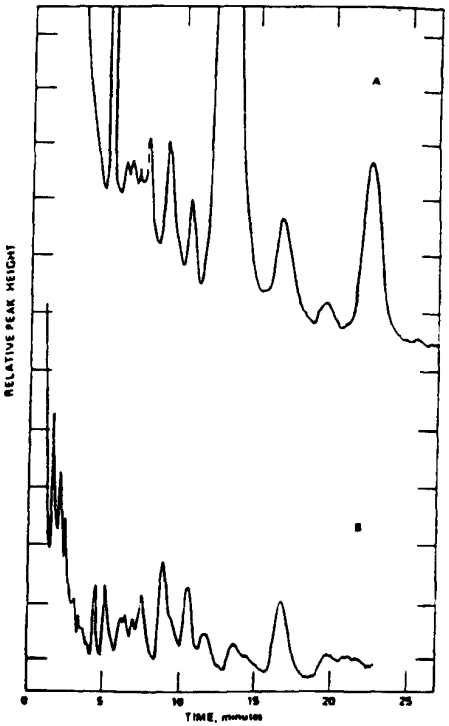


Figure 6-4. PGC/ECD Chromatograms (A) Before and (B) After Alumina Column Chromatographic Cleanup

The sample is a personal air monitoring sample collected at Inez, North Carolina.

Reprinted from MacLeod (1979).

Traage, 1979a; Tuinstra et al., 1981; Teichman et al., 1978), sediment (Goerlitz and Law, 1974; Teichman et al., 1978), soil (Tuinstra and Traag, 1979a; Teichman et al., 1978), air (Lewis et al., 1977; MacLeod, 1979; Lewis, 1982), water (United Kingdom Department of Environment, 1979; Devenish and Harling-Bowen, 1980), and oil (Kohli et al., 1979; Nagayama et al., 1975, 1976; Telling et al., 1977; Sonchik et al., 1984).

6. Detailed procedure: As an example of the alumina cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Adjust the activity of the alumina (Fisher A540 or equivalent) by heating to 200°C for at least 2 hr. When cool, add 3% water (wt:wt) and mix until uniform. Allow the deactivated alumina to equilibrate at least 1/2 hr before use. Store in a tightly sealed bottle.

2. Variations between batches of alumina may affect the elution volume of the various PCBs. For this reason, the volume of solvent required to completely elute all of the PCBs must be verified by the analyst. The weight of alumina can then be adjusted accordingly.

3. Place a 50-g charge of alumina into a Chromaflex column. Settle the alumina by tapping. Add about 1 cm of anhydrous sodium sulfate. Pre-elute the column with 70 to 80 mL of hexane. Just before exposure of the sodium sulfate layer to air, stop the flow. Discard the eluate.

4. Add the sample extract to the column.

5. Carefully wash down the inner wall of the column with 5 mL of hexane.

6. Add 295 mL of hexane to the column.

7. Discard the first 50 mL.

8. Collect 250 mL of the hexane in a Kuderna-Danish flask. All of the PCBs should be in this fraction. Concentrate to an appropriate volume.

MONS 005356

9. Analyze the sample.

E. Carbon

Carbon (or charcoal) has long been used to decolor reaction mixtures and otherwise clean up organic solutions. The chemical properties of the graphitic lattice make carbon not only a strong, but also a selective adsorbent. Thus, carbon can be used to both clean up samples and also fractionate PCBs and other organics according to their structural properties.

The carbon column techniques exhibit excellent selectivity, but poor capacity. Thus, they are generally used as a second cleanup after major interferences have been removed by another technique. Dougherty et al. (1980) used gel permeation chromtography (see Section V, below) to remove the lipids and other major interferences from fish extracts before applying a carbon/foam cleanup. Smith et al. (1984) used a series of silica-based sorbents prior to the carbon/fiber column, as described later in this section.

1. Separation of PCBs from other compounds: Chau and Bakjak (1979) used a carbon/foam mixture to separate PCBs from chlorinated pesticides. Following a general cleanup on Florisil column, mirex, photomirex, heptachlor and aldrin were quantitatively separated from PCBs and certain other organochlorines by elution of the carbon/foam column with cyclohexane. The cleanup scheme is shown in Figure 6-5. Greater than 95% of the target chlorinated compounds, including PCBs, were recovered in their respective fractions. The columns were prepared by chopping pesticide quality polyurethane foam (Analabs) in chloroform and slurrying with carbon (Norit C-170; four parts carbon per six parts foam, by weight). The mixture was then dried, dry-packed into a 5 mm ID column to a depth of 5 cm (about 0.2 g), and topped with 1 cm Na_2SO_4.

A charcoal column has also been used to separate PCBs from several pesticides which co-eluted from an alumina column (Teichman et al., 1978). The column, 140 x 6 mm ID was slurry-packed to a height of 90 mm with 50-200 mesh charcoal (Fisher No. 5-690). Aldrin, heptachlor, p,p'-DDE, p,p'-DDT, p,p'-DDD, lindane, and chlordane eluted in a first fraction of 90 mL acetone/diethyl ether (25:75). Recoveries ranged from 81 to 112% at a fortification level of 1 to 4 ppb in soil. The PCBs eluted in a second fraction of 60 mL benzene. Recoveries of 100% were reported for Aroclor 1254 at a fortification level of 7 ppb in soil.

MONS 005357

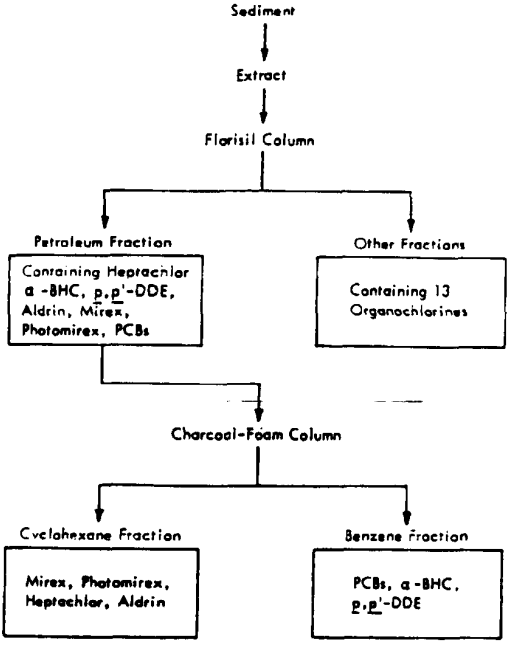


Figure 6-5. Flow Chart of Extraction and Cleanup Using Florisil and Carbon/Foam Column Chromatography to Separate PCBs from Other Organochlorine Compounds in Sediment Samples

Reprinted, with permission, from Chau and Babjak (1979); copyright 1979 by Association of Official Analytical Chemists, Inc.

2. Separation of PCBs by structural features: Carbon has a high selectivity for those PCBs which can assume a planar conformation. These PCBs contain no ortho-chlorines. As the degree of ortho-substitution increases (up to four chlorines in o,o' positions), the retention decreases. Thus, a PCB with four ortho-chlorines would elute from a carbon column before other PCBs. This selectivity is useful for fractionation of PCBs. The degree of ortho-substitution affects the toxicity of PCBs (see Chapter 2 for a more detailed discussion and references). Therefore, isolation and characterization of different fractions from commerical mixtures has been of interest.

Jensen and Sundström (1974) used a carbon column to separate PCBs according to the number of o,o'-chlorines. By combining this procedure with high resolution gas chromatography, better separation and identification of individual PCB congeners was achieved. As illustrated in Figure 6-6, nearly 60 PCB congeners were identified in the technical mixtures of Clopnen A50 and A60. This charcoal column (1.5 x 20 cm) was a modification of that reported by Berg et al. (1972) to separate DDT, DDD, and DDE from PCBs. The Jensen and Sundström (1974) modification of the procedure consisted of using Darco G-60 activated charcoal mixed with equal weight of Celite 545. The column was eluted with tetrahydrofuran and then benzene. PCBs with four ortho-chlorines eluted essentially with the dead volume of the column (10 mL tetrahydrofuran; Fraction 1; Trace B in Figure 6-6) and those with three ortho-chlorines eluted with an additional 20 mL of tetrahydrofuran (Fraction 2; Trace C in Figure 6-6). However, the compounds with only one or two ortho-chlorines required at least 100 mL of benzene for elution. The substitution pattern of additional chlorine atoms in the non-ortho positions of the PCB molecule did not noticeably affect the order of elution.

The carbon column cleanup was applied to the analysis of human adipose tissues following removal of DDD, DDT, DDE and metabolites by hydrolysis and oxidation (Jensen and Sundström, 1974). Most of the PCBs present in the pooled adipose extracts contained one to three ortho-chlorines. The only PCB with four ortho-chlorines that was positively identified in these samples was decachlorobiphenyl.

Jensen and Sundström (1974) suggested that the coplanarity of the phenyl rings might be affected by the number of chlorine atoms ortho to the biphenyl bridge. This difference in molecular conformation could explain the separation properties of activated charcoal based on the interactions between the graphite structure and aromatic character of the PCBs. The authors also suggested that this mechanism might explain the elution of o,p'-DDT and its metabolites before

MONS 005359

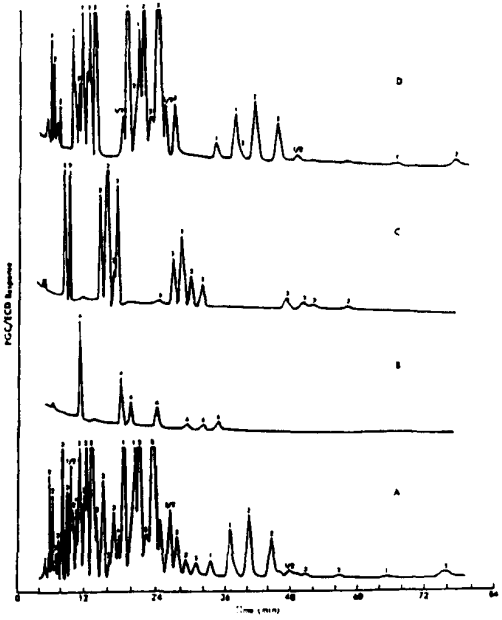


Figure 6-6. Chromatograms of PCBs Fractionated According to Number of Ortho Chlorines Using a Charcoal Column

The number of ortho chlorines is indicated above the peaks in (A) Chlophen A50 starting material; (B) Fraction 1, containing PCBs with 4 ortho chlorines, eluted with 10 mL tetrahydrofuran; (C) Fraction 2, containing PCBs with 3 ortho chlorines, eluted with 20 mL tetrahydrofuran, and (D) Fraction 3, containing PCBs with 2 and 1 ortho chlorines, eluted with 100 mL benzene. PGC/ECD chromatograms were obtained on a 5.2 m glass column packed with 4% Apiezon L on Chromosorb W, operated isothermally at 250°C.

Reprinted, with permission, from Jensen and Sundström (1974) copyright 1974 by the Royal Swedish Academy of Science, Stockholm, Sweden.

the corresponding p,p' isomers. Jensen and Sundström (1974) noted several considerations for working with activated carbon systems: (1) additional effort is required to analyze more than one fraction of an extract containing PCBs (three injections versus one); (2) and the elution profiles of each batch of activated carbon adsorbent must be established.

Stalling et al. (1978, 1979a,b) and Huckins et al. (1980) have used activated charcoal dispersed on either polyurethane foam or, more recently, on glass fibers (Smith et al., 1984), to separate structurally similar components of Aroclor mixtures in structure-toxicity correlation studies. The results presented by Stalling et al. (1978) corroborated the previous work by Jensen and Sundström (1974). Those PCBs with more chlorines in the ortho positions eluted first from a column of 1.75 g of activated carbon (Amoco PX-21) as shown in Figure 6-7. In addition, within each of the six possible o,o'-chlorine substitution groups shown in Figure 6-7, elution volumes generally increased with additional chlorine substitution. This conflicts with the findings of Jensen and Sundström (1974) and may be a function of solubility. Using the activated charcoal cleanup procedure, separation and detection of Aroclor 1248 and 1254 components lacking o,o'-chlorine substitution was feasible at concentrations less than 1 μg/g Aroclor using high resolution gas chromatography/election capture detection.

Huckins et al. (1980) determined the concentration of non ortho-ortho'-substituted PCBs in several Aroclor mixtures (Table 6-1) and fish. The non ortho-ortho'-substituted PCBs are of interest because of the higher toxicological activity of these compounds relative to other PCB congeners. Carbon-14-labeled 3,3',4,4'-tetrachlorobiphenyl, added to the Aroclor mixtures, averaged 89% recovery from the carbon/foam column. As indicated in Table 6-1, the highest concentrations of the 3,3',4,4'-tetrachlorobiphenyl were found in Aroclors 1248 and 1242 which correlated well with the higher toxicity of these mixtures to fish (Huckins et al. 1980). In addition, 3,3',4,4'-tetrachlorobiphenyl was isolated and identified as a major constituent of the non ortho-ortho'-substituted PCB fraction from composite fish samples. Huckins et al. (1978) and Stalling et al. (1978) have also used the carbon/foam chromatographic procedure to isolate other planar polychlorinated aromatics such as dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in formulations of the Herbicide Agent Orange, Aroclors, and as trace environmental contaminants in fish tissues.

MONS 005361

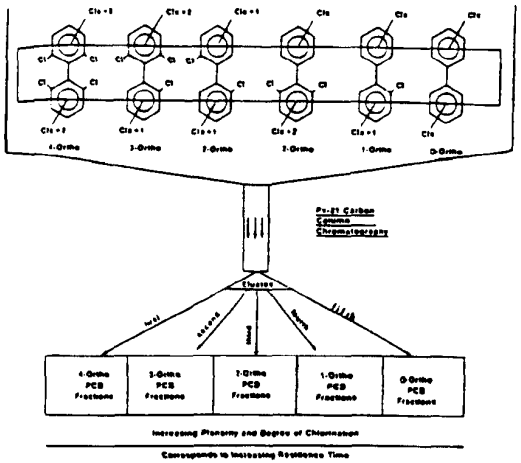


Figure 6-7. Elution Order of PCBs from Carbon Column, Illustrating Dependance on Number of ortho Chlorines

Two 10 cm x 1 cm ID columns containing 1.75 g PX-21 carbon (> 325 mesh) were eluted in series with a step gradient of 60-mL portions of toluene/cyclohexane (2:98 and 100:0).

Reprinted, with permission, from Stalling et al. (1979a); copyright 1979 by New York Academy of Sciences.

Table 6-1. Concentration of Non-o,o-Chlorine Substituted PCB Congeners in Aroclor Mixtures[a]

Aroclor	3,4,4'-TriCB			3,3',4,4'-TetraCB			3,3',4,4',5,5'-PentaCB	3,3',4,4',5,5'-HexaCB
	N	Found, µg/g	Std. dev.	N	Found, µg/g	Std. dev.	Found, µg/g	Found, µg/g
1016	3	13,200	1,700		ND[b]		ND	ND
1242	3	16,600	3,100	3	2,400	200	+[c]	ND
1248	5	6,100	1,200	5	3,400	330	+	ND
1254	3	300	40	3	210	12	+	ND
1260	3	67	7		ND		ND	ND

a Aroclor sample size ranged from 50 to 103 mg and separations were made by using columns (1 cm ID x 10 cm) of Amoco PX-21 carbon dispersed on foam (15% w/w, carbon/foam). N = number of samples.

b ND = None detected; minimum detection limit was 0.4 µg/g for experimental conditions described in methods section, also see methods for recovery values.

c Plus sign indicates that 3,3',4,4',5'-PentaCB was present in concentrations < 250 µg/g; lack of standards of known concentrations prevented exact measurements. No 3,3',4,4',5,5'-HexaCB was detected in any of the five Aroclors.

Source: Huckins et al., 1980; reproduced with permission of the Association of Official Analytical Chemists, Copyright 1980.

MONS 005363

The carbon/foam columns suffered from breakdown of the foam during use and a carbon/glass fiber system has been adopted. The most recent version of this system utilized the carbon/glass fiber column in series with other columns to extract, clean up and fractionate tissue samples in a two-part continuous process (Stalling et al., 1982; Smith et al., 1984). The serial columns are connected by tubing and valves to provide semiautomated operation with gravity flow. In part I (Figure 6-8) the sample, in a mixture with sodium sulfate, is extracted with dichloromethane/benzene (50:50) and the extract is, in the same process, passed through the sorbent columns. Specifically, the extract passes through silica-based adsorbents in the following order: potassium silicate, silica gel, cesium silicate, and finally silica gel. The residues of interest (PCDFs, PCDDs, specific PCB isomers, PCNs, as well as other aromatic chemical classes) are retained on the carbon/fiber adsorbent and are subsequently recovered by reverse elution with toluene. In part II (Figure 6-8), following a change of solvent to hexane, the sample is applied to a second series of adsorbents contained in two columns. The first column contains small amounts of cesium silicate and sulfuric acid-impregnated silica gel. The effluent from this column flows directly onto an activated alumina column on which several classes of residues are fractionated. Following reduction of sample volume, GC/ECD or GC/MS analyses are carried out. A similar system has been automated, using pressurized flow, solenoid values, and microcomputer control (O'Keefe et al., 1985).

II. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

A. Characteristics

High performance liquid chromatography (HPLC) can be used either as a cleanup technique, as discussed here, or as a final determination technique, as discussed in Chapter 7. As a cleanup technique, HPLC follows the same chromatographic principles as the open column adsorption column techniques discussed above. Molecules are selectively retarded by their adsorptive interactions with the solid phase. Under the proper conditions, PCBs are separated from interferences. If an appropriate fraction is collected, the PCB content may be subsequently determined by GC or other techniques.

The advantages of HPLC over the open column techniques are resolution, speed, reproducibility, and the ability to monitor the effluent. HPLC, as the name implies, has much better resolution than open column systems because the sorbent particles are smaller, more uniform, and more tightly

MONS 005364

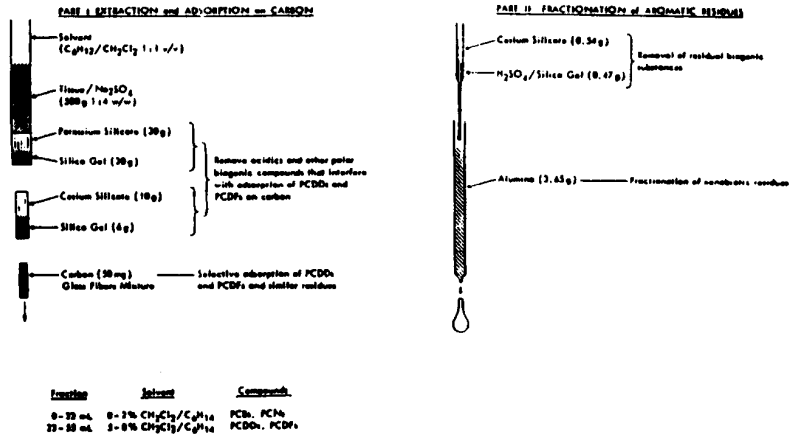


Figure 6-8. Enrichment and Fractionation of PCBs, PCNs, PCDDs, and PCDFs from Tissue Samples Using Carbon Column

Reprinted, with permission, from Smith et al. (1984); copyright 1984 by American Chemical Society.

MONS 005365

packed. HPLC can be faster because the solvent flow is controlled by a high pressure pump, instead of gravity. Because the same column is used repeatedly, the separations are reproducible. The UV detector normally associated with an HPLC system provides a real-time indication of the compounds eluting from the column, which allows the analyst to make precise fraction cuts.

The disadvantages of HPLC are low capacity and high cost. In general, HPLC has less capacity for very dirty samples (e.g., fat extracts) than an open column system using the same sorbent. In addition to the substantial cost of the instrumentation and accessories, the per-sample cost may be higher, since only one HPLC system is generally operated at a time. In contrast, 8-12 open columns are typically monitored by one analyst.

B. Applications

1. Tissue: Despite the aforementioned capacity problems, HPLC has been successfully used to clean up animal and plant samples for PCB and pesticide analysis (Rohlender et al., 1976). PCBs and organochlorine pesticides from a silica column with n-hexane and the triglycerides eluted with acetone. Recoveries of about 95% were noted.

2. Paper: Figure 6-9 presents an example of an HPLC cleanup of a paperboard extract (Dark and Crossman, 1973). The composition of the large peak after the PCB region was not identified. The sample was extracted with acetonitrile in a blender, filtered, and concentrated. The HPLC conditions are given on the figure. The authors noted that the PCB retention time was roughly proportional to the number of chlorines, with dichlorobiphenyls eluting in the 3-5 min region and trichlorobiphenyls eluting in the 8-10 min region. Aitzetmüller (1975) used a 10-μm silica column with petroleum ether as the solvent to clean up cardboard extracts for subsequent PCB determination by PGC/ECD. Large amounts of wax present in the sample required additional cleanup. The wax was saponified and the resulting wax alcohols removed by Florisil column chromatography. Without the Florisil step, the alcohols overloaded the HPLC column. DDE and DDT were separated from Aroclors 1254 and 1260, indicating that, with proper fraction collection, this HPLC system could be useful for separation of DDE, DDT, and other interfering pesticides from PCBs. Krull (1977) reviewed this and similar previous work on HPLC fractionation.

MONS 005366

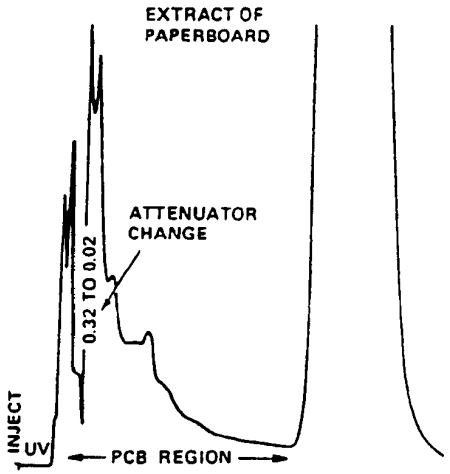


Figure 6-9. Preparative Reversed-Phase HPLC Cleanup of Paperboard Extract

A Bondapak C_{18}/Corasil column was eluted with acetonitrile water.

Reprinted, with permission, from Dark and Crossman (1973); copyright 1973 by Waters Associates.

MONS 005367

3. Oil: Oil samples have also been cleaned up by HPLC for subsequent HRGC/ECD analysis (Chesler et al., 1979, 1981; Parris et al., 1984). The preparative aminosilane column (see Figure 6-10) removed more ECD interferences than solvent extraction, sulfuric acid treatment, or open column chromatography. In addition, the HPLC cleanup was more rapid. A total analysis time of 70 min was required for the HPLC cleanup and HRGC/ECD determination as compared to 8 hr for a procedure which employed solvent extraction, column chromatography, and sulfuric acid partitioning prior to the gas chromatographic analysis. The latter procedure did not clean up the sample sufficiently to yield an identifiable chromatogram of Aroclor 1254, which had been spiked into waste crankcase oil at 10 ppm. The HPLC cleanup of Chesler et al. (1979, 1981; Parris et al., 1984) was used in my laboratory to clean up transformer oil samples after chemical PCB destruction. The resultant oil was clean enough for GC/ECD determination, but did not remove sufficient mineral oil for HRGC/EIMS determination.

An HPLC cleanup for oils removed 96% of the oil background which was sufficient for analysis of PCBs by HRGC/EIMS at the 100 ppb level (Nero and Hudson, 1984). The NO_2-bonded column (Nucleosil 5 NO_2; 3-(4-nitrophenyl)propyl bonded to silica) was eluted with an isooctane/tetrahydrofuran gradient.

4. Commercial PCB mixture: Preparative HPLC has been used to characterize commercial PCB mixtures (Krupcik et al., 1977). A 42% chlorine PCB mixture was first fractionated into 70 fractions by vacuum distillation. Four of these fractions were further fracticnated into 10-14 subfractions on a 25 cm x 8.0 mm ID column packed with 5 um silica gel. The PCBs were eluted with n-pentane at a flow rate of 400 mL/hr. These subfractions were then analyzed by HPLC and HRGC/FID. Individual congeners were identified by comparison with authentic standards.

5. Separation of PCDDs from PCBs: PCBs are separable from PCDDs on an alumina HPLC column (Dolphin and Willmott, 1978). Using a 10 µm Alox T column (250 x 4.6 mm ID), n-hexane at 1.8 mL/min, and UV detection at 270 nm, Aroclor 1268 eluted with the solvent at about 2 min. PCDDs eluted from 2.9 to 4.0 min. Separations of PCBs and other chlorinated organics on silica columns were also presented.

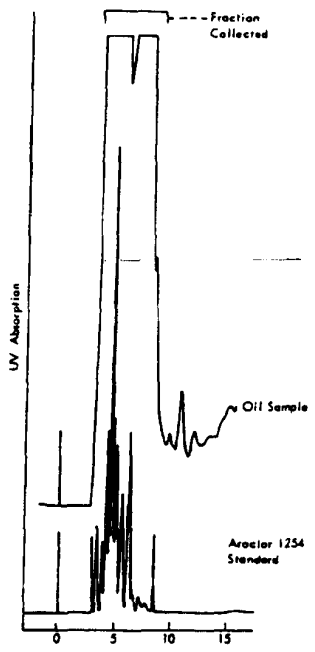


Figure 6-10. Preparative-Scale HPLC Fractionation of Oil

Conditions: Column, preparative-scale aminosilane, 7.9 mm ID x 30 cm; mobile phase, pesticide grade hexane; flow rate, 4 mL/min; detection, ultraviolet absorption, 254 nm; sample injected, 100 µL.

Reprinted, with permission, from Chesler et al. (1981) and Parris et al. (1984).

MONS 005369

C. Detailed Procedure

As an example of the HPLC cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Quantitatively transfer the concentrated extract into the sample loop or the barrel of a syringe. Rinse the vial with several small portions of solvent. It may be necessary to inject several fractions.

2. Inject the extract and washes onto the amine column (Waters μBondapak 3.9 x 300 mm or equivalent) and elute the PCBs with 1.0 mL/min hexane. The UV at 254 nm or lower should be monitored.

3. Collect the eluent from 3 min to 9.5 min as it exits UV cell. The elution time should be verified using PCB standards covering a range from mono- to decachlorobiphenyls.

4. After collection, wash the column by eluting with methylene chloride until the absorbance attains a stable minimum. Return the system to hexane.

5. Concentrate the hexane eluate under a gentle stream of purified nitrogen to an appropriate volume and analyze.

III. THIN-LAYER CHROMATOGRAPHY

As with HPLC, thin layer chromatography (TLC) can be used either as a cleanup technique or as a final determination technique, as discussed in Chapter 7. The chemical separation mechanisms of TLC are also discussed in Chapter 7.

Silica gel (Kieselgel G) TLC plates were used to clean up fish extracts for PCB and organochlorine pesticide analysis by GC/ECD (Hattula, 1974b). The technique was a useful supplement to the routine sulfuric acid cleanup for confirming the concentrations of dieldrin, endrin, and the DDT-type compounds. Up to 15-mg fish fat could be applied per spot. The TLC cleanup involved a two-stage elution, first with dichloromethane to half of the plate height and second with n-heptane. Plates were sprayed with diphenylamine reagent and developed under UV light for 3 min to yield colored spots. PCBs were light violet. PCBs, aldrin, and

MONS 005370

p,p-DDE co-eluted in an upper spot, while p,p'-DDT, o,p'-DDT, p,p'-DDD, dieldrin, and endrin were separated into a lower spot. The fat remained much lower on the plate. The TLC technique gave PCB recoveries comparable to both a sulfuric acid cleanup and an alumina column cleanup. Nevertheless, the TLC technique was recommended for routine use only for samples with very low fat content (less than 10 mg) such as plankton, bottom invertebrates, and water plants. Silica gel TLC has also been used to clean up extracts of bird eggs (Koeniger et al., 1975) and bald eagle carcasses (Bagley et al., 1970) for PCB determination.

Animal feed extracts were cleaned up on alumina TLC plates using n-heptane as the developing solvent (Westoo and Noren, 1970). The PCBs, along with p,p'-DDE, o,p'-DDE, and o,p'-DDT were contained in one area of the plate, which was scraped from the plate and extracted. The extract could then be analyzed by GC or further cleaned up to remove p,p'-DDE by oxidation with chromium trioxide or by saponification with sodium hydroxide to remove o,p'-DDT.

A reversed phase TLC system was used to separate PCB mixtures into seven fractions for GC determination (De Vos and Peet, 1971). Paraffin-impregnated silica gel plates were developed with a solvent mixture of acetonitrile/acetone/methanol/water (40:18:40:2). Silver nitrate and UV light were used to visualize the spots. For preparative work, a small part of the plate was visualized and the remaining, unvisualized portions of the bands were scraped off the plates.

IV. ADSORBENT SLURRY TECHNIQUES

Adsorbent materials can be used in a simple slurry with the sample to effect a cleanup. As noted above, carbon has been used to decolor chemical reaction mixtures in a slurry, although the technique has not been reported for PCB analysis. The only adsorbent slurry technique commonly used for PCB analysis is the Florisil slurry for cleanup of transformer oil and similar matrices (EPA, 1981a; Bellar and Lichtenberg, 1981; ASTM, 1983). Although no articles have been published showing either the extent of cleanup or PCB recovery, this technique appears to be in common application. It may be speculated that the Florisil slurry removes ECD-active oxidation products formed during transformer oil use and also the phenolic and epoxide antioxidants which are added to askarels, mineral oil dielectric fluid, and other oil matrices.

MONS 005371

As an example of the Florisil slurry cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Place the sample extract into a 20-mL narrow-mouth screw-cap container. Add 0.25 g of Florisil (PR grade or equivalent). Seal with a Teflon-lined screw cap and shake for 1 min.

2. Allow the Florisil to settle; then decant the treated solution into a second container with rinsing. Concentrate the sample to an appropriate volume. Analyze the sample.

V. GEL PERMEATION CHROMATOGRAPHY

A. Properties

Gel permeation chromatography (GPC), also called size-exclusion chromatography, separates molecules primarily by size. Large molecules are not well retained by the solid phase and elute early, while small molecules elute later. The stationary phase is a hydrophobic gel which is swollen with the elution solvent. Smaller molecules permeate into the gel particles, are retarded, and elute later than larger molecules. In addition to the separation based on molecular dimensions, adsorption phenomena in the GPC column can also separate compounds of similar molecular weight but different polarity. Thus, GPC cannot be regarded as solely a size separation technique. Common GPC packing materials are copolymers of styrene and divinylbenzene, often modified with different functional groups (e.g., Styragel, Bio-Beads); and polydextran (Sephadex). A more detailed description of GPC is available in general chromatography monographs (e.g., Zweig and Sherma, 1972).

Gel permeation chromatography (GPC) is a popular cleanup technique for complex matrices, especially those containing macromolecular interferents. Examples include biological materials containing high levels of lipid materials or oils with molecular weights in the range of 600 to 1500 amu. GPC has been fully automated to accommodate large number of sample extracts.

B. Eluting Solvents

The use of GPC to clean up biogenic extracts for PCB analysis was introduced by Stalling et al. (1971, 1972), using Biobeads SX-2 with cyclohexane as the solvent. Recoveries of PCBs as well as endrin, methoxychlor, lindane,

MONS 005372

dieldrin, malathion, parathion, DDE, DDD and DDT were reported to be > 95% for samples containing up to 500 mg of lipid materials. Stalling et al. (1971) recommended that lipid material should not exceed 500 mg for a single analysis with this size column.

A mixed dichloromethane/cyclohexane solvent was used to elute polar compounds such as chlorophenols along with the PCBs and organochlorine pesticides (Kuehl and Leonard, 1978). Retention volumes and recovery studies for the polar and nonpolar compounds were measured on a Bio-Rad SX-2 column using the following mixtures of dichloromethane/hexane: (a) 100:0, (b) 10:90, (c) 50:50, and (e) 75:25. The 50:50 mixture was the best compromise between high recoveries and compound separation. Figure 6-11 is an example of the resolution with the 50:50 mixture on a similar column (Ribick et al., 1982).

Dichloromethane alone was used as a rapid and efficient eluent for the bulk separation of lipids from low molecular weight organic compounds, while the dichloromethane/hexane (50:50) solvent system was used to fractionate low molecular weight organics into polar and nonpolar solvents. Figure 6-12 is an example of the two-step cleanup. The upper trace (100% methylene chloride) represents bulk lipid separation for a fish extract and the lower trace (50% methylene chloride) is the fractionation into polar and nonpolar constituents. Fractions 1 and 2 from the second cleanup contained PCBs and chlorobenzene, while fractions 3 through 10 contained phenols, anisole, and heterocyclic aromatics. Kuehl et al. (1980a,b) used the combination of GPC and negative chemical ionization mass spectrometry to analyze fish tissues for PCBs, organochlorine pesticides and a number of polar compounds.

A micro-GPC system consisting of a column of Bio-Rad SX-2 beads (500 mm x 10 mm) using dichloromethane/cyclohexane (50:50) as eluent was described by Kuehl et al. (1980b) for the cleanup of 5 to 50 mg of human adipose tissue. Larger sample masses overloaded the column and the PCBs were not resolved from the fat. Steinwandter (1982b) reported a similar GPC cleanup with dichloromethane as the elution solvent for a Bio-Beads SX-3 column.

C. Calibration

A variety of substances have been used to calibrate the elution of sample components on GPC. A traditional calibrant is corn oil. The PCBs are collected in the fraction that elutes after the corn oil (Haile and Lopez-Avila, 1984).

MONS 005373

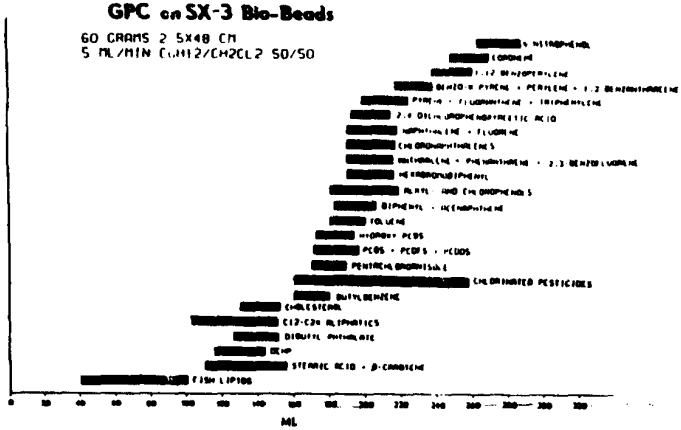


Figure 6-11. GPC Elution Profiles of Selected Biogenic Compounds and Environmental Contaminants

Conditions: 60 g SX-3 BioBeads, 2.5 cm x 48 cm column, cyclohexane/dichloromethane (1:1), 5 mL/min.

Reprinted, with permission, from Ribick et al. (1982); copyright 1982 by American Chemical Society.

MONS 005374

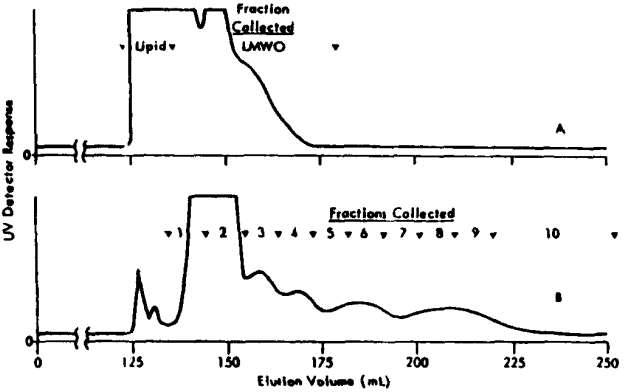


Figure 6-12. GPC Chromatograms of Fat Sample Showing the Separation of Low Molecular Weight Organic Chemicals (LMWO) from Lipids (Top) and Fractionation of LMWOs (Bottom)

In the first step (Chromatogram A), the LMWO fraction is collected, eliminating most of the lipids, which elute first. In the second step (Chromatogram B), 10 fractions were collected for PGC/ECD analysis. PCBs were in fractions 1-4.

Reprinted, with permission, from Kuehl and Leonard (1977); copyright 1977 by American Chemical Society.

A more elegant calibration uses Vitamin E acetate and Vitamin K_3 to bracket the PCB window (Pellizzari et al., 1983a). The vitamins are detected in the column effluent by a UV detector at 254 nm. Degradation of the vitamins has been observed, so solutions should be fresh and their quality monitored (unpublished results, J. Stanley, Midwest Research Institute, Kansas City, Missouri).

D. Comparison to Other Cleanup Techniques

Griffitt and Craun (1974) compared GPC cleanup with acetonitrile partitioning for the analysis of PCBs and organochlorine pesticides in fat-containing food. In most cases 98% of the fat or oil eluted from the column before the pesticides or PCBs. Cleanup efficiency was better than that obtained with acetonitrile partitioning. Recoveries of Aroclor 1254 from milk fat were generally better with GPC (92-100%) than with a combined acetonitrile partitioning and Florisil column cleanup (77%).

Since a GPC column is generally used repetitively, Griffith and Craun (1974) investigated the potential for analyte carryover. High concentrations (500 µg each) of heptachlor epoxide, malathion, and Aroclor 1242 were loaded in alternate sample loops with the intermediate loops containing cyclohexane only as blanks. The analysis of the "blanks" showed that carryover was less than 0.10% (0.5 µg) for each of the spikes. The study authors concluded that this carryover was insignificant at the residue levels encountered in oils and fats.

The use of automated GPC was shown by Tessari et al. (1980) to be faster and more economical than the classic Mills-Onley-Gaither acetonitrile partioning and Florisil column chromatographic techniques (Mills et al., 1963; Watts, 1980) for cleanup of human adipose samples. Comparable results for PCBs and 19 organochlorine pesticides were obtained by the two techniques for 21 adipose samples.

E. Automation

Tindle and Stalling (1972) reported an automated apparatus for GPC cleanup in residue analysis with specific applications for fish lipids. The automated system allowed continuous operation with capability to process up to 23 samples, in sequence. Recoveries were reproducible (< 5% RSD) and cross-contamination from one sample to another was less than 1%. Since the introduction of the automated apparatus, gel permeation chromatography has been successfully used as a cleanup for high molecular weight matrices and has provided a cost-effective approach cleanup of large numbers of samples

MONS 005376

(Albro, 1979; Caragay and Levins, 1979; Griffitt and Craun, 1974; Haile and Lopez-Avila, 1984; Hopper and Hughes, 1976; Kohli et al., 1979; Kuehl et al., 1980a, 1980b; Rodriguez et al., 1980; Stalling, 1971, 1976; Stalling et al., 1972, 1979; Tessari, 1980).

F. Applications

The use of GPC cleanup in PCB analysis has been reviewed (Krull, 1977). In addition to the applications cited in the paragraphs above, GPC has been used to clean up fish (Kloepfer, 1982; Kuehl et al., 1980a; Dougherty et al., 1980; Stalling et al., 1972; Stalling, 1971, 1976; Tuinstra et al., 1983); adipose (Egestad et al., 1982; Tessari et al., 1980); oil (Kohli et al., 1979; Young and Kamps, 1982); milk (Egestad et al., 1982); fatty foods (Griffitt and Craun, 1974); blood (Needham et al., 1981); sludge (Rodriguez et al., 1980; EPA, 1979e); and wastewater (Caragay and Levins, 1979).

G. Detailed Procedure

As an example of the GPC cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Set up and calibrate the gel permeation chromatograph with an SX-3 column according to the Autoprep instruction manual. Use methylene chloride/cyclohexane (15:85; v:v) as the mobile phase.

2. Inject 5.0 mL of the sample extract into the instrument. Collect the fraction containing the PCBs (see Autoprep operator's manual) in a Kuderna-Danish flask equipped with a 10-mL ampul.

3. Concentrate the PCB fraction to an appropriate volume.

4. Analyze the sample.

VI. LIQUID-LIQUID PARTITIONING

Liquid-liquid partitioning is used in both cleanup and extraction (see Chapter 5) steps. Partitioning is generally used to remove polar interference which have much different partition coefficients from PCBs. As described in Chapter 5, an acetonitrile-hexane partition is often used to

MONS 005377

remove bulk lipids from hexane extracts of fatty samples. These include adipose (Watts, 1980; Swift and Settle, 1976; Porter and Burke, 1973), food (Mills et al., 1963; Leoni et al., 1973; AOAC, 1980a; FDA, 1977; Tanabe, 1976; Leoni et al., 1973), milk (Watts, 1980; Tessari, 1977; Tessari and Savage, 1980), blood (Welborn et al., 1974) and eggs (Mulhern et al., 1972).

Acetonitrile partition has also been used as part of the extraction cleanup for both mineral oil (Gordon et al., 1982) and silicone oil (Klimisch and Ingebrigtson, 1980) transformer dielectric fluids, as described in Chapter 5.

Either a hexane-dimethylformamide (DMF) partition or a Florisil column cleanup were recommended as cleanups for determination of lighter PCB mixtures such as Clophen A-30 and Aroclor 1242 (Seidl and Ballschmiter, 1976b). Both techniques gave > 90% recovery of Clophen A-30 from olive oil with only 5-10% of the matrix carried into the extract. These cleanups were judged adequate for GC/ECD determination. In the partition cleanup, 5-10 g oil were dissolved in 50 mL hexane, and extracted 4 times with 15 mL DMF. The combined DMF extracts were diluted with 100 mL water and back-extracted with 2 x 20 mL hexane. The hexane layers were combined, dried, concentrated and then determined by HRGC/ECD. Two other cleanup techniques gave inferior recoveries: hexane/acetonitrile partition (45-60% recovery) and saponification/sulfuric acid extraction (80% recovery).

As an example of a liquid-liquid partition cleanup technique, the acetonitrile partition section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Place the sample extract into a 125-mL separatory funnel with enough hexane to bring the final volume to 15 mL. Extract the sample four times by shaking vigorously for 1 min with 30-mL portions of hexane-saturated acetonitrile. Retain hexane layer for combination with other hexane extracts in step 3.

2. Combine and transfer the acetonitrile phases to a 1-L separatory funnel and add 650 mL of distilled water and 40 mL of saturated sodium chloride solution. Mix thoroughly for about 30 sec. Extract with two 100-mL portions of hexane by vigorously shaking about 15 sec.

3. Combine the hexane extracts in a 1-L separatory funnel and wash with two 100-mL portions of

MONS 005378

distilled water. Discard the water layer and pour the hexane layer through an 8- to 10-cm anhydrous sodium sulfate column into a 500-mL Kuderna-Danish flask equipped with a 10-mL receiver. Rinse the separatory funnel and column with three 10-mL portions of hexane.

4. Concentrate the extracts to an appropriate volume.

5. Analyze the sample.

VII. CHEMICAL DEGRADATION

Most of the cleanup techniques discussed in this chapter involve physical separation of the PCBs from interferences. In this section, however, selective chemical degradation of the matrix is discussed as a technique for removing interferences. Chemical degradation techniques must be used with caution to ensure that PCBs are not destroyed along with the interferences.

A. Specific Reactions

Specific chemical reactions can be used to destroy the matrix or interferents if they are already known. For example, technical-grade products can be selectively degraded during by-product PCB analyses (Erickson et al., 1982, 1983e, 1984d; Erickson, 1984a). Benzoyl chloride has been hydrolyzed using 1 M NaOH, with a small amount of hexane present to extract any PCBs. After the hydrolysis, the aqueous layer was extracted three times with hexane and the combined hexane extracts back-extracted with 0.1 M NaOH to remove any residual benzoic acid. The hexane extract was dried and concentrated to an appropriate level for HRGC/EIMS determination. Methyl esters and anhydrides have been similarly treated (unpublished data, Mitchell D. Erickson, Midwest Research Institute, Kansas City, Missouri).

B. Sulfuric Acid

This cleanup usually involves a simple shaking of the sample extract with concentrated sulfuric acid for a short time. The sulfuric acid oxidizes both potential GC interferents and organic macromolecules. An organic-water partition is sometimes used after the sulfuric acid treatment to remove residual acid and also any polar materials which did not fully partition into the acid. The technique has the advantage of both speed and ease relative to most column cleanups.

MONS 005379

The technique was validated for the more acid-susceptible monochlorobiphenyls (Haile and Baladi, 1977). Specifically, 105 to 107% recoveries were observed for 2- and 4-chlorobiphenyl in 5 mL hexane after shaking for 1 min with 5 mL concentrated sulfuric acid. Additional cleanup with Florisil column chromatography was recommended. On the other hand, losses of mono- through trichlorobiphenyls were reported when pigment samples were heated with sulfuric acid for at least 15 min at 40-50°C to dissolve the matrix (DCMA, 1982).

A related technique utilized mixtures of sulfuric and nitric acids. Various reports prior to 1970, reviewed by Lincer (1973), conflicted on whether or not PCBs were lost by nitration. The use of sulfuric and nitric acid mixtures has not been reported since that time.

Sulfuric acid treatment is often used to cleanup transformer and other oil samples for PCB analysis (Bellar and Lichtenberg, 1981; Sonchik et al. 1984). It was recommended as the best cleanup for PCB fluid (askarel) and mineral oil; while column chromatographic cleanups were recommended for waste oil, hydraulic fluids, and capacitor fluids (Sonchik et al., 1984).

A sulfuric acid cleanup was found to be sufficient for PGC/ECD analysis and PGC/EIMS confirmation of PCBs in oil samples (Veierov and Aharonson, 1980). Unlike most other sulfuric acid cleanups, in which the sample and acid are simply shaken together, the sulfuric acid was eluted through the organic phase. Specifically, the sample was placed in a chromatographic column and concentrated sulfuric acid added dropwise. The heavier acid phase was drawn off occasionally and discarded. Acid was passed through the sample until twice the amount needed for the acid to emerge colorless had been added. This usually required about 10 mL acid/g fat. For cleanup of large samples, an alternating acid treatment-sample addition scheme was used. A small aliquot of sample was first dissolved in the solvent and acid-treated, then another aliquot of sample was added to the solvent and treated, and so on. This method allowed cleanup of up to 200 g fat in one day with no need for solvent evaporation, and with lipid carryover of only 0.02%. Greater than 85% recoveries were measured for soybean and safflower oil samples spiked with Aroclor 1254.

Another alternate configuration for sulfuric acid cleanup is to elute the sample through a column of acid-treated silica gel (Lamparski and Nestrick, 1980). At least 40% H_2SO_4 can be loaded onto a silica gel column. This technique has been found to be efficient and considerably less

messy than the traditional shakeout, especially for large-volume samples (unpublished data, Mitchell D. Erickson, Midwest Research Institute, Kansas City, Missouri).

Sulfuric acid has been used to clean up fish (Hattula, 1974b; Ofstad et al., 1978); adipose (United Kingdom et al., 1972); biological materials (Murphy, 1972); oil (Kohli et al., 1979a; Sonchik et al., 1984; Levine et al., 1983; Veierov and Aharonson, 1980); stack gas (Haile and Baladi, 1977); paper products (Serum et al., 1973; Becker and Schulte, 1976). Fuming sulfuric (7%) has been used to clean up sewage sludge samples (Mattsson and Nygren, 1976).

As an example of the acid cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Place 5 mL of concentrated sulfuric acid into a 40-mL narrow-mouth screw-cap bottle. Add the sample extract. Seal the bottle with a Teflon-lined screw cap and shake for 1 min.

2. Allow the phases to separate, transfer the sample (upper phase) with three rinses of 1-2 mL solvent to a clean container.

3. Back-extract the sample extract with 5 to 10 drops of distilled water. Pass through a short column of anhydrous sodium sulfate and concentrate to an appropriate volume.

4. Analyze the sample.

5. If the sample is highly contaminated, a second or third acid cleanup may be employed.

C. Chromium Trioxide

The presence of p,p'-DDE, usually at a much higher concentration, can interfere with the determination of PCBs by PGC/ECD, since the p,p'-DDE peak elutes with pentachlorobiphenyls (Webb and McCall, 1974). Because of the chemical and physical similarity of p,p'-DDE and PCBs, most column cleanups yield both analytes in the same fraction. Often, analysts have simply quantitated the p,p'-DDE peak and ignored interference by co-eluting PCBs. In addition, the PCB quantitation is affected since some PCBs are buried under the large p,p'-DDE peak.

p,p'-DDE can be chemically degraded to p,p'-dichlorobenzophenone, which can then be readily fractionated with a

MONS 005381

column chromatographic cleanup. A chromium trioxide (CrO_3, chromic acid) degradation, followed by a silica gel column chromatography has been shown to remove the p,p'-DDE with 91% PCB recovery (Underwood, 1979). Specifically, the Florisil column eluate of fatty food sample (AOAC, 1980b) was shaken with a solution of 8% CrO_3 in glacial acetic acid. The chromium trioxide layer was back-extracted with hexane and discarded. The combined hexane fractions were back-extracted with water and then analyzed. The PCB peak at the retention time of p,p'-DDE was quantitated and subtracted from the p,p'-DDE value obtained before the chromium trioxide treatment to yield a "true" value for p,p'-DDE. The extract can also be further cleaned up using silica gel column. It was noted that high lipid content of some extracts would interfere with the p,p'-DDE degradation. Therefore, for such samples, GPC or another efficient lipid removal cleanup was recommended prior to the chromium trioxide cleanup. Chromium trioxide oxidation was also used to remove p,p'-DDE from pelican egg samples for TLC determination (Mulhern et al., 1972). p,p'-DDE had the same R_f as Aroclor 1254, while the dichlorobenzophenone product was well separated from the PCBs.

In a related technique, Mizutani and Matsumoto (1973) prepared liquid chromatographic column using chromium trioxide and acetic acid on a silica gel support, which quantitatively degraded DDE to dichlorobenzophenone to remove the DDE interference from the PCB chromatogram.

Chlorinated naphthalenes (PCNs) can be selectively oxidized by chromium trioxide to permit reliable determination of PCBs (Holmes and Walen, 1972). The PCNs, which occur in environmental samples as complex mixtures similar to PCBs, were oxidized by chromium trioxide in a boiling water bath for 20 min. No validation data were presented.

Losses of PCBs, especially the lower chlorinated homologs, during chromium trioxide cleanup have been reported (Szelewski et al., 1979). For the oxidation step, recoveries from spiked fish extracts ranged from 30 to 90% for eight replicates each of Aroclor 1016 and 1254, while no Aroclor 1221 was recovered. The lower PCBs may have been lost by oxidation, by volatilization due to the highly exothermic nature of the oxidative process, or a combination of the two. Similar losses and potential causes were observed by Trotter (1975).

A similar but more elaborate procedure separated DDT and its analogs from PCBs, as shown in Figure 6-13 (Trotter, 1975). The PCB-containing fraction from a Florisil

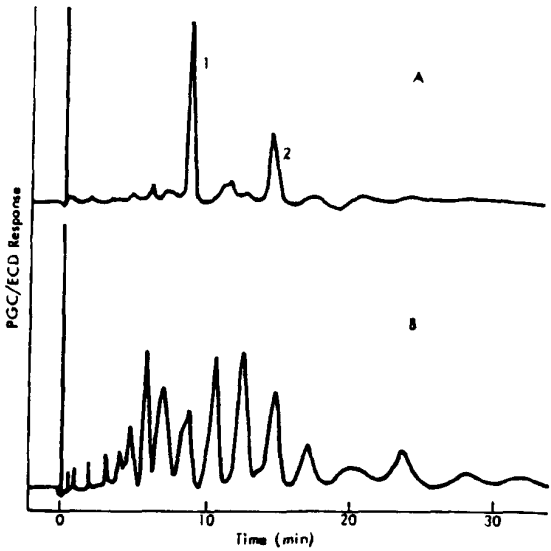


Figure 6-13. PGC/ECD Chromatograms of Fish Extract (A) Before and (B) After Treatment with KOH and Chromium Trioxide to Degrade the p,p'-DDE (Peak 1) and p,p'-DDT (Peak 2)

The sample, Lake Michigan chub, contained 1.3 ppm p,p'-DDE and 2.2 ppm p,p'-DDT as measured in Chromatogram A and 2.3 ppm PCBs, calculated as Aroclor 1254, from Chromatogram B.

Reprinted, with permission, from Trotter (1975); copyright 1975 by Association of Official Analytical Chemists, Inc.

column cleanup of fish extracts was first treated with ethanolic KOH (see below) to dehydrochlorinate DDT and related compounds to their respective olefins. The DDT products, DDE, and other olefins were then oxidized with chromium trioxide to dichlorobenzophenone. The PCBs were eluted in a petroleum ether fraction from a micro Florisil column. Recoveries for Aroclors 1254 and 1260 were > 80% in the ppm range, but were poorer for lower chlorinated Aroclors and for lower concentrations.

D. Base

Treatment of a sample with strong base can selectively degrade many interferences without affecting the PCBs. The most common reaction is saponification of fats to their corresponding glycerols and carboxylates. These products are water-soluble and can be back-extracted. Another common reaction is dehydrochlorination of organochlorine pesticides. In addition, and generally unreported, are a variety of other reductive degradations which remove both chromatographable and nonchromatographable interferences along with the fats or organochlorine pesticides. As noted below, losses of the lower chlorinated PCBs have been reported, so analysts must exercise both caution and appropriate QC when using base treatment to clean up samples.

Saponification of fat-containing samples with base is a commonly used technique to eliminate the lipids, as discussed in Chapter 5. For instance, milk fat can be saponified by refluxing in ethanolic KOH. The digestate can then be diluted with water and the PCBs extracted with hexane (Yakushiji et al., 1978; Tuinstra et al., 1980, 1981; Tuinstra and Traag, 1979a,b). A similar technique was applied to soil and tissue (Tatsukawa and Wakimoto, 1972). Many of the standard procedures (Chapter 3) utilize saponification of sediment, soil, water, food and adipose matrices.

Another application of base to sample cleanup is dehydrochlorination of organochlorine pesticides (Young and Burke, 1972; Trotter, 1975). In conjunction with several other cleanup techniques, Trotter used ethanolic KOH to degrade DDT and similar compounds to their corresponding olefins, which were then oxidized with CrO_3 to their corresponding dibenzophenones, as described above. Specifically, the PCB fraction from a Florisil column was concentrated to 2 mL and 1 mL of 2% ethanolic KOH was added. The mixture was refluxed for 15 min or until the volume reached 0.2 mL. The PCBs and other organics were then extracted from the residue with hexane. The dehydrochlorination reaction can also be used to confirm the identity of pesticides by observing the changes in the chromatograms (Young and Burke, 1972).

As an example of the base cleanup technique, the appropriate section of the Bellar and Lichtenberg (1981) procedure for PCBs in transformer oils is given below.

1. Quantitatively transfer the concentrated extract to a 125-mL extraction flask with the aid of several small portions of solvent.

2. Evaporate the extract just to dryness with a gentle stream of dry filtered nitrogen, and add 25 mL of 2.5% alcoholic KOH.

3. Add a boiling chip, put a water condenser in place, and allow the solution to reflux on a hot plate for 45 min.

4. After cooling, transfer the solution to a 250-mL separatory funnel with 25 mL of distilled water.

5. Rinse the extraction flask with 25 mL of hexane and add it to the separatory funnel.

6. Stopper the separatory funnel and shake vigorously for at least 1 min. Allow the layers to separate, and transfer the lower aqueous phase to a second separatory funnel.

7. Extract the saponification solution with a second 25-mL portion of hexane. After the layers have separated, add the first hexane extract to the second separatory funnel and transfer the aqueous alcohol layer to the original separatory funnel.

8. Repeat the extraction with a third 25-mL portion of hexane. Discard the saponification solution, and combine the hexane extracts.

9. Concentrate the hexane layer to an appropriate volume, and analyze the sample.

VIII. CLEANUP OF OIL SAMPLES

Determining the extent of PCB contamination in oil has been a major analytical application. While many laboratories have prescribed procedures for cleanup of specific matrices, few studies have been published recommending a given cleanup for these matrices. Table 6-II presents the cleanup techniques recommended by Sonchik et al. (1984) for a

MONS 005385

Table 6-II. Recommended Sample Preparation Procedures for GC/ECD Analysis

Oil Type	Procedure
Waste oil	Florisil column chromatography
Hydraulic fluid (excluding water glycols)	Alumina column chromatography
Water glycol hydraulic fluids	Hexane extraction
Capacitor fluids (excluding PCB fluid)	Alumina column chromatography
PCB fluid	Dilution; sulfuric acid wash
Transformer oil	Sulfuric acid wash

Source: Sonchik et al., 1984; reproduced from J. Chrom. Sci. with permission of Preston Publications, Inc., Copyright 1984.

variety of oil matrices. For some matrices different cleanups were compared, but many of the recommendations appear to be based on experience and subjective evidence.

A simple Florisil slurry cleanup (see Section IV) is recommended by ASTM (1983) to remove interferences from mineral insulating oils for PGC/ECD determination. Prior to the cleanup, the sample is diluted with hexane or isooctane. Florisil (0.25 g) is then added, the mixture shaken, and the supernatant solution decanted to another vial for instrumental analysis. Shaking with concentrated sulfuric acid and a Florisil microcolumn cleanup are given in the procedure as alternative cleanup techniques. The Florisil slurry cleanup was preferred because it is safer to use and dispose of than the sulfuric acid and simpler than the adsorbent column cleanup. ASTM (1983) also notes that a combination of the Florisil slurry and acid treatment may be beneficial in some cases.

MONS 005386

IX. SULFUR REMOVAL

Elemental sulfur frequently occurs in sediment, sewage sludge, and similar matrices. As seen in Figure 6-14, sulfur can significantly interfere with the early portion of a GC/ECD chromatogram. Several chemical treatments have been reported for sulfur removal, including mercury (Bellar and Lichtenberg, 1975, 1980; Goerlitz and Law, 1971, 1974; Rodriguez et al., 1980); tetrabutylammonium sulfite (Jensen et al., 1977; Bellar and Lichtenberg, 1980); cyanide (Mattsson and Nygren, 1976); and barium hydroxide (Mattsson and Nygren, 1976). Treatment with mercury appears to be the most widely used sulfur removal. A simple shaking for at least 1 min with 0.1 to 0.2 mL mercury removes sulfur (Goerlitz and Law, 1971, 1974). If the mercury darkens or causes precipitation, the sample is filtered with glass wool and the treatment repeated. In contrast, Rodriguez et al. (1980) found it advisable to shake sludge samples with 0.4 mL mercury for 2 hr.

The tetrabutylammonium sulfite reagent is prepared by saturating a 0.1 molar aqueous solution of tetrabutylammonium hydrogen sulfate with sodium sulfite (Jensen et al., 1977). The reagent (1 mL) and 2 mL isopropanol are added to a 2-mL sample extract in isooctane and shaken for at least 1 min. Additional sodium sulfite is added, if necessary, until a solid residue persists. When the treatment is complete, 5 mL water is added, the mixture shaken, and the organic phase removed. Greater than 93% recoveries of PCBs were observed for both mercury and tetrabutylammonium sulfite treatment, and the techniques judged equivalent (Bellar and Lichtenberg, 1980).

The cyanide treatment illustrated in Figure 6-14 was used by Mattsson and Nygren (1976), since mercury did not remove all of the sulfur. However, the cyanide degraded the hexachlorocyclohexane insecticides (BHCs) and a milder barium hydroxide treatment was recommended. Specifically, 1.5 mL of 0.1 M aqueous barium hydroxide is added to a 1-2 mL sample in hexane. Acetone (3 mL) is added dropwise and the solution will turn yellow-brown if sulfur is present. A second 3-mL aliquot of acetone is added and, upon shaking, a light green color appears. After 2 min the green color should disappear; if not, the treatment is repeated. When the color has disappeared, 10 mL water is added and the hexane phase separated and injected onto a gas chromatograph.

MONS 005387

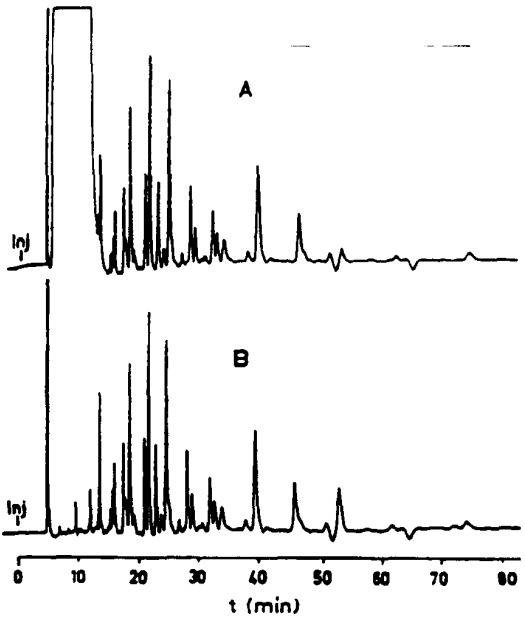


Figure 6-14. HRGC/ECD Chromatograms Illustrating Interference by Sulfur in the Early Portion of Chromatogram A

A sewage sludge sample was extracted and the lipids removed by shaking with 7% fuming sulfuric acic (Chromatogram A). The sulfur was then removed by addition of potassium cyanide (Chromatogram B). The samples were analyzed on a 50-m SF 96 glass capillary column at 185°C isothermal.

Reprinted, with permission, from Mattsson and Nygren (1976); copyright 1976 by Elsevier Science Publishers, B.V.

X. CRITERIA FOR CHOICE OF A CLEANUP TECHNIQUE

This chapter has presented a review of the cleanup techniques used for removing many different interfering chemicals from a variety of matrices. The confusing and even conflicting data often makes the choice of cleanup technique difficult. This section discusses the criteria for choosing a sample cleanup.

Where possible, one of the standard procedures discussed in Chapter 3 should be used. However, many analytical problems do not fit within the confines of any of the standard procedures. Thus, the analyst is often forced to adapt a cleanup to the problem at hand. The criteria for choice of a cleanup include:

1. Reported success at removing the interferences.
2. Reported success at retaining any PCBs in the sample extract.
3. Appropriate capacity for the sample size to be used.
4. Previous experience in the laboratory.
5. Cost of setup and execution relative to other candidate cleanups.

If the analyst has previous experience with the cleanup, the setup and validation time will be shorter and it will require less practice to gain proficiency with the technique.

Often a cleanup requires more than one stage. First, major interferences (e.g., lipids in adipose tissue) are removed. This is often done in the extraction step, as discussed in Chapter 5. Liquid-liquid partitioning and macro columns are widely used for this step. Second, a general cleanup will separate the PCBs from other trace level interferences, such as organochlorine pesticides. Since these interferences are usually chemically and physically similar to PCBs, the cleanup must involve a well-defined cut between the interference and PCB fractions. Adsorbent column chromatography is most often employed for this step. The third stage of a cleanup is fractionation of the PCBs by structural category. Since many analyses require only determination of total PCB content, this stage is not usually employed. Carbon columns and other specialized chromatographic techniques are generally used for fractionation of PCBs.

MONS 005389

The choice of a cleanup technique is also dependent on the degree of purification required. In some cases, the concentration of the interferences is a million or more higher than the PCB concentration. In these cases, the cleanup and determination steps must effect a 10^6 concentration of the PCBs relative to the interferences. This will require a very efficient removal of the interferences with very little loss of the PCBs. Often a combination of techniques is used. For example, a chemical degradataion may change the bulk of the interferences into polar compounds which are easily removed in a solvent partition. An adsorbent column can then be used to remove the remaining interferences.

Unfortunately, there is insufficient agreement among the research reviewed in the preceeding sections to make specific recommendations for cleanup of individual matrices. Nevertheless, there is a general consensus on some of the more general approaches for specific interferences. These are discussed in the following paragraphs.

A. Lipids

Lipids and other polar, relatively fragile biological molecules have been most often removed by acetonitrile partition (see Chapter 5). As noted in Section V.D, above, the acetonitrile partitioning does not yield quantitative recoveries, so other techniques should be considered. Other candidate primary cleanups are gel permeation chromatography, Florisil column chromatography, and saponification with alcoholic KOH. Regardless of the primary cleanup, an adsorbent column cleanup will probably be necessary to fully remove the lipids.

Removal of a wide variety of less-stable interferences may be done with a chemical degradation cleanup (sulfuric acid, alconolic KOH, or chromium trioxide). In the literature, these cleanups are generally targeted at a specific interference, such as lipids or DDE; however, in reality, many other interferences are often removed. This is quite often expressed by an instruction to repeat the treatment until all color is gone. Analysts should seriously consider the use of the chemical degradation cleanups (sulfuric acid, base, etc.) with PCB samples. Unlike many other organic analytas, PCBs are generally resistant to attack by these reagents and thus survive the cleanup. Since most aliphatic and many aromatic compounds are degraded, these chemical cleanups can be quite effective at removing matrix interferences. As long as the chemical degradation is shown to not affect the PCBs, these techniques should be considered for cleanup of most samples.

MONS 005390

B. Macromolecules

Macromolecules can be efficiently removed by GPC. Applicable matrices include sediment, sludge, and biota of all kinds. The macromolecules may be cellulose, sugars, proteins, or even synthetic polymers. The major impediment to use of GPC appears to be the cost and effort of the initial setup. If GPC cannot be justified, most of the adsorbent column techniques will efficiently remove macromolecules, although they may suffer from capacity problems. In addition, the adsorbent columns will probably not be reusable.

C. Organochlorine Pesticides

Fractionation of PCBs from similar compounds such as organochlorine pesticides usually requires one of the adsorbent columns. Florisil is the classic adsorbent for this purpose and is still widely used. Silica gel and alumina have also been extensively used. Arguments can be made for the use of any one of these. Both silica gel and alumina can be deactivated with water to alter the adsorbent properties and control the elution volumes. On the other hand, "bad batches" of alumina seem to be reported more often than with the other adsorbents. Any of the three adsorbents will work adequately for most cleanups, provided that the column and solvent volumes are scaled to the sample size and the elution volumes are carefully validated. A visual indicator such as azulene can be effective in monitoring the elution characteristics of individual columns.

XI. VALIDATION OF CLEANUP TECHNIQUES

Even when a well-documented technique is being used, it must be validated for use by each laboratory and for each sample type. Subtle differences in execution, reagents (especially adsorbent activity), solvent composition, matrix, and PCB composition can affect the effectiveness of a cleanup.

A thorough validation would include assessment of the PCB recovery (accuracy), reproducibility (precision), and enrichment factors. As noted in Chapter 9, these are all part of good general quality control. Ongoing QC measures constitute a reassurance that the cleanup remains valid. With adsorbant column cleanups, the sorbent must be properly activated and characterized (Edwards, 1974; Zitko, 1972). The levels of interferences are assessed by eluting a blank column with each sample set. In addition, deactivation of the sorbent by the sample, column overloading, and impure solvents can adversely affect the performance (Edwards,

MONS 005391

1977). Particular care must be taken with cleanups which use columns only once. The column-to-column variability can often change the elution volume by several percent (Erickson et al., 1983e). The elution volume must allow for the variability to assure full recovery of all PCB congeners in the PCB fraction. Alternatively, a visual indicator such as azulene can be used to check the elution pattern for each individual column as discussed in Section I.A. of this chapter (Griffin et al., 1980; Nowicki, 1981; Erickson et al., 1983e).

MONS 005392

7

DETERMINATION

All analytical methods are designed to answer "is the analyte present?", "how much analyte is in the sample?", or both questions. The identification and quantitation is generally accomplished in the same step. This determination step is the foundation of any method around which all other steps (cleanup, data reduction, QC, etc.) are centered. With PCBs, a chromatographic separation has almost always been an integral part of the determination technique. This chapter presents the three major separation techniques, gas chromatography (GC), thin layer chromatography (TLC), and high performance liquid chromatography (HPLC). The GC section contains subsections on separation, where both packed column (PGC) and high resolution (capillary) (HRGC) techniques are discussed, and detection, where electron capture (ECD), Hall electrolytic conductivity (HECD), mass spectrometry (MS), and other detectors are discussed. Other, non-chromatographic, techniques are presented separately.

Confirmation and screening represent the two extremes of analysis; the former striving for the maximum confidence in the results and the other sacrificing confidence for speed and/or simpler apparatus. These two topics are discussed, where appropriate, along with the determination techniques. Separate subsections at the end of this chapter discuss the techniques devoted specifically to either confirmation or screening.

Although often integral to the determination step, the reduction of data (interpretation of chromatograms and quantitation) is presented separately in Chapter 8.

I. CRITERIA FOR CHOICE OF TECHNIQUES

Most of the determination techniques used for PCBs employ a chromatographic separation coupled to a detector. The choice of technique depends upon:

MONS 005393

1. anticipated PCB concentration (limit of detection required),
2. anticipated number, level, and type of interferences,
3. resolution needed (congener-specific or total PCB),
4. qualitative discrimination power (are false positives acceptable?),
5. quantitative accuracy and precision,
6. availability of instrumentation, and
7. analysis time and cost.

Clearly, no one technique is the best for all analyses, or else the plethora of techniques discussed below would not exist. Needless to say, the extraction, cleanup, and determination techniques are all interrelated and must be appropriately mated in a method design.

In an analysis where "total PCB" is the desired output, packed column GC, TLC, or HPLC may provide sufficient resolution. On the other hand, if congener-specific analysis is required for a metabolism study, HRGC would be the technique of choice.

The qualitative discrimination power of a detector is a major factor in selection of a determination technique. This is especially relevant when considering the variety of PCB mixtures giving rise to complex chromatographic patterns. If the concentrations are high enough (e.g., percent level) and the interferences are minimal (e.g., transformer Askarels), a "universal" detector such as low resolution (packed column) GC/FID or GC/TCD may be appropriate. If additional discrimination is required, GC/ECD may be appropriate if there are few other non-electron capturing compounds (i.e., non-halogenated) in the matrix. In these cases, PCB mixtures which fit the classic Aroclor patterns are identified by visual pattern recognition. When visual pattern recognition cannot be used, where interferences are too complex, or where higher qualitative confidence is required, a more discriminating technique such as HRGC/MS must be employed.

Another aspect of the qualitative discrimination power of a technique is the acceptability of false positives or negatives. A false positive may be acceptable in a survey of transformers for PCB contamination, if the false positive would simply result in the added expense of unnecessary

MONS 005394

changing of the transformer dielectric fluid. On the other hand, false positives in human milk samples collected near a PCB incinerator would cause undue public concern and would therefore be highly undesirable. A false negative may arise from selection of a technique which has insufficient sensitivity for the anticipated concentrations (e.g., GC/EIMS analysis of blood samples as described above). False negatives may also arise from visual pattern recognition of GC/ECD chromatograms in which the PCB pattern is skewed from that of the standard due to weathering, retention time shifts, or other factors.

High quantitative accuracy and precision can, in theory, be met by most of the common techniques, provided that appropriate calibration, chromatographic separation, and data reduction steps are employed. One exception is TLC, which is generally regarded as "semiquantitative." Calibration using individual congeners is more difficult with ECD than EIMS because the ECD response can vary by an order of magnitude for different isomers of one homolog. Instrument availability is obviously a major factor in choice of technique. A laboratory with GC/EIMS capabilities is much more likely to choose this technique than one which must purchase instrumentation or employ an outside laboratory.

The analysis time and cost are also factors to be considered. TLC is quick, inexpensive, and requires no major capital equipment expenditures. At the other extreme, some HRGC/EIMS analyses can take well over an hour per sample, not counting the time required to set up and calibrate the instrument. Time-consuming analyses such as HRGC can be made more cost-effective by automation of the sample introduction and data reduction steps so that the instrumentation can be used beyond the customary 8-hr work day.

ii. GAS CHROMATOGRAPHY

Gas chromatography (GC), also called gas-liquid chromatography, has been a workhorse technique in most analytical laboratories for over 20 years. The function of a GC is to separate complex mixtures and detect the components. The instrumentation consists of a pressurized gas (generally purified nitrogen, helium, or hydrogen) source, an injector, the separation column, and a detector. A very small (generally 1-10 μL) amount of sample is injected at the head of the column with a microsyringe, where it is vaporized. The vapors are swept by the carrier gas onto the column, where the components are separated, and then to the detector, where they are detected. The detection output consists of a series of peaks with time. The intensity of the peaks is generally

proportional to the amount of compound present. The separation is effected by the interaction of the compounds with the gas and liquid phases. The more soluble the compound in the liquid phase, the more time it will spend dissolved in the liquid phase and the later it will elute. In addition, GC analyses use elevated temperatures or a programmed temperature range to enhance separation, so compound volatility also affects the retention time. PCBs generally elute in order of chlorination: $C_{12}H_9Cl$ first, $C_{12}Cl_{10}$ last; although there is considerable overlap in the middle homologs. Many liquid phases are available with different separating powers based on polarity, solubility, and other factors. The liquid phases are usually high molecular weight, low viscosity oils, gums, or waxes, which may be coated on the inside wall of a long, thin tube ("column") or they may be coated on an inert granular solid which is then packed into a column. In the former case, the columns are usually 0.2-0.5 mm ID and 10-100 m long and may be made of steel, glass, or, more recently, fused silica ("quartz"). GC using these "capillary" columns gives very high resolution and is therefore called high resolution gas chromatography (HRGC). Other terms for the same technique include capillary GC (CGC), glass capillary GC [$(GC)^2$], and fused silica capillary GC (FSCGC). The second alternative, packed column GC (PGC), utilizes columns which are usually 2-4 mm ID and 1-3 m long. PGC exhibits less resolution than HRGC, so more peaks tend to overlap, but is simpler to use and was preferred in the United States until the mid 1970's.

Common GC detectors include flame ionization (FID), which detects anything which burns and is therefore a "universal" detector, electron capture (ECD), which is selective for halogenated organics and a few other compounds, and mass spectrometry (MS), which detects all compounds and provides a characteristic spectrum for identification. Many other detectors are available, some of which are discussed below.

The separated peaks exit ("elute") from the GC column and are detected at different times. Measurement of the time required to elute through a given column yields a retention time (RT) which is reproducible for a given compound. To enhance the measurement precision, RTs are often measured relative to an internal standard to compensate for fluctuations in temperature or carrier gas flow rate. The relative retention time, RRT, can be used to identify components by comparison to RRTs of an authentic standard. Selective detectors provide an added dimension to the identification of PCBs. GC is discussed in detail in most analytical chemistry texts and in many monographs. Examples include McNair and Bonnelli (1969) and Jennings (1980).

MONS 005396

Gas chromatography, in combination with various detectors, has been by far the most popular and useful analytical procedure for PCBs. In recent years, HRGC has been used increasingly, although many analysts still use PGC. The popularity of GC for PCB analysis lies in its resolution and speed (most PGC analyses take less than 30 min) and the sensitivity (ECD), selectivity (ECD, HECD), and specificity (MS) of the available detectors. This section is divided into separation, which is subdivided by PGC and HRGC techniques, and detection, which is subdivided by the various detectors.

A. Separation

As noted above, the separation of a complex mixture not only provides an identification of PCBs by their retention times, but also effects an in situ cleanup. The retention time of each component is generally measured relative to a standard run on the same system under the same conditions, preferably on the same day. This is not generally possible due to the large number of PCB congeners and their lack of availability. Several investigators have tabulated retention times or related parameters of individual congeners, as shown in Table 7-I. These data, especially the half-retention indices (Table 7-II) reported by Albro et al. (1977), may be useful to analysts who need to identify individual congeners. The analyst must exercise caution in using literature data without validating the reproducibility with selected authentic standards. Since many analyses center on identification of components of commercial mixtures, Table 7-III summarizes the literature references to peak identifications in these commercial mixtures.

1. Packed column GC (PGC): Packed column gas chromatography (PGC), has been the most widely used analytical separation technique for PCBs. The vast majority of the literature references have used PGC in a routine manner with a common liquid phase. The quality of PGC chromatography (resolution and tailing) is adequate for low resolution separation of Aroclor-derived samples into "fingerprints" for identification or quantitation, as shown in Appendix D and Figure 7-1. Since the Aroclor mixtures are too complex for resolution into peaks containing single congeners by PGC, little or no emphasis was placed on improving resolution. The most common PGC detector has been ECD. ECD has historically required isothermal GC operation (not so with modern instruments).

MONS 005397

Table 7-1 Retention Times of PCB Congeners

No. of Congeners	Liquid Phase	(Gas Chromatographic Parameters) Column Type	Temp. (°C)	Reporting Mode[c]	Internal Standard	Reference
1,5	Apiezon L	[illegible][a]	205	RI	n-Alkanes	Vissers and Wells, 1971
17	SE-30	[illegible][b]	190	RRT	DDM	Webb and McCall, 1973
65	[illegible]	[illegible]	200	RI	DDM	Albro and Fishbein, 1972a
60	Apiezon L SE-30	[illegible]	250	RRT	2,2',3,4,4',5'-Hexachlorobiphenyl	Jensen and Sundström, 1974
All[d]	[illegible]	[illegible]	[illegible]	[illegible] RI	DDM	Albro et al., 1977
80	SE-30	[illegible]	180	RI	n-Alkylbenzenes chloronaphthalenes	Zell et al., 1978
70	OV-1	[illegible]	220	RRT	DDM	Duc and Egaas, 1979
109[e]	Apiezon L	[illegible]	200-240 @ 50 240-290 @ 1.6 290, 290, 210	RI	n-Alkanes	Ballschmiter and Zell, 1980
11	OV-1	[illegible]	190, 200, 210	RI	n-Alkanes	Hannegan, 1982
75	Apiezon L	[illegible]	70-160 @ 10 180-230 @ 4	RS		Bush et al., 1982
77	OV-1	[illegible]	110-325 @ 10	RRT	4,4'-Tetrachlorobiphenyl	Erickson et al., 1982
56	Apiezon M	[illegible]	100-240 @ 3	RRT	1,2-Dichloronaphthalene 1,2,3,4-Tetrachloronaphthalene Octachloronaphthalene	Pellizzari et al., 1981a,b
45	SP-2100	[illegible]	70-190 @ 10, 190-270 @ 1	RRT	DDM	Singer et al., 1983
209	SE-54	[illegible]	100-290 @ 5	RRS	Octachloronaphthalene	Mullin et al., 1984

a RI = retention index, RRT = retention time relative to internal standard listed, RI = retention time in minutes
b SCOT column
c RIs were determined on OV-101, I-60, Apiezon L, OV-17, OV-225, and CHDMS packed columns
d % RI values reported for substitution on one ring. RIs for all 209 congeners may be calculated
e Ten packed columns with different phases, dimensions, and temperatures
f RI measured, RS calculated

MONS 005398

Table 7.11 I/2 (RI) Values for All Ring Substitution Patterns[a]

Substitution Pattern (I/2 RIB)	Column No.[b] 1	2	3	4	5	6	7	8	9	10	11	12	13
None	678	703	747	830	733	828	877	870	916	1.000	733	927	777
2	911	914	933	950	852	960	1.074	1.093	1.055	1.127	876	1.095	900
3	877	906	952	1.067	923	1.026	1.083	1.096	1.146	1.252	950	1.221	964
4	887	926	945	1.060	928	1.047	1.096	1.120	1.169	1.273	962	1.245	980
2,6	923	953	951	1.032	967	1.085	1.164	1.220	1.280	1.254	984	1.220	987
2,5	906	930	997	1.119	1.003	1.116	1.175	1.176	1.220	1.319	1.025	1.205	1.017
2,4	930	928	1.010	1.135	1.010	1.115	1.184	1.171	1.229	1.322	1.037	1.201	1.046
2,3	990	999	1.026	1.100	1.046	1.167	1.253	1.232	1.279	1.370	1.069	1.251	1.080
3,5	1.023	1.026	1.096	1.223	1.060	1.154	1.240	1.241	1.292	1.420	1.109	1.284	1.111
3,4	1.022	1.025	1.116	1.205	1.126	1.253	1.310	1.284	1.401	1.525	1.169	1.290	1.182
2,6,6	1.000	1.037	1.026	1.179	1.070	1.176	1.250	1.205	1.259	1.361	1.109	1.251	1.097
2,5,6	1.000	1.000	1.085	1.257	1.137	1.246	1.327	1.289	1.340	1.438	1.196	1.344	1.189
2,4,6	1.020	1.033	1.068	1.220	1.159	1.272	1.345	1.318	1.391	1.490	1.200	1.386	1.185
2,4,5	1.132	1.126	1.178	1.311	1.165	1.270	1.360	1.351	1.396	1.514	1.216	1.397	1.216
2,4,4	1.168	1.166	1.233	1.405	1.212	1.350	1.440	1.411	1.480	1.605	1.269	1.568	1.270
2,4,3	1.233	1.230	1.314	1.480	1.275	1.404	1.476	1.446	1.508	1.630	1.340	1.559	1.340
2,3,5,6	1.200	1.190	1.300	1.383	1.280	1.355	1.430	1.391	1.434	1.500	1.230	1.330	1.263

[a] Ring Substitution Patterns

[b] Column Numbers

MONS 005399

Table 7.11 (continued)

Substitution Pattern (1/2 PIR)	Column No.[b] 1	2	3	4	5	6	7	8	9	10	11	12	13
2,3,4,6	1,200	1.140	1.102	1.190	1.212	1.360	1.335	1.400	1.417	1.488	1.288	1.500	1.265
2,3,4,5	1.312	1.101	1.109	1.513	1.150	1.475	1.554	1.543	1.644	1.673	1.530	1.370	1.021
2,3,4,5,6	1.300	1.103	1.197	1.620	1.417	1.549	1.670	1.576	1.648	1.702	1.480	1.773	1.419
2,3,5,6[c]	1.252	1.256	1.273	1.444	1.110	1.393	1.481	1.471	1.536	1.612	1.276	1.637	1.307
2,3,4,6[c]	1.255	1.210	1.260	1.450	1.206	1.419	1.503	1.473	1.535	1.592	1.362	1.640	1.309
2,3,4,5[c]	1.301	1.139	1.100	1.556	1.177	1.502	1.593	1.583	1.654	1.750	1.467	1.772	1.422
2,3,4,5,6[c]	1.400	1.425	1.415	1.650	1.472	1.655	1.723	1.687	1.748	1.782	1.578	1.913	1.523

a To use the $\frac{1}{2}$ PIR value table, determine the substitution pattern on each ring. Find the two entries corresponding to these substitutions in the appropriate column and add them together.

b Chromatography columns used

Number	Packing	Dimensions (cm)	Temperature (°C)
1	10% OV 101, 80/100 mesh Chromosorb W HP	300 × 0.2	240
2	5% Versilube F-50, 80/100 mesh Chromosorb W HP	275 × 0.2	180
3	6% Apiezon L, 100/120 mesh Chromosorb W DW	200 × 0.2	215
4	10% OV 210, 80/100 mesh Supelcoport	150 × 0.2	260
5	10% OV 1, 100/120 mesh Gas Chrom Z	300 × 0.2	200
6	10% OV 17, 80/100 mesh Supelcoport	300 × 0.2	255
7	10% OV 25, 100/120 mesh Gas Chrom Z	300 × 0.2	240
8	10% QF 1(FV), 100/120 mesh Chromosorb W HP	300 × 0.2	190
9	10% OV 225, 80/100 mesh Supelcoport	300 × 0.2	240
10	1% SE30, 100/120 mesh Gas Chrom Q	400 × 0.2	200
11	5% Dexsil 300 GC, 80/100 mesh Supelcoport	200 × 0.2	235
12	5% Poly MPE 5-ring, 80/100 mesh, Chrom Z	200 × 0.2	260
13	10% Dexsil 410, 80/100 mesh Anakrom AS	200 × 0.2	280

c These values apply when each ring is substituted

Source: Albro et al. (1977, with permission) Chromatogr. 131, 403 (1977), reproduced with permission from copyright 1977, by Elsevier Science Publishers, B.V.

MONS 005400

Table 7 (A1) Identification of PCB Congeners in Commercial Mixtures

Mixture	Technique	Number of Congeners Identified	Quantitated?	Reporting Mode[a]	Reference
Aroclor 1242	HRGC MS of fractions authentic standards	70	No	MI	Sissons and Welti 1971
1254		116			
1260	" MI	170			
Aroclor 1242	Pd/110 on 17 columns	90	Yes		Albro and Parker 1979
1016	" MI GLMS	31			
Aroclor 1248	HRGC 110 HRGC/110	67	Yes	MI	Albro et al 1981
1254	MI	81			
1260		96			
Aroclor 1221	Pd/110 IR	30	No	MNI	Webb and Mckay 1972
1232		36			
1242		77			
1248		63			
1254		77			
Aroclor 1221	Previous work authentic standards GC/MS	75	Yes	MI	Bush et al 1982, 1981
1016		27			
1254		48			
1260		41			
Aroclor 1016/ 1254/ 1:1	HRGC 110 HRGC/MS MS authentic standards	65[b]			Pellizzari et al 1982a,b
Aroclor 1221	HRGC 110 of authentic standards	15	Yes	MNI	Ramsey and Haug 1981
1232		18			
1242		45			
1248		49			
1254		51			
1260		75			
Chlophen A50	HRGC 110 of authentic standards	61	No	MI	Zell et al 1978
A60		54			

MONS 005401

Table 7.111 (concluded)

Matrix	Technique	Number of Components Identified	Quantitated	Reporting Mode[a]	Reference
Chlorpheno A/W	Previous work	59	No	RI	Ballschmiter and Zell, 1980
A/W	Authentic standards	71			
A/W	Calculated RIs	67			
Chlorpheno A/W	HRGC/ECD with column switching	71	Yes	RR[b]	Schulte and Malisch, 1983; 1984
A/W		57			
Chlorpheno A/W	HRGC/ECD, HRGC/LRMS	61	Semi[c]	RR	Duinker and Hillebrand, 1983
A/W	Authentic standards	57			
A/W		67			
A/W		67			
Naphthalene Sed	GC/ECD and GC/MS	17		RR	Lunder, 1976
Sed		20			
Sed		22			
Sed		23			

a RI = retention index, RRT = relative retention time, RT = retention time
b RR = not reported
c Many peaks identified as number + letter (number = carbon number, with up to five possibilities for some peaks. Thirty eight additional peaks identified only by homolog
d Relative peak heights given in five categories

MONS 005402

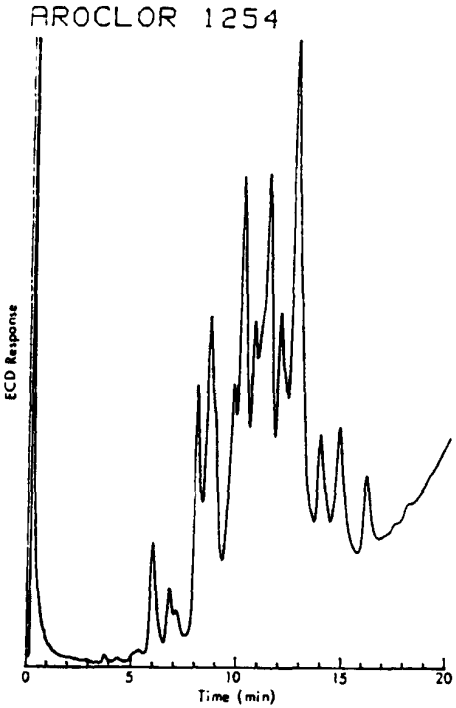


Figure 7-1. Temperature-Programmed PGC/ECD Chromatogram of Aroclor 1254

A 0.2 cm ID x 180 cm glass column, packed with 1.5% SP-2250/ 1.95% SP-2401 on 100/120 mesh Supelcoport was programmed from 150°C to 250°C at 10°C/min. The nitrogen carrier gas flow rate was 30 mL/min.

By 1971 sufficient work in PCB analysis by PGC had been completed to merit a review (Reynolds, 1971). This was followed by several other reviews (Fishbein, 1972; Hutzinger et al., 1974a; Fuller et al., 1976; Krull, 1977; Margeson, 1977; and CMA, 1981). One review by Sherma (1975) was devoted to PGC analysis of PCBs and related chlorinated aromatic pollutants. PGC is the recommended analytical separation technique in most of the standard procedures listed in Table 3-I, a testimony to its reliability and popularity.

Albro et al. (1977) evaluated 13 packed columns ranging in polarity from Apiezon L to OV-225 (Table 7-II). The number of observed theoretical plates ranged from 491 to 3,833. None of the columns could successfully resolve all PCBs. It was calculated that of the 21,945 theoretically possible pairs of PCB congeners, 465 would be indistinguishable using the best column tested. The researchers discussed the use of multiple columns for resolving indistinguishable pairs and concluded that five columns were necessary to resolve all isomers. Thus, using this scheme, each sample would have to be analyzed once on each of five PGC columns to resolve all congeners. Albro and Parker (1979) applied this technique to the identification of the components in Aroclor 1016 and 1242. The identity of 44 congeners was reported. A report by Jensen and Sundström (1974) presents what may be the highest resolution PGC chromatogram of PCBs (Figure 6-6). Even though it was operated isothermally, this 5.2-m Apiezon L column resolved 59 peaks in a Chlophen mixture.

A recent development, bonded phases, gives more rugged and stable columns. The lighter loading of liquid phase also reportedly reduces the analysis time. In the example shown in Figure 7-2, a 1-hr PGC analysis was reduced to 18 min using the bonded liquid phase (Driscoll and Krull, 1983).

2. High resolution gas chromatography: HRGC has not been as popular as PGC, although its use has increased dramatically in the past few years. This increase in popularity can be traced primarily to the advent of flexible fused silica capillary columns, which are easier to use, longer-lasting, and yield better chromatography than the glass and metal columns used previously. The quality of the HRGC separation currently achievable is illustrated in Figure 7-3 (Safe et al., 1983a). While this example represents the state of the art, a more "routine" chromatogram is presented in Figure 7-4 (Erickson and Stanley, 1982). Even the routine HRGC chromatogram provides substantially more resolution and information than a PGC chromatogram. As noted below, this can have both positive and negative ramifications. Generally speaking, any analysis which may be done by PGC may also be

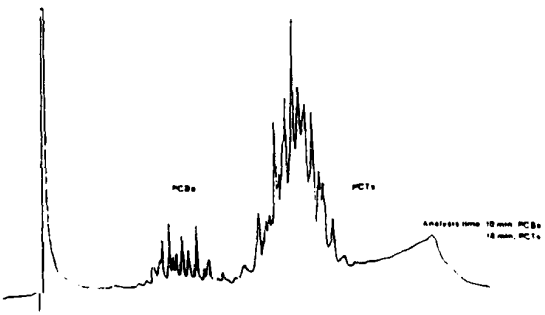


Figure 7-2. PGC/FID Chromatogram of PCBs and PCTs Using a Bonded Liquid Phase

A Permabond methyl silicone column was programmed from 140°C at 10°C/min to 350°C.

Reprinted, with permission, from Driscoll and Krull (1983); copyright 1983 by International Scientific Communications, Inc.

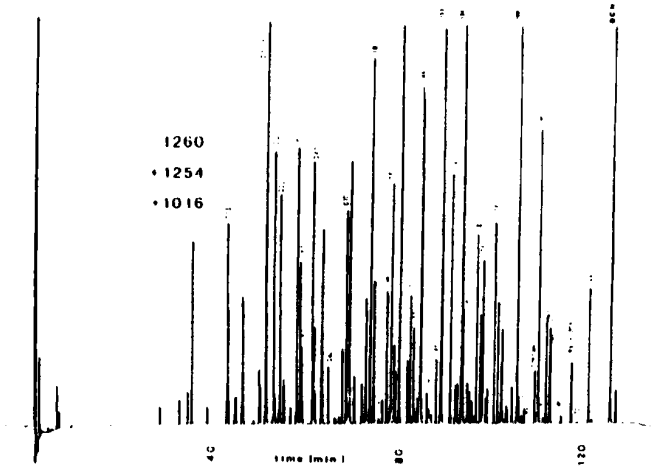


Figure 7-3. HRGC/ECD Chromatogram of Aroclor 1016, 1254, and 1260 (5:3:2, w/w/w)

A 50-m fused silica capillary column, coated with SE54 was programmed from 100°C at 1°C/min to 240°C. Numbers above peaks refer to PCB congener. The PCB congeners are numbered according to Ballschmiter and Zell (1980). The octachloronaphthalene internal standard is denoted by OCN

Reprinted, with permission, from Safe et al. (1983a), copyright 1983 by Butterworth Publishers

MONS 005406

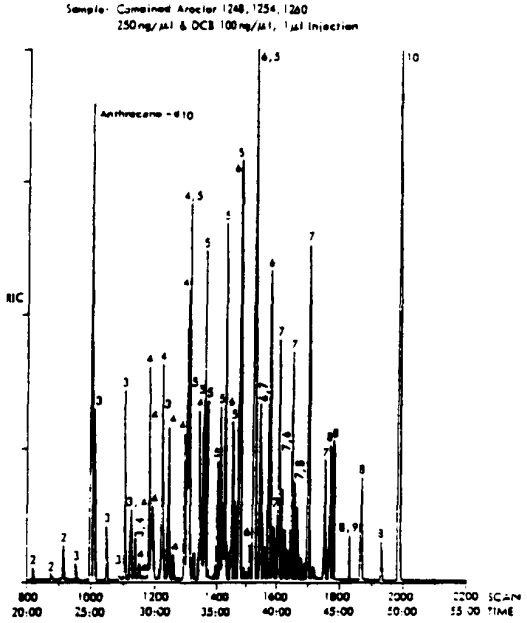


Figure 7-4. HRGC/EIMS Reconstructed Full Scan Ion Chromatogram of PCBs and d_{10}-Anthracene (Internal Standard)

The number of chlorines is denoted above each peak. Instrumental parameters: column - 15 m, DB-5, fused silica; column temperature - 80°C for 2 min, 8°C/min to 300°C, helium carrier at 2.5 psi; 1 µL injected on J&W on-column injector.

Reprinted, with permission, from Erickson and Stanley (1982) and Haile et al. (1983b).

achieved by HRGC, although the converse may not always be true. For instance, congener-specific analysis of complex PCB mixtures requires HRGC.

Figure 7-5 shows the relative retention times of 77 congeners using a DB-5 bonded phase column (Erickson et al., 1982; Stanley et al., 1983). This figure illustrates the overlap of the homologs. There is no way to separate congeners into homolog groups based solely on retention time. Relative retention times (RRT) for 77 PCB congeners as well as a mixture of Aroclors (1016, 1242, 1260) were determined with respect to the internal standard, 3,3',4,4'-tetrachlorobiphenyl-d_6, to establish relative retention windows that are required for identification of specific PCB homologs. The RRT data can also be used in selecting standard isomers which elute in the middle of the range as well as establishing the proper retention windows for HRGC/EIMS data acquisition for particular PCB homologs.

HRGC was briefly cited (five references) in one review (Sherma, 1975). An Aroclor HRGC/ECD chromatogram was included in a HRGC monograph (Jennings, 1980) as an application of HRGC. One of the standard methods in Table 3-1 recommends HRGC, specifically a support coated open tubular (SCOT) column coated with FFAP (free fatty acid phase) for analysis of PCBs in capacitor Askarels. EPA Method 625 (EPA, 1979b) recommends PGC or if desired, capillary or SCOT columns may be used. High resolution gas chromatography is also allowed, if desired, for the analysis of PCBs in transformer fluids or waste oils (EPA, 1981a). HRGC/EIMS is the technique used for analysis of PCBs, PCDDs, and PCDFs in stack gas during incinerator tests (Ackerman et al., 1983a; Haile et al., 1983a, 1983b, 1984a, 1984b).

The resolution and column specifications for HRGC analysis of PCBs span a wide range. Although the resolution was poor by today's standards, Biros et al. (1970) used HRGC/EIMS to determine PCBs in human adipose in 1970. Sissons and Welti (1971) published an early article which characterized many of the PCB isomers in Aroclor 1254. Using an Apiezon L packed column, 23 peaks were resolved, while the same phase on a SCOT column (24,000 to 27,000 plates) separated 65 peaks.

Many investigators have used Apiezon L, a purified hydrocarbon grease, as an HRGC liquid phase (Albro et al., 1981; Stalling et al., 1980; Bush and Barnard, 1982; Bush et al., 1983; Jensen and Sundström, 1974; Nakamura and Kashimato, 1977; United Kingdom Department of Environment, 1979). Apiezon L has been reported by several groups to be the most selective phase for PCB congeners after comparison with other

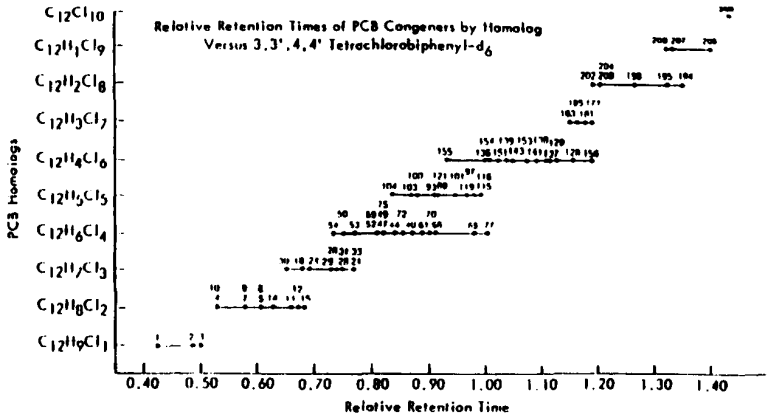


Figure 7-5. Retention Times of 77 PCB Congeners Relative to d_6-3,3',4,4'-Tetrachlorobiphenyl (RRT of 1.00)

The numbers refer to the IUPAC sequence number for each congener. Relative retention times were determined on a J&W DB-5, 15-m fused silica column in a Finnigan 4023 GC/EIMS system temperature program: 110°C for 2 min, then 10°C/min to 325°C.

Reprinted, with permission, from Erickson et al. (1982) and Stanley et al. (1983).

phases (Sissons and Welti, 1971; Albro et al., 1977; Bush et al., 1982, 1983, 1984; Pellizzari, 1981; Pellizzari et al., 1981, 1983b). Figure 7-6 presents examples of PCB separations on an Apiezon L capillary column (Bush et al., 1982).

Krupcik et al. (1976) evaluated metal wall-coated open tubular (WCOT) columns coated with Apiezon L or OV-101 and found them unsuitable. However, OV-101 on a glass WCOT column gave good results. Krupcik et al. (1982) have also reported the optimization of experimental conditions for the analysis of complex mixtures by capillary gas chromatography. The optimization procedure for complex materials was demonstrated with Aroclor 1242. Forty PCBs were separated at 170°C using a 40 m Carbowax 20M glass capillary column connected to a 76 m Apiezon L glass capillary column.

Using a 50-m Dexsil 410 glass capillary, Albro et al. (1981) achieved 175,000 effective theoretical plates for 2,2',3,3',5,5'-hexachlorobiphenyl. Resolution of Aroclor 1260, which required an isothermal chromatogram of 5 h, generated 110 peaks, of which only 4 were unidentified. Even at this resolution, the Dexsil 410 did not resolve all congener pairs. Less efficient columns coated with Silar 5C, Apiezon L, and OV-25 were used to provide different separations which resolved the congener pairs not previously resolved.

Mullin and co-workers have achieved impressive resolution by temperature-programmed HRGC/ECD on C-87 columns (Mullin and Filkins, 1981; Mullin et al., 1981) and SE-54 columns (Safe et al., 1983a; Mullin et al., 1983, 1984). The retention times on an SE-54 column of all 209 congeners are listed in Table 7-IV (Mullin et al., 1984). Figure 7-7 illustrates the general trend of increasing retention time with chlorine content. For isomeric PCBs (same degree of chlorination), the retention time is dependent on structure. Mullin et al. (1984) noted a general increase in retention time as the chlorines are placed further from the bridge between the two benzene rings (i.e., decreasing ortho-chloro substitution and increasing para-chloro substitution. For the monochlorobiphenyls, the elution order is 2- < 3- < 4-. For the dichlorobiphenyls with chlorines all on one ring, the elution order is 2,6- < 2,5- < 2,4- < 2,3- < 3,5- < 3,4-. The limited data on boiling points (Table 2-III) indicate that the more non-planar PCBs have lower boiling points, which is consistent with the observed retention times. In addition, it may be that those congeners which can more readily assume a planar conformation are more soluble in the liquid phase and are therefore retained longer in the column.

MONS 005410

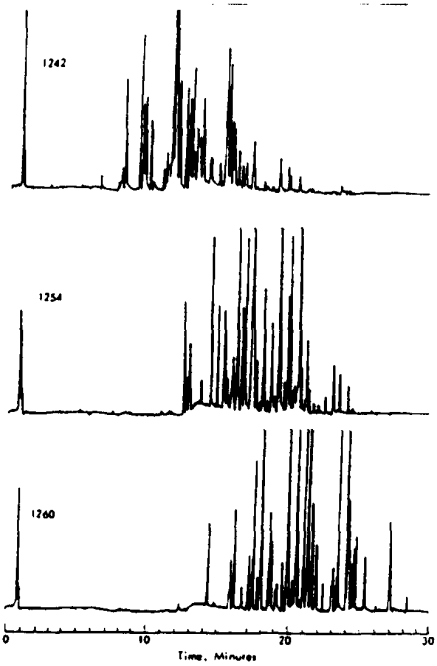


Figure 7-6. HRGC/ECD Chromatograms of Aroclors 1242, 1254, and 1260, on a 0.29 mm ID x 20-m Apiezon L Column

The column temperature was 70°C, programmed at 10°C/min to 130°C, then at 4°C/min to 230°C, with a 10-min hold. Samples (2 µL) were injected using splitless injection.

Reprinted, with permission, from Bush et al. (1982); copyright 1982 by Association of Offical Analytical Chemists, Inc.

Table 7-IV. Relative Retention Times and ECD Response Factors for 209 PCB Congeners[a]

IUPAC No.[b]	Relative Retention Time[c]	Relative Response Factor[d]	IUPAC No.[b]	Relative Retention Time[c]	Relative Response Factor[d]
0	0.0997	0.0251	43	0.4587	0.503
1	0.1544	0.0393	44	0.4832	0.524
2	0.1937	0.04[e]	45	0.4334	0.54
3	0.1975	0.0193	46	0.445	0.468
4	0.2245	0.0374	47	0.4639	0.848
5	0.2785	0.119	48	0.4651	0.556
6	0.2709	0.38	49	0.461	0.648
7	0.2566	0.69	50	0.4007	0.6817
8	0.2783	0.206	51	0.4242	0.6[e]
9	0.257	0.388	52	0.4557	0.418
10	0.2241	0.262	53	0.4187	0.3606
11	0.3238	0.0449	54	0.38	0.3643
12	0.3298	0.179	55	0.5562	0.829
13	0.3115	0.2[e]	56	0.5676	0.829
14	0.2973	0.3047	57	0.5155	0.6[e]
15	0.3387	0.107	58	0.5267	0.609
16	0.3625	0.447	59	0.486	0.6[e]
17	0.3398	0.412	60	0.5676	1.0164
18	0.3378	0.313	61	0.5331	1.2227
19	0.3045	0.3037	62	0.4685	1.1478
20	0.417	0.7238	63	0.529	0.728
21	0.4135	1.0598	64	0.4999	0.607
22	0.4267	1.0935	65	0.4671	0.8408
23	0.377	0.5[e]	66	0.5447	0.646
24	0.3508	0.793	67	0.5214	0.6[e]
25	0.3937	0.5[e]	68	0.504	0.726
26	0.3911	0.603	69	0.451	0.8024
27	0.3521	0.495	70	0.5407	0.658
28	0.4031	0.854	71	0.4989	0.468
29	0.382	0.6339	72	0.4984	0.5515
30	0.4165	0.8202	73	0.4554	0.5805
31	0.4024	0.562	74	0.5241	0.671
32	0.3636	0.278	75	0.4643	0.6461
33	0.4163	0.447	76	0.5408	0.5795
34	0.3782	0.6092	77	0.6295	0.3812
35	0.4738	0.3746	78	0.6024	1.1151
36	0.4375	0.2948	79	0.5894	0.881
37	0.4858	0.58	80	0.5464	0.7278
38	0.4593	0.4698	81	0.6149	0.7159
39	0.4488	0.347	82	0.6453	0.773
40	0.5102	0.722	83	0.6029	0.6339
41	0.499	0.5469	84	0.5744	0.386
42	0.487	0.792	85	0.6224	0.7396

MONS 005412

Table 7-IV (continued)

IUPAC No.[b]	Relative Retention Time[c]	Relative Response Factor[d]	IUPAC No.[b]	Relative Retention Time[c]	Relative Response Factor[d]
86	0.6105	0.7968	131	0.6853	0.8492
87	0.6175	1.021	132	0.7035	0.7303
88	0.5486	0.6892	133	0.6871	1.148
89	0.5779	0.561	134	0.6796	0.7331
90	0.5814	0.611	135	0.6563	0.7031
91	0.5549	0.571	136	0.6257	0.444
92	0.5742	0.5375	137	0.7329	1.112
93	0.5437	0.6676	138	0.7403	0.827
94	0.5331	0.4514	139	0.6707	0.7219
95	0.5464	0.443	140	0.6707	0.6732
96	0.5057	0.4308	141	0.7203	1.352
97	0.61	0.631	142	0.6848	1.218
98	0.5415	0.6246	143	0.6789	0.7088
99	0.588	0.613	144	0.6563	0.8764
100	0.5212	0.5871	145	0.6149	0.6789
101	0.5816	0.668	146	0.6955	0.728
102	0.5431	0.4561	147	0.6608	0.6[e]
103	0.5142	0.6068	148	0.6283	0.554
104	0.4757	0.4561	149	0.6672	0.572
105	0.7049	0.94	150	0.5969	0.5676
106	0.668	1.0046	151	0.6499	0.785
107	0.6628	0.8183	152	0.6062	0.5235
108	0.6626	1.0654	153	0.7036	0.688
109	0.6016	0.9625	154	0.6349	0.57
110	0.6314	0.65[e]	155	0.5666	0.586
111	0.6183	0.6601	156	0.8105	1.389
112	0.5986	0.8286	157	0.8184	1.1965
113	0.5862	0.604	158	0.7429	1.132
114	0.6828	1.0261	159	0.7655	0.9934
115	0.6171	1.1328	160	0.7396	1.1914
116	0.6132	1.3987	161	0.6968	0.9672
117	0.615	0.8895	162	0.7737	1.0322
118	0.6693	0.87	163	0.7296	0.9976
119	0.5968	0.8239	164	0.7299	0.9848
120	0.6256	0.7444	165	0.692	1.0777
121	0.5518	0.7659	166	0.7572	1.0421
122	0.6871	0.7247	167	0.7814	1.0658
123	0.6658	0.6645	168	0.7068	0.8375
124	0.6584	0.848	169	0.9625	0.8355
125	0.6142	0.556	170	0.874	0.75
126	0.7512	0.4757	171	0.8089	1.1712
127	0.7078	0.5834	172	0.8278	1.172
128	0.7761	1.188	173	0.8152	2.044
129	0.7501	0.997	174	0.7965	0.806
130	0.7284	0.952	175	0.7611	0.381

MONS 005413

Table 7-IV (concluded)

IUPAC No[b]	Relative Retention Time[c]	Relative Response Factor[d]	IUPAC No[b]	Relative Retention Time[c]	Relative Response Factor[d]
176	0.7305	1.0589	193	0.8397	1.4167
177	0.8031	1.009	194	0.962	1.868
178	0.7537	0.621	195	0.9321	0.415
179	0.7205	0.8237	196	0.8938	1.2121
180	0.8362	1.295	197	0.8293	0.9522
181	0.7968	1.6046	198	0.8845	1.07
182	0.7653	1.1272	199	0.8494	1.1508
183	0.772	0.976	200	0.8197	0.369
184	0.7016	1.0046	201	0.8875	0.803
185	0.7848	1.437	202	0.8089	1.165
186	0.7416	1.2236	203	0.8938	1.629
187	0.7654	1.122	204	0.8217	0.8034
188	0.692	0.7337	205	0.9678	1.406
189	0.9142	1.5091	206	1.0103	1.673
190	0.874	1.31	207	0.9423	1.3257
191	0.8447	1.4741	208	0.932	1.1756
192	0.8269	1.599	209	1.0496	1.139

a The high-resolution capillary gas chromatography was performed on a Varian Model 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector. A 50-m fused silica capillary column (0.2 mm ID) coated with SE-54 (Hewlett-Packard) was used to separate the PCB isomers and congeners. The oven temperature was programmed at a rate of 1.0°C min^{-1} from 100 to 240°C. The injector and detector temperatures were 270 and 330°C, respectively. Sample volume, 6.0 μL, was injected by using an automatic sampler with splitting in the injector (10:1 split ratio, vented from 0.75 to 1.75 min). The hydrogen carrier gas was held at a constant pressure of 2.25 kg cm^{-2} to give the optimized linear velocity (u) at 100°C of 45 cm s^{-1}.

b Ballschmiter and Zell, 1980.

c Retention times (RT) of the PCBs were expressed relative to the octachloronaphthalene (RT = 124.9 min) standard.

d Response factors (by weight) for the PCBs expressed relative to octachloronaphthalene (R_f = 1.0 for 1 ng of OCN) by using integrated peak areas.

e Estimated relative response factor based on other isomeric PCBs.

Source: Mullin et al., 1984; reproduced with permission, copyright 1984 by American Chemical Society.

MONS 005414

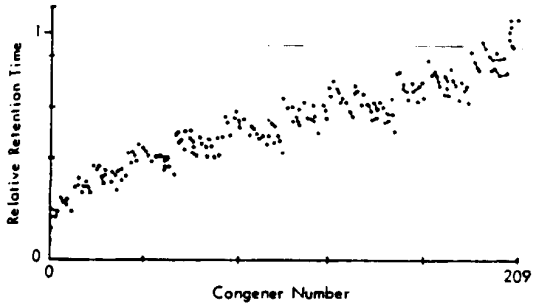


Figure 7-7. Plot of HRGC Relative Retention Time Versus Congener Number for all 209 PCBs

See Table 7-IV for more detailed data and chromatographic conditions.

Reprinted, with permission, from Mullin et al. (1984), copyright 1984 by American Chemical Society.

Recently, bonded liquid phases have been made available on capillary GC columns. These exhibit low bleed and background and have long lifetimes. Figure 7-5 presents a HRGC/EIMS chromatogram of a PCB standard on a DB-5 column. Narrow-bore capillary columns produce both high resolution and fast analyses, although the capacity is reduced since less liquid phase is present. For example, an 8-min chromatogram of Aroclor 1260 has been reported using a short (4.1 m) capillary column operated isothermally at 222°C (Schutjes et al., 1984). A resolution of 70,000 theoretical plates was obtained with the 55-μm ID fused silica column coated with OV-1. Similarly, Onuska (1984) demonstrated nearly double the resolution with about half the analysis time (35 versus 60 min) for a mixture of Aroclor 1242, 1254, and 1260 with a 25 m x 104 μm ID column relative to a 50 m x 300 μm ID column. Both columns were coated with OV-1, prepared in a similar way.

Despite the advances in column technology, no GC method reported or predicted will separate all 209 PCB congeners. As an example of the overlap problem, Mullin et al (1984) noted that 11 pairs of congeners coelute on an SE-54 column. Using their conditions, as shown in Table 7-IV, congener numbers 94/61, 70/76, 95/80, 60/56, 145/81, 144/135, 140/139, 133/122, 163/160, 202/171, and 203/196 exhibited similar or identical retention times. In addition to the problem of congener separation, interferences may coelute. While EIMS can readily discriminate against non-PCBs, coeluting major components may affect the mass spectral response of PCBs.

3. Comparison of PGC and HRGC: The relative merits of PGC and HRGC are well-known (Jennings, 1980) and apply to the separation of PCBs. As seen in Figure 7-8 (Bush et al., 1982), HRGC provides better resolution, and thus higher qualitative reliability. PGC yields a simple chromatogram (less data reduction), permits higher sample loading (and therefore possibly lower limits of quantitation), and is generally considered easier to use.

The inherent low resolution of PGC has been further hindered since PGC analyses traditionally have been done isothermally due to requirements of the ECD (see below). This has not only degraded the resolution of later-eluting peaks (see Figures 7-1 and 7-8) but also lengthened the analysis time. On the other hand, HRGC chromatograms are generally temperature-programmed, which yields similar resolution throughout the chromatogram. Until recently, the emphasis with HRGC has been "ultimate" resolution, achieved by slow temperature program rates, low carrier gas flow rates, and, especially, long (> 50 m) capillary columns. This has resulted in very long chromatograms (see Figure 7-3) relative to PGC (see Figure 7-1). An extreme example is the 5-hr chromatogram published by Albro et al. (1981). In the past few years the trend has shifted toward practical applications of HRGC. Using shorter columns and faster temperature program rates, at the sacrifice of some resolution, chromatographers have produced rapid HRGC separations (Figure 7-9).

Properly utilized, HRGC transmits more of the sample injected to the detector than PGC. With less surface area, there are fewer active sites and less chance for adsorptive losses or catalytic degradation. This advantages translates into lower detection limits.

In a direct comparison of PGC and HRGC, no significant difference was observed in the results for the analysis of PCBs in oils at the 30-500 ppm levels (Levine et al., 1983). The PGC analyses were done on a 180 cm x 2 mm ID

MONS 005416

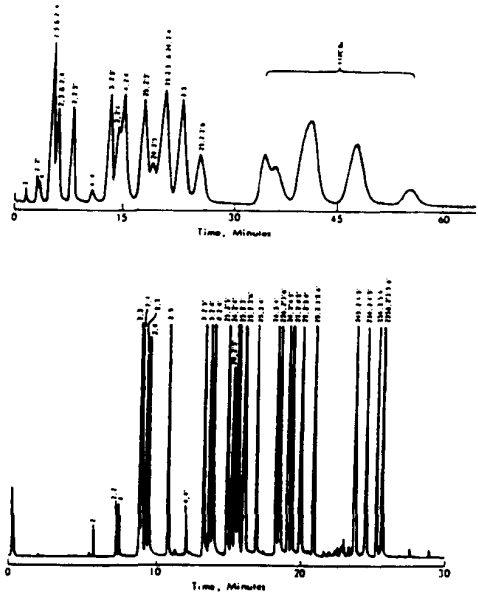


Figure 7-8. Comparison of PGC/ECD (Top) and HRGC/ECD (Bottom) Chromatograms of 29 PCB Congeners

The PGC/ECD chromatogram was obtained on a 5.2 m Apiezon L column operated isothermally at 250°C, as described by Jensen and Sundström (1974). The HRGC/ECD chromatogram was obtained on a 20 m x 0.29 mm ID glass capillary coated with Apeizon L and operated at an initial temperature of 70°C, programmed at 10°C/min to 130°C, then at 4°C/min to 230°C.

Reprinted, with permission, from Bush et al. (1982); copyright 1982 by Association of Official Analytical Chemists, Inc.

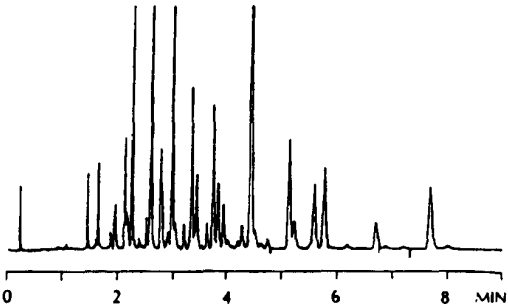


Figure 7-9. HRGC/ECD Chromatogram of Aroclor 1260 Short Capillary Illustrating Rapid Separation

The 4.1 m x 55 µm ID fused silica column was coated with OV-1 and operated isothermally at 222°C.

Reprinted, with permission, from Onuska (1984); copyright 1984 by Elsevier Science Publishers BV.

---

glass column packed with 3% OV-1, operated isothermally. The HRGC analyses were done on a 30-m fused silica capillary coated with SE-54. A Grob injector was used and the column was programmed from 50-250°C at 10°C/min. Both ECD and HECD were used as detectors.

B. Injection

The injector is an integral and important part of the chromatographic process. While often overlooked and not even reported, the type of injector can affect resolution, discriminations, and sensitivity. In PGC, most modern instruments have "on-column" injectors, while earlier work favored injection into a chamber, with the analytes being swept onto the column after vaporization. This latter technique is the basis of HRGC's split and splitless injectors. Recently, on-column injectors have become available for HRGC and provide generally superior chromatography. One detriment of on-column injectors is that, with dirty matrices, inorganics,

polymeric materials, etc., stay on the front of the column, degrading performance and increasing the background. The common solution is to break off the front portion of the column periodically.

C. Detection

The GC detector is a transducer, converting a chemical signal (molecules in a gas stream) to an electrical signal. Some detectors (e.g., FID) destroy the compounds in the detection process, while others (e.g., ECD) are non-destructive. GC detectors are discussed in more detail in several monographs and reviews (David, 1974; Sevcik, 1976; Adlard, 1978; McNair and Bonnelli, 1969).

GC detectors may be categorized as either universal or selective. The ECD and Hall electrolytic conductivity detector (HECD) are selective toward halogenated compounds. This selectivity, coupled with its extreme sensitivity, has made ECD very popular for analysis of trace levels (residues) of pesticides and PCBs and has, in fact, had a significant role in regulatory actions on these classes of compounds. FID is the most common GC detector and is an universal detector, giving similar responses for most organic compounds. Thus, FID would be unsuitable for detection of PCBs in a complex matrix.

Mass spectrometry and Fourier transform infrared spectrometry (FTIR) are in essence both universal and selective GC detectors. By focusing on a spectral property characteristic of a compound or class of compounds, these detectors can be quite specific. However, by using the full spectral range, any compound eluting from the GC will be detected. Due to the much higher information content of mass and infrared spectra, identifications made by GC/MS or GC/FTIR generally have much greater certainty than those made by other detectors.

The analysis of PCBs generally requires selectivity and sensitivity. Even after cleanup, PCBs are usually a minor component of the sample; mixed in with other halocarbons (e.g., DDE), hydrocarbons, lipids, etc. Thus, the detector often must selectively detect PCBs in the presence of other compounds present at orders of magnitude higher concentration. Furthermore, the levels typically observed in food, biota, tissue, soil, and other matrices of interest are in the parts per billion range. These levels strain the capabilities of even the most sensitive detection device such as ECD, resulting in a large number of "not detected" values in many reports.

MONS 005419

The choice of detector often depends upon the level of analytes. Low concentrations demand a detector capable of detecting low amounts (high sensitivity). Figure 7-10 presents the typical range and detection limits for most of the GC detectors used in analysis for PCBs. The detection limit of the HECD is 10^{-11} g with a linear range up to about 10^{-2} g, as measured for lindane (Anderson and Hall, 1980). As can be seen, ECD exhibits the lowest limit of detection (LOD).

The reported LOD for PCBs in a variety of matrices are listed in Table 7-V. Comparison of the reported LODs is difficult because no standard definition of LOD was used. Glaser et al. (1981) followed a rigorous definition and experimentally determined the LOD with a fair degree of confidence, while other investigators clearly approximated the LOD. The issue is further clouded by inconsistency in presenting the LOD as a measure of the instrumental determination or the entire procedure. Some LODs are reported for standard solutions, while others take into account the interferences in the matrix which raise the detection limit considerably.

Every review article (Risebrough, 1971; Reynolds, 1971; Fishbein, 1972; Lincer, 1973; Hutzinger et al, 1974a; Sherma, 1975; Fuller et al., 1976; Margeson, 1977; Krull, 1977; Safe, 1976) has covered the subject of ECD detection of GC effluents. Fishbein (1972), Sherma (1975), and Hutzinger et al. (1974a) all reviewed the use of electrolytic conductivity detectors for PCB determination. Safe (1976) and Hutzinger et al. (1974a) discussed the use of flame ionization detection (FID), mostly with respect to calibration of ECD or establishing ECD response factors. Hutzinger et al. (1974a) noted that for the mono- and dichlorobiphenyls FID and ECD sensitivities are comparable.

As noted in Table 3-1, most of the standard methods specify ECD as either the detector or one of the options. FID is the detector prescribed in the American Society for Testing and Materials (1980) procedure for determining PCBs in capacitor Askarels. In this case, the matrix is well-characterized and generally contains no other compounds in the PCB retention window. HECD is permitted as an alternate detector in three procedures (EPA, 1978; EPA, 1981a; FDA, 1977).

1. Electron capture detection: The electron capture detector (ECD) detects the drop in current caused by the absorption of electrons by the sample compound. A radioactive source emits β particles (electrons) which are swept toward the anode by an applied voltage across the electrodes

MONS 005420

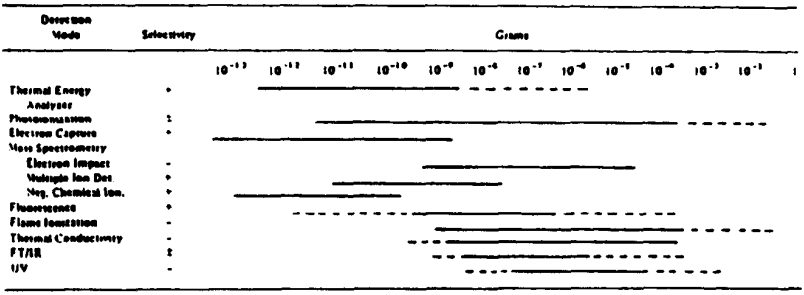


Figure 7-10. Detection Limits and Dynamic Range for Several Instrumental Methods

Reprinted, with permission, from Pellizzari (1981); copyright 1984 by Butterworth Publishers

MONS 005421

Table 7-9 Reported Limits of Detection for PCBs

Instrument	Reported LOD	Converted LOD[a] (µg/g or ppm)	PCB Type	Matrix	Reference
GC/ECD	0.005 µg/l	0.0005[b]	Aroclor 1262	Distilled water	Glaser et al., 1981
	0.5 ppb	0.0005	Aroclors	River water	Kuehl et al., 1980a
	6.5 ppb	0.0065	Aroclors	Pure solution	Jennings et al., 1978
	50 ppb	0.05	Aroclors	Milk	Tessari and Savage, 1980
	1-10 ng/g (wet weight)	0.005-0.01	Isomers	Vegetable	Iwamoto et al., 1981
	0.5 ppm	0.5	Aroclors	Transformer fluid	Axelson, 1981a,b
	1 ppm	1.0	Total PCB	Oil	Chesler et al., 1981
	0.5 ppm	0.5	Total PCB	Oils	Baltz and Farrah, 1980
	0.6 µg/l	0.0006	Perchlorinated	Ground water	Stratton et al., 1979
	1 mg/m³	NA[b]	Perchlorinated	Air	Stratton et al., 1978b
	0.1 mg/m³	NA[b]	Theoretical per isomer	Air	Lewis et al., 1977a
	1 µg/l	0.001	Aroclor 1254	Blood serum	Bretz et al., 1981
	1 ppm	1	18 homologs	Pigments	DHHA, 1982
	10 ppb	0.01	Aroclor 1254	Milk	McKinney et al., 1980
	4 ppb	0.004	Aroclor 1254	Serum	McKinney et al., 1984
GC/ECD	10 pg		Aroclor 1254	Air	Barton and Arsenault, 1987
GC/MECD	1 ng/kg	1.0	Aroclors	Oil	EPA, 1981a
GC/ITMS	90 pg/l	0.090	Aroclor 1221	Distilled water	Glaser et al., 1981
	96 µg/l	0.096	Aroclor 1254	Distilled water	Glaser et al., 1981
	0.03-0.2 µg/l	0.03-0.2	Single component	Industrial sample extract	Tindall and Wineman, 1980
	1.4 ppb[c]	0.001-0.002	Single component	Air	Westberg et al., 1984
	5 ppm	5	Single component	Chlorinated hydrocarbons	Collard and Lewis, 1981a,b, 1981
	1 µg/g	1	Single component	Products and wastes	Erickson et al., 1981a
NMR/IMS	10 ppb	0.01	Aroclors	Biological extracts	Safe et al., 1975

MONS 005422

Table 7-V (concluded)

Instrument	Reported LOD	Converted LOD[a] (µg/g or ppm)	PCB Type	Matrix	Reference
GC/MC DMS	10 ppb[c]	0.01	Mono- to penta-isomers	NS[d]	Westerberg et al., 1980
	1.8 to 0.09 ppb[c]	0.004 to 0.0001	Hexa- to deca-isomers	NS	Westerberg et al., 1980
Dir. Probe MC DMS	~ 1 ppb	0.001	NS	Biological extracts	Dougherty et al., 1980
ECC	0.5 ppm	0.5	Aroclor	Adipose	Bush and Ia, 1971
	0.04 ppm	0.04	Aroclor	Milk	Savage et al., 1971a
	0.1 µg	-	Aroclor	Animal tissue	De Vos and Poot, 1971
	0.05 µg	-	Aroclor	NS	Koch, 1979
	0.7 µg	-	Aroclor	Animal tissue	Melhorn et al., 1971
	1 µg	-	Aroclor	NS	Ismail and Bonner, 1974

a Converted to common units of micrograms per gram (parts per million) assuming 1 ml = 1 g density
b NA = not applicable
c See Table 7-XVII for additional details
d NS = not specified

MONS 005423

(10-50 V). This electron migration produces a current, approximately 10^{-9} amperes. If a molecule or ion capable of absorbing an electron enters the detector, $M + e^- = [Me]^-$ energy. The absorption or capture of electrons by M will reduce the current, since the species $[Me]^-$ migrates more slowly than an electron. In older ECDs the drop in current yielded the detector response. Most ECDs now sold use pulsing circuitry to maintain a constant current. The frequency of the pulses required to maintain the constant current is the detector response. Pulsed ECDs exhibit a greater linearity range than the old constant current models.

Because of its extreme sensitivity and selectivity toward halogenated compounds, ECD has been the most common detector for GC analysis of PCBs. While it is considered a selective detector, it does detect many non-PCB compounds (halogenated pesticides, PCNs, chloroaromatics, phthalate and adipate esters, and other compounds) which may be differentiated from PCBs only on the basis of retention time. Figure 7-11 illustrates the potential interferences from chlorinated pesticides. Figure 7-12 illustrates the actual interferences observed in a chlorinated organic process intermediate (Hanneman, 1982). Clearly, ECD was not a suitable detector for this sample.

In addition to ECD-active compounds such as halogenated organics and phthalate esters, there are other interferences which do not give discrete peaks. As mentioned in Chapter 6, elemental sulfur can interfere with PCB analysis in sediment and other samples which have been subjected to anaerobic degradation conditions. Another non-specific interference is mineral oil (ASTM, 1983). Mineral oil, a complex mixture of hydrocarbons, often contains PCBs as a result of cross-contamination of transformer oils. A typical analysis of mineral oil for PCBs entails simple dilution with hexane to reduce the viscosity and also achieve a concentration in the linear range of the ECD. The mineral oil in the diluted sample reduces the ECD response (ASTM, 1983). In order to minimize the effects of the mineral oil interference on the quantitation, ASTM (1983) recommends that the sample and standard contain the same amount of mineral oil.

A major disadvantage of ECD is the range of response factors (Tables 7-IV, 7-VI, 7-VII, and 7-VIII and Figure 7-13) which different PCB congeners exhibit. The earlier PGC/ECD work (Table 7-VI) has a response factor range of about 7000, while recent HRGC/ECD work (Table 7-VII) has a range of only about 100. Data sets similar to that in Table 7-VI were published by Zitko et al. (1971) and Hattori et al.

MONS 005424

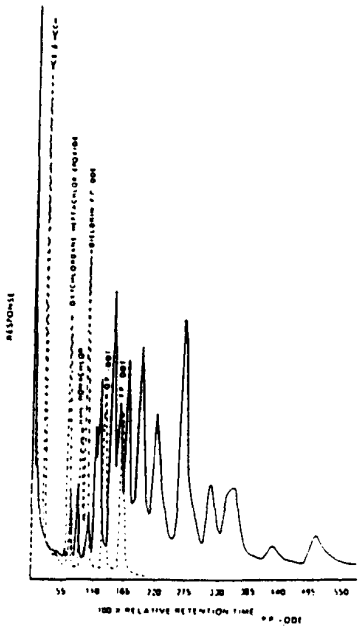


Figure 7-11. PGC/ECD Chromatograms of Aroclor 1260 (921 pg, Solid Line) and Nine Common Pesticides (38 pg Each, Dashed Line) Illustrating the Potential for Interference

A 183 x 0.4 cm ID glass column packed with 3% SE-30 was operated at 195°C, isothermal with a nitrogen flow of 15 mL/min.

Reprinted, with permission, from Needham et al. (1980); copyright 1980 by American Chemical Society.

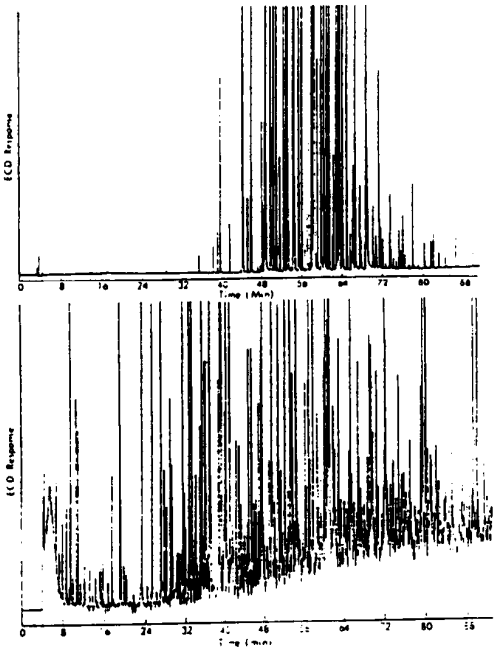


Figure 7-12. HRGC/ECD Chromatogram of Process Intermediate (Bottom) and Aroclor 1248 (Top)

The sample contained mono- and dichlorobiphenyls and over 500 ECD-responsive interferences. A 60-m DB-1 (bonded polydimethylsiloxane) fused silica capillary column was programmed from 100°C to 290°C at 2°/min.

Reprinted, with permission, from Hanneman (1982); copyright 1982 by Dow Corning Corporation.

MONS 005426

Table 7-VI Relative Molar Responses of Electron Capture and Flame Ionization Detectors to Some Chlorobiphenyls

Chlorobiphenyl	Relative Molar Response	
	Electron Capture	Flame Ionization
2-	1.00	1.00
3-	0.20	0.92
4-	1.10	0.87
2,2'-di	5.16	0.99
2,4-di	17.7	0.86
2,6-di	32.0	0.91
3,3'-di	6.10	0.94
3,4-di	15.2	0.86
4,4'-di	5.97	0.81
2,4,4'-tri	135	0.78
2,2',4,4'-tetra	106	0.87
2,2',6,6'-tetra	20.6	0.90
3,3',4,4'-tetra	396	0.87
3,3',5,5'-tetra	320	0.85
2,3,4,5-tetra	367	0.87
2,3,5,6-tetra	259	0.71
2,2',4,4',6,6'-hexa	347	
3,3',4,4',5,5'-hexa	726	
2,2',3,3',4,4',6,6'-octa	1,180	
2,2',3,3',5,5',6,6'-octa	1,150	
deca	1,410	
N	21	16
Mean	310	0.88
SD	438	0.07
RSD (%)	140	8.3

Source: Hutzinger et al., 1974a, reproduced with permission, copyright 1974 by CRC Press, Inc., Boca Raton, Florida.

MONS 005427

Table 7-VII. Summary of ECD Relative Response Factors[a] (Mullin et al., 1984)

Homolog	No. of Isomers	Mean	SD	RSD (%)	Minimum Value	Maximum Value
0	1	0.0251	-	-	-	-
1	3	0.0329	0.0118	36	0.0193	0.04
2	12	0.2432	0.1825	75	0.0374	0.69
3	24	0.5631	0.2287	41	0.313	1.0935
4	42	0.6750	0.1992	30	-	-
5	46	0.7172	0.2115	29	0.4308	1.3987
6	42	0.8550	0.2567	30	0.444	1.389
7	24	1.1529	0.3705	32	0.381	2.044
8	12	1.0720	0.4452	42	0.369	1.868
9	3	1.3914	0.2551	18	1.1756	1.673
10	1	1.139	-	-	-	-

a Values summarized from Table 7-IV.

MONS 005428

Table 7 VIII Comparison of PCB/ECD Response Factors Obtained by Different Laboratories[a]

PCB Congener	Concentration[b] (ng/ml)	Laboratory Number 1	2	3	4	5	6	Mean	S.D (%)
2-Chlorobiphenyl	0.073415	1.00[c]	1.00	1.00	1.00	1.00	1.00		
3,4'-Dichlorobiphenyl	0.088035	1.95	0.9949	0.729	0.7386	0.605	1.199	1.036	40
2,4,5-Trichlorobiphenyl	0.088188	0.19	0.134	0.065	0.0850	0.056	0.11	0.107	40
2,2',4,4'-Tetrachlorobiphenyl	0.018625	0.17	0.138	0.090	0.0671	0.058	0.095	0.103	42
2,3',4,5'-Pentachlorobiphenyl	0.005670	0.11	0.130	0.032	0.0558	0.027	0.074	0.068	50
2,2',3,3',6,6'-Hexachlorobiphenyl	0.011265	0.17	0.141	0.081	0.0555	0.070	0.110	0.105	42
2,2',3,4,5,5',6-Heptachlorobiphenyl	0.005545	0.053	0.0425	0.026	0.0265	0.015	0.041	0.037	40
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	0.006305	0.062	0.0489	0.026	0.0260	0.011	0.038	0.036	50
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0.006715	0.099	0.0695	0.042	0.0411	0.024	0.056	0.054	51
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	0.004700	0.086	0.0564	0.026	0.0176	0.023	0.049	0.046	57
Reported value for 2-chlorobiphenyl		2.03	22.89	0.0310	40.70	0.2790	0.0715		
Reported ratio for 2-chlorobiphenyl		0.84	4.4	0.0247	15	0.0421	0.0054		

a Study conducted as part of a collaborative validation of the Dry Color Manufacturers's Association method for by-product PCBs in pigments (DCMA, 1985, see Chapter 10). All laboratories analyzed four dilutions over one order of magnitude to obtain the response factor. Laboratories 1 and 5 used integrators to measure peak heights. The other laboratories used manual measurement of peak heights in various units.

b The stock standard mixture # 9427-104A was supplied to the laboratories at the concentration shown. The laboratories selected the appropriate dilutions to obtain a working range.

c All values were recalculated and normalized to 2-chlorobiphenyl to make the data comparable. The reported value and range for 2-chlorobiphenyl are shown below to illustrate the scatter.

Source: DCMA, 1985, reproduced with permission, by Dry Color Manufacturers' Association

MONS 005429

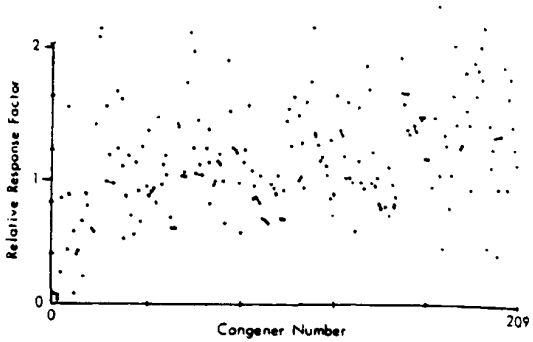


Figure 7-13. Plot of HRGC/ECD Relative Response Factor Versus Congener Number for All 209 PCBs

See Table 7-IV for more detailed data and chromatographic conditions.

Reprinted, with permission, from Mullin et al. (1984); copyright 1984 by American Chemical Society.

(1981) with response factors ranges about 540 and 9000, respectively. The opposite trend in response factors in Table 7-VIII, relative to the other tables, presumably results from differences in the equations used (i.e., whether the PCB response is in the denominator or numerator). Boe and Egaas (1979), Onuska et al. (1983) and Singer et al. (1983) have also published ECD response factors. The range of response factors seriously inhibits reliable quantitation.

The difference in response factors noted above may be a function of the differences in detector design and GC column throughput. In addition, the HRGC is temperature-programmed, while PGC data were presumably obtained isothermally. Despite these differences, all four tables clearly illustrate that, even within a homolog, the RSD is very large and would result in poor accuracy if quantitation involves extrapolation from one isomer to another. For example, the ECD relative response factors for all 12 octachlorobiphenyls showed a range from 1.007 to 2.644 (range of 2.6X) with a RSD of 35% (Mullin et al., 1981). A more recent tabulation (Table 7-IV and 7-VII) of the response factors for these same

compounds by the same authors (Mullin et al., 1984) yielded much different results. While the values would be expected to differ by virtue of changing the internal standard (2,2',4,4',5,5'-hexachlorobiphenyl in the former publication and octachloronaphthalene in the latter), the trends among the sets of response factors were not similar (i.e., the highest in one set was not the highest in the other). This illustrates the importance of calibration of instruments at the time of the analysis.

The ECD response factors for a solution of one isomer of each homolog were compared for six laboratories as part of a collaborative validation of the Dry Color Manufacturers Association method for by-product PCBs in pigments (DCMA, 1982; see Chapter 10 for further discussion). The laboratories reported a mean value for the response factor (RF) and the range of the RFs obtained by analysis of four dilutions of the stock solution ranging from one order of magnitude in concentration. As shown at the bottom of Table 7-VIII, the intralaboratory range was quite large. The study authors attributed the wide range to the nonlinearity of ECD detectors and lack of amplifiers with linearizers in older instruments. They noted that samples should be concentrated or diluted to within ± 25% of the standard to get reliable results. The results presented in Table 7-VIII were recalculated from the original data to normalize the response factors. These normalized RFs permit direct comparison of the data from the different laboratories. The subject of ECD response factor variability is also discussed in the Quantitation section of Chapter 8.

To further complicate its quantitative use, ECD has notoriously variable sensitivity. On the same day, an instrument's response can drift enough to dramatically affect the quantitation of PCBs. The sensitivity (i.e., limit of detection) of GC/ECD is affected by the brand, individual instrument, daily instrumental response, attenuation, injection volume, and detector temperature (Rust, 1984).

Aue and Kapila (1978) presented a novel dual GC where selected peaks from the first ECD were "heart-cut" routed to a second PGC column, and detected by a second ECD. The chemical degradation of PCBs in the first detector yielded new electron-capturing species and provided confirmatory evidence of PCBs. The system probably is not suited to routine application.

PGC/ECD is generally the method of choice for analysis of transformer oils, hydraulic oils, askarels, mineral oil dielectric fluid, and other similar matrices which must

be assayed for PCB content prior to incineration or other destruction (Copland and Gohmann, 1982). The PCBs generally resemble Aroclor standards, halogenated interferences are almost nonexistent, GC/ECD is highly selective against the hydrocarbon matrix, and the technique is relatively inexpensive to operate.

A field-portable PGC/ECD was used to obtain rapid measurements of PCBs in sediment and soil (Spittler, 1983, 1984). The sample preparation consisted of a single solvent extraction and the PCBs were eluted within 9 min. In a 6-hr period, 40 soils and 10 QC samples were analyzed, with concentrations ranging from 0.2 to 24,000 ppm. The use of field analysis permits rapid decisions in a cleanup operation and reduces the need for either return visits to a site by a cleanup crew or excessive excavation of uncontaminated soils. Similar portable systems have been reported (Colby et al., 1983; Picker and Colby, 1984).

The only novel aspects of most articles deals with qualitative or quantitative aspects of the detector and are discussed in Chapter 8. Two studies comparing ECD with the electrolytic conductivity detector are discussed below.

2. Electrolytic conductivity: The Hall electrolytic conductivity detector (HECD) measures the change in conductivity of a solution containing HCl or HBr which is formed by pyrolysis of halogenated organic GC effluents. The column eluent is oxidized in a microcombustion furnace in a quartz tube. The reaction products are absorbed into the liquid electrolyte in the gas-liquid contactor and the electrolytic conductivity of the liquid measured between the two electrodes. The reaction products of non-halogenated organics are CO_2, H_2O, N_2, and SO_2. The SO_2 is scrubbed out with CaO and the other components give little or no response, leaving HCl, HBr, and the other hydrogen halides as the detected species. The HECD exhibits 10^5-10^6 selectivity for halogenated compounds over other compounds. It also gives a linear response over at least a 10^4 range. It is much less subject to interference from nonhalogenated compounds than ECD and the response is proportional to the number of chlorines. The high limit of quantitation and difficulty of operation are the disadvantages of this detector.

Webb and McCall (1973) and Sawyer (1978a) used HECD in the characterization of Aroclor standards. Serum et al. (1973) used HECD, ECD, and electron impact mass spectrometry as PGC detectors in analysis of paper products for PCBs and other compounds. Hofstader et al. (1974) determined that

MONS 005432

sulfur compounds in certain petroleum oils gave positive interferences in PGC/ECD determinations of PCBs. Flame photometric, microcoulometric, and Hall detectors were used to characterize the PCBs and interferences. Chesler et al. (1981) characterized oil products in the preparation of National Bureau of Standards standard reference materials for PCBs in oil. They used both ECD and HECD as HRGC detectors. The ECD was found to be more sensitive than the HECD by two orders of magnitude and easier to maintain in a noncontaminated state. However, ECD response factors varied for different PCB isomers, while the molar response to chlorine which is obtained from the HECD appeared to be constant. The HECD exhibited a wider linearity range and was more selective as it responded only to halogenated compounds. Butler (1981) demonstrated the application of HECD coupled to both packed and HRGC columns in several matrices: milk, fish, transformer oil, and water. Detection of 1 ng of Aroclor 1254 was shown.

An interesting, though tangential, use of HECD was presented by Dolan et al. (1972), Dolan and Hall (1973), and Su and Price (1973). By adjusting the HECD operating parameters they selectively detected organochlorine pesticides in the presence of PCB interferences.

HECD and ECD were compared for their use in detecting PCBs in waste oil, hydraulic fluid, capacitor fluid, and transformer oil (Sonchik et al., 1984). They found both detectors acceptable, but noted that the HECD gave higher results with less precision than the ECD. The method detection limits ranged from 3-12 ppm for HECD and 2-4 ppm for ECD. Greater than 100% recovery of spikes analyzed by the HECD indicated a non-specific response to non-PCB components, since extraneous peaks were not observed. Nevertheless, the authors recommended HECD for general applications, because simple dilution may be employed for the sample preparation. They noted, however, that injection of such large amounts of oil was injurious to both the column and the reactor tube in the detector. It was especially difficult to analyze butylated monochlorodiphenyl ether and phthalate ester dielectrics without sample pretreatment. They also noted that ECD is easier to operate, maintain, and troubleshoot than the HECD.

Another comparison of HECD and ECD for the analysis of PCBs in oils at the 30-500 ppm levels found that the type of detector made no significant difference in the results (Levine et al., 1983). The authors noted that higher accuracy had been expected from the more specific HECD. They postulated that the cleanup procedures (Florisil, alumina, and sulfuric acid) all had effectively removed the non-PCB species which would have caused interferences in the ECD and degraded its accuracy.

MONS 005433

3. Mass spectrometry: Mass spectrometers have only recently come into common use as GC detectors, although they have been widely used for decades in other areas. Mass spectrometers contain three major components: a region where ions are generated (source), a mass analyzer (magnet or quadrupole), and an ion detector. Molecules introduced to a mass spectrometer via a GC are generally ionized by a beam of high-energy electrons ("electron impact") or by reaction with ionized molecules such as methane ("chemical ionization"). The ionized molecule and/or its fragments are then swept to the analyzer section. In a magnetic sector instrument, the strength of the applied magnetic field controls the mass (actually mass-to-charge ratio, m/z) of the ions which can pass through the curved flight path. A quadrupole analyzer has a flight path down the center of four rods. Oscillating RF and DC fields of opposing polarities are applied to the rods. Only those ions of the desired mass pass through the quadrupole; the others oscillate out of the path and strike the rods. Ions passing through either type of analyzer are focused on an electron multiplier for detection. The polarity of the applied voltages determine whether positive ions (usually) or negative ions are transmitted and detected. Associated electronics control all of the components and rapidly change the mass analyzer conditions to scan a mass range.

A GC/MS produces a chromatogram consisting of data points at about 1-sec intervals, which are actually full mass spectra. The data are stored by a dedicated computer and may be retrieved in a variety of ways. The data file contains information on the amount of compound (signal intensity), molecular weight ("parent" ion), and chemical composition (fragmentation patterns and isotopic clusters). A reconstructed ion chromatogram (RIC or total ion current profile) is the sum of all measured ions and is analogous to the response of a flame ionization detector (see Figures 7-4 and 7-14). Extracted ion current profiles (EICPs) or ion plots are chromatograms of only selected portions of the data, usually a single ion. As illustrated in Figure 7-15, the EICPs for PCBs allow comparison of the isotopic ratios and also exhibit characteristic patterns for commercially derived PCBs. Finally, the individual spectra may be used to identify compounds. The spectrum in Figure 7-16 is typical of a hexachlorobiphenyl. More complete descriptions of GC/MS instrumentation, principles, and data interpretation are available from many monographs and analytical text books. One example is McLafferty (1980).

MS is particularly suited to detection of PCBs because of their intense molecular ion and the characteristic

MONS 005434

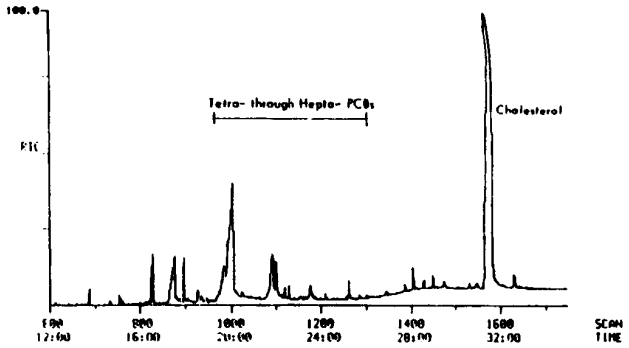


Figure 7-14. Reconstructed Ion Current Chromatogram of HRGC/EIMS Analysis of a Fish Sample from Chesapeake Bay

The area where the tetra- through heptachlorobiphenyls would elute is marked on the chromatogram. The PCBs in the sample are not apparent in this figure because of the higher levels of interferences. The fish was extracted with hexane and cleaned up with gel permeation chromatography. The chromatogram was obtained on a 30-m DB-5 column, with a temperature of 60°C for 2 min, programmed at 10°C/min to 410°C. Full scan, low resolution electron impact (70 eV) data were collected for masses from m/z 143 to 517.

Unpublished data, Mitchell D. Erickson and Stephen E. Swanson, April 2, 1984, Midwest Research Institute, Kansas City, Missouri.

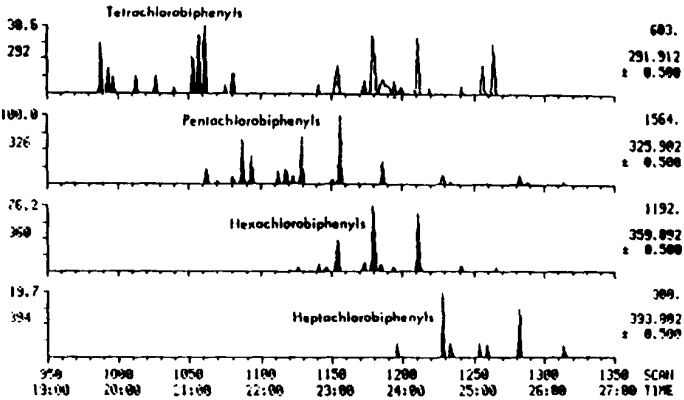


Figure 7-15. Extracted Ion Current Profiles for Tetra- Through Heptachlorobiphenyls in Fish Sample from Chesapeake Bay

See Figure 7-14 for analysis details. Shaded peaks are PCBs. Unshaded peaks are either not PCBs or fragments of higher chlorinated homologs. For example, the peaks at Scan Nos 1155, 1180, and 1211 in the m/z 292 EICP are fragments (M-70) of hexachlorobiphenyls.

Unpublished data, Mitchell D. Erickson and Stephen E. Swanson, April 2, 1984, Midwest Research Institute, Kansas City, Missouri

MONS 005436

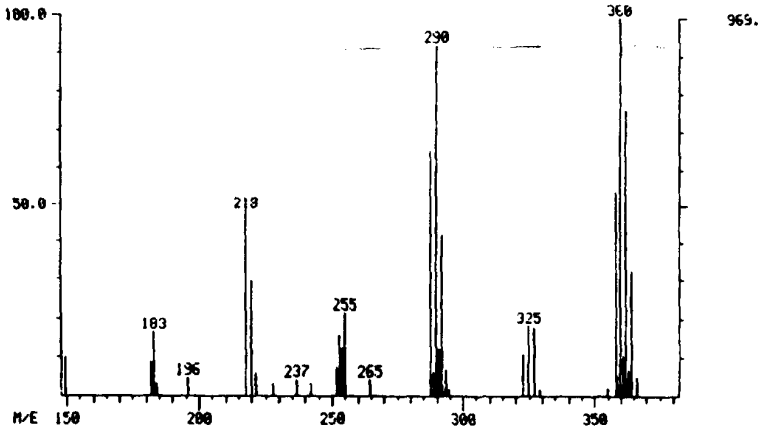


Figure 7-16. Mass Spectrum of Hexachlorobiphenyl in Fish Sample from Chesapeake Bay

Spectrum No. 1180 in Figures 7-14 and 7-15; see Figure 7-14 for details on analysis.

Unpublished data, Mitchell D. Erickson and Stephen E. Swanson, April 2, 1984, Midwest Research Institute, Kansas City, Missouri.

MONS 005437

chlorine cluster. Chlorine has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl, which occur in a ratio of 100:33. Thus, a molecule with one chlorine atom will have a parent ion, M, and an M+2 peak at 33% relative intensity. With two chlorine atoms, M+2 has an intensity of 66% and M+4, 11%. Appendix C gives more detailed presentations of the isotope ratios.

Mass spectrometry may be subdivided by the type of ionization and polarity of ions detected (electron impact ionization/positive ion detection, EI; chemical ionization/positive ion detection, CI; and chemical ionization/negative ion detection, NCI) or by the resolution, low (able to separate at least unit masses, i.e., m/z 321 from m/z 322) or high (able to separate ions of the same unit mass, but different molecular formulae, i.e., $C_{12}Cl_5H$, m/z 319.8529--a PCB fragment--from $C_{12}H_4O_2Cl_4$, m/z 319.8967--TCDD. The differences and relative applicabilities to toxic compounds, including PCBs, have been reviewed (Dougherty, 1980). These different modes of operation are discussed separately in the subsections below.

Because of its expense, complexity of data, and lack of sensitivity, GC/MS has not been used as extensively as other detectors (particularly GC/ECD), despite its inherently higher information content. As the above factors have improved, GC/MS has become much more popular for analysis of PCBs, and will probably continue to increase in importance. For example, the sensitivity of GC/MS has steadily improved over the years. As noted in Table 7-V and Figure 7-10, GC/EIMS is still best characterized as a moderately sensitive technique. Several factors including the introduction of "routine" instruments without costly accessories, decreases in data system costs, and mass-marketing techniques, have combined to keep the costs of GC/MS down while prices of other instruments have risen steadily. Nevertheless, a GC/MS is still considerably more expensive than a GC/ECD ($40,000 and up versus $10,000-$20,000). With larger data systems and more versatile and "user-friendly" software, the large amount of data is more easily handled. However, data reduction of a GC/MS chromatogram still requires substantially more time than for a GC/ECD chromatogram.

GC/EIMS has found increasing use in trace analysis of PCBs as pollutants, including human milk (Yakushiji et al., 1978), municipal sewage sludge (Erickson and Pellizzari, 1979), and stack gas from incinerators and power plants (Levins et al., 1979; Haile et al., 1983a,b, 1984). One area where GC/EIMS (or possibly other MS modes) is indispensible as the primary analytical technique is for samples which contain large amounts of other chlorinated organics. In these

MONS 005438

samples, chlorine-specific detectors (ECD or HECD) cannot discriminate between PCBs and interferents. An example is the analysis of chlorinated organic products and wastes in which the PCBs are generated as by-products. GC/EIMS has been recommended as the technique of choice for these types of samples (CMA, 1981; Erickson and Stanley, 1982).

a. Electron impact mass spectrometry: Electron impact mass spectrometry (EIMS) ranks second only to ECD in popularity as a GC detector for PCBs. Electron impact has been and continues to be the most widely used MS ionization technique. While the chemical ionization (CI) and negative chemical ionization (NCI) techniques are often more sensitive (Table 7-V, Figure 7-10), their operation is more complicated and the spectral patterns and response factors are much less reproducible.

EIMS has been applied to PCB determination using both direct probe and gas chromatography for sample introduction. Early work generally employed the then-exotic technique for confirmation of GC/ECD results. In recent years, as GC/EIMS has become more routine, analysts have increasingly chosen GC/EIMS as the primary technique. As listed in Table 3-1, several standard procedures use GC/EIMS, either as the primary analytical technique or as the confirmatory technique. The application of EIMS to analysis for PCBs has been reviewed by Fishbein (1972), Oswald et al. (1974b), Hutzinger et al. (1974a), Safe (1976), and Stan (1981).

Among the pioneers, Biros et al. (1970) used HRGC/EIMS to determine PCBs in human adipose tissue. Bagley et al. (1970) determined PCBs in bald eagles by PGC/EIMS, and Bonelli (1972a,b) presented PGC/EIMS data for an Aroclor 1254/chlorinated pesticide mixture. In addition, Sissons and Welti (1971), Webb and McCall (1972, 1973), Ugawa et al. (1973), Duinker and Hillebrand (1983) and Tuinstra and Traag (1983) employed GC/EIMS in characterization of commercial PCB mixture. Using both electron impact and chemical ionization mass spectrometry, Oswald et al. (1974a) were able to differentiate some isomers in complex mixtures from their spectra.

While full spectra provide the most qualitative information, the use of selected ion monitoring enhances both instrument sensitivity and selectivity and simplifies data interpretation. Examples of this technique have been presented by Beggs and Banks (1976), Eichelberger et al. (1974), Tressl and Wessely (1976), Martelli et al. (1981), Collard and Irwin (1982a,b, 1983), and Erickson and Pellizzari (1977, 1979). Eichelberger et al. (1974) gave ion selection criteria which were based on their intensity and

the probability of interference from higher homologs or other compounds. Table 7-IX presents a set of SIM ions appropriate for PCBs originally published by Rote and Morris (1973) and expanded upon by Erickson et al. (1982, 1983d). Generally, only the ratio of the primary to secondary ions is necessary for qualitative identification. The tertiary ion is used only when the other data are questionable. The analyst must also include ions for the internal standards and recovery surrogates added to the sample.

A compromise between full scan and SIM techniques is mass chromatography, also called extracted ion current profiles. Full spectra are collected and then ion intensity versus file position plots are extracted from the data by the computer. Thus, mass chromatography has the ease of interpretation of SIM but higher LOQs since full spectra are collected. These full spectra are available for qualitative use if needed. Canada and Regnier (1976) presented a technique which used mass chromatography to monitor the ion ratios in the PCB isotopic clusters.

Another compromise technique, limited mass scanning (LMS), involves scanning the spectrometer only over the mass range of interest (e.g., molecular ion cluster). This permits the spectrometer to spend more time on the ions of interest and thus achieve better sensitivity than the full scan mode. Figure 7-17 presents an example of an LMS analysis (Erickson et al., 1983b). The lower portion of the figure, the "reconstructed ion chromatogram" (RIC), is a sum of all of the ranges scanned. The plots of the individual ions for the octachlorobiphenyl and ^{13}C-octachlorobiphenyl clearly show fewer peaks and thus, less complexity than the RIC.

Tindall and Wininger (1980), Erickson et al. (1982, 1983a,b,d) and Westerberg et al. (1984) utilized LMS in their GC/EIMS analysis of commercial products for by-product PCBs. Table 7-X presents a set of suggested LMS ranges, developed by Tindall and Wininger (1980) and modified by Erickson et al. (1982). The analyst must adjust these ranges or add new mass ranges to cover internal standards and recovery surrogates. The mass ranges cover at least the ions for SIM analysis (Table 7-VIII) and also include the two masses below the parent ion. These ions are included both to monitor the background, since M-1 and M-2 losses are uncommon, and also to permit the system to settle down electronically before it is measuring a mass which would be used for quantitation. A similar approach was used by Westerberg et al. (1984).

MONS 005440

Table 7-IX. Characteristic SIM Ions for PCBs

Homolog	Ion (Relative Intensity)		
	Primary	Secondary	Tertiary
$C_{12}H_9Cl$	188 (100)	190 (33)	-
$C_{12}H_8Cl_2$	222 (100)	224 (66)	226 (11)
$C_{12}H_7Cl_3$	256 (100)	258 (99)	260 (33)
$C_{12}H_6Cl_4$	292 (100)	290 (76)	294 (49)
$C_{12}H_5Cl_5$	326 (100)	328 (66)	324 (61)
$C_{12}H_4Cl_6$	360 (100)	362 (82)	364 (36)
$C_{12}H_3Cl_7$	394 (100)	396 (98)	398 (54)
$C_{12}H_2Cl_8$	430 (100)	432 (66)	428 (87)
$C_{12}HCl_9$	464 (100)	466 (76)	462 (76)
$C_{12}Cl_{10}$	498 (100)	500 (87)	496 (68)
$C_{10}H_4I$[a]	254 (100)	-	-
$C_{12}D_6Cl_4$[a]	298 (100)	300 (49)	296 (76)
$C_{18}D_{12}$[a]	240 (100)	-	-
$^{13}C_6{}^{12}C_6H_9Cl$[b]	194 (100)	196 (33)	-
$^{13}C_{12}H_6Cl_4$[b]	304 (100)	306 (49)	302 (76)
$^{13}C_{12}H_2Cl_8$[b]	442 (100)	444 (65)	440 (87)
$^{13}C_{12}Cl_{10}$[b]	510 (100)	512 (87)	508 (68)

a Internal standards added to sample before HRGC/EIMS analysis.

b Recovery surrogates added to sample before extraction.

Source: Erickson et al., 1985c.

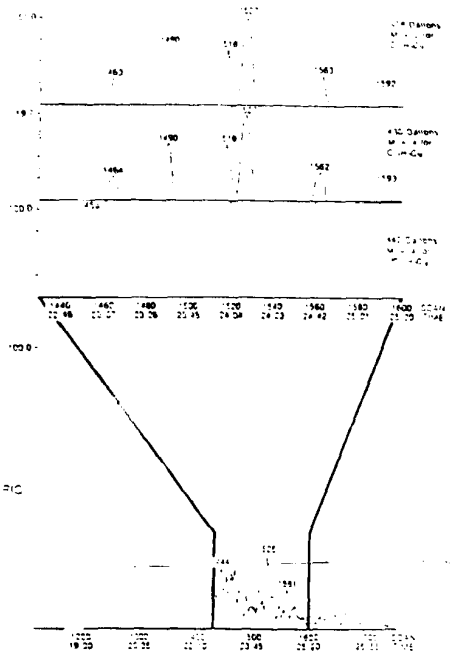


Figure 7-17. HRGC/EIMS Data for a Chlorinated Aromatic Waste Showing Presence of Octachlorobiphenyls as By-products

Extracted ion current profiles (upper) of octachlorobiphenyl congeners identified (428, 430 Daltons), the ^{13}C-octachlorobiphenyl surrogate (442 Daltons), and portion of reconstructed ion chromatogram.

Reprinted, with permission, from Erickson et al. (1983b). copyright 1983 by Battelle Press.

MONS 005442

Table 7-X. Limited Mass Scanning (LMS) Ranges for PCBs

Compound	Mass Range (m/z)
$C_{12}H_9Cl_1$ + $^{13}C_6{}^{12}C_6H_9Cl$[a]	186-198
$C_{12}H_8Cl_2$	220-226
$C_{12}H_7Cl_3$	254-260
$C_{12}H_6Cl_4$ + $C_{12}D_6Cl_4$[b] + $^{13}C_{12}H_6Cl_4$[a]	288-310
$C_{12}H_5Cl_5$	322-328
$C_{12}H_4Cl_6$	356-362
$C_{12}H_3Cl_7$	390-396
$C_{12}H_2Cl_8$	426-434
$C_{12}HCl_9$	460-468
$C_{12}Cl_{10}$	496-502
$C_{10}H_9I$[b]	254
$C_{18}D_{12}$[b]	240
$^{13}C_{12}H_2Cl_8$[a]	440-446
$^{13}C_{12}Cl_{10}$[a]	508-514

a Recovery surrogates added to sample before extraction.

b Internal standards added to sample before HRGC/EIMS analysis.

Source: Erickson et al., 1985c.

In contrast to ECD, the responses of the PCB congeners are relatively well-behaved. As seen in Tables 7-IV, 7-VI, 7-VII, and 7-VIII, the ECD response factors can range over at least two orders of magnitude and can even vary widely among isomers of one homolog. The EIMS data of Martelli et al. (1981) are presented in Table 7-XI. These response factors are somewhat confusing, in that the lowest response for each homolog was set at 1.000. Thus, there is no way to compare the responses of the different homologs.

A more complete set of response factors (RFs) is presented in Table 7-XII (Erickson et al., 1982, 1983b; Stanley et al., 1983). Comparison of the data (Table 7-XIII and Figure 7-18) indicated that there was a statistically significant difference in the RF values from the quadrupole and magnetic instruments for all but the mono-, tetra-, and pentachlorobiphenyl homologs. Differences between instrument types were expected due to differences in mass discrimination and hence sensitivity between the quadrupole and magnetic sector instruments. Further comparison of the data showed no significant difference in the variance of the RF within each homolog. Based on the consistency of the RF data, standards were selected for calibration and quantitation of all PCB isomers for each homolog (Table 7-XIV). The RF values indicate that HRGC/EIMS should provide more accurate quantitation of PCBs than can be obtained by other instrumental methods.

b. Positive chemical ionization mass spectrometry. Positive chemical ionization (CI) mass spectromery (CIMS) is one of the "soft" ionization techniques which tend to produce fewer fragments. Thus, the spectra are simple and the molecular ion is generally one of the most intense peaks. However, with PCBs, the electron impact spectra generally exhibit good molecular ions, reducing the advantages of CI. Another problem with CI is that the ionization process depends on a reagent gas introduced with the sample into the source. Slight changes in gas pressure, source temperature, and electronic conditions can affect the reaction conditions and thus the spectrum (both fragmentation patterns and overall intensity). Thus, CI is not as reproducible as electron impact, either qualitatively or quantitatively.

Several researchers have utilized GC/CIMS for determination of PCBs. Oswald et al. (1974a), Sawyer (1978a), and Cairns and Siegmund (1981a) characterized standard solutions. Oswald et al. (1974b), Iida and Kashiwegi (1975), Stalling (1976), Cairns and Jacobsen (1977), and Iida et al. (1983) applied GC/CIMS to PCB metabolites, environmental samples, and food samples.

MONS 005444

Table 7-XI. Molecular Ion Response of PCBs Congeners to EIMS[a]

Compound	Relative[b] Response Mean ± SD, N = 4
Monochlorobiphenyls	
4-	1.000 ± 0.004
3-	1.060 ± 0.015
2-	1.090 ± 0.015
Mean[c]	1.050 ± 0.046 (4.4)
Dichlorobiphenyls	
2,2'-	1.000 ± 0.078
2,6-	1.505 ± 0.148
2,3-	1.689 ± 0.021
3,4-	1.738 ± 0.016
2,5-	1.821 ± 0.023
2,4-	1.851 ± 0.021
4,4'-	1.868 ± 0.033
3,5-	1.909 ± 0.140
3,3'-	1.922 ± 0.082
2,4'-	2.062 ± 0.035
Mean	1.736 ± 0.30 (17.2)
Trichlorobiphenyls	
2,5,2'-	1.000 ± 0.066
2,3,4-	1.273 ± 0.064
2,4,6-	1.288 ± 0.087
2,3,6-	1.315 ± 0.122
3,4,2'-	1.319 ± 0.079
2,4,4'-	1.356 ± 0.143
2,5,3'-	1.358 ± 0.103
2,4,5-	1.474 ± 0.097
2,5,4'-	1.627 ± 0.081
Mean	1.334 ± 0.221 (16.4)
Tetrachlorobiphenyls	
2,3,2',3'-	1.000 ± 0.039
2,3,2',5'-	1.253 ± 0.094
2,4,2',4'-	1.315 ± 0.092
3,4,3',4'-	1.418 ± 0.146
2,4,2',5'-	1.478 ± 0.090
2,5,2',5'-	1.536 ± 0.086
2,4,3',4'-	1.749 ± 0.097
2,6,2',6'-	1.766 ± 0.045
2,5,3',4'-	1.828 ± 0.133
2,3,4,5-	1.854 ± 0.208
2,3,5,6-	2.146 ± 0.092
Mean	1.577 ± 0.32 (20.7)

MONS 005445

Table 7-XI (concluded)

Compound	Relative[b] Response Mean ± SD, N = 4
Pentachlorobiphenyls	
2,4,5,2',3'-	1.000 ± 0.041
2,4,5,2',5'-	1.001 ± 0.072
2,3,4,2',5'-	1.013 ± 0.047
Mean	1.005 ± 0.007 (0.7)
Hexachlorobiphenyls	
2,3,5,6,2',5'-	1.000 ± 0.077
2,3,4,5,2',5'-	1.092 ± 0.100
2,3,4,2',3',4'-	1.100 ± 0.047
2,3,4,2',4',5'-	1.107 ± 0.071
2,3,6,2',3',6'-	1.184 ± 0.038
2,4,6,2',4',6'-	1.265 ± 0.022
2,4,5,2',4',5'-	1.321 ± 0.103
Mean	1.153 ± 0.13 (10.8)
Octachlorobiphenyls	
2,3,4,5,2',3',4',5'-	1.000 ± 0.056
2,3,5,6,2',3',5',6'-	1.359 ± 0.034

a Data obtained on an LKB 2091-051 gas chromatograph low resolution mass spectrometer operated in the EI mode with selected ion monitoring acquisition, equipped with an LKB-2130 computer for data acquisition and calculation. The GC conditions were as follows: glass column, 2 m x 2 mm ID, packed with 3% OV-1 on Gas Chrom Q (100-120 mesh); helium flow, 25 mL/min^{-1}; electron energy, 70 eV; trap current, 100 μA; ion temperature, 250°C; separator temperature, 250°C.

b Relative to the isomer with the lowest response, for each homolog.

c Mean ± standard deviation (relative standard deviation) of the responses for the congeners in the homolog.

Source: Martelli et al., 1981; reproduced with permission, copyright 1981 by John Wiley and Sons, Ltd.

MONS 005446

Table 7-411 HMX/TNT Relative Response Factors[a]

Congener No.	Degree of Chlorination	Quadruple (4 Measurements)[b,c] Average Relative Response Ratio	Standard Deviation	Coefficient of Variation (%)	Quadruple[b,d] (Single Measurement)	Regression Value[b,e] (Single Measurement)
1	1	0.871	0.110	2.9	2.708	2.516
2	1	2.951	0.056	1.9	2.596	2.619
3	1	2.969	0.028	1.0	3.011	2.911
4	2	1.212	0.006	0.5	1.278	1.212
5	2	1.959	0.035	1.8	1.727	1.819
7	2	2.688	0.027	1.0	2.295	1.648
8	2	2.964	0.023	1.1	2.357	1.748
9	2	2.116	0.061	2.8	2.164	1.692
10	2	1.888	0.031	1.7	1.946	1.558
11	2	1.971	0.073	3.4	2.208	2.170
12	2	1.629	0.016	1.0	2.081	1.648
14	2	2.081	0.098	4.7	2.308	1.765
15	2	1.989	0.089	4.7	2.337	1.619
18	3	1.310	0.017	1.1	1.140	0.977
21	3	1.586	0.018	1.1	1.195	1.168
24	3	1.954	0.033	1.1	1.140	0.661
26	3	1.736	0.013	0.7	1.759	1.297
28	3	1.987	0.028	1.2	1.836	1.287
29	3	2.195	0.048	2.2	1.680	1.549
30	3	1.536	0.067	4.4	1.780	1.754
31	3	1.746	0.026	1.4	1.853	1.208
33	3	1.688	0.031	1.9	1.821	1.771
40	4	0.597	0.013	2.2	0.595	0.698
44	4	0.712	0.007	0.9	0.659	0.758
47	4	1.067	0.059	5.6	0.916	1.069
49	4	0.831	0.019	2.2	0.883	0.838
50	4	0.957	0.025	2.6	1.003	0.974
52	4	0.732	0.011	1.5	0.771	0.758
53	4	0.798	0.008	1.0	0.738	0.781
59	4	0.956	0.013	1.3	0.948	0.913
61	4	0.675	0.007	1.1	0.727	0.667
63	4	1.086	0.022	2.0	0.961	0.913
66	4	1.139	0.068	6.0	1.131	1.054
70	4	1.042	0.012	1.1	1.090	1.116

TABLE 7-III (continued)

Compound No	Degree of Chlorination	Quadrupole (4 Measurements)[b,c] Average Relative Response Factor	Quadrupole (4 Measurements)[b,c] Standard Deviation	Quadrupole (4 Measurements)[b,c] Coefficient of Variation (%)	Quadrupole[c,d] (Single Measurement)	Magnetic Sector[c,e] (Single Measurement)
70	4	1.01	0.050	4.9	1.135	0.868
72	4	1.08	0.046	4.3	0.948	0.912
75	4	1.05	0.061	5.8	1.121	1.012
77	4	1.05	0.050	4.8	1.179	1.116
87	5	0.827	0.041	4.9	0.930	0.744
98	5	0.831	0.035	4.2	0.926	0.826
99	5	0.928	0.050	5.4	0.972	0.915
100	5	0.719	0.038	5.3	0.850	0.693
101	5	0.777	0.041	5.3	0.736	0.804
103	5	0.651	0.034	5.3	0.735	0.720
104	5	0.766	0.045	5.9	0.856	0.672
114	5	0.824	0.035	4.2	0.836	0.801
115	5	0.851	0.061	7.1	0.792	0.768
118	5	0.785	0.033	4.2	0.835	0.768
119	5	0.767	0.022	2.9	0.855	0.682
121	5	0.788	0.029	3.7	0.792	0.682
126	5	0.773	0.044	5.7	0.688	0.771
128	6	0.649	0.035	5.4	0.723	0.638
129	6	0.649	0.035	5.4	0.723	0.638
130	6	0.649	0.035	5.4	0.723	0.638
131	6	0.649	0.035	5.4	0.723	0.638
132	6	0.649	0.035	5.4	0.723	0.638
133	6	0.649	0.035	5.4	0.723	0.638
134	6	0.649	0.035	5.4	0.723	0.638
135	6	0.649	0.035	5.4	0.723	0.638
136	6	0.649	0.035	5.4	0.723	0.638
171	7	0.484	0.032	6.6	0.775	0.566
173	7	0.492	0.028	5.6	0.715	0.581
174	7	0.480	0.028	5.7	0.728	0.496
175	7	0.476	0.028	5.7	0.707	0.495

MONS 005448

Table 7 (11 (concluded)

Congener No	Degree of Chlorination	Quadrupole (4 Measurements)[b,c] Average Relative Response Factor	Standard Deviation	Coefficient of Variation (%)	Quadrupole[b,d] (Single Measurement)	Magnetic Sector[d,e] (Single Measurement)
194	H	0.221	0.001	0.6	0.159	0.372
195	H	0.265	0.003	1.2	0.217	0.497
198	H	0.262	0.010	2.9	0.213	0.414
200	H	0.101	0.007	2.4	0.750	0.464
202	H	0.250	0.007	2.7	0.272	0.575
204	H	0.221	0.007	3.2	0.237	0.451
206	N	0.193	0.003	1.7	0.153	0.346
207	N	0.217	0.006	3.5	0.230	0.510
208	N	0.259	0.003	1.1	0.208	0.516
209	Dc	0.139	0.006	4	0.124	0.300

a Relative to $^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl. Calculated as the average of four replicate measurements made on the same day. Compounds separated on a 0.255 mm ID x 15 m DB-5 (0.25 µm thick) fused silica capillary column (J&W Scientific) with 4% ca/sec helium carrier gas, on-column injection (1&W) of 1.0 µl hexane solutions. The column temperature was programmed from 110 to 125°C at 10°C/min. The column outlet was placed in the source, with a transfer line temperature of 290°C.

b Finnigan 8230 Quadrupole Mass Spectrometer with electron impact ionization. The spectrometer was scanned from m/z 95-500 with a 1 sec cycle time, unit resolution, source temperature of 200°C, 70 eV electron energy, 0.2 mA trap current, 1600 V multiplier voltage, and 10^-5 A/V preamplifier sensitivity. The mass spectrometer was tuned daily according to rigorous criteria (Erickson et al., 1982) to ensure system reproducibility.

c Four replicate measurements made on the same day for each congener.

d Single measurement for each congener; all data collected on a single day to minimize effects of tuning drift, etc., which have day-to-day variance.

e Finnigan MAT 311A magnetic sector mass spectrometer with electron impact ionization. The spectrometer was scanned from m/z 90-500 exponentially with a 1.2 sec cycle time, resolution of 1000, source temperature of 200°C, 70 eV electron energy, 1.2 mA emission current, and 1600 V multiplier voltage.

Source: Erickson et al. (1982, 1981b), Stanley et al. (1983), and unpublished data, Midwest Research Institute, Kansas City, Missouri.

MONS 005449

Table 7 XIII. Summary of HRGC/ELMS Response Factors in Table 7 XII[a]

Homolog	No. of Isomers Measured	Quadrupole (1 measurement/congener) Mean	SD	RSD %[b]	Quadrupole (1 measurement/congener) Mean	SD	RSD %	Magnetic Sector Mean	SD	RSD %
Cl_4	1	1.111	0.601	19.3	2.745	0.758	9.3	2.179	0.199	8.5
Cl_5	10	2.098	0.467	22.8	2.048	0.722	35.7	1.661	0.229	13.8
Cl_6	9	1.573	0.681	21.7	1.592	0.789	38.1	1.167	0.248	21.2
Cl_7	16	0.951	0.175	18.4	0.946	0.189	20.0	0.903	0.138	13.2
Cl_8	12	0.720	0.120	16.7	0.739	0.130	17.6	0.751	0.135	18.0
Cl_9	14	0.511	0.078	15.3	0.500	0.096	19.3	0.644	0.124	19.3
Cl_{10}	4	0.364	0.024	6.6	0.369	0.025	8.0	0.497	0.060	12.0
Cl_{11}	6	0.255	0.036	13.7	0.274	0.049	17.5	0.461	0.071	15.4
Cl_{12}	3	0.200	0.031	14.6	0.199	0.030	14.2	0.467	0.105	22.5
Cl_{13}	1	0.213			0.179			0.586		

a Relative to [4,4'-tetrachlorobiphenyl]. See footnotes to Table 7 XII for experimental conditions.
b Relative standard deviation.
Source: Erickson et al. (1982, 1983b), Stanley et al. (1981), and unpublished data, Midwest Research Institute, Kansas City, Missouri.

MONS 005450

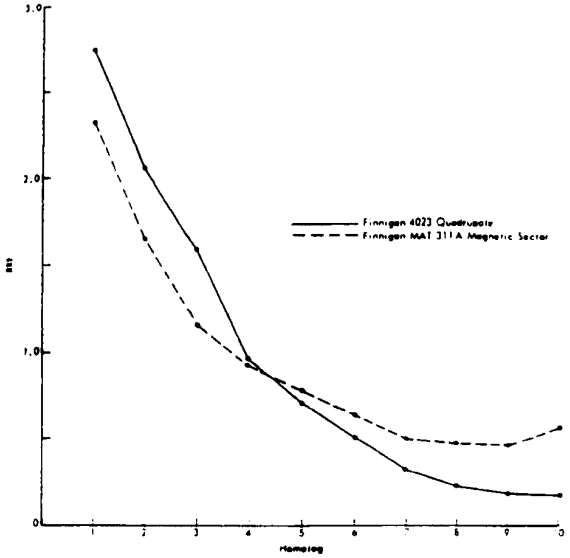


Figure 7-18. Plot of Average Response Factors Versus PCB Homolog

Response factors were determined relative to d_6-3,3',4,4'-tetrachlorobiphenyl for 77 congeners on a single day to minimize instrumental effects. See Table 7-XII for instrumental conditions.

Reprinted, with permission, from Erickson et al. (1982, 1983b) and Stanley et al. (1983).

Table 7-XIV. Pairings of Analyte and Calibration Congeners for Homolog-Specific GC/EIMS Determination of PCBs

Analyte		Calibration Standard[a]	
Congener[b] No.	Compound	Congener No	Compound
1	$C_{12}H_9Cl$	1	2
4-15	$C_{12}H_8Cl_2$	7	2,4
16-39	$C_{12}H_7Cl_3$	30	2,4,6
40-81	$C_{12}H_6Cl_4$	50	2,2',4,6
82-127	$C_{12}H_5Cl_5$	97	2,2',3',4,5
128-169	$C_{12}H_4Cl_6$	143	2,2',3,4,5,6'
170-193	$C_{12}H_3Cl_7$	183	2,2',3',4,4',5',6
194-205	$C_{12}H_2Cl_8$	202	2,2',3,3',5,5',6,6'
206-208	$C_{12}HCl_9$	207	2,2',3,3',4,4',5,6,6'
209	$C_{12}Cl_{10}$	209	$C_{12}Cl_{10}$

a The congeners are prepared in a mixture along with internal standards and used to generate the response factors for the analytes in the same row.

b Ballschmiter and Zell, 1980.

Source: Erickson et al., 1985c.

MONS 005452

The fragmentation patterns of hydrogen CI mass spectra are isomer-dependent for the lower homologs (Cl_4 and lower) and may be useful in identification of PCB isomers (Harrison et al., 1981). The higher homologs did not fragment enough to be of qualitative value.

Dougherty et al. (1973) reported the use of direct probe positive and negative CIMS for the analysis of human adipose tissues for PCBs. Stalling et al. (1980b) reported an HPLC/MS technique for PCBs which is presumed to use the CI mode. This preliminary report speculated that HPLC/MS could be useful as a screening technique for environmental samples.

A related (but often defined as separate) technique, atmospheric pressure chemical ionization (APCI) has been reported for PCB determination. Dzidic et al. (1975) reported subpicogram detection of 2,3,4,5,6-pentachlorobiphenyl. An instrument in a van has been used for in situ detection of PCBs in clay and soil (Thomson et al., 1980; Thomson and Roberts 1980, 1982; Lovett et al., 1983). It has been used for direct sampling and analysis of mono- through hexachlorobiphenyls in stack gas (Lovett et al., 1983) and ambient air (Thomson et al., 1980). Data were available about 2 min after the sample was collected. A detection limit for total PCBs of 8 $\mu g/m^3$ was reported.

c. Negative chemical ionization mass spectrometry: Negative chemical ionization (NCI) mass spectrometry (NCIMS) is similar to both CIMS and ECD. The basic difference between negative and positive CI is the polarity of the various voltage potentials in the spectrometer and the detector. Many of the chemical reactions in the NCI source and the ECD are the same. NCI and ECD exhibit similar detection limits and selectivities toward chlorinated compounds, thus the interest in NCI. The reproducibility problems of CI are also present in NCI. The range of response factors found with ECD are also found with NCI (see Table 7-XV). NCIMS, only recently available, is still considered to be a research technique.

The major reasons for use of NCIMS for PCB analysis are its sensitivity and selectivity. The sensitivity is highly dependent on the degree of chlorination. As shown in Table 7-XVI, the sensitivity of NCIMS is much worse than EIMS for the lower homologs and up to 40 times better for the higher homologs (Westerberg et al., 1984). Nevertheless, the lower MDL for the higher homologs can be a decided advantage for trace work. It should be noted that the magnitude of the homolog discrimination may be dependent on conditions or instrument configuration.

Table 7-XV Relative Response Factors for HRGC/MCIMS Detection of PCBs (m/z 35) for Homologous Series of PCBs

Homolog	No. of Isomers Possible	No. of PCB Isomers Measured	Range[a]	Mean ± SD	% RSD
1Cl	3	3	0.456-1.787	0.924 ± 0.75	81
2Cl	12	8	2.881-21.199	8.343 ± 6.17	74
3Cl	24	7	0.721-10.901	2.921 ± 3.64	125
4Cl	42	16	0.102-4.267	2.058 ± 1.02	50
5Cl	46	12	0.465-1.216	0.805 ± 0.27	33
6Cl	42	16	0.369-1.440	0.817 ± 0.29	36
7Cl	24	13	0.236-1.192	0.703 ± 0.30	43
8Cl	12	8	0.241-1.116	0.573 ± 0.26	46
9Cl	3	3	0.068-0.565	0.354 ± 0.26	73
10Cl	1	1	-	0.410	-

a All values are relative to octachloronaphthalene
Source: Pellizzari et al., 1983b.

MONS 005454

Table 7-XVI Limits of Detection for PCBs

PCB Isomer	MW	EI MDL[a] (ppb)	NCI MDL[a] (ppb)
2-Monochlorobiphenyl	188	1.3	> 10
4,4'-Dichlorobiphenyl	222	3.1	> 10
2,4,5-Trichlorobiphenyl	256	2.6	> 10
2,2',4,4'-Tetrachlorobiphenyl	290	2.0	> 10
2,3',4,5',6-Pentachlorobiphenyl	324	1.2	> 10
2,2',4,5,5'-Pentachlorobiphenyl	324	1.9	> 10
2,2',3,3',6,6'-Hexachlorobiphenyl	358	1.3	3.5
2,2',3,3',4,4'-Hexachlorobiphenyl	358	2.8	1.8
2,2',3,4,5,5',6-Heptachlorobiphenyl	392	2.2	0.16
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	426	3.2	0.09
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	460	4.5	0.13
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	494	4.3	0.10

a MDL = Amount which corresponds to a peak height of twice the average noise level above baseline.

Source: Westerberg et al., 1984, reproduced with permission, copyright by Elsevier Science Publishers, B.V.

MONS 005455

The selectivity of NCIMS was illustrated by Kuehl et al. (1980a), who used both HRGC/EIMS and HRGC/NCIMS to analyze fish samples for a variety of chloro-organics, including PCBs. The electron impact spectra were used for primary identification, although the NCI spectra were also of great value. Figure 7-19 presents the NCI and electron impact RICs for comparison. The NCI is much more selective toward the halogenated compounds, eliminating the broad hump which is presumably a complex mixture of lipids and oils from the fish matrix. Other investigators have applied GC/NCIMS to analysis for PCBs in Lake Ontario sediment (Kaminsky and Hites, 1982) and marine sediments (Lewis and Jamieson, 1983).

The group led by Dougherty has published extensively on the methods and application of (direct probe) NCIMS (Dougherty, 1980, 1981a,b; Dougherty et al., 1973, 1980; Kuehl et al., 1980b). The technique is described as rapid and highly selective toward halogenated compounds. The latter advantage reduces the need for cleanup and, according to Dougherty (1981a), permits the analysis without the customary GC separation.

HRGC/NCIMS proved much more sensitive than HRGC/EIMS for PCBs in the analysis of ambient air samples collected during a demonstration of PCB destruction at the ENSCD incinerator in El Dorado, AR (Erickson et al., 1980a). Extracts of the polyurethane foam air sampling sorbent contained no detectable PCBs when analyzed by HRGC/EIMS, whereas the analysis of the same extracts by HRGC/NCIMS found mono- through hexachlorobiphenyls in most of the samples at concentrations up to 51 ng/m^2/homolog.

The HRGC/NCIMS instrumental operating parameters have been characterized (Pellizzari et al., 1981, 1983a, 1983b). The choice of reagent gas and its pressure markedly affect the relative intensities of the major peaks (m/z 35 and 37, molecular ion, etc.). The response factors for several PCB congeners are summarized in Table 7-XV (Pellizzari et al., 1983b). As with ECD, the range of the response factors is broad. Thus quantitation by extrapolation from a single calibration isomer presents similar problems. They have compared the quantitation of single congeners obtained by HRGC/ ECD and HRGC/NCIMS (Pellizzari et al., 1983b). In both cases, there was a one-to-one correspondence between the calibration and analyte congeners. For nine congeners in serum and 38 in adipose, the analyses generally correlated well. For some congeners, however, there was a distinct bias toward one or the other technique, which may have been due to discrepancies in calibration. They also note that the HRGC/ECD is more sensitive than HRGC/NCIMS: 109 versus 50 peaks were quantitated by the two techniques, respectively.

MONS 005456

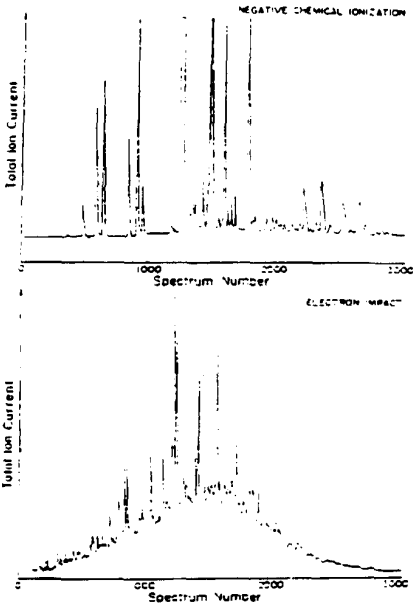


Figure 7-19. Comparison of HRGC/NCIMS (Top) and HRGC/EIMS (Bottom) Total Ion Current Profiles for a Fish Sample

The fish sample was extracted with dichloromethane/hexane (50:50), cleaned up by Florisil column chromatography and further cleaned up by gel permeation chromatography. The sample was injected via a Grob injector onto a 30-m x 0.25 mm glass capillary column coated with SE-30 which was programmed from 100°C to 225°C at 4°C/min with a 30-min hold. A Finnigan 4000 quadrupole mass spectrometer was operated at 70 eV ionization energy for the EIMS mode and with 0.5 torr methane for the NICMS mode.

Reprinted, with permission, from Kuehl et al. (1980a); copyright 1980 by Association of Official Analytical Chemists, Inc.

MONS 005457

While not directly used for PCB determination, HRGC/atmospheric pressure negative chemical ionization mass spectrometry was shown to be both sensitive and selective for PCDDs in the presence of PCBs (Mitchum et al., 1982). With proper selection of masses and ionization conditions, this technique may be highly selective for PCBs.

d. High resolution electron impact mass spectrometry: HREIMS is capable of obtaining precise and accurate mass measurements of a peak. As reviewed by Safe (1976), HREIMS is particularly useful for chlorinated compounds because the chlorine mass defect clearly distinguishes a halocarbon from a molecule containing only carbon, hydrogen, nitrogen, and oxygen. Safe (1976) and Safe et al. (1975) have reported the application of direct probe HREIMS to the analysis of crude goat urine extracts and other biological samples for PCB and polychloroterphenyl metabolites. The reported 10-ppb detection limit and the rapid analysis time (no GC separation is used) would appear to make this technique a suitable technique for rapid screening of samples for the presence of PCBs.

Figure 7-20 illustrates the need for HREIMS to separate interferences if they are not chromatographically separated. The direct probe mass spectrum in Figure 7-20 shows that ODE, TCDD, and PCB would have given one peak under low resolution conditions (Baughman and Meselson, 1973). Similar spectra have been published by Hass and Friesen (1979) and Dougherty (1980).

HRGC/HREIMS has been applied to the analysis of fat and blood samples for PCBs (Voyksner et al., 1983). As discussed in the next section, the technique proved more reliable than direct probe MS/MS analysis.

Several factors have inhibited the wide usage of GC/HREIMS for routine analytical work. Instrumentation is more expensive, more difficult to use, and much less available. Nevertheless, HREIMS does provide much higher qualitative confidence than most other detectors and should be considered as an excellent candidate for confirmation, when required.

e. Mass spectrometry/mass spectrometry (MS/MS): MS/MS couples two or more mass analyzers in one instrument so that a fragment of a molecule (e.g., M-70 for a PCB) may be selected out of the entire spectrum, further fragmented and, in a subsequent analyzer, its fragments analyzed. MS/MS may be operated in several different modes to produce different outputs from this multidimensional ion map. The technique has been reviewed (Kondrat and Cooks, 1978; Yost

MONS 005458

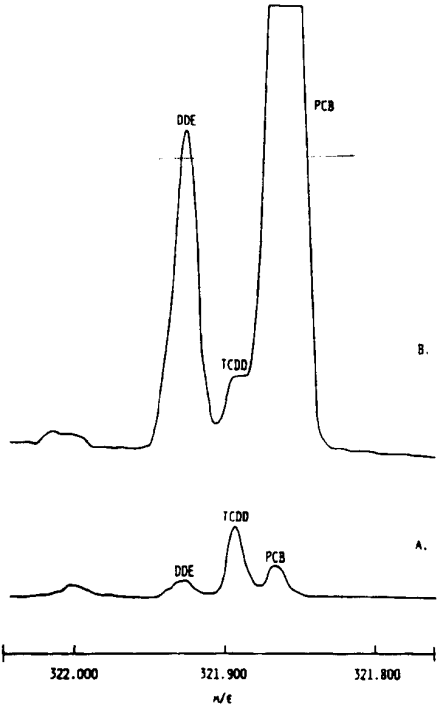


Figure 7-20. HREIMS Spectrum of Fish Sample After Sulfuric Acid and Alumina Column Chromatographic Cleanups

The CH_2Cl_2/hexane (20:80) fraction was analyzed after preelution with A - CCl_4/hexane (20:80) or B - CH_2Cl_2/hexane (1:99).

Reprinted, with permission, from Baughman and Meselson (1973).

and Enke, 1979). A triple quadrupole was used to analyze marine sediments (Bonner, 1983). By normal GC/EIMS analysis, PCBs were indistinguishable from the hydrocarbon background, while GC/MS/MS was able to detect (but not quantitate) tetra- through heptachlorobiphenyls with little interference. For each homolog, the first quadrupole filtered only the $C_{12}H_{n}{}^{35}Cl_{10-n}$ (i.e., the lowest ion in the molecular cluster) ion. The second quadrupole, the collision chamber, generated daughter ions, and the third quadrupole scanned the spectrum of the daughter ions ($M-Cl^{+}$, $M-HCl^{+}$, $M-Cl_2^{+}$, etc.). The major advantage cited was the ability to use the instrument to filter out interferences, reducing or eliminating the often lengthy sample preparation.

Voyksner et al. (1983) also found MS/MS useful in analyzing complex samples for PCBs; however, they noted that interferences caused the PCB quantitation to be erroneously high. In the first stage of the MS/MS analysis, $[M]^{+}$ ions (e.g., 358 for hexachlorobiphenyl) were passed by the magnetic sector. The electrostatic analyzer was then scanned to observe the loss of one and two chlorines. Samples were introduced by direct probe. The values by MS/MS were 2 to 10 times larger than the GC/HREIMS values. The results obtained by direct probe HREIMS on the blood samples were higher than those obtained by GC/HREIMS. These results suggest that the direct probe HREIMS and MS/MS techniques are detecting more interferences, possibly due to aliphatics (cholesterol, etc.) in blood and fat (large $[M-CH_3]$ present) or from higher PCB homologs. The GC/HREIMS was presumed to be the more accurate method since it gave lower quantitative results, which indicated less influence from the matrix. The accuracy of the analyses could not be checked since the true levels in the samples were not known a priori. The advantages of speed and less sample preparation were, in Voyksner's opinion, outweighed by the fact that the results were consistently and unpredictably high and did not agree with other techniques. They further noted that GC introduction reduces the probability of encountering interferences compared to direct probe techniques.

4. Flame ionization detection: The flame ionization detector (FID) measures the change in electrical conductivity of a flame which is proportional to the number of charged particles in the flame. The GC column effluent enters the base of a hydrogen/air microburner and is burned. An electrode at the base and one at the top measure the current. FID is the most commonly used GC detector because of its sensitivity and universality. Although some investigators have used FID for determination of PCBs in samples, it has generally been used only for calibration of response factors, to check purity of standards, or other method development work.

MONS 005460

FID has been used for determination of PCBs in environmental samples (Mizutani and Matsumoto, 1972; Modi et al., 1976; Lao et al., 1976; Onuska and Comba, 1980). Biros (1971) split the GC effluent to FID for quantitation and EIMS for identification. Cook et al. (1978) and Zimmerli (1974) used FID to detect biphenyl following dehydrochlorination of PCBs; a technique termed carbon skeleton chromatography.

Most of the FID applications have been in establishing response factors, characterizing Aroclors, or other method development areas (Webb and McCall, 1972; Albro and Fishbein, 1972a; Ogawa et al., 1973; Dexter and Pavlou, 1976; Boe and Egaas, 1979; Pavlou et al., 1980; Albro and Parker, 1980; Albro et al., 1981; Stalling et al., 1982). An example of the use of FID is presented in Table 7-V, where the molar responses of FID and ECD were compared (Hutzinger et al., 1974a; Safe, 1976).

FID is not selective enough for general application to PCB problems.

5. Photoionization: The photoionization detector (PID) uses a high intensity UV source to ionize molecules in the GC effluent. The ions are then detected at an electrode. The energy of the UV source (measured in electron volts) determines the selectivity of the PID.

GC/PID was studied for possible application as a portable PCB monitor (Bostick et al., 1983; Denton et al., 1981). PID was found to be about 40 times more sensitive than FID. However, using the standard 10.2 eV lamp, the PID was not selective for PCBs in hydrocarbon matrices. Better selectivity was obtained with an experimental 8.3 eV lamp. The lack of selectivity and problems with portability made the technique impractical. Therefore, the approach was not pursued further.

6. Thermal conductivity (TCD): Hirwe et al. (1974) used TCD to characterize Aroclor mixtures. This application is similar to many of the FID applications. GC/TCD was used to determine PCBs in ethylene glycol impingers used to collect the gaseous effluent from a bench-scale plasma arc destruction test (Barton and Arsenault, 1982). A 10 µg/10 µL detection limit for Aroclor 1254 was reported, which was adequate to demonstrate > 99% destruction efficiency.

Since TCD is neither selective nor sensitive, it is not generally considered a detector of choice for PCB analysis.

D. Perchlorination

Perchlorination methods are based on the exhaustive chlorination of the biphenyl ring of the PCB congeners. The major disadvantage of the perchlorination reactions is that biphenyl can also be perchlorinated. Thus, the presence of biphenyl can lead to erroneously high levels of quantitation. Quantitative analysis is typically accomplished by GC/ECD (Figure 7-21) although GC/MS identification has been used in some instances. Perchlorination reactions are reportedly troublesome because of contamination of reagents with decachlorobiphenyl or brominated compounds (Trotter and Young, 1975).

Perchlorination reaction methods were first studied using antimony pentachloride (Berg et al., 1972; Masumoto, 1972; Armour, 1973) and thionyl chloride in the presence of aluminum chloride (Nose, 1972). Armour (1973) reported greater than 90% recovery of PCBs by perchlorination and found the technique comparable to PGC/ECD comparison with Aroclor standards. Nose (1972) reported approximately 100% conversion of tri-, tetra-, and hexachlorobiphenyls to decachlorobiphenyl with the thionyl chloride system. Antimony pentachloride is apparently the most frequently used reagent. Hutzinger et al. (1973) studied trichlorosulfur tetrachloroaluminate to quantitatively convert Aroclor 1254 to decachlorobiphenyl. A rapid perchlorination technique, which utilizes an iron catalyst, has also been reported (Steinwandter and Bruene, 1982; Steinwandter, 1984). Complete perchlorination was reported in 10 min after addition of 10 mg iron powder and 0.2 mL $SbCl_5$ and heating to 205°C.

One of the major disadvantages of perchlorination arises from blank problems (Trotter and Young, 1975). This has resulted in the need to carefully characterize perchlorination reagents prior to reaction (Huckins et al., 1974). The other major disadvantage of perchlorination is the conversion of biphenyl to decachlorobiphenyl. Chlorine-37 labeled perchlorination reagents have been studied as a means to clarify this problem and at the same time distinguish the contribution of various PCB homologs to the final decachlorobiphenyl by computer assisted isotope dilution interpretation (Burkhard and Armstrong, 1981). This technique, although unique in approach, requires optimum reaction and MS conditions for successful analysis. A recent study claimed that the perchlorination yield is constant regardless of the degree of chlorination of the starting material and that a constant factor (0.9X) could be used to convert the decachlorobiphenyl mass back to the original commercial mixture (Takamiya, 1983). This method was reported to be an accurate

MONS 005462

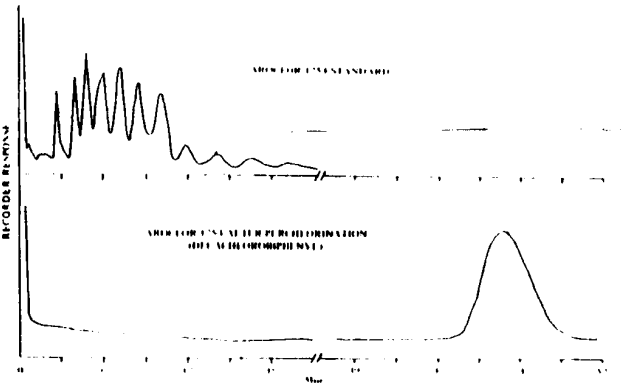


Figure 7-21. PGC/ECD Chromatograms of Aroclor 1254 Before (Top) and After Perchlorination (Bottom)

The sample was chromatographed on a 6 ft x 4 mm glass column containing 4% SE-30 on acid-washed Chromosorb W 60-80 mesh at 260°C with a nitrogen carrier gas at 60 mL/min.

Reprinted, with permission, from Hutzinger et al. (1974a); copyright 1974 by CRC Press, Inc., Boca Raton, Florida.

and rapid screen for PCBs. Perchlorination has been used successfully for numerous studies in recent years (Leoni et al., 1976a; Vannucchi et al., 1976; Crist and Moseman, 1977; Haile and Baladi, 1977; Margeson, 1977; Mes et al., 1977; Brinkman et al., 1978; Stratton et al., 1978a,b, 1979; Kohli et al., 1979a; Mes and Davies, 1979; Robbins and Willhite, 1979; Albro et al., 1979; Trevisani, 1980; Sherma, 1981).

E. Carbon Skeleton Chromatography

Carbon skeleton chromatography is based on the dechlorination of PCBs to biphenyl. Catalysts for the dechlorination are typically platinum or palladium. The disadvantage of carbon skeleton chromatography is that background levels of biphenyl in the sample extract will yield erroneously high concentrations of total PCBs as noted for perchlorination. Also, since the product of dechlorination is biphenyl, mass spectrometry must be used to reliably identify the compound, especially in extracts from complex matrices.

Quantitative carbon skeleton chromatography by catalytic decomposition of the PCBs over platinum or palladium to biphenyl has been discussed in three articles (Berg et al., 1972; Zimmerli, 1974; Cooke et al., 1978). Zimmerli (1974) and Cooke et al. (1978) studied conversion of PCBs as well as halogenated terphenyls, napthalenes, dioxins, furans, and DDT. Effective catalysts were found to be effective as 3% palladium at 305°C and 5% platinum at 180°C. Reaction products for the various compounds were identified by GC/MS.

III. THIN-LAYER CHROMATOGRAPHY

Thin-layer chromatography employs a liquid as the mobile phase and a thin layer (e.g., 100-250 μm) of solid adsorbent as the solid phase. The thin layer is generally adhered to a glass plate for mechanical stability. The TLC plate is spotted with the mixture solution near one end. The plate is then placed vertically, spot down, in a developing tank containing a small amount of the mobile phase in the bottom. The mobile phase climbs the plate by capillary action and draws components of the mixture upward. Since the components interact with the mobile phase and adsorbent differently, they migrate at different rates, thereby effecting the separation. The different components of the mixture are subsequently detected as spots either visually or with an optical scanner. Occasionally derivatizing reagents are used to enhance visualization. Compounds are identified by comparison of the height they climb the plate (R_f) with the R_f of authentic standards, preferably run on the same plate. Quantitation is generally only approximate and is done by

MONS 005464

comparison of the intensity of the color with that of a standard. TLC is discussed in more detail in most analytical chemistry texts and many monographs. One example is Stahl (1969).

In addition to its use as a cleanup technique (Chapter 6), TLC has been used as a determination technique. TLC was used extensively in early work (latter 1960s, early 1970s) because HPLC was not readily available and the GC techniques were not well-developed. Most of the early TLC reports were normal phase (silica gel) and included elaborate cleanup steps to remove interferents (e.g., oxidation of DDE to a benzophenone derivative). In the mid-1970s when packed column gas-liquid chromatography/electron capture detection (PGC/ECD) became the method of choice, emphasis on TLC methods dwindled. Several articles have been published which take advantage of modern TLC techniques: high performance TLC, two-dimensional TLC, reverse phase TLC, and new detection methods. TLC has been shown to be an effective technique for determination of (Aroclor) PCBs in a wide variety of matrices. The advantages included its ease of use and the simplicity of the apparatus. The disadvantages include lack of resolution, moderate sensitivity, and low specificity.

A. Historical Perspective

TLC analysis of PCBs was reviewed by Fishbein (1972). TLC is included as an alternate technique for "semiquantitation" analysis of PCBs in human adipose tissue in EPA manuals (Watts, 1980; Sherma, 1981). It is also included in the Association of Official Analytical Chemists methods for confirmation of identity (AOAC, 1980a,b). TLC is mentioned by the Food and Drug Administration (1977) as a technique which they feel may also be useful. The TLC properties of commercial polychlorinated terphenyls have also been investigated (De Kok et al., 1982).

Since the publication of a TLC method for PCBs by Mulhern (1968) and Mulhern et al. (1971), several researchers have used a similar method for analysis of PCBs in food (Stijve and Cardinale, 1974), animal feeds (Westöö and Noren, 1970), food packaging (Zimmerli et al., 1973), bald eagles (Bagley et al., 1970), Aroclor mixtures (Willis and Addison, 1972), animal tissue (Collins et al., 1972; Koeniger et al., 1976; Bush and Lo, 1973; Hattula, 1974b; Mes et al., 1977), human adipose tissue (Price and Welch, 1972; Lucas et al., 1980), human milk (Savage et al., 1973a, 1973b; Mes and Davies, 1979), soil (Piechalak, 1984), and oil (Stahr, 1984). Many of these researchers employed TLC in conjunction with other techniques such as GC/ECD. Often, TLC has been used as a qualitative confirmation technique.

MONS 005465

Bruggeman et al. (1982) used reverse phase TLC (C_{18} bonded phase) to study the relationship between PCB retention and hydrophobicity (water solubility and octanol-water partition coefficients). Anomalous behavior was observed for ortho-substituted PCBs relative to other PCBs, chlorobenzenes, alkylbenzenes, and polynuclear aromatic hydrocarbons. The authors attributed the results to the non-planarity of the ortho-substituted PCBs, which apparently reduces the ability of the solute molecule to interact with the stationary phase.

Several developments have improved the technique. Circular TLC reportedly improves sensitivity by an order of magnitude with a PCB limit of detection of about 0.05 μg (Koch, 1979). Fused glass TLC has been reported as yielding longer plate life (Okumura et al., 1973). Proper selection of the solid phase and eluting solvent permit separation of Aroclor components into discrete bands, as shown in Figure 7-22 (Brinkman et al., 1976a). Reverse phase (Figure 7-22) gives better resolution, but normal phase is more convenient and less time-consuming. Reverse phase TLC has been reported to yield better separation of PCBs from interferences (DeVos and Peet, 1971; DeVos, 1972; Stalling and Huckins, 1973; Brinkman et al., 1976a). An impregnated silica gel plate has been reported (Bergman et al., 1976) which improves selectivity apparently on the basis of ion-pairing. The use of surfactant micellar solutions as the mobile phase is certainly novel and reportedly has potential for separation of chlorinated aromatics, including decachlorobiphenyl (Armstrong and Terrill, 1979). Improvements in detection have included an $AgNO_3$ spray followed by UV irradiation (DeVos and Peet, 1971; DeVos, 1972; Kawabata, 1974) and fluorescence (Kan et al., 1973; Ueta et al., 1974; Stahr, 1984). A two-dimensional TLC method was developed which barely separated the DDT analogs from PCBs, as shown in Figure 7-23 (Fehringer and Westfall, 1971).

This last reference points to one of the major problems with TLC determination of PCBs. Many common interferences (e.g., DDE in biological tissues) have similar elution characteristics and are not easily resolved. One common technique for removal of DDE prior to TLC is oxidation of the DDE to dichlorobenzophenone with chromium trioxide or other oxidant (Biros et al., 1972; Sharma, 1981; Watts, 1980; Collins et al., 1972). Thielemann (1976) reported separation of PCBs from DDE on paraffin-impregnated Kieselguhr 9 plates.

Quantitation can be improved with the use of a densitometer (Stahr, 1984). Reverse-phase TLC was performed on C_{18} plates with methanol/water (95:5) as the eluting solvent. A limit of detection of 10 ng was reported, with 5% repeatability in the linear quantitation range of 1-4 μg.

MONS 005466

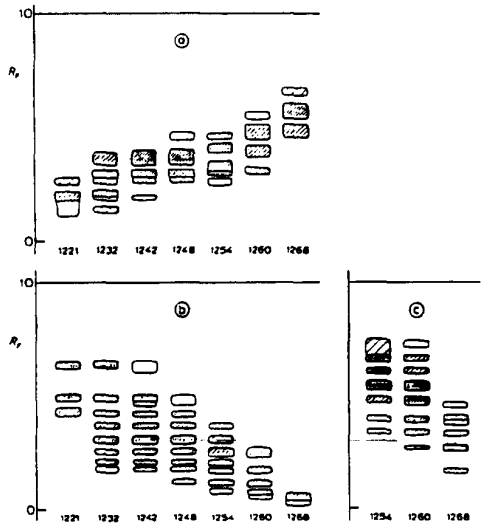


Figure 7-22. TLC of Aroclors 1221 Through 1268 in Three Systems

(a) Silica gel/n-hexane; (b) Kieselguhr impregnated with paraffin oil/acetonitrile-methanol-water (8:9:3); (c) Kieselguhr impregnated with paraffin oil/acetonitrile-methanol-acetone-water (20:20:9:1)

Reprinted, with permission, from Brinkman et al. (1976a); copyright 1976 by Elsevier Science Publishers, B.V.

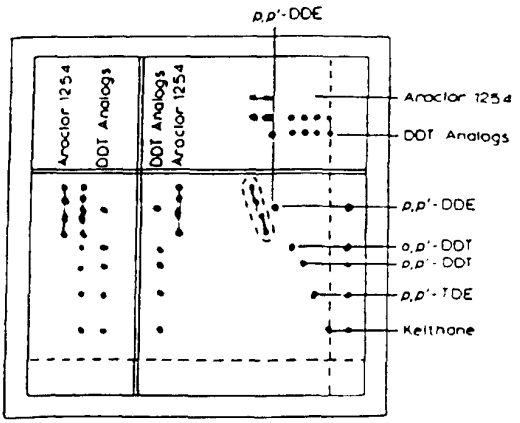


Figure 7-23. Two Dimensional TLC of Aroclor 1254 and DDT Analogs on a Silver Nitrate-Impregnated Silica Gel Plate

The sample was spotted at the intersection of the two dashed lines and several standards along the top third of the vertical dashed line. The plate was then developed (from right to left in this figure) with n-heptane until the solvent front had reached 10 cm, as denoted by the double vertical line. The plate was then turned 90° to the orientation shown, additional standards spotted along the bottom dashed line, and the plate developed with acetone/n-heptane (2:98) to the horizontal double solid line. The Aroclor 1254 from the sample is within the dashed oval. The DDT analogs from the sample are in a diagonal line to the right and below the Aroclor 1254.

Reprinted, with permission, from Fehringer and Westfall (1971); copyright 1971 by Elsevier Science Publishers, B.V.

MONS 005468

B. Comparison to Other Techniques

Two studies (Bush et al., 1975; Collins et al., 1972) compared TLC and GC/ECD. In both studies the PCB values obtained were comparable, although in the study by Bush et al., the TLC results were generally lower than GC/ECD.

Lucas et al. (1980) reported a statistical analysis of semiquantitative determinations of PCBs in human adipose tissue generated by the EPA's National Human Monitoring Program (Kutz and Strassman, 1976) during FY 1972 to 1976. Results were reported only as ranges (not determined, < 1, 1 to 3, and > 3 ppm) for 5,259 samples. The EPA TLC technique (Watts, 1980; Sherma, 1981) was used in this study through November 1974 and a GC/ECD technique involving a single PCB peak quantitation was used thereafter. A total of 3,802 TLC results and 1,457 PGC/ECD results were compared and found to be not significantly different.

Reverse-phase TLC compared favorably with GC/ECD for the analysis of PCBs in transformer oil in the 4-55 ppm range (Stahr, 1984). The difference in the results of the two methods averaged ± 20%.

C. Current and Potential Applications

TLC lacks the congener resolution of GC, so it is not applicable to detailed analysis for individual PCBs. However, the low setup and per-analysis costs (no capital equipment) and rapid analysis make it ideal for screening samples where a simple "yes" or "no" answer for total PCBs is sufficient. Examples could include screening of industrial products for by-product PCBs and screening of soil or hazardous waste samples for PCB contamination. In samples where PCBs are ubiquitous, such as human adipose, TLC may be of less utility, since more detailed qualitative and quantitative information is generally sought. However, it should be noted that the LODs quoted for TLC are not as sensitive as those for other techniques, so it will be less applicable where trace level analysis is required.

IV. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

High performance liquid chromatography, also called high pressure or high speed liquid chromatography (HPLC), is essentially an instrumental version of the common open column chromatographic techniques used for sample cleanup (see Chapter 6). The instrumentation consists of a pumping system, injector, separation column, and a detector. All components are linked by tubing, so the separation and detection

MONS 005469

are done in one continuous operation. The separation may be based on liquid-solid partitioning (e.g., hexane on silica gel), liquid-liquid partitioning (e.g., bonded alkane columns such as C_{18}), size exclusion (gel permeation), or chemical functionality interactions (e.g., amine columns). Liquid-solid and liquid-liquid chromatography are collectively known as adsorption chromatography, since the interaction with the stationary phase occurs at the surface. Separation of analytes by adsorption chromatography may be effected using either of two modes of operation controlled by the nature of the mobile phase: normal or reverse phase. In normal phase adsorption chromatography, the mobile phase or solvent (e.g., hexane, methylene chloride, benzene) is less polar than the stationary phase (e.g., silica or alumina). Reverse phase chromatography utilizes a more polar solvent (e.g., water, acetonitrile, methanol) relative to the stationary phase (e.g., chemically bonded C_8 or C_{18}- silica gel).

Common detectors include ultraviolet (not very selective), fluorescence (somewhat selective), and electrochemical (selective, depending on compound classes). Several other detectors are employed less commonly, including mass spectrometry. Compounds are identified by their retention time (RT) when compared to that of a standard and by detection with a selective detector. The intensity (height or area) of the peak is used for quentitation by comparison to the response obtained from a standard.

HPLC is discussed in detail in most analytical chemistry texts and in many monographs. Two examples are Yost et al. (1980) and Snyder and Kirkland (1979).

A. Literature Citations

High performance liquid chromatography (HPLC), with ultraviolet and other detectors, has been reported in the characterization of commercial PCBs, as a cleanup technique, and as a determination technique. Despite its general applicability in analytical chemistry, HPLC has not been as popular as gas chromatography for PCB analysis. The major reason is that GC detectors, especially those selective toward halogens, exhibit much lower limits of detection.

Since HPLC is basically an instrumental version of the column chromatographic cleanup techniques, described in Chapter 6, it is applicable both as a cleanup and a determination technique. Some researchers have exploited this and combined cleanup and determination into one step with HPLC (Hanai and Walton, 1977; Van Vliet et al., 1979).

MONS 005470

Krull (1977) discussed HPLC and its utility as a cleanup technique, especially for removing similar chlorinated hydrocarbons such as the DDT family. Lawrence and Turton (1978) reviewed the HPLC data on pesticides and PCBs. Their review provides a useful tabulation of HPLC chromatographic systems (column packings, dimensions, mobile phases, detectors) and elution volumes for 166 pesticides and PCBs.

Although HPLC has been used for measurement of PCBs from a variety of matrices discussed below, this technique has not been used with any of the standard procedures identified in Chapter 3.

1. Characterization of commercial mixtures. Several authors (Brinkman et al., 1976a,b; Veith and Austin, 1976; Albro and Parker, 1979; Brinkman and De Vries, 1979) have used HPLC in characterization of commercial PCB products or establishing the chemical behavior of PCBs. Krupcik et al. (1977) used HPLC/UV and HRGC/FID to characterize fractions obtained by vacuum distillation of an Aroclor 1242 mixture. The HPLC separation was performed on silica gel with n-pentane as the elution solvent. Figure 7-24 illustrates the chromatography and also the effect of different UV wavelengths on sensitivity. About 20 congeners were identified in this and other fractions by comparison of retention times to those of authentic standards. Brinkman et al. (1976a,b) used a similar system to characterize Aroclors and listed retention times and UV data for 51 congeners.

Kaminsky and Fasco (1978) used reverse phase (RP) HPLC/UV to characterize Aroclor 1221, 1016, and 1254. The retention times on a uBondapak C_{18} column with a water/acetonitrile gradient and relative response at 254 nm were reported for 48 congeners. Figure 7-25 illustrates the separation power of RP HPLC. Clearly the reverse phase is much better at resolving PCBs than normal phase (Figure 7-24). Issaq et al. (1984) also used a C_{18} bonded column to obtain an RP HPLC/UV separation of Aroclor 1254 into 15 peaks.

Brinkman and De Vries (1979) used silica gel and alumina columns with n-hexane as the eluent to characterize a variety of haloaromatics, including PCBs, relating chromatographic behavior to structure. Planarity and linearity of the molecule were found to affect adsorption on alumina, but not silica gel. The presence of substituents ortho to each other or the central C-C bond promotes retention on both adsorbents. Veith and Austin (1976) found that the HPLC retention time on a C_{18} column with methanol/water eluent was proportional to the octanol/water partition coefficient.

MONS 005471

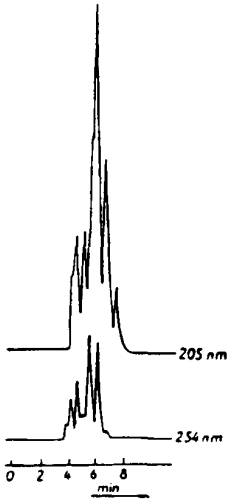


Figure 7-24. HPLC Chromatogram of PCBs with UV Detection at Two Wavelengths (205 nm and 254 nm)

The sample was the last fraction (No. 70) from a distillation of Aroclor 1242. A 25 cm x 4.7 mm ID glass column was packed with 5 µm spherical silica gel. The solvent was n-pentane at 40 mL/min.

Reprinted, with permission, from Krupcik et al. (1977), copyright 1977 by Elsevier Science Publishers B.V.

MONS 005472

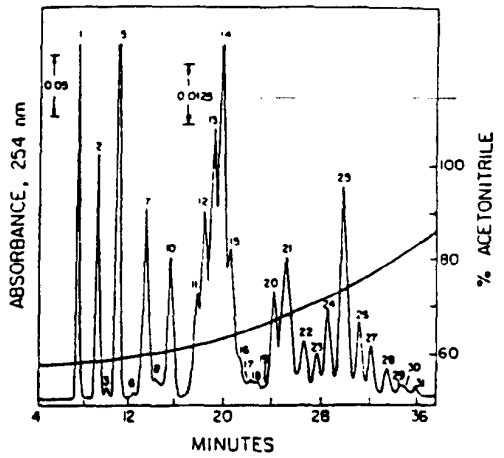


Figure 7-25. Reverse Phase HPLC/UV Separation of Aroclors 1221, 1016, and 1254 (1:1:1, w/w/w) in Tetrahydrofuran on a μBondapak C_{18} Column Monitored at 254 nm

Initial conditions, 40% water-acetonitrile (9:1) and 60% water-acetonitrile (1:9); final conditions, 100% water-acetonitrile (1:9); gradient time, 40 min; flow rate, 2 mL/min; injection volume, 10 μL; amount injected, 50 μg total.

Reprinted, with permission, from Kaminsky and Fasco (1978); copyright 1978 by Elsevier Science Publishers B.V.

Recently, high resolution HPLC using capillary or micropacked columns has revolutionized the resolving power of HPLC. The pioneers in this field, Ishii and Takeuchi (1983) have illustrated the high resolution RP HPLC of PCBs, as shown in Figure 7-26. This is by far the highest resolution HPLC chromatogram of those in the literature reviewed. The high resolution, however, is achieved only at a cost in time. The analysis in Figure 7-26 took about 8 hr to elute all of the PCBs.

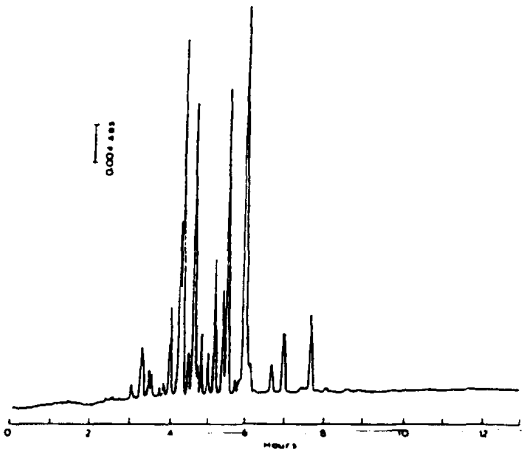


Figure 7-26. High Resolution Reversed-Phase HPLC/UV Chromatogram of PCB Mixture Containing 48% Chlorine

The column was a 1.5 m x 0.26 mm ID fused silica capillary packed with 5 µm silica ODS SC-01. Acetonitrile/water (85:15, v/v) was pumped at 0.6 µL/min. The sample was 5% PCB in acetonitrile; 0.2 µL was injected. The UV detector wavelength was 254 nm.

Reprinted, with permission, from Ishii and Takeuchi (1983); copyright 1983 by Elsevier Science Publishers B.V.

De Kok et al (1982b) used HPLC to characterize commercial polychlorinated terphenyls (PCTs). Hernandez and Walton (1982) reported the retention volumes of polychlorinated biphenylols by RP HPLC/UV using a C_{18} column and methanol/water as the eluent.

HPLC has been used as a cleanup technique prior to gas chromatographic determination (Aitzetmüller, 1975; Dark and Crossman, 1973; Rohleder et al., 1976; Krupcik et al., 1977; Dolphin and Willmott, 1978). More recently it has been

used on a preparative scale to clean up waste and transformer oils prior to HRGC/ECD determination (Anonymous, 1982a; Chesler et al., 1981). In the course of these investigations, the researchers noted that the HRGC/ECD limit of detection was about 100 times lower than the HPLC/UV limit of detection.

2. Trace analysis: As HPLC became increasingly popular in the early 1970s, Eisenbeiss and Sieper (1973) performed preliminary investigations of the use of HPLC for pesticide (and PCB) residue analysis. They concluded that HPLC can be regarded as "an alternative or supplementary method to conventional methods such as gas chromatography," and also would be applicable as a confirmatory analysis. Electron capture detection of HPLC effluents has been described (Willmott and Dolphin, 1974) for the analysis of PCBs. The LOD of HPLC/ECD was reported to be about 10 times higher than for GC/ECD in a study of decachlorobiphenyl following perchlorination (Brinkman et al., 1978).

Room temperature phosphorescence in liquid solutions (RTPL) was used as a RP HPLC detector for PCBs (*Donkerbroek et al.*, 1982, 1983). Detection limits were reported for nine congeners ranging from 0.21-5.6 ng. Ortho-substituted PCBs are poorly detected, so the technique may be useful for qualitative identification of compounds when used in conjunction with UV detection. Stalling et al. (1980b) gave a preliminary description of an HPLC/MS (presumably the chemical ionization MS mode) system for rapid screening for PCBs.

Hanai and Walton (1977) developed an HPLC/UV method for determining PCBs in water. No LOD was determined, but good recoveries were obtained for 250 µg/L of Aroclor 1232 spiked into distilled water. The water was pumped directly through the HPLC system and the PCBs subsequently eluted by gradient elution. A similar application (Van Vliet et al., 1979) used an HPLC precolumn to concentrate PCBs from water and then elute them onto the analytical column for separation and determination. The example presented was for 20 µg/16.5 mL of water or 1,200 µg/L.

Belliardo et al. (1979) developed a RP HPLC/UV procedure for PCBs in oil and compared it with a PGC/ECD method. The HPLC method was judged suitable to approximate, but not quantitate, the PCB content. Compared with GC/ECD methods, the RP HPLC/UV was termed rapid, convenient, and applicable to routine analysis. Klimisch and Ingebrigtson (1980) reported a RP HPLC/UV method for determination of PCBs in polydimethylsiloxane (silicone) fluids. PCBs were extracted with

acetonitrile and then injected on a C_{18} column with acetonitrile/water eluent. A method detection limit (MDL) of 100 ppb and repeatability of less than ± 4% at the 0.1-3% level were reported. A PGC/ECD method had an MDL of 25 ppb and was judged to be preferable for low level analyses and for routine screening where a single dilution is the only preparation required. For PCB levels over 1%, HPLC was recommended for quantitative work since the serial dilutions required to get within the PGC/ECD linearity are more time-consuming.

Seidl and Ballschmiter (1979) used silica gel HPLC/UV to detect biphenyl after dehydrochlorination of PCBs in soil and olive oil. A detection limit of 100 ng absolute was reported, which translates to about 0.05-0.5 µg/g depending on sample size and other factors.

A simple, rapid method for quantitation of PCBs removes interferences by the DDT family by oxidation to dichlorobenzophenone and then determination by normal phase HPLC/UV (Chiosi et al., 1982). The PCB detection limit (as Aroclor 1242) was reported as 2.57 ng. The precision of the HPLC step was in the range of ± 2%. The method was applied to snails and tuna with no observed interferences.

B. Current and Potential Applications

HPLC has found little use in analysis for trace PCBs in environmental samples. With the shift toward analysis of commercial products and assessment of transformer and other fluids for PCB contamination (often at the high ppm to percent levels), HPLC should be more useful. The poor inherent sensitivity of most HPLC detectors is partially compensated for by the large injection volumes (often more than 100 µL). Another drawback of HPLC is that the specific detectors available for GC (e.g., ECD and MS) are not as widely applied to HPLC. Thus, most applications have utilized the UV detection, which is not very selective. Perhaps the greatest potential advantage of HPLC is when it can be used as a one-step cleanup/determination technique. This could be easily automated to provide PCB analysis with virtually no labor costs. Sample matrices which are much different from PCBs, such as water, would be particularly amenable to this approach.

V. NONCHROMATOGRAPHIC METHODS

This section presents a variety of miscellaneous methods reported for the determination of PCBs. Some of the MS techniques (notably HREIMS and MS/MS) are used either as GC detectors, or as stand-alone techniques with direct probe

MONS 005476

sample introduction. Both applications were discussed in the respective subsections above. While many of the nonchromatographic techniques are of great use in characterizing PCBs, few of them have the required specificity and sensitivity for trace determinations.

A. Nuclear Magnetic Resonance (NMR) Spectrometry

Wilson and Anderson (1973) used both ^{13}C and ^{1}H nuclear magentic resonance (NMR) to characterize the chemistry of selected PCBs. No attempt at analysis of real samples was made. Levy and Hewitt (1977) reported the analysis of PCB mixtures by ^{13}C NMR, but noted that the technique was not as useful for higher homologs. Hutzinger et al. (1974a) included a discussion of the NMR characteristics of PCBs in their review book. Synthetic congeners have been characterized by proton NMR (Mullin et al., 1981, 1984).

B. Infrared (IR) Spectrometry

Hutzinger et al. (1974a) discussed the infrared (IR) spectral properties of PCBs. Webb and McCall (1972) used IR and other techniques to identify 24 PCB congeners in Aroclor 1221. The spectra of 14 pentachlorobiphenyls and two trichlorobiphenyls were studied in detail by Nyquist et al. (1983). Spectra were obtained on a Fourier transform infrared spectrometer (FTIR) using the diffuse reflectance technique. In addition to spectra, major peaks were assigned to the various bending and stretching modes and the group frequency contributions presented. The authors noted that this data base should be useful in the identification of other congeners.

Chen and Gardner (1983) used the higher sensitivity and data manipulation capabilities of FTIR to identify and quantitate the individual congeners in mixtures. The method was applied to fractions collected from a gas chromatograph. Up to three components were accurately identified and quantitated. FTIR has been used as an on-line GC detector (Erickson, 1979) and could probably be applied to PCB analyses, where the concentrations are sufficient and the identity of individual congeners is needed. This technique would be especially applicable as a confirmatory technique.

FTIR has been studied as a field-usable instrumental technique for rapidly determining PCBs in transformer oil (Nordstrom, 1983; Nordstrom and McIntosh, 1981). For regulatory purposes (EPA, 1979d), transformer oils must be categorized as "clean" (< 50 ppm), "contaminated" (50-500 ppm), or "PCB-containing" (> 500 ppm). Transmittance spectra

are collected and the concentration determined by a least-squares fit of the absorbance to a standard curve. In order to clean up the sample sufficiently for reliable measurement in the 50-500 ppm concentration range, an automated dimethyl formamide extraction and concentration apparatus is attached to the FTIR spectrometer. The entire procedure can analyze a sample in 10 min with ± 10% accuracy in the 50-500 ppm range. The technique was judged impractical and further research discontinued (Hinganori, 1984).

A filter IR instrument has been studied for use as a portable field monitor (Denton et al., 1981; Bostick et al., 1983; Denton and Walker, 1983). The authors selected IR because of its ability to detect PCBs in the presence of mineral oil. In fact, mineral oil is the well-known Nujol used to mull solid samples in classic infrared spectroscopy. The authors found the 8.5 μm (1,180 cm^{-1}) and 9.2 μm (1,090 cm^{-1}) bands selective for Aroclor 1260 in the presence of mineral oil or trichlorobenzene (a common component of transformer askarels). The major limitation of the technique was the high limit of detection--500-1,000 μg/g. The authors also used IR to detect PCBs in soil. The PCBs were extracted from the soil matrix with a volatile solvent (e.g., acetonitrile) and then spotted onto the window of a multiple internal reflectance (MIR) cell. After the solvent had evaporated, the absorbance was measured. The authors were able to detect a "few dozen micrograms" of Aroclor 1260.

C. Radioimmunoassay

Albro and coworkers reported preliminary results in the development of a radioimmunoassay (RIA) method for PCBs (Albro et al., 1979; Kohli et al., 1979a; Luster et al., 1979, 1981). The evidence indicated the feasibility of employing radioimmunoassays for determining the Aroclor number and concentration in environmental samples (Luster et al., 1979). The assay required an antiserum for each isomer but was termed fairly specific.

A radioimmunoassay was developed capable of determining Aroclor 1260 in milk at levels of from 20 to 80 ppb and in blood from 2 to 16 ppb (Newsome and Shields, 1981). The values obtained by radioimmunoassay correlated well with those determined by gas-liquid chromatography but were up to 25% lower. Antiserum was produced in rabbits and was specific for 2,2',4,4',5,5'-hexachlorobiphenyl. It cross-reacted with congeners and isomers in Aroclor 1254 and 1260 to the extent that a 20% decrease in binding was observed with 0.1 ng of either mixture. The method required preliminary cleanup of the extract on alumina.

MONS 005478

D. Other Techniques

Interrupted-sweep voltametry has been applied to the identification of PCBs, yielding positive identifications (Farwell et al., 1975). Plasma chromatography has been reported to give characteristic qualitative data for PCBs (Karasek, 1971). One report utilized neutron activation analysis for the determination of PCBs in dosed rats (Manri et al., 1971). Low temperature luminescence has been proposed as a simplified method for the identification and quantitation of PCBs (EPA, 1972; Brownrigg and Hornig, 1974, 1976). The limit of detection was reported to be as low as 0.01 ppm.

VI. CONFIRMATION

Confirmatory techniques have been used frequently in PCB analysis. The term confirmation may be loosely defined as any operation performed to increase the confidence of the results beyond the primary analysis. Qualitative confirmation is much more often reported than quantitative confirmation. Confirmatory techniques involve variation of the same technique (PGC/ECD on two dissimilar columns), confirmation by a lesser technique (PGC/ECD with TLC confirmation), or confirmation by a more advanced technique (PGC/ECD with PGC/EIMS confirmation). A review on confirmatory tests presents a general overview of confirmation as it relates to pesticides (Lawrence, 1981).

A. Literature Citations

Hutzinger et al. (1974a) reviewed confirmation. While mass spectrometry was briefly mentioned, most of the discussion centered on perchlorination. Table 3-I lists all of the standard methods and notes the type of confirmation suggested. All of these confirmations are optional and qualitative.

As early as 1969, the need for confirmation of PCB findings was discussed (Reynolds, 1969). An exchange of comments following a presentation by Risebrough (1971) led to a proposal for confirmation, covering mass spectrometry, dechlorination, and perchlorination. Price and Welch (1972) are typical of many early investigators who backed up their PGC/ECD analysis with a TLC confirmation (see also the standard methods: AOAC, 1980a; FDA, 1977). Hannan et al. (1973) utilized a cumbersome ultraviolet irradiation method to confirm PGC/ECD results. A dual GC to heart-cut a chromatogram and separate the decomposition products from the first ECD has been proposed as a confirmation technique for pesticides

MONS 005479

and PCBs (Aue and Shubhender, 1978). A HPLC/room temperature phosphorescence system has been reported which not only provides a second detection in addition to UV, but also aids in identification of isomers, since ortho-substituted PCBs are not detected by the phosphorescence technique (Donkerbroek et al., 1982, 1983).

Mes and co-workers have utilized a variety of techniques to confirm the PCB concentration in the analysis of adipose and milk samples (Mes et al., 1977, 1980; Mes and Davies, 1979). The methods include two dissimilar GC columns, perchlorination, and GC/EIMS.

GC/EIMS was used by Biros et al. (1972) and Kutz and Strassman (1976) to confirm TLC results. GC/EIMS confirmation has also been reported (Haile and Baladi, 1977; Teichman et al., 1978; Musial et al., 1974; Lucas et al., 1980; Pastel et al., 1980; Rodriguez et al., 1980; Erickson et al., 1983e). HREIMS has been reported as a confirmatory technique (Safe et al., 1975; Safe, 1976; Musial et al., 1974). Kuehl et al. (1980b) used HRGC/NCIMS to qualitatively confirm their HRGC/EIMS PCB identifications in fish. Hass and Friesen (1979), placing particular emphasis on polychlorinated dibenzodioxins, reviewed the advanced mass spectrometric techniques for both high sensitivity and high reliability analysis: HREIMS and NCIMS.

B. Current and Potential Applications

The choice of a confirmation technique depends on (1) the information content from the primary technique, (2) the PCB and interferent concentrations, (3) the level of confidence needed, and (4) availability of instrumentation. Clearly, the confirmation technique must increase knowledge about the sample. Confirmation by GC/ECD after a successful analysis by GC/EIMS therefore makes little sense, while the reverse may often make sense. The analytical technique must be sufficiently sensitive for the level of PCBs in the sample. This frequently means that GC/EIMS cannot be used to confirm residue levels in trace environmental samples. The higher the level of interferences, the more selective the confirmation technique must be. Even with the high selectivity of MS, high levels of dissimilar compounds (e.g., an oil matrix) can totally obscure PCBs at the part-per-million level in a GC/EIMS confirmation. The level of analytical confidence required can often be a political or financial decision. In addition, it depends on the prior knowledge of the sample. Detection of PCBs at 10 μg/g in human adipose by GC/ECD would not normally require confirmation, since this is a typical level and they are ubiquitous (Lucas et al., 1982).

MONS 005480

On the other hand, confirmation would most certainly be required if an Aroclor-like pattern were observed in a GC/ECD chromatogram of a commercial product sample which should not be contaminated and had a negative assay for chlorine.

With ECD detection of either GC or HRGC, second-column confirmations are often appropriate. All of the more advanced MS techniques (NCIMS, HREIMS, MS/MS), with direct probe or preferably as GC sample introduction, are useful confirmation techniques.

Quantitative confirmation has rarely been noted in the literature. Confirmation of the quantitation is almost as important as the confirmation of the identity of the analyte. Not only can interferences mask or augment the peak identified as a PCB, but calibration by a second technique is often sufficiently different to minimize systematic bias. Quantitative confirmation can be viewed as a portion of a good QC program since it verifies the reported values.

VII. SCREENING

A. Screening for PCBs

Screening techniques sacrifice the confidence in the analysis for speed and/or simplicity of apparatus. Often a screening analysis provides only qualitative or semiquantitative information. Samples should be screened where immediate analysis is needed, such as during an incinerator trial burn to make sure that the PCBs are being destroyed, or where most of the samples should contain no PCBs above the detection limit of either the screening or primary analytical technique and may be efficiently eliminated by the screen.

1. Chromatographic screening: As discussed earlier, TLC, HPLC, and GC all have application for screening samples. In addition, the perchlorination and carbon skeleton chromatography techniques can serve for screening samples. Finally, abbreviated analytical procedures can be used to quickly screen samples. An example is a PGC/ECD analysis of fish tissue with a quick extraction/cleanup using miniature chromatographic columns (Erney, 1974a).

Another aspect of screening is simple range-finding. If there is a possibility of an extremely high concentration sample, such as in transformer oil samples or in hazardous waste samples, very dilute or very small volume injections can prevent a catastrophic overloading of the analytical system.

2. Total organic halide: An increasingly popular screening technique is total organic halide (TOX) or total organic chlorine (TOCl or RCl). TOCl values are required for incinerator testing for PCBs (EPA, 1979d). While TOX is one of the least selective techniques since it detects "all" organic halides, it is quite sensitive and can be useful when there are low levels of other chlorinated compounds relative to the PCBs. TOX have been monitored using a very short column (2.5 cm long) PGC/HECD method, shown in Figure 7-27 (Stanley et al., 1982; Haile et al., 1983a; Nulton et al., 1984), or extraction/GC/EIMS method (Beard and Schaum, 1978). Both employ a Soxhlet extraction of the XAD-2 resin from the modified Method 5 train (EPA, 1977; Haile and Baladi, 1977). The TOX values for stack gas and fly ash from a power plant and an incinerator obtained by HRGC/EIMS averaged about 14% higher than the values obtained by the short column GC/HECD technique (Nulton et al., 1984). It should be noted that these methods do not in fact measure total chlorinated organics, but rather semivolatile, gas chromatographable, chlorinated organics. The GC/HECD TOX measurement was applied to background air particulate, stack gas particulate, and ash samples from a municipal incinerator and a co-fired power plant (Haile et al., 1983a,b; Nulton et al., 1984). Values ranged from 0.9 to 46,000 ng/g. In water samples they ranged from 100 to 1,000 ng/L.

Two techniques for total chlorinated organics involve concentration of the organic halides on a sorbent trap, and reduction to HCl at 950°C. In one system the HCl gas is detected by electrolytic conductivity (Model 610 Total Organic Halogen Analyzer, O.I. Corporation, College Station, Texas). In the other system, the HCl gas is detected by microcoulometry (Model DX-20 Total Organic Halide Analyzer, Dohrmann Xertex, Santa Clara, California). Both techniques have the advantage over previously used methods in that volatile, semivolatile, and non-volatile organic chlorides can be detected. The extraction/GC methods detect only the semivolatile organic chlorides. The electrolytic conductivity technique was characterized by Bernard and Russell (1983). As shown in Figure 7-28, the analyses with the electrolytic conductivity technique are quite rapid and reproducible. The response is linear with concentration. The coefficients of variation at both PCB levels were less than 2% and about 2.6% for the blank. This technique features an optional dedicated data system. The microcoulometric technique was characterized by Berger (1984).

3. Chemical determination of total chloride: The classic organic reduction of organochlorine to free chloride ion with metallic sodium has been used to develop screening techniques for PCBs. The free chloride ion can be detected by a chloride ion-specific electrode or colorimetrically.

MONS 005482

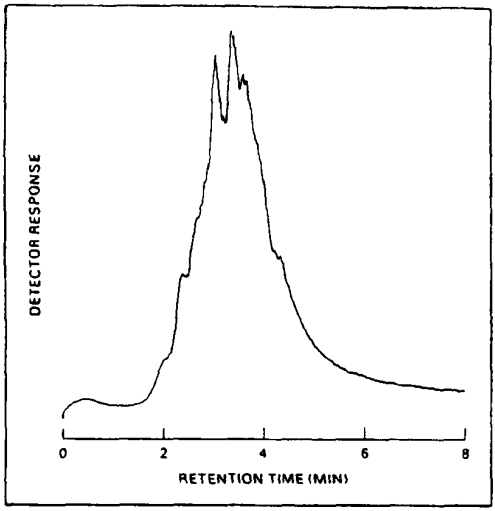


Figure 7-27. Total Organic Halide (TOX) Analysis Using a Short Column PGC/HECD

The sample (5-20 µL) is injected onto a 1-m column containing 2.5 cm of 10% SP-2100 on Ultrabond packing with a helium flow rate of 60 mL/min. The column temperature was 60°C for 3 min, then programmed at 40°C/min to 230°C. The total area under the chromatogram is integrated and compared to the response for monochlorobiphenyl.

Reprinted, with permission, from Nulton et al. (1984); copyright 1984 by American Chemical Society.

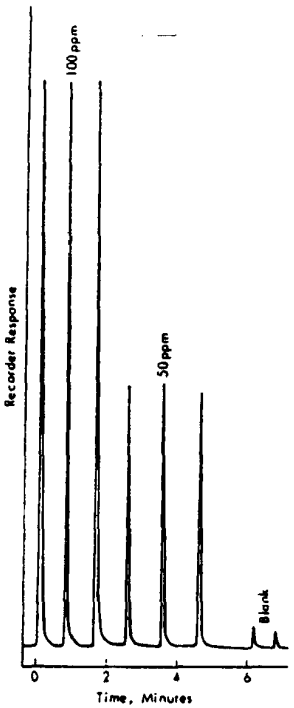


Figure 7-28. TOCl Measurements of Aroclor 1248 Using Electrolytic Conductivity

Eight sample injections (5 μL) are shown.

Reprinted, with permission, from Bernard and Russell (1983).

Using the colorimetric detection principle, an inexpensive, rapid, self-contained kit has been developed for field-testing transformer oil samples (Fisher et al., 1984). The object is to determine whether the oil is "contaminated" (50-500 ppm) with PCBs and therefore requires special handling and disposal in the United States (EPA, 1979d). The kit (Chlor-N-Oil®), developed for the Electric Power Research Institute and marketed by Dexsil Corporation, is based on the quantitative conversion of the chlorine atoms on PCBs to chloride ions which in turn are extracted into an aqueous solution and measured colorimetrically. Chlorine is converted to chloride ions by sodium salts formed by naphthalene together with the dimethyl ether of diethylene glycol ("diglyme") as stabilizing ligand. The chloride ions are extracted into an aqueous buffer solution and reacted with a carefully controlled amount of dissolved mercuric nitrate. Diphenylcarbazone is added. Reaction of any excess mercuric ion with the diphenylcarbazone will form a vivid blue complex. If the chloride ion content exceeds that taken up by the available mercuric ion, the complex is not formed and the reaction mixture remains colorless to pale yellow. The reactions are carried out in soft plastic test tubes containing premeasured reagents in breakable glass ampules. Proper control of the sample size and of the quantity of mercuric nitrate allows the blue-colorless response level in the mineral transformer oil to be set at levels from a few ppm to several thousand ppm.

The lowest ratio of chlorine to PCB found in an askarel is 0.42 (Aroclor 1242). Therefore, an oil sample containing less than 21 ppm chlorine cannot contain more than 50 ppm PCB. A color response level set at 21 ppm chlorine for the kit should assure that no contaminated oil (i.e., 50-500 ppm) gives blue responses. Samples giving colorless responses can be checked by gas chromatography to determine whether they actually contain more than 50 ppm PCB. It has been estimated that the use of a colorimetric test kit can reduce the number of GC/ECD analyses required to determine whether or not a transformer oil is contaminated by 50-60% (Walsh, 1983). This would result in a significant reduction in cost of a monitoring program.

The test was validated by 40 utilities with a total of 824 samples tested. Using a 50-ppm regulator cutoff, 27% of the samples yielded false positives and only 2.3% were false negatives when compared to GC/ECD results, which were assumed to be accurate (Tahiliani, 1984). Minor changes in the kit and instructions promise to improve the accuracy of the test.

4. X-Ray fluorescence: X-ray fluorescence (XRF) has been studied as a PCB screening technique. When an atom like chlorine is bombarded with x-rays, electrons are dislodged from inner orbitals, creating "holes." These holes are rapidly filled by electrons from outer orbitals. The energy difference between an inner and outer orbital results in the emission of a secondary x-ray when a hole is filled. This secondary x-ray is measured by XRF. McQuade (1982) showed that XRF could accurately detect and quantitate chlorine down to a concentration equivalent to about 10 ppm of an Aroclor. The technique cannot differentiate between PCBs and other chlorine species (including inorganic chlorides). The total analysis time is about 5 min/ sample and the instrument is small enough (40 kg) for field use. The portable analyzer was used to test transformer oils at electrical substations (Schwalb and Marquez, 1982). The main objective was to categorize the oils as "clean" (< 50 ppm), "contaminated" (50-500 ppm), or "PCB-containing" (> 500 ppm) for EPA regulatory purposes (EPA, 1979d). The XRF results compared well with those obtained off-site by GC, although there were occasional false negatives.

8. Screening for Interferences

Samples may also be screened to assess the effectiveness of cleanup before submission to a final determination technique such as GC/EIMS. The objective is to assess the overall level of chromatographable compounds, not to specifically detect PCBs. Background screening for samples which will be analyzed by a gas chromatographic technique is best accomplished using GC/flame ionization detection (FID). FID is a "universal" detector and thus provides a relatively uniform response to all eluting components of the mixture.

Interference screening is especially applicable for unfamiliar samples, when major interferences may contaminate the analytical instrumentation. Indications for screening include: highly colored samples or extracts; evidence of cleanup technique overloading; precipitation on solvent evaporation; sample history (e.g., solid hazardous waste of unknown composition); and matrices which have similar physical properties to PCBs (e.g., oils).

VIII. SUMMARY

As discussed in this chapter, a wide variety of instrumental techniques are available to determine the PCB content of a sample. The choice of the technique depends on a number of factors, as presented in "Criteria for Choice of Techniques" at the beginning of this chapter. For routine

analysis, GC/ECD, GC/HECD, or GC/EIMS would probably be most appropriate. The selection of PGC or HRGC depends on the need for isomer specificity and, to some extent, individual preference. Several screening techniques may be applicable if the probability of PCB occurrence is low and the matrix composition permits their use. TLC, TOX, GC/FID, and GC/ECD are all candidate screening techniques under the right circumstances. Confirmation generally involves either reanalysis on a second column using the same detector, or stepping up in instrumental sophistication to improve the qualitative reliability of the analysis. Thus, EIMS, HREIMS, MS/MS, and NCIMS are often considered confirmatory techniques.

MONS 005487

8

DATA REDUCTION

Data reduction is a key element in sample analysis. In this step, the analyst converts the instrumental output into information for the user. Specifically, any PCBs present in the samples are identified and quantitated. Depending on the detection and output system, data may be presented to the analyst as analog chromatograms, numerical tabulations, MS extracted ion current plots, etc. Computers and integrators can reduce the analyst's work in data acquisition and reduction; however, the judgement of a qualified analyst is critical to reliable data reduction.

The importance of data reduction cannot be overemphasized, especially with PCBs. In a collaborative study, Delfino and Easty (1979) reported an RSD of ± 15.6% for direct injection of an Aroclor 1242. They noted that the PGC/ECD analysis appeared to provide the principal source of variation in the overall determination. Similarly, Erickson et al. (1983c) noted that data reduction constituted about one-third of the error associated with a HRGC/EIMS procedure for by-product PCB analysis. See Chapter 10 for more details on both studies.

The first task in data reduction is to qualitatively identify the analyte, answering the question "is the analyte present?" Quantitation can be attempted only after a compound has been identified, although the required level of confidence in the identification can vary widely, as discussed below.

I. QUALITATIVE

A. The Importance of Proper Qualitative Data Interpretation

The qualitative aspects of the analysis are all too often overlooked. Especially with complex mixtures of PCBs, differences in the qualitative assessment of a sample can

MONS 005488

dramatically affect the number of peaks quantitated. Qualitative assessment of results depends to a large extent on sample type. For samples where the presence of PCBs has been well-established (e.g., human or adipose tissue) the qualitative burden is not nearly so great as for samples in which PCBs are not expected.

The cleanup and determination techniques used to generate the data also dictate the level and type of data assessment needed. PCB-specific methods reduce the probability of interference and ease the qualitative burden. In some cases, the cleanup involves a rather specific liquid chromatographic separation which separates PCBs from most organochlorine pesticides and other potential interferences. In addition, the use of specific GC detectors (ECD, HECD) reduces the probability of interferences and increases confidence in the identification. Better still, MS provides spectra of the eluent which may be compared with those of authentic compounds to give higher confidence in the identifications. The retention time of the unknown should match that of a standard or at least be within a PCB window. HRGC gives much more precise retention times than PGC and increases qualitative confidence. In the case of samples contaminated by commercial mixtures (e.g., Aroclor), the pattern of chromatographic peaks often resembles the pattern of a standard. This visual pattern recognition has been a common qualitative technique in residue analyses, especially when PGC/ECD is the analytical procedure.

For many analyses, qualitative identification of PCBs is trivial. For example, human adipose samples will most assuredly have a characteristic PCB pattern in sample after sample. In cases where the presence of PCBs is less likely, the qualitative criteria should be established before the analysis, generally as part of the QA plan. To some extent, qualitative criteria are controlled by external factors: economics, politics, organizational policy, etc. For example, a regulated industry may set relatively low qualitative criteria, so that samples even suspected of containing PCBs will be properly disposed of. Also, if confirmation of suspected PCBs in a waste is more expensive than disposal, then further analysis is clearly not warranted; the waste is simply labeled "PCB-contaminated" and shipped off for disposal. Not only should the qualitative criteria establish limits (retention time windows, ion ratios, etc.), but they should direct the analyst to alternate courses of action (consult supervisor, confirm by alternate technique, analyze by standard addition, etc.).

MONS 005489

In addition to the various gas chromatographic identification techniques discussed here, thin-layer chromatography and high performance liquid chromatography yield qualitative information, as discussed in Chapter 7. More exotic techniques such as specialized mass spectrometric techniques, Fourier transform infrared spectrometry, and nuclear magnetic resonance spectroscopy are not used routinely for PCB analysis and were discussed in Chapter 7.

B. Interpretation of Retention Data

Regardless of the detector used, the retention time data from a gas chromatogram provides the first dimension of information used to identify PCBs. The peaks must be within the PCB window before any of the other qualitative criteria are applied. With ECD and HECD data, the detector selectivity reduces, but does not eliminate, the probability that non-PCB peaks will interfere with the qualitative interpretation. With mass spectromtric detection, the mass spectrum provides a second qualitative dimension, as discussed in Section I.C, below.

Only a few of the references using ECD or other analog detectors have mentioned the qualitative criteria used in identification of PCBs. In PGC/ECD procedures, visual pattern recognition is normally the qualitative technique. Often two GC columns of different polarity are used to enhance the confidence of the identification. With HRGC data, individual congeners may be identified by use of retention time or retention index tables or by comparison to a characterized commercial mixture. Increasingly, formal computerized pattern recognition routines are used to compare the PCB composition of samples.

1. Low resolution chromatograms: The low resolution chromatograms generated by PGC/ECD or PGC/HECD can be compared to the retention windows established with standards (either congener mixtures, or commercial mixtures). The only other qualitative assessment which can be made is comparison of the pattern with that of a commercial mixture. A representative qualitative criterion in the literature that the chromatogram exhibit a "typical Aroclor pattern" (Gordon et al., 1982; Giam et al., 1972; Ofstad et al., 1978; Kirshen, 1981a,b). For many purposes, visual pattern recognition is entirely satisfactory. However, the PCB mixtures in many samples do not resemble a single Aroclor mixture, so identification is difficult.

Computerized pattern recognition has been applied to the relatively simple task of identifying which Aroclor is

present in transformer oils and related samples (Colby and Picker, 1983). The goal was to minimize both the analysis time and operator intervention with an automated field analyzer (Colby et al., 1983; Picker and Colby, 1983). An algorithm was written for the dedicated microprocessor which identified PGC/ECD peaks in the Aroclor retention windows and then converted the retention time-intensity data pairs into an n-dimensional vector. The cosine of the angle of this vector in n-space was calculated and compared with the cosine of the angle for the various Aroclor standards. Pure and major-component Aroclors in a sample were readily distinguished. The algorithm was unreliable for components of less than 20% relative to the total amount of Aroclor. The authors noted that visual interpretation was also unreliable at this level.

Lerman et al. (1982) developed an algorithm for analysis of PCBs in transformer oils which calculates the concentration of an unknown against standard Aroclors 1242, 1254, and 1260 using both the total area and a mean of five key peaks for each. An error factor is calculated and an "error score" reported. The analyst can then review the data and decide which Aroclor best fits the unknown. The article does not present the routine in detail. Another routine (Lea et al., 1983) to identify Aroclors 1242, 1254, and 1260 is designed to be used with common chromatographic data systems (e.g., Varian Vista 401) and integrators (e.g., Varian CDS-111). Peaks are identified by retention time and then integrated. The peak areas are compared to those in the standard Aroclors by a ratio technique. The relative standard deviation of these ratios indicates how well the unknown matches the standard. Statistical tests ("Q test") are also incorporated to test for outliers, which can then be eliminated from the calculation.

A novel data reduction approach is to treat a PGC/ECD *chromatogram as a spectrum and use infrared* spectral subtraction software to match the unknown to a standard(s) in an interactive mode. Gossman (1983) presented this concept as applied to PCB-contaminated wastes. The ability to reject peaks which did not fit with an Aroclor standard was used to fit "only the good data." The concept, used with discretion, has particular appeal in analysis of mixed or degraded Aroclors. After a subtraction of one Aroclor, the residual peaks are observable on a screen and the analyst can visually assess the data.

2. High resolution gas chromatograms

a. Use of retention times and retention indices: Several researchers have compared retention times (RTs) or relative retention times (RRTs) between the sample

MONS 005491

and an Aroclor standard for PCB identification (Webb and McCall, 1972; Onsuka and Comba, 1978; Erickson et al., 1983e; Pellizzari et al., 1983a,b; Tuinstra et al., 1980). Another identification technique involves use of one of the retention index (RI) schemes (e.g., Kovats). Several publications contain tabulations of RIs of PCB congeners as shown in Table 7-I (Sissons and Welti, 1971; Zell et al., 1978; Ballschmiter and Zell, 1980; Albro et al., 1981; Albro and Fishbein, 1972a,b; Hanneman, 1982). Since all 209 PCB congeners are not readily available, a scheme of predicting RIs has been developed based on the half-RI values (see Table 7-II) for the various chlorination positons on one of the benzene rings. Sissons and Welti (1971) first proposed this system, which was expanded upon and further validated by Albro and Fishbein (1972a) and Albro et al. (1977). The use of half RIs permits the analyst to qualitatively identify all 209 PCBs on the basis of their retention time, although the level of confidence in this identification has not been determined. Using state-of-the-art chromatography, RI measurement precision of ± 0.05% has been reported for PCBs (Neu et al., 1978), and with full optimization, precision of ± 0.01% has been predicted (Neu and Zinburg, 1979).

b. Individual congener identification: Several publications, dating back to the landmark work of Sissons and Welti (1971), concentrated on the identification of PCB congeners in commercial mixtures such as Aroclor or Chlophen (Tas and de Vos, 1971; Tas and Kleipool, 1972; Armour, 1972; Willis and Addison, 1972; Paasivirta and Pitkänen, 1975; Jensen and Sundström, 1974; Neu et al., 1978; Zell et al., 1978; Ballschmiter and Zell, 1980; Pellizzari et al., 1981; Tuinstra et al., 1981; Bush et al., 1982; Duinker and Hillebrand, 1983). The objective of most of these papers was to characterize the commercial mixture as an aid to quantitation in environmental samples or for toxicological information. The recent work by Bush et al. (1982) expanded on previous work and assigned 72 peaks in a mixture of Aroclors 1221, 1016, 1254, and 1260 (2 μg/mL each). Where there were ambiguities in previous work which they could not resolve, only the homolog is listed (e.g., Cl_5). They note that the confidence of the peak identities differs, depending on availability of standards, number of isomers eluting in the same region, etc. They also note that the confidence in the assignments will increase with time as more standards become available and further work is done to corroborate the assignments. Using the four-Aroclor calibration mixture and the peak tables, Bush et al. (1982) can identify all of the major and most of the minor PCB peaks found in environmental samples from the northeast United States. They state that:

MONS 005492

> "...although chromatographic matching of retention parameters does not necessarily constitute perfect authentication of peak assignment, several authors are reaching a consensus on the structure of compounds separated on Apiezon L (Mullin et al., 1981; Ballschmiter and Zell, 1980) and other phases (Albro et al., 1981). We consider that the structures of the major peaks are now well enough established to warrant reporting them quantitatively as described here. This will enable the task of determining the toxicological significance of residues of PCB to be started, a hopeless task when results are expressed in terms of Aroclor mixtures as has been the practice hitherto."

For environmentally derived samples where specification of congeners is useful and where PCB concentrations are very low, this HRGC/ECD method holds great promise.

Zell and Ballschmiter (1980) interpreted any deviation of an environmental PCB pattern from the pattern of combinations of commercial mixtures as the result of degradation or weathering. These authors established which congeners are indicative of metabolism, or other degradation process for different types of environmental samples. This method allows the analyst to focus attention on those components of interest--either because of their constancy from matrix to matrix, or because of their change with environmental conditions.

c. Comparison of retention times on two HRGC columns. Singer et al. (1983) used two HRGC columns (OV-1 and SE-54) with ECD detection for both qualitative and quantitative analysis. The data from the two analyses were correlated and the following criteria supplied using a program written on the chromatograhpic data system:

> "1. The retention time of the peak must have been within limits (usually ± 0.1%) of the expected retention time, otherwise the peak was rejected.
>
> 2. If the peak for a given PCB was identified on both columns and the quantities were within limits (usually ± 20%), the average was calculated and printed followed by the word 'confirmed.'
>
> 3. If the peak for a given PCB was identified on both columns, but the quantities were not within given limits, then the lower value was taken as the result, followed by word 'interference' (we assumed

that the higher value was caused by an impurity co-eluting with the PCB).

4. If the peak for a given PCB was identified on one column only, the value was rejected and identified by the words 'not PCB.'

5. Although the capillary columns have very high resolving power, some PCBs could not be resolved at all or could be resolved on one column only. If this happened, then the determined quantities of unresolved PCBs on one or both columns were summed up and evaluated under identical criteria."

d. Pattern recognition: As noted at the beginning of this section, GC/ECD data have traditionally been evaluated by visual pattern recognition. In the past few years some analysts have used computerized pattern recognition. Bush et al. (1983) have used a rather simple technique to study differential concentrations of PCB congeners in maternal and fetal cord blood. They used histograms of the frequency of detection at different concentration intervals to compare the two matrices. They were able to detect several congeners which are differentiated by the placenta. Gassiot et al. (1982) compared the Zobel and simplex computer algorithms for the identification and quantitation of up to three Aroclors in fish sample. The simplex routine was judged easier and more flexible to use.

Dunn et al. (1982) have used a computerized pattern recognition technique to evaluate HRGC/ECD data on PCBs. HRGC/ECD data for 69 congeners in about 700 samples of sediment, suspended sediment, benthos, and fish were examined using the SIMple Classification by Analogy (SIMCA) principal components modeling technique. SIMCA performs a vector analysis of all of the relationships (e.g., concentration of a congener in water) and derives a set of artificial coordinates which best separate the data into classes. The two dimensional eigenvector plots of the data readily indicated samples that were (a) either incorrectly assigned to a class, i.e., fish instead of water, or (b) those that were experimentally abnormal. SIMCA proved to be especially valuable for identifing outlier samples for reanalysis and also provided a basis for defining "trace" concentration levels. Dunn et al. (1984) also compared SIMCA, K-nearest neighbor (KNN) and partial least squares (PLS) techniques to categorize HRGC/ECD data by Aroclor. A transformer oil from a dump site was found to contain predominantly Aroclor 1260 with about 8% Aroclor 1254 (Figure 8-1). Pattern recognition appears to be a most promising technique for interpretation of large numbers of PCB determinations.

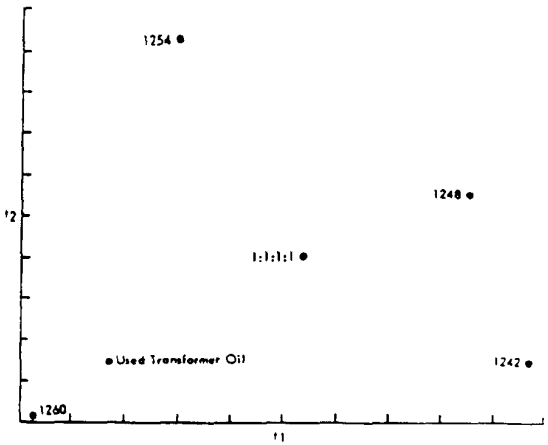


Figure 8-1. Principal Components Plot of PCB Data

The data for four Aroclors, a transformer oil, and a 1:1:1:1 mixture of the Aroclors showing that the transformer oils are similar, but not equivalent, to Aroclor 1260. The axes denoted t_1 and t_2, are arbitrary, unitless scales depicting the relationship of the data in n-dimensional space.

Reprinted, with permission, from Dunn et al. (1984); copyright 1984 by American Chemical Society.

MONS 005495

3. Recommended qualitative techniques for GC data: Where "total PCBs" or similar general identification is desired, simple pattern recognition (visual or computerized) of the PCBs relative to Aroclor standards may be appropriate. However, as noted above, many types of samples can be weathered or metabolized to skew the Aroclor patterns. In these cases, more advanced identification techniques are necessary. The precise relative retention times on HRGC columns represent a high level of confidence in the identity of the peaks. Use of a dual column analysis and correlation of the data provide additional confidence.

Automated data quality assessment is becoming increasingly popular as old strip chart recorders and integrators are replaced by chromatographic data systems, which are becoming increasingly sophisticated. Retention time windows, peak height ratios, and other criteria are already in use. More sophisticated statistical techniques, correlation and pattern recognition, will become more popular as the programs become more available and chemists become familiar with their utility. Automated injectors, better instrumentation control, and possibly improved columns can all be utilized to improve the retention time precision. As the precision improves, the time window for an identification can be narrowed, reducing the possibility of other compounds being identified as PCBs.

C. Interpretation of Mass Spectrometric Data

1. General: When a mass spectrometer is used as the GC detector, a second qualitative dimension is available in addition to the retention time. The mass spectra of PCBs are distinctive due to the cluster of masses generated by the presence of two chlorine isotopes in nature (see Appendix C). If sufficient material is present to obtain full mass spectra, an unknown can be reliably identified by comparison with spectra of authentic standards or from spectral compilations (Stenhagen et al., 1974; Mass Spectrometry Data Centre, 1970; Heller and Milne, 1978).

As mentioned above, the natural isotopic abundance ratios yield a characteristic pattern (Appendix C). The ratios have been tabulated for PCBs (Appendix C; Erickson et al., 1983d; Rote and Morris, 1973). The use of these ratios in selected ion monitoring can provide qualitative information when full mass spectra are not obtained (Canada and Regnier, 1976; Erickson and Pellizzari, 1977, 1979; Erickson et al., 1982). Even though the natural isotopic abundance ratios are constant, instrumental variances and interferences can affect the observed ratio. Thus, ratios observed with

standards may be more appropriate than the natural ratio for comparison to an unknown (Erickson et al., 1983b).

2. Specific criteria: Tindall and Wininger (1980), in a method designed to determine PCBs even if they are not "Aroclor-derived," established qualitative criteria.

> Each peak in the chromatogram is evaluated to determine if it is a PCB peak. Peaks must meet these criteria to be labeled PCB peaks for quantitation: (1) the peaks of the characteristic ions must maximize at the same retention time; (2) the peak must be in the proper retention time window; and (3) the relative peak intensities of the molecular ions must be within ± 15% of the theoretical ratio. This tolerance is arbitrary and can be made larger for very low concentrations of PCBs where statistical variations in peak intensity become large.

Work by Collard and Irwin (1982a,b, 1983) and Dow (1981) established similar qualitative criteria:

> Identify the chlorinated biphenyl homologs by their mass ion response, relative retention time, and ion intensity ratio (± 20% relative). Secondary confirmation of trichloro- through decachlorobiphenyl may rely upon the M-70+ ion response.

The procedure developed for EPA's enforcement of by-product PCBs in chemical products and wastes (Erickson et al., 1982, 1983d; Erickson, 1984a) includes similar qualitative criteria for data collected under full scan, selected ion monitoring (SIM), or limited mass scan (LMS) conditions. For full scan data

> "1. The peak must elute within the retention time windows set for that homolog.
>
> 2. The unknown spectrum should be compared to that of an authentic PCB. The intensity of the three largest ions in the molecular cluster (two largest for monochlorobiphenyls) must match the ratio observed for a standard within ± 20%. Fragment clusters with proper intensity ratios should also be present. System noise at low concentration or interferences may skew the ion ratio beyond the ± 20% criteria. If the analyst's best judgement is that a peak, which does not meet the qualitative criteria, is a PCB, the peak may be included in the calculation, with a footnote explaining the data and the reason for relaxing the criteria.

MONS 005497

3. Alternatively, a spectral search may be used to automatically reduce the data. The criteria for acceptable identification include a high index of similarity."

The criteria for selected ion monitoring and limited mass scanning data are similar, but add the specific requirement that the analyst search higher mass windows, in particular M+70 to prevent misidentification of a PCB fragment ion cluster as the parent. If there is reasonable doubt as to the identity of a peak as a PCB, "the analyst must either identify the peak as a PCB or proceed to a confirmational analysis." This approach for marginal data reflects regulatory constraints to err on the high side of the true value. These three works (Tindall and Wininger, 1980; Collard and Irwin, 1983; and Erickson et al., 1983d) suggest a new awareness that qualitative criteria must be stipulated in any method if the results are to have any significance.

A novel use of GC/MS data in identifying the relative concentrations of different Aroclors was described by Liu et al. (1983). A multiple regression algorithm identified the percent of each Aroclor (1242, 1248, 1254, or 1260) contributing to each of 40 GC peaks. This data base was then used to compare unknowns and identify the relative concentrations of the different Aroclors. The authors noted that lower correlations were obtained with samples which had been subjected to degradation.

3. Recommended qualitative techniques for GC/MS data: The qualitative criteria of Tindall and Wininger (1980), Collard and Irwin (1983), and Erickson et al. (1983d) are the most complete guidance on mass spectral identification of PCBs. These criteria cannot cover all cases. At low levels, or with interferences, the PCB clusters can become skewed. In addition, data massaging techniques (summing spectra, background subtract, etc.) can be used (and misused) to bring a peak ratio which had been out of the proper ion intensity ratio requirement (e.g., ± 20% relative) within the requirement. Rules for data manipulation have not been well-defined for general GC/MS analysis a well as for PCBs. Better guidance for data acceptance are needed.

Future software packages will undoubtedly permit automated identification of PCBs based on isotopic abundance ratios. Although the technology is available, high precision retention times with GC/MS, have not been widely used. As noted above, HRGC/ECD can give fairly high confidence identifications of over 70 congeners, based solely on relative retention times. With the added dimension of the mass spectrum, data of very high qualitative confidence can easily be generated.

II. QUANTITATIVE

Quantitation (or less accurately, quantification) is the final step in a chemical analysis sequence. Some measure of signal intensity (peak height, or peak area) is converted into concentration. For most detectors used in PCB analysis, the mass of analyte in a peak, M_a, is proportional to the signal for the analyte, A_a

$$M_a = RF \times A_a \qquad \text{Eq. 8-1}$$

The response factor, RF, is a constant which accounts for instrument attenuation, response of the compound, and other factors. RFs are derived by injection of a standard of known M_a and back-calculating Equation 8-1. Quantitation can be improved by injection of several standards of different M_a to give a plot of response versus amount (or concentration). Then RF can be read off the response curve at the precise area for the unknown. Since there can be instrumental variation from run to run (different injection volumes, instrumental drift, etc.) additional precision can usually be obtained with the internal standard (IS) method. A known amount of an internal standard, M_{is}, is added to each sample. Then the equation becomes

$$M_a = RF \times A_a \times \frac{M_{is}}{A_{is}} \qquad \text{Eq. 8-2}$$

For this equation, the RF is derived using the internal standard areas, and would not have the same value as in Equation 8-1. Once the mass of the analyte in the peak is known, the concentration in the extract, C_e, can be derived.

$$C_e = \frac{M_a}{V_i} \qquad \text{Eq. 8-3}$$

where V_i is the volume injected onto the instrument. The concentration in the extract may be converted to concentration in the original sample, C_s, by

$$C_s = C_e \times \frac{V_e}{M_s} \qquad \text{Eq. 8-4}$$

where M_s is the mass of the sample (volume may be used for water and air samples). V_e, the volume of the extract, is often 1.0 mL and care must be taken to ensure that proper units are used to prevent miscalculation by a factor of 1,000, since V_i is often 1 µL.

MONS 005499

Equations 8-3 and 8-4 are often combined with either Equations 8-1 or 8-2 so that the calculation is done in one equation.

$$C_s = RF \times A_a \times \frac{M_{is}}{A_{is}} \times \frac{1}{V_i} \times \frac{V_e}{M_s} \qquad \text{Eq. 8-5}$$

If all of the values for the terms in Equation 8-5 were known, the only error in quantitation could be a mistake in calculation or transcription. Unfortunately, deriving the value for RF (the calibration step) and A_a (the determination step) from the raw data can easily induce significant errors in the overall analysis. This is particularly true for PCBs, as discussed below.

With most organic compounds, quantitation is relatively straightforward. The instrumental response is calibrated using standard solutions of the compound. The amount of unknown is measured by comparison of the signal it generates with the calibration factor or curve. Quantitation of PCBs is not nearly so simple since the analyte is not a single compound but rather a complex mixture of 209 possible congeners. In addition, standards of all 209 congeners are not readily available for calibration. Given these problems, analysts have devised alternate quantitation methods, often based on the similarity of the sample PCB mixture to a commercial product (e.g., Aroclor). Aroclor-based quantitation schemes may be appropriate if the sample and standard "fingerprints" are similar. As the similarity diverges, the quantitative confidence diminishes.

A. Calibration

Three calibration techniques are available: external standard, internal standard response factors, and internal standard multipoint calibration.

1. External standard calibration: Calibration of the analysis system versus an external standard and then quantitation using the absolute intensities of the peaks lacks precision (Haefelfinger, 1981) and is not generally recommended for gas chromatographic analysis. Often, a major source of imprecision is the reproducibility of injection volume. Nevertheless, many PCB analyses, especially those using PGC/ECD, have successfully used external standard calibration.

2. Internal standard calibration: In this technique, internal standard(s) are added to the sample extract immediately prior to the instrumental determination, and the analytes are quantitated using the ratio of the analyte and

internal standard responses. A previously determined response factor (essentially a one-point calibration curve, with an assumed intercept at the origin) is used in converting the response ratio to the mass.

For PCBs, which can span a large retention time range, three or four internal standards which span the PCB window may improve the precision of the response factors, and therefore the final quantitation. Response factor precision is related to how close the analyte peak and internal standard elute (Haefelfinger, 1981; Bickford et al., 1980). Other factors to be considered in the selection of internal standards are chromatographic resolution from analytes and interferences, different mass spectral properties to assure identification in GC/MS analysis, chemical similarity to analyte (to minimize effects of changes in system selectivity), very low probability of occurrance in samples, and chemical stability. Candidates for internal standards in PCB analysis include PCB congeners known not to be present in the matrix, other halobiphenyls (e.g., tribromobiphenyl), related haloaromatics (e.g., chloronaphthalenes), and isotopically labeled compounds (e.g., d_6-3,3',4,4'-tetrachlorobiphenyl or d_{12}-chrysene).

Since the internal standard technique is a one-point calibration, the response factor must be determined at a concentration close to that of the analyte. Differences of more than one order of magnitude may induce significant error.

3. Internal standard multipoint calibration: This technique is essentially the same as the response factor technique, above, except multiple calibration points (typically three, spanning up to two orders of magnitude) are used to establish a calibration curve. This has the potential for greater precision, but requires much more time and several standard solutions. In cases where detector sensitivity (signal response versus amount or concentration) is either nonlinear or the curve does not intercept close to the origin, a multipoint curve is especially advisable.

4. Selection of compounds for calibration: Since PCBs consist of 209 separate congeners, most of which are not readily available, a subset must generally be employed for calibration. This subset must be judiciously selected, since quantitation based on a calibration factor obtained for another congener introduces an error. The options for selection of compounds to be used in calibration are:

1. Establish and use relative responses for all 209 congeners.

MONS 005501

2. Establish and use relative responses for several congeners and extrapolate the responses for the other congeners.

3. Characterize a secondary standard prepared from commercial mixtures to span the range of congeners.

4. Calibrate against one or more Aroclor mixtures.

5. Calibrate for only a few selected available congeners.

Option 1 is the ultimate technique; however, all 209 congeners are not readily available. Option 2 is a compromise. Option 3 would utilize a well-characterized mixed Aroclor or similar mixture. This has the advantages of low cost (once the characterization has been completed) and uniformity. One disadvantage is that the concentrations of the congeners range over two or more orders of magnitude, so calibration of the instrument would be difficult. Another problem is that non-Aroclor constituents cannot be quantitated. Option 4 has been utilized extensively, especially with PGC/ECD analysis. As discussed elsewhere, this approach is valid only if the standard and the unknown "fingerprints" are similar. Option 5 will not yield a "total PCB" value, but may be the most appropriate approach for many applications where information about selected congeners is sufficient.

B. Quantitation Techniques

It is obvious that PCBs were quantitated in most references in the bibliography, since quantitative data were presented. However, many authors neglected to mention how the detector signal was converted into a concentration value. Many other articles only made a brief mention of "integration" or "comparison with Aroclor 1260 standard" with respect to the quantitation.

As shown in Table 3-I, all standard procedures give at least cursory instructions on quantitation. At one extreme, the general purpose semivolatile organic procedures (EPA, 1978, 1979a,b; Ballinger, 1978) contain vague direction to "integrate the area under the peak." Much more complete quantitation guidelines are given in EPA's (Bellar and Lichtenberg, 1981; EPA, 1981a) procedure for analysis of PCBs in transformer fluids and waste oils.

MONS 005502

1. Packed column gas chromatography/electron capture detection

a. Webb-McCall: The most prominent PGC/ECD quantitation technique was originated by Webb and McCall (1973). The weight percent and homolog identification (relative proportions where more than one homolog was present) were determined PGC/EIMS for several Aroclors, and retention times relative to p,p'-DDE were specified. An example is presented in Table 8-1 and Figure 8-2. The general procedure is as follows:

1. Chromatograph known amounts of the standards and measure the area for each peak.

2. Using the tables of data determine the response factor for each peak.

3. Chromatograph the sample and measure the area of each peak.

4. Multiply the area of each peak by the response factor for that peak.

5. Add the nanograms of PCB found in each peak to obtain the total nanograms of PCB present.

6. Samples containing one or more Aroclors can be quantitated by comparison with appropriate standards.

Regarding the last point, Webb and McCall devised the chromatogram division scheme shown in Figure 8-3. This scheme accounts for the chromatographic overlap of the three common Aroclors. Their article presents a detailed explanation of the rationale for this flowchart. Validation of the multi-Aroclor quantitation with nine known mixtures found recoveries ranging from 96 to 107%.

Following an interlaboratory survey, Chau and Sampson (1975) recommended that the Webb-McCall technique be adopted as the uniform quantitation technique. They cited the general applicability, elimination of mixed standards, the more realistic results, and simplicity of the method as reasons for their recommendations. Another interlaboratory study (Lee and Chau, 1981a) also found Webb-McCall quantitation preferable. Half of the 14 participants used Webb-McCall, while the others used either selected peaks or a summation of all peaks. The mean of the results by the Webb-McCall quantitation was only 3% higher than the design value, while the other quantitations averaged 22% higher.

Exact replication of the Webb-McCall quantitation requires either reproducing the chromatographic pattern using the same lot of Aroclor standards as Webb and McCall used or determining the composition of the peaks obtained with different chromatographic conditions or Aroclor lots. These stringent requirements have led most researchers to characterize their quantitation practice as a modified Webb-McCall (Sawyer, 1978a; Kreiss et al., 1981; Harris et al., 1981; Steichen et al., 1982; Erickson et al., 1983e). These users have not replicated the Webb-McCall chromatography or Aroclor lot number, but have decided that the chromatographic patterns are similar enough to use Webb-McCall's data tables. The error induced by this practice is probably not significant, since participants in the interlaboratory studies discussed in the previous paragraph reported a variety of chromatographic conditions and undoubtedly used several lots of Aroclors. Ugawa et al. (1973) devised a quantitation technique similar to Webb-McCall which was based on Kanechlors, the Japanese commercial PCB mixtures. A scheme similar to Webb-McCall (Dexter and Pavlou, 1976; Pavlou et al., 1980) used PGC/FID to characterize the Aroclor mixtures, with analysis of samples by PGC/ECD. Several standard procedures have adopted the Webb-McCall quantitation technique for analysis of PCBs in a variety of matrices as summarized in Table 3-I (NIOSH, 1977b, 1977c; Beard and Schaum, 1978; EPA, 1978, 1981a; Bellar and Lichtenberg, 1981; Harris et al., 1981).

The calculations required with the Webb-McCall technique can be easily automated using common GC integrators or data systems (Needham et al., 1981; Kirshen, 1981a,b; Newton and Laski, 1983; Erickson et al., 1983e). Newton and Laski (1983) reported a computer routine for quantitation of Aroclor 1242, 1254, and 1260 and their combinations. The routine, essentially an automation of the Webb and McCall (1973) procedure using BASIC, compared favorably with manual calculation by peak height or peak area. About 5 minutes of operator time is required per analysis. One apparent flaw of the routine, in addition to the assumption that the analyte PCBs are unmodified Aroclors, is that it does not consider the chromatographic overlap of the Aroclors. The three Aroclors are segregated into non-overlapping time windows.

b. Total areas: Several researchers (Collins et al., 1972; Bellar and Lichtenberg, 1975) and standard methods (AOAC, 1980a,b; ASTM, 1981a,b) advocate comparison of the total areas under the "Aroclor region" in the sample and standard chromatograms. This is a simple approach and has been recommended by Sawyer (1973) as the most reliable method for obtaining interlaboratory precision. In a later collaborative study (Sawyer, 1978b), the individual peak height,

Table 8-1. Composition of Aroclor 1254 According to Webb and McCall (1973)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	No. of Chlorines[c]
47	6.2	3.7	4
54	2.9	2.6	4
58	1.4	2.8	4
70	13.2	2.7	4 (25%) 5 (75%)
84	17.3	1.9	5
98	7.5	5.3	5
104	13.6	3.8	5
125	15.0	2.4	5 (70%) 6 (30%)
146	10.4	2.7	5 (30%) 6 (70%)
160	1.3	8.4	6
174	8.4	5.5	6
203	1.8	18.6	6
232	1.0	26.1	7
Total	100.0		

a Retention time relative to p,p'-DDE = 100. Measured from first appearance of solvent.

b Standard deviation of six results as a percentage of the mean of the results.

c From GC/MS data. Peaks containing mixtures of isomers are bracketed.

Source: Webb and McCall (1973), reprinted with permission, copyright 1973 by Preston Publications, Inc.

MONS 005505

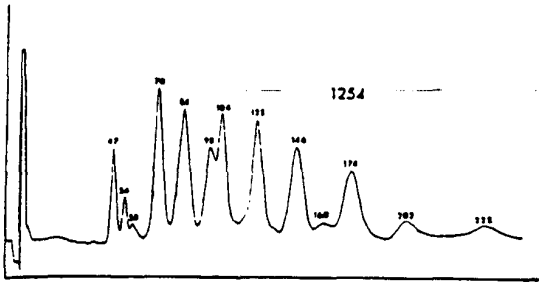


Figure 8-2. PGC/ECD Chromatogram of Aroclor 1254

The sample was chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE = 100. See Table 8-I for peak compositions.

Reprinted, with permission, from Webb and McCall (1973); copyright 1973 by Preston Publications, Inc.

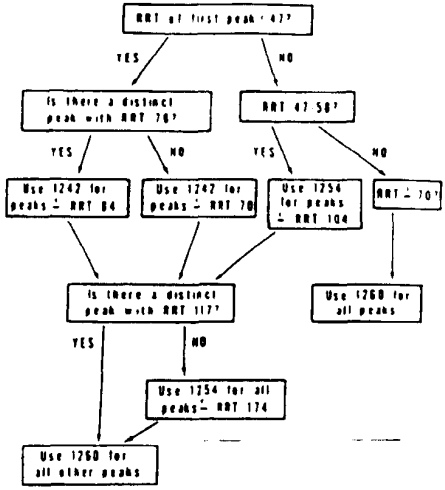


Figure 8-3. Flow Chart for Division of PGC/ECD Chromatograms Into Retention Time Regions for Quantitation of Samples With Mixed Aroclor Patterns

Reprinted, with permission, from Webb and McCall (1973); copyright 1973 by Preston Publications, Inc.

MONS 005507

total peak height and total peak area methods were all compared and gave similar results, although the individual peak method (Webb and McCall, 1973; Sawyer, 1978a), was judged slightly better. On this basis, AOAC (1980a,b) permits either individual peak (Webb-McCall) or total area quantitation of PCBs. Bellar and Lichtenberg (1975) used either the total peak height for samples closely resembling Aroclors or Webb-McCall for patterns "not representing a single Aroclor."

Transformer oils must often be analyzed to comply with regulations regarding their use and disposal. The objective in the United States has been to classify the oil as "PCB-containing" if it contains over 500 ppm PCBs and "PCB contaminated" if it contains 50 to 500 ppm PCBs. Thus, quantitation has focused on deriving a "total PCB" concentration. Transformer oil analysis is relatively simple, the sample matrices are relatively consistent and unmodified Aroclor patterns are almost always observed. Thus, sophisticated analytical techniques have not generally been necessary. In addition, rapid results from on-site laboratories have often been desired.

The EPA (Bellar and Lichtenberg, 1981; EPA, 1981a) has issued an analytical method for PCBs in transformer fluid and waste oils. If the parent Aroclor is identifiable, it may be used as the standard for quantitation:

> "The concentration of the PCBs in the sample is calculated by comparing the sum of the responses for each PCB in the standard to the sum of all of the PCBs in the sample. This is particularly important as sample concentrations approach within 20% of 50 mg/kg or any other EPA-regulated concentration. If calculations are based upon a single PCB peak or upon a small percentage of the total PCB peaks, serious errors may result. Peaks comprising less than 50% of the total can be disregarded only if (a) interference problems persist after cleanup; (b) the source of PCBs is obvious; or (c) the concentration of PCBs are not within ± 20% of an EPA-controlled value such as 50 mg/kg."

The method directs the analyst to use the following formula to calculate the concentration of PCBs in the sample:

$$\text{"Concentration (mg/kg)} = \frac{B \times V_t}{A \times W} \quad \text{Eq. 8-6}$$

MONS 005508

where:

$$A = \frac{\text{Sum of Standard Peak Heights (Areas)}}{\text{ng of Standard Injected}} \times \text{mm/ng},$$

$$B = \frac{\text{Sum of Sample Peak Heights (Areas)}}{\mu\text{L Injected}} = \text{mm/}\mu\text{L},$$

V_t = dilution volume of sample in milliliters, and

W = weight of the sample in grams."

If the parent Aroclor is not apparent, the analyst is directed to calculate the concentration according to the procedure of Webb and McCall (1973). The concentration of the PCBs in each peak is determined individually. These concentrations are then added together to determine the total PCB content of the sample. Each PCB identified in the sample must be included in these calculations. Specific instructions are given.

2. High resolution gas chromatography/electron capture detection

a. Single congener quantitation: The application of HRGC to PCB determination complicates an already difficult quantitation problem: more peaks are present. Since the peaks are presumably single congeners instead of the mixtures obtained by PGC, quantitation of single congeners has been emphasized by many authors. Boe and Egaas (1979) devised a calibration factor system that permits the analyst to calculate the ECD response factor for a given congener, once its structure is known. More recently, the ECD response factors for all 209 congeners were measured (Mullin et al., 1984; Tables 7-IV and 7-VII). As discussed in Chapter 7 the ranges over homologs and within a homolog indicate that calibration with each congener would be necessary for accurate results.

b. Calibration with commercial mixtures: One option for calibration is to use a commercial mixture (i.e., Aroclor) as a secondary standard, as mentioned in Section II.A.4. This is the approach taken with the Webb and McCall (1973) quantitation for PGC/ECD data (see Section II.B.1.a, above). With HRGC/ECD data, similar approaches can be used, although identification and quantitation of all of the components in the Aroclor mixture is much more tedious. The various publications which characterize commercial PCB mixtures are reviewed in Table 7-III and Appendix B. Among the more recent and complete tabulations, Albro et al. (1981) determined the relative molar percentages of the individual

MONS 005509

components of about 100 different PCB congeners in Aroclors 1248, 1254, and 1260. They recommend using the Aroclor mixtures as secondary standards to determine HRGC/ECD response factors. Schulte and Malisch (1984) have published a similar approach based on the known composition of Chlophen A60. This approach has been further refined by Bush et al. (1982, 1983) and the mass for 72 peaks in four common Aroclors determined (Table 8-II). The accuracy was assessed by comparison of the gravimetric versus GC-calculated concentrations. The total amount calculated by the chromatographic data system was 12% higher than the gravimetric value. The precision, based on replicate injections of a mixture of 27 authentic congeners, ranged from ± 1.17% RSD to ± 8.26% RSD for individual peaks, with a precision on the total of ± 2.25% RSD.

A menu-driven computer program was recently reported which gives congener-specific quantitation of over 100 components of Aroclors 1242, 1248, 1254, and 1260 (Schwartz et al., 1984). The data may be presented in several ways, such as by congener, by homolog, or by number of ortho chlorines. The data may also be fed into a pattern recognition program for additional qualitative studies (Dunn et al., 1984).

The use of a well-characterized secondary standard has several advantages. The preparation of standards is relatively simple and cheap. All of the congeners likely to occur in environmental samples will be calibrated and will be in roughly similar proportions in the samples and standards. A disadvantage is that, like the Webb-McCall quantitation, it presupposes that all PCBs are derived from the commercial mixtures and does not quantitate all PCBs. This can be detrimental in analysis of true unknowns, especially where by-product PCBs or partially destroyed PCBs may be present.

c. Statistical evaluation of HRGC/ECD data: A rigorous statistical quantitation was described (Kafadar and Eberhardt, 1983) for the certification of the NBS standard reference material of Aroclors in oil (Uriano, 1982). The linear statistical model recognized that the data for the individual peaks determined by HRGC/ECD were not independent. Each of four SRMs were analyzed six times as described by Chesler et al. (1981) and Parris et al. (1984), yielding 10 PCB peaks and 3 internal standard areas. The statistical analysis yielded the certified concentrations shown in Table 8-III.

d. Quantitation using selected diagnostic peaks: Zell and Ballschmiter (1980) presented a simplified

MONS 005510

Table 8-II. Analysis of 1:1:1.1 Mixture and Separate Aroclor Mixture

Retention Time, min	Structure	Calib. Amt. µg/mL	Aroclor (2.0 µg/mL) 1221	1016	1254	1260	Sum of Aroclors
5.33	2	0.794	1.264				1.264
6.59	2,2'	0.182	0.118	0.094			0.212
6.79	4	0.425	0.400				0.400
7.86	2,5	0.028	0.018	0.008			0.026
7.96	2,4	0.035	0.033	0.008			0.041
8.10	2,3'	0.092	0.065	0.034			0.103
8.21	2,3	0.047	0.030	0.028			0.059
8.36	2,4'	0.323	0.213	0.166			0.379
9.37	2,2',5'	0.216	T	0.185			0.202
9.82	2,2',4'	0.074	T	0.065			0.073
9.79	2,2',3' + 3,2',6'	0.096	T	0.094			0.102
10.18	2',4,6'	0.074	T	0.057			0.074
10.41	4,4'	0.158	0.104	0.064			0.168
11.09	2,2',3',5'	0.018	T	0.015			0.018
11.32	2',3,5'	0.040	T	0.032			0.039
11.39	2,3',5'	0.038	T	0.034			0.037
11.49	Cl_3	0.021	T	0.017			0.020
11.55	Cl_3	0.029	T	0.023			0.024
11.65	2',3,6'	0.157	T	0.149			0.166
11.85	2',3,3' + 2',4,4'	0.267	T	0.238			0.271
12.12	2',3',6	0.146	T	0.127			0.147
12.62	2,2',5,5'	0.233	T	0.115	0.133		0.268
12.90	2,2',6,5'	0.151	T	0.123	0.042		0.161
13.07	2,2',3,5'	0.166	T	0.105	0.067		0.179
13.22	2,2',4,4'	0.057	T	0.047	0.011		0.063
13.40	Cl_4	0.050		0.039	0.008		0.047
13.56	2,2',3,3'	0.049		0.039	0.011		0.050
13.65	Cl_4	0.050		0.043	0.015		0.058
13.82	Cl_4	0.110		0.107	0.057		0.164
14.52	Cl_5	0.185			0.115	0.001	0.196
15.03	2,2',3,3',6'	0.085			0.078	0.025	0.103
15.45	2,3',4',5	0.134			0.105	0.013	0.118
15.66	2,3',4,4'	0.042			0.032	0.006	0.038
16.03	2',3',4,4'	0.053			0.059	0.015	0.074
16.13	2,2',3,3',6,6'	0.086			0.041	0.056	0.097
16.36	2,2',4',5,5'	0.181			0.136	0.172	0.298
16.68	2,2',4,4',5'	0.070			0.069	0.006	0.075
16.85	[illegible]	0.080				Not integrated	
16.92	2,2',3',4',5	0.116			0.149	0.024	0.173
17.37	2,2',3,3',6'	0.269			0.289	0.049	0.338
17.66	2,2',3',5,5',6'	0.112			0.037	0.087	0.124
17.97	2,2',3,3',5',6'	0.029			0.012	0.021	0.033
18.16	2,2',3,3',4,6'	0.206			0.083	0.145	0.228

MONS 005511

TABLE 8-II (concluded)

Retention Time, min	Structure	Calib. Amt. µg/mL	Aroclor (2.0 µg/mL) 1221	1016	1254	1260	Sum of Aroclors
18.50	Cl_5	0.014			0.013	0.007	0.020
18.78	2,2',3,3',5',6,6'	0.096			0.091	0.064	0.105
18.95	2',3,4,4',5'	0.058			0.035	0.051	0.066
19.28	2,2',3,3',4',6,6'	0.135			0.128	0.017	0.145
19.44	2,2',3,4',5,5'	0.032			0.015	0.020	0.035
19.72	Cl_5	0.051			0.024	0.034	0.058
19.87	2',3,3',4,4'	0.082			0.080	0.005	0.085
20.06	2,2',4,4',5,5'	0.369			0.127	0.253	0.380
20.29	Cl_6	0.025			0.015	0.011	0.026
20.46	Cl_6	0.045			0.027	0.021	0.048
20.66	2,2',3,4,4',5'	0.288			0.130	0.165	0.295
20.87	2,2',3,3',5,5',6'	0.051			0.035	0.028	0.063
21.01	2,2',3',4,5,5',6'	0.010				0.008	0.008
21.18	Cl_5	0.118			0.009	0.127	0.136
21.27	2,2',3,3',4,4'	0.053			0.040		0.040
21.51	2,2',3,3',5,5',6,6'	0.193			0.022	0.170	0.192
21.79	2,2',3,3',4,4',6'	0.068			0.011	0.060	0.071
22.13	2,3',4,4',5,5'	0.048			0.008	0.047	0.055
22.38	2,2',3,3',4',5',6,6'	0.026			0.009	0.018	0.027
23.13	2',3,3',4,4',5'	0.047			0.033	0.019	0.052
23.27	2,2',3,3',4',5,5'	0.029			0.005	0.023	0.028
23.63	2,2',3',4,4',5,5'	0.278			0.027	0.250	0.277
24.32	2,3',3,3',4,4',5'	0.120			0.020	0.102	0.122
24.37	2,2',3,3',4,5,5',6'	0.064			T	0.059	0.064
24.54	Cl_7	0.033			T	0.028	0.035
24.71	2,2',3,3',4,4',5,6'	0.035			T	0.032	0.036
24.86	2,2',3',4,4',5,5',6'	0.042			T	0.038	0.043
25.49	2,2',3,3',4,4',5',6'	0.033				0.030	0.030
27.27	2',3,3',4,4',5,5'	0.065			T	0.062	0.063
	Total	8.230	2.249	2.044	2.393	2.339	9.225

a T = Trace.

Source: Bush et al., 1982; reprinted with permission, copyright 1982 by Association of Official Analytical Chemists.

Table 8-III. Quantitation of NBS Standard Reference Material 1581 Polychlorinated Biphenyls in Oil

Matrix	Aroclor Type	Certified Concentration (μg/g)[a,b]	Statistical Concentration μg/g[c]	95% Confidence Units (μg/g)[c]
Motor oil	1242	100 ± 1	100.07	98.65, 101.48
Motor oil	1260	100 ± 2	100.69	98.70, 102.74
Transformer oil	1242	100 ± 1	100.39	99.18, 101.62
Transformer oil	1260	100 ± 3	100.07	98.65, 101.48

a From Uriano, 1982.
b Uncertainty is expressed at the 95% confidence level.
c From Kafadar and Eberhardt, 1983.

MONS 005513

approach to quantitation using "diagnostic peaks." The rationale for selection of these diagnostic peaks is discussed in Section I.B.2.b, above. Although subject to some error, the authors consider the inherent error small relative to total PCB quantitation at the parts per billion range. They also assert that the small, unresolved peaks are more likely to be (or contain) nonPCB components such as polychloroterpenes (toxaphene). The validity of the approach has not been reported.

Tuinstra et al. (1983) presented an extension of the above approach. For regulatory analyses, where the full quantitation of samples below the regulatory cut-off level is of no interest, they selected six PCB congeners (Table 8-IV) for use in quantitation. The six are present in at least one Aroclor mixture, tend to accumulate in biological samples, are commercially available, and are chromatographically resolved from other congeners. This approach may be especially useful in large sample screening programs, where the Aroclor-derived PCB patterns are similar and compliance with a regulatory cut-off is the primary concern.

Simplistic quantitation routines are still used with HRGC, even though most analysts choose it over PGC for the increased information content. Gordon et al. (1982) used only three peaks from each Aroclor standard to quantitate PCBs in transformer oil by HRGC/ECD. While PCBs do not weather extensively in transformer oil and are thus more likely to resemble the parent Aroclor, this method utilizes only a small portion of the available information. Schulte et al. (1976) recommended quantitation of HRGC/ECD chromatograms based on two selected characteristic peaks in food extracts.

3. Comparison of quantitation by PGC/ECD and HRGC/ECD: Wolff et al. (1982a) used one tri-, penta-, and hexachlorobiphenyl as standards for HRGC/ECD quantitation of trithrough heptachlorobiphenyls in plasma and adipose samples of occupationally exposed people. Quantitation by this sum of individual peaks gave comparable results to the Webb-McCall method using PGC/ECD. Both methods gave lower values than the sum of peak areas method using PGC/ECD data.

A collaborative study of PCBs and organochlorine pesticides in open ocean waters come to an emphatic conclusion that PCB concentrations in seawater should not be reported in terms of Aroclor 1254 (Palmork et al., 1982). Almost all of the literature had previously reported seawater concentrations as an Aroclor 1254 equivalent. The study showed that the measured amounts of individual PCB congeners

Table 8-IV. Six PCBs Used for Regulatory Tolerance Purposes

Compound	IUPAC No.	Maximum Percentage in Technical Aroclors	Derived Tolerance[a] (mg/kg)
2,4,4'-Trichlorobiphenyl	28	10 (In Aroclor 1242)	0.5
2,2',5,5'-Tetrachlorobiphenyl	52	4 (In Aroclor 1254)	0.2
2,2',4,5,5'-Pentachlorobiphenyl	101	8 (In Aroclor 1254)	0.4
2,2',3,4,4',5-Hexachlorobiphenyl	138	10 (In Aroclor 1260)	0.5
2,2',4,4',5,5'-Hexachlorobiphenyl	153	10 (In Aroclor 1260)	0.5
2,2',3,4,4',5,5'-Heptachlorobiphenyl	180	12 (In Aroclor 1260)	0.6

[a] Derived from The Netherlands official tolerance of 5 mg/kg in fish assuming (worst case) that only one technical Aroclor mixture is present in a sample.

Source: Tuinstra et al. (1983); reproduced with permission, copyright 1983, Gordon and Breach Science Publishers, Ltd.

MONS 005515

in a single sample varied from the equivalent of 0.06 to 1.57 ng/L Aroclor 1254 indicating severe distortion of the Aroclor pattern. The study authors recommended that congener-specific PCB measurement was the only valid method for determining PCBs in open ocean water.

The PCB concentrations in air samples were measured by PGC/ECD, HRGC/ECD on three different columns, and by dual column HRGC/ECD, as shown in Table 8-V (Singer et al., 1983). The dual column approach involved simultaneous injection of the sample onto two columns in one GC oven. The quantitative results decreased about one order of magnitude for each of the levels of increased analytical sophistication. The HRGC analyses on the different single columns agree fairly well and are roughly an order of magnitude less than the PGC data and an order of magnitude greater than the dual column HRGC data. Singer et al. believe that the higher values result from erroneous quantitation of interferences along with the PCBs and speculate that most of the data for PCB concentrations in ambient air may be biased high. This conclusion should be verified by independent confirmatory techniques. It is unclear from the article whether the dual column HRGC approach is eliminating only interferences, as the authors claim, or applying overly-stringent identification criteria (see Section I.B.2.c, above).

4. Gas chromatography/electron impact ionization mass spectrometry: The ability of EIMS to easily sort PCBs by homolog has led to a tendency among GC/EIMS users to quantitate by homolog (i.e., summing all peaks for each homolog). Another major difference from ECD is the ability to quantitate using either a single PCB-specific m/z peak or the total ion current. The latter corresponds to an analog detector output.

The first reported GC/EIMS quantitation of PCBs was a simple translation of classical GC/ECD quantitation: comparison of "the area under one or more of the eight PCB peaks to the area of a known amount of a standard" (Bonelli, 1972a,b). Eichelberger et al. (1974) chose what they termed "the conventional approach" and assumed that the PCB mixture was one of the commercial mixtures. The total peak area for each selected ion monitoring (SIM) mass in the sample and standard were compared using an internal standard to normalize the peak areas. Williams and Benoit (1979) used the summed total integrated area for six to eight selected peaks for quantitation of PCBs in several household products.

A multiple regression statistical analysis program quantitated HRGC/EIMS data for sediment samples using standard areas for 40 peaks in Aroclors 1242, 1248, 1254 and 1260

Table B-V Comparison of PCB Concentrtions in Air Samples Determined by PGC, HRGC, and Dual Column HRGC[a]

No	Sample Code	Packed	Single Capillary Column SP-2100	Single Capillary Column OV-1	Single Capillary Column SE-54	Dual Column OV-1/SE-54
1	HAM-S1-12-16	66	4.2	5.3	1.4	0.4
2	HAM-S1-12-17	44	1.0	2.7	3.0	0.7
3	HAM-S1-12-18	7.1	2.2	2.6	1.2	0.0
4	SAR-S1-U1-16	58	4.6[b]	6.1	4.3	0.6
5	SAR-S1-U1-18	6.2	1.6[b]	3.2	1.0	0.02
6	SUD-S1-S1-18	52	3.8[b]	2.3	2.1	0.0
7	SUD-S1-S1-17	53	1.7[b]	2.9	2.0	0.0
8	SUD-S1-S1-4	47	4.1[b]	3.9	2.8	0.3
9	SUD-S1-S1-1	66	3.9[b]	3.9	3.1	0.8
10	SAR-S1-U1-15	115	3.5[b]	3.7	14	0.6
11	SAR-S1-U1-17	19	3.7[b]	3.3	2.3	0.2
12	HAM-S1-U-4	173	4.8[b]	5.2	4.1	1.4
13	HAM-S1-U-1	317	11[b]	11	7.0	3.3
14	TOR-S1-U1-1	28	12[b]	10	10	5.4
15	TOR-S1-U1-2	238	23[b]	16	15	6.9
16	TOR-S1-U1-18	6.4	4.1[b]	5.5	4.7	1.6
17	HAM-S1-U2-16	31	3.6[b]	2.3	1.7	0.2
18	MIS-S1-U4-15	6.7	2.4[b]	3.4	3.3	0.2
19	MIS-S1-U4-19	13	3.9[b]	3.2	3.4	0.2
20	MIS-S1-U4-17	1.5	4.0[b]	2.4	1.8	0.4
21	HAM-S1-U2-4	128	2.4[b]	3.8	3.0	0.9
22	MIS-S1-U4-16	19	1.8[b]	2.5	2.9	0.1
23	HAM-S1-U2-18	25	4.4[b]	2.2	1.6	0.2
24	HAM-S1-U-5	52	8.7[b]	0.7	1.6	0.2
25	LON-S1-S1-18	35	11[b]	9.4	9.1	6.3
26	SAR-S1-U-2	1,615	6.8[b]	4.3	6.5	2.1
27	HAM-S1-U-15	68	20[b]	5.9	9.7	1.9
28	MIS-S1-U1-3	-	11[b]	2.9	3.1	0.6

a Samples analyzed on Hewlett-Packard 5840A or 5880A GC with splitless injection and ECD detection. The packed column was 9' x 1/8" od SS, packed with 1% Dexsil 400 on Anachrom Q. The capillary columns were all 25 m x 0.2 mm ID. Concentrations are expressed as ng PCBs/m³ air

b A poorly resolved peak is present around RT = 26 min, which was originally considered as PCB. In this set of data the peak was excluded.

Source: Singer et al. (1983), reproduced with permission, copyright 1983 by Butterworths Publishers (Ann Arbor Science).

MONS 005517

(Liu et al., 1984) to yield an "Aroclor" concentration. Unweathered Aroclor mixtures yielded very low deviations from the expected value, while weathered PCBs extracted from field sediment samples gave less reliable quantitations.

A single isomer for each homolog has been used to calibrate HRGC/EIMS for quantitation of PCBs in sludge (Erickson and Pellizzari, 1977, 1979) and stack gases (Haile et al., 1983a,b, 1984). Stack gas samples from the M/T Vulcanus I were analyzed by HRGC/HREIMS (Ackerman et al., 1983b). The analytical system was calibrated using a suite of three isomers for each homolog (except $C_{12}Cl_{10}$), as shown in Table 8-VI. An average response factor for the three isomers was used to quantitate the unknown isomers for that homolog. 2,3,6-Tribromobiphenyl was added to the sample before extraction or cleanup to monitor recovery and d_{12}-chrysene was coinjected with each sample as an internal standard. Instrumental detection limits were either 25 pg/μL or 100 pg/μL for each homolog.

In one of the few papers addressing analysis of noncommercial PCBs, Tindall and Wininger (1980), established homolog response ratios using an unspecified number of isomers per homolog. The highest and lowest response factors for a homolog were averaged to give the average response factor relative to tribromobiphenyl. Collard and Irwin (1982a,b, 1983) and Dow (1981) used 22 congeners to establish response factors. For homologs with more than one isomer in the standard, a summed intensity was used. A daily calibration plot at three concentrations was used for comparison of the summed peak heights for one homolog.

Martelli et al. (1981) reported the EIMS relative response factors for 45 PCB congeners (Table 7-XI). The relative standard deviation per homolog ranged from 0.7% (3 of 46 possible isomers measured) to 21% (11 of 42 isomers measured). They proposed using these average response factors on GC/EIMS quantitation of PCBs by homolog.

The relative response factors (RRF) for 77 PCB congeners (Tables 7-XII and 7-XIII and Figure 7-15), obtained by both quadrupole and magnetic sector instruments, were used to determine the average RRFs by homolog (Erickson et al., 1982, 1983b; Stanley et al., 1983). A subset of 11 congeners having average RRFs and RRTs (Table 7-XIV) were recommended for use as calibrants in a method for analysis of by-product PCBs in product and product waste samples (Erickson et al., 1982, 1983b). The approach, similar to those discussed above, utilizes the most complete set of EIMS response factors available.

MONS 005518

Table 8-VI. PCB Congeners Used to Determine Response Factors

Homolog	PCB Stock Solution 1	2	3
Monochloro	2	3	4
Dichloro	2,2'	2,4	2,6
Trichloro	2',3,4	2,4,6	2,4,4'
Tetrachloro	2,2',6,6'	3,3',4,4'	2,2',4,4'
Pentachloro	2,2',4,6,6'	2,3,4,4',6	2,3,3',5,6
Hexachloro	2,2',3,3',6,6'	2,2',4,4',6,6'	2,2',3,5,5',6
Heptachloro	2,2',3,4,5,5',6	2,2',3,4,4',5,6	2,2',3,3',4,4',6
Octachloro	2,2',3,3',4,5,6,6'	2,2',3,3',4,4',5,5'	2,2',3,3',5,5',6,6'
Nonochloro	2,2'3,3',4,5,5',6,6'	2,2',3,3',4,4',5,5',6	2,2',3,3',4,4',5,6,6'
Decachloro	2,2',3,3',4,4',5,5',6,6'	-----	-----

Source: Ackerman et al (1983b).

MONS 005519

5. Miscellaneous: Cairns and Jacobson (1977) advocated PCB quantitation by PGC/CIMS because of the reduction in interferences by other halogenated compounds such as DDE relative to GC/ECD. They did not compare CIMS with EIMS, however.

As discussed in Chapter 7, perchlorination and dehydrochlorination, followed by PGC/ECD and PGC/FID determinations, respectively, have been proposed as PCB quantitation techniques which eliminate many of the problems arising from multiple congeners. An advantage of these techniques is that the area of a single peak is being measured, so there is less potential for error. A disadvantage is that the derivatization step introduces its own source of error. In addition qualitative information about the PCB congener distribution is lost. Safe (1976) suggested that perchlorination would be more consistently accurate than quantitation of the complex chromatogram of the original PCB mixtures because of the variability in ECD response factors (see Table 7-VI).

TLC and HPLC have also been employed as quantitative techniques. TLC spots can only be semiquantitated with visual interpretation. Probably order-of-magnitude estimations of concentration are possible. With a densitometer, TLC spots can be quantitated with more precision. HPLC quantitation is at least as precise as most GC quantitations. However, problems of quantitating multiple peaks, insufficient standards, coelution of homologs, etc., afflict HPLC in much the same way as GC. The absorption maxima and extinction coefficients for 27 congeners (Hutzinger et al., 1974a; see Chapter 2) indicate considerable variability can be expected in the of HPLC/UV response factors.

6. Automated quantitation: For many analyses, quantitation of PCBs is the most labor-intensive step. Even with electronic integration of all of the peaks in a chromatogram, the analyst often faces a long task of eliminating nonPCB peaks and totaling the areas. Thus, it is only logical that analysts have increasingly sought to automate the data reduction. The automated data reduction techniques which have been reported can be categorized as either simple integration routines or pattern recognition routines. Pattern recognition routines were discussed above under qualitative data reduction.

The simplest automated integration routine sums the area of all peaks within a given retention window. The total area is then compared to the corresponding area for a standard (usually an Aroclor) and the concentration reported. A more complex variation involves individual peak quantitation by comparison of the peaks to those in an Aroclor cocktail.

Bush et al. (1982; 1983) have automated such a system. Individual response factors were used for quantitation of 72 peaks in unknowns.

Zobel (1974) devised a computer fit routine for PGC data which matched the sample chromatogram with various "co-added" Aroclor chromatograms to obtain a best fit. "Spuriously large or small peak heights, caused by interfering compounds or metabolism, are automatically sorted and rejected." The method reports results in terms of the different Aroclors and can be modified to generate an estimate of "premetabolism" PCB content.

Several authors have reported computerized quantitation techniques for PCBs in transformer oils (Newton and Laski, 1983; Colby et al., 1983; Colby and Picker, 1983; Gossman, 1983; Lea et al., 1983; Picker and Colby, 1983). While automation of this time-consuming step is appealing for economic reasons, trained analysts must both validate the quantitation with real samples and audit the results during routine application for QC purposes.

In an intralaboratory comparison of several matrix/cleanup/GC column/detector/quantitation combinations, Levine et al. (1983) found some significant differences in quantitation results. For instance, the PGC/HECD/area quantitation results for ~ 150 ppm Aroclor 1254 in waste road oil were about twice as high as those obtained by PGC/HECD/peak heights, PGC/ECD/area, PGC/ECD/peak height, or a similar set of four HRGC/detector/quantitation combinations. The authors concluded that a computerized data system did not yield more accurate results than either a low-cost printer/plotter integrator or a ruler (for peak heights).

7. Measurement of PCB recovery with surrogates: Recovery surrogates are added prior to any sample treatment and are used to assess the recovery of the native PCBs through the extraction and cleanup. Like the native PCBs, surrogates may also be quantitated against the internal standard. Since the amount added is known, the surrogate recovery can be calculated. The criteria for selection of recovery surrogates are similar to those for internal standards discussed above. ^{13}C-Labeled PCB congeners have been used as recovery surrogates in by-product PCB analysis (Erickson et al., 1982, 1983b, 1983d; Erickson, 1984a, 1984b, 1984c, 1984d). Knowledge of the percent recovery is useful in monitoring extraction/cleanup performance. The final reported concentration may be corrected for recovery if desired, or the value found and percent recovery reported separately. It should be noted that if the recovery surrogates and analytes

MONS 005521

are not, in fact, equally recovered, then the reported recovery is meaningless. This can happen if the surrogates are not fully incorporated into the matrix.

8. Discussion: The applicability of the different quantitation techniques depends on the analytical technique, the PCB concentrations, consistency of the PCB pattern within a sample set, and analytical objectives. HRGC permits identification and quantitation of individual congeners, while PGC is generally limited to either reporting an "Aroclor" concentration, or "total PCB" concentration. If MS is used as the detector, the different homologs are readily discernable, and concentration by homolog is often reported. If the PCB pattern is consistent with that of a commerical mixture (e.g., transformer askarels), quantitation of GC/ECD data against a known quantity of Aroclor may be appropriate and can yield satisfactory data. This approach must be utilized with increasing caution as the chromatographic pattern diverges from that of the standard. The objectives of the data user also affect the appropriateness of the quantitation techniques. A study of selective degradation of congeners in an Aroclor mixture would require quantitation of individual peaks, while analysis of a waste to determine disposal requirements may only require a total PCB quantitation.

The analyst employing PGC/ECD for trace environmental samples will probably obtain the best results using the Webb-McCall technique. The best technhique for quantitation of environmental samples using HRGC/ECD is not as clearly defined. "Total PCB" values may be obtained by integration of all of the peaks, using response factors generated from an Aroclor cocktail (see Bush et al., 1982). The approach, used by Zell and Ballschmiter (1980), of quantitating only a selected few "diagnostic peaks" may be appropriate for some applications, provided the PCB patterns are similar and provided that the approach is thoroughly validated. For regulatory cutoff analyses, the approach used by Tuinstra et al. (1983) which uses six specific, diagnostic congeners appears to be both reasonable and expedient.

If the PCB pattern closely resembles that of the commercial mixtures (e.g., transformer oils), quantitation against an Aroclor standard, either by total area, or by the area of selected peaks may be appropriate. These analyses are often automated to reduce the labor costs. The analyst must review the data and employ appropriate QC measures to monitor the data quality.

When the PCBs are present at sufficient levels, when there are significant levels of chlorinated interferences, or when the situation demands additional qualitative

confidence, EIMS should be used as the GC detector. With mass spectral data, PCBs are most often quantitated by homolog, generally with only one calibration isomer per homolog. The added information of congener-specific quantitation may be obtained the same way as with HRGC/ECD data, i.e., the response factors and retention times for each congener of interest are obtained with authentic standards.

Regardless of the quantitation technique employed, it should be described in detail or adequately referenced in the analysis report or publication. As noted repeatedly in this book, the data reduction can be a significant or even major source of analytical error. Thus, the analyst must document this step with the same detail as is customary for instrumentation and procedure.

III. DATA REPORTING

The data report must be formatted to fulfill the analytical objectives. If individual congener concentrations are needed, the report will be complex, while if "total PCB" is sufficient, the data report may consist of a single value. The report must specify the reporting units. Units such as micrograms per gram (solids), micrograms per liter (water), and micrograms per cubic meter (air) are recommended. Parts per million and parts per billion can be confusing. Not only is there international disagreement on the term "billion" (10^9 in American System; 10^{12} in British System), but also it may be unclear in some matrices whether the measure is weight/weight or weight/volume. For high density liquid samples (e.g., a halogenated solvent), the difference can be significant.

The analyst should include on the data report some measure of the qualitative confidence. This is often done in the text, or as a footnote.

The data report should include mention of any recovery correction employed and the correction factor. Recovery correction has not been customary practice in residue analysis. Often the error associated with the recovery measurement is larger than the error associated with the PCB quantitation, so a recovery correction may add to rather than reduce uncertainty of the reported value.

The analyst must treat values near the detection limit appropriately. "Zero" should never be reported; only "not detected," "trace," or other expression of the limit of detection (LOD) or the limit of quantitation (LOQ). If samples or congeners are reported as "not detected," "trace,"

MONS 005523

"not quantitatable," etc., the numerical value or estimate of the LOD or LOQ should be stated in the data report. Additional guidance is available (Keith et al., 1983; Crummett, 1979; MacDougall et al., 1980; Glaser et al., 1981; Long and Winefordner, 1983).

Finally, as a QC measure, the data report should include sufficient information to trace the data. In addition to the customer's sample number, an internal sample code, data file code, notebook number, analyst identifier, etc., may be appropriate.

MONS 005524

9

QUALITY ASSURANCE

I. GENERAL CONSIDERATIONS

Emphasis on quality assurance (QA) in chemical analysis has increased dramatically in the past few years with the realization that data of unknown quality are virtually useless. In previous chapters, QA considerations have occasionally been mentioned with regards to specific techniques. This chapter focuses on both general QA considerations and specific quality control (QC) measures applied to PCBs.

The terms "quality assurance" and "quality control" have often been inappropriately used. QA is generally defined as the program or structure within an organization which plans, designs, and monitors the QC procedures and affirms the data quality in reports. The elements of a QA program plan for the Office of Toxic Substances in the USEPA (EPA, 1983c) are listed in Table 9-I. The specific requirements for other QA plans can vary from this list, but the general content should be similar.

QC is the term used to describe the activities in the QA program which control errors and define the data quality. Some of the potential QC elements or activities are listed in Table 9-II. Few QC programs, if any, will implement all of these measures. The selection of measures and the degree to which they are applied (e.g., frequency of calibration) are dependent on the analytical objectives of the program and on the procedures, people, and equipment being used. A third term, quality assessment, describes the data verification process. For more details on quality assurance the reader is referred to more detailed reviews on the subject (Keith et al., 1983; MacDougall et al., 1980; EPA, 1979c,f, 1980a,b, 1983c; Cardone, 1983a,b; Cairns and Rogers, 1983; Horwitz, 1983; Kateman and Pijpers, 1981; Kirchmer, 1983; Sherma, 1981; Watts, 1980).

MONS 005525

Table 9-1. Suggested Table of Contents for QA Project Plan

1.0	Title page
2.0	Table of contents
3.0	Project description and objectives
4.0	Project organization and management
5.0	Personnel qualifications
6.0	Facilities, equipment, consumables, and services
	6.1 Facilities and equipment
	6.1.1 Evaluation
	6.1.2 Inspection and maintenance
	6.1.3 Calibration procedures and reference materials
	6.2 Consumables
	6.3 Services
7.0	Data generation
	7.1 Experimental design
	7.2 Sample collection
	7.3 Sample custody
	7.4 Laboratory analysis procedures
	7.5 Internal quality control checks
	7.6 Performance and system audits
8.0	Data processing
	8.1 Collection
	8.2 Validation
	8.3 Storage
	8.4 Transfer
	8.5 Reduction
	8.6 Analysis
9.0	Data quality assessment
	9.1 Precision
	9.2 Accuracy
	9.3 Representativeness
	9.4 Comparability
	9.5 Completeness
10.0	Corrective action
11.0	Documentation and reporting
	11.1 Documentation
	11.2 Document control
	11.3 Quality assurance reports to management
	11.4 Report design

Source: EPA, 1983c.

MONS 005526

Table 9-II. Quality Control Considerations in PCB Analysis

METHOD VALIDATION
- Analyze blanks
- Analyze spikes
- Analyze standard addition samples
- Analyze replicates (precision)
- Assess potential interferences
- Conduct a ruggedness test
- Compare to other methods (accuracy)
- Select and validate PCBs to be used for instrumental calibration
- Assess transferability to other analysts
- Establish instrumental performance criteria (e.g., sensitivity, resolution)
- Determine instrumental limit of detection
- Determine instrumental limit of quantitation
- Determine method limit of detection/quantitation
- Determine range of quantitation
- Decide on treatment of questionable identifications
- Decide on treatment of trace data
- Conduct a collaborative study

SAMPLING
- Use field controls (e.g., 10%) to assess losses
- Use field blanks (e.g., 10%) to assess contamination
- Use a well-designed sampling scheme to fit study objectives
- Evaluate representativeness of sampling scheme
- Use a validated sample preservation and storage procedure
- Use clear, unambiguous, informative, permanent labels

METHOD EXECUTION
- Monitor instrumental performance (e.g., sensitivity, resolution)
- Calibrate instrumentation
- Calibrate apparatus (e.g., 1-mL volume marks on sample vials)
- Verify reagent and standard purity
- Verify reagent and standard identity
- Verify reagent and standard concentration
- Periodically check stability of standard solutions
- Control glassware contamination
- Monitor glassware contamination with blanks
- Use either sample traceability (not legally defensible) or chain of custody (legally defensible)

MONS 005527

Table 9-II (continued)

SAMPLE PREPARATION AND ANALYSIS
- Include blanks (e.g., 10%) with each sample set
- Include replicates (e.g., 10%) with each sample set
- Include spikes (e.g., 10%) with each sample set
- Include check samples (e.g., 10%) with each sample set
- Include blind check samples on a regular basis
- Repeat analyses on a regular basis
- Use surrogates to measure method recovery on each sample
- Use internal standards for quantitation
- Determine LOD, LOQ, MDL, or MQL for each analysis day or sample set
- Monitor retention times for PCB identification

DATA REDUCTION AND REPORTING
- Validate equations, algorithms, or programs
- Check selected identifications by a second analyst (e.g., 10%)
- Check selected quantitations by a second analyst (e.g., 10%)
- Label and annotate all chromatograms and other output
- Include sample number, date of analysis, notebook reference, or other information in analysis report so that data may be traced
- Cite method and document all deviations in the analysis report
- Report data in uniform, unambiguous units
- Report analytical uncertainty
- Report any blank or recovery corrections
- Report results of QC samples
- Footnote any questionable identifications or quantitations
- Do not report any quantitation below the LOQ
- Report the LOD, LOQ, MDL, or MQL and when it was determined
- Report results only to the appropriate number of significant figures
- Review data with another analyst
- Repeat questionable analyses

CONFIRMATION
- Analyze sample using an alternate technique (e.g., additional column cleanup)
- Use a confirmatory technique (e.g., alternate GC columns, more specific detector)
- Send to another laboratory for a repeat analysis

MONS 005528

Table 9-II (concluded)

NETWORKS OF MULTIPLE LABORATORIES
- Designate a QA laboratory
- Use the same procedure
- Use a consistent reporting format
- Use aliquots of the same standard solution and critical reagents
- Use similar apparatus and instrumentation
- Provide assistance to the analysts from both QA lab and others in network
- Conduct periodic informal site visits for information exchange
- Conduct periodic formal systems audits
- Conduct periodic informal QC check sample analyses
- Conduct periodic formal performance audits
- Use a central sample tracking, coding, scheduling, and distribution system
- Incorporate blind duplicates, blanks, and spikes into the sample set
- Have blind duplicates analyzed by different laboratories
- Have a central data review organization
- Conduct periodic confirmatory analyses

The QA program for a given laboratory, if already in place and operational, should need little adjustment for analysis of samples for PCBs. The QC, however, must be tailored not only to the general considerations discussed in this paragraph, but also to the analytical peculiarities of PCBs discussed in the following sections and in other chapters of this book. The first step in planning a QC program is to establish the data quality needed by the end user. At this point, the analyst and user must agree (or at least compromise) on the data quality objectives; specifically the degree of qualitative confidence, limit of detection, data confidence level (i.e., precision and accuracy), validity of the method, and the amount of QC needed. Next, the analyst must design the QC program to fit these needs in the context of the analytical program. Finally, the analytical program is conducted. During this last phase, it is critical that all of the plans for QC be executed. The analyst must insert appropriate blanks and replicates. The QA staff must conduct audits. Management must insist on timely QA/QC reports so that corrective action can be taken. Last, and most importantly, the QC data and a data quality assessment should accompany the analytical report so that the user will know the data quality. The vast majority of the PCB publications omit the last step, forcing the reader to speculate on the data quality.

MONS 005529

II. SPECIAL CONSIDERATIONS IN PCB ANALYSES

Since PCBs generally occur as complex mixtures of analytes, special QC measures must be considered. The PCBs used for calibration of the analytical instrument may be a mixture (e.g., Aroclor 1254) similar to that found in the samples or a group of individual congeners. Any realistic option is a compromise from calibration with all 209 congeners. Thus, an estimate of the error induced by the compromise should accompany the data. The selection of calibration mixtures was discussed in Chapter 8.

Because of the complexity of the data, special precautions should be taken to assure both the qualitative and quantitative aspects. Many quantitation techniques involve summing the calculated response or concentration for many individual PCB peaks to yield a total PCB value. Any systematic error replicated through several quantitations could result in a magnified error in the reported result. The complexity of the calculations also increases the chance of calculation and transcription mistakes.

A. Reference Materials

A major component of a good QC program is the inclusion of reference materials as QC check samples. These may be routine daily accuracy checks, or may be part of a performance audit. Regardless of their use, reference materials must be validated prior to use. While in-house preparation may be appropriate in many cases, the use of reference materials certified by an external organization lends much more credence to the results. Table 9-III lists some reference materials. The availability of standards of neat PCB mixtures and individual congeners was discussed in Chapter 2.

B. QA in Multiple Laboratory Networks

When data from more than one laboratory are to be compared, special measures must be taken to assure data comparability. In a formal multi-laboratory network, it is advisable that one organization function as a QA laboratory. The QA laboratory must ensure that all laboratories in the network:

- Use the same procedure.
- Execute these procedures without significant variation.

MONS 005530

Table 9-III. Reference Materials for PCB Analysis

Matrix	PCB Composition	PCB Concentration	Code	Availability	Reference
Wet sediment	Aroclor 1254/1260 (1:1)	1 ppm	-	Marine Analytical Chemistry Standards Program Atlantic Research Laboratory National Research Council 1411 Oxford Street Halifax, Nova Scotia B3H 3Z1	Chau et al., 1979 Chau and Lee, 1980
Dried sediment	Aroclor 1254/1260 (1:1)	2 ppm	-		
Water oil	Aroclor 1242	100 µg/g	SRM 1581	U.S. National Bureau of Standards Washington, DC 20234	Uriano, 1982
Water oil	Aroclor 1260	100 µg/g			
Transformer oil	Aroclor 1242	100 µg/g			
Transformer oil	Aroclor 1260	100 µg/g			
Methanol[a]	Aroclor 1242	5,000 µg/mL	E 104	QA Branch EMSL - Cincinnati U.S. EPA Cincinnati, OH 45268	EPA, 1983b
Methanol[a]	Aroclor 1254	5,000 µg/mL	E 105		
Methanol[a]	Aroclor 1232	5,000 µg/mL	E 107		
Methanol[a]	Aroclor 1248	5,000 µg/mL	E 108		
Methanol[a]	Aroclor 1260	5,000 µg/mL	E 109		
Methanol[a]	Aroclor 1016	5,000 µg/mL	E 110		
Methanol[a]	Aroclor 1221	5,000 µg/mL	E 126		
Methanol[a]	Aroclor 1262	5,000 µg/mL	E 130		
Acetone[a]	Aroclor 1268	2,500 µg/mL	E 131		
Isooctane	Aroclor 1016	1,000 µg/mL	E 125		
Isooctane	Aroclor 1242	1,000 µg/mL	E 132		
Isooctane	Aroclor 1254	1,000 µg/mL	E 135		
Isooctane	Aroclor 1260	1,000 µg/mL	E 129		
Capacitor oil	Aroclor 1016	3 levels[b]	-		
Capacitor oil	Aroclor 1242	3 levels[b]	-		

MONS 005531

Table 9-III (continued)

Matrix	PCB Composition	PCB Concentration	Code	Availability	Reference
Capacitor oil	Aroclor 1254	3 levels[b]	-		
Capacitor oil	Aroclor 1260	3 levels[b]	-		
Hydraulic oil	Aroclor 1016	3 levels[b]	-		
Hydraulic oil	Aroclor 1242	3 levels[b]	-		
Hydraulic oil	Aroclor 1254	3 levels[b]	-		
Hydraulic oil	Aroclor 1260	3 levels[b]	-		
Transformer oil	Aroclor 1016	3 levels[b]	-		
Transformer oil	Aroclor 1242	3 levels[b]	-		
Transformer oil	Aroclor 1254	3 levels[b]	-		
Transformer oil	Aroclor 1260	3 levels[b]	-		
Fish	Aroclor 1242	2 levels[b]	-		
Fish	Aroclor 1254	2 levels[b]	-		
Fish	Aroclor 1260	2 levels[b]	-		
Sediment	Aroclor 1242	3 levels[b]	-		
Sediment	Aroclor 1254	3 levels[b]	-		

a for spiking water to prepare a water check sample for priority pollutant or other analyses
b levels not specified in catalog.

MONS 005532

- Obtain similar performance (i.e., precision and accuracy).

- Report results in a consistent format.

It is advisable that all network members use aliquots of the same standard solutions, use commonly obtained reagents where critical (e.g., Florisil for column cleanup), and use similar apparatus and instrumentation. The QA measures specifically applicable to multiple laboratory analysis networks are listed in Table 9-II.

As an example of such a network, the U.S. EPA has operated a network of laboratories for pesticide analysis in a variety of sample matrices (blood, adipose, milk, urine, soil, water, air, wildlife, and others) since the late 1960s. As part of this network, an EPA laboratory (the QA Section of the Health Effects Research Laboratory, ORD, EPA, Research Triangle Park, NC, until 1982; now Environmental Monitoring and Support Laboratory, ORD, EPA, Las Vegas, NV)) functions as a central QA laboratory. Analysis of composites, development of methods, revision of the methods manual, supply of special reagents and standards, maintenance of instruments, site visits, analyst assistance, assessment of method execution, and conduct of a periodic QC check sample program are among this group's duties. The check sample program consists of issuing a standard pesticide reference material (e.g., fat spiked with pesticides and PCBs), receiving results, and evaluating laboratory performance. The results from the 10-20 participating laboratories are tabulated and each laboratory given a numerical performance score based on both qualitative and quantitative results. Results for three fat samples spiked with PCBs at 0.5-1.5 ppm levels averaged between 93% and 105% of the formulated concentration, with relative standard deviations between 12 and 34% (Personal communications, R. R. Watts, U.S. EPA, Research Triangle Park, NC, 1980-1981). However, several participants--50% in one case--did not report PCBs in these samples. It is not known whether participants "missed" the PCBs or simply chose not to report their findings. Despite the relatively good performances noted above, at least one participant was found (Lucas et al., 1980) to be short-cutting the prescribed analytical method (Watts, 1980). The participating laboratory had eliminated a liquid chromatographic fractionation and was quantitating only a single heptachlorobiphenyl peak against an Aroclor 1260 standard.

MONS 005533

III. PREVIOUS QC MEASURES

The U.S. EPA has taken steps to implement strong QC programs in various standard methods of analysis and as part of long-term project goals (EPA, 1979c, 1980a,b, 1981a; Bellar and Lichtenberg, 1981). Table 3-I listed the standard procedures that acknowledge the need to follow some type of QC program. QC measures have also been cited in several collaborative studies (DCMA, 1982; Sawyer, 1973, 1978b; Delfino and Easty, 1979; Devenish and Harling-Bowen, 1980; Pittaway and Horner, 1982). These and other collaborative studies are also discussed in Chapter 10.

The QC program for the Dry Color Manufacturers Association (DCMA, 1982) collaborative study included instrument calibration specifications, performance evaluation of the gas chromatography column with a standard mixture of PCBs, and measurement of sensitivity for PCBs by serial dilution of the standard, method blanks, specification of quantitation procedures and validation of sample preparation procedure. The validation of sample extraction, cleanup and analysis included workup of blind and known spike samples. The results of the DCMA study indicate that variance in reported PCB levels between laboratories was significantly reduced when a commercially prepared quantitation standard was used by all participating laboratories. Data from the DCMA report indicated relative standard deviations of 3.1 to 9.1% within a laboratory, 2.4 to 40% between laboratories, and 7.3 to 41% for the total reproducibility for analysis of three different pigments.

The Chemical Manufacturers Association sponsored a collaborative study of PCB concentrations in five different byproduct PCB samples (Pittaway and Horner, 1982). Eight different laboratories participated in the study. In contrast to the DCMA study, no defined protocol or QC programs were specified for analysis of the matrices. Each laboratory was allowed to choose the method of extraction, cleanup, instrumental determination and quantitation, and QC program it desired. This study indicated that there are many sources of potential error in the quantitative analysis of PCBs. The lack of agreement of the measurements between laboratories indicated a true need for a strong QC program to produce comparable data.

In a study of emissions from a municipal incinerator and a co-fired (refuse-derived fuel plus coal) power plant, Haile et al. (1983a) used three laboratories to analyze the different samples. Sets of spiked fly ash were sent periodically to the laboratories to serve as QC check

MONS 005534

samples. Recovery of decachlorobiphenyl spiked at the 500-2,500 ng/g level ranged over an order of magnitude. Duplicate analyses within a laboratory differed by as much as a factor of 3.

Bush et al. (1983) have illustrated a good quality control technique for single laboratory analyses. In routine analyses of environmental samples for PCBs by automated HRGC/ECD, they utilized a quality control chart (Figure (9-1) to monitor the instrumental response. The standard was run after every sixth sample. The chart in Figure 9-1 also illustrates the additive effects of random errors. While the fluctuation of the plots for the individual congeners is small, much larger fluctuations are seen for the "Total PCB" plot.

IV. RECOMMENDED QA/QC MEASURES

A good working QA program requires a set of written standard operating procedures for instrumental operation, routine laboratory operations, data review, reporting, and all other aspects of data generation. More importantly, the QA program must have support from all levels in the organization. The goal must be to assure that data of known quality are being reported while minimizing interference with the analysis process.

Once a working QA program is in place, the specific QC aspects pertaining to PCBs are relatively simple to implement. The QC will differ from organization to organization, and indeed, according to the individual project. The QC should be discussed with the data user (i.e., the client) to reach agreement on the desired precision and accuracy.

Summaries of the QC recommendations from three analytical procedures are presented in this section as examples of thorough QC programs.

A. Transformer Oil (Jung, 1981)

In a review of analytical methods for PCB analysis in transformer oil, Jung (1981) recommended several QC measures:

1. Analyze a quality check sample daily to assess accuracy.

2. Analyze 10% of all samples in duplicate, selected at random, to assess the precision.

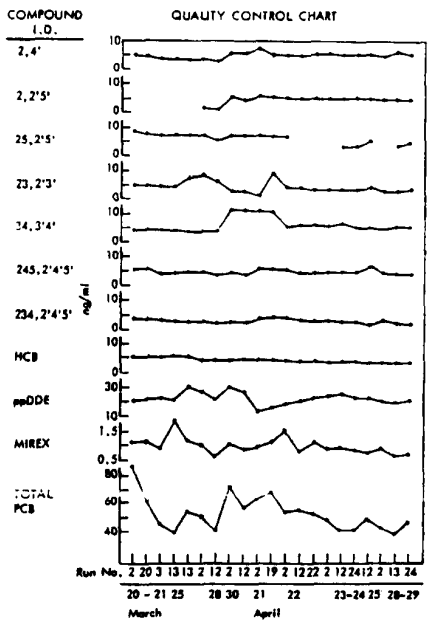


Figure 9-1. Quality Control Chart for HRGC/ECD Analysis of PCBs and Other Organochlorine Compounds in Human Milk

A "quasi-milk" QC sample, containing individual PCB congeners and insecticides at known concentrations, was analyzed after every sixth milk sample. The results, plotted above, indicate immediately whether the previous analyses are within the QC tolerances.

Reprinted, with permission, from Bush et al. (1983); copyright 1983 by Association of Official Analytical Chemists, Inc.

3. Maintain a log of precision and accuracy data.

4. Maintain a record of the retention times of unknown PCBs.

5. Analyze a certified sample, if available, at least quarterly.

8. Transformer Fluids and Waste Oils (Bellar and Lichtenberg, 1981)

The elements of a section entitled "Precision and Accuracy" include:

1. A formal QC program must be operational.

2. The laboratory must demonstrate its capability with check samples on a periodic basis.

3. The analyst must demonstrate precision and accuracy by analyzing at least four replicate standard addition samples. The recovery and standard deviation must meet EPA performance criteria (these were to be established at a later date).

4. Using the recovery and standard deviation from slope, control charts are to be constructed to serve as performance criteria.

5. At least 10% of all samples or one sample per month, whichever is greater, must be analyzed by standard addition techniques to monitor spike recoveries.

6. Each time a set of samples is analyzed or there is a change in reagents, a laboratory reagent blank should be processed.

7. Additional QC measures should be considered by each laboratory. These may include field duplicates to monitor sampling precision, qualitative confirmation with a dissimilar GC column, halogen-specific detector or MS.

8. A standard sample of PCBs in a typical oil matrix must be analyzed daily before any samples are analyzed. The results of this analysis serve as instrument status checks, calibration curve validation, and long-term precision measures.

9. An EPA QC sample must be analyzed on a quarterly basis. Results within 15% of the true value are acceptable. If the results are unacceptable, the analyst must resolve the problem.

MONS 005537

C. By-product PCBs (Erickson et al., 1983d)

The elements of the QA section of this document are:

1. A formal QA plan is required.

2. A formal QC program must be in operation, including recordkeeping, certification, and performance checks.

3. Procedural QC measures include:

a. GC performance criteria.

b. MS performance criteria.

c. Confirmation of at least 10% of all qualitative identifications by a second analyst.

d. Confirmation of at least 10% of all calculations by a second analyst.

4. Sample QC measures include:

a. Acceptable recoveries of ^{13}C-labeled surrogates (e.g., 50-150%).

b. Spectral data quality must be evaluated. The chlorine isotope intensities must be of the proper ratios (e.g., within ± 20% of the ratios observed for standards).

c. Internal standard areas must be within ± 20% from injection to injection.

d. For small (1-10) sample sets, 1 method blank, 1 duplicate (triplicate preferred), and 1 standard addition sample must accompany the set.

e. For intermediate (10-100) sample sets, the number of method blanks, replicates, and standard addition samples must comprise at least 10% each.

f. With large (> 100) sample sets, alternate QC measures may be proposed. For example, if contamination has never been observed in blanks, the frequency of method blanks may be reduced.

5. Additional QC, specific to each organization and analytical problem, should be considered.

MONS 005538

10

COLLABORATIVE STUDIES

A collaborative study is the validation of an analytical method by several laboratories. Collaborative studies are generally considered the ultimate in method validation and are required by most organizations before a method is accepted as "official," "final," etc. Collaborative studies are also termed interlaboratory studies, round robins, etc.

Guidelines for a collaborative test are available (Youden and Steiner, 1975; AOAC, 1982) although many studies differ markedly in both objectives and execution. Ideally, each participating laboratory receives the same sample set, performs the analysis according to a written protocol and reports the results to a coordinator for evaluation. Two areas of fundamental disagreement are the degree of control over the participants and the data evaluation. The objective of a true collaborative study is to evaluate a given protocol, so all variables are held as constant as possible. Many studies, however, have permitted the participants to use any method they choose. These studies, then, evaluate either the "current state of the art" or the laboratories. The other point of disagreement is the data evaluation. In a true collaborative study, where the objective is to evaluate the method performance, the statistical evaluation summarizes the precision, accuracy, and any other performance measures and then attempts to evaluate potential sources of error (random, systematic, and laboratory-specific). Many studies, however, have been used to also evaluate the participant's performance. Labs are rated by how closely they meet target values.

This chapter discusses several PCB collaborative studies in some detail because they (a) demonstrate the quality of the data obtainable for many procedures, (b) emphasize those few out of the myriad methods discussed in earlier chapters which have been subjected to this level of validation, (c) illustrate the different approaches to the conduct of collaborative studies, and (d) permit direct comparison of some of the techniques for those studies which allowed the participants to select various techniques.

MONS 005539

I. WILDLIFE (HOLDEN, 1973)

This study used three test samples containing known amounts of organochlorine pesticides, PCBs, or mercury. Sixteen of the 26 participants reported values for both a hexane solution of Chlophen A-60 and a cormorant homogenate sample (Table 10-I). The average accuracy was 99% and the precision was about ± 13% for the hexane solution and ± 22% for the cormorant sample. The participants were allowed to use their customary in-house procedures, which covered the range of extraction, cleanup, GC column, and quantitation techniques. All participants apparently used PGC/ECD.

II. CHICKEN FAT AND FISH (SAWYER, 1973)

Nine laboratories collaborated on the analysis of PCBs in hexane, chicken fat, and fish. Existing AOAC multipesticide methods with PGC/ECD or PGC/halogen specific detector (HECD or microcoulometric) quantitation were employed. The results shown in Table 10-I indicate excellent performance of the method for direct injection GC/ECD analysis with peak height quantitation. With the chicken fat which required laboratory preparation, the precision was poorer, but the accuracy was very near 100%. The accuracy for the fish was much lower (~ 75%). Similar results were obtained for all three matrices using PGC/ECD or PGC/halogen specific detector with total area quantitation.

III. PAPERBOARD (FINSTERWALDER, 1974)

Eleven laboratories participated in this AOAC study to validate a method for PCBs (Aroclor 1242 and 1254) in paperboard. The method involves alcoholic KOH extraction, Florisil column cleanup, and PGC/ECD determination. The results, shown in Table 10-I, indicate an average precision of about ± 20% relative standard deviation (RSD) and an average accuracy of about 85%. In addition to tabulation of the data and discussing potential outliers, the study author ranked the laboratories for each sample with a "1" for the highest reported concentration, a "2" for the next highest, etc. The sum of a laboratory's rank for each sample yielded a collaborative score. This technique is useful for identifying systematic errors which make a participant consistently either high or low. Laboratory ranking is discussed in more detail by Youden and Steiner (1975).

MONS 005540

Table IV-1 Summary of Collaborative Studies

Matrix	Number of Participants	Method	PCB Composition	Prepared Concentration	Mean Concentration Found[1]	Precision (S.Dev)	Accuracy[2] (%)	Reference
Hexane	16	Unspecified	Chlophen A-60	9.0 mg/l	9.71 mg/l	12.9	99.1	Holden, 1973
Effluent			Raw residue	-	111 mg/kg	22		
Hexane	9	ASAE (PGC/ECD,	Aroclor 1254/1260	5 ppm	5.66 ppm	6.3	106.9	Sawyer, 1973
Chicken fat		PN Quant.)	Aroclor 1242	8.04 ppm	8.15 ppm	12.6	Ref 1	
Fish			Aroclor 1254	5.46 ppm	5.71 ppm	13.9	75.4	
Paperboard	11	ASAE (PGC/ELCD)	Aroclor 1242	12.5 ppm	10.1 ppm	20.2	80.8	Firstenberger, 1974
			Aroclor 1242	4.7 ppm	7.2 ppm	19.6	97.5	
			Aroclor 1254	17.1 ppm	18.7 ppm[3]	15.3[3]	87.8	
			Aroclor 1254	8.5 ppm	7.6 ppm[3]	22.9[3]	89.4	
			Aroclor 1242	-	5.6 ppm	15.8		
Marine sediment	10	Unspecified	Raw residue	-	612 mg/g	21.9	-	Pavlou and Dexter, 1975
Milk	10	ASAE (PGC/ECD)	Aroclor 1254	1.30 ppm	1.15 ppm	14.5	84	Sawyer, 1974b
				2.72 ppm	2.35 ppm	17.1	86	
Solvent	8	Direct GC/ECD	Aroclor 1242	2.50 mg/ml	2.47 mg/ml	15.6	98	Battine and Tasky
Distilled water	8	Extract/GC/ECD	Aroclor 1260			18.7	95.6	1979
Paper mill effluent	5	Extract/GC/ECD	Unknown		2.76 ug/l	49.6		
Paper mill effluent	5	Extract/GC/ECD	Unknown		5.11 ug/l	36.8	91.7	
Sediment	16	Unspecified	A1242/A1254	1.00 mg/g	1.17 mg/g	19.1	117	Lee and Chow, 1980a
Wet lake sediment[4]	16	Unspecified	A1260/A1260	5.46 ppm		18.3	92.8	
			A1254/A1260	3.22 ppm		16.1	98.5	
Sediment	15	Unspecified	A1242/A1254/A1260	400 ug/g	372 ug/g[4]	12.8	93.4[4]	Lee and Chow, 1980b
Dry lake sediment	15	Unspecified	Raw residue	-	2.054 ug/g	29.8	88.9 ± 10.4[4]	
			Raw residue	-	1.200 ug/g	28.3		
Dry pigments	10	GC/ECD	2,3'-dichlorobiphenyl	-	66.6 ppm[3]	10	-	GCMA, 1982
			Decachlorobiphenyl	-	37.2 ppm[3]	7.3		
			$C_{12}H_6Cl_4$ + $C_{12}H_5Cl_5$ isomers	-	72.7 ppm	12.9		
			$C_{12}H_5Cl_5$ + $C_{12}H_4Cl_6$ isomers	-	73.8 ppm[3]	21		
			$C_{12}H_5Cl_5$ + $C_{12}H_4Cl_6$ isomers	-	66.6 ppm[3]	17		
			$C_{12}H_4Cl_6$ + $C_{12}H_3Cl_7$ isomers	-	90.1 ppm[3]	23		
			$C_{12}H_4Cl_6$ + $C_{12}H_3Cl_7$ isomers	-	69.7 ppm[3]	41		
Gas (extracts)	9	Unspecified	Raw residue	-	7.1 mg/m³	26	-	Dickinson, 1981
					4.6 mg/m³	39		

MONS 005541

Table IV-1 (continued)

Matrix	Number of Participant	Method	PCB Composition	Prepared Concentration	Mean Concentration Found[a]	Precision (% RSD)	Accuracy[b] (%)	Reference
Insulating oils	10	GC/ECD	A1242/A1254	42.0	49.0 ppm	11	105	Rouse, 1982
			A1242	5.0	5.0 ppm	0		
			A1242/A1254	48.1	48.4 ppm	13	96	
			A1260	50.1	49.0 ppm	10	97	
			A1254/A1260	35.7	39.2 ppm	16	107	
			A1254	11.4	10.5 ppm	14	98	
Sea water collected on ARE-2	7	Unspecified	Low residue		0.1 ng/l	45	-	Petrasek et al., 1982
Sediments collected on ARE-2	12	Unspecified	Aroclor 1254	75 ug/Kg	705.9 ng/Kg	23	108	Williamson, 1982
Sea water	11	Unspecified	Aroclor 1254	5 ng/l	7.7 ng/l	57	154	Williamson, 1982
Chlorinated benzene waste	16[c]	Unspecified	~ 80 components[f]		283 ppm	14		Pittsburgh and Denver, 1982; Hodges et al., 1983
Mixture of chlorinated benzenes	10	Unspecified	A1254	5	7.0 ppm	42	75	
Mixture of chlorinated benzenes	10	Unspecified	~ 23 components[f]	8 - 64 ppm[f]	64 ppm	46	75	
Mixture of aliphatic waste	10	Unspecified	$C_xH_yCl \cdot C_xH_yCl_2$	-	179 ppm	22		
Mixture of aromatic waste	10	Unspecified	$C_xH_yCl \cdot C_xH_yCl_2$	-	9.2 ppm	53		
Hexane (# 7)	4	DI GC/MS	11 components	5.0 ug/ml	4.6 ug/ml	11	117 ± 15	Erickson et al., 1983b
Hexane (# 8)	4	DI GC/MS	11 components[f]	5.0 ug/ml	10.9 ug/ml	19	186 ± 44	
Chlorinated benzene waste (# 9)	4	DI GC/MS	~ 80 components[f]	-	39.7 ug/ml	20		
Chlorinated benzene waste (# 10)	4	DI GC/MS	~ 80 components	-	11.0 ug/ml	16		
Chlorinated benzene waste (# 11)	4	Florisil GC/MS	~ 80 components	-	7.704 ug/g[d]	144		
Chlorinated benzene waste (# 12)	4	Florisil GC/MS	~ 80 components	-	4.420 ug/g[d]	102		
Chlorinated benzene waste (# 13)	4	Interpret	~ 80 components	-	23.9 ug/ml	12		
Herring oil	23	GC/MS	Low residue	5	3.19 mg/kg	93		Mestel and Wise, 1980
Herring oil			A1254	4 - 1.00 mg/kg	2.03 mg/kg	20	87 ± 23	
Bovine serum	12	GC/MS	A1254[e]	9.97 ppb[g]	23.86 ppb	37.0	239.3	Duree et al., 1980[e]
Bovine serum				49.54 ppb[g]	78.00 ppb	38.7	165.4	

MONS 005542

Table 10-1 (concluded)

Matrix	Number of Participants	Method	PCB Composition	Prepared Concentration	Mean Concentration Found	Precision (S_RSD)	Accuracy[b] (%)	Reference
Lubricating oil	19	GC/ECD	A1260	5.10 ppm	5.9	64	188	Becker, 1984
			A1247	41.0 ppm	17	18	98	
			A1260	140.1 ppm	12	57	98	
			Blank	< 1 ppm	0.55			
			A1242 and 1260	50 ppm	50	44	98	
				90 ppm	59	42	92	
			A1254	96.6 ppm	107	55	111	
			Industrial contamination	Unknown	105	63	-	
			Industrial contamination	Unknown	196	51		
			Interferences	< 1	10.1	251		

[a] Values termed "outlier" in the studies are included without elimination here.
[b] Accuracy defined as mean concentration found divided by the prepared concentration
[c] Outliers excluded by study authors.
[d] One environmental residue and two spiked samples. Values were reported as percent recovery of the spike after subtraction of the native PCBs
[e] Accuracy assessed by comparison of the results reported for duplicate dry sediment samples analyzed through the full analysis scheme against an extract of this sediment which was analyzed by direct injection onto the GC
[f] Preparation B, methylene chloride extraction with Florisil column cleanup
[g] Preparation A, hexane/KOH partition
[h] Eight participants submitted 30 data sets (two participants reported results using two methods, i.e., GC/MS and GC/ECD)
[i] Between 80 congeners over all 10 homologs were found
[j] Twenty-three congeners (all 10 homologs) spiked into previous sample
[k] Second sample ("B," mean = 3 ppm) spiked with 7-5 ppm of 72 congeners for a total spike of 69 ppm
[l] Two isomers of $C_{12}H_6Cl_4$ and 4 isomers of $C_{12}H_4Cl_6$
[m] Simplified number of isomers of each homolog
[n] One participant was much higher than all others. With the outlier omitted, the mean was 107 µg/g, 950 = %, and the range was 100-920
[o] One participant was much higher than all others. With the outlier omitted, the mean was 107 µg/g, 850 = %, and the range was 200-650
[p] In ring bound
[q] Based on in-house analysis by study coordinators

MONS 005543

IV. MARINE SEDIMENTS (PAVLOU AND HOM, 1976)

Ten participants were asked to analyze a sediment sample to assess the reliability of chlorinated hydrocarbon measurements. All participants presented values for total PCBs, seven presented a sum of DDT metabolites, and one quantitated dieldrin, cis-chlordane, and trans-chlordane. As can be seen in Table IO-I, the RSD of the PCB values for all of the laboratories was ± 22%. The participants used a variety of techniques for all steps of the analysis. The reported concentration was slightly dependent on whether the sediment was dried and on the weight of sediment used; the authors recommended drying the sediment before extraction. The quantitation technique also affected the results. "Total PCB" and "Aroclor" quantitations both led to much less accurate results than a Webb and McCall (1973) type approach, which the authors incorrectly termed a homolog quantitation. They recommended the latter approach.

V. QUANTITATION TECHNIQUES AND MILK (SAWYER, 1978b)

Ten collaborators quantitated a synthetic mixture of one tri-, two tetra-, and one pentachlorobiphenyl; one tri- and two tetrachlorobiphenyls; and another mixture of two Aroclor 1254-fortified milk samples; one milk sample containing bioincurred PCBs; and one chicken fat sample containing bioincurred Aroclor 1242. The study was conducted by the AOAC to evaluate (a) different PGC/ECD quantitation techniques and (b) the applicability of the AOAC multiresidue pesticide method to milk.

A. Quantitation Techniques

Each collaborator was asked to analyze the two synthetic PCB mixtures and the chicken fat sample by direct injection onto a PGC/ECD system which met certain specifications. The data were to be quantitated against standard Aroclor solutions supplied by the coordinator. Three quantitation techniques were to be used: (a) summation of the height of peak matching the retention time of peaks in the Aroclor standard, (b) summation of the area of peaks matching the retention time of peaks in the Aroclor standard, and (c) the individual peak comparison of Webb and McCall (1973). The first two techniques were those recommended in Section 29.018 of the AOAC method (1980a). The Webb-McCall technique was being considered for inclusion in the method as an alternate quantitation technique.

MONS 005544

Based on the results summarized in Table 10-II, the study author concluded that the Webb-McCall technique was generally an improvement over the other two techniques. The author also recommended that AOAC adopt the Webb-McCall technique as the technique of choice when residues do not exhibit a PCB pattern similar to that of an Aroclor standard.

B. Milk

The two milk samples were extracted, cleaned up, and determined by PGC/ECD using the AOAC method for quantitating PCB residues. The 85% average recovery and RSDs ranging from ± 14% to ± 17% (see Table 10-I) were considered adequate and consistent with previous results for PCBs in fatty foods (Sawyer, 1973). The author recommended that the AOAC method be modified to include milk and other fatty dairy products as applicable matrices.

VI. PAPER MILL EFFLUENT (DELFINO AND EASTY, 1979)

The collaborative study reported by Delfino and Easty (1979) focused on the analysis of PCBs in paper mill effluents. The study consisted of two phases. The first phase was used to determine the comparability of PCB methodologies between six different laboratories and the abilities of the participating analysts to perform the basic operations required for PCB analysis. These factors were determined by direct injection of a performance standard and also the simple extraction and analysis of a spiked aqueous solution. The second phase required analysis of both known and blind samples by a single method. A modified EPA wastewater analysis procedure (EPA, 1973) was followed by all participating laboratories, which involved liquid-liquid extraction, a Florisil column cleanup, and PGC/ECD determination. The silica gel microcolumn step for separation of PCBs from pesticides was deleted for this study, since pesticides were judged to be unlikely constituents of paper mill effluents.

The results of the first phase, extraction from distilled water, yielded an average recovery of 95.6% with a relative standard deviation of 14.7%. The relative standard deviation for direct injection of a standard solution was 15.6%. The results for paper mill effluent yielded similar results with 93.6% average recovery with a 16.0% relative

Table 10-11 Summary of Collaborative Test of PCB Quantitation Techniques

Matrix Solvent	Quantitation Technique[a]	Aroclor Standard	PCB Composition	Prepared Concentration	Mean Concentration Found	Precision (% RSD)	Accuracy (%)[b]
Solvent[c]	W-H	1248	2,2',5	0.19 mg/µl	0.166 mg/µl	17.1	87.4
	W-H	1248	2,2',5,5'	0.53 mg/µl	0.476 mg/µl	30.9	89.5
	W-H	1248	2,3',4',5	0.55 mg/µl	0.572 mg/µl	28.1	104.1
	W-H	1248	2,3',4,5,5'[d]	0.10 mg/µl	0.232 mg/µl	19.7	232.0
	PH	1248	Total (3)	1.28 mg/µl	1.39 mg/µl	27.9	108.6
	A	1248	Total (3)	1.28 mg/µl	1.21 mg/µl	18.5	94.5
	W-H	1248	Total (3)	1.28 mg/µl	1.22 mg/µl	6.3	95.3
	PH	1248	Total (4)[e]	1.38 mg/µl	1.49 mg/µl	16.6	115.9
	A	1248	Total (4)	1.38 mg/µl	1.54 mg/µl	28.9	111.6
	W-H	1248	Total (4)	1.38 mg/µl	1.44 mg/µl	6.5	104.4
Chicken fat[c]	PH	1242	Aroclor 1242	-[f]	6.78 ppm	12.6	-
	PH	1248	Aroclor 1242	-	6.94 ppm	5.5	-
	A	1242	Aroclor 1242	-	7.54 ppm	16.0	-
	A	1248	Aroclor 1242	-	5.89 ppm	7.7	-
	W-H	1242	Aroclor 1242	-	5.62 ppm	8.1	-
	W-H	1248	Aroclor 1242	-	6.11 ppm	7.8	-
Milk[g]	PH	1254	Aroclor 1254	1.38 ppm	1.14 ppm	16.8	82.6
	A	1254	Aroclor 1254	1.38 ppm	1.18 ppm	11.1	85.5
	W-H	1254	Aroclor 1254	1.38 ppm	1.16 ppm	15.2	84.1
	PH	1254	Aroclor 1254	2.72 ppm	2.32 ppm	18.8	85.3
	A	1254	Aroclor 1254	2.72 ppm	2.37 ppm	14.3	87.1
	W-H	1254	Aroclor 1254	2.72 ppm	2.36 ppm	10.2	86.8
	PH	1254	Aroclor 1254	-	1.38 ppm	30.4	-
	A	1254	Aroclor 1254	-	1.66 ppm	31.4	-
	W-H	1254	Aroclor 1254	-	1.15 ppm	10.4	-

a W-H = Webb and McCall (1973) individual peak quantitation, PH = total peak height versus Aroclor standard, A = total area versus Aroclor standard.

b Accuracy measured as mean concentration found divided by the prepared concentration

c Three samples analyzed by direct injection into the HGC/ECD

d All individual components, except 2,2',4,5,5'-pentachlorobiphenyl

e All four individual components

f Background residue, prepared concentration not determinable

g Sample analyzed by AOAC multiresidue extraction, cleanup, and HGC/ECD method with quantitation technique as shown

Source: Sawyer (1980b); reprinted with permission, Copyright 1980 by Association of Official Analytical Chemists

MONS 005546

standard deviation, and indicated that the method was satisfactory for paper mill effluents. The similarity of the precision and accuracy of direct injection, a distilled water sample, and the papermill samples indicated that the PGC/ECD analysis (including quantitation) was the principal source of error.

VII. WET LAKE SEDIMENT (LEE AND CHAU, 1981a)

Fourteen laboratories were given one isooctane solution and three sediment samples for analysis by the method of their choice. One sediment sample contained the native PCBs and the other two were aliquots of the first to which 1.01 and 1.22 ppm of a 1:1 mixture of Aroclor 1254 and 1260 had been added. The participants used a variety of techniques, with the only common denominator being PGC/ECD for the instrumental determination. The results for the unspiked sample of Lake Ontario sediment were generally low, trace or not detected and were not summarized by the authors. The results for the spiked samples were summarized in terms of the percent recovery of the spike. The mean percent recoveries were 93 and 99%, with RSDs of ± 18 and ± 19%, respectively. The fourth sample, 1.00 ng/μL of a 1:1 mixture of Aroclor 1254 and 1260, was analyzed by direct injection onto the GC. The 112% recovery with an RSD of ± 19% was surprisingly poorer than the results for the samples which went through the entire method. The authors used a Youden plot (Youden and Steiner, 1975) to compare the results for the two spiked sediment samples (Figure 10-1). The 45° diagonal line represents the true ratio of the PCB content in the two samples. As can be seen in Figure 10-1, the plot easily distinguishes the systematic error (distance along the 45° line from the design value) from random error (distance from the 45° line). The value reported by Laboratory No. 4 for Sample No. 3 was rejected as an outlier.

Lee and Chau presented some discussion of the relative merits of the various extraction, cleanup, and notably, quantitation techniques employed. Eight participants used the Webb and McCall (1973) quantitation technique and had a mean accuracy of 103% with a RSD of ± 4.5% for the sample of Aroclors in isooctane for direct injection. The other eight participants used a variety of multiple-peak quantitation techniques and had a mean accuracy of 122% with a RSD of ± 23%. Clearly, for these laboratories and this sample, the Webb and McCall technique was both more accurate and more precise.

The authors concluded that the RSD for these samples was ± 20%, the method detection limit was between 0.01

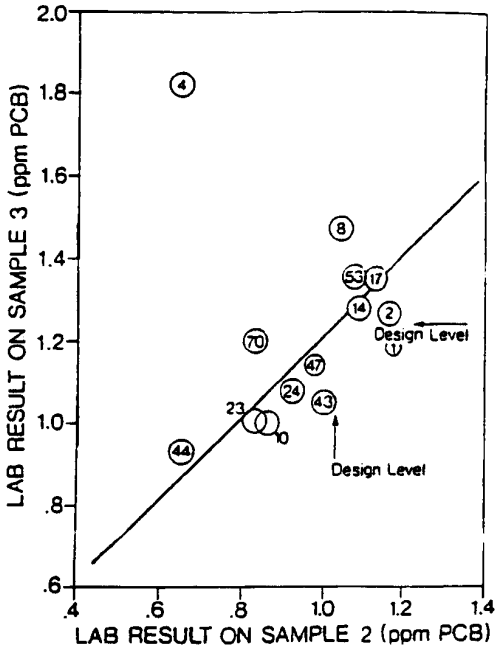


Figure 10-1. Paired Sample (Youden) Plot for Two Wet Sediment Samples

Numbers in circles are the participant's identification numbers.

Reprinted, with permission, from Lee and Chau (1981a).

MONS 005548

and 0.02 ppm, the various extraction and cleanup methods appear to be equally efficient, and quantitation was a major source of error.

VIII. NATURALLY CONTAMINATED DRY SEDIMENTS (LEE AND CHAU, 1981b)

A companion to the wet lake sediment study (Lee and Chau, 1981a) discussed above, this study required 15 participants to analyze four samples (actually two duplicate aliquots) of naturally contaminated dry sediment, a cleaned up extract of one of the sediments, and a 600 pg/μL mixture of Aroclor 1242, 1254, and 1260 (1:1:1). As can be seen in Table 10-I, the results for the Aroclor mixture had accuracy and precision similar to the other studies. The precision for the sediment samples, however, was about ± 25%, even after rejection of outliers. Furthermore, the intralaboratory precision (RSD of the values reported for the blind duplicate samples) ranged from less than 1% to over 100%. Typically, the results were in fair agreement (e.g., 1.4 and 1.7 μg/g for an RSD of 14%).

The participants used a variety of techniques for all stages of the analysis. One participant used HRGC/ECD; the rest, PGC/ECD. The authors attributed the poor performance of the participants in this study relative to that in the wet sediment study to the fact that this study utilized real samples. They recommended the use of these sediment reference materials for both internal and interlaboratory QC studies to improve the data quality.

IX. AMBIENT AIR (BIDLEMAN, 1981)

High-volume air samples from Boston, Massachusetts, and Columbia, South Carolina, were collected on a glass fiber filter-polyurethane foam sorbent trap. Aliquots of the organic extracts were sent to nine laboratories. The laboratories were permitted to use any procedure in the analysis. Most groups used either Florisil or silica gel column chromatography in the cleanup. Several used a chemical degradation (sulfuric acid, base, or chromium trioxide) as an additional cleanup step. Most of the participants used PGC/ECD for the sample analysis. Two laboratories used HRGC/ECD and one used GC/EIMS. The precision for the PCB measurements (± 26% to ± 39%, see Table 10-I) was comparable to that observed for most pesticides; however, the precision for the polychloroterpenes (toxaphene) was ± 116%. Bidleman (1981) recommended that the validity of sample collection also be studied in a collaborative study.

MONS 005549

X. DRY PIGMENTS (DCMA, 1982)

The Dry Color Manufacturers Association (DCMA) developed a method for the analysis of pigments using PGC/ECD. The method has two sample preparation options, a hexane/sulfuric acid partition for phthalocyanine blue pigments and a methylene chloride extraction/Florisil column cleanup for diarylide yellow, phthalocyanine blue, and phthalocyanine green pigments. The 10 participants of a collaborative study conducted by DCMA were all DCMA member companies. They were asked to analyze five samples (one yellow, two blue, and two green pigments). The two blue pigment samples were analyzed by both cleanup options. Several of the participants did not adhere to the method and their data were not included in the summaries presented in Table 10-I. The average RSD for the seven values in Table 10-I was about ± 19%.

The participants reported their repeatability on four different days, which permitted an evaluation of the within- and between-laboratory components of the RSD. For diarylide yellow (first sample in Table 10-I), the quantitation of the 3,3'-dichlorobiphenyl in the sample had similar within- and between-laboratory error components. The source of error in the quantitation of the decachlorobiphenyl in the two phthalocyanine green samples could not be deduced. The between-laboratory error contribution accounted for almost 80% of the total error for the four analyses of phthalocyanine blue, which contained several penta- and hexachlorobiphenyl congeners. The higher RSDs for these samples was attributed to the greater number of congeners and also to the large number of interferences.

XI. INSULATING OILS (ROUSE, 1982)

This study was conducted to test the precision of a proposed American Society for Testing Materials (ASTM) method (Method D 4059) for the analysis of PCBs in mineral insulating oils by GC/ECD. The study was conducted by ASTM Committee D27 - Electical Insulating Liquids and Oils. Ten participants reported results for six transformer oil samples containing Aroclor 1242, 1254, 1260, or mixtures thereof. As shown in Table 10-I, the average recovery was 98% and the average RSD was 15%.

MONS 005550

XII. BY-PRODUCTS FROM INDUSTRIAL PROCESSES (PITTAWAY AND HORNER, 1982; HODGES ET AL., 1982; WESTERBERG ET AL., 1984)

This study was conducted by the Chemical Manufacturer's Association (CMA) to evaluate the available analytical methodologies for analysis of commercial products and wastes. The eight participants were mostly industrial laboratories experienced in the analysis of by-product PCBs in industrial matrices. The study was designed to "simulate the situation in which a company independently attempts to determine the number and quantity of incidentally generated chlorobiphenyls in its process and/or waste streams" (Pittaway and Horner, 1982). The participants were asked to analyze a set of five samples: a chlorinated benzene waste, two mixtures of chlorinated benzenes, a chlorinated aliphatic waste stream sample, and a chlorinated aromatic sample. The samples were chosen to typify process stream matrices that were regulated by EPA. The coordinators made no attempt at controlling sample preparation, analysis, quantitation, reporting format, or QA. Most participants used either direct injection or a simple dilution for sample preparation. Most participants used GC/EIMS, although one participant used PGC/ECD and one used PGC/FID. The latter's results were 100 to 1000 times higher than the average and were excluded from the data analysis (Pittaway and Horner, 1982).

As can be seen from the results in Table 10-I, the precision ranged from ± 34% to ± 92% RSD. The accuracy for one sample, which was a spike of another sample, was found to be 75%. Since the data were tabulated by homolog, the error contribution by homolog was assessed. As shown in Figure 10-2 for one of the samples, the lower homologs tended to contribute more of the error. This may be a function of the techniques used, but is more likely a function of the matrix interferences, which were chlorinated benzenes and chlorinated aliphatics. In addition to the differences in techniques, the reporting units were often vague or unspecified. Some of the overall error may have been caused by differences in data reporting, since it is unknown whether the all of the respondents corrected for density in their reporting of "ppm."

Pittaway and Horner (1982) concluded that, under uncontrolled conditions, one cannot expect to receive PCB analytical results which are sufficiently reliable for regulatory decision-making. It should be noted that the complexity of the PCB mixtures and the matrices in this study were much greater than those in studies involving Aroclor-derived PCBs in environmental matrices.

MONS 005551

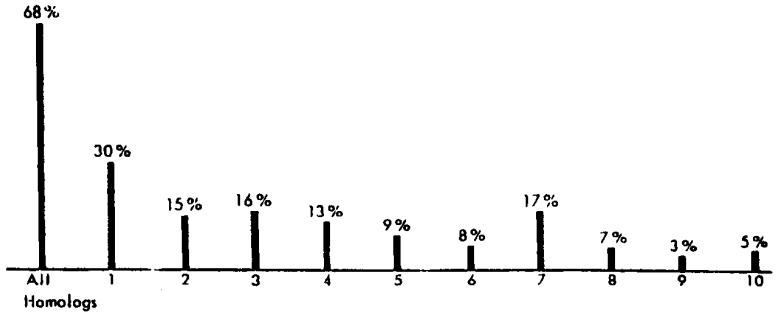


Figure 10-2. Histogram of Error Contribution by Homologs for Sample A from CMA Study Reprinted from Hodges et al. (1983).

XIII. BY-PRODUCTS IN A CHLORINATED AROMATIC WASTE (ERICKSON ET AL., 1983c)

This study was conducted to assess a method for the analysis of incidentally generated chlorinated biphenyls in commercial products and product wastes (Erickson et al., 1982). Four participants received calibration solutions at known concentrations, instructions for analysis and data reporting, and a set of samples. The sample set included paired samples of (a) additional ampules of the calibration solution of 11 PCB congeners at unknown and slightly differing concentrations which required only GC/EIMS determination (samples 7 and 8), (b) a chlorinated aromatic waste which required only GC/EIMS determination (samples 9 and 10), and (c) the same chlorinated aromatic waste which required both laboratory preparation (Florisil column cleanup) and GC/EIMS determination (samples 11 and 12). An additional sample, again the chlorinated aromatic waste, was supplied in the form of a magnetic tape (sample 14). This last sample required only data interpretation by the participants. Figure 10-3 presents a schematic of the entry points into the sample analysis scheme.

The results are summarized in Table 10-I. The overall errors ranged from ± 12 to ± 182%. The two RSDs over 100% were inflated by one participant who appeared to be an outlier. The first two samples were dilutions of the calibration solution. Since the concentrations were known, the accuracy could be assessed as shown in Table 10-I. A comparison of the Youden pair samples (samples differing only in concentration by about 10%; Youden and Steiner, 1975) were compared using a Student's t-test. At the 95% confidence level none of the participants correctly differentiated among the samples. This indicates that the method precision is > 10%.

One of the samples consisted simply of a magnetic tape containing a calibration analysis and an analysis of the same original sample used for four of the other samples in this study. The interpretation of this magnetic tape provided a direct assessment of the data reduction error. The qualitative analyses identified from 55-109 peaks as PCBs although the participant reporting the highest number clearly did not evaluate the data since they reported 14 monochlorobiphenyls. Two of the three reporting participants calculated equivalent response factors from the standard run, while one participant reported response factors two times higher. The ± 25% RSD for this sample was the largest individual contribution to the total error, as shown in Figure 10-4.

MONS 005553

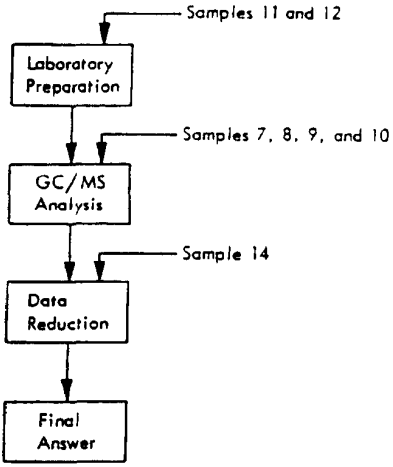


Figure 10-3. Analysis Flow Scheme for By-product Collaborative Study, Showing Sample Entry Points

Reprinted, with permission, from Erickson et al. (1983c).

MONS 005554

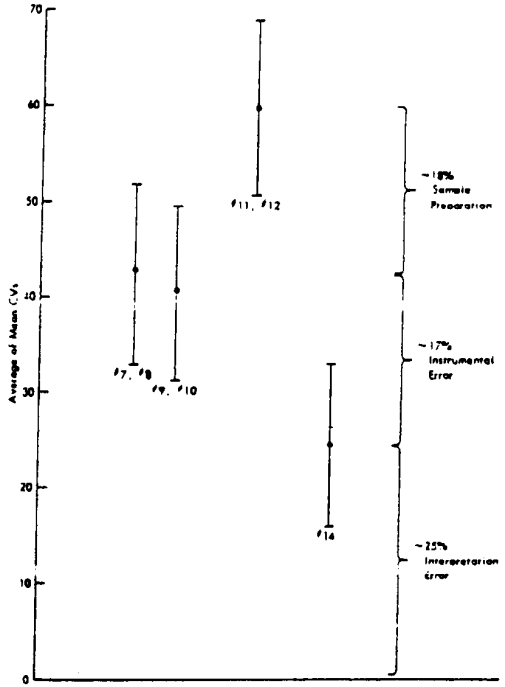


Figure 10-4. Plot of Error in By-product Collaborative Study by Sample Type, Showing Contributions of the Analysis Steps

Reprinted, with permission, from Erickson et al. (1983c).

The data indicate that the overall method variation appears to be ± 60% RSD. This is shown in Figure 10-4 (outliers excluded). There is about ± 25% variation associated with the data interpretation step. About ± 17% variation appears to be associated with instrumental error and ± 18% variation is associated with sample preparation. The results of this study indicate that the precision and accuracy of this method are lower than for many other methods. This collaborative study, however, was operating at the lower limit of instrumental sensitivity (selected ion monitoring mode) where precision is poor and also employed samples containing about 80 PCB congeners in a matrix containing many other chlorinated compounds. Thus, this was an extremely tough challenge to the method. A second study of the method using more collaborators, simpler PCB mixtures, and higher concentrations is currently being conducted. Preliminary results indicate that the precision, accuracy, and surrogate recovery are better at higher PCB concentrations (Bishop and Gebhart, 1984).

XIV. HERRING (MUSIAL AND UTHE, 1983)

In this international study, 23 participants reported results for PCBs in unspiked and spiked (1.00 mg/kg Aroclor 1254 in oil) samples of herring oil. Each participant was free to choose the analytical method, although Aroclor 1254 standard solutions were provided for use as a quantitation standard. The overall precision of the higher level (spiked) sample was substantially better than the precision for the lower level sample. There was no significant difference in the quantitation based on four calculations: either the participant's usual method or the sum of three prominent Aroclor 1254 peaks compared to either the participant's own standards or a standard solution of Aroclor 1254 supplied by the coordinators. Also, no significant difference was found when the GC column efficiencies were compared. There did, however, appear to be a dependence of the results on the type of liquid phase in the GC column; the authors recommended the use of high grade silicone stationary phases. They also noted that the in-house calibration standards were as much as 6% different than that supplied by the coordinators. The authors also observed significantly higher values for participants who used Florisil cleanup as opposed to those who used alumina. A lengthy discussion of the causes was inconclusive.

XV. BOVINE SERUM (BURSE ET AL., 1983b)

Twenty-five laboratories which are engaged in routine analysis of blood samples for PCBs and other chlorinated

hydrocarbons collaborated in this study coordinated by the Centers for Disease Control (CDC). The participants were free to choose the analytical method and employed a wide variety of techniques. Only 12 participants which reported the prescribed duplicate analyses on a low- and high-level sample were included by the study authors in the statistical analyses presented in Table 10-I. The total precision of ± 37.0% and ± 30.7% for the two samples (Table 10-I) was further broken down. The intra-laboratory variance wes ± 16.8% and ± 11%, while the inter-laboratory variance was ± 33.0% and ± 28.6% for the low and high level samples, respectively.

The accuracy reported in Table 10-I is highly misleading. The prepared value used for comparison with the participants' values is actually a CDC analysis of the samples which were prepared from in vivo-bound PCBs (Burse et al., 1983a). There is no data on the accuracy of the in-house analysis. Nevertheless, the two samples were dilutions of the same pool, so it may be reasonable to assume that the relative ratios are reasonably correct. Thus, the collaborative date show that there is a higher bias at lower concentrations (239% recovery for the lower concentration sample versus 165% for the higher). The authors attributed most of the accuracy error (i.e., high values by the collaborators) to two sources: high reagent blanks and failure to completely separate PCBs from DDT and its metabolites. They noted that the three participants which were within ± 3 standard deviations of the CDC mean either used a small volume of solvent to minimize the background or oxidized the DDT analogs.

XVI. LUBRICATING OILS (BECKER, 1984)

This study was part of a cooperative program between the U.S. National Bureau of Standards and the American Society for Testing and Materials to develop an accurate and relative simple method for determining PCBs in used and rerefined lubricating oils. Eleven samples were prepared, some containing known amount of Aroclors in clean oil, and some containing industrially incurred PCBs as shown in Table 10-I. Two duplicates and a blank were included in the sample set. In addition, one sample contained only an oil additive package which was suspected of causing interferences with some PCB analyses. The samples were analyzed using the participants' in-house procedures. The 19 participants all used GC/ECD, some packed and some capillary column. All laboratories used external standard calibration and quantitated the PCBs as individual Aroclors. A variety of cleanup techniques were reported, although a combination of Florisil and sulfuric acid was most widely used.

As noted in Table 10-I, most of the results were very close to the prepared concentrations; i.e., the accuracy was high. However, the 40 to 60% relative standard deviation on most of the samples indicates that the precision was not nearly as good. An examination of the data by Becker (1984), including Youden plots of the duplicate samples, indicated that most of the error was systematic. The intralaboratory precision was generally good. Becker inferred that problems with standardization and/or quantitation caused the bias in some of the participants' results.

MONS 005558

BIBLIOGRAPHY

Aaronson, M. J., J. D. Tessari and S. M. Bergin. "PCBs in Transformer Oils," Bull. Environ. Contam. Toxicol. 28:584-591 (1982).

Acker, L. and F. Schulte. "Occurrence of Hexachlorobenzene and Polychlorinated Biphenylenes Besides Chlorinated Insecticides in Human Fat Tissues and Milk," Ernaehrungsforschung 16(4):559-67 (1972), Chem. Abst. 78:80552c (1973).

Ackerman, D. G., L. L. Scinto, P. S. Bakshi, R. G. Delumyea, R. J. Johnson, G. Richard and A. M. Takata. "Guidelines for the Disposal of PCBs and PCB Items by Thermal Destruction," USEPA, IERL, Research Triangle Park, NC, EPA-600/ 2-81-022, February 1981, 317 pp.

Ackerman, D. G., L. L. Scinto, P. S. Bakshi, R. G. Delumyea, R. J. Johnson, G. Richard, A. M. Takata and E. M. Sworzyn. "Destruction and Disposal of PCBs by Thermal and Non-Thermal Methods," TRW, Inc., Redondo Beach, CA, Noyes Data Corporation, Park Ridge, New Jersey, 1983a, 417 pp.

Ackerman, D. G., J. F. McGaughey and D. E. Wagoner. "At-Sea Incineration of PCB-Containing Wastes Onboard the M/T Vulcanus," TRW Inc., Redondo Beach, CA, for the U.S. Environmental Protection Agency, Office of Research and Development, Contract No. 68-02-3174, Work Assignment No. 103 (April 1983b), 273 pp.

Adams, J. D. and J. H. Caro. "Polyurethane Foam as Trapping Agent for Airborne Pesticides, Analytical Method Development," Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, GA, EPA-600/4-80-008 (January 1980).

Adams, J., K. Menzies and P. Levins. "Selection and Evaluation of Sorbent Resins for the Collection of Organic Compounds," U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/7-77-044 (April 1977).

MONS 005559

Adams, T. T., N. J. Williams, R. J. McElhaney and R. A Viator. "Analysis for Polychlorinated Biphenyls in Environmental Samples," Union Carbide report prepared for the U.S. Department of Energy, Contract No. W 7405 eng 26 (June 1979).

Addis, G. and R. Y. Komai, Eds. "Proceedings: 1983 PCB Seminar," Electric Power Research Institute, Palo Alto, CA, EPRI-EL-3581, June 1984.

Addis, G. and J. Marks, Eds. "Proceedings: 1981 PCB Seminar," Electric Power Research Inst., Palo Alto, CA, EPRI-EL-2572, CONF-811260 (NTIS No. DE82906457), September 1982, 296 pp.

Addison, J. B. and M. E. Nearing. "An Approach to the Preparation of Standard Reference Material for the Analysis of Polychlorinated Biphenyls in Marine Sediments," Intern. J. Environ. Anal. Chem. 11:9-16 (1982).

Adlard, E. R. "A Review of Detectors for Gas Chromatography," in CRC Critical Reviews in Analytical Chemistry 5:1 (1978).

Afghan, B. K. and D. Mackay (Eds.). Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, Plenum Publishing Corporation, New York. Proceedings of International Symposium on the Analysis of Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, Ontario, Canada, 1978 (1980).

Ahling, B. and S. Jensen. "Reversed Liquid-Liquid Partition in Determination of Polychlorinated Biphenyl (PCB) and Chlorinated Pesticides in Water," Anal. Chem. 42(13):1483-1486 (1970).

Ahnoff, M., G. Eklund and B. Josefsson. "Analysis of PCB in Water from the Swedish West Coast," Acta Hydrochim. Hydrobiol. 7(2):171-178 (1979).

Ahnoff, M. and B. Josefsson. "Confirmation Studies on Polychlorinated Biphenyls (PCB) from River Waters Using Mass Fragmentography," Anal. Lett. 6(12):1083-1093 (1973).

Ahnoff, M. and B. Josefsson. "Simple Apparatus for On-Site Continuous Liquid-Liquid Extraction of Organic Compounds from Natural Waters," Anal. Chem. 46(6): 658-663 (1974).

Ahnoff, M. and B. Josefsson. "Clean Up Procedures for PCB Analysis on River Water Extracts, Bull. Environ. Contam. Toxicol. 13(2):159-166 (1975).

Ahnoff, M. and B. Josefsson. "Apparatus for in Situ Solvent Extraction of Nonpolar Organic Compounds in Sea and River Water," Anal. Chem. 48(8):1268-1270 (1976).

Aitzetmüller, K. "Adsorption Liquid Chromatography of DDT and Polychlorinated Biphenyls," J. Chromatogr. 107:411-415 (1975).

Alben, K. and E. Shpirt. "Distribution Profiles of Chloroform, Weak Organic Acids, and PCBs on Granular Activated Carbon Columns from Waterford, New York," Environ. Sci. Technol. 17(4):187-192 (1983).

Albro, P. W. "Problems in Analytic Methodology: Sample Handling, Extraction, and Cleanup," Ann. N.Y. Acad. Sci. 320: 19-27 (1979).

Albro, P. W. "Validation of Extraction and Cleanup Procedures for Environmental Analysis," Chapter 8 in Environmental Health Chemistry, The Chemistry of Environmental Agents as Potential Human Hazards, J. D. McKinney, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980), pp. 163-175.

Albro, P. W. and L. Fishbein. "Quantitative and Qualitative Analysis of Polychlorinated Biphenyls by Gas-Liquid Chromatography and Flame Ionization Detection. I. One to Three Chlorine Atoms," J. Chromatogr. 69:273-283 (1972a).

Albro, P. W. and L. Fishbein. "Intestinal Absorption of Polychlorinated Biphenyls in Rats," Bull. Environ. Contam. Toxicol. 8(1):26-31 (1972b).

Albro, P. W., J. K. Haseman, T. A. Clemmer and B. J. Corbett. "Identification of the Individual Polychlorinated Biphenyls in a Mixture by Gas-Liquid Chromatography," J. Chromatogr. 136:147-153 (1977). Errata published in J. Chromatogr. 139: 404 (1977).

Albro, P. W. and B. J. Corbett. "Extraction and Clean-up of Animal Tissues for Subsequent Determination of Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans," Chemosphere 7:381-385 (1977).

Albro, P. W., J. R. Hass and W. B. Crummett. "Summary of the Workshop on Recent Advances in Analytical Techniques for Halogenated Aromatic Compounds," Ann. N.Y. Acad. Sci. 320: 125-130 (1979).

MONS 005561

Albro, P. W. and C. E. Parker. "Comparison of the Compositions of Aroclor 1242 and Aroclor 1016," J. Chromatogr. 169: 161-166 (1979).

Albro, P. W. and C. E. Parker. "General Approach to the Fractionation and Class Determination of Complex Mixtures of Chlorinated Aromatic Compounds," J. Chromatogr. 197:155-169 (1980).

Albro, P. W., J. T. Corbett and J. L. Schroeder. "Quantitative Characterization of Polychlorinated Biphenyl Mixtures (Aroclors® 1248, 1254 and 1260) by Gas Chromatography Using Capillary Columns," J. Chromatogr. 205:103-111 (1981).

Albro, P. W., J. S. Schroeder, D. J. Harvan, and B. J. Corbett. "Characteristics of an Extraction and Purification Procedure for Chlorinated Dibenzo[p]dioxins and Dibenzofurans in Soil and Liver," J. Chromatogr. 312:165-182 (1984).

American National Standards Institute, Inc. "American National Standard Guidelines for Handling and Disposal of Capicator- and Transformer-Grade Askarels Containing Polychlorinated Biphenyls, ANSI C107.1-1974," New York, NY (1974).

American Society of Mechanical Engineers. "Test Protocol: Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions" (1984). Unpublished report from Environmental Standards Workshop.

American Society for Testing and Materials. "Standard Specifications for Chlorinated Aromatic Hydrocarbons (Askarels) for Capacitors, ANSI/ASTM D 2233-74" in Annual Book of ASTM Standards Part 40, Philadelphia, Pennsylvania (1978a), p. 647-649.

American Society for Testing and Materials. "Standard Specifications for Chlorinated Aromatic Hydrocarbons (Askarels) for Transformers, ANSI/ASTM D 2283-75," in Annual Book of ASTM Standards, Part 40, Philadelphia, Pennsylvania (1978b), p. 650-653.

American Society for Testing and Materials. "Standard Method for Rapid Gas Chromatographic Estimation of High Boiling Homologues of Chlorinated Biphenyls for Capacitor Askarels, ANSI/ASTM D 3303-74 (Reapproved 1979)," in Annual Book of ASTM Standards, Part 40, Philadelphia, Pennsylvania (1980a), pp. 870-876.

American Society for Testing and Materials. "Standard Practice for Sampling Water, ASTM D 3370," in Annual Book of ASTM Standards, Part 31, Philadelphia, Pennsylvania.

MONS 005562

American Society for Testing and Materials. "Standard Method for Polychlorinated Biphenyls (PCBs) in Water, ANSI/ASTM D 3534-80," in Annual Book of ASTM Standards Part 31, Philadelphia, Pennsylvania (1981a), pp. 816-833.

American Society for Testing and Materials. "Standard Method for Analysis of Environmental Materials for Polychlorinated Biphenyls, ASNI/ASTM D 3304-77," in Annual Book of ASTM Standards Part 31, Philadelphia, Pennsylvania (1981b), pp. 877-885.

American Society for Testing and Materials. "Standard Method for Analysis of Polychlorinated Biphenyls in Mineral Insulating Oils by Gas Chromatography," ANSI/ASTM D 4059-83," in Annual Book of ASTM Standards, Part 40, Philadelphia, Pennsylvania (1983), pp. 542-550.

Anderson, R. J. and R. C. Hall. "Hall Bipolar Pulse, Differential Electrolytic Conductivity Detector for GC," Amer. Lab. 108-124 (February 1980).

Anderson, T. "The Role of Legislature in the Regulation of Toxic Materials," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 375-382.

Andren, A. W. "Processes Determining the Flux of PCBs Across Air/Water Interfaces," in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), 442 pp.

Anonymous. New Scientist, 612 (1966).

Anonymous. "Toxic Impurities in Polychlorinated Biphenyls - Environmental Impact," in Environ. Res. 5:308-312 (1972).

Anonymous. "Extraction of PCBs from Transformer Oil for GC-ECD Analysis with 'Baker' Disposable Extraction Column Octyl(C_8) (7087-6)," Application Note SS-AN017 (J. T. Baker Chemical Co., Phillipsburg, NJ), November 1981.

Anonymous. "NBS Develops Improved Technique for Measuring PCBs in Oils," J. Assoc. Offic. Anal. Chem. 65(4):1033 (1982a).

Anonymous. "Method Improves PCB Measurements in Oil," Chem. Eng. News 19, March 1, 1982b.

Appleby, A. "Atmospheric Freons and Halogenated Compounds," U.S. Environmental Protection Agency, Office of Research and Development, EPA-600/3-76-108 (November 1976).

MONS 005563

Araki, Y. and K. Tanaka. "Simple Screening Method for [Hepatic] Enzyme-inducing Agents of Polychlorinated Biphenyl (PCB) Type," Fukuoka-Igaku-Zasshi 65(1):47-52 (1974); Chem. Abst. 81:146433n (1974).

Armour, J. A. "Gas Chromatographic Data for Polychlorinated Biphenyl Components in Six Aroclors®," J. Chromatogr. 72:275-282 (1972).

Armour, J. A.. "Quantitative Perchlorination of Polychlorinated Biphenyls as a Method for Confirmatory Residue Measurement and Identification," J. Assoc. Offic. Anal. Chem. 56(4): 988-993 (1973).

Armour, J. A. and J. A. Burke. "Method for Separating Polychlorinated Biphenyls from DDT and Its Analogs," J. Assoc Offic. Anal. Chem. 53(4):761-768 (1970).

Armour, J. A. and J. A. Burke. "Behavior of Chlorinated Naphthalenes in Analytical Methods for Organochlorine Pesticides and Polychlorinated Bipnenyls," J. Assoc. Offic. Anal. Chem. 54:175-177 (1971).

Armstrong, D. E. and D. L. Swackhamer. "PCB Accumulation in Southern Lake Michigan Sediments: Evaluation from Core Analysis," in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich, M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), 442 pp.

Armstrong, D. W. and R. Q. Terrill. "Thin Layer Chromatographic Separation of Pesticides, Decachlorobiphenyl, and Nucleosides with Micellar Solutions," Anal. Chem. 51(13): 2160-2163 (1979).

Arnoux, A., J. L. Monod, and T. Schembri. "Gas-Chromatographic and Gas Chromatographic/Mass Spectrometric Identification of PCBs, Linear Saturated Hydrocarbons, Polynuclear Aromatic Hydrocarbons and Phthalates in Deep Sediments from the Western Mediterranean Sea," Journ. Etud. Pollut. Mar. Mediterr., 6:469-474 (1983); Chem. Abstr. 101:177066f (1984).

Arpino, P. J., B. G. Dawkins and F. W. McLafferty. "A Liquid Chromatography/Mass Spectrometry System Providing Continuous Monitoring with Nanogram Sensitivity," J. Chromatogr. Sci. 12:574-578 (1974).

Association of Official Analytical Chemists. "General Method for Organochlorine and Organophosphorus Pesticides, Method 29.001," Official Methods of Analysis of the Association of Official Analytical Chemists, W. Horwitz, Ed. (13th ed., Washington, DC 1980a), pp. 466-474.

Association of Official Analytical Chemists. "PCB in Paper and Paperboard, Method 29.029," Official Methods of Analysis of the Association of Official Analytical Chemists, W. Horwitz, Ed. (13th ed., Washington, DC 1980b), p. 475-476.

Association of Official Analytical Chemists. Handbook for AOAC Members (5th Edition, 1982), 109 pp.

Atlas, E., and C. S. Giam. "Global Transport of Organic Pollutants: Ambient Concentrations in the Remote Marine Atmosphere," Science, 211:163-165 (1981).

Aue, W. A. and S. Kapila. "The Electron Capture Detector--Controversies, Comments, and Chromatograms," J. Chromatogr. Sci. 11:255-263 (1973).

Aue, W. A. and S. Kapila. "Use of Electron Capture-Induced Products for Confirmation of Identity in Pesticide Residue Analysis," Anal. Chem. 50:536-538 (1978).

Augood, D. R., D. H. Hey, and G. H. Williams. "Homolytic Aromatic Substitution. Part III. Ratio of Isomerides Formed in the Phenylation of Chlorobenzene. Competitive Experiments on the Phenylation of p-Dichlorobenzene and 1,3,5-Trichlorobenzene. Partial Rate Factors for Chlorobenzene," J. Chem. Soc. (London) pp. 44-50 (1953).

Ayer, F. A. (Ed.), "National Conference on Polychlorinated Biphenyls (November 19-21, 1975, Chicago, Illinois)," Report of proceedings prepared for the U.S. Environmental Protection Agency, Office of Toxic Substances, Report No. EPA-560/6-75-004, NTIS No. PB-253 248 (March 1976), 471 pp.

Babkina, E. I., T. P. Fanaskova and T. V. Shpotova. "Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in the Ground and the Water," Gidrobiol. Zh. 18(3): 86-91 (1982); Chem. Abstr. 97:86886f (1982).

Bagley, G. E., W. L. Reichel and E. Cromartie. "Identification of Polychlorinated Biphenyls in Two Bald Eagles by Combined Gas-Liquid Chromatography-Mass Spectrometry," J. Assoc. Offic. Anal. Chem. 53(2):251-261 (1970).

Bagley, G. E. and E. Cromartie. "Elimination Pattern of Aroclor 1254 Components in the Bobwhite," J. Chromatogr. 75:219-226 (1973).

Bailey, R. E., S. J. Gonsior and W. L. Rhinehart. "Biodegradation of the Monochlorobiphenyls and Biphenyl in River Water," Environ. Sci. Technol. 17(10):617-621 (1983).

MONS 005565

Baird, W. M. J. "Responding to Public Concern Over Environmental Pollution Hazards," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 91-100.

Baker, E. L., P. J. Landrigan, C. J. Glueck, H. M. Zack, Jr., J. A. Liddle, V. W. Burse, W. J. Housworth and L. L. Needham. "Metabolic Consequences of Exposure to Polychorinated Biphenyls (PCB) in Sewage Sludge," Amer. J. Epidemiol. 112(4): 553-563 (1980).

Ballinger, D. G. "Test Procedures for Priority Organics in Municipal Wastewater and Sludges," U.S. Environmental Protection Agency, Cincinnati, Ohio, December 11, 1978.

Ballschmiter, K. "High Resolution Gas Chromatography in Environmental Analysis," in Reviews in Analytical Chem. 4:139-156 (1983a); Chem. Abstr. 99:63564b (1983).

Ballschmiter, K. "Sample Treatment Techniques for Organic Trace Analysis," Pure Appl. Chem. 55(12):1943-1956 (1983b); Chem. Abstr. 100:95791d (1984).

Ballschmiter, K. and M. Zell. "Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography. Composition of Technical Aroclor- and Clophen-PCB Mixtures," Fresenius' Z. Anal. Chem. 302:20-31 (1980).

Ballschmiter, K., Ch. Unglert and H. J. Neu. "Abbau Von Chlorierten Aromaten: Mikrobiologischer Abbau Der Polychlorierten Biphenyle (PCB). III: Chlorierte Benzoesäuren als Metabolite Der PCB," Chemosphere 6(1):51-56 (1977).

Balya, D. R. and G. H. Farrah. "Column Chromatographic Procedure for the Determination of Polychlorinated Biphenyls in Certain Industrial Oils," Anal. Lett. 13(B8):655-671 (1980).

Bartle, K. D. "Identification of Polychlorobiphenyls by High Resolution Proton Magnetic Resonance," J. Assoc. Offic. Anal. Chem. 55(5):1101-1103 (1972).

Barton, T. G. and G. P. Arsenault. "Ultimate Disposal of Polychlorinated Biphenyls," Chapter 10 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp. 185-199.

Bauer, U.. "Combination of Thin-layer and Gas Chromatography for Identifying Halogenated Hydrocarbons," Vom Wasser 38:49-62 (1971); Chem. Abstr. 76:136672x (1972).

Baughman, R. and M. Meselson. "An Analytical Method for Detecting TCDD (Dioxin): Levels of TCDD in Samples from Vietnam," Environ. Health Perspect. 5:27-35 (1973).

Beard, J. H., III and J. Schaum. "Sampling Methods and Analytical Procedures Manual for PCB Disposal: Interim Report, Revision 0," Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC (February 10, 1978).

Becker, D. A. "Analysis for PCBs in Oil: The NBS/ASTM Round Robin," in National Bureau of Standards Special Publication 674. Proceedings, Conference on Measurements and Standards for Recycled Oil. - IV, Gaithersburg, Maryland, pp. 33-41 (1984).

Becker, D. A. "Used Lube Oil: Hazardous Waste vs. Valuable Resource," Trace Subst. Environ. Health 16:22-27 (1982); Chem. Abstr. 99:160990v (1983).

Becker, G. and E. Schulte. "Presence of PCB in Packaging Materials," Mitteilungsbl. GDCh-Fachgruppe Lebensmittelchem. Gerichtl. Chem. 30(6):101-108 (1976); Chem. Abstr. 85:107564u (1976).

Beezhold, F. L. and V. F. Stout. "The Use and Effect of Mixed Standards on the Quantitation of Polychlorinated Biphenyls," Bull. Environ. Contam. Toxicol. 10(1):10-15 (1973).

Beggs, D. P. and D. B. Banks. "Qualitative Analysis of PCB by GC/MS," Application Note AN 176-20, Hewlett-Packard, Avondale, Pennsylvania (1976).

Bellar, T. A. and J. J. Lichtenberg. "Some Factors Affecting the Recovery of Polychlorinated Biphenyls (PCB's) from Water and Bottom Samples," in Special Technical Publication 573, American Society for Testing and Materials, Philadelphia, Pennsylvania (1975), pp. 206-219.

Bellar, T. A., J. J. Lichtenberg and S. C. Lonneman. "Recovery of Organic Compounds from Environmentally Contaminated Bottom Materials," Chapter 4 in Contaminants and Sediments, Vol. 2, R. A. Baker, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1980).

Bellar, T. A. and J. J. Lichtenberg. "The Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils," Prepared for U.S. Environmental Protection Agency, EPA-600/4-81-045 (1981).

MONS 005567

Bellar, T. A. and B. Froning. "Application of Methods 606 and 608 for Analysis of PCBs Organochlorine Pesticides and Phthalate Esters Contained in Landfill Leachates," U.S. Environmental Protection Agency, Cincinnati, OH, EPA-600/4-82-044, NTIS No. PB82 227463 (1982), 16 pp.

Belliardo, F., E. Gionchiglia and G. M. Nano. "Analysis of Polychlorinated Biphenyl Residues in Waste Oils by High-Performance Liquid Chromatography," J. Liq. Chromatogr. 2(1): 77-83 (1979).

Benville, P. E. and R. C. Tindle. "Dry Ice Homogenization Procedure for Fish Samples in Pesticide Residue Analysis," J. Agr. Food Chem. 18(5):948-949 (1970).

Bercovici, B., M. Wassermann, S. Cucos, M. Ron, D. Wasserman and A. Pines. "Serum Levels of Polychlorinated Biphenyls and Some Organochlorine Insecticides in Women with Recent and Former Missed Abortions," Environ. Res. 30:169-174 (1983).

Berg, O. W., P. L. Diosady and G. A. V. Rees. "Column Chromatographic Separation of Polychlorinated Biphenyls from Chlorinated Hydrocarbon Pesticides, and their Subsequent Gas Chromatographic Quantitation in Terms of Derivatives," Bull. Environ. Contam. Toxicol. 7(6):338-347 (1972).

Berger, D. L. "Screening Procedure for Total Organic Halogen," Anal. Chem. 56:2271-2272 (1984).

Bergman, Å., R. Göthe and C. A. Wachtmeister. "Impregnation of Silica Gel with Tetraalkylammonium Salts in Adsorption Chromatography of Neutral Aromatic Compounds," J. Chromatogr. 123: 231-236 (1976).

Bergman, Å., B. Jansson, and I. Bamford. "Methylthio- and Methylsulfonylpolychlorobiphenyls: Synthesis and Studies of Correlations Between Structure and Fragmentation Pattern on Electron Impact," Biomedical Mass Spectrometry, 7(1):20-27 (1980).

Bergman, Å., L. Reutegardh, and M. Ahlman, "Determination of Polychlorinated Biphenyls in Commercial Silica Gel by Capillary Gas Chromatography," J. Chromatogr. 291:392-397 (1984a).

Bergman, Å., A. Hagman, S. Jacobsson, B. Jansson, and M. Ahlman. "Thermal Degradation of Polychlorinated Alkanes," Chemosphere, 13(2):237-250 (1984b).

Bernard, B. B. and B. D. Russell. "Rapid Determination of PCBs in Insulating Fluids," unpublished report, O. I. Corporation, College Station, TX (1983), 5 pp.

Bezot, P., C. Hesse-Bezot and B. Quentrec. "Transmission of Light and Local Order in Viscous Liquids. IV. Angular Dependence of Depolarized Spectra," Mol. Phys. 43(6):1407-1418 (1981); Chem. Abstr. 96:76686p (1982).

Bezot, P., C. Hesse-Bezot. "Fabry-Perot Study of Polarized and Depolarized Spectra of Liquid Pentachlorobiphenyl from -54 to 150°C," Can. J. Phys. 60(11):1709-1715 (1982).

Bickford, B., J. Bursey, L. Michael, E. Pellizzari, R. Porch, D. Rosenthal, L. Sheldon, C. Sparacino, K. Tomer, R. Wiseman, S. Yung, J. Gebhart, L. Rando, O. Perry and J. Ryan. "Preliminary Draft Report, Master Scheme for the Analysis of Organic Compounds in Water, Part III: Experimental Development and Results," EPA Contract No. 68-03-2704 (March 1980).

Bidleman, T. F. "Interlaboratory Analysis of High Molecular Weight Organochlorines in Ambient Air," Atmos. Environ. 15: 619-624 (1981).

Bidleman, T. F. "Estimation of Vapor Pressures for Nonpolar Organic Compounds by Capillary Gas Chromatography," Anal. Chem., 56:2490-2496 (1984).

Bidleman, T. F. and C. E. Olney. "High-volume Collection of Atmospheric Polychlorinated Biphenyls," Bull. Environ. Contam. Toxicol. 11(5):442-450 (1974).

Bidleman, T. F., C. P. Rice, and C. E. Olney. "High Molecular Weight Chlorinated Hydrocarbons in the Air and Sea: Rates and Mechanisms of Air/Sea Transfer," in Marine Pollutant Transfer, H. L. Windom and R. A. Duce, Eds. (Lexington, MA: Lexington Books, 1976), pp. 323-351.

Bidleman, T. F., J. R. Matthews, C. E. Olney and C. P. Rice. "Separation of Polychlorinated Biphenyls, Chlordane, and p,p'-DDT from Toxaphene by Silicic Acid Column Chromatography," J. Assoc. Offic. Anal. Chem. 61(4):820-828 (1978).

Bidleman, T. F., W. N. Billings and C. G. Simon. "Evaluation of Solid Adsorbents for Collecting Atmospheric Chlorinated Hydrocarbons," EPA 600/2-80-167 (1980).

MONS 005569

Bidleman, T. F., E. J. Christensen and H. W. Harder. "Aerial Deposition of Organochlorines in Urban and Coastal South Carolina," Chapter 24 in Atmospheric Pollutants in Natural Waters, S. J. Eisenreich, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981a), pp. 481-508.

Bidleman, T. F., E. J. Christensen, W. N. Billings and R. Leonard. "Atmospheric Transport of Organochlorines in the North Atlantic Gyre," J. Marine Res. 39(3):443-464 (1981b).

Bidleman, T. F. and R. Leonard. "Aerial Transport of Pesticides over the Northern Indian Ocean and Adjacent Seas," Atmos. Environ. 16:1099-1107 (1982).

Bidleman, T. F., N. F. Burdick, J. W. Westcott and W. N. Billings. "Influence of Volatility on the Collection of Airborne PCB and Pesticides with Filter-Solid Adsorbent Samplers," Chapter 2 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 15-48.

Bidleman, T. F., C. G. Simon, N. F. Burdick, and F. You. "Theoretical Plate Measurements and Collection Efficiences for High-Volume Air Samplers Using Polyurethane Foam," J. Chromatogr. 301:448-453 (1984).

Billings, W. N., and T. F. Bidleman, "Field Comparison of Polyurethane Foam and Tenax-GC Resin for High-Volume Air Sampling of Chlorinated Hydrocarbons," Environ. Sci. Technol. 14(6): 679-683 (1980).

Billings, W. N. and T. F. Bidleman. "High Volume Collection of Chlorinated Hydrocarbons in Urban Air Using Three Solid Adsorbents," Atmos. Environ. 17:383-391 (1983).

Biocca, M., J. A. Moore, B. N. Gupta and J. D. McKinney. "Toxicology of Selected Symmetrical Hexachlorobiphenyl Isomers: I. Biological Responses in Chicks and Mice," Conf. Proc. - Natl. Conf. Polychlorinated Biphenyls pp. 67-72 (1976); Chem. Abstr. 85:73086x (1976).

Biocca, M., B. N. Gupta, K. Chae, J. D. McKinney and J. A. Moore. "Toxicity of Selected Symmetrical Hexachlorobiphenyl Isomers in the Mouse," Toxicol. Appl. Pharmacol. 58(3):461-474 (1981).

MONS 005570

Biros, F. J. "An Integrated Gas Chromatograph-Flame Ionization Detector-Mass Spectrometer System for Pesticide Residue Analysis," Pestic. Chem. Proc. Int. IUPAC Congr. Pestic. Chem. 2nd 4:149-169 (1971).

Biros, F. J., A. C. Walker and A. Medbery. "Polychlorinated Biphenyls in Human Adipose Tissue," Bull. Environ. Contam. Toxicol. 5(4):317-323 (1970).

Biros, F. J., H. F. Enos, A. C. Walker and J. F. Thompson. "Analytical Aspects of Polychlorinated Biphenyl Determinations in Human and Animal Adipose Tissue," Prepr. Pap. Natl. Meet. (New York); Div. Water, Air and Waste Chem.; Amer. Chem. Soc. 12:61-66 (1972); Chem. Abstr. 81:386c (1972).

Bishop, T. A., and J. E. Gebhart. "Method Validation for Incidental Generation of Polychlorinated Biphenyls in Products and Waste Streams," Final Report, Task 68, EPA Contract No. 68-01-6721, Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, DC (1984).

Boe, B. and E. Egaas. "Qualitative and Quantitative Analyses of Polychlorinated Biphenyls by Gas-Liquid Chromatograpny," J. Chromatogr. 180:127-132 (1979).

Bonelli, E. J.. "GC/MS Techniques for the Determination of Interferences in Pesticide Analysis," Inst. Environ. Sci. Proc. 18:251-254 (1972a).

Bonelli, E. J. "Gas Chromatograph/Mass Spectrometer Techniques for Determination of Interferences in Pesticide Analysis," Anal. Chem. 44(3):603-606 (1972b).

Boniforti, L., G. Citti and G. Laguzzi. "Identification and Quantitative Determination of Polychlorinated Biphenyls and Polynuclear Aromatic Hydrocarbons in Fly Ash from Municipal Incinerators by Gas Chromatography with Electron-Capture Detection and Gas Chromatography-Mass Spectrometry," Anal Chem. Symp. Ser. 7:219-225 (1981); Chem. Abstr. 96:90803y (1982).

Bonner, R. F. "Environmental Analysis with a Triple Quadrupole," Int. J. Mass Spectrometry Ion Phys. 48:311-314 (1983).

Bopp, R. F., "Revised Parameters for Modeling the Transport of PCB Components Across an Air Water Interface," J. Geophysical Research, 88(C4):2521-2529 (1983).

Bostick, W. D., M. S. Denton and S. R. Dinsmore. "Development of a Portable Field Monitor for PCBs," Prepared for Electric Power Research Institute, Palo Alto, CA, EPRI CS-2828 (1983); NTIS No. DE83 007425.

MONS 005571

Bourke, J. B. "PCB's and Pesticides," N.Y. State Assoc. Milk and Food Sanitarians, Ann. Rept. 46:41-43 (1972).

Bowes, G. W. and J. A. Lewis. "Extraction of Polychlorinated Biphenyls: Evaluation of A Column Technique Applied to Polar Bear and Seal Tissue," J. Assoc. Offic. Anal. Chem. 57(1): 138-144 (1974).

Bowes, G. W., M. J. Mulvihill, M. R. DeCamp and A. S. Kende. "Gas Chromatographic Characteristics of Authentic Chlorinated Dibenzofurans; Identification of Two Isomers in American and Japanese Polychlorinated Biphenyls," J. Agric. Food Chem. 23(6):1222-1223 (1975a).

Bowes, G. W., M. J. Mulvihill, B. R. T. Simoneit, A. L. Burlingame and R. W. Risebrough. "Identification of Chlorinated Dibenzofurans in American Polychlorinated Biphenyls," Nature 256:305-307 (1975b).

Bowes, G. W., M. J. Mulvihill, B. R. T. Simoneit, A. L. Burlingame and R. W. Risebrough. "Isolation and Identification of Chlorinated Dibenzofurans from Polychlorinated Biphenyls (PCB) and from Yusho Rice Oil Containing PCB," Chapter 8 in Dioxin--Toxicological and Chemical Aspects, F. Cattabeni, A. Cavallaro and G. Galli, Eds. (New York, NY: SP Medical and Scientific Books, 1978), pp. 79-98.

Bremer, K. E. "Dealing with Multi-Agency and Multi-State Regulation of Polychlorinated Biphenyls," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 367-374.

Brinkman, U. A. Th., A. De Kok, G. De Vries and H. G. M. Reymer. "High-speed Liquid and Thin-layer Chromatography of Polychlorinated Biphenyls," J. Chromatogr. 128:101-110 (1976a).

Brinkman, U. A. Th., J. W. F. L. Seetz and H. G. M. Reymer. "High-speed Liquid Chromatography of Polychlorinated Biphenyls and Related Compounds," J. Chromatogr. 116:353-363 (1976b).

Brinkman, U. A. Th., G. De Vries, A. De Kok and A. L. De Jonge. "Discrimination Between Polychlorinated Naphthalenes and Polychlorinated Biphenyls," J. Chromatogr. 152: 97-104 (1978).

Brinkman, U. A. Th. and G. De Vries. "Relationship Between Structure and Retention of Polyhalogenated Aromatics in Two Adsorption Chromatographic Systems," J. Chromatogr. 169: 167-182 (1979).

MONS 005572

Brinkman, U. A. Th. and A. De Kok. "Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products. Production, Properties and Usage," Chapter 1. R. D. Kimbrough, Ed. (New York: NY: Elsevier/North-Holland Biomedical Press, 1980), pp. 1-40.

Broto-Puig, F., M. Gassiot-Matas, R. Martinez-Fonrodona. "Application of an On-Line Potassium Hydroxide Microreactor to the Resolution of Interferences Between PCBs and DDTs in the Gas Chromatography of High-Molecular-Weight Organochlorinated Contaminants," Journ. Etud. Pollut. Mar. Mediterr. 6:449-454 (1983); Chem. Abst. 101:157348w (1984).

Brown, D. P. and M. Jones. "Mortality and Industrial Hygiene Study of Workers Exposed to Polychlorinated Biphenyls," Archives of Environmental Health 36(3):120-129 (1981).

Brown, J. F. Jr., J. T. Coe and H. O. Pocock Jr. "Human Health Effects of Electrical-Grade PCB's," Corporate Health and Safety Operation, General Electric Company, Fairfield, CT (August 1981a).

Brown, J. F. Jr., M. E. Lynch, J. C. Carnahan, and J. Singleton. "Chemical Destruction of PCBs in Transformer Oil," General Electric Company, Schenectady, NY, Technical Information Series, 81CRD257 (November 1981b).

Brown, J. F. Jr., M. E. Lynch, J. C. Carnahan and J. Singleton. "Chemical Destruction of Polychlorinated Biphenyls in Transformer Oil," Chapter 11 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp.201-214.

Brown J. F., Jr., and R. W. Lawton. "Polychlorinated Biphenyl (PCB) Partitioning Between Adipose Tissue and Serum," Bull. Environ. Contam. Toxicol. 33:277-280 (1984).

Brownrigg, J. T. and A. W. Hornig. "Estimation of Polychlorinated Biphenyls in the Presence of DDT-Type Compounds," Prepared for the U.S. Environmental Protection Agency, NTIS Publication No. PB-233 599 (June 1974).

Brownrigg, J. T. and A. W. Hornig. "Identification of PCB's in the Presence of DDT-Type Compounds Using Low Temperature Luminescence," Arch. Environ. Contam. Toxicol. 4:175-182 (1976).

MONS 005573

Bruggeman, W. A., J. van der Steen and O. Hutzinger. "Reversed-Phase Thin-Layer Chromatography of Polynuclear Aromatic Hydrocarbons and Chlorinated Biphenyls. Relationship with Hydrophobicity as Measured by Aqueous Solubility and Octanol-Water Partition Coefficient," J. Chromatogr. 238(2): 335-346 (1982).

Brugger, J. E., J. J. Yezzi Jr., I. Wilder, F. J. Freestone, R. A. Miller and C. Pfrommer, Jr. "The EPA-ORD Mobile Incineration System: Present Status," Proceedings in: 1982 Hazardous Material Spills Conference Paper No. 167 (April 19-22, 1982).

Brunelle, D. J. "Reaction of Polychlorinated Biphenyls with Mercaptans in Non-polar Media: Formation of Polychlorobiphenyl Sulfides," Chemosphere 12(2):167-181 (1983).

Brunelle, D. J. and D. A. Singleton. "Destruction/Removal of Polychlorinated Biphenyls from Non-polar Media. Reaction of PCB with Poly(Ethylene Glycol)/KOH," Chemosphere 12(2):183-196 (1983).

Brunn, H. "Quantitative Gas Chromatographic Detection of Residues of Polychlorinated Biphenyls in Raw and Processed Foods of Animal Origin," Arch. Lebensmittelhyg 33(5):118-122 (1982); Chem. Abstr. 98:33135z (1983).

Burdick, N. F. and T. F. Bidleman. "Frontal Movement of Hexachlorobenzene and Polychlorinated Biphenyl Vapors through Polyurethane Foam," Anal. Chem. 53(12):1926-1929 (1981).

Burke, J. A. "Report on Chlorinated Insecticides," J. Assoc. Offic. Anal. Chem. 58(2):233-235 (1975).

Burke, J. A. "Report on Chlorinated Pesticides," J. Assoc. Offic. Anal. Chem. 59(2):338-340 (1976).

Burkhard, L. P. and D. E. Armstrong. "Labeled Perchlorination Reagent for Determination of Polychlorinated Biphenyls," Anal. Chem. 53(3):523-528 (1981).

Burns, J. E. "Pesticides in People: Organochlorine Pesticide and Polychlorinated Biphenyl Residues in Biopsied Human Adipose Tissue--Texas 1969-1972," Prepared for the U.S. Environmental Protection Agency, NTIS No. PB-280 613/1, 5 pp. (1974).

Burse, V. W., R. F. Moseman, G. W. Sovocool and E. C. Villanueva. "PCB Metabolism in Rats Following Prolonged Exposure to Aroclor 1242 and Aroclor 1016," Bull. Environ. Contam. Toxicol. 15(1): 122-128 (1976).

MONS 005574

Burse, V. W., L. L. Needham, J. A. Liddle, D. D. Bayse and M. A. Price. "Interlaboratory Comparison for Results of Analyses for Polychlorinated Biphenyls in Human Serum," J. Anal. Toxicol. 4:22-26 (1980).

Burse, V. W., L. L. Needham, M. P. Korver, C. R. Lapeza Jr., J. A. Liddle and D. D. Bayse. Gas-Liquid Chromatographic Determination of Polychlorinated Biphenyls and a Selected Number of Chlorinated Hydrocarbons in Serum," J. Assoc. Off. Anal. Chem. 66(1):32-39 (1983a).

Burse, V. W., L. L. Needham, M. P. Korver, C. R. Lapeza Jr., J. A. Liddle and D. D. Bayse. "Assessment of Methods to Determine PCB Levels in Blood Serum: Interlaboratory Study," J. Assoc. Off. Anal. Chem. 66(1):40-45 (1983b).

Buser, H. R. "Analysis of TCDDs by Gas Chromatography-Mass Spectrometry Using Glass Capillary Columns," Chapter 4 in Dioxin--Toxicological and Chemical Aspects, F. Cattabeni, A. Cavallaro and G. Galli, Eds. (New York, NY: SP Medical and Scientific Books, 1978), pp. 27-41.

Buser, H. R., H. P. Bosshardt and C. Rappe. "Formation of Polychlorinated Dibenzofurans (PCDFs) From the Pyrolysis of PCBs," Chemosphere 7:109-119 (1978a).

Buser, H. R., H. P. Bosshardt, C. Rappe and R. Lindahl. "Identification of Polychlorinated Dibenzofuran Isomers in Fly Ash and PCB Pyrolyses," Chemosphere 7(5):419-429 (1978b).

Buser, H. R. and C. Rappe. "Formation of Polychlorinated Dibenzofurans (PCDFs) from the Pyrolysis of Individual PCB Isomers," Chemosphere 8(3):157-174 (1979).

Buser, H. R. and C. Rappe. "Isomer-Specific Separation of 2378-Substituted Polychlorinated Dibenzo-p-dioxins by High-Resolution Gas Chromatography/Mass Spectrometry," Anal. Chem. 56:442-448 (1984).

Bush, B. and F.-C. Lo. "Thin-layer Chromatography for Quantitative Polychlorinated Biphenyl Analysis," J. Chromatogr. 77: 377-388 (1973).

Bush, B., F. Baker, R. Dell'Acqua, C. L. Houck and F.-C. Lo. "Analytical Response of Polychlorinated Biphenyl Homologues and Isomers in Thin-layer and Gas Chromatography," J. Chromatogr. 109:287-295 (1975).

MONS 005575

Bush, B. and E. L. Barnard. "Determination of Nonpolar Chlorinated Hydrocarbons and PCB in Microsamples," Anal. Lett. 15(A20):1643-1648 (1982).

Bush, B., S. Connor and J. Snow. "Glass Capillary Gas Chromatography for Sensitive, Accurate Polychlorinated Biphenyl Analysis," J. Assoc. Off. Anal. Chem. 65(3):555-566 (1982).

Bush B., J. T. Snow, and S. Connor, "High Resolution Gas Chromatographic Analysis of Nonpolar Chlorinated Hydrocarbons in Human Milk," J. Assoc. Off. Anal. Chem. 66(2):248-255 (1983).

Bush, B., J. Snow, and R. Koblintz, "Polychlorobiphenyl (PCB) Congeners, p,p'-DDE, and Hexachlorobenzene in Maternal and Fetal Cord Blood from Mothers in Upstate New York," Arch. Env Cont. Tox. 13(5):517-527 (1984).

Butler, J. "Analysis of Diverse Sample Matrices for Polychlorinated Biphenyls Using the 700A Hall Electrolytic Conductivity Detector," 1981 Pittsburgh Conference, Abstract No. 041.

Cairns, T and R. A. Jacobson. "New Approaches to FDA Analytical Problems," J. Chem. Infor. Comp. Sci. 17(2):105-109 (1977).

Cairns, T. and E. G. Siegmund. "Determination of Polychlorinated Biphenyls by Chemical Ionization Mass Spectrometry," Anal. Chem. 53(11):1599-1603 (1981a).

Cairns, T. and E. G. Siegmund. "PCBs: Regulatory History and Analytical Problems," Anal. Chem. 53(11):1183A-1193A (1981b).

Cairns, T. and W. M. Rogers. "Acceptable Analytical Data for Trace Analysfs," Anal. Chem. 55(1):54A-57A (1983).

Calandra, J. C. "Summary of Toxicological Studies on Commercial PCBs," in National Conference on Polychlorinated Biphenyls, Franklin A. Ayer, Ed. U.S. Environmental Protection Agency, Office of Toxic Substances, EPA-560/6-75-004, NTIS No. PB-253 248, pp. 35-42 (1976).

Call, D. J., Y. A. Greichus and J. J. Worman. "A Gas Chromatographic-mass Spectrometric Comparison of Polychlorinated Biphenyl Residues in the Japanese Quail Brain to an Aroclor Standard," Bull. Environ. Contam. Toxicol. 11(4):333-338 (1974).

Canada, D. C. and F. E. Regnier. "Isotope Ratios as a Characteristic Selection Technique for Mass Chromatography," J. Chromatogr. Sci. 14:149-154 (1976).

Cantlon, J. E. "The PCB Problem: An Overview," in PCBs: Human and Environmental Hazards, F. M. O'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 5-10.

Caragay, A. B. and P. L. Levins. "Evaluation of Protocols for Pesticides and PCB's in Raw Wastewater," Final Report, Arthur D. Little, Inc., Contract No. 68-01-3857, Office of Research and Development, Environmental Protection Agency, Report No. EPA-600/2-79-166 (November 1979).

Carcich, I. G., and T. J. Tofflemire. "Distribution and Concentration of PCB in the Hudson River and Associated Management Problems," Environmental International 7:73-85 (1982).

Cardone, M. J. "Detection and Determination of Error in Analytical Methodology. Part I. In the Method Verification Program," J. Assoc. Off. Anal. Chem. 66(5):1257-1282 (1983a).

Cardone, M. J. "Detection and Determination of Error in Analytical Methodology. Part II. Correction for Corrigible Systematic Error in the Course of Real Sample Analysis," J. Assoc. Off. Anal. Chem. 66(2):1283-1294 (1983b).

Carey, A. E. and J. A. Gowen. "PCB's in Agricultural and Urban Soil," In: Proceedings of the National Conference on PCBs, pp. 195-198, EPA 560/6-75-004 (1976).

Carson, L. J. "Interlaboratory Study of the Hall 700A Halogen Electrolytic Conductivity Gas Chromatographic Detector," J. Assoc. Off. Anal. Chem. 66(6):1335-1344 (1983).

Carson, R. Silent Spring, (Greenwich, CT: Fawcett Publications, Inc., 1962), 304 pp.

Castelli, M. G., G. P. Martelli, C. Spagone, L. Cappellini and R. Fanelli. "Quantitative Determination of Polychlorinated Biphenyls (PCB) in Marine Organisms Analyzed by High-Resolution Gas Chromatography Selected Ion Monitoring," Chemosphere 12(3): 291-298 (1983).

Chau, A. S. Y. and C. J. Sampson. "Electron Capture Gas Chromatographic Methodology for the Quantitation of Polychlorinated Biphenyls: Survey and Compromise," Environ. Lett. 8(2):89-101 (1975).

MONS 005577

Chau, A. S. Y. and L. J. Babjak. "Column Chromatographic Determination of Mirex, Photomirex, and Polychlorinated Biphenyls in Lake Sediments," J. Assoc. Off. Anal. Chem. 62(1): 107-113 (1979).

Chau, A. S. Y., J. Carron and H.-B. Lee. "Analytical Reference Materials. II. Preparation and Sample Integrity of Homogeneous Fortified Wet Sediment for Polychlorinated Biphenyl Quality Control Studies," J. Assoc. Off. Anal. Chem. 62(6):1312-1314 (1979).

Chau, A. S. Y. and H.-B. Lee. "Analytical Reference Materials. III. Preparation and Homogeneity Test of Large Quantities of Wet and Dry Sediment Reference Materials for Long Term Polychlorinated Biphenyl Quality Control Studies," J. Assoc. Off. Anal. Chem. 63:947-951 (1980).

Chemical Manufacturers Association, "The Analysis of Chlorinated Biphenyls," submitted to the Environmental Protection Agency, August 21, 1981, in reference to OPTS-62017.

Chen, J-Y. T. and A. M. Gardner. "Multicomponent Analyses of PCBs by FTIR Spectroscopy," Amer. Lab. pp. 26-33 (1983).

Chen, K. "The Reclamation of PCB-Contaminated Transformer Oils by The Sunohio PCBX Process," Interim Report, TVA/OP/EDT--82/45, NTIS No. DE82 906112, 49 pp. (1982).

Chen, K. "Evaluation of the Sunohio PCBX Process for Reclamation of Transformer Oils Containing PBCs," IEEE Trans. Power Appar. Syst. PAS-102(12):3893-3898 (1983); Chem. Abstr. 100:106079f (1984).

Chen, P. H., J. M. Gaw, C. K. Wong and C. J. Chen. "Levels and Gas Chromatographic Patterns of Polychlorinated Biphenyls in the Blood of Patients After PCB Poisoning in Taiwan," Bull. Environ. Contam. Toxicol. 25:325-329 (1980).

Chen, P. H., K. T. Chang and Y. O. Lu. "Polychlorinated Biphenyls and Polychlorinated Dibenzofurans in the Toxic Rice-Bran Oil that Caused PCB Poisoning in Taichung," Bull. Environ. Contam. Toxicol. 26:489-495 (1981).

Chen, P. H., M. L. Luo, C. K. Wong and C. J. Chen. "Comparative Rates of Elimination of Some Individual Polychlorinated Biphenyls from the Blood of PCB-Poisoned Patients in Taiwan," Food Chem. Toxicol. 20:417-425 (1982).

Chen, P. H. and R. A. Hites. "Polychlorinated Biphenyls and Dibenzofurans Retained in the Tissues of a Deceased Patient with Yucheng in Taiwan," Chemosphere 12(11-12):1507-1516 (1983).

Chesler, S. N., W. E. May, P. A. White, R. M. Parris and F. R. Guenther. "Determination of Polychlorinated Biphenyls in Waste and Lubricating Oils," *National Bureau of Standards* Special Publication 584, Proceedings of Joint Conference on Measurements and Standards for Recycled Oil/Systems Performance and Durability, Gaithersburg, MD, October 23-26, 1979, pp. 295-297, NBS, (Issued November 1980).

Chesler, S. N., F. R. Guenther, W. E. May and R. M. Parris. "SRM's for Accurate Analyses of PCBs in Oil," Abstract, Center for Analytical Chemistry, National Bureau of Standards, Washington, DC, 20234 (1981).

Chiosi, S., A. Evidente, G. Randazzo and D. Scalorbi. "Analysis of a Mixture of Polychlorinated Biphenyls, DDT and Its Analogues by High-Performance Liquid Chromatography," J. Liquid Chromatogr. 5(9):1653-1663 (1982).

Chittim, B. G., B. S. Clegg, S. H. Safe and O. Hutzinger. "Chlorinated Dibenzofurans and Dibenzo-p-dioxins: Detection and Quantitation in Electrical Equipment and Their Formation During the Incineration of PCBs," prepared under Contract No.: OSS78-00067 for Fisheries and Environment Canada (September 1979) 79 pp.

Choudhry, G. G. and O. Hutzinger, Eds. Mechanistic Aspects of the Thermal Formation of Halogenated Organic Compounds Including Polychlorinated Dibenzo-p-dioxins (New York: Gordon and Breach Science Publishers, 1983), 194 pp.

Christensen, E. J., C. E. Olney and T. F. Bidleman. "Comparison of Dry and Wet Surfaces for Collecting Organochlorine Dry Deposition," Bull. Environ. Contam. Toxicol. 23:196-202 (1979).

Claeys, R. R. "Analysis of PCBs in Pulp Mill Effluent," Special Report-NCASI (National Council of the Paper Industry for Air and Stream Improvement), No. 77-04, pp. 46-49 (1977).

Coburn, J. A., I. A. Valdmanis and A. S. Y. Chau. "Evaluation of XAD-2 for Multiresidue Extraction of Organochlorine Pesticides and Polychlorinated Biphenyls from Natural Waters," J. Assoc. Off. Anal. Chem. 60(1):224-228 (1977).

Colby, B. N. and J. E. Picker. "Automated Recognition of Aroclor GC Patterns," Abstract No. 574, 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy (1983).

MONS 005579

Colby, B. N., E. A. Burns and P. L. Lagus. "The S-Cubed PCBA 101, an Automated Field Analyzer for PCBs," Abstract No. 731, 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy (1983).

Coleman, W. E. and R. G. Tardiff. "Contaminant Levels in Animal Feeds Used for Toxicity Studies," Arch. Environ. Contam. Toxicol. 8:693-702 (1979).

Colenutt, B. A. and S. Thorburn. "Optimisation of a Gas Stripping Concentration Technique for Trace Organic Water Pollutants," Intern. J. Environ. Anal. Chem. 7:231-244 (1980).

Collard, R. S. and M. M. Irwin, Jr. "GC/MS Determination of Chlorinated Biphenyls in Complex Chlorinated Hydrocarbon Process and Waste Streams," The Dow Chemical Company (1982a).

Collard, R. S. and M. M. Irwin, Jr. "Determination of Chlorinated Biphenyls (Incidental PCBs) in Chlorinated Hydrocarbon Process and Waste Streams," Abstract, 184th Annual American Chemical Society National Meeting, September 12-17, 1982b.

Collard, R. S. and M. M. Irwin. "GC/MS Determination of Incidental PCBs in Complex Chlorinated-Hydrocarbon Process and Waste Streams," Talanta 30(11):811-818 (1983).

Collins, G. B., O. C. Holmes and F. J. Jackson. "The Estimation of Polychlorobiphenyls," J. Chromatogr. 71:443-449 (1972).

Cone, M. V., M. F. Baldauf, D. M. Opresko and M. S. Uziel. "Chemicals Identified in Human Breast Milk, A Literature Search," U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, DC, EPA 560/5-83-009; NTIS No. PB84-118538 (October 1983), 125 pp.

Connors, T. F., J. F. Rusling, and A. Owlia. "Determination of Standard Potentials and Electron-Transfer Rates for Halobiphenyls from Electrocatalytic Data," Anal. Chem. 57:170-174 (1985).

Cook, W. J. "Some Chemical Aspects of Polychlorinated Biphenyls (PCBs)," Environ. Health Perspec. 1:3-13 (1972).

Cooke, M., G. Nickless, A. M. Prescott and D. J. Roberts. "Analysis of Polychlorinated Naphthalenes, Polychlorinated Biphenyls and Polychlorinated Terphenyls via Carbon Skeleton Gas-Liquid Chromatography," J. Chromatogr. 156:293-299 (1978).

Copeland, R. A. Letter to U.S. Environmental Protection Agency, Office of Toxic Substances, Re. Manufacturing Ban Exemption Petition (TS-794), from Monochlorobiphenyl Task Force, Dow Chemical U.S.A., July 31, 1979.

Copland, G. B. and C. S. Gohmann. "Improved Method for Polychlorinated Biphenyl Determination in Complex Matrices," Environ. Sci. Technol. 16:121-124 (1982).

Cordle, F., P. Corneliussen, C. Jelinek, B. Hackley, R. Lehman, J. McLaughlin, R. Rhoden and R. Shapiro. "Human Exposure to Polychlorinated Biphenyls and Polybrominated Biphenyls," Environ. Health Perspec. 24:157-172 (1978).

Cordle, F., R. Locke and J. Springer. "Risk Assessment in a Federal Regulatory Agency: An Assessment of Risk Associated with the Human Consumption of Some Species of Fish Contaminated with Polychlorinated Biphenyls (PCBs)," Environ. Health Perspec. 45:171-182 (1982).

Corneliussen, P. E. "Report on Multiresidue Methods (Interlaboratory Studies)," J. Assoc. Off Anal. Chem. 58(2):238-239 (1975).

Crist, H. L. and R. F. Moseman. "Simplified Micro Perchlorination Method for Polychlorinated Biphenyls in Biological Samples," J. Assoc. Off. Anal. Chem. 60(6):1277-1281 (1977).

Crummett, W. B. "The Problem of Measurements Near the Limit of Detection," Ann. N. Y. Acad. Sci. 320:43-47 (1979).

Cull, M. R., and A. J. Dobbs, "Analysis of Polychlorobiphenyls from Used Transformers for Polychlorodibenzofurans," Chemosphere 13(9):1085-1089 (1984).

Curley, A., V. W. Burse, M. E. Grim, R. W. Jennings and R. E. Linder. "Polychlorinated Biphenyls: Distribution and Storage in Body Fluids and Tissues of Sherman Rats," Environ. Res. 4:481-495 (1971).

Dale, W. E., A. Curley and C. Cueto, Jr. "Hexane Extractable Chlorinated Insecticides in Human Blood," Life Sci. 5:47-54 (1966).

Dark, W. A. and L. W. Crossman, Jr. "Applications Highlights - Polychlorinated Biphenyls," Waters Associates, Milford, Massachusetts, AH-324 (1973).

MONS 005581

Das, K. G. and P. S. Kulkarni. "Gas-Liquid Chromatography," Chapter 2 in Pesticide Analysis, K. G. Das, Ed. (New York, NY: Marcel Dekker, Inc. 1981), pp 45-98.

Davenport, R. J. and B. K. Bernard (Eds.). Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, DC, LSI-TR-507-137B, NTIS No. PB84-135771 (December 1983) 365 pp.

David, D. J. "Gas Chromatographic Detectors," Corporation (New York, NY: Wiley-Interscience Publication, 1974).

deAlencastro, L. F., V. Prélax, and J. Tarradellas. "Contamination of Silos in Switzerland by PCB Residues in Coatings," Bull. Environ. Contam. Toxicol. 33:270-276 (1984).

De Kanel, J., S.-Y. Tang and R. C. Dougherty. "Capillary GC/MS Profiling of Xenobiotic Chemicals in Biofluids in EI and NCI Modes," American Society for Mass Spectrometry, 30th Annual Conference on Mass Spectrometry and Allied Topics, Abstract, June 6-11, pp. 197 (1982).

De Kok, A., R. B. Geerdink, R. W. Frei and U. A. Th. Brinkman. "The Use of Dechlorination in the Analysis of Polychlorinated Biphenyls and Related Classes of Compounds," Intern. J. Environ. Anal. Chem. 9:301-318 (1981).

De Kok, A., R. B. Geerdink, R. W. Frei and U. A. Th. Brinkman. "Limitations in the Use of Perchlorination as a Technique for the Quantitative Analysis of Polychlorinated Biphenyls," Intern. J. Environ. Anal. Chem. 11:17-41 (1982a).

De Kok, A., R. B. Geerdink, G. De Vries and U. A. Th. Brinkman. "An Evaluation of Chromatographic Methods for the Analysis of Polychlorinated Terphenyls in Environmental Samples," Intern. J. Environ. Anal. Chem. 12:99-122 (1982b).

De Kok, A., R. B. Geerdink and U. A. Th. Brinkman. "The Determination of Polychlorinated Naphthalenes in Soil Samples by Means of Various Gas and Liquid Chromatographic Methods," Chromatogr. Biochem., Med. Environ. Res., 1, A. Frigerio, Ed. (1983), pp. 203-216.

Delfino, J. J. "Toxic Substances in the Great Lakes," Environ. Sci. Technol. 13(12):1462-1468 (1979).

Delfino, J. J. (Ed.). Methods for Analysis of Organic Compounds in the Great Lakes, Proceedings of an Invitational Workshop, April 1-2, 1980, University of Wisconsin Great Lakes Research Facility, Milwaukee, Wisconsin, WIS-SG-80-236 (1980).

Delfino, J. J. and O. B. Easty. "Interlaboratory Study of the Determination of Polychlorinated Biphenyls in a Paper Mill Effluent," Anal. Chem. 51(13):2235-2239 (1979).

Dennis, O. S. "Polychlorinated Biphenyls in the Surface Waters and Bottom Sediments of the Major Drainage Basins of the United States," Prepared for the U.S. Environmental Protection Agency, Office of Pesticide Programs, NTIS No. PB-276 313/4 (1974), 12 pp.

Denton, M. S. "Portable Field Monitor for PCBs," Abstract No. 629, 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 7-12, 1983.

Denton, M. S., S. R. Dinsmore and W. D. Bostick. "Portable Field Monitor for PCBs," in Proceedings: 1981 PCB Seminar, G. Addis and J. Marks, Eds. Report No. EPRI-EL-2572 (Palo Alto, CA: Electric Power Research Institute, 1982), pp. 3-3 to 3-21.

Denton, M. S., and M. H. Walker. "Portable Infrared Fieic Monitor for PCBs: Phase II." in Proceedings: 1983 PCB Seminar, G. Addis and R. Y. Komai Eds. Report No. EPRI-EL-358: (Palo Alto, CA: Electric Power Research Institute, 1984).

Department of Health, Education and Welfare, "Final Report of the Subcommittee on the Health Effects of Polychlorinated Biphenyls and Polybrominated Biphenyls of the DHEW Committee to Coordinate Toxicology and Related Programs," Env. Health Persp. 24:129-208 (1978a).

Department of Health, Education and Welfare. "DHEW Subcommittee on Health Effects of PCBs and PBBs, General Recommendations," Env. Health Persp. 24:187-189 (1978b).

Department of Health, Education and Welfare. "DHEW Subcommittee on Health Effects of PCBs, General Summary and Conclusions," Env. Health Persp. 24:191-198 (1978c).

Department of Transportation. "Polychlorinated Biphenyls (PCBs) in Transit System Electrical Equipment," Final Report, Urban Mass Transportation Administration, Office of Technical Assistance, Washington, DC, UMTA-MA-06-0098-84-1; NTIS No. PB84-222207 (1984) 104 pp.

Dequidt, J., F. Erb, C. Van Aerde and P. Colain. "Determination of Polychlorinated Biphenyls in Biological Media," Bull. Soc. Pharm. Lille 31(2-3):149-155 (1975); Chem. Abst., 84:39391n (1976).

MONS 005583

DeRoos, F. L., M. Cooke, J. E. Gebhart, L. E. Slivon, and P. J. Mondron. "An Update on Analytical Methods for Polychlorinated Biphenyls (PCB), Polychlorinated Dibenzofurans (PCDF) and Polychlorinated Dibenzo-p-dioxins (PCDD)," in Proceedings: 1983 PCB Seminar, G. Addis and J. Marks Eds., Report No. EPRI-EL-3581, (Palo Alto, CA, Electric Power Research Institute, 1984).

Devenish, I. W. and L. Harling-Bowen. "The Examination and Estimation of the Performance Characteristics of a Standard Method for Organo-Chlorine Insecticides and PCB," in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, B. K. Afghan and D. Mackay, Eds. (New York: Plenum Press, 1980), pp. 231-253.

deVera, E. R., B. P. Simmons, R. D. Stephens and D. L. Storm. "Samplers and Sampling Procedures for Hazardous Waste Streams," Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH, EPA-600/2-80-018 (January 1980).

De Voogt, P., J. C. Klamer and U. A. T. Brinkman. "Identification and Quantification of Polychlorinated Biphenyls in Paper Board Using Fused Silica Capillary Gas Chromatography," Bull. Environ. Contam. Toxicol. 32(1):45-52 (1984).

De Vos, R. H. "Analytical Techniques in Relation to the Contamination of the Fauna," TNO-nieuws 27:615-622 (1972).

De Vos, R. H. and E. W. Peet. "Thin-Layer Chromatography of Polychlorinated Biphenyls," Bull. Environ. Contam. Toxicol. 6(2):164-170 (1971).

Dexter, R. N. and S. P. Pavlou. "Characterization of Polychlorinated Biphenyl Distribution in the Marine Environment," Bull. Environ. Contam. Toxicol. 16(4):477-482 (1976).

D'Itri, F. M. and M. A. Kamrin, Eds. PCBs: Human and Environmental Hazards (Boston: Butterworth Publishers, 1983) 443 pp.

Dilling, W. L., G. E. Miracle and G. U. Boggs. "Organic PhotoChemistry. XVIII. Tropospheric Phototransformation Rates of 2-, 3-, and 4-Chlorobiphenyl," Preprints, Division of Environmental Chemistry, American Chemical Society National Meeting, Washington, DC, pp. 343-346 (August 1983).

DiNardi, S. R. and A. M. Desmarais. "Polychlorinated Biphenyls in the Environment," Chemistry, 49(4):14-17 (1976).

MONS 005584

Di Toro, D. M. and L. M. Horzempa. "Reversible and Resistant Component Model of Hexachlorobiphenyl Adsorption-Desorption Resuspension and Dilution," Chapter 6 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp 89-113.

Di Toro, D. M., L. M Horzempa and M. C. Casey. "Adsorption and Desorption of Hexachlorobiphenyl. A. Experimental Results and Discussions. B. Analysis of Exchangeable and Non-exchangeable Components," EPA-600/3-83-088, PB83-261677 (September 1983), 322 pp.

Doguchi, M. and S. Fukano. "Residue Levels of Polychlorinated Terphenyls, Polychlorinated Biphenyls and DDT in Human Blood," Bull. Environ. Contam. Toxicol. 13:57-63 (1975).

Dolan, J. W. and R. C. Hall. "Enhancement of the Sensitivity and Selectivity of the Coulson Electrolytic Conductivity Detector to Chlorinated Hydrocarbon Pesticides," Anal. Chem. 45(13): 2198-2204 (1973).

Dolan, J. W., R. C. Hall and T. M. Todd. "Selective Detection of Chlorinated Insecticides in the Presence of Polychlorinated Biphenyls," J. Assoc. Off. Anal. Chem. 55(3): 537-538 (1972).

Dolphin, R. J. and F. W. Willmott. "Separation of Chlorinated Dibenzo-p-dioxins from Chlorinated Congeners," J. Chromatogr. 149:161-168 (1978).

Donkerbroek, J. J., N. J. R. van Eikema Hommes, C. Gooijer, N. H. Velthorst and R. W. Frei. "Sensitized Room-Temperature Phosphorescence for Detection in Continuous Flow and Chromatographic Systems," Chromatographia 15(4):218-222 (1982).

Donkerbroek, J. J., N. J. R. van Eikema Hommes, C. Gooijer, N. H. Velthorst and R. W. Frei. "Phosphorescence Detection of Polychloronaphthalenes and Polychlorobiphenyls in Liquid Chromatography," J. Chromatogr. 255:581-590 (1983).

Donkin, P., S. V. Mann and E. I. Hamilton. "Microcoulometric Determination of Total Organochlorine Pesticide and Polychlorinated Biphenyl Residues in Grey Seal (Halichoerus grypus) Blubber," Anal. Chim. Acta 88:289-301 (1977).

Doskey, P. V. and A. W. Andren. "High-Volume Sampling of Airborne Polychlorobiphenyls with Amberlite XAD-2 Resin," Anal. Chim. Acta 110:129-137 (1979).

MONS 005585

Dougherty, R. C. "Toxic Residues and Pollutants," Chapter 32A in Biochemical Applications of Mass Spectrometry, First Supplemental Volume, G. R. Waller and O. C. Dermer, Eds. (New York, NY: Wiley-Interscience Publication, 1980), pp. 951-968.

Dougherty, R. C. "Negative Chemical Ionization Mass Spectrometry: Applications in Environmental Analytical Chemistry," Biomed. Mass Spectrom. 8(7):283-291 (1981a).

Dougherty, R. C. "Chemical Geometrodynamics: Physical Fields can Cause Asymmetric Synthesis," Origins of Life 11:71-84 (1981b).

Dougherty, R. C., J. D. Roberts, H. P. Tannenbaum, and F. J. Biros, "Positive and Negative Chemical Ionization Mass Spectra of Polychlorinated Pesticides," in Mass Spectrometry and NMR Spectroscopy in Pesticide Chemistry, R. Haque and F. J. Biros (Eds.), New York-London (1973). pp. 33-47.

Dougherty, R. C., M. J. Whitaker, L. M. Smith, D. L. Stalling, and D. W. Kuehl, "Negative Chemical Ionization Studies of Human and Food Chain Contamination with Xenobiotic Chemicals," Environ. Health Persp., 36:103-118 (1980).

Dougherty, R. C., M. J. Whitaker, S.-Y. Tang, R. Bottcher, M. Keller, and D. W. Kuehl, "Sperm Density and Toxic Substances: A Potential Key to Environmental Health Hazards," Chapter 13 in Environmental Health Chemistry, The Chemistry of Environmental Agents as Potential Human Hazards, J. D. McKinney (Ed.), Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan (1981). pp. 263-278.

Dow Chemical Company, "Determination of Chlorinated Biphenyls in the Presence of Chlorinated Benzenes," Midland MI, July 1, 1981.

Driscoll, J. N. and I. S. Krull. "Improved GC Separations with Chemically Bonded Supports," Amer. Lab. pp. 42-52 (May 1983).

Dry Color Manufacturers Association, "An Analytical Procedure for the Determination of Polychlorinated Biphenyls in Dry Phthalocyanine Blue, Phthalocyanine Green, and Diarylide Yellow Pigments," Arlington, VA (1982).

Dudenbostel, B. F. "Tentative Method of Test for Polychlorinated Biphenyls in Water," Attachment 8 in "Sampling Methods and Analytical Procedures Manual for PCB Disposal: Interim Report," J. H. Beard, III and J. Schaum, Office of Solid Waste, U.S. Environmental Protection Agency, Washington, DC (February 10, 1978).

Dufek, P., V. Pacáková and K. Zivny. "Gas Chromatographic Behaviour of Mono- and Dihydroxybiphenyls on Various Silicone Phases," J. Chromatogr. 211:150-154 (1981).

Duinker, J. C. and M. T. J. Hillebrand. "Characterization of PCB Components in Clophen Formulations by Capillary GC-MS and GC-ECD Techniques," Environ. Sci. Technol. 17:449-456 (1983).

Dunn, W. D., E. Johannson, D. L. Stalling, T. R. Schwartz, B. K. Marlow, J. D. Petty, and J. D. Hogan, "Application of SIMCA to the Characterization of PCB Residue Profiles in Sediment, Water, and Aquatic Biota," Abstract, 184th Annual Chemical Society National Meeting, September 12-17, 1982.

Dunn, W. J., III, D. L. Stalling, T. R. Schwartz, J. W. Hogan J. D. Petty, E. Johansson, and S. Wold. "Pattern Recognition for Classification and Determination of Polychlorinated Biphenyls in Environmental Samples," Anal. Chem. 56:1308-1313 (1984).

Durfee, R. L., G. Contos, F. C. Whitmore, J. D. Barden, E. E. Hackman, III and R. A. Westin. "PCBs in the United States - Industrial Use and Environmental Distributions," Prepared for the U.S. Environmental Protection Agency, Office of Toxic Substances, Report No. EPA 560/6-76-005 (NTIS No. PB-252 012), 488 pp. (1976).

Duvall, D. S. and W. A. Rubey. "Laboratory Evaluation of High-Temperature Destruction of Polychlorinated Biphenyls and Related Compounds," U.S. Environmental Protection Agency, EPA-600/2-77-228; NTIS No. PB 279 139 (December 1977).

Dyer, N. "PCBs - The Federal View," in Proceedings: 1981 PCB Seminar, G. Addis and J. Marks, Eds. (Palo Alto, CA: Electric Power Research Institute, 1981), pp. 1-1 to 1-10.

Dyment, P. G., L. M. Hebertson, E. D. Gomes, J. S. Wiseman and R. W. Hornabrook. "Absence of Polychlorinated Biphenyls in Human Milk and Serum from Texas and Human Milk from New Guinea," Bull. Environ. Contam. Toxicol. 6(6):532-534 (1971).

Dzidic, I., D. I. Carroll, R. N. Stillwell and E. C. Horning. "Atmospheric Pressure Ionization (API) Mass Spectrometry: Formation of Phenoxide Ions from Chlorinated Aromatic Compounds," Anal. Chem. 47(8):1308-1312 (1975).

Eadie, B. J., C. P. Rice and W. A. Frez. "The Role of the Benthic Boundary in the Cycling of PCBs in the Great Lakes," Chapter 12 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983) 442 pp.

MONS 005587

Easty, D. B. "Quantitation of Mixtures of Polychlorinated Biphenyls Isolated from Paperboard Containing Recycled Fiber," Tech. Assoc. Pulp and Paper Ind. 56(5):131-134 (1973).

Easty, D. B. and B. A. Wabers. "Determination of Polychlorinated Biphenyls in Paper Mill Effluents and Process Streams," Analytical Letters, 10(11):857-867 (1977).

Easty, D. B. and B. A. Wabers. "Determination of Polychlorinated Biphenyls in Paper Mill Effluents," Tech. Assoc. Pulp and Paper Ind. 61(10):71-74 (1978).

Ecology and Environment, Incorporated. "Summary of the Health Effects of PCBs," Report Submitted to U.S. Environmental Protection Agency and Admitted as Part of the "Official Rulemaking Record PCB Regulations for Closed and Controlled Waste Manufacturing Processes," Fed. Reg. 47:46993-5 (1982).

Eder, G. "Polychlorinated Biphenyls and Compounds of the DDT Group in Sediments of the Central North Sea and the Norwegian Depression," Chemosphere 5(2):101-106 (1976a).

Eder, G. "Evaluation of Environmental Polychlorobiphenyls and DDE in Terms of Mixtures of Commercial Preparations from Peak Heights of Packed-Column Gas Chromatograms Using a Programmable Calculator," J. Chromatogr. 121:269-277 (1976b).

Edison Electric Institute and The National Rural Electric Cooperative Association. "Comments and Studies on the Use of Polychlorinated Biphenyls in Response to an Order of the United States Court of Appeals for the District of Columbia Circuit, Vol. III, Report of the Study of PCBs in Equipment Owned by the Electric Utility Industry," submitted to the U.S. Environmental Protection Agency, Washington, D.C. (February 12, 1982).

Edwards, R. "Some Factors in the Separation of Polychlorobiphenyls (PCBs) from Organochlorine Pesticides by Column Chromatography Combined with Gas-Liquid Chromatography," Pestic. Sci. 5:293-304 (1974).

Egestad, B., T. Curstedt and J. Sjövall. "Simple Procedures for Enrichment of Chlorinated Aromatic Pollutants from Fat, Water and Milk for Subsequent Analysis by High-Resolution Methods," Anal. Lett. 15(A3):293-307 (1982).

Eichelberger, J. W., L. E. Harris and W. L. Budde. "Application of Gas Chromatography-Mass Spectrometry with Computer Controlled Repetitive Data Acquisition from Selected Specific Ions," Anal. Chem. 46(2):227-232 (1974).

Eisenbeiss, F. and H. Sieper. "The Potential Use of High-Performance Liquid Chromatography on Residue Analysis," J. Chromatogr. 83:439-446 (1973).

Eisenreich, S. J., G. J. Hollod and T. C. Johnson. "Atmospheric Concentrations and Deposition of Polychlorinated Biphenyls to Lake Superior," Chapter 21 in Atmospheric Pollutants in Natural Waters, S. J. Eisenreich, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981a) pp. 425-444.

Eisenreich, S. J., B. B. Looney and J. D. Thornton. "Airborne Organic Contaminants in the Great Lakes Ecosystem," Environmental Science and Technology 15:30-38 (1981b).

Eisenreich, S. J. and T. C. Johnson. "PCBs in the Great Lakes: Sources, Sinks, Burdens," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 49-76.

Eisenreich, S. J., P. D. Capel and B. B. Looney. "PCB Dynamics in Lake Superior Water," Chapter 11 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983a), 442 pp.

Eisenreich, S. J., B. B. Looney and G. J. Hollod. "PCBs in the Lake Superior Atmosphere 1978-1980," Chapter 7 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983b), 442 pp.

Eisenreich, S. J. and B. B. Looney. "Evidence for the Atmospheric Flux of Polychlorinated Biphenyls to Lake Superior," Chapter 9 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), 442 pp.

Elder, D. "PCBs in N.W. Mediterranean Coastal Waters," Marine Pollution Bulletin, 7(4):63-64 (1976).

Elder, V. A., B. L. Proctor and R. A. Hites. "Organic Compounds Near Dumpsites in Niagara Falls, New York," Biomedical Mass Spectrometry 8:409-415 (1981).

Environmental Defense Fund, Natural Resources Defense Council, and Chemical Manufacturers Association. "Recommendation of the Parties for a Final EPA Rule on Inadvertent Generation of PCBs," Submitted to Don R. Clay, Acting Assistant Administrator, Environmental Protection Agency, Office of Toxic Substances, Washington, DC, April 13, 1983.

Environmental Protection Agency. "Identification of Polychlorinated Biphenyls in the Presence of DDT-Type Compounds," *Office of Research and Monitoring*, Washington, D.C., EPA-R2-72-064 (NTIS No. PB-213 900) (October 1972).

Environmental Protection Agency. "Sample Collection Manual, Ecological Monitoring Branch," Office of Pesticides Programs, Benefits and Field Studies Division, Washington, D.C. (1976).

Environmental Protection Agency, "40 CFR Part 60 - Standards of Performance for New Stationary Sources," Fed. Reg. 42: 41754-41789 (August 18, 1977).

Environmental Protection Agency. "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," Interim Report, Environmental Monitoring and Support Laboratory, Cincinnati, OH, September 1978.

Environmental Protection Agency. "Organochlorine Pesticides and PCBs-- Method 608," Fed. Reg. 44:69501-69509 (December 3, 1979a).

Environmental Protection Agency. "Base/Neutrals, Acids, and Pesticides--Method 625," Fed. Reg. 44:69540-69552 (December 3, 1979b).

Environmental Protection Agency. "Appendix III - Example Quality Assurance and Quality Control Procedures for Organic Priority Pollutants," Fed. Reg. 44:69553-69559 (December 3, 1979c).

Environmental Protection Agency. "40 CFR 761, Polychlorinated Biphenyls (PCBs) in Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions; Final Rule," Fed. Reg. 44:31514-31568 (1979d).

Environmental Protection Agency. "Analytical Protocol for Screening Publicly Owned Treatment Works (POTW) Sludges for Organic Priority Pollutants," Environmental Monitoring and Support Laboratory, Cincinnati, OH (September 1979e).

Environmental Protection Agency. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories," Environmental Monitoring and Support Laboratory, Cincinnati, OH (March 1979f).

Environmental Protection Agency. "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans," *Office of Monitoring Systems and Quality Assurance*, Washington, D.C., QAMS-005/80, December 27, 1980a.

MONS 005590

Environmental Protection Agency. "Quality Assurance Program Plan for the Office of Toxic Substances, Office of Pesticides and Toxic Substances," Washington, D.C. October 1980b.

Environmental Protection Agency. "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," Office of Water and Waste Management, Washington, D.C., SW-846 (1980c).

Environmental Protection Agency. "Ambient Water Quality Criteria for: Polychlorinated Biphenyls (PCBs)," Report for Office of Water Regulations and Standards, Criteria and Standards Division, Washington, D.C., EPA 440/5-80-068 NTIS No. PB81-117798), October 1980d.

Environmental Protection Agency. "The Analysis of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils," Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH (February 1981a).

Environmental Protection Agency. "PCB Disposal by Thermal Destruction," Report by Solid Waste Branch, Air and Hazardous Materials Division, U.S. Environmental Protection Agency, Region 6, Dallas, TX, EPA-200/9-81-001 (NTIS No. PB82 241 860), 606 pp. (1981b).

Environmental Protection Agency. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Report by Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, Cincinnati, OH, EPA 600/4-81-055 (1981c).

Environmental Protection Agency. "Toxic Substances Control Act Inspection Manual; Volume I, TSCA Base Manual; Volume II, PCB Inspection Manual," U.S. Environmental Protection Agency, Pesticides and Toxic Substances Enforcement Division, Washington, DC (March 1981d).

Environmental Protection Agency. "40 CFR Part 761, Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions; Recodification," Fed. Reg. 47:19526-19527 (May 6, 1982a).

Environmental Protection Agency. "40 CFR Part 761, Polychlorinated Biphenyls (PCBs); Manufacture, Processing, Distribution, and Use in Closed and Controlled Waste Manufacturing Processes," Fed. Reg. 47:24976-24989 (June 8, 1982b).

Environmental Protection Agency. "40 CFR Part 761, Polychlorinated Biphenyls (PCBs); Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions; Use in Closed and Controlled Waste Manufacturing Processes," Fed. Reg. 47:46980-46986 (October 21, 1982c).

MONS 005591

Environmental Protection Agency. "Analysis of Pesticides, Phthalates, and Polychlorinated Biphenyls in Soils and Bottom Sediments," HWI Sample Management Office, Alexandria, VA, unpublished method (November 4, 1982d), 12 pp.

Environmental Protection Agency. "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods, SW-846, 2nd Edition," Office of Solid Waste and Emergency Response, Washington, DC (July 1982e).

Environmental Protection Agency. "40 CRF Part 761, Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce and Use Prohibitions; Use in Electrical Equipment," Fed. Reg. 47:37342-34360 (August 25, 1982f).

Environmental Protection Agency. "40 CFR Part 761, Procedural Amendment of the Approval Authority for PCB Disposal Facilities and Guidance for Obtaining Approval," Fed. Reg. 48:13181-13186 (1983a).

Environmental Protection Agency. "Quality Assurance Newsletter," Vol. 5, No. 3, Environmental Monitoring and Support Laboratory, Cincinnati, OH (April 1983b).

Environmental Protection Agency. "Quality Assurance Program Plan for the Office of Toxic Substances, Office of Pesticides and Toxic Substances," Washington, D.C. (September 30, 1983c).

Environmental Protection Agency. "40 CFR Part 761, Polychlorinated Biphenyls (PCBs); Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions," in Code of Federal Regulations, Title 40, Part 425 to End (Revised as of July 1, 1983d), U.S. Government Printing Office, Washington, DC (1983d) pp. 530-566.

Environmental Protection Agency. "40 CFR Part 761, Polychlorinated Biphenyls (PCBs); Manufacture, Processing, Distribution in Commerce and Use Prohibitions; Use in Electrical Transformers, Advanced Notice of Proposed Rulemaking," Fed. Reg. 49:11070-11083 (March 23, 1984a).

Environmental Protection Agency. "40 CFR Part 761, Polychlorinated Biphenyls (PCBs); Manufacturing, Processing, Distribution in Commerce and Use Prohibitions; Response to Individual and Class Petitions for Exemptions; Exclusions, Exemptions, and Use Authorizations, Final Rule," Fed. Reg. 49:28154-28209 (July 10, 1984b).

MONS 005592

Environmental Protection Agency. "40 CFR Part 761, Polychlorinated Biphenyls (PCBs); Manufacture, Processing, Distribution in Commerce and Use Prohibitions; Use in Electrical Transformers," Fed. Reg. 49:39966-39989 (October 11, 1984c).

Environmental Protection Agency. "Mass Spectrometric Identification and Measurement of Polychlorinated Biphenyls as Isomer Groups," Draft Report by Physical and Chemical Methods Branch, Office of Research and Development, Cincinnati, OH (October 1984d).

Environmental Protection Agency, "Organochlorine Pesticides and PCBs--Method 608," Fed. Reg. 49(209):89-104 (October 26, 1984e).

Environmental Protection Agency. "Base/Neutrals, Acids, and Pesticides--Method 625," Fed. Reg., 49(209):153-174 (October 26, 1984f).

Erickson, M. D. "Gas Chromatography/Fourier Transform Infrared Spectroscopy Applications," Appl. Spectrosc. Rev. 15(2): 261-325 (1979).

Erickson, M. D. "Review of the Report 'Statistical Analysis of Data from a Round Robin Experiment on PCB Samples,'" Letter Report, U.S. EPA Contract No. 68-01-5915, Task D6, February 1982.

Erickson, M. D. "Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Commercial Products and Product Wastes, Revision 2," U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, EPA 560/5-85-010 (1984a).

Erickson, M. D. "Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Air, Revision 2," U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, EPA 560/5-85-011 (1984b).

Erickson, M. D. "Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Water, Revision 2," U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, EPA 560/5-85-012 (1984c).

Erickson, M. D. and E. D. Pellizzari. "Identification and Analysis of Polychlorinated Biphenyls and Other Related Chemicals in Municipal Sewage Sludge Samples," U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., EPA-560/6-77-021 (August 1977).

MONS 005593

Erickson, M. D. and E. D. Estes. "Evaluation of Chlorinated Hydrocarbon Catalytic Reduction Technology" U.S. Environmental Protection Agency, Office of Research and Development, Washington, D. C., EPA-600/2-78-059 (March 1978).

Erickson, M. D., L. C. Michael, R. A. Zweidinger and E. D. Pellizzari. "Development of Methods for Sampling and Analysis of Polychlorinated Naphthalenes in Ambient Air," Environ. Sci. Technol., 12:927-931 (1978).

Erickson, M. D. and E. D. Pellizzari. "Analysis of Municipal Sewage Sludge Samples by GC/MS/Computer for Polychlorinated Biphenyls and Other Chlorinated Organics," Bull. Environ. Contam. Toxicol. 22:688-694 (1979).

Erickson, M. D., C. M. Sparacino, E. D. Pellizzari and K. B. Tomer. "Point Source Ambient Monitoring to Determine Impact of ENSCO Incinerator Located at El Dorado, Arkansas," Draft Report submitted to Phillip Schwindt, U.S. Environmental Protection Agency, Region 6, Sampling and Analysis Division, Dallas, TX, EPA Contract No. 68-01-4141, Task 29, October 1980a, 135 pp.

Erickson, M. D., B. S. H. Harris, E. D. Pellizzari, K. B. Tomer, R. D. Waddell and D. A. Whitaker, "Acquisition and Chemical Analysis of Mother's Milk for Selected Toxic Substances," Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., EPA 560/13-80-029, 1980b.

Erickson, M. D. and John S. Stanley. "Methods of Analysis for By-Product PCBs--Literature Review and Preliminary Recommendations," Interim Report No. 1, Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., EPA-560/5-82-005, NTIS No. PB83 126 573 (1982). 135 pp.

Erickson, M. D., J. S. Stanley, K. Turman, G. Radolovich, K. Bauer, J. Onstot, D. Rose and M. Wickham. "Analytical Methods for By-Product PCBs--Preliminary Validation and Interim Methods," Interim Report No. 4, Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D. C., EPA-560/5-82-006, NTIS No. PB83 127 696 (1982), 243 pp.

Erickson, M. D. and R. V. Shah. "Guidelines for PCB Destruction Permit Applications and Demonstration Test Plans," Draft Interim Report No. 5, Revision 1, EPA Contract No. 68-01-5915, Task 51, May 17, 1983, 80 pp.

MONS 005594

Erickson, M. D., J. S. Stanley, J. K. Turman, G. Radolovich, J. Onstot, M. Wickham and J. Going. "Determination of Incidentally Generated PCBs in Commerical Products and Wastes by Capillary GC/EIMS." Abstract from 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 1983a.

Erickson, M. D., J. S. Stanley, J. K. Turman, J. E. Going and D. P. Redford. "Methods for Analysis of Complex Mixtures in Complex, Variable Matrices--Chlorinated Biphenyls in Commercial Products and Wastes," in Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement, M. Cooke and A. J. Dennis, Eds. (Columbus, OH: Battelle Press, 1983b), pp. 483-492.

Erickson, M. D., K. M. Bauer, F. J. Bergman. "Analytical Methods for By-Product and Destruction Derived PCBs--Interlaboratory Validation A," Draft Interim Report No. 6, Task 51, EPA Contract No. 68-01-5915, August 23, 1983c.

Erickson, M. D., J. S. Stanley, G. Radolovich and R. B. Blair. "Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Commercial Products and Product Wastes," Revision 1, Prepared by Midwest Research Institute for Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, DC, under Subcontract No. A-3044(8149)-271, Work Assignment No. 17 to Battelle, Washington, DC August 15, 1983d.

Erickson, M. D., J. P. Goforth, M. A. Jones, M. C. Saylor, K. B. Tomer, and E. D. Pellizzari, B. T. Cook, M. Frankenberry, J. J. Breen and F. W. Kutz. "Analysis of Blood and Adipose Tissue Samples from GSA Workers for Polychlorinated Biphenyls (PCBs) Phase I: Packed Column GC/ECD and GC/MS Analyses," Interim Report, Contract No. 68-01-3849, Task 4, U.S. Environmental Protection Agency (1983e).

Erickson, M. D., P. G. Gorman, and D. T. Heggem. "Relationship of Destruction Parameters to the Destruction/Removal Efficiency (DRE) of PCBs," Journal of the Air Pollution Control Association, in press (1984a).

Erickson, M. D., C. J. Cole, J. D. Flora, Jr., P. G. Gorman, C. L. Haile, G. D. Hinshaw, F. C. Hopkins, and S. E. Swanson. "Thermal Degradation Products from Dielectric Fluids," U.S. Environmental Protection Agency, Washington, DC, EPA 560/5-84-009; NTIS No. PB 85/38535 (1984b).

Erickson, M. D., C. J. Cole, J. D. Flora, Jr., P. G. Gorman, C. L. Haile, G. D. Hinshaw, F. C. Hopkins, S. E. Swanson, and D. T. Heggem, "PCDF Formation from PCBs Under Fire Conditions," Chemosphere (submitted) (1984c).

MONS 005595

Erickson, M. D., J. S. Stanley, J. K. Turman, J. E. Going, O. P. Redford, and D. T. Heggem. "Determination of By-Product PCBs in Commercial Products and Wastes by High Resolution GC/EIMS," Anal. Chem. (submitted) (1984d).

Erickson, M. D., C. J. Cole, J. D. Flora, Jr., P. G. Gorman, C. L. Haile, G. D. Hinshaw, F. C. Hopkins, S. E. Swanson, and D. T. Heggem. "Formation of PCDFs Under 'Optimized' Combustion Conditions from Low-Level PCB Dielectric Fluids," Presented at EPRI PCDF Workshop, Palo Alto, California (1984e).

Erickson, M. D., C. J. Cole, J. D. Flora, Jr., P. G. Gorman, C. L. Haile, G. D. Hinshaw, F. C. Hopkins, S. E. Swanson, and D. T. Heggem. "Formation of PCDFs Under 'Optimized' Combustion Conditons from Low-Level PCB Dielectric Fluids," in Proceedings: 1984 EPRI PCDF Workshop, G. Addis and R. Komai, Eds., Electric Power Research Institute, (1985a) in press.

Erickson, C. J. Cole, J. D. Flora, P. G. Gorman, C. L. Haile, G. D. Hinshaw, F. C. Hopkins, S. E. Swanson, and D. T. Heggem. "Thermal Degradation Products from Dielectric Fluids," Presented at 189th ACS National Meeting, Miami Beach, Florida (May 1985b).

Erickson, M. D., J. S. Stanley, J. K. Turman, and G. Radolovich. "Analytical Method: The Analysis of Chlorinated Biphenyls in Liquids and Solids," U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, EPA-560/5-85-023 (February 1985c).

Erney, D. R. "A Feasibility Study of Miniature Silica Gel Columns for the Separation of Some Polychlorinated Biphenyls, DDT, and Analogs," Bull. Environ. Contam. Toxicol. 12(6):710-716 (1974a).

Erney, D. R. "Rapid Screening Method for Analysis of Chlorinated Pesticide and Polychlorinated Biphenyl Residues in Fish," J. Assoc. Offic. Anal. Chem. 57(3):576-579 (1974b).

Ernst, W., R. G. Schaefer, H. Goerke and G. Eder. "Aufarbeitung von Meerestieren für die Bestimmung von PCB, DDT, DDE, DDD, γ-HCH und HCB," Z. Anal. Chem. 272:358-363 (1974).

Exner, J. H. (Ed.). Detoxication of Hazardous Waste, Ann Arbor Science, Ann Arbor, MI (1982a), 362 pp.

Exner, J. H. "Summary of Polychlorinated Biphenyl Treatment Alternatives," Chapter 6 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982b), pp. 119-120.

MONS 005596

Farrington, J. W., E. D. Goldberg, R. W. Risebrough, J. H. Martin and V. T. Bowen. "U.S. 'Mussel Watch' 1976-1978: An Overview of the Trace-Metal, DDE, PCB, Hydrocarbon, and Artificial Radionuclide Data," Environ. Sci. Technol. 17:490-496 (1983).

Farwell, S. O., F. A. Beland and R. D. Geer. "Interrupted-Sweep Voltammetry for the Identification of Polychlorinated Biphenyls and Naphthalenes, Anal. Chem. 47(6):895-902 (May 1975).

Feairheller, W., P. J. Marn, D. H. Harris and D. L. Harris. "Technical Manual for Process Sampling Strategies for Organic Materials," Prepared for the U.S. Environmental Protection Agency, Office of Research and Development, Washington, D. C., Report No. EPA-600/2-76-122 (April 1976).

Fehringer, N. V. and J. E. Westfall. "Separation and Identification of DDT Analogs in the Presence of Polychlorinated Biphenyl Compounds by Two-Dimensional Thin-Layer Chromatography," J. Chromatogr. 57:397-405 (1971).

Femia, R. A., S. Scypinski, and L. J. Cline Love. "Fluorescence Characteristics of Polychlorinated Biphenyl Isomers in Cyclodextrin Media," Environ. Sci. Technol., 19(2):155-159 (1985).

Finklea, J. D., L. E. Priester, J. P. Creason, T. Hauser, T. Hinners and D. I. Hammer. "Polychlorinated Biphenyl Residues in Human Plasma Expose a Major Urban Pollution Problem," Amer. J. Publ. Health 62:645-651 (1972).

Finlay, D. J., F. H. Siff and V. J. DeCarlo. "Review of PCB Levels in the Environment," EPA-560/7-76-001; NTIS No. PB-253 735 (1976).

Finsterwalder, C. E. "Industrial Chemicals: Collaborative Study of the Determination of Polychlorinated Biphenyls in Paperboard," J. Assoc. Off. Anal. Chem. 57(3):518-521 (1974).

Fishbein, L. "Chromatographic and Biological Aspects of Polychlorinated Biphenyls," J. Chromatogr. 68:345-426 (1972).

Fishbein, L. "Toxicity of Chlorinated Biphenyls," Ann. Rev. Pharmacol. 14:139-156 (1974).

Fishbein, L. (Ed.). Potential Industrial Carcinogens and Mutagens, (Amsterdam: Elsevier, 1979).

MONS 005597

Fisher, D. J., T. O. Rouse, and T. R. Lynn, "Field Determination of PCB in Transformer Oil 'CLOR-N-OIL Kit'," in Proceedings: 1983 PCB Seminar, G. Addis and R. Y. Komai, Eds. Report No. EPRI-EL-3581 (Palo Alto, CA: Electric Power Research Institute, 1984).

Food and Drug Administration. "Pesticide Analytical Manual," Vol. I, August 1, 1977.

Fradkin, L. and S. Barisas. "Technologies for Treatment, Reuse, and Disposal of Polychorinated Biphenyl Wastes," Argonne National Laboratory, Argonne, IL, Report No. ANL/EES-TM-168 (NTIS No. DE 82013715], 51 pp. (1982).

Frank, R., M. Holdrinet, H. E. Braun, D. P. Dodge and G. E. Sprangler. "Residues of Organochlorine Insecticides and Polychlorinated Biphenyls in Fish from Lakes Huron and Superior, Canada, 1968-76," Pestic. Monit. J. 12(2):69-80 (1978).

Frank, R., R. L. Thomas, M. Holdrinet, A. L. W. Kemp, H. E. Braun and R. Dawson. "Organochlorine Insecticides and PCB in the Sediments of Lake Huron (1969) and Georgian Bay and North Channel (1973)," Sci. Total Environ. 13:101-117 (1979).

Fries, G. F. "Polychlorinated Biphenyl Residues in Milk of Environmentally and Experimentally Contaminated Cows," Environ. Health Perspec. 1(1):55-62 (April 1972).

Friess, S. L., V. A. Drill, H. W. Hays, T. A. Loomis and C. B. Schaffer. "Potential Health Effects from Exposure to Polychlorinated Biphenyls; Laboratory Studies," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D. C., Report No. LSI-TR-507-1378, NTIS No. PB84-135771 (December 1983), pp. 212-228.

Frimmel, F. "Differentiation of Polychlorinated Biphenyls from Pesticides with Combined Gas Chromatography-Mass Spectrometry," Z. Wasser Abwasser Forsch 6(4):113-116 (1973).

Fukano, S. and M. Doguchi. "PCT, PCB and Pesticide Residues in Human Fat and Blood," Bull. Environ. Contam. Toxicol. 17(5): 613-617 (1977).

Fuller, B., J. Gordon and M. Kornreich. "Environmental Assessment of PCBs in the Atmosphere," U.S. Environmental Protection Agency, Washington, D. C., EPA-450/3-77-045 (April 1976).

Furukawa, K., K. Tonomura and A. Kamibayashi. "Effect of Chlorine Substitution on the Biodegradability of Polychlorinated Biphenyls," Appl. Environ. Microbiol. 35(2):223-227 (1978).

Gaffey, W. R. "The Epidemiology of PCBs," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983a), pp. 279-298.

Gaffey, W. R. "Recent Epidemiologic Studies of PCBs," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U. S. Environmental Protection Agency, Washington, D. C., Report No. LSI-TR-507-1378, NTIS No. PB84-135771 (December 1983b), pp. 189-201.

Gaffney, P. E. "Chlorobiphenyls and PCBs: Formation During Chlorination," Journal Water Pollution Control Federation, 49(3):401-404 (March 1977).

Gallis, D., A. Defner-Hallowel, J. C. White and J. Waber. "Optimization of a Reversed Phase Partitioning Technique for the Analysis of Polychlorinated Biphenyls in Aqueous Samples by Gas Chromatography/Mass Spectrometry," Bull. Environ. Contam. Toxicol. 31(3):285-291; Chem. Abstr. 99:145823z (1983).

Garcia-Gutierrez, A., A. E. Mcintyre, J. N. Lester and R. Perry. "Determination of Organochlorine Compounds in Waste Water Samples by Gas Chromatography and Gas Chromatography-Mass Spectrometry Using Capillary Columns," Environ. Technol. Lett. 4:129-140; Chem. Abstr. 98:204072h (1983).

Garty, J., A. S. Perry and J. Mozel. "Accumulation of Polychlorinated Biphenyls (PCBs) in the Transplanted Lichen Ramaline Duriaei in Air Quality Biomonitoring Experiments," Nord. J. Bot. 2(6):583-586 (1983); Chem. Abstr. 98:148790b (1983).

Gassiot, M., X. Tomás, F. Broto, L. G. Sabaté and G. Codinas. "Algorithms for the Quantitative Determination of PCBs in Chromatograms of Organochlorinated Contaminants: Application to Samples of Sediments and Marine Organisms," Analytical Techniques in Environmental Chemistry 2, J. Albaiges, Ed. (New York, NY: Pergamon Press, 1982) pp. 249-258.

Gast, R. "Studies into Quantitative PCB Determination," Muench. Beitr. Abwasser, Fisch.-Flussbiol. 30:215-225 (1978); Chem. Abst. 90:115924e (1979).

General Accounting Office. "EPA Slow in Controlling PCBs," GAO/CED-82-21, 39 pages, December 30, 1981.

Gesser, H. D., A. Chow and F. C. Davis. "The Extraction and Recovery of Polychlorinated Biphenyls (PCB) Using Porous Polyurethane Foam," Anal. Letters 4(12):883-886 (1971).

Giacin, J. R. and S. G. Gilbert. "Analysis of Polychlorinated Biphenyls in Packaging Materials," in Technical Advances in Packaging with Flexible Barrier Materials, ASTM STP 548, 10-19 (1973).

Giam, C. S., A. R. Hanks, R. L. Richardson, W. M. Sackett and M. K. Wong. "DDT, DDE, and Polychlorinated Biphenyls in Biota from the Gulf of Mexico and Caribbean Sea - 1971," Pestic. Monit. J. 6(3):139-143 (1972).

Giam, C. S., H. S. Chan and G. S. Neff. "Rapid and Inexpensive Method for Detection of Polychlorinated Biphenyls and Phthalates in Air," Anal. Chem. 47(13):2319-2320 (1975).

Giam, C. S., H. S. Chan, and G. S. Neff. "Concentrations and Fluxes of Phthalates, DDTs, and PCBs to the Gulf of Mexico," in Marine Pollutant Transfer, H. L. Windom and R. A. Duce, Eds. (Lexington, MA: Lexington Books, 1976) pp. 375-386.

Giger, W., M. Reinhard, C. Schaffner and F. Zürcher. "Analyses of Organic Constituents in Water by High-Resolution Gas Chromatography in Combination With Specific Detection and Computer-Assisted Mass Spectrometry," Chapter 26 in Identification and Analysis of Organic Pollutants in Water, L. H. Keith Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1976), pp. 433-452.

Gilman, A. P. "Monitoring for PCBs in Fish: The Human Health Perspective," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 115-122.

Glaser, J. A., D. L. Foerst, G. D. McKee, S. A. Quave and W. L. Budde. "Trace Analyses for Wastewaters," Environ. Sci. Technol. 15:1426-1435 (1981).

Godefroot, M., M. Stechele, P. Sandra and M. Verzele. "A New Method for the Quantitative Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls," J. High Resol. Chrom. and Chrom. Comm. 5:75-79 (1982a).

MONS 005600

Godefroot, M., M. Stechele, P. Sandra and M. Verzele. "A New Method for the Quantitative Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls," Comm. Eur. Communities, [Rep.] EUR 1982, EUR 7623, Anal. Org. Micropollut. Water 16-23; Chem. Abstr. 97:133257p (1982b).

Goerlitz, D. F., and L. M. Law. "Note on Removal of Sulfur Interferences from Sediment Extracts for Pesticide Analysis," Bull. Environ. Contam. Toxicol. 6:9-10 (1971).

Goerlitz, D. F. and L. M. Law. "Determination of Chlorinated Insecticides in Suspended Sediment and Bottom Material," J. Assoc. Off. Anal. Chem. 57(1):176-181 (1974).

Goldstein, J. A. "Structure-Activity Relationships for the Biochemical Effects and the Relationship to Toxicity," Chapter 4 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzo-dioxins and Related Products, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980), pp. 151-190.

Goldstein, J. A., J. D. McKinney, G. W. Lucier, P. Hickman, H. Bergman and J. A. Moore. "Toxicological Assessment of Hexachlorobiphenyl Isomers and 2,3,7,8-Tetrachlorodibenzofuran in Chicks," Toxicol. Appl. Pharmacol. 36(1):81-92 (1976).

Goodman, J. I. "Concepts in Toxicology and Carcinogenesis: A Basis for Discussing the Potential Environmental Hazard Posed by PCBs," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 179-186.

Gordon, R. J., J. Szita and E. J. Feeder. "Determination of Polychlorinated Biphenyls in Transformer Oils by Capillary Gas Chromatography," Anal. Chem. 54:478-481 (1982).

Gorski, T. and T. Syrowatka. "Simplified Method for the Separation and Determination of Residues of Organochlorine Pesticides and Polychlorinated Biphenyls in Human Fatty Tissue," Chem. Abst. 91:885W (1979).

Gossman, D. G. "Data Processing as an Alternative to Extensive Sample Cleanup in the Gas Chromatographic Determination of PCBs," Abstract from the 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 7-12, 1983.

Gothe, R. "Oxidation with Tetrabutylammonium Permanganate for Quantitation of DDT Residues in GLC Determination of Chlorinated Hydrocarbons," Bull. of Environ. Contam. Toxicol. 11(5):451-455 (1974).

MONS 005601

Grant, D. L. "Regulation of PCBs in Canada," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 383-392.

Greichus, Y. A., J. J. Worman, M. A. Pearson and D. J. Call. "Analyses of Polychlorinated Biphenyls in Bird Tissues and Aroclor Standards with Gas Chromatography and Mass Spectrometry," Bull. of Environ. Contam. Toxicol. 11(2):113-120 (1974).

Griffin, D. A., A. B. Marin and M. L. Deinzer. "Optimization of Chromatographic Conditions for the Separation of p,p'-DDE from Aroclor 1254 on Silica, Using Azulene as Indicator," J. Assoc. Off. Anal. Chem. 63(5):959-964 (1980).

Griffitt, K. R. and J. C. Craun. "Gel Permeation Chromatographic System: An Evaluation," J. Assoc. Off. Anal. Chem. 57(1): 168-172 (1974).

Gross, M. L., J. O. Lay, Jr., P. A. Lyon, D. Lippstreu, N. Kangas, R. L. Harless, S. E. Taylor and A. E. Dupuy, Jr. "2,3,7,8-Tetrachlorodibenzo-p-dioxin Levels in Adipose Tissue of Vietnam Veterans," Environ. Res. 33(1):261-268 (1984); Chem. Abstr. 100:108498r (1984).

Gu, T. and M. Manes. "Adsorptive Displacement from Activated Carbon: Recovery of 4,4'-Dichlorobiphenyl," Environ. Sci. Technol. 18:55-57 (1984).

Gutierrez, A. G., A. E. McIntyre, J. N. Lester and R. Perry. "Comparison of Gas Chromatography and Gas Chromatography/Mass Spectrometry for the Analysis of Polychlorinated Biphenyls and Organochlorine Insecticides in Sewage Sludges," Environ. Technol. Lett. 4(12):521-528 (1983); Chem. Abstr. 100:56357x (1984).

Hadorn, H. and K. Zuercher. "Contamination of Food With Polychlorinated Biphenyls (PCB) by Packaging Material and Environmental Pollution," Gordian 73(12):458-462 (1973).

Haefelfinger, P. "Limits of the Internal Standard Technique in Chromatography," J. Chromatogr. 218:73-81 (1981).

Hahn, G. E. and C. A. Ward. "The Determination of PCBs in Human Blood," Presented at the FACSS 10th Annual Meeting, September 25-30, 1983.

Haile, C. L. and E. Baladi. "Methods for Determining the Total Polychlorinated Biphenyl Emissions From Incineration and Capacitor and Transformer Filling Plants," U. S. Environmental Protection Agency, EPA-600/4-77-048, NTIS No. PB-276 745/7G1 (November 1977), 90 pp.

MONS 005602

Haile, C., J. Stanley, R. M. Lucas, D. Melroy, C. Nulton and W. Yauger, Jr. "Comprehensive Assessment of Specific Compounds Present in Combustion Processes. Vol. 1-Pilot Study of Combustion Emissions Variability," Office of Toxic Substance, U.S. Environmental Protection Agency, Washington, D.C., EPA-560/ 5-83-004 (June 1983a).

Haile, C. L., J. S. Stanley, T. Walker, G. R. Cobb and B. A. Boomer. "Comprehensive Assessment of the Specific Compounds Present in Combustion Processes, Volume 3, National Survey of Organic Emissions from Coal Fired Utility Boiler Plants," Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., EPA-560/5-83-006 (1983b).

Haile, C. L., and V. Lopez-Avila. "Development of Analytical Test Procedures for the Measurement of Organic Priority Pollutants--Project Summary," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA-600/S4-84-001; (Full Report available as NTIS No. PB 84-129 048) (1984).

Haile, C. L., J. S. Stanley, A. M. Magin, R. V. Northcutt and D. P. Redford. "Emissions of Organic Pollutants from Coal-Fired Utility Boiler Plants," in Identification and Analysis of Organic Pollutants in Air, L. H. Keith, Ed. (Boston: Butterworth Publishers, 1984a), pp. 443-458.

Haile, C. L., R. B. Blair, T. Walker, and R. M. Lucas. "Assessment of Emissions of Specific Compounds from a Resource Recovery Municipal Refuse Incinerator," U.S. Environmental Protection Agency, EPA 600/5-84-002, (June 1984b).

Hall, J., F. Record, P. Wolf, G. Hunt, S. Zelenski, P. Fenneily, A. Fisher, A. Garwick, T. Hockman, W. Kilgore and D. Koenig. "Evaluation of PCB Destruction Efficiency in an Industrial Boiler," Report by GCA/Technology Division, Bedford, MA, to David C. Sanches, USEPA, Office of Research and Development, IERL, Research Triangle Park, NC, EPA-600/2-81-055a and b (NTIS Nos. PB 82-224 940 and PB 81-187 270), 172 pp. (1982).

Hammer, D. I., J. F. Finklea, L. E. Priester, J. E. Keil, S. H. Sandifer and K. Bridbord. "Polychlorinated Biphenyl Residues in the Plasma and Hair of Refuse Workers," Environ. Health Perspec. 1(1):83 (1972).

Hammond, P. B. "Biological Effects in Polychlorinated Biphenyls - Environmental Impact," Environ. Res. 5:312-338 (1972).

MONS 005603

Hanai, T. and H. F. Walton, "Chromatography of Chlorinated Biphenyls on an Ion-Exchange Resin," Anal. Chem. 49(6):764-766 (1977).

Hanks, A. R. and B. M. Colvin. "High-Performance Liquid Chromatography," Chapter 3 in Pesticide Analysis, K. G. Das, Ed. (New York, NY: Marcel Dekker, Inc., 1981), pp 99-174.

Hannan, E. J. and D. D. Bills. "Separation of Aldrin from Aroclor 1254," Bull. Environ. Contam. Toxicol., 8(6):327-328 (1972).

Hannan, E. J., D. D. Bills and J. L. Herring. "Analysis of Polychlorinated Biphenyls by Gas Chromatography and Ultraviolet Irradiation," J. Agr. Food Chem. 21(1):87-90 (1973).

Hanneman, L. F. "The New PCB Issue - Analysis of Specific Congeners Produced by Unintentional By-Product Chemistry," Presented at Capillary Chromatography '82--An International Symposium, Tarrytown, NY, October 4-6, 1982.

Haque, R., D. W. Schmedding and V. H. Freed. "Aqueous Solubility, Adsorption, and Vapor Behavior of Polychlorinated Biphenyl Aroclor 1254," Environ. Sci. Tech. 8(2):139-142 (1974).

Haque, R. and D. Schmedding. "A Method of Measuring the Water Solubility of Hydrophobic Chemicals: Solubility of Five Polychlorinated Biphenyls," Bull. Environ. Contam. Toxicol. 14(1): 13-18 (1975).

Haque, R. and D. Schmedding. "Studies on the Adsorption of Selected Polychlorinated Biphenyl Isomers on Several Surfaces," J. Environ. Sci. Health B11(2):129-137 (1976).

Haraguchi, H., H. Kuroki, Y. Masuda, and N. Shigematsu. "Determination of Methylthio- and Methylsulfone Polychlorinated Biphenyls in Tissues of Patients with 'Yusho'," Food Chem. Toxicol. 22(4):282-288 (1984).

Harris, J. C., D. J. Larsen, C. E. Rechsteiner and K. E. Thrun. "Sampling and Analysis Methods for Hazardous Waste Incineration (First Edition)," Report to Larry D. Johnson, U.S. Environmental Protection Agency, IERL, Research Triangle Park, NC, EPA Contract No. 68-02-3111, Technical Directive No. 124, February 1982, 400 pp.

Harris, R. W., C. F. Grainger and W. J. Mitchell. "Validation of a Method for Measuring Polychlorinated Biphenyls in Natural Gas Pipelines," EPA 600/4-81-048; NTIS No. PB82-207556 (1981).

MONS 005604

Harrison, A. G., F. I. Onuska, and C. W. Tsang. "Chemical Ionization Mass Spectrometry of Specific Polychlorinated Biphenyl Isomers," Anal. Chem., 53:1183-1186 (1981).

Harvey, G. R., H. P. Miklas, V. T. Bowen and W. G. Steinhauer. "Observations in the Distribution of Chlorinated Hydrocarbons in Atlantic Ocean Organisms," J. Marine Res. 32:103-118 (1974).

Harvey, G. R., and W. G. Steinhauer. "Transport Pathways of Polychlorinated Biphenyls in Atlantic Water," J. Marine Res. 34:561-575 (1976).

Harvey, J., Jr., G. Zweig, R. Cannizzaro, H. Dishburger and J. Sherma (Ed.), "Pesticide Analytical Methodology," ACS Symposium Series 136 (Washington, D. C.: Amer. Chem. Soc., 1980).

Harz, A., and U. Muelder. "Gas Chromatographic Determination of Mirex and Polychlorinated Biphenyls," Lebensmittelchem. Gerichtl. Chem. 37(6):146-174 (1983); Chem. Abst. 101:5594k (1984).

Hass, J. R. and M. D. Friesen. "Qualitative and Quantitative Methods for Dioxin Analysis," Ann. N.Y. Acad. Sci. 320:28-42 (1979).

Hass, J. R., M. D. Friesen and M. K. Hoffman. "Recent Mass Spectrometric Techniques for the Analysis of Environmental Contaminants," Chapter 11 in Environmental Health Chemistry, The Chemistry of Environmental Agents as Potential Human Hazards, J. D. McKinney, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981), pp. 219-243.

Hattori, Y., Y. Kuge and M. Nakamoto. "The Correlation Between the Electron-Capture Detector Response and the Chemical Structure for Polychlorinated Biphenyls," Bull. Chem. Soc. Jpn. 54(9):2807-2810; Chem. Abstr. 96:34427s (1981).

Hattula, M. L. "Some Aspects of the Recovery of Chlorinated Residues (DDT-Type Compounds and PCB) From Fish Tissue by Using Different Extraction Methods," Bull. Environ. Contam. Toxicol. 12(3):301-307 (1974a).

Hattula, M. L. "Simultaneous Clean Up of Fish Fat Containing Low Levels of Residues and Separation of PCB From Chlorinated Pesticides by Thin-Layer Chromatography," Bull. Environ. Contam. Toxicol. 12(3):331-337 (1974b).

Hattula, M. L. and O. Karlog. "Adsorption of Polychlorinated Biphenyls (PCB) on Glass Surfaces," Dan. Tidsskr. Farm. 45(7): 259-261 (1971).

MONS 005605

Heeg, F. J., R. Zinburg, H. J. Neu and K. Ballschmiter. "Retention Index Calculation Based on a Non-Linear Relationship Between Net Retention Time and Carbon Number of n-Alkanes," Chroma-tographia 12(7):451-458 (1979).

Heesen, T. C., and D. R. Young. "Precision of Chlorinated Hydrocarbon Measurements," in Southern California Coastal Water Research Project Annual Report for the Year Ended June 30, 1977, p. 69-74 (1977) (NTIS No. PB274 463/9GI).

Heesen, T. C., D. R. Young, and D. McDermott-Ehrlich. "Evaluation of a Technique for Measuring Dry Atmospheric Deposition Rates of DDT and PCB Residues," Atmospheric Environment 13:1677-1680 (1979).

Heller, S. R., J. M. McGuire and W. L. Budde. "Trace Organics by GC/MS," Environ. Sci. Technol. 9(3):210-213 (March 1975).

Heller, S. R. and G. W. A. Milne. "1978 Indices to EPA/NIH Mass Spectral Data Base," U.S. G.P.O., Washington, D.C. (1978). p. 25409.

Henderson, J. E. and W. H. Glaze. "GC/MS Analysis of XAD-2 Extracts of Superchlorinated Septage," Water Res. 16:211-218 (1982).

Hernandez, A. and H. F. Walton. "Liquid Chromatography of Chlorinated Biphenylols," J. Chromatogr. 242:346-348 (1982).

Herzel, F. "Polychlorinated Biphenyls and Their Discrimination from Organochlorine Insecticides," Vom Wasser 38:71-80 (1971).

Hesselberg, R. J. and J. L. Johnson. "Column Extraction of Pesticides from Fish, Fish Food and Mud," Bull. Environ. Contam. Toxicol. 7:115-120 (1972).

Higuchi, K. (Ed.). PCB Poisoning and Pollution. (New York, NY: Academic Press, 1976).

Hilker, D. R., K. M. Aldous, R. M. Smith, P. W. O'Keefe and J. Jurusik. "Comparison of Methods for the Determination of PCDDs and PCDFs in Transformer Oil and Transformer Oil Soot," Presented at the American Society for Mass Spectrometry, Thirty-First Annual Conference on Mass Spectrometry and Allied Topics, Boston, MA, May 8-13, 1983.

Hingoreni, N. G., "PCB Technical Report from EPRI, No. 9," EPRI Technical Newsletter, Electrical Power Reserch Institute, Palo Alto, California (November 28, 1984).

Hirota, K., Y. Takata, Y. Arikawa, T. Yoshihara, H. Akimori and S. Ganno. "Preparation and Application of Glass Capillary Columns," Bunseki Kagaku 23(10):1194-1201 (1974).

Hirwe, S. N., R. E. Borchard, L. G. Hansen and R. L. Metcalf. "Gas-Liquid Chromatography - Mass Spectrometric Characterization of Aroclor 1242 and 1254 Components," Bull. Environ. Contam. Toxicol. 12(2):138-144 (1974).

Hodges, K. L., T. A. Robinson, C. J. Hensler, R. S. Kaley, H. Caspers, F. Ewald and A. R. Pittaway. "Exposure Studies Relating to Industrial Processes Containing Incidental PCB," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-1378, NTIS No. PB84-135771 (December 1983), pp. 137-181.

Hoeting, A. L. "FDA Regulation of PCB in Food," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 393-408.

Hofstader, R. A., C. A. Bache and D. J. Lisk. "Interference in the Electron-Capture Technique for Determination of Polychlorinated Biphenyls by Sulfur-Containing Compounds in Petroleum Products," Bull. Environ. Contam. Toxicol. 11(2):136-138 (1974).

Holden, A. V. "The Analysis of Fish for Organochlorine Residues," International Symposium on Identification and Measurement of Environmental Pollutants, Ottawa, Ontario, Canada (June 1971).

Holden, A. V. "International Cooperative Study of Organochlorine and Mercury Residues in Wildlife, 1969-71," Pestic. Monit. J. 7(1): 37-52 (1973).

Holden, A. V. "Report on the Fourth ICES Organochlorine Intercalibration Exercise," International Council for the Exploration of the Sea, Copenhagen, Denmark, CM 1980/E:40 (1980).

Holden, A. V. and K. Marsden. "Single-Stage Clean-Up of Animal Tissue Extracts for Organochlorine Residue Analysis," Journal of Chromatography, 44:481-492 (1969).

Holdrinet, M. V. H. "Preliminary Results of an Interlaboratory PCB Check Sample Program," Environ. Qual. Safety Suppl. 3 (Pesticides):51-56 (1975).

Holdrinet, M. V. H. "Confirmation of Mirex and cis- and trans-Chlordane in the Presence of Other Organochlorine Insecticides and Polychlorinated Biphenyls," Bull. Environ. Contam. Toxicol. 21:46-52 (1979).

Hollod, G. J. and S. J. Eisenreich. "Collection of Atmospheric Polychlorinated Biphenyls on Amberlite XAD-2 Resins," Anal. Chim. Acta 124:31-38 (1981).

Holmes, D. C. and M. Wallen. "A Simple Differentiation of Polychlorobiphenyls from Chlorinated Naphthalenes," J. Chromatogr. 71:562-563 (1972).

Hopper, M. L. and D. D. Hughes. "An Improved GPC System for Pesticides in Fats," Laboratory Information Bulletin No. 1958, FSB/EDRO, U.S. Food and Drug Administration, Kansas City, MO, p. 50-55 (July 1976).

Horn, E. J., L. J. Hetling and T. J. Tofflemire. "The Problem of PCBs in the Hudson River System," Ann. N. Y. Acad. Sci. 320:591-609 (1979).

Hornig, A., and H. Masters. "Destruction of PCB-Contaminated Soils with a High-Temperature Fluid-Wall (HTFW) Reactor," Municipal Environmental Research Laboratory--Cincinnati, OH, Office of Research and Development, EPA-600/D-84-072 (1984).

Horwitz, W. "Evaluation of Analytical Methods Used for Regulation of Foods and Drugs," Anal. Chem. 54(1):67A-76A (1982).

Horwitz, W. "Today's Chemical Realities," J. Assoc. Off. Anal. Chem. 66(5):1295-1301 (1983).

Horzemoe, L. M. and D. M. Di Toro. "Extent of Reversibility of Polychlorinated Biphenyl Adsorption," Water Research 17: 851-859 (1983).

Hubbard, H. L. "Chlorinated Biphenyl and Related Compounds," in Encyclopedia of Chemical Technology, 2nd Ed. (New York, NY: Kirk-Othmer, Publishers - Wiley and Sons Interscience, 1964), Vol. 5 pp. 289-297.

Huckins, J. N., J. E. Swanson and D. L. Stalling. "Perchlorination of Polychlorinated Biphenyls," J. Assoc. Off. Anal. Chem. 57(2):416-417 (1974).

Huckins, J. N., D. L. Stalling and J. L. Johnson. "Silicic Acid Chromatographic Separation of Polychlorinated Biphenyls and Pesticides: Some Contaminants and Limitations," J. Assoc. Off. Anal. Chem. 59(5):975-981 (1976).

MONS 005608

Huckins, J. N., D. L. Stalling and W. A. Smith. "Foam-Charcoal Chromatography for Analysis of Polychlorinated Dibenzodioxins in Herbicide Orange," J. Assoc. Off. Anal. Chem. 61:32-38 (1978).

Huckins, J. N., D. L. Stalling and J. D. Petty. "Carbon-Foam Chromatographic Separation of Non-o,o'-Chlorine Substituted PCBs from Aroclor Mixtures," J. Assoc. Off. Anal. Chem. 63(4): 750-755 (1980).

Humphrey, H. E. B. "Population Studies of PCBs in Michigan Residents," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 299-310.

Hunt, D. F., J. Schabanowitz, T. M. Harvey, and M. Coates. "Scheme for the Direct Analysis of Organics in the Environment by Tandem Mass Spectrometry," Anal. Chem., 57:525-537 (1985).

Hunt, G. T., P. Wolf and P. F. Fennelly. "Incineration of Polychlorinated Biphenyls in High-Efficiency Boilers: A Viable Disposal Option," Environ. Sci. Technol. 18:171-179 (1984).

Hunter, R. G. "Environmental Effects of Polychlorinated Biphenyls: Important Ecological Aspects," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-137B, NTIS No. PB84-135771 (December 1983), pp. 265-291.

Hutzinger, O. "PCB Symposium," Chemosphere 12(7/8):N39-N43 (1983a).

Hutzinger, O. "Summary of Recent Advances in Exposure, Health and Environmental Effects Studies of PCBs," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings," R. J. Davenport and B. K. Bernard (Eds.), Office to Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-137B, NTIS No. PB84-135771 (December 1983b), pp. 340-345.

Hutzinger, O., S. Safe, and V. Zitko, "Analysis of Chlorinated Aromatic Hydrocarbons by Exhaustive Chlorination: Qualitative and Structural Aspects of the Perchloro-Derivatives of Biphenyl, Naphthalene, Terphenyl, Dibenzofuran, Dibenzodioxin and DDE," Intern. J. Environ. Anal. Chem., 2, 95-106 (1972a).

MONS 005609

Hutzinger, O., S. Safe and V. Zitko. "Photochemical Degradation of Chlorobiphenyls (PCBs)," Environ. Health Perspec. 1(1): 15-20 (1972b).

Hutzinger, O., W. D. Jamieson, S. Safe and V. Zitko. "Exhaustive Chlorination as a Technique in the Analysis of Aromatic Hydrocarbons," J. Assoc. Off. Anal. Chem. 56(4):982-986 (1973).

Hutzinger, O., S. Safe, and V. Zitko, The Chemistry of PCB's, (CRC Press: Cleveland, Ohio, 1974a) 269 pp.

Hutzinger, O., S. Safe and V. Zitko. "Preparation, Gas Chromatographic Behavior, and Spectroscopic Properties of Hydroxylated Chlorobiphenyls," J. Assoc. Off. Anal. Chem. 57(5):1061-1067 (1974b).

Hutzinger, O., R. A. Heacock and S. Safe. "Thin-Layer Chromatography and Colour Reactions of Some Hydroxylated Chlorobiphenyls," J. Chromatogr. 97:233-247 (1974c).

Hutzinger, O. and A. A. M. Roof. "Polychlorinated Biphenyls and Related Halogenated Compounds," in Analytical Techniques in Environmental Chemistry, J. Albaiges, Ed. (New York, NY: Pergamon Press, 1980a), pp. 167-184.

Hutzinger, O. and A. A. M. Roof. "Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment: The Thoughts on the Philosophy and Practice of Environmental Analytical Chemistry," Environ. Sci. Res. 16:9-20 (1980b).

Iida, Y. and T. Kashiwagi. "Analysis of Polychlorinated Biphenyls by Gas Chromatography-Chemical Ionization Mass Spectrometry," Seikei Daigaku Kogakubu Kogaku Hokoku 19:1461-1462 (1975).

Iida, Y., S. Daishima and T. Kashiwagi. "Determination of Polychlorobiphenyls by Chemical Ionization Mass Spectrometry," Bunseki Kagaku 32(2):80-86; Chem. Abstr. 98:154737f (1983).

International Agency for Research on Cancer. "IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans--Polychlorinated Biphenyls and Polybrominated Biphenyls," Volume 18 (Lyon, France, 1978), pp. 43-103.

International Joint Commission. "Great Lakes Water Quality - Appendix E. Status Report on the Persistent Toxic Pollutants in the Lake Ontario Basin," IJC (1977).

MONS 005610

Ishii, D. and T. Takeuchi. "High-Performance Liquid Chromatography Using Flexible Fused-Silica Micro-Packed Columns," J. Chromatogr. 255:349-358 (1983).

Ismail, R. J. and F. L. Bonner. "New, Improved Thin Layer Chromatography for Polychlorinated Biphenyls, Toxaphene, and Chlordane Components," J. Assoc. Off. Anal. Chem. 57(5):1026-1032 (1974).

Issaq, H. J., J. Klose, and G. M. Muschik. "Separation of Polychlorinated Biphenyls (Aroclor 1254) by High Performance Liquid Chromatography," J. Chromatogr. 302:159-166 (1984).

IT Corporation. "Initial Report for Destruction of Polychlorinated Biphenyls in a Mobile Incineration System at EPA Region II Facility, Edison, NJ, Volume I," U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory-Ci, Oil and Hazardous Material Spills Branch, Edison, NJ, September 18, 1981, 16 pp.

IT Corporation. "Trial Burn Plan for the U.S. Environmental Protection Agency Mobile Incineration System at EPA Region II Facility, Edison, NJ." Prepared for: U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory-Ci, Oil and Hazardous Material Spills Branch, Edison, NJ, February 26, 1982a, 148 pp.

IT Corporation. "USEPA Mobile Incineration System SPCC Plan," Prepared for U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Oil and Hazardous Material Spills Branch, Edison, NJ, July 16, 1982b.

IT Corporation. "USEPA Mobile Incineration System, Phase II Interim Trial Burn Results," Prepared for: U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Oil and Hazardous Materials Spills Branch, Edison, NJ, December 10, 1982c, 22 pp.

IT Corporation. "Mobile Incineration System Trial Burn Quality Assurance Project Plan EERU/QA-2," Prepared for: U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Solid and Hazardous Waste Research Division, Oil and Hazardous Spills Branch, Edison, NJ, December 30, 1982d.

Jacobson, S. W., J. L. Jacobson, P. M. Schwartz and G. G. Fein. "Intrauterine Exposure of Human Newborns to PCBs: Measures of Exposure," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 311-344.

MONS 005611

James, R. C. and R. D. Harbison. "Assessment of the Human Risks to PCBs Associated with the Expected Environmental Exposures," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-137B, NTIS No. PB84-135771 (December 1983), pp. 300-336.

Jennings, W. "Gas Chromatography with Glass Capillary Columns," 2nd Edition (New York, NY: Academic Press, 1980).

Jensen, S. Ambio 1:123 (1972).

Jensen, S., A. G. Johnels, M. Olsson, and G. Otterlind. "DDT and PCB in Marine Animals from Swedish Waters," Nature 224: 247-250 (1969).

Jensen, S., L. Renberg and R. Vaz. "Problems in the Quantification of PCB in Biological Material," Committee Proceeding PCB 2nd Conference, Wenner-Gren Center, 1972, 7-14 (1973).

Jensen, S. and G. Sundström. "Structures and Levels of Most Chlorobiphenyls in Two Technical PCB Products and in Human Adipose Tissue," Ambio 3(2):70-76 (1974).

Jensen, S., L. Renberg and R. Vaz. "Methods for Analysis of DDT and PCB in Environmental Samples Using Chromatographic Methods," FAO Fisheries Technical Paper, Rome, FIRI/T137 (1975). pp. 229-236.

Jensen, S., L. Renberg and L. Reutergardh. "Residue Analysis of Sediment and Sewage Sludge for Organochlorines in the Presence of Elemental Sulfur," Anal. Chem. 49(2):316-318 (1977).

Jiang, K., Z. Kang and Y. Bian. "Quantitative Analysis of Polychlorinated Biphenyl Residues in Environmental Samples by GC-MS," Huanjing Kexue Xuebao 2(1):85-89; Chem. Abstr. 96: 194988d (1982a).

Jiang, K., R. Chen, J. Wang, Z. Kang and Y. Bian. "Environmental Analysis of Polychlorinated Biphenyls by Gas Chromatography and Mass Spectroscopy - Use of Chinese Commercial Products as References," Fenxi Huaxue 10(12):711-715 (1982b); Chem. Abstr. 98:185022y (1983).

Jiang, K., Z. Kang and Y. Bian. "Determination of Polychlorinated Biphenyl Residues in the Environment by GC-MS with Multiion Detection," Huanjing Hauxue 1(4): 274-280 (1982c); Chem. Abst. 98:29072j (1983).

MONS 005612

Jiang, K., Z. Kang, and Y. Bian. "Determination of Polychlorinated Biphenyl Residues in the Environment by Quantitative GC/MS Analysis--o,p'-DDE Internal Standard Method," Huanjing Huaxue 3(3):71-75 (1984); Chem. Abst. 101:150579p (1984).

Johnson, L. D. and R. G. Merrill. "Stack Sampling for Organic Emissions, Toxicol. Environ. Chem. 6:109-126 (1983).

Jones, J. W. and H. S. Alden. "An Acneform Dermatergosis," Arch. Dermatol. Syphilol. 33:1022-1034 (1936).

Jung, J. D. "A Review of Methods for PCB Analysis of Transformer Oil," Proc. Electr./Electron. Insul. Conf. 15th, 231-236 (1981); Chem. Abst. 97:16335b (1982).

Junk, G. A. and J. J. Richard. "Vapor-Phase Sampling of Organic Compounds," in Identification and Analysis of Organic Pollutants in Air, L. H. Keith, Ed. (Boston: Butterworth Publishers, 1984), pp. 61-78.

Kafadar, K. and K. R. Ebernardt. "Statistical Analysis of Some Gas Chromatography Measurements," J. Res. Nat. Bur. Stand. 88(1):37-46 (1983).

Kalmaz, E. V., R. B. Craig and G. W. Zimmerman. "Kinetics Model and Simulation of Concentration Variations of Species of Polychlorinated Biphenyls Involved in Photochemical Transformation," Chapter 14 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp. 233-240.

Kaminsky, L. S. and M. J. Fasco. "High-Performance Liquid Chromatography of Polychlorinated Biphenyls," J. Chromatogr. 155:363-370 (1978).

Kaminsky, R. and R. A. Hites. "Analysis of Compounds from Niagara Falls Dump Sites Using NCI GC/MS," Abstract from 30th Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, June 6-11, 1982.

Kamps, L. R., W. J. Trotter, S. J. Young, L. J. Carson, J. A. G. Roach, J. A. Sphon, J. T. Tanner and B. McMahon. "Polychlorinated Quaterphenyls Identified in Rice Oil Associated with Japanese 'Yusho' Poisoning," Bull. Environ. Contam. Toxicol. 20:589-591 (1978).

MONS 005613

Kamps, L. R., W. J. Trotter, S. J. Young, A. C. Smith, J. A. G. Roach and S. W. Page. "Separation and Quantitation of 3,3',4,4'-Tetrachlorobiphenyl and 3,3',4,4',5,5'-Hexachlorobiphenyl in Aroclors Using Florisil Column Chromatography and Gas-Liquid Chromatography," Bull. Environ. Contam. Toxicol. 23: 51-56 (1979).

Kan, T., K. Kamata, T. Ueta, R. Yamazoe and T. Totani. "Fluorescence Reactions of Organohalogen Compounds. I. Fluorometry of Polychlorinated Biphenyls (PCB) with Diphenylamine on Thin-Layer Chromatograms," Tokyo Toritsu Eisei Kenkyusho Kenky Nempo 24:137-145 (1973); Chem. Abst. 80:115771w (1974).

Kapila, S. and W. A. Aue. "Chemical Degradation of Single Gas Chromatographic Peaks for Confirmation of Pesticide Residue Identity," J. Chromatogr. Sci. 15:569-572 (1977).

Karasek, F. W. "Plasma Chromatography of the Polychlorinated Biphenyls," Anal. Chem. 43(14):1982-1986 (1971).

Karppanen, E. and L. Kolho. "The Concentration of PCB in Human Blood and Adipose Tissue in Three Different Research Groups," PCB Conference II, 1972, Stockholm, Natl. Swedish Environ. Protection Board, Publication No. 1973:4E, 124-8 (1973).

Kashimoto, T., H. Miyata, S. Kunita, T.-C. Tung, S.-T. Hsu, K.-J. Chang, S.-Y Tang, G. Ohi, J. Nakagawa and S.-I. Yamamoto. "Role of Polychlorinated Dibenzofuran in Yusho (PCB Poisoning)," Archives of Environmental Health 36(6): 321-326 (1981a).

Kashimoto, T., H. Miyata and N. Kunita. "The Presence of Polychlorinated Quaterphenyls in the Tissues of Yusho Victims," Food Cosmet. Toxicol. 19:335-340 (1981b).

Kashimoto, T., H. Miyata, S. Fukushima, N. Kunita, T. C. Tung, S. T. Hsu, C. J. Chang, S. Y. Tang, G. Ohi and S. Yamamoto. "Chlorinated Compounds in Taiwanese 'Yusho' Patients' Blood," Abstract from 30th Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, June 6-11, 1982, pp. 198-199.

Kateman, G. and F. W. Pijpers (Eds.). Quality Control in Analytical Chemistry (John Wiley and Sons: Wiley-Interscience Publishers, 1981).

MONS 005614

Kauss, P. B., K. Suna and A. F. Johnson. Montiroing of PCBs in Water, Sediments and Biota of the Great Lakes - Some Recent Examples," Chapter 20 in Physical Behavior of PCBs in The Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 385-409.

Kawabata, J. "Simple Method for the Determination of PCBs [Polychlorinated Biphenyls] by a Combination of Thin-Layer Chromatography and UV Absorption," Kogai To Taisaku 10(10): 1112-1116 (1974); Chem. Abst. 83:201652b (1975).

Kawaguchi, T., S. Hiratsuka, T. Yoneshima and Y. Nagao. "A Method of Analysis for Polychlorobiphenyl Gas Chromatograms," Tokyo-Toritsu Kogyo Gijutsu Senta Kenkyu Hokoku 5:57-60 (1975); Chem. Abst. 86:83287y (1977).

Keith, L. H., W. Crummett, J. Deegan Jr., R. A. Libby, J. K. Taylor and G. Wentler. "Principles of Environmental Analysis," Anal. Chem. 55:2210-2218 (1983).

Kelso, G. L., M. D. Erickson, B. A. Boomer, S. E. Swanson, D. C. Cox, and B. D. Schultz. "Cleanup of PCB Spills from Capacitors and Transformers," Draft Interim Report No. 1, Work Assignment Task 37, EPA Contract No. 68-02-3938, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC (January 1985).

Kennedy, P. A., D. J. Roberts and M. Cooke. "Determination of Polychlorinated Naphthalenes in the Presence of Polychlorinated Biphenyls by Capillary Gas Chromatography," J. Chromatogr. 249:257-265 (1982).

Kerkhoff, M. A. T, A. De Vries, R. C. C. Wegman and A. W. M. Hofstee. "Analysis of PCBs in Sediments by Glass Capillary Gas Chromatography," Chemosphere 11(2):165-174 (1982).

Khan, M. A., A. F. Novak and R. M. Rao. "Comparative Evaluation of Polychlorinated Biphenyl Solutions," Bull. Environ. Contam. Toxicol. 16(3):360-367 (1976).

Kilikidis, S. D., J. E. Psomas, A. P. Kamarianos and A. G. Panetsos. "Monitoring of DDT, PCBs, and Other Organochlorine Compounds in Marine Organisms from the North Aegean Sea," Bull. Environ. Contam. Toxicol. 26:496-501 (1981).

Kimbrough, R. D. "The Toxicity of Polychlorinated Polycyclic Compounds and Related Chemicals," CRC Crit. Rev. Toxicol. 2: 445-498 (1974).

MONS 005615

Kimbrough, R. O., (Ed.) Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products (New York: Elsevier/North-Holland Biomedical Press, 1980a), 406 pp.

Kimbrough, R. D. "Environmental Pollution of Air, Water and Soil," Chapter 3 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980b), pp. 77-80.

Kimbrough, R. D. "Occupational Exposure," Chapter 9 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Compounds, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980c), pp. 333-398.

Kimbrough, R., J. Buckley, L. Fishbein, G. Flamm, L. Kasza, W. Marcus, S. Shibko and R. Teske. "Animal Toxicology," Environ. Health Persp. 24: 173-184 (1978).

Kirchmer, C. J. "Quality Control in Water Analyses," Environ. Sci. Technol. 17(4):174A-181A (1983).

Kirshen, N. A. "PCBs in Transformer Fluids," Varian Instrum. Appl. 15(2): 1-10; Chem. Abst. 94(26):219095j (1981a).

Kirshen, N. A. "PCBs in Transformer Fluids," Amer. Lab. 65-69 (December 1981b).

Kitchens, J. F., W. E. Jones, III, G. L. Anspach and D. C. Schubert. "Light-Activated Reduction of Chemicals for Destruction of Polychlorinated Biphenyls in Oil and Soil," Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp. 215-226.

Klimisch, H. M. and O. N. Ingebrigtson. "Determination of Polychlorinated Biphenyls in Silicone Fluids," Anal. Chem. 52:1675-1678 (1980).

Kloepfer, R. D. "Preparation of Fish Tissue for Extractable Organics Analysis," Method No. EE015TR, U.S. Environmental Protection Agency, Region VII, Kansas City, MO (October 19, 1983), 3 pp.

Koch, R. "Circular Thin-Layer Chromatography as a Rapid Method for a Qualitative Detection of Organochlorine Compounds," Acta Hydrochim. Hydrobiol. 7(3):355-356 (1979); Chem. Abst. 91:101574z (1979).

Kodama, H., N. Kawamura and H. Ota. "A Simple Method for the Determination of PCB in Human Milk and Blood Using an Improved Essential Oil Distillator," Nippon Eiseigaku Zasshi 31(6):644-651 (1977); Chem. Abst. 87:96853a (1977).

Kodama, H. and O. Hideo. "Transfer of Polychlorinated Biphenyls to *Infants From Their Mothers*," Arch. Environ. Health 35(2):95-100 (1980).

Koeniger, M., P. Wallnoeer and G. Engelhardt. "Residue Determination of Polychlorinated Biphenyl (PCBs) in the Presence of Chlorinated Hydrocarbon Pesticides in Eggs of Wild Birds," Nachrichtenbl. Dtsch. Pflanzenschutzdienstes 27(9): 131-135 (1975); Chem. Abst. 84:85033v (1976).

Kohli, K. K., P. W. Albro and J. D. McKinney. "Radioisotope Dilution Assay (RIDA) for the Estimation of Polychlorinated Biphenyls (PCBs)," J. Anal. Toxicol. 3:125-128 (1979a).

Kohli, P., W. Albro and J. D. McKinney. "Radioisotope Dilution Assay (RIDA) for the Estimation of Polychlorinated Biphenyls (PCBs)," Environ. Health Persp. 33:347 (1979b).

Kolbye, A. C., Jr. "Regulatory Considerations Regarding Limiting Human Exposures to PCBs," in PCBs: Human and Environmental Hazards. F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 77-90.

Kondrat, R. W. and R. G. Cooks. "Direct Analysis of Mixtures by Mass Spectrometry," Anal. Chem. 50(1):81A-92A (1978).

Kováts, von E. "Gas-Chromatographische Charakterisierung Organischer Verbindungen. Teil 1: Retentionsindices Aliphatischer Halogenide, Alkohole, Aldehyde und Ketone," Helv. Chim. Acta 41:1915-1932 (1958).

Kratochvil, B., D. Wallace and J. K. Taylor. "Sampling for Chemical Analysis," Anal. Chem. 56:113R-129R (1984).

Kraul, I. and O. Karlog. "Persistent Organochlorinated Compounds in Human Organs Collected in Denmark 1972-73," Acta Pharmacol. et Toxicol. 39:39-48 (1976).

Kreiss, K., M. M. Zack, R. D. Kimbrough, L. L. Needham, A. L. Smrek and B. T. Jones. "Association of Blood Pressure and Polychlorinated Biphenyl Levels," J. Amer. Med. Assoc. 245(24):2505-2509 (1981).

Krull, I. S. "Recent Advances in PCB Analysis," in Residue Reviews, F. A. Gunther and J. D. Gunther (Eds.), 66, New York (1977).

Krupcik, J., P. A. Leclercq, A. Simova, P. Suchanek, M. Collak and J. Hrivnak. "Possibilities and Limitations of Capillary Gas Chromatography and Mass Spectrometry in the Analysis of Polychlorinated Biphenyls," J. Chromatogr. 119:217-283 (1976).

MONS 005617

Krupcik, J., J. Kriz, D. Prusova, P. Suchanek and Z. Cervenka. "Analysis of Polychlorinated Biphenyls by High-Performance Liquid Chromatography and Capillary Gas-Liquid Chromatography," J. Chromatogr. 142:797-807 (1977).

Krupcik, J., P. A. Leclercq, J. Garaj and A. Simova. "Analysis of Alkylated Mixtures of Polychlorinated Biphenyls by Capillary Gas Chromatography-Mass Spectrometry," J. Chromatogr. 191:207-220 (1980).

Krupcik, J., J. Mocak, A. Simova, J. Garaj and G. Guiochon. "Optimization of Experimental Conditions for the Analysis of Complex Mixtures by Gas Chromatography," J. Chromatogr. 238: 1-12 (1982).

Kuehl, D. W. and E. N. Leonard. "Isolation of Xenobiotic Chemicals from Tissue Samples by Gel Permeation Chromatography," Anal. Chem. 50(1):182-185 (1978).

Kuehl, D. W., E. N. Leonard, K. J. Welch and G. D. Veith. "Identification of Hazardous Organic Chemicals in Fish from the Ashtabula River, Ohio, and Wabash River, Indiana. J. Assoc. Off. Anal. Chem. 63(6):1238-1244 (1980a).

Kuehl, D. W., M. J. Whitaker and R. C. Dougherty. "Micromethods for Toxic Residue Screening by Negative Chemical Ionization Mass Spectrometry," Anal. Chem. 52:935-940 (1980b).

Kuge, Y. "Pollution Analysis and Examples of Measurement," Kankyo Gijutsu 12(10):659-665 (1983); Chem. Abstr. 100: 79161t (1984).

Kuratsune, M. "An Abstract Results of Laboratory Examinations of Patients with Yusho and of Animal Experiments," Environ. Health Perspec. 1:129-136 (1972).

Kuratsune, M. "Yusho," Chapter 981 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980), pp. 287-302.

Kuratsune, M. and Y. Masuda. "Polychlorinated Biphenyls in Non-Carbon Copy Paper," Env. Health Persp., 1:61-62 (1972).

Kuratsune, M., T. Yoshimura, J. Matsuzaka and A. Yamaguchi. "Epidemiologic Study on Yusho, A Poisoning Caused by Ingestion of Rice Oil Contaminated with a Commerical Brand of Polychlorinated Biphenyls," Environ. Health Perspec. 1:119-128 (1972).

MONS 005618

Kuroki, H. and Y. Masuda. "Determination of Polychlorinated Dibenzofuran Isomers Retained in Patients with Yusho," Chemosphere 7(10):771-777 (1978)

Kutz, F. W. and S. C. Strassman. "Residues of Polychlorinated Biphenyls in the General Population of the United States," in Proceedings of the National Conference on Polychlorinated Biphenyls, (Chicago, IL: November 19-21, 1975), F. A. Ayer, Ed. Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., EPA-560/6-75-004, NTIS No. PB 253 248 (March 1976), pp. 139-143.

Kutz, F. W., S. C. Strassman and J. F. Sperling. "Survey of Selected Organochlorine Pesticides in the General Population of the United States: Fiscal Years 1970-1975," Ann. N. Y. Acad. Sci. 320:60-68 (1979).

Kveseth, N. J. and E. M. Brevik. "Column Chromatographic Method for Cleaning Up Extracts from Biological Material and Simultaneous Separation of PCBs and DDE," Bull. Environ. Contam. Toxicol. 21:213-218 (1979).

LaBrosse, J. and R. J. Anderegg. "Using the Mass Spectrometer as a Chlorine-Selective Detector," Abstract from 30th Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, June 6-11, 1982.

Laitem, L. and P. Gaspar. "A T.L.C. Procedure for Identification of DDT and Its Metabolites in Presence of PCB," Bull. Environ. Contam. Toxicol. 19:264-265 (1978).

Lam, N. K., and M. Kopanica. "Determination of Trichlorobiphenyl by Adsorptive Stripping Voltammetry," Anal. Chim. Acta 161:315-324 (1984).

Lamparski, L. L., T. J. Nestrick, and R. H. Stehl. "Determination of Part-per-Trillion Concentrations of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Fish," Analytical Chemistry, 51(9):1453-1458 (1979).

Lamparski, L. L., and T. J. Nestrick, "Micro Chlorination Procedure for Synthesis of Higher Chlorinated Dibenzo-p-dioxins from [^{13}C]-2,3,7,8-Tetrachlorodibenzo-p-dioxin," Anal. Chem., 54:402-406 (1982).

Landrigan, P. J. "General Population Exposure to Environmental Concentrations of Halogenated Biphenyls," Chapter 9A in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980), pp. 267-286.

MONS 005619

Lao, R. C., R. S. Thomas, and J. L. Monkman, "Application of Computerized Gas Chromatography-Mass Spectrometry to the Analysis of Polychlorinated Biphenyls," Dynamic Mass Spectrom., 4: 107-131 (1976).

Lawrence, J. F. "Confirmatory Tests," Chapter 10 in Pesticide Analysis, K. G. Das, Ed. (New York, NY: Marcel Dekker, Inc., 1981), pp 425-460.

Lawrence, J., and H. M. Tosine, "Adsorption of Polychlorinated Biphenyls from Aqueous Solutions and Sewage," Environ. Sci. Technol., 10(4):381-383 (1976).

Lawrence, J. F. and D. Turton, "High-Performance Liquid Chromatographic Data for 166 Pesticides," J. Chromatogr., 159: 207-266 (1978).

Lea, Robert E., R. Bramston-Cook and J. Tschida. "Pattern Recognition for Identification and Quantitation of Complex Mixtures in Chromatography," Anal. Chem. 55:826-829 (1983).

Lech, J. J. and R. E. Peterson. "Biotransformation and Persistence of Polychlorinated Biphenyls (PCBs) in Fish," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 187-202.

Lederman, T. C. and G-Y. Rhee. "Bioconcentration of a Hexachlorobiphenyl in Great Lakes Planktonic Algae," Canadian J. of Fisheries and Aquatic Sci. 39:380-387 (1982).

Lee, H. B. and A. S. Y. Chau. "National Interlaboratory Quality Control Study No. 25. PCBs in Wet Sediments," Rep. Ser. - Inland Waters Dir. (Can.) Report Series No. 71:12 pp. (1981a); Chem. Abst. 97: 222636d (1982).

Lee, H. B. and A. S. Y. Chau. "National Interlaboratory Quality Control Study No. 27. PCBs in Naturally Contaminated Dry Sediments," Rep. Ser. - Inland Waters Dir. (Can.) Report Series No. 72, 15 pp. (1981b); Chem. Abst. 97:22263 (1982).

Leib, A. J., and D. D. Bills, "Influence of Storage Temperature of Florisil on Analysis of Polychlorinated Biphenyls," Bull. Environ. Contam. Toxicol., 12(3):328-330 (1974).

Leifer, A., R. H. Brink, G. C. Thom, and K. G. Partymiller. "Environmental Transport and Transformation of Polychlorinated Biphenyls," U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, D.C., EPA-560/5-83-025, NTIS No. PB84-142579 (1983).

MONS 005620

Lentzen, D. E., D. E. Wagoner, E. D. Estes and W. F. Gutknecht. "IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition)," Prepared for U.S. Environmental Protection Agency, Office of Research and Development, EPA-600/7-78-201, October 1978.

Leoni, V., "The Separation of Fifty Pesticides and Related Compounds and Polychlorobiphenyls into Four Groups by Silica Gel Microcolumn Chromatography," J. Chromatogr., 62:63-71 (1971).

Leoni, V., E. d'Allessandro de Luca and A. M. Simeone. "Techniques of Qualitative and Quantitative Analysis of Polychlorinated Biphenyls in Food Products and Packing Materials," Rass. Chim. 25(2):99-111 (1973); Chem. Abst. 79:77061j (1973).

Leoni, V., M. Biocca and E. d'Allessandro de Luca. "I Policlorodifenili Nei Tessuti Adiposi Umani: Accertamento Sperimentale E Possibile Significato Igienico," Il Farmaco 31(2): 57-79 (1976a).

Leoni, V., G. Puccetti, R. J. Colombo and A. M. d'Ovidio. "The Use of Tenax for the Extraction of Pesticides and Polychlorinated Biphenyls from Water. II. Tests with Artificially Polluted and Natural Waters," J. Chromatogr. 125: 399-407 (1976b).

Leoni, V. and C. Vannucchi. "Analytical Methods for Water. 6. Determination of Polychlorinated Biphenyls and Polychlorinated Terphenyls in Wastewater," Quad. - Ist. Ric. Acque 11: 41 pp. (1981); Chem. Abst. 97:115204f (1982).

Lerman, S. I. and J. P. Hendricks. "Determination of Polychlorinated Biphenyls in Transformer Oil," Chromatogr. Newsl. 9(1):5-6 (1981); Chem. Abst. 95(7):55674r (1981).

Lerman, S. I., H. Gordon and J. P. Hendricks. "A Study in Laboratory Automation - Analysis of PCBs in Transformer Oils," Amer. Lab. 14(2):176-181 (February 1982).

Lavine, S. P., M. T. Homsher and J. A. Sullivan. "Comparison of Methods of Analysis of Polychlorinated Biphenyls in Oils," J. Chromatogr. 257:255-266 (1983).

Levins, P. L., C. E. Rechsteiner and J. L. Stauffer. "Measurement of PCB Emissions from Combustion Sources," U.S. Environmental Protection Agency, Report No. EPA-600/7-79-047 (February 1979).

MONS 005621

Levins, P. L., C. E. Rechsteiner, Jr. and J. L. Stauffer. "A New Procedure for the Measurement of Polychlorinated Biphenyls (PCBs) in Combustion Sources," AIChE Sym. Series 76(196):330-337 (1980).

Levy, G. C. and J. M. Hewitt. "Analysis of Polychlorinated Biphenyls by Carbon-13 Nuclear Magnetic Resonance Spectroscopy," J. Assoc. Offic. Anal. Chem. 60(1):241-242 (1977).

Lewis, E. and W. D. Jamieson. "Use of Negative Chemical Ionization GC/MS to Study Polychlorinated Biphenyls in Marine Sediments," Int. J. Mass Spectrom. Ion Physics 48:303-306 (1983).

Lewis, R. G. "Procedures for Sampling and Analysis of Polychlorinated Biphenyls in the Vicinities of Hazardous Waste Disposal Sites," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 16, 1982, 14 pp.

Lewis, R. G., A. R. Brown and M. D. Jackson. "Evaluation of Polyurethane Foam for Sampling of Pesticides, Polychlorinated Biphenyls and Polychlorinated Naphthalenes in Ambient Air," Anal. Chem. 49(12):1668-1672 (1977a).

Lewis, R. G., A. R. Brown and M. D. Jackson. "Sampling for Low Levels of Airborne Pesticides, Polychlorinated Biphenyls, and Polychlorinated Naphthalenes,". Paper No. 78, 173rd National Meeting, American Chemical Society, New Orleans, Louisiana (1977b).

Lewis, R. G. and M. D. Jackson. "Modification and Evaluation of a High-Volume Air Sampler for Pesticides and Semivolatile Industrial Organic Chemicals," Anal. Chem. 54:592-594 (1982).

Lewis, R. G. and K. E. MacLeod. "Portable Sampler for Pesticides and Semivolatile Industrial Organic Chemicals in Air," Anal. Chem. 54:310-315 (1982).

Liberti, A., D. Brocco, V. Di Palo and M. Possanzini. "Evaluation of Organochlorine Compounds in the Emissions of Urban Incinerators," in Analytical Techniques in Environmental Chemistry, J. Albaiges, Ed. (New York, NY: Pergamon Press, 1980), pp. 157-166.

Liddle, J. A. "Method Standardization and Interlaboratory Compatibility of Serum Polychlorinated Biphenyl Analysis," Abstract, 184th Annual Chemical Society National Meeting, September 12-17, 1982.

MONS 005622

Lincer, J. L. "Polychlorinated Biphenyls: Their Potential Interference with Pesticide Residue Analysis and Present Analytical Status," Progr. Anal. Chem. 5:109-131 (1973).

Liu, R. H., S. Ramesh and J. Y. Liu. "Qualitative and Quantitative Determinations of Aroclor Formulations," Abstract from the Thirty-First Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, May 8-13, pp. 213 (1983).

Liu, R. H., S. Ramesh, J. Y. Liu, and S. Kim. "Qualitative and Quantitative Analyses of Commercial Polychlorinated Biphenyl Formulation Mixtures by Single Ion Monitoring Gas-Liquid Chromatography/Mass Spectrometry and Multiple Regression," Anal. Chem. 56:1808-1812 (1984).

Long, G. L. and J. D. Winefordner. "Limit of Detection - A Closer Look at the IUPAC Definition," Anal. Chem. 55(7): 712A-724A (1983).

Longanbach, J. R. and W. H. Mink. "Development of a Process for PCB Removal from Triaryl Phosonate Hydraulic Fluids by Vacuum Distillation," Environ. Sci. Technol. 17(5):305-307 (1983).

Longbottom, J. E. and J. J. Lichtenberg, Eds. "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," U. S. Environmental Protection Agency, Report No. EPA-600/4-82-057 (July 1982).

Lovell, R. J., R. A. Miller, C. Pfommer, Jr., J. E. Brugger, and J. J. Yezzi, Jr. "Trial Burn Testing of the EPA-ORD Mobile Incineration System," Enviroscience, Inc., Knoxville, TN, EPA-600/D-84-054, NTIS No. PB84-175520 (1984.

Lovett, A. M., S. Nacson, N. H. Hijazi, and R. Chan. "Real Time Ambient Air Measurements for Toxic Chemical," in Proceedings: A Specialty Conference on: Measurement and Monitoring of Non-Criteria (Toxic) Contaminants in Air, E. R. Frederick, Ed., The Air Pollution Control Association, Pittsburgh, PA (1983), pp. 113-125.

Lucas, R. M., M. D. Erickson, P. V. Piserchia and S. R. Williams. "PCB Residue Levels in Human Adipose Tissue, A Statistical Evaluation by Racial Grouping," Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., EPA-650/13-79-015 (November 1980).

MONS 005623

Lucas, R. M., V. G. Iannacchione and K. D. Melroy. "Polychlorinated Biphenyls in Human Adipose Tissue and Mother's Milk," Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., EPA-560/5-83-011, NTIS No. PB83-253179 (1982).

Luckas, B., H. Pscheidl and D. Haberland. "Determination of Chlorinated Pesticides and Polychlorinated Biphenyls by Derivatization Gas Chromatography," J. Chromatogr. 147:41-46 (1978).

Lunde, G. and E. B. Ofstad. "Determination of Fat-Soluble Chlorinated Compounds in Fish," Z. Anal. Chem. 282:395-399 (1976).

Luster, M. I., P. W. Albro, G. Clark, K. Chae, S. K. Chaudhary, L. D. Lawson, J. T. Corbett and J. D. McKinney. "Production and Characterization of Antisera Specific for Chlorinated Biphenyl Species: Initiation of a Radioimmunoassay for Aroclors," Toxicol. Appl. Pharmacol. 50:147-155 (1979).

Luster, M. I., P. W. Albro, K. Chae, S. K. Chaudhary and J. D. McKinney "Development of Radioimmunoassays for Chlorinated Aromatic Hydrocarbons," Chapter 14 in Environmental Health Chemistry, The Chemistry of Environmental Agents as Potential Human Hazards, J. D. McKinney Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981), pp. 279-297.

MacDougall, D. et al. "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," Anal. Chem. 52:2242-2249 (1980).

Mackay, D. "Environmental Pathways of Polychlorinated Biphenyls," in Comments and Studies on the Use of Polychlorinated Biphenyls in Response to an Order of the United States Court of Appeals for the District of Columbia Circuit, Vol. IV, Submitted by The Utility Solid Waste Activities Group, The Edison Electric Institute and The National Rural Electric Cooperative Association to The U. S. Environmental Protection Agency, February 12, 1982a, 61 pp.

Mackay, D. "Correlation of Bioconcentration Factors," Environ. Sci. Technol. 16(5):274-278 (1982b).

Mackay, D., R. Mascarenhas, W. Y. Shiu, S. C. Valvani, and S. H. Yalkowsky. "Aqueous Solubility of Polychlorinated Biphenyls," Chemosphere 9:257-264 (1980).

Mackay, D., A. Bobra, D. W. Chan, and W. Y. Shiu. "Vapor Pressure Correlations for Low-Volatility Environmental Chemicals," Environ. Sci. Technol. 16:645-649 (1982).

MONS 005624

Mackay, D. and S. Paterson. "Fugacity Models of Indoor Exposure to Volatile Chemicals," Chemosphere 12(2):143-154 (1983).

Mackay, D., S. Paterson, S. J. Eisenreich, and M. S. Simmons. Physical Behavior of PCBs in the Great Lakes, Ann Arbor Science, Ann Arbor, MI, (1983a), 442 pp.

Mackay, D., W. Y. Shiu, J. Billington and G. L. Huang. "Physical Chemical Properties of Polychlorinated Biphenyls," Chapter 4 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983b), pp 59-69.

Mackay, D., and A. I. Hughes. "Three-Parameter Equation Describing the Uptake of Organic Compounds by Fish," Environ. Sci. Technol. 18(6):439-444 (1984).

MacLeod, K. E. "Sources of Emissions of Polychlorinated Biphenyls into the Ambient Atmosphere and Indoor Air," U.S. Environmental Protection Agency, Report No. EPA-600/4-79-022 (Marcn 1979).

MacNeil, J. D., S. Safe and O. Hutzinger. "The Ultraviolet Absorption Spectra of Some Chorinated Biphenyls," Bull. Environ. Contam. Toxicol. 15(1):66-77 (1976).

Manri, T., Y. Shinbori, S. Murakawa and Y. Mochizuki. "Determination of Chlorobiphanyl in Rat Adipose Tissues by Neutron Activation Analysis," Radioisotopes 20(8):371-375 (1971); Chem. Abst. 76:11738s (1972).

Marchand, M., D. Vas, and E. K. Duursma. "Levels of PCBs and DDTs in Mussels from the N.W. Mediterranean," Marine Pollut. Bull. 7(4):65-69 (1976).

Margeson, J. H. "Methodology for Measurement of Polychlorinated Biphenyls in Ambient Air and Stationary Sources - A Review," U.S. Environmental Protection Agency, Report No. EPA-600/4-77-021 (April 1977).

Markovec, L. M., and R. J. Magee. "Identification of Major Perchloroaromatic Compounds in Waste Products from the Production of Carbon Tetrachloride and Tetrachloroethylene," Analyst, 109(4):497-501 (1984).

Martelli, G. P., M. G. Castelli and R. Fanelli. "Analytical Response of Single Polychlorinated Biphenyls Analysed by Selected Ion Monitoring," Biomed. Mass Spectrom. 8(8):347-350 (1981).

MONS 005625

Mason, B. J. "Preparation of Soil Sampling Protocol: Techniques and Strategies," ETHURA, McLean, Virginia, under subcontract to Environmental Research Center, University of Nevada, Cooperative Agreement No. CR808529-01-2, for U.S. Environmental Protection Agency, Las Vegas (October 1982).

Mass Spectrometry Data Centre, in collaboration with *ICI* Ltd. Eight Peak Index of Mass Spectra, 2nd ed., Vol. 1-3, AWRE, Aldermaston, Reading RG 7/4PR, United Kingdom (1970).

Masuda, Y. and H. Shiokawa. "Experimental File. 42. Chromatography. Three Experiments," Kagaku No Jikken 23(7):669-671 (1972); Chem. Abst. 77:87143k (1972).

Masuda, Y., H. Kuroki, T. Yamaryo, K. Haraguchi, M. Kuratsune and S. T. Hsu. "*Comparison of Causal Agents in Taiwan and* Fukuoka PCB Poisonings," Chemosphere 11(2):199-206 (1982).

Masuda, Y., KH. Kuroki, and J. Nagayama. "Polychlorinated Dibenzofurans in the Tissues of Patients with Yusho and Their Enzyme-Inducing Activities on Aryl Hydrocarbon Hydroxylase," Chlorinated Dioxins Dibenzofurans Total Environ. 375-384 (1983); Chem. Abst. 100:152051p (1984).

Masui, T., M. Yamamoto and S. Kimura. "Problems in Polychlorinated Biphenyl Analysis," Shizuoka-ken Eisei Kenkyusho Hokoku 19:59-64 (1976); Chem. Abst. 90:109442e (1979).

Masumoto, H. T. "Study of the Silicic Acid Procedure of Armour and Burke for the Separation of Polychlorinated Biphenyls from DDT and Its Analogs," J. Assoc. Offic. Anal. Chem. 55(5):1092-1100 (1972).

Masumoto, H. T. "Total Polychlorinated Biphenyl Quantitation by Reduction," EDRO SARAP Res. Tech. Rep. 1:Paper 20-73, 30 pp. (1976); Chem. Abst. 88:73094k (1978).

Mathar, W., and H. Beck. "Simple Use of Fat-Containing Foods *for the Determination of PCB Residues by Distillation with* Steam," Lebensmittelchem. Gerichtl. Chem., 37(6):147-148 (1983); Chem. Abst. 100:173236t (1984).

Matthews, H. B. "Metabolism of PCBs in Mammals: Routes of Entry, Storage, and Excretion," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 203-214.

Matthews, H., G. Fries, A. Gardner, L. Garthoff, J. Goldstein, Y. Ku and J. Moore "Metabolism and Biochemical Toxicity of PCBs and PBBs," Env. Health Persp. 24:147-155 (1978).

Matthews, H. B. and S. Kato. "The Metabolism and Disposition of Halogenated Aromatics," Ann. N. Y. Acad. Sci. 320:131-137 (1979).

Mattsson, P. E. and S. Nygren. "Gas Chromatographic Determination of Polychlorinated Biphenyls and Some Chlorinated Pesticides in Sewage Sludge Using a Glass Capillary Column," J. Chromatogr. 124:265-275 (1976).

McCallum, R. L. "Order Dismissing Interlocutory Appeal," Before the Administrator U.S. Environmental Protection Agency, Washington, DC. In the Matter of: The Dow Chemical Company, Appellant. Docket No. TSCA (16(a))-1, July 28, 1982.

McClure, V. E. "Transport of Heavy Chlorinated Hydrocarbons in the Atmosphere," Environ. Sci. Technol. 10(13):1223-1229 (1976).

McConnell, E. E. "Acute and Chronic Toxicity, Carcinogenesis, Reproduction, Teratogenesis and Mutagenesis in Animals," Chapter 5 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products. R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980), pp. 109-150.

McConnell, E. E., J. R. Hass, N. Altman, J. A. Moore. "A spontaneous Outbreak of Polychlorinated Biphenyl (PCB) Toxicity in Rhesus Monkeys (Macaca Mulatta): Toxicopathology," Lab. Anim. Sci. 29(5):666-673 (1979).

McCracken, W. E. "Edible Tissue Sampling for Fish Contaminant Analysis," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 123-140.

McInnes, R. G. "Technical Assistance in Support of Permitting Activities for the Thermal Destruction of PCBs," USEPA, Office of Research and Development, IERL, Research Triangle Park, NC, EPA 600/2-81-240 (NTIS No. PB82 231 325), 70 pp. (1982).

McInnes, R. G. and R. J. Johnson. "Provision of Technical Assistance to Support Regional Office Implementation of the PCB Regulations--East and West," Draft Project Summary Report by GCA Corporation, New Bedford, MA, and TRW, Inc., Redondo Beech, CA, on EPA Contract No. 68-02-3168, Work Assignment No. 45, and Contract No. 68-02-3174, Work Assignment No. 68, for David C. Sanchez, USEPA, Office of Research and Development, IERL, Research Triangle Park, NC, 186 pp. (1982).

MONS 005627

McKinney, J. D., K. Chae, B. N. Gupta, J. A. Moore, and J. A. Goldstein. "Toxicological Assessment of Hexachlorobiphenyl Isomers and 2,3,7,8-Tetrachlorodibenzofuran in Chicks. I. Relationship of Chemical Parameters," Tox. and Appl. Pharma., 36:65-80 (1976).

McKinney, J. D. "Environmental Health Chemistry--Definitions and Interrelationships: A Case in Point," Chapter 1 in Environmental Health Chemistry, The Chemistry of Environmental Agents as Potential Human Health Hazards, J. D. McKinney, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981), pp. 3-15.

McKinney, J. D., L. Moore, A. Prokopetz and D. B. Walters. "Validated Extraction and Cleanup Procedures for Polychlorinated Biphenyls and DDE in Human Body Fluids and Infant Formula," J. Assoc. Off. Anal. Chem. 67(1):122-129 (1984).

McKone, H. T. and A. Daub. "A Rapid and Efficient Cleanup Technique for the Quantitative Determination of Polychlorinated Biphenyls in Fish," Chromatogr. Mass Spectrom. Biomed. Sci. 2:497-503 (1983).

McLafferty, F. W. Interpretation of Mass Spectra, 3rd Edition, (Mill Valley, CA: University Science Books, 1980).

McLafferty, F. W., R. Knutti, R. Venkataraghavan, P. J. Arpino and B. G. Dawkins. "Continuous Mass Spectrometric Monitoring of a Liquid Chromatograph with Subnanogram Sensitivity Using an On-Line Computer," Anal. Chem. 47(9):1503-1505 (1975).

McLeod, H. A. and P. J. Wales. "A Low Temperature Cleanup Procedure for Pesticides and Their Metabolites in Biological Samples," J. Agr. Food Chem. 20(3):624-627 (1972).

McMahon B. and J. A. Burke. "Analytical Behavior Data for Chemicals Determined Using AOAC Multiresidue Methodology for Pesticide Residues in Foods," J. Assoc. Off. Anal. Chem., 81(3):640-652 (1978).

McMurtrey, K. D., N. J. Wildman and H. Tai. "Pyrolysis Gas Chromatography-Mass Spectrometry of Polychlorinated Biphenyls on Sediment," Bull. Environ. Contam. Toxicol. 31(6):734-737 (1983).

McNair, H. M. and E. J. Bonelli. Basic Gas Chromatography, 5th Edition. (Walnut Creek, CA, Varian Aerograph, March 1969.)

McQuade, J. M. "PCB Analysis by X-Ray Fluorescence," in Proceedings: 1981 PCB Seminar, G. Addis and J. Marks, Eds., Report No. EPRI-EL-2572, (Palo Alto, CA: Electric Power Research Institute, 1982), pp. 2-9.

Menzie, C. "Metabolism of Pesticides - Update II," U. S. Department of Interior, Fish and Wildlife Service, Washington, D.C. Special Scientific Report - Wildlife No. 212 (1978).

Menzie, C. M. "Metabolism of Pesticides Update III," U.S. Department of the Interior, Fish and Wildlife Service, Washington, D.C., Special Scientific Report--Wildlife 232, NTIS No. PB83-175349 (1980).

Mes, J. and D. S. Campbell. "Extraction Efficiency of Polychlorinated Biphenyl, Organochlorine Pesticides, and Phthalate Esters from Human Adipose Tissue," Bull. Environ. Contam. Toxicol. 16(1):53-60 (1976).

Mes, J., D. S. Campbell, R. N. Robinson and D. J. A. Davies. "Polychlorinated Biphenyl and Organochlorine Pesticide Residues in Adipose Tissue of Canadians," Bull. Environ. Contam. Toxicol. 17(2):196-203 (1977).

Mes, J. and D. J. Davies. "Variation in the Polychlorinated Biphenyl and Organochlorine Pesticide Residues During Human Breastfeeding and Its Diurnal Pattern," Chemosphere 7(9): 699-706 (1978).

Mes, J. and D. J. Davies. "Presence of Polychlorinated Biphenyl and Organochlorine Pesticide Residues and the Absence of Polychlorinated Terphenyls in Canadian Human Milk Samples," Bull. Environ. Contam. Toxicol. 21:381-387 (1979).

Mes, J., D. Davies and J. Truelove. "The Determination of Polychlorinated Biphenyl in Small Samples of Monkey Milk and Tissues. I.." Intern. J. Environ. Anal. Chem. 9:99-98 (1980).

Mes, J. and P. Y. Lau. "Distribution of Polychlorinated Biphenyl Congeners in Human Milk and Blood During Lactation," Bull. Environ. Contam. Toxicol. 31(6):639-643 (1983).

Mes, J., J. A. Doyle, B. R. Adams, D. J. Davies, and D. Turton. "Polychlorinated Biphenyls and Organochlorine Pesticides in Milk and Blood of Canadian Women During Lactation," Arch. Environ. Contam. Toxicol. 13(2):217-223 (1984); Chem. Abst. 100:152123r (1984).

MONS 005629

Messier, F. M-F. Lévesque and R. Massé. "Metabolism of 4-Chlorobiphenyl by the Achromobacter Strain B-218 and Bacillus Brevis Strain B-257," Abstract from the Thirty-First Annual Conference on Mass Spectrometry and Allied Topics, American Society for Mass Spectrometry, May 8-13, 1983, p. 225.

Mestres, R., C. Chevallier and M. Pagnon. "Mass Spectrometric Confirmation of the Identity and Content of Pesticide and Chlorinated Biphenyl Residues in the Sediments of the Mediterranean Sea," Trav. Soc. Pharm. Montpellier 36(2):151-160 (1976); Chem. Abst. 85:73422d (1976).

Mestres, R. and C. Chevallier. "XXXII. Method of Research and Determination of PCB and Phthalate Pesticide Residues in Water," Ann. Falsif. Expert. Chim. 70(750):101-111 (1977), Chem. Abst. 87:79446c (1977).

Mestres, R., C. Chevallier, C. Espinoza and R. Cornet. "Application of Coupled Gas Chromatography-Mass Spectrometry in Methods for the Study and Determination of Pesticide Residues and Organic Micropollutants in Environmental and Food Materials," Ann. Falsif. Expert. Chim. 70(751):177-188 (1977); Chem. Abst. 87:63535v (1977).

Metcalf, R. L. "Screening Compounds for Early Warnings About Environmental Pollution," in Trace Substances in Environmental Health - VIII, D. D. Hemphill (Ed.), Proceedings of University of Missouri's 8th Annual Conference on Trace Substances in Environmental Health," Columbia, Missouri, June 11-13, 1974. pp. 213-217.

Meuser, J. M. and W. C. Weimer. "Amine-Enhanced Photodegradation of Polychlorinated Biphenyls," Battelle Pacific Northwest Labs, Richland, WA, Report No. EPRI-CS-2513 (NTIS No. DE82 021378), 57 pp. (July 1982).

Middleditch, B. S., S. R. Missler and H. B. Hines. Mass Spectrometry of Priority Pollutants, Plenum Press, New York (1981).

Mieure, J. P., O. Hicks, R. G. Kaley and V. W. Saeger. "Characterization of Polychlorinated Biphenyls," in National Conference on Polychlorinated Biphenyls (November 19-21, 1975, Chicago, Illinois), F. A. Ayer (Ed.), prepared for U.S. Environmental Protection Agency, Report No. EPA-560/6-75-004; NTIS No. PB253 248 (March 1976).

Miki, T. "PCBs [Polychlorinated Biphenyls] and Organochlorine Pesticide Residues in Sugars," Seito Gijutsu Kenkyukaishi 25: 32-38 (1975); Chem. Abst. 83:149456z (1975).

MONS 005630

Millar, J. D., R. E. Thomas and H. J. Schattenberg, III. "Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Water by Gas Chromatography," Anal. Chem. 53:214-219 (1981).

Millar, J. D., R. E. Thomas and D. E. Johnson. "Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters," U.S. Environmental Protection Agency, Contract No. 68-03-2606, Report No. EPA-600/4-82-023 (NTIS No. PB82-214222) (March 1982).

Millar, J. D., R. E. Thomas, and H. J. Schattenberg. "EPA Method Study 18, Method 608--Organochlorine Pesticides and PCB's," Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA-600/4-84-061; NTIS No. PB84 211358 (1984) 197 pp.

Miller, R. A. and R. D. Fox. "Catalyzed Wet Oxidation of Hazardous Wastes," Chapter 13 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp. 227-232.

Miller, S. "The Persistent PCB Problem," Environ. Sci. Technol. 16(2):98A-99A (1982).

Mills, P. A., J. H. Onley and R. A. Gaither. "Rapid Method for Chlorinated Pesticide Residues in Nonfatty Foods," J. Ass. Offic. Anal. Chem. 46(2):186-191 (1963).

Mills, P. A. "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and Its Use in Standardizing Florisil Columns," J. Assoc. Offic. Anal. Chem. 51(1):29-32 (1968).

Mitchum, R. K., W. A. Korfmacher and G. F. Moler. "Capillary Gas Chromatography/ Atmospheric Pressure Negative Chemical Ionization Mass Spectrometry of the 22 Isomeric Tetrachlorodibenzo-p-dioxins," Anal. Chem. 54:719-722 (1982).

Miyata, H. and T. Kashimoto. "The Finding of Polychlorodibenzofurans in Commercial PCBs (Aroclor, Phenoclor and Clophen)," Shokuhin Eiseigaku Zasshi 17(6):434-437 (1976).

Miyata, H., T. Kashimoto and N. Kunita. "Detection and Determination of Polychlorodibenzofurnas in Normal Human Tissues and Kanemi Rice Oils Caused 'Kanemi Yusho'," J. Food Hyg. Soc. 18(3):260-265 (1977).

Mizushima, Y. and H. Mukai. "Study of Cleanup Operations in PCB Analysis," Niigata-ken Kogai Kenkyusho Kenkyu Hokoku 6: 110-114 (1982); Chem. Abst. 98:10864x (1983).

MONS 005631

Mizutani, T. and M. Matsumoto. "Determination of Polychlorinated Biphenyls by an Exhaustive Chlorination Method," Shokuhin Eiseigaku Zasshi 13(5):398-404 (1972); Chem. Abst. 78:66686v (1973).

Mizutani, T. and M. Matsumoto. "Separation and Determination of Polychlorinated Biphenyls and DDE by Oxidation in a Solid Support," Eisei Kagaku 19(5): 287-292 (1973); Chem. Abst. 80: 116981b (1974).

Modi, G., M. Piccinini and S. Bonciani. "Study of Pesticide Contamination in Some Tuscany Wines," Boll. Chim. Unione Ital. Lab. Prov. 2(3):133-147 (1976); Chem. Abst. 85:141275k (1976).

Moein, G. J. "Study of the Distribution and Fate of Polychlorinated Biphenyls and Benzenes After Spill of Transformer Fluid," Report No. EPA 904/9-76-014, NTIS No. PB288484 (1976).

Moolenaar, R. J. "Distribution and Fate of Chlorobiphenyls in the Environment," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-1378, NTIS No. PB84-135771 (December 1983), pp. 67-96.

Morita, M., J. Nakagawa, K. Akiyama, S. Mimura and N. Isono. "Detailed Examination of Polychlorinated Dibenzofurans in PCB Preparations and Kanemi Yusho Oil," Bull. Environ. Contam. Toxicol. 19(1):67-73 (1977).

Morita, M., J. Nakagawa, and C. Rappe. "Polychlorinated Dibenzofuren (PCDF) Formation From PCB Mixture by Heat and Oxygen," Bull. Environ. Contam. Toxicol. 19:665-670 (1978).

Moseley, M. A. and E. D. Pellizzari. "Development and Evaluation of Wall Coated Open-Tubular Columns for GC Anelysis of Individual Polychlorinated Biphenyl Isomers," J. High Res. Chromatogr. and Chromatogr. Commun. 5:404-412 (1982).

Moser, J. H. and K. R. Huibregtse. "Handbook for Sampling and Sample Preservation of Water and Wastewater," EPA-600/4-76-049 (NTIS No. PB-259 946) (1976).

Moye, H. A. "High Speed Liquid Chromatography of Pesticides," J. Chromatogr. Sci. 13:268-278 (1975).

MONS 005632

Muldrew, D. H., B. L. Worobey and G. R. B. Webster. "Sorption of [^{14}C] 2,4,5,2',4',5'-Hexachlorobiphenyl to Glass and Plastic Surfaces," Proc. - Annu. Workshop Pestic. Residue Anal. (West. Can.), 16th, D. C. G. Muir, Ed., pp. 98-100 (1981); Chem. Abstr. 96:1520p (1982).

Mulhern, B. M. "An Improved Method for the Separation and Removal of Organochlorine Insecticides from Thin-layer Plates," J. Chromatogr. 34:556-558 (1968).

Mulhern, B. M., E. Cromartie, W. L. Reichel and A. Belisle. "Semiquantitative Determination of Polychlorinated Biphenyls in Tissue Samples by Thin Layer Chromatography," J. Assoc. Offic. Anal. Chem. 54(3):548-550 (1971).

Mullin, M. D. and J. C. Filkins. "Analysis of Polychlorinated Biphenyls by Glass Capillary and Packed-Column Chromatography," Chapter 11 in Advances in the Identification and Analysis of Organic Pollutants in Water, L. H. Keith Ed., Vol. 1 (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981), pp. 187-196.

Mullin, M., G. Sawka, L. Safe, S. McCrindle and S. Safe. "Synthesis of the Octa- and Nonachlorobiphenyl Isomers and Congeners and Their Quantitation in Commercial Polychlorinated Biphenyls and Identification in Human Breast Milk," J. Anal. Toxicol. 5:138-142 (1981).

Mullin, M. D., C. M. Pochini, S. H. Safe and L. M. Safe. "Analysis of PCBs Using Specific Isomer High-Resolution Capillary Gas Chromatography," Chapter 12 in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 165-176; Chem. Abstr. 100:79164w (1984).

Mullin, M. D., C. M. Pochini, S. McCrindle, M. Romkes, S. H. Safe and L. M. Safe. "High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of All 209 PCB Congeners," Environ. Sci. Technol. 18:468-476 (1984).

Murphy, P. G. "Sulfuric Acid for the Cleanup of Animal Tissues for Analysis of Acid-Stable Chlorinated Hydrocarbon Residues," J. Assoc. Offic. Anal. Chem. 55(6):1360-1362 (1972).

Murphy, T. J., A. Schinsky, G. Paolucci and C. P. Rzeszutko. "Inputs of Polychlorinated Biphenyls from the Atmosphere to Lakes Huron and Michigan," Chapter 22 in Atmospheric Pollutants in Natural Waters, S. J. Eisenreich, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981a), pp. 445-458.

MONS 005633

Murphy, T. J., T. C. Heesen, and D. R. Young. "Exchange of Comments: Evaluation of a Technique for Measuring Dry Aerial Deposition Rates of DDT and PCB Residues," Atmos. Environ 15:206-208 (1981b).

Murphy, T. J., and A. W. Schinsky. "Net Atmospheric Inputs of PCBs to the Ice Cover on Lake Huron," J. Great Lakes Res 9(1):92-96 (1983).

Murphy, T. J., J. C. Pokojowczyk and M. D. Mullin. "Vapor Exhange of PCBs with Lake Michigan: The Atmosphere as a Sink for PCBs," *Chapter 3 in* Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp 49-58.

Musial, C. J., D. Hutzinger, V. Zitka and J. Crocker. "Presence of PCB, DDE and DDT in Human Milk in the Provinces of New Brunswick and Nova Scotia, Canada," Bull. Environ. Contam. Toxicol. 12(3):258-267 (1974).

Musial, C. J. and J. F. Uthe, "Interlaboratory Calibration Results of Polychlorinated Biphenyl Analyses in Herring," J. Assoc. Off. Anal. Chem. 66(1):22-31 (1983).

Musty, P. R. and G. Nickless. "Use of Amberlite XAD-4 for Extraction and Recovery of Chlorinated Insecticides and Polychlorinated Biphenyls from Water," J. Chromatogr. 89:185-190 (1974a).

Musty, P. R. and G. Nickless. "The Extraction and Recovery of Chlorinated Insecticides and Polychlorinated Biphenyls from Water Using Porous Polyurethane Foams," J. Chromatogr. 100(1): 83-94 (1974b).

Musty, P. R. and G. Nickless. "Extractants for Organochlorine Insecticides and Polychlorinated Biphenyls from Water," J. Chromatogr. 120:369-378 (1976).

Myers, D. S., S. D. Myers and J. J. Kelly. "PCB White Paper, Part II," Natl. Eng. 86(9):26-32; Chem. Abstr. 94:194024g (1982).

Nagayama, J., Y. Masuda and M. Kuratsune. "Chlorinated Dibenzofurans in Kanechlors and Rice Oils Used by Patients with Yusho," Fukuoka Igaku Zasshi 66(10):593-599 (1975).

Nagayama, J., M. Kuratsune and Y. Masuda. "Determination of Chlorinated Dibenzofurans in Kanechlors and 'Yusho Oil'," Bull. Environ. Contam. Toxicol. 15(1):9-13 (1976).

Nakagawa, H., M. Kayama and E. Ariyoshi. "Measurements of Polychlorinated Biphenyl (PCB) in Water, Sediments, and Organisms of Two Rivers in Hiroshima Prefecture," J. Fac. Fish Anim. Husb. Hiroshima Univ. 14(2):253-259 (1975); Public Health Abst. 62(6).34268 (1976).

Nakagawa, J., M. Morita and Y. Higuchi. "Analysis of Polychlorinated Oibenzofurans by Gas Chromatography Using Glass Capillary Columns," Tokyo-toritsu Eisei Kenkyusho Kenkyu Nempo 30-1:260-264 (1979); Chem. Abst. 93:160694c (1980).

Nakamura, A. and T. Kashimoto. "Studies on a Calculation Method for Polychlorinated Biphenyl (PCB) Isomers. Analysis Using an Apiezon L. Column," Shokuhin Eiseigaku Zasshi 18(1): 1-12 (1977); Chem. Abst. 87:63524r (1977).

Nakatsu, K., J. F. Brien, H. Taub, W. J. Racz and G. S. Marks. "Gram Quantity Synthesis and Chromatographic Assessment of 3,3',4,4'-Tetrachlorobiphenyl," J. Chromatogr. 239: 97-106 (1982).

Namovicz, R. M. (Ed.). Environ. Health Perspec., Experimental Issue Number One, National Institute of Environmental Health Sciences, Research Triangle Park, NC, 181 pp. (April 1972).

Napier, J. M., M. A. Travaglini, E. G. Laggis and M. A. Makerewicz. "Evaluation and Development of Polychlorinated Biphenyl Removal Processes," Oak Ridge Y-12 Plant, Oak Ridge, TN, Report No. Y/OZ-1, February 5, 1982.

National Bureau of Standards. "Standard Reference Material 1581. Polychlorinated Biphenyls in Oil," U.S. Department of Commerce, Washington, D.C., Summer 1982, 1 pp.

National Institute for Occupational Safety and Health. NIOSH Manual of Analytical Methods, Second Edition, Part I, NIOSH Monitoring Methods, Vol. 1, "Polychlorinated Biphenyls (PCB) in Air, Analytical Method P&CAM 244," U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, April 1977a.

National Institute for Occupational Safety and Health. NIOSH Manual of Analytical Methods, Second Edition, Part I, NIOSH Monitoring Methods, Vol. 1, "Polychlorinated Biphenyls (PCB) in Air, Analytical Method P&CAM 253," U.S. Department of Health, Education, and Welfare, Cincinnati, Ohio, April 1977b.

MONS 005635

National Institute for Occupational Safety and Health. "Criteria for a Recommended Standard....Occupational Exposure to Polychlorinated Biphenyls (PCBs)," U.S. Department of Health, Education, and Welfare, (Public Health Service, Center for Disease Control, and National Institute for Occupational Safety and Health), DHEW (NIOSH) Publication No. 77-225, 224 pp. (September 1977c).

National Research Council. Polychlorinated Biphenyls, National Academy of Sciences, Washington, D.C., 182 pp. (1979).

National Technical Information Service. "Polychlorinated Biphenyls in the Environment, 1980-September, 1981," PB82-803867, 70 pp. (1982).

National Technical Information Service. "Polychlorinated Biphenyls in the Environment. 1977-January, 1983," PB83-859322, 199 pp. (1983a).

National Technical Information Service. "Polychlorinated Biphenyls in the Environment. September 1980-February 1983," PB83-804716, 154 pp. (1983b).

National Technical Information Service. "Polychlorinated Biphenyls: Occurrence in Sediments and Soils. 1977-January 1984 (Citations from the Selected Water Resource Abstracts Data Base)," PB84-860790, 124 pp. (1984a).

National Technical Information Service. "Polychlorinated Biphenyls: Occurrence and Treatment in Municipal and Industrial Wastes, 1977-1983, (Citations from the Selected Water Resource Abstracts Data Base)," PB84-860949 (1984b).

National Technical Information Service. "Polychlorinated Biphenyls in the Freshwater Environment, 1977-January 1984 (Citations from the Selected Water Resources Abstracts Data Base)," PB84-857358, 118 pp. (1984c).

National Technical Information Service. "Polychlorinated Biphenyls in the Environment, September 1980-April 1984 (Citations from the NTIS Data Base)," PB84-865724, 188 pp. (1984d).

Needham, L. L., A. L. Smrek, S. L. Head, V. W. Burse and J. A. Liddle. "Column Chromatography Separation of Polychlorinated Biphenyls from Dichlorodiphenyltrichloroethane and Metabolites," Anal. Chem. 52:2227-2229 (1980).

Needham, L. L., V. W. Burse and H. A. Price. "Temperature-Programmed Gas Chromatographic Determination of Polychlorinated And Polybrominated Biphenyls in Serum," J. Assoc. Off. Anal. Chem. 64(5):1131-1137 (1981).

MONS 005636

Neely, W. B. "Reactivity and Environmental Persistence of PCB Isomers," Chapter 5 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983) pp 71-88.

Neidert, E., and P. W. Saschenbrecker. "Improved Storherr Tube for Assisted and Sweep Co-Distillation Cleanup of Pesticides, Polychlorinated Biphenyls, and Pentachlorophenol from Animal Fats," J. Assoc. Off. Anal. Chem., 67(4):773-775 (1984).

Nelson, N. "Comments on Research Needs," Environ Health Perspec. 1:181-185 (1972).

Nero, V. P., and R. O. Hudson. "Liquid Chromatographic Cleanup Prior to Determination of Polychlorinated Biphenyls in Oil by Gas Chromatography/Mass Spectrometry," Anal. Chem. 56:1041-1043 (1984).

Neu, H. J., M. Zell and K. Ballschmiter. "Identifizierung von Einzelkomponenten in komplexen Gemischen durch Retentions-Index-Vergleich nach Capillar-Gas-Chromatographie mit Elektroneneinfangdetektor (ECD)," Fresenius' Z. Anal. Chem. 293: 193-200 (1978).

Neu, H. J. and R. Zinburg. "Are We Using the Full Resolving Power of Capillary GC?" J. High Resol. Chromatogr. & Chromatogr. Commun., 2:395-399 (1979).

Neulicht, R. M., M. D. Erickson, and R. V. Shah. "Guidelines for PCB Destruction Permit Applications and Demonstration Test Plans," Work Assignment No. 6, Draft Interim Report No. 1, Revision No. 2, EPA Contract No. 68-02-3938, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC (March 1985).

Newsome, W. H. and J. B. Shields. "Radioimmunoassay of PCBs in Milk and Blood," Intern. J. Environ. Anal. Chem. 10:295-304 (1981).

Newton, D. A. and R. R. Laski. "A Computer Routine for the Rapid Quantitation of Combinations of Aroclors 1242, 1254 and 1260," J. Chromatogr. Sci. 21:161-165 (1983).

Nicholson, W. J. and J. A. Moore (Eds.). "Health Effects of Halogenated Aromatic Hydrocarbons," Ann. N. Y. Acad. Sci. Vol. 320 (1979).

Nickerson G. B. and S. T. Likens. "Quantitative Analysis of Organochlorine Pesticides and PCB's," J. Chromatogr. 21:1-5 (1966).

Nisbet, I. C. T. "Environmental Occurrence and Human Exposure in Polychlorinated Biphenyls - Environmental Impact," Environ. Res. 5:287-308 (1972a).

Nisbet, I. C. T. "Transport Models and Monitoring Schemes for PCBs in Polychlorinated Biphenyls - Environmental Impact," Environ. Res. 5:348-352 (1972b).

Nisbet, C. T. and A. F. Sarofim. "Rates and Routes of Transport of PCBs in the Environment," Environ. Health Perspec. 1:21-38 (1972a).

Nisbet, I. C. T. and A. F. Sarofim. "Transport and Transformation in the Environment in Polychlorinated Biphenyls - Environmental Impact," Environ. Res. 5:213-287 (1972b).

Nordstrom, R. J. "Detection of PCBs by Infrared Spectroscopy," in Proceedings: 1983 Seminar. G. Addis and R. Y. Komai, Eds., Report No. EPRI-EL-3581 (Palo Alto, CA: Electric Power Research Institute), 1984.

Nordstrom, R. J. and B. McIntosh. "Infrared Spectroscopy for Field Measurements of PCBs," in Proceedings: 1981 PCB Seminar, G. Addis and J. Marks, Eds., Report No. EPRI-EL-2571 (Palo Alto, CA: Electric Power Research Institute), 1982.

Norstrom, R. J., R. W. Risebrough and D. J. Cartwright. "Elimination of Chlorinated Dibenzofurans Associated with Polychlorinated Biphenyls Fed to Mallards (Anas platyrhynchos)," Toxicol. Appl. Pharmacol. 37:217-228 (1976).

Nose, K. "Decachlorination of Polychlorinated Biphenyls and Its Application to Soil and Rice Analyses," Nippon Nogei Kagaku Kaishi 46(12):579-681 (1972); Chem. Abst. 78:146633r (1973).

Nose, K. "Assay of Residual PCB [Polychlorinated Biphenyl] in Water, Soil, and Agricultural Products," Noyaku Seisan Gijutsu 30:29-36 (1973); Chem. Abst. 79:101513f (1973).

Nose, K. "Determination of PCB (Polychlorinated Biphenyls)," Yukagaku 25(10):638-644 (1976); Chem. Abst., 86:26565p (1977).

Nowicki, H. G. "Application of Azulene as Visual Aid to Monitor Column Chromatographic Fractionation of Samples for Pesticide and Polychlorinated Biphenyl Determination," J. Assoc. Offic. Anal. Chem. 64(1):16-18 (1981).

MONS 005638

Nulton, C. P., C. L. Haile, and D. P. Redford. "Determination of Total Organic Halogen in Environmental Extracts by Gas Chromatography with Hall Detection," Anal. Chem. 56:598-599 (1984).

Nygren, S. and P. E. Mattsson. "Flow Programming in Glass Capillary Column-Electron Capture Gas Chromatograpy by Using the Valve in the Splitter Line," J. Chromatogr. 123:101-108 (1976).

Nyquist, R. A., C. L. Putzig and D. P. Peterson. "Identification of Pentachlorobiphenyl Isomers by Application of Diffuse Reflectance Fourier Transform Infrared Spectroscopy," Appl. Spectrosc. 37(2):140-153 (1983).

Oehme, M., and H. Stray, "Quantitative Determination of Ultra-Traces of Chlorinated Compounds in High-Volume Air Samples from the Arctic Using Polyurethane Foam as Collection Medium," Fresenius' Z. Anal. Chem., 311:665-673 (1982).

Oehme, M. and B. Ottar. "Toxic Organic Air Pollutants in the Arctic," in Proceedings: A Speciality Conference On: Measurement and Monitoring of Non-Criteria (Toxic) Contaminants in Air, E. R. Frederick (Ed.), The Air Pollution Control Association, Pittsburgh, PA, pp. 60-67 (1983).

Ofstad, E. B., G. Lunde, and K. Martinsen, "Chlorinated Aromatic Hydrocarbons in Fish from an Area Polluted by Industrial Effluents," Sci. Total Environ., 10:219-230 (1978).

Ogata, J. N., J. D. Okun, J. W. Hylin, and A. Bevenue, "Gas Chromatographic Method for the Analysis of Polychlorinated Biphenyls in Transformer Oil," J. Chromatogr., 189:425-427 (1980).

O'Keefe, P. W., R. M. Smith, D. R. Hilker, K. M. Aldous, and W. Gilday. "A Semiautomated Cleanup Method for Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in Environmental Samples," in Chlorinated Dioxins and Dibenzofurans in the Total Environment, II, L. H. Keith, C. Rappe, and G. Choudhary, Eds. (Boston: Butterworth Publishers, 1985) pp. 111-124.

Okumura, T., T. Kadono, and M. Nakatani, "Thin-layer Chromatography on Precoated Adsorbents Fixed with Fused Glass. V. Thin-layer Chromatography on Kieselguhr Sintered Plate," Yakugaku Zasshi 93(1):79-86 (1973); Chem. Abst. 78:105744j (1973).

O'Mara, T. and B. Nagel. "Sample Analysis for Neal's Landfill Case," unpublished memorandum, U.S. Environmental Protection Agency Region V, Chicago, IL, October 27, 1982.

Onuska, F. I. and M. Comba, "Identification and Quantitative Analysis of Polychlorinated Biphenyls on WCOT Glass Capillary Columns," in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, B. K. Afghan and D. Mackay, Eds. (New York: Plenum Press, 1980) pp. 285-302.

Onuska, F. I., R. J. Kominar and K. A. Terry. "Identification and Determination of Polychlorinated Biphenyls by High-Resolution Gas Chromatography," J. Chromatogr. 279:111-118 (1983).

Onuska, F. I. "Narrow-Bore Wall-Coated Open-Tubular Columns for Fast High-Resolution Gas Chromatographic Separations of Toxicants of Environmental Concern," Journal of Chromatography, 289:207-221 (1984).

Organization for Economic Cooperation and Development. Polychlorinated Biphenyls, Their Use and Control, Environmental Directorate, Paris (1973).

Organization for Economic Cooperation and Development. OECD Report on Protection of the Environment by Control of Polychlorinated Biphenyls, Paris (1979).

Osterroht, C., "Development of a Method for the Extraction and Determination of Non-polar, Dissolved Organic Substances in Sea Water," J. Chromatogr. 101:289-298 (1974).

Osterroht, C., "Dissolved PCB's and Chlorinated Hydrocarbon Pesticides in the Baltic, Determined by Two Different Sampling Procedures," Marine Chem. 5:113-121 (1977).

Oswald, E. O., E. Levy, B. W. Dorsett, and M. P. Walker, "Differentiation and Characterization of Isomeric Polychlorinated Biphenyls by Gas-Liquid Chromatography Coupled with Electron Impact and Chemical Ionization Mass Spectrometry," J. Chromatogr. 93:63-90 (1974a).

Oswald, E. O., P. W. Albro, and J. D. McKinney, "Utilization of Gas-Liquid Chromatography Coupled with Chemical Ionization and Electron Impact Mass Spectrometry for the Investigation of Potentially Hazardous Environmental Agents and Their Metabolites," J. Chromatogr. 98:363-448 (1974b).

Ouw, H. K., G. R. Simpson, and D. S. Siyali, "Use and Health Effects of Aroclor 1242, a Polychlorinated Biphenyl, in an Electrical Industry," Arch. Environ. Health, 31:189-194 (1976).

Paasivirta, J. and M. Pitkänen. "Structure Analysis of the Main Components in PCB Mixture Clophen A 60," Finn. Chem. Lett. 89-93 (1975).

MONS 005640

Pacco, J. M. and A. K. Mukherji. "Determination of Polychlorinated Biphenyls in a Polymer Matrix by Gel Permeation Chromatography Using Micro-Styragel® Columns," J. Chromatogr. 144: 113-117 (1977).

Palmork, K. H., J. C. Duinker, A. H. Knap, and J. P. Villeneuve. "Organochlorines," in Scientific Report of the Intercalibration Exercise, Intergovernmental Oceanographic Commission Technical Series, Report No. 22, UNESCO, Paris (ISBN 92-3-102077-3) (1982) pp. 60-83.

Pankow, J. F., L. M. Isabelle, and W. E. Asher. "Trace Organic Compounds in Rain. 1. Sampler Design and Analysis by Adsorption/Thermal Desorption (ATD)," Environ. Sci. Technol. 18:310-318 (1984); Errata published in Environ. Sci. Technol. 18:987 (1984).

Parker, C. E., P. W. Albro, M. J. Bobenrieth, T. W. Cochran and J. D. Robinson. "Quantitation of Halogenated Aromatic Compounds by Gas Chromatography-Mass Spectrometry," J. Chromatogr. 278(1):1-11 (1983).

Parkinson, A., R. Cockerline, and S. Safe. "Polychlorinated Biphenyl Isomers and Congeners as Inducers of Both 3-Methylcholanthrene- and Phenobarbitone-Type Microsomal Enzyme Activity," Chem.-Biol. Interactions, 29:277-289 (1980a).

Parkinson, A., L. Robertson, L. Safe, and S. Safe. "Polychlorinated Biphenyls as Inducers of Hepatic Microsomal Enzymes: Structure-Activity Rules," Chem.-Biol. Interactions, 30:271-285 (1980b).

Parlar, H. and M. Mansour. "Gaschromatographic Determination of Several Cyclodiene Insecticides in the Presence of Polychlorinated Biphenyls by Photoisomerisation Reactions," in Analytical Techniques in Environmental Chemistry 2. J. Albaiges, Ed. (New York: Pergamon Press, 1982), pp. 241-247.

Parris, R. M., F. R. Guenther, W. E. May, and S. N. Chesler. "Analysis of PCBs in Oil: Technique and SRM Development," in National Bureau of Standards Special Publication 674; Proceedings, Conference on Measurements and Standards for Recycled Oil - IV, held at NBS, Gaithersburg, Maryland (July 1984) pp. 27-32.

Pastel, M., B. Bush and J. S. Kim. "Accumulaton of Polychlorinated Biphenyls in American Shad During Their Migration in the Hudson River, Spring 1977," Pestic. Monit. J. 14(1): 11-22 (1980).

MONS 005641

Pavlou, S. P. "Environmental Dynamics of Trace Organics Contaminants in Estuarine and Coastal Zone Ecosystems," in Analytical Techniques in Environmental Chemistry, J. Albaiges, Ed. (New York: Pergamon Press, 1980), pp. 387-399.

Pavlou, S. P. and W. Hom. "Interlaboratory Calibration Results from Chlorinated Hydrocarbon Analyses in Marine Sediments," Marine Chem. 4:155-163 (1976).

Pavlou, S. P., R. N. Dexter and W. Hom. "Characterization of Chlorinated Hydrocarbons in the Marine Environment: Sampling and Analytical Aspects," in Analytical Techniques in Environmental Chemistry, J. Albaiges, Ed. (New York: Pergamon Press, 1980), pp. 185-196.

Pearson, C. R. "Halogenated Aromatics," in The Handbook of Environmental Chemistry, O. Hutzinger, Ed. (New York, NY: Springer-Verlag, 1982), pp. 89-116.

PEDCo Environmental, Inc. "Substitutes for PCB's for Use in Indoor Electrical Transformers," Contract No. 68-01-3935, Work Assignment 1-16, PN 3607-6, Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C. (January 6, 1984).

Pellizzari, E. D. "Electron Capture Detection in Gas Chromatography," J. Chromatogr. 98:323-361 (1974).

Pellizzari, E. D. "State-of-the-Art Instrumental Organic Analysis in Environmental Chemistry," Chapter 10 in Environmental Health Chemistry, J. D. McKinney, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981), pp. 195-218.

Pellizzari, E. D. "Analysis of Adipose and Blood Sera Samples for Individual PCB Isomers," MRI Subcontract No. 82-4900-21, EPA Contract No. 68-01-5915, Monthly Tech. Prog. Report No. 2, March 1, 1982.

Pellizzari, E. D., K. B. Tomer and M. A. Moseley. "High-Resolution Gas Chromatography and Negative Ion Chemical Ionization Mass Spectrometry of Polychlorinated Biphenyls," Chapter 12 in Advances in the Identification and Analysis of Organic Pollutants in Water, L. H. Keith, Ed., Vol. 1 (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981), pp. 197-218.

Pellizzari, E. D., S. D. Cooper, T. D. Hartwell and D. A. Whitehurst. "Analysis of Adipose and Blood Sera Samples for Individual PCB Isomers," Final Report, Midwest Research Institute, Kansas City, MO, Prepared for Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Contract No. 68-01-5915, Task 46 (1983a).

MONS 005642

Pellizzari, E. D., M. A. Moseley, S. D. Cooper, J. V. Harry B. A. Demian and M. D. Mullin. "Recent Advances in the Analysis of Polychorinated Biphenyls in Environmental and Biological Media," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-1378, NTIS No. PB84-135771 (December 1983b), pp. 4-60.

Pepe, M. G. and J. J. Byrne. "Adhesion-Binding of 2,2',4,4',5,5'-Hexachlorobiphenyl to Glass and Plastic: A Posible Source of Error for PCB Analysis," Bull. Environ. Contam. Toxicol. 25:936-940 (1980).

Perlman, H. L. "Accelerated Decision," U.S. Environmental Protection Agency, Before the Administrator, in re: Dow Chemical Company, Respondent. Docket No. TSCA (16(a))-1, September 22, 1980.

Perry, T. W., R. J. Everson, K. S. Hendrix, R. C. Peterson and F. R. Robinson. "Placental Transfer of Ingested Aroclor 1254 in the Bovine," in Trace Substances in Environmental Health 16:326-330 (1982).

Peterman, P. H., J. J. Delfino, D. J. Dube, T. A. Gibson and F. J. Priznar. "Chloro-organic Compounds in the Lower Fox River, Wisconsin," in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, B. K. Afghan and D. Mackay, Eds. (New York: Plenum Publishing Corporation, 1980), pp. 145-160.

Peyton, T. O. "Biological Disposal of Hazardous Waste," Enzyme Microb. Technol. 6(4):146-154 (1984).

Picer, M. and M. Ahel. "Separation of Polychlorinated Biphenyls from DDT and its Analogues on a Miniature Silica Gel Column," J. Chromatogr. 150:119-127 (1978).

Picer, N. and M. Picer. "Evaluation of Macroreticular Resins for the Determination of Low Concentratons of Chlorinated Hydrocarbons in Sea Water and Tap Water," J. Chromatogr. 193: 357-369 (1980).

Picker, J. E., and B. N. Colby, "Field Determination of Aroclors Using an Automated Electron Capture Detector Gas Chromatograph," in Proceedings: 1983 PCB Seminar, G. Addis and R. Y. Komai, Eds., Report No. EPRI-EL-3581 (Palo Alto, CA: Electric Power Research Institute), 1984.

Piechalak, B. "The Semiquantitative Detection of Polychlorinated Biphenyls (PCBs) in Contaminated Soils by Thin-Layer Chromatography," in Proceedings: 1983 PCB Seminar, G. Addis and R. Y. Komai, Eds., Report No. EPRI-EL-3581 (Palo Alto, CA: Electric Power Research Institute), 1984.

Pittaway, A. R., R. S. O'Connor and E. J. Heiden. "A Report of a Survey on the Incidental Manufacture, Processing, Distribution, and Use of Polychlorinated Biphenyl at Concentrations Below 50 ppm," Report prepared for Chemical Manufacturers Association by Regulatory Research Service (November 1981).

Pittaway, A. R. and T. W. Horner. "Statistical Analysis of Data from a Round Robin Experiment on PCB Samples," Report prepared for Chemical Manufacturers Association, Washington, D.C. (March 18, 1982).

Plumb, R. H., Jr. "Procedures for Handling and Chemical Analysis of Sediment and Water Samples," Prepared for U.S. Environmental Protection Agency/Corps of Engineers Technical Committee on Criteria for Dredged and Fill Material, Contract No. EPA-4805572010, NTIS No. AD A103788 (May 1981).

Polcyn, A. J., S. A. Whitlock and T. E. Siedhoff. "PCB Waste Destruction Study: High Efficiency Boiler," in Proceedings: A Specialty Conference on: Measurement and Monitoring of Non-Criteria (Toxic) Contaminants in Air, E. R. Frederick, Ed., (Pittsburgh, PA: The Air Pollution Control Association, 1983), pp. 361-373.

Polishuk, Z. W., M. Ron, M. Wassermann, S. Cucos, D. Wassermann and C. Lemesch. "Pesticides in People. Organochlorine Compounds in Human Blood Plasma and Milk," Pestic. Monit. J. 10(4):121-129 (1977).

Pomerantz, I., J. Burke, D. Firestone, J. McKinney, J. Roach and W. Trotter. "Chemistry of PCBs and PBBs," Environ. Health Perspec. 24:133-146 (1978).

Poole, C. F. and S. A. Schuette. "Isolation and Concentration Techniques for Capillary Column Gas Chromatographic Analysis," J. Chromatogr. pp. 526-549 (1983).

Porter, M. L., and J. A. Burke. "An Isolation and Cleanup Procedure for Low Levels of Organochlorine Pesticide Residues in Fats and Oils," J. Assoc. Offic. Anal. Chem. 56:733-738 (1973).

MONS 005644

Pressley, T. A. and J. E. Longbottom. "The Determination of Organohalide Pesticides and PCBs in Industrial and Municipal Wastewater: Method 617," U.S. Environmental Protection Agency, Report No. EPA-600/4-82-006, 35 pp.; NTIS PB82-156001 (1982).

Price, H. A., and R. L. Welch. "Occurrence of Polychlorinated Biphenyls in Humans," Environmental Health Perspectives, I:73-78 (1972).

Pyysalo, H., K. Wickström, and R. Litmanen. "A Baseline Study on the Concentrations of Chlordane-, PCB- and DDT-Compounds in Finnish Fish Samples in the Year 1982," Chemosphere, 12(6):837-842 (1983).

Que Hee, S. S., J. A. Ward, M. W. Tabor and R. R. Suskind. "Screening Method for Aroclor 1254 in Whole Blood," Anal. Chem. 55:157-160 (1983).

Rapaport, R. A. and S. J. Eisenreich. "Chromatographic Determination of Octanol-Water Partition Coefficients (K_{ow}'S) for 58 Polychlorinated Biphenyl Congeners," Environ. Sci. Technol. 18:163-170 (1984).

Rappe, C. "Analysis of Polychlorinated Dioxins and Furans," Environ. Sci. Technol. 18(3):78A-90A (1984).

Rappe, C., H. R. Buser, H. Kuroki, and Y. Masuda. "Identification of Polychlorinated Dibenzofurans (PCDFs) Retained in Patients with Yusho," Chemosphere 8(4):259-266 (1979).

Rappe, C. and H. R. Buser. "Chemical Properties and Analytical Methods," Chapter 2 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980), pp. 41-76.

Rappe, C., S. Marklund, P.-A. Bergqvist and M. Hansson. "Polychlorinated Dibenzo-p-dioxins, Dibenzofurans and Other Polynuclear Aromatics Formed During Incineration and Polychlorinated Biphenyl Fires," in Chlorinated Dioxins and Dibenzofurans in the Total Environment, G. Choudhary, L. H. Keith, C. Rappe (Eds.) (Ann Arbor Science Book: Butterworth Publishers, 1983), pp. 99-124.

Reggiani, G. "Toxicology of TCDD and Related Compounds: Observations in Man," in Chlorinated Dioxins and Related Compounds, O. Hutzinger, R. W. Frei, E. Merian and F. Pocchiari, Eds. (New York, NY: Pergamon Press, 1982), pp. 463-493.

MONS 005645

Reynolds, L. M. "Polychlorobiphenyls (PCB's) and Their Interference with Pesticide Residue Analysis," Bull. Environ. Contam. Toxicol. 4(3):128-143 (1969).

Reynolds, L. M., and T. Cooper. "Analysis of Organochlorine Residues in Fish," Water Quality Parameters, ASTM STP 573, American Society for Testing and Materials, pp. 196-205 (1975).

Ribick, M. A., G. R. Dubay, J. D. Petty, D. L. Stalling, and C. J. Schmitt. "Toxaphene Residues in Fish: Identification, Quantification, and Confirmation at Part per Billion Levels," Environ. Sci. Technol. 16:310-318 (1982).

Rice, C. P. and W. A. Frez. "Application of Capillary Chromatography to the Study of the Cycling of PCBs on Suspended Particles," Final Report Prepared for the Great Lakes Environmental Research Laboratory - The National Oceanographic and Atmospheric Administration, Department of Commerce, Grant NA79RA000006, NTIS No. PB82-245903 (1981).

Rice, C. P., P. A. Meyers and G. S. Brown. "Role of Surface Microlayers in the Air-Water Exhange of PCBs," Chapter 10 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 157-179.

Rice, C. P., B. J. Eadie, and K. M. Erstfeld. "Enrichment of PCBs in Lake Michigan Surface Films," J. of Great Lakes Research, 8(2):265-270 (1982).

Richardson, W. L., V. E. Smith and R. Wethington. "Dynamic Mass Balance of PCB and Suspended Solids in Saginaw Bay--A Case Study," Chapter 18 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 329-366.

Ringer, R. K. "Toxicology of PCBs in Mink and Ferrets," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 227-240.

Risebrough, R. W. "Determination of Polychlorinated Biphenyls in Environmental Samples." Presented at the International Symposium on Identification and Measurement of Environmental Pollutants, Ottawa, Ontario, Canada, June 14-17, 1971.

Risebrough, R. W., B. W. de Lappe, and W. Walker II. "Transfer of Higher Molecular Weight Chlorinated Hydrocarbons to the Marine Environment," in Marine Pollutant Transfer, H. L. Windom, R. A. Duce, Eds. (Lexington, MA: Lexington Books, 1976). pp. 261-321.

Riva, M., A. Carisano and A. Gaghetta. "Rapid GLC-ECD [Gas-Liquid Chromatography-Electron Capture Detector] Determination of Chlororganic Pesticide and Polychlorobiphenyl (PCB's) Residues in Animal Foods. General Considerations about Ecological Contamination," Riv. Ital. Sostanze Grasse 50(12):434-442 (1973); Chem. Abst. 81:11924c (1974).

Robbins, A. L. and C. R. Willhite. "A Rapid Method for the Analysis of Polychlorinated Biphenyls in Milk," Bull. Environ. Contam. Toxicol. 21:428-431 (1979).

Roberts, J. R., D. W. Rodgers, J. R. Bailey and M. A. Rorke. "Polychorinated Biphenyls: Biological Criteria for an Assessment of Their Effects on Environmental Quality," Associate Committee on Scientific Criteria for Environmental Quality. Ottawa, Canada: National Research Council of Canada (1978).

Rodgers, P. W. "Model Simulation of PCB Dynamics in Lake Michigan," Chapter 17 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 311-327.

Rodriguez, C. F., W. A. McMahon and R. E. Thomas. "Method Development for Determination of Polychlorinated Hydrocarbons in Municipal Sludge," Final Report, Contract No. 68-03-2606, Environmental Protection Agency, EPA-600/2-80-029; NTIS No. PB 82-234 071 (March 1980).

Rogan, W. J., B. C. Gladen, J. D. McKinney, and P. A. Albro. "Chromatographic Evidence of Polychlorinated Biphenyl Exposure From a Spill," J. Amer. Med. Assoc. 249(8):1057-1058 (1983).

Rohleder, H., H. Staudacher and W. Suemmermann. "High-pressure Liquid Chromatography for the Separation of Lipophilic Organochlorine Xenobiotics from Triglycerides in Trace Analysis," Fresenius' Z. Anal. Chem. 279(2):152-153 (1976); Chem. Abst. 84:160197g (1976).

Ross, P. F., O. L. Osheim and H. A. Nelson. "PCB Residues in Feedlot Steers," Bull. Environ. Contam. Toxicol. 26:485-488 (1981).

MONS 005647

Rouse, T. O., "PCB Round Robin Analysis," in Proceedings: 1981 PCB Seminar, G. Addis and J. Marks, Eds., Report No EPRI-EL-2572 (Palo Alto, CA: Electric Power Research Institute), 1982.

Rote, J. W. and W. J. Morris. "Use of Isotopic Abundance Ratios in Identification of Polychlorinated Biphenyls by Mass Spectrometry," J. Assoc. Offic. Anal. Chem. 56(1):188-199 (1973).

Roth, R. W., J. R. Heys, D. H. T. Chien, G. A. Rotert, J. H. Saugier and M. D. Erickson. "Methods of Analysis for Incidentally Generated PCBs--Synthesis of ^{13}C-PCB Surrogates," Draft Interim Report No. 3, Revision No. 1, EPA Contract No. 68-01-5915, Task 51, prepared by Midwest Research Institute, Kansas City, MO, for Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., November 22, 1982. 91 pp.

Rubenstein, H. M. "Polychlorinated Biphenyls: Single Isomer Formation from 2,4-Dichlorobenzoyl Peroxide," Abstract No. 614, 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 7-12, 1983.

Russell, D. J. and B. McDuffie. "Analysis for Phthalate Esters in Environmental Samples: Separation from PCB's and Pesticides Using Dual Column Liquid Chromatography," Int. J. Environ. Anal. Chem. 15(3):165-183; Chem. Abstr. 99:151456y (1983).

Rust, S. W. "Study of Errors Generated in the Chemical Analysis of Environmental Samples," Final Report, Task 67, Contract No. 68-01-6721, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC (1984).

Ruzo, L. O., M. J. Zabik and R. D. Schuetz. "Polychlorinated Biphenyls: Photolysis of 3,4,3',4'-Tetrachlorobiphenyl and 4,4'-Dichlorobiphenyl in Solution," Bull. Environ. Contam. Toxicol. 8(4):217-218 (1972).

Ryan, J. J., P-Y Lau, J. C. Pilon, D. Lewis, H. A. McLeod, and A. Gervais. "Incidence and Levels of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Lake Ontario Commercial Fish," Environ. Sci. Technol., 18:719-721 (1984).

Ryan, R. M., D. R. Pendleton and J. M. Jenks. "Coastal Impacts of PCB Incineration Operations in the Gulf of Mexico," in Proceedings: A Specialty Conference on: Measurement and Monitoring of Non-criteria (Toxic) Contaminants in Air, E. R. Frederick, Ed. (Pittsburgh: The Air Pollution Control Association, 1983), pp. 351-360.

Sabate, L. G., X. Tomas, M. A. Colom and A. Garcia-Carrillo. "Quantitation of PCB - Chesbyshev's Method," Comput. Appl. Lab. 1(2):146; Chem. Abstr. 99:224441b (1983).

Saeki, S., A. Tsutsui, K. Oguri, H. Yoshimura and M. Hamana. "Isolation and Structure Elucidation of the Amino Component of KC-400 (Chlorobiphenyls)," Fukuoka-Igaku-Zasshi 62(1): 21-24 (1971); Chem. Abst. 74:146294y (1971).

Safe, S. "Overview of Analytical Identification and Spectroscopic Properties," in National Conference on Polychlorinated Biphenyls (November 19-21, 1975, Chicago, Illinois), F. A. Ayer, Ed., EPA-560/6-75-004; NTIS No. PB 253-248, March 1976.

Safe, S. "Metabolism, Uptake, Storage and Bioaccumulation," Chapter 4 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980). pp. 81-107.

Safe, S. "Polychlorinated Biphenyls (PCBs) and Polybrominated Biphenyls (PBBs): Biochemistry, Toxicology, and Mechanism of Action," CRC Crit. Rev. Toxicol. 13:319-395 (1984).

Safe, S., N. Platonow, O. Hutzinger and W. D. Jamieson. "Analysis of Organochlorine Metabolites in Crude Extracts by High Resolution Photoplate Mass Spectrometry," Biomed. Mass Spectrom. 2:201-203 (1975).

Safe, S., C. Wyndham, A. Parkinson, R. Purdy and A. Crawford. "Halogenated Biphenyl Metabolism," in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, B. K. Afghan and D. Mackay, Eds. (New York, NY: Plenum Press, 1980), pp. 537-544.

Safe, S. and R. K. Boyd. "Pesticide Analysis by Mass Spectrometry," in Pesticide Analysis Conf. Proc., K. G. Das, Ed. (New York: Dekker, 1981), pp. 329-368. Chem. Abst. 95: 110007b (1981).

Safe, S., A. Parkinson, L. Robertson, R. Cockerline, L. Safe, S. Bandiera and A. Okey. "PCBs as AHH Inducers," in Chlorinated Dioxins and Related Compounds, O. Hutzinger, R. W. Frei, E. Merian and F. Pocchiari, Eds. (New York: Pergamon Press, 1981), pp. 383-392.

Safe, S., L. W. Robertson, L. Safe, A. Parkinson, S. Bandiera, T. Sawyer, and M. A. Campbell. "Halogenated Biphenyls: Molecular Toxicology," Can J. Physiol. Pharmacol., 60:1057-1064 (1982).

MONS 005649

Safe, S., M. Mullin, L. Safe, C. Pochini, S. McCrindle and M. Romkes. "High Resolution PCB Analysis," Chapter 1 in Physical Behavior of PCBs in The Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983a), pp. 1-13

Safe, S., L. Robertson, T. Sawyer, A. Parkinson, S. Bandiera, L. Safe and M. Campbell. "PCDDs and Related Compounds: Metabolism and Biochemistry," in Human and Environmental Risks of Chlorinated Dioxins and Related Compounds, R. E. Tucker, A. L. Young and A. P. Gray, Eds. (New York, NY: Plenum Press, 1983b), pp. 393-403.

Safe, S., M. Mullin, L. Safe, C. Pochini and S. McCrindle. "High Resolution PCB (Polychlorinated Biphenyls) Analysis," Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, MN, EPA-600/D-83-095; NTIS No. PB83-246124; Chem. Abstr. 100:61153g (1983c).

Safe, S., A. Parkinson, L. Robertson, T. Sawyer and S. Bandiera. "PCBs (Polychlorinated Biphenyls): Structure-Activity Relationships," Environmental Research Laboratory, U.S. Environmental Protection Agency, Washington, D.C., EPA-600/D83-096, NTIS No. PB83-247486 (1983d).

Safe, S., A. Parkinson, L. Robertson, T. Sawyer, S. Bandiera, L. Safe, M. A. Campbell and M. Mullin. "PCBs: Structure-Activity Relationships," in Advances in Exposure, Health and Environmental Effects of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-137B; NTIS No. PB-84-135771 (December 1983e), pp. 229-248.

Sans, W. W. "Multiple Insecticide Residue Determination Using Column Chromatography, Chemical Conversion, and Gas-Liquid Chromatography," J. Agr. Food Chem. 15:192-198 (1967).

Saperstein, M. D., R. J. Gordon and E. J. Faeder. "PCB Contamination in Distribution Transformers," J. Environ. Sci. Health A17(2):241-251 (1982).

Sarofim, A. F. "Properties, Production, and Uses in Polychlorinated Biphenyls - Environmental Impact," Environ. Res. 5:258-273 (1972a).

Sarofim, A. F. "Analytical Methods in Polychlorinated Biphenyls - Environmental Impact," Environ. Res. 5:338-348 (1972b).

MONS 005650

Sarro, T. L., O. R. Moore and D. G. Ackerman. "Emissions Testing During Incineration of PCBs at Energy Systems Company, El Dorado, Arkansas," Draft Report by TRW, Inc., Redondo Beach, CA, to Philip C. Schwindt, U.S. Environmental Protection Agency, Region VI, Dallas, TX, EPA Contract No. 68-02-2174, Work Assignment 56 (September 1981a), 171 pp.

Sarro, T. L., O. R. Moore and D. G. Ackerman. "Emissions Testing During Incineration of PCBs at Rollins Environmental Services, Inc., Deer Park, TX," Draft Report by TRW, Inc., Redondo Beach, CA, to Philip C. Schwindt, U.S. Environmental Protection Agency, Region VI, Dallas, TX, EPA Contract No. 68-02-3174, Work Assignment 56 (September 1981b), 128 pp.

Sauter, A. D., P. E. Mills, W. L. Fitch and R. Dyer. "Interlaboratory GC/MS Response Factor Precision," J. High Resol. Chromatogr. & Chromatogr. Commun. 5:27-30 (1982).

Savage, E. P., J. D. Tessari, J. W. Malberg, H. W. Wheeler and J. R. Bagby. "A Search for Polychlorinated Biphenyls in Human Milk in Rural Colorado," Bull. Environ. Contam. Toxicol. 9(4):222-226 (1973a).

Savage, E. P., J. D. Tessari, J. W. Malberg, H. W. Wheeler and J. R. Bagby. "Organochlorine Pesticide Residues and Polychlorinated Biphenyls in Human Milk, Colorado--1971-72," Pestic. Monit. J. 7(1):1-3 (1973b).

Sawyer, L. D. "Collaborative Study of the Recovery and Gas Chromatographic Quantitation of Polychlorinated Biphenyls in Chicken Fat and Polychlorinated Biphenyl-DDT Combinations in Fish," J. Assoc. Offic. Anal. Chem. 56(4):1015-1023 (1973).

Sawyer, L. D. "Quantitation of Polychlorinated Biphenyl Residues by Electron Capture Gas-Liquid Chromatography: Reference Material Characterization and Preliminary Study," J. Assoc. Offic. Anal. Chem. 61(2):272-281 (1978a).

Sawyer, L. D. "Quantitation of Polychlorinated Biphenyl Residues by Electron Capture Gas-Liquid Chromatography: Collaborative Study," J. Assoc. Offic. Anal. Chem. 61(2):282-291 (1978b).

Schneider, J. F., S. Bourne, and A. S. Boparai, "Parallel Capillary Column Gas Chromatography in the Determination of Chlorinated Pesticides and PCBs," Journal of Chromatographic Science, 22 (1984).

Schulte, E. and L. Acker. "Identifizierung und Metabolisierbarkeit von polychlorierten Biphenylen," Naturwissenschaften 61:79-80 (1974a).

MONS 005651

Schulte, E. and L. Acker. "Gas-Chromatographie mit Glascapillaren bei Temperaturen bis zu 320°C und ihre Anwendung zur Trennung von Polychlorbiphenylen," Fresenius' Z. Anal Chem. 268(4):260-267; Chem. Abst. 81:115377t (1974b).

Schulte, E., H. P. Thier and L. Acker. "Residual Analysis of Polychlorinated Biphenyls in Foods of Animal Origin: Experiences and Proposals for Standardization," Dtsch. Lebensm.-Rundsch. 72(7):229-232 (1976); Chem. Abst. 85:121894h (1976).

Schulte, E. and R. Malisch. "Berechnung der Wahren PCB-Gehalte in Umweltproben I. Ermittlung der Zusammensetzung Zweier Technischer PCB-Gemische," Fresenius' Z. Anal. Chem 314:545-551 (1983).

Schulte, E., and R. Malisch. "Calculation of the Real PCB Content in Environmental Samples II. Gas Chromatographic Determination of the PCB Concentration in Human Milk and Butter," Fresenius' Z. Anal. Chem. 319:54-59 (1984).

Schutjes, C. P. M., E. A. Vermeer, G. J. Scherpenzeel, R. W. Bally, and C. A. Cramers. "Practical Aspects of Fast Gas Chromatography on 50 µm I.D. Capillary Columns: Combination with Electron-Capture Detection," Journal of Chromatography, 289:157-162 (1984).

Schwalb, A. L. and A. Marquez. "Salt River Project's Experience with the Horiba Sulfur/Chlorine-in-Oil Analyzer," in Proceedings: 1981 PCB Seminar, G. Addis and J. Marks, Eds. Report No. EPRI-EL-2572 (Palo Alto, CA: Electric Power Research Institute, 1982), pp. 2-23.

Schwartz, P. M., J. W. Jacobson, G. Fein, J. L. Jacobson and H. A. Price. "Lake Michigan Fish Consumption as a Source of Polychlorinated Biphenyls in Human Cord Serum, Maternal Serum, and Milk," Am. J. Public Health 73(3):293-296 (1983).

Schwartz, T. R. and R. G. Lehmann. "Determination of Polychlorinated Biphenyls in Plant Tissue," Bull. Environ. Contam. Toxicol. 28:723-727 (1982).

Schwartz, T. R., J. D. Petty, D. L. Stalling, J. W. Hogan, M. K. Marlow, R. D. Campbell and R. L. Little. "A MUMPs (DSM-11) Derived Data Base for Congener Specific PCB Analysis Leading to Pattern Recognition Studies," Abstract, 184th Annual Chemical Society National Meeting, September 12-17, 1982.

Schwartz, T. R., J. D. Petty and E. M. Kaiser. "Preparation of n-Alkyl Trichloroacetates and Their Use as Retention Index Standards in Gas Chromatography," Anal. Chem. 55:1839-1840 (1983).

MONS 005652

Schwartz, T. R., R. D. Campbell, D. L. Stalling, R. L. Little, J. D. Petty, J. W. Hogan and E. M. Kaiser. "Laboratory Data Base for Isomer-Specific Determination of Polychlorinated Biphenyls," Anal. Chem. 56:1303-1308 (1984).

Scinto, L. L., P. A. Painter, A. M. Takata and T. J. Hennings. "Preliminary Operations Plan and Guidelines for the At-sea Incineration of Liquid PCB Wastes," Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/2-82-068, NTIS No. PB83-181834 (1982).

Seiber, J. N. "Reversed-Phase Liquid Chromatography of Some Pesticides and Related Compounds. Solubility-Retention Relationships," J. Chromatogr. 94:151-157 (1974).

Seidl, G. and K. Ballschmiter. "Isolation of PCB's from Soil. Recovery Rates Using Different Solvent Systems," Chemosphere 5:373-376 (1976a).

Seidl, G. and K. Ballschmiter. "Isolation of PCB's from Vegetable Oils: Recovery and Efficiency of 'Clean Up' Methods," Chemosphere 5:363-366 (1976b).

Seidl, G. and K. Ballschmiter. "Quantitation of Polychlorinated Biphenyl (PCB)-Residues after Hydrodechlorination to Biphenyl Using Liquid Chromatography with UV-Detection," Fresenius' Z. Anal. Chem. 296:281-284 (1979).

Serum, J. W., S. C. Tong, L. E. St. John Jr., C. A. Bache, D. R. Mertens and D. J. Lisk. "Electron-Capturing Compounds and Selected Elements in Paper," Bull. Environ. Contam. Toxicol. 10(2):88-96 (1973).

Sevcik, J. "Detectors in Gas Chromatography," J. Chromatogr. Library Vol. 4 (New York, NY: Elsevier Scientific Publishers, 1976).

Sexton, F. W. and D. E. Lentzen. "Audit of the Vulcanus Incineration Ship Prior to the August 1982 PCB Burn, Mobile, Alabama," U.S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Research Triangle Park, NC, Report No. EPA-600/7-83-023; NTIS No. PB83-193698 (April 1983).

Shahied, S. I., R. P. Stanovick, D. E. McInturff and E. Missaghi. "Determination of Polychlorinated Biphenyl (PCB's) Residues in Grades of Pulp, Paper and Paperboard," Bull. Environ. Contam. Toxicol. 10(2):80-87 (1973).

MONS 005653

Shaw, D. G. "Discrimination Between PCB and DDT Residues by a Gas Chromatographic-Mass Spectrometric Technique," Bull. Environ. Contam. Toxicol. 8(4):208-211 (1972).

Shaw, G. R., H. C. Chapman and G. W. Roache. "Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Sediment Samples Containing Oil Residues," Residue (Melbourne) 3(2):2-8 (1976); Chem. Abst. 88:1362y (1978).

Shaw, G. R. and D. W. Connell. "Physiochemical Properties Controlling Polychlorinated Biphenyl (PCB) Concentrations in Aquatic Organisms," Environ. Sci. Technol. 18:18-23 (1984).

Sherma, J. "Gas-Chromatography Analysis of Polychlorinated Biphenyls and Other Nonpesticide Organic Pollutants," Chapter 5 in Advances in Chromatography, J. C. Giddings, E. Grushka, R. A. Keller and J. Cazes, Eds. (New York, NY: Marcel Dekker, Inc., 1975), pp. 141-176.

Sherma, J. Manual of Analytical Quality Control for Pesticides and Related Compounds in Human and Environmental Samples, EPA-600/2-81-059; NTIS No. PB81-222721 (April 1981).

Shirai, F. "Detection of Polychlorinated Terphenyls on Food Wrappers by Reversed-Phase Partition Thin-Layer Chromatography," Eisei Kagaku 20(5): 282-286 (1974); Chem. Abst. 82: 84559t (1975).

Skrentny, R. F., R. W. Hemken and H. W. Dorough. "Silo Sealants as a Source of Polychlorobiphenyl (PCB) Contamination of Animal Feed," Bull. Environ. Contam. Toxicol. 6(5):409-416 (1971).

Simon, C. G. and T. F. Bidleman. "Sampling Airborne Polychlorinated Biphenyls with Polyurethane Foam--Chromatographic Approach to Determining Retention Efficiencies," Anal. Chem. 51(8):1110-1113 (1979).

Singer, E., T. Jarv and M. Sage. "Survey of Polychlorinated Biphenyls in Ambient Air Across the Province of Ontario," Chapter 19 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp 367-383.

Sissons, D. and D. Welti. "Structural Identification of Polychlorinated Biphenyls in Commercial Mixtures by Gas-Liquid Chromatography, Nuclear Magnetic Resonance and Mass Spectrometry," J. Chromatogr. 60:15-32 (1971).

MONS 005654

Siyali, D. S. "Polychlorinated Biphenyls, Hexachlorobenzene and Other Organochlorine Pesticides in Human Milk," Med. J. Aust. 2:815-818 (1973).

Sleight, S. D. "Pathologic Effects of PCBs in Mammals," in PCBs: Human and Environmental Hazards. F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 215-226.

Smith, A. B., J. Schloemer, L. K. Lowry, A. W. Smallwood, R. N. Ligo, S. Tanaka, W. Stringer, M. Jones, R. Hervin and C. J. Glueck. "Metabolic and Health Consequences of Occupational Exposure to Polychlorinated Biphenyls," Br. J. Ind. Med. 39:361-369 (1982).

Smith, G. C., G. A. Gauger and R. M. Frey "Using Capillary Gas Chromatography to Determine Polychlorinated Biphenyls (PCBs) in Electrical Insulating Liquids," IEEE Trans. Power Appar. Syst. PAS-101(7):2260-2267 (1982); Chem. Abstr. 97: 229462c (1982).

Smith, J. "Quality Assurance Plan for Measurment of Incidentally Generated Chlorinated Biphenyls (PCBs)," Unpublished Memorandum, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC, April 6, 1982.

Smith, L. M., D. L. Stalling, and J. L. Johnson. "Determination of Part-per-Trillion Levels of Polychlorinated Dibenzofurans and Dioxins in Environmental Samples," Anal. Chem. 56: 1830-1842 (1984).

Smodlaka, N. "Unidentified Compounds in Seawater Chromatographically Similar to PCBs," Marine Pollut. Bull. 5:84-86 (1974); Chem. Abstr. 83:12063d (1975).

Smrek, A. L. and L. L. Needham. "Simplified Cleanup Procedures for Adipose Tissue Containing Polychlorinated Biphenyls, DDT, and DDT Metabolites," Bull. Environ. Contam. Toxicol. 28:718-722 (1982).

Snyder, D. and R. Reinert. "Rapid Separation of Polychlorinated Biphenyls from DDT and Its Analogues on Silica Gel," Bull. Environ. Contam. Toxicol. 6(5):385-390 (1971).

Snyder, L. R. and J. J. Kirkland. Introduction to Modern Liquid Chromatography, 2nd Ed. (New York, NY: Wiley-Interscience, 1979), 863 pp.

Sonchik, S., D. Madeleine, P. Macek and J. Longbottom. "Evaluation of Sample Preparation Techniques for the Analysis of PCBs in Oil," J. Chromatogr. Sci. 22:265-271 (1984).

MONS 005655

Spaw, S. N., D. R. Pendleton and J. M. Jenks. "Environmental Sampling and Analysis of Airborne Contaminants Identified as Skin Irritants: Deer Park, Texas," in Proceedings: A Specialty Conference on: Measurement and Monitoring of Non-criteria (Toxic) Contaminants in Air, E. R. Frederick, Ed. (Pittsburgh: The Air Pollution Control Association, 1983), pp. 156-167.

Spearman, R. I. C. "Biochemistry of Adipose Tissue and its Regulation," in The Physiology and Pathophysiology of the Skin (London, New York: Academic Press, 1982), pp. 2283-2325; Chem. Abstr. 98:14654b (1982).

Spies, D. N. "Rapid Field Extraction Technique for Determining Extent of PCB Contaminated Sediments," in Hazardous Materials Spills, Conference Proceedings, J. Ludwigson (Ed.), pp. 435-437 (1982); Chem. Abst. 97:60688t (1982).

Spittler, T. M. "Field Measurement of PCB's in Soil and Sediment Using a Portable Gas Chromatograph," Natl. Conf. Manage. Uncontrolled Hazard. Waste Sites, pp. 105-107 (1983); Chem. Abst. 100:220890p (1984).

Spittler, T. M. "Field Measurement of Polychlorinated Biphenyls in Soil and Sediment Using a Portable Gas Chromatograph," in Environmental Sampling for Hazardous Wastes, G. E. Schweitzer and J. A. Santolucito, Eds., ACS Symposium Series 267 (Washington, DC, American Chemical Society, 1984) pp. 37-42.

Stahl, E., Ed. Thin-Layer Chromatography: A Laboratory Handbook (New York: Springer-Verlag, 1969).

Stahr, H. M. "Analysis of PCBs by Thin-Layer Chromatography," J. Liq. Chromtogr. 7(7):1393-1402 (1984).

Stalling, D. L. "Analysis of Organochlorine Residues in Fish: Current Research at the Fish-Pesticide Research Laboratory," in Pestic. Chem., Proc. Intl. IUPAC Congr. Pest. Chem., 2nd 4:413-438 (1971).

Stalling, D. L. "Application of Analytical Methods Research to Monitoring Organic Residues in Fish," The Institute of Electrical and Electronics Engineers, Inc., Annals No. 75CH1004-1 7-5 (1976).

Stalling, D. L. and J. N. Huckins. "Gas-Liquid Chromatography--Mass Spectrometry Characterization of Polychlorinated Biphenyls (Aroclors) and ^{36}Cl-Labeling of Aroclors 1248 and 1254," J. Assoc. Offic. Anal. Chem. 54(4):801-807 (1971).

MONS 005656

Stalling, D. L., R. C. Tindle and J. L. Johnson. "Cleanup of Pesticide and Polychlorinated Biphenyl Residues in Fish Extracts by Gel Permeation Chromatography," J. Assoc. Offic. Anal. Chem. 55(1):32-38 (1972).

Stalling, D. L. and J. N. Huckins. "Reverse Phase Thin Layer Chromatography of Some Aroclors, Halowaxes, and Pesticides," J. Assoc. Offic. Anal. Chem. 56(2):367-372 (1973).

Stalling, D. L., J. Johnson and J. N. Huckins. "Automated Gel Permeation--Carbon Chromatographic Cleanup of Dioxins, PCBs, Pesticides, and Industrial Chemicals," in Environmental Quality and Safety, Supplement Vol. III, Pesticides Lectures of the IUPAC, Third International Congress of Pesticide Chemistry, Helsinki, July 1974, F. Coulson and F. Korte, Eds. (Stuttgart, Germany: G. Thieme Publishing, 1975), pp. 12-18.

Stalling, D. L., J. N. Huckins, J. D. Petty, J. L. Johnson and H. O. Sanders. "An Expanded Approach to the Study and Measurement of PCBs and Selected Planar Halogenated Aromatic Environmental Pollutants," Ann. N.Y. Acad. Sci. 320:48-59 (1979a).

Stalling, D. L., L. M. Smith and J. D. Petty. "Approaches to Comprehensive Analyses of Persistent Halogenated Environmental Contaminants," in Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, C. E. Van Hall, Ed. (American Society for Testing and Materials, 1979b), pp. 302-323.

Stalling, D. L., J. N. Huckins and J. D. Petty. "Presence and Potential Significance of o-o'-Unsubstituted PCB Isomers and Trace Aroclor® 1248 and 1254 Impurities," in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, B. K. Afghan and D. Mackay, Eds. (New York: Plenum Press 1980a), pp. 131-139.

Stalling, D. L., J. D. Petty, G. R. Dubay and R. A. Smith. "Application of LC/MS to Chromatographic Separation of Aromatics Using Carbon as the Stationary Phase," J. Chromatogr. Sci. 18:107-108 (1980b).

Stalling, D. L., J. D. Petty, L. M. Smith and G. R. Dubay. "Contaminant Enrichment Modules and Approaches to Automation of Sample Extract Cleanup," Chapter 9 in Environmental Health Chemistry, The Chemistry of Environmental Agents as Potential Human Hazards, J. D. McKinney, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1981), pp. 177-193.

MONS 005657

Stalling, D. L., J. D. Petty, L. M. Smith, C. Rappe, and H. R. Buser. "Isolation and Analysis of Polychlorinated Furans in Aquatic Samples," in Chlorinated Dioxins and Related Compounds: Impact on the Environment, O. Hutzinger, R. W. Frei, E. Merian, F. Pocchari, Eds. (Pergamon Press, 1982).

Stan, H.-J. "Combined Gas Chromatography-Mass Spectrometry," Chapter 9 in Pesticide Analysis, K. G. Das, Ed. (New York: Marcel Dekker, Inc., 1981), pp. 369-423.

Stanley, J., C. Haile, A. Small and E. Olson. "Sampling and Analysis Procedures for Assessing Organic Emissions from Stationary Combustion Sources for Exposure Evaluation Division Studies. Methods Manual," U.S. Environmental Protection Agency, EPA-560/5-82-014 (1982).

Stanley, J. S., M. D. Erickson, J. K. Turman, G. Radolovich, J. Onstot, K. Bauer and J. E. Going. "Relative Response Factors and Relative Retention Times of PCBs Obtained by Capillary GC/EIMS," Abstract No. 801 presented at the 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 7-12, 1983.

Stanley, J. S., C. L. Haile, A. M. Magin, R. V. Northcutt and O. P. Redford. "Quality Assurance Program for Combustion Source Studies," in Identification and Analysis of Organic Pollutants in Air, L. H. Keith, Ed. (Boston: Butterworth Publishers, 1984), pp. 459-473.

Stanovick, R. P., S. Shahied and E. Missaghi. "Determination of Polychlorinated Biphenyl (Aroclor 1242) Migration Into Food Types," Bull. Environ. Contam. Toxicol. 10(2):101-107 (1973).

Steichen, R. J., R. G. Tucker and E. Mechon. "Standardization of Aroclor Lots for Individual-Peak Gas Chromatographic Calibration," J. Chromatogr. 236:113-126 (1982).

Steinwandter, H. "Contributions to Silica Gel Application in Pesticide Residue Analysis," Fresenius' Z. Anal. Chem. 312: 342-345 (1982a).

Steinwandter, H. "Contributions to the Application of Gel Chromatography in Residue Analysis," Fresenius' Z. Anal. Chem. 313:536-538 (1982b).

Steinwandter, H. "Contributions to Silica Gel Application in Residue Analysis. V. Simple Micro Method for Liquid Chromatographic Separation of Chlorinated Hydrocarbon Pesticides and Polychlorinated Biphenyls (PCB's), Fresenius' Z. Anal. Chem. 316(5):493-494 (1983).

Steinwandter, H. "Chlorination of Organic Compounds. II. Kinetics of PCB Perchlorination," Fresenius' Z. Anal. Chem. 317:869-871 (1984).

Steinwandter, H. and H. Bruene. "Chlorination of Organic Compounds. I. A Simple 10 Min Perchlorination Technique for the Quantitative Determination of Polychlorinated Biphenyls (PCB's)," Fresenius' Z. Anal. Chem. 314(2):160 (1983).

Stenhagen, E., S. Abrahamsson and F. W. McLafferty Registry of Mass Spectral Data Vol. 1-4, Wiley, New York (1974).

Stijve, T. and E. Cardinale. "Rapid Determination of Chlorinated Pesticides, Polychlorinated Biphenyls, and a Number of Phosphated Insecticides in Fatty Foods," Mitt. Geb. Lebensmittelunters. Hyg. 65(1):131-150 (1974); Chem. Abst. 82: 137862v (1975).

Stolzenburg, T. R. and A. W. Andren. "Determination of the Aqueous Solubility of 4-chlorobiphenyl," Anal. Chim. Acta 151(1):271-274 (1983).

Strachan, W. M. J., H. Huneault, W. M. Schertzer, and F. C. Elder. "Organochlorines in Precipitation in the Great Lakes Region," in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment, B. K. Afghan and D. Mackay, Eds. (New York: Plenum Press, 1980), pp. 387-396.

Strachan, W. M. J., and H. Huneault. "Automated Rain Sampler for Trace Organic Substances," Environ. Sci. Technol. 18: 127-130 (1984).

Stratton, C. L. and P. C. Geiszler. "Analysis of Polychlorinated Biphenyl (PCB) in Human Blood Serum Samples," Report prepared for U.S. Environmental Protection Agency, EPA-560/6-78-007, NTIS No. PB-291 458/8 (October 1977).

Stratton, C. L., K. L. Tuttle and J. M. Allan. Environmental Assessment of Polychlorinated Biphenyls (PCBs) near New Bedford, MA Municipal Landfill," Report prepared for U.S. Environmental Protection Agency, Report No. EPA 560/6-78-006 (May 1978a).

Stratton, C. L., S. A. Whitlock and J. M. Allan. "A Method for the Sampling and Analysis of Polychlorinated Biphenyl (PCB) in Air," Report prepared for U.S. Environmental Protection Agency, Report No. EPA-600/4-78-048, NTIS No. PB 288 410/4 (August 1978b).

MONS 005659

Stratton, C. L., J. M. Allan and S. A. Whitlock. "Advances in the Application of the Perchlorination Technique for the Quantitation and Confirmation of Polychlorinated Biphenyls (PCBs)," Bull. Environ. Contam. Toxicol. 21:230-237 (1979).

Straub, C. P. and J. M. Sprafka. "Environmental Levels of PCB in Great Lakes Fish," Environmental Research Laboratory, U.S. Environmental Protection Agency, Duluth, MN, EPA-600/8-83-094, NTIS No. PB83-264481 (1983).

Strik, J. J. T. W. A., F. M. H. Debets and G. Koss. "Chemical Porphyria," Chapter 7 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, R. D. Kimbrough, Ed. (New York: Elsevier/North-Holland Biomedical Press, 1980), pp. 191-240.

Su, G. C. C. and H. A. Price. "Element Specific Gas Chromatographic Analyses of Organochlorine Pesticides in the Presence of PCB's by Selective Cancellation of Interfering Peaks," J. Agr. Food Chem. 21:1099-1102 (1973).

Sundaram, K. M. S and P. G. Davis. "Analysis of DDT Residues in Animal Tissues and Soils Collected from Different Regions of Canada," File Rep. - Chem. Control Res. Inst., Ottawa 3: 63 pp. (1974); Chem. Abst. 82:93952t (1975).

Sundström, G. and C. A. Wachtmeister. "Synthesis of ^{14}C-Labelled and Unlabelled PCB Compounds," in PCB Conference II, National Swedish Environment Protection Board, Stockholm, Publications 1973:4E (1972), pp. 73-86.

Sundström, G., O. Hutzinger, F. W. Karasek and J. Michnowicz. "Environmental Chemistry of Substitutes for Polychlorinated Biphenyls. I. Composition and Properties of an Alkylchlorobiphenyl Product," J. Assoc. Offic. Anal. Chem. 59(5): 982-988 (1976).

Supelco, Chromatography Supplies Catalog 20, p. 26.

Sutcliffe, C. R. and S. O. Nielson. "Adsorption of Polychlorinated Biphenyls on Glass Surfaces," Presented at FACSS 10th Annual Meeting, September 25-30, 1983.

Swain, W. R. "An Overview of the Scientific Basis for Concern with Polychlorinated Biphenyls in the Great Lakes," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 11-48.

Swanson, S. E., M. O. Erickson, and L. Mood. "Products of Thermal Degradation of Dielectric Fluids," U.S. Environmental Protection Agency, Office of Toxic Substances, Report No. EPA-560/5-85-022 (1985) 23 pp.

Swift, R. and H. Settle. "A Procedure for the Determination of Polychlorinated Biphenyls in Fat Samples," Residue (Melbourne) 3(2):9-12 (1976); Chem. Abst. 87:199289a (1977).

Sworzyn, E. M. and D. G. Ackerman. "Interim Guidelines for the Disposal/Destruction of PCBs and PCB Items by Non-thermal Methods," Environmental Protection Agency, Contract No. 68-02-3174, Task 41, Report No. EPA-600/2-82-069 (1981).

Sworzyn, E. M. and D. G. Ackerman, "Interim Guidelines for the Disposal/Destruction of PCBs and PCB Items by Non-thermal Methods," Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/2-82-069; NTIS No. PB82-217 498, 177 pp. (1982).

Szelewski, M. J., D. R. Hill, S. J. Spiegel and E. C. Tifft, Jr. "Loss of Polychlorinated Biphenyl Homologues during Chromium Trioxide Extraction of Fish Tissue," Anal. Chem. 51(14):2405-2407 (1979).

Tahiliani, V. H., "CLOR-N-OIL Field Test Program," in Proceedings: 1983 PCB Seminar, G. Addis and R. T. Komai, Eds. Report No. EPRI-EL-3581 (Palo Alto, CA: Electric Power Research Institute), 1984.

Tai, H., M. T. Williams and K. D. McMurtrey. "Separation of Polychlorinated Biphenyls from Toxaphene by Silicic Acid Column Chromatography," Bull. Environ. Contam. Toxicol. 29:64-67 (1982).

Takamiya, K. "Perchlorination Reaction Applied to the Rapid Determination of PCBs, Bull. Environ. Contam. Toxicol. 30: 600-605 (1983).

Takei, G. H., S. M. Kauahikaua and G. H. Leong. "Analysis of Human Milk Samples Collected in Hawaii for Residues of Organochlorine Pesticides and Polychlorobiphenyls," Bull. Environ. Contam. Toxicol. 30:606-613 (1983).

Takeshita, R. and T. Yamashita. "Reversed-Phase Partition Thin-Layer Chromatography of Chlorinated Pesticides and Polychlorinated Biphenyls," Eisei Kagaku 18(6):388-392 (1972); Chem. Abst. 78:144191w (1973).

MONS 005661

Talhelm, D. R. "Economic Impacts of PCB Regulations in Food and Fish," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 409-422.

Tanabe, H. "Methods of Analysis of PCB [Polychlorinated Biphenyls] in Edible Oil and Fat," Yukagaku 22(1):35-40 (1973); Chem. Abst. 78:119783h (1973).

Tanabe, H. "PCB Microanalysis," in PCB Poisoning and Pollution, K. Higuchi, Ed. (Tokyo: Kodansha, Ltd; New York: Academic Press 1976), pp. 127-145.

Tanabe, S., and R. Tatsukawa. "Chlorinated Hydrocarbons in the North Pacific and Indian Oceans," Journal of the Oceanographical Society of Japan 36:217-226 (1980).

Tanabe, S., M. Kawano, and R. Tatsukawa. "Chlorinated Hydrocarbons in the Antarctic, Western Pacific, and Eastern Indian Oceans," Transactions of the Tokyo University of Fisheries 5:97-109 (1982).

Tanabe, S., and R. Tatsukawa. "Vertical Transport and Residence Time of Chlorinated Hydrocarbons in the Open Ocean Water Column," Journal of the Oceanographical Society of Japan 39:53-62 (1983).

Tanabe, S., H. Hidaka and R. Tatsukawa. "PCBs and Chlorinated Hydrocarbon Pesticides in Antarctic Atmosphere and Hydrosphere," Chemosphere 12(2):277-283 (1983).

Tanner, H. A. "Regulation of PCBs in Michigan," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 347-352.

Tarradellas, J., P. Biercxsens and M. B. Bouche. "Methods of Extraction and Analysis of PCBs from Earthworms," Intern. J. Environ. Anal. Chem. 13:55-67 (1982).

Tas, A. C. and R. H. de Vos. "Characterization of Four Major Components in a Technical Polychlorinated Biphenyl Mixture," Environ. Sci. Technol. 5(12):1216-1218 (1971).

Tas, A. C. and R. J. C. Kleipool. "Characterization of the Components of Technically Polychlorinated Biphenyl Mixtures--II," Bull. Environ. Contam. Toxicol. 8(1):32-36 (1972).

Tatsukawa, R. and T. Wakimoto. "Pollution Analysis. Determination of Polychlorinated Biphenyl in Soil," Kogai Bunseki Shishin 6:45-56 (1972), Chem. Abst. 82:11793e (1975).

MONS 005662

Tausch, H., G. Stehlik and H. Wihlidal. "Analyse von Organochlorpestizid-und PCB-Rückständen in Fischen mittels Kapillargaschromatographie/Massenspecktrometrie," Chromatographia 14(7):403-410 (1981).

Taylor, J. K. "Validation of Analytical Methods," Anal. Chem. 55(6): 600A-608A (1983).

Teichman, J., A. Bevenue and J. W. Hylin. "Separation of Polychlorobiphenyls from Chlorinated Pesticides in Sediment and Oyster Samples for Analysis by Gas Chromatography," J. Chromatogr. 151:155-161 (1978).

Telling, G. M. and D. J. Sissons. "Determination of Organochlorine Insecticide Residues in Fatty Foodstuffs Using a Clean-up Technique Based on a Single Column of Activated Alumina," Journal of Chromatography, 137:405-423 (1977).

Tenzner, R. B. Ford, Jr., W. Mattox, and J. E. Brugger, "Mobile System for the Detoxification/Incineration of Cleanup Residuals from Hazardous Material Spills," in Disposal of Oil and Debris Resulting from a Spill Cleanup Operation, ASTM STP 703, J. S. Farlow and C. Swanson, Eds., American Society for Testing and Materials (1980) pp. 118-136.

Tessari, J. D. "Analytical Methods for PCBs in Human Milk," Env. Chem: Human & Animal Health 5:227-229 (1977).

Tessari, J. D. and E. P. Savage. "Gas-Liquid Chromatographic Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Human Milk," J. Assoc. Offic. Anal. Chem. 63(4): 736-741 (1980).

Tessari, J. D., L. Griffin and M. J. Aaronson. "Comparison of Two Cleanup Procedures (Mills, Onley, Gaither vs Automated Gel Permeation) for Residues of Organochlorine Pesticides and Polychlorinated Biphenyls in Human Adipose Tissue," Bull. Environ. Contam. Toxicol. 25:59-64 (1980).

Thielemann, H. "Dünnschicht-chromatographische Auftrennung und Identifizierung eines Gemisches von polychlorierten Biphenylen (PCB) und p,p'-DDE an parraffinimprägnierten Kieselgur G-Schichten," Fresenius' Z. Anal. Chem. 282:144 (1976).

Thielemann, H. "Dünnschichtchromatographische Nachweisgrenzen (semiquantitative Bestimmung) von polychloriertem Biphenyl (Chlophen A_{50}) sowie Identifizierung des Insektizids Thiodan (Endosulfan)," Z. Chem. 18:147-148 (1978).

MONS 005663

Thielemann, H. "Separation and Identification of Polychlorinated Biphenyls and p,p'-DDE in Paraffin-Impregnated Commercial Sheets by Repeated Thin-Layer Chromatography," Z. Gesamte Hyg. Ihre Grenzgeb. 26(6):463-464 (1980); Chem. Abst. 94:202208a (1981).

Thomann, R. V. and J. P. Connolly. "Age Dependent Model of PCB in a Lake Michigan Food Chain," U.S. Environmental Protection Agency, Report No. EPA-600/3-84-026; NTIS PB84-155993 (1984). 122 pp.

Thomann, R. V. and J. A. Mueller. "Steady State Modeling of Toxic Chemical-Theory and Application to PCBs in the Great Lakes and Saginaw Bay," Chapter 16 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp 283-309.

Thomas, R. L. and R. Frank. "PCBs in Sediment and Fluvial Suspended Solids in the Great Lakes," Chapter 14 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp 245-267.

Thomson, B. A. and J. R. Roberts. "The Development of an Analytical Technique for the Rapid in situ Detection of PCBs and Trichlorobenzene in Clay," in A Case Study of A Spill of Industrial Chemicals--Polychlorinated Biphenyls and Chlorinated Benzenes, National Research Council of Canada, Associate Committee on Scientific Criteria for Environmental Quality (NRCC No. 17586), Section VII (Appendix 2) (1980). 22 pp.

Thomson, B. A., T. Sakuma, J. Fulford, D. A. Lane, N. M. Reid, and J. B. French. "Fast In Situ Measurement of PCB Levels in Ambient Air to ng m^{-3} Levels Using a Mobil Atmospheric Pressure Chemical Ionization Mass Spectrometer System," in Advances in Mass Spectrometry, Vol. 8B, A. Quayle, Ed., (Heyden and Son Ltd., London, 1980) pp. 1422-1428.

Thomson, B. A. and J. R. Roberts. "A New Technique for the Rapid Analysis of Soil for the Presence of Polychlorinated Biphenyls," Intern. J. Environ. Anal. Chem. 11:139-151 (1982).

MONS 005664

Tiernan, T. O., M. L. Taylor, J. G. Solch, G. F. Vanness, J. H. Garrett and M. D. Porter. "Incineration of Chemical Wastes Containing Polychlorinated Biphenyls: Assessment of Tests Conducted at Rollins Environmental Services, Deer Park, Texas, and Energy Systems Company, El Dorado, Arkansas," Chapter 9 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp. 143-183.

Tindall, G. W. and P. E. Wininger. "Gas Chromatography-Mass Spectrometry Method for Identifying and Determining Polychlorinated Biphenyls," J. Chromatogr. 196:109-119 (1980).

Tindle, R. C. and D. L. Stalling. "Apparatus for Automated Gel Permeation Cleanup for Pesticide Residue Analysis. Applications to Fish Lipids," Anal. Chem. 44(11):1768-1773 (1972).

Tofflemire, T. J., T. T. Shen and E. H. Buckley. "Volatilization of PCB from Sediment and Water: Experimental and Field Data," Chapter 21 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp 411-422.

Tong, H. Y., D. L. Shore, and F. W. Karasek. "Identification of Organic Compounds Obtained from Incineration of Municipal Waste by High-Performance Liquid Chromatographic Fractionation and Gas Chromatography-Mass Spectrometry," Journal of Chromatography, 285:423-441 (1984).

Trench, W. C. "New PCB Rulemaking - A Repeat of History or Final Conclusions?" in Proceedings: 1981 PCB Seminar, G. Addis and J. Marks, Eds., Report No. EPRI-EL-2572 (Palo Alto, CA: Electric Power Research Institute, 1981), Section 1, pp. 11-34.

Tressl, G. and K. Wessely. "Analysis of Chloropesticides and PCB's in Cheese by Glass Capillary GC/MS Using the Selected Ion Monitoring Technique," Application Note AN 176-22, Hewlett-Packard Company, Avondale, Pennsylvania (1976).

Trevisani, G. R. "Simultaneous Studies on Chlorinated Pesticides, Polychlorinated Biphenyls, Polychlorinated Triphenyls, and Polychlorinated Naphthalenes in Fatty Foods of Various Types," Boll. Chim. Unione Ital. Lab. Prov., Parte Sci. 6(2): 117-142 (1980); Chem. Abst. 93:202765j (1980).

Trotter, W. J. "Removing the Interference of DDT and Its Analogs in the Analysis for Residues of Polychlorinated Biphenyls," J. Assoc. Offic. Anal. Chem. 58(3):461-465 (1975).

MONS 005665

Trotter, W. J. and S. J. V. Young. "Limitation on the Use of Antimony Pentachloride for Perchlorination of Polychlorinated Biphenyls," J. Assoc. Offic. Anal. Chem. 58(3):466-468 (1975).

Trotter, W. J., S. J. V. Young, J. L. Casterline, Jr., J. A. Bradlaw and L. R. Kamps. "Industrial Chemcals: Induction of Aryl Hydrocarbon Hydroxylase Activity in Cell Cultures by Aroclors, Residues from Yusho Oil Samples, and Polychlorinated Biphenyl Residues from Fish Samples," J. Assoc. Off. Anal. Chem. 65(4):838-841 (1982).

Tsushimoto, G., S. Asano, J. E. Trosko and C-C. Chang. "Inhibition of Intercellular Communications by Various Congeners of Polybrominated Biphenyl and Polychlorinated Biphenyl," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 241-252.

Tuinstra, L. G. M. Th. and W. A. Traag. "Automated Glass Capillary Gas Chromatograpic Analysis of PCB and Organochlorine Pesticide Residues in Agricultural Products," J. High Resol. Chromatogr. & Chromatogr. Commun. 2:723-728 (1979a).

Tuinstra, L. G. M. Th. and W. A. Traag. "Automated $(GC)^2$ Analysis of PCB and Organochlorine Pesticide Residues in Agricultural Products," Med. Fac. Landbouww. Rijksuniv. Gent 44(2): 885-893 (1979b).

Tuinstra, L. G. M. Th., W. A. Traag and H. J. Keukens. "Quantitative Determination of Individual Chlorinated Biphenyls in Milkfat by Splitless Glass Capillary Gas Chromatograpny," J. Assoc. Offic. Anal. Chem. 63(5):952-958 (1980).

Tuinstra, L. G. M. Th., W. A. Traag and A. J. Van Munsteren. "Determination of Individual Chlorinated Biphenyls in Agricultural Products by Automated Capillary Gas Chromatography. Determination in Cattle Feed and Its Relation to Milk Residues," J. Chromatogr. 204:413-419 (1981).

Tuinstra, L. G. M. Th. and W. A. Traag. "Capillary Gas Chromatographic-Mass Spectrometric Determination of Individual Chlorobiphenyls in Technical Aroclors," J. Assoc. Off. Anal. Chem. 66(3):708-717 (1983).

Tuinstra, L. G. M. Th., J. J. M. Driessen, H. J. Keukens, T. J. Van Munsteren, A. H. Roos and W. A. Traag. "Quantitative Determination of Specified Chlorobiphenyls in Fish with Capillary Gas Chromatograpny and Its Use for Monitoring and Tolerance Purposes," Intern. J. Environ. Anal. Chem. 14:147-157 (1983).

Ueta, T., K. Kamata, T. Kan, M. Kazama and T. Totani. "Fluorescence Reactions for Organic Halogen Compounds. II. In Situ Fluorometry of Polychlorinated Biphenyls and Their Isomers on Thin-Layer Chromatograms Using Diphenylamine," Tokyo Toritsu Eisei Kenkyusho Kenkyu Nempo 25:111-118 (1974); Chem. Abst. 83:21991c (1975).

Ugawa, M., A. Nakamura and T. Kashimoto. "Calculation Method for Polychlorinated Biphenyl (PCB) Isomers in Gas Chromatographic Determination," Shokuhin Eiseigaku Zasshi 14(5):415-424 (1973); Chem. Abst. 80:90955u (1974).

Ugawa, M., A. Nakamura and T. Kashimoto. "Studies on a Calculation Method for Polychlorinated Biphenyl Isomers (PCBs)," in New Methods in Environmental Chemistry and Toxicology, Collection of Papers Presented at the Research Conference on New Methodology in Ecological Chemistry, Susono, Japan, November 23-25, 1973, F. Coulston, F. Korte, and M. Goto (Eds.), International Academic Printing Co., Ltd., Tokyo (1973). pp 253-267.

Uk, S., C. M. Himel and T. Dirks. "Mass Spectrometric Identification of Mirex Residues in Crude Extracts and in the Presence of Polychlorinated Biphenyls," Bull. Environ. Contam. Toxicol. 8(2):97-104 (1972).

United Kingdom Department of the Environment. "Organochlorine Insecticides and Polychlorinated Biphenyls in Waters 1978; Tentative Method. Methods for the Examination of Waters and Associated Materials," Organochlorine Insectic. Polychlorinated Biphenyls Waters 28 pp. (1979).

United States Congress, Toxic Substances Control Act, Public Law 94-469, October 11, 1976.

Underwood, J. C. "Separation of Polychlorinated Biphenyls from DDT and Its Analogs Using Chromic Acid and Silica Gel," Bull. Environ. Contam. Toxicol. 21:787-790 (1979).

Urabe, H., H. Koda and M. Asahi. "Present State of Yusho Patients," Ann. N. Y. Acad. Sci. 320:273-283 (1979).

Uriano, G. A. "National Bureau of Standards Certificate of Analysis, Standard Reference Material 1581 - Polychlorinated Biphenyls in Oils," Washington, DC, June 25, 1982.

Uthe, J. F., J. Reinke and H. O'Brodovich. "Field Studies on the Use of Coated Porous Polyurethane Plugs as Indwelling Monitors of Organochlorine Pesticides and Polychlorinated Biphenyl Contents of Streams," Environ. Lett. 6(2):103-115 (1974).

MONS 005667

Uthe, J. F. and C. J. Musial. "Report of the Fifth ICES Intercalibration Study of PCBs in Biological Material," International Council for the Exploration of the Sea, Copenhagen, Denmark, ICES C.M. 1980/E:8, Marine Environmental Quality Committee (1980).

Utility Solid Waste Activities Group, Edison Electric Institute, and National Rural Electric Cooperative Association. "Comments and Studies on the Use of Polychorinated Biphenyls in Response to an Order of the United States Court of Appeals for the District of Columbia Circuit," U.S. Environmental Protection Agency, February 12, 1982, Volumes I-IV.

Uyeta, M., S. Taue, K. Chikasawa and M. Mazaki. "Photoformation of Polychlorinated Biphenyls from Chlorinated Benzenes." Nature 264:583-584 (1976).

Vannucchi, C., R. Salvadori, R. Nottoli, G. Ghimenti and G. Taponeco. "Identification and Quantification of Aromatic Polychlorinated Hydrocarbon Residues in the Environment," Riv. Sci. Tecnol. Alimenti Nutr. Um. 6(2):101-114 (1976); Chem. Abst. 85:175663a (1976).

Vannucchi, C. and M. Berlincioni. "Sampling and Analytical Method to Determine PCB Concentrations in the Air of the Working Areas of an Electrical Industry," Am. Ind. Hyg. Assoc. J. 41:352-360 (1980).

Van Ravenswaay, E. O. "The Science-Policy Interface in Regulatory Decision-Making," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 353-366.

Van Vliet, H. P. M., Th. C. Bootsman, R. W. Frei and U. A. Th. Brinkman. "On-Line Trace Enrichment in High-Performance Liquid Chromatography Using a Pre-Column," J. Chromatogr. 185:483-495 (1979).

Veierov, D. and N. Aharonson. "Economic Method for Analysis of Fluid Milk for Organochlorine Residues at the 10 ppb Level," J. Assoc. Offic. Anal. Chem. 63(3):532-535 (1980).

Veierov, D. and N. Aharonson. "Improved Cleanup of Large Lipid Samples for Electron Capture Gas Chromatographic Quantitation and Gas Chromatographic-Mass Spectrometric Confirmation of Organochlorine Residues," J. Assoc. Offic. Anal. Chem. 63(2): 202-207 (1980).

Veith, G. D. "Baseline Concentrations of Polychlorinated Biphenyls and DDT in Lake Michigan Fish, 1971," Pestic. Monit. J. 9(1):21-29 (1975).

Veith, G. D. and N. M. Austin. "Detection and Isolation of Bioaccumuable Chemicals in Complex Effluents," Chapter 20 in Identification and Analysis of Organic Pollutants in Water, L. H. Keith, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1976), pp. 297-302.

Veith, G. D. and L. M. Kiwus. "An Exhaustive Steam-Distillation and Solvent-Extraction Unit for Pesticides and Industrial Chemicals," Bull. Environ. Contam. Toxicol. 17: 631-636 (1977).

Veith, G. D., D. W. Kuehl, E. N. Leonard, K. Welch and G. Pratt. "Polychlorinated Biphenyls and Other Organic Chemical Residues in Fish from Major United States Watersheds Near the Great Lakes, 1978," Pestic. Monit. J. 15:1-8 (1981).

Veith, G. D. and P. Kosian. "Estimating Bioconcentration Potential from Octanol/Water Partition Coefficients," Chapter 15 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp 269-282.

Velie, M. and G. Kuntz. "Federal Polychlorinated Biphenyl Regulations," Chapter 7 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp. 121-130.

Ver Duin, C. "The Commerical Fishermen's View of the PCBs Problem in the Great Lakes," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 109-112.

Versar, Inc. "Revised Materials Balance for Inadvertently Produced PCBs," Report to U.S. Environmental Protection Agency, Washington, DC (April 22, 1982).

Villeneuve, J. P. "Intercalibration of Organochlorine Standard Solutions," in Scientific Report of the Intercalibration Exercise, Intergovernmental Oceanographic Commission Technical Series Report No. 22, UNESCO, Paris (ISBN 92-3-102077-3), (1982) pp. 84-91.

Vodicnik, M. J. "Factors Affecting the Bioaccumulation and Persistence of Polychlorinated Biphenyls," in Advances in Exposure, Health and Environmental Effects Studies of PCBs: Symposium Proceedings, R. J. Davenport and B. K. Bernard (Eds.), Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., Report No. LSI-TR-507-1378; NTIS No. PB84-135771 (December 1983), pp. 97-127.

MONS 005669

Vogel, G., K. Brooks, I. Frankel, S. Haus and W. Jacobsen. "Guidance Manual for Evaluating Permit Applications for the Operation of Incinerator Units," Report by The Mitre Corporation, McLean, VA, to U.S. Environmental Protection Agency, Contract No. 68-01-6092, December 31, 1980, 221 pp.

Voice, T. C., C. P. Rice and W. J. Weber, Jr. "Effect of Solids Concentration on the Sorptive Partitioning of Hydrophobic Pollutants in Aquatic Systems," Environ. Sci. Technol. 17(9):513-518 (1983).

Vos, J. G., J. H. Koeman, H. L. van der Maas, M. C. ten Noever de Brauw and R. H. de Vos. "Identification and Toxicological Evaluation of Chlorinated Dibenzofuran and Chlorinated Naphthalene in Two Commerical Polychlorinated Biphenyls," Food Cosmet. Toxicol. 8:625-633 (1970).

Vos, J. G., R. E. Faith and M. I. Luster. "Immune Alterations," Chapter 8 in Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products, R. D. Kimbrough, Ed. (New York, NY: Elsevier/North-Holland Biomedical Press, 1980), p. 241-266.

Voyksner, R. D., J. R. Hass, G. W. Sovocool and M. M. Bursey. "Comparison of Gas Chromatography/High-Resolution Mass Spectrometry and Mass Spectrometry/Mass Spectrometry Detection of Polychlorinated Biphenyls and Tetrachlorodibenzofuran," Anal. Chem. 55:744-749 (1983).

Vuceta, J., J. R. Marsh, S. Kennedy, L. Hildemann and S. Wiley. "State-of the-Art Review: PCDDs and PCDFs in Utility PCB Fluid," CS-3308, Research Project 1263-11, Final Report, Electric Power Research Institute, Palo Alto, CA (November 1983).

Wakimoto, T., R. Tatsukawa and T. Ogawa. Kogai to Taisaku 7:517 (1971); Fish Res. Bd. Can. Translation No. 2185.

Wakimoto, T., M. Fukushima, R. Tatsukawa and T. Ogawa. "Separation of PCBs [Polychlorinated Biphenyls] from p,p'-DDE and Other Organochlorine Pesticides by a Newly Developed Silica Gel," Nippon Nogei Kagaku Kaishi 49(10):499-503 (1975); Chem. Abst. 84:116448r (1976).

Walsh, E. J. "Interpretation of PCB Field Testing Kits," in Proceedings: 1983 PCB Seminar, G. Addis and R. Y. Komai, Eds. Report No. EPRI-EL-3581 (Palo Alto, CA: Electric Power Research Institute), 1984.

MONS 005670

Ward, R. S. and A. Pelter. "The Analysis of Mixtures of Closely Related Naturally-occurring Organic Compounds Using High Performance Liquid Chromatography," J. Chromatogr. Sci. 12:570-574 (1974)

Wardall, G. L. "Method for the Extraction of Organochlorine Compounds from Quail Eggs," Analyst 102:54-55 (1977).

Warshaw, R., A. Fischbein, J. Thornton, A. Miller and I. J. Selikoff. "Decrease in Vital Capacity in PCB-Exposed Workers in a Capacitor Manufacturing Facility," Ann. N. Y. Acad. Sci. 320:277-283 (1979).

Washington, T. L. "The Environmentalist's View of the PCBs Problem in the Great Lakes," in PCBs: Human and Environmental Hazards, F. M. O'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 101-108.

Wassermann, M., D. Wassermann, S. Cucos and H. J. Miller. "World PCBs Map: Storage and Effects in Man and His Biologic Environment in the 1970s," Ann. N.Y. Acad. Sci. 320:69-124 (1979).

Wassermann, M., M. Ron, B. Bercovici, D. Wassermann, S. Cucos and A. Pines. "Premature Delivery and Organochlorine Compounds: Polychlorinated Biphenyls and Some Organochlorine Insecticides," Environ. Res. 28:106-112 (1982).

Watanabe, I., T. Yakushiji, K. Kuwabara, S. Yoshida, K. Koyama, I. Hara and N. Kunita. "Studies on Polychlorinated Biphenyl (PCB) Isomers in Blood of Ordinary Persons, Oil Sickness Patients, and Occupationally Exposed Workers. 2. Apiezon L Column Analysis," Osaka-furitsu Kosnu Eisei Kenkyusho Kenkyu Hokoku, Shokuhin Eisei Hen 8:51-55 (1977); Chem. Abst. 88: 183989b (1978).

Watanabe, I., T. Yakushiji and N. Kunita. "Distribution Differences Between Polychlorinated Terphenyls and Polychlorinated Biphenyls in Human Tissues," Bull. Environ. Contam. Toxicol. 25:810-815 (1980).

Watts, R. R. (Ed.), Analysis of Pesticide Residues in Human and Environmental Samples, A Compilation of Methods Selected for Use in Pesticide Monitoring Programs, U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/8-80-038 (June 1980).

Weast, R. C. and S. M. Selby (Eds.). CRC Handbook of Chemistry and Physics 48th Ed. (Cleveland, OH: The Chemical Rubber Co., 1967).

MONS 005671

Weaver, G. "PCB Contamination in and Around New Bedford, Mass," Environ. Sci. Technol. 18(1):22A-27A (1984).

Webb, R. G. and A. C. McCall. "Identities of Polychlorinated Biphenyl Isomers in Aroclors," J. Assoc. Offic. Anal. Chem. 55(4):746-752 (1972).

Webb, R. G., and A. C. McCall. "Quantitative PCB Standards for Electron Capture Gas Chromatography," J. Chromatogr. Sci. 11:366-373 (1973).

Weinberger, R., P. Yarmchuk and L. J. Cline Love. "Micelle-Stabilized Room Temperature Phosphorescence and Fluorescence of Polychlorinated and Polybrominated Biphenyls," Abstract No. 295 from the 1983 Pittsburgh Conference and Exposition on Analytical Chemistry and Applied Spectroscopy, March 7-12, 1983.

Weininger, D., D. E. Armstrong and D. L. Swackhamer. "Application of a Sediment Dynamics Model for Estimation of Vertical Burial Rates of PCBs in Southern Lake Michigan," Chapter 22 in Physical Behavior of PCBs in the Great Lakes, D. Mackay, S. Paterson, S. J. Eisenreich and M. S. Simmons, Eds. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1983), pp. 423-439.

Weitzman, L. "Treatment and Destruction of Polychlorinated Biphenyls and Polychlorinated Biphenyl-Contaminated Materials," Chapter 8 in Detoxication of Hazardous Waste, J. H. Exner, Ed. (Ann Arbor, MI: Ann Arbor Science Publishers, Inc., 1982), pp. 131-142.

Welborn, M. E., R. E. Borchard, L. G. Hansen and R. L. Metcalf. "Extraction and Analysis of Aroclor 1254 Components in Blood," J. Assoc. Offic. Anal. Chem. 57(6):1248-1252 (1974).

Wells, D. E. and A. A. Cowan. "Use of Gas Chromatography - Mass Spectrometry in the Environmental Analysis of Industrial Pollutants," in Recent Advances in Chromatography-Mass Spectrometry (Anal. Proc.) pp. 242-246 (1982).

Welsch, F. "Effects of Polychlorinated Biphenyls on the Expression of Embryotoxicity Caused by Model Teratogens," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 253-276.

Welti, D. and D. Sissons. "The Proton Chemical Shifts of Polychlorinated Biphenyls," Organic Magnetic Resonance 4: 309-319 (1972).

MONS 005672

West, P. R., S. K. Chaudhary and R. H. Mitchell. "Photodechlorination of Polychlorinated Biphenyls Induced by Hydroquinone in Basic Media." Extended Abstracts, Division of Environmental Chemistry, American Chemical Society, Washington, D.C., pp. 384-187 (September 1983).

Westcott, J. W., and T. F. Bidleman. "Determination of Polychlorinated Biphenyl Vapor Pressures by Capillary Gas Chromatography," J. Chromatogr. 210:331-336 (1981).

Westerberg, R. B., S. L. Alibrando and F. J. van Lenten. "Determination of Polychlorinated Biphenyls Using Limited Mass Scan Gas Chromatography Mass Spectrometry," J. Chromatogr. 294(2):447-456 (1984).

Westin, R. A. "Polychlorinated Biphenyls 1929-1979," Office of Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C., EPA-560/6-79/004; NTIS No. PB-2965591/8 (1979).

Westöö, G. and K. Norén. "Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Animal Foods," Acta Chem. Scand. 24(5):1639-1644 (1970).

Whitmore, F. C. "Destruction of Polychlorinated Biphenyls in Sewage Sludge During Incineration," Report by Versar, Inc., Springfield,VA, to U.S. Environmental Protection Agency, Washington, DC, EPA Contract No. 68-01-1587 (NTIS No. PB-258 162) 73 pp. (1976).

Whitmore, F. C. and J. O. Barden. "A Study of PCB Destruction Efficiency and Performance for a Coal-Fired Utility Boiler; Volume 1. Test and Evaluation," U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, EPA-600/2-82-101a (NTIS No. PB84-110147) 79 pp. (October 1983a).

Whitmore, F. C. and J. O. Barden. "A Study of PCB Destruction Efficiency and Performance for a Coal-Fired Utility Boiler; Volume 2. Test Protocol," U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, EPA-600/2-83-101b (NTIS No. PB84-110154) 89 pp. (1983b).

Williams, C. H., C. L. Prescott, P. B. Stewart and G. Choudhary. "Formation of Polychlorinated Dibenzofurans and Other Potentially Toxic Chlorinated Pyrolysis Products in PCB Fires," Extended Abstract, Division of Environmental Chemistry, American Chemical Society, Washington, D.C., pp. 265-266 (September 1983).

MONS 005673

Williams, C. H. Jr., C. L. Prescott, and L. O. Garretson, "Detection of Polychlorinated Dibenzofurans and Other Chlorinated Pyrolysis Products in the Soot Formed in PCB Fires," Proceedings: 1983 PCB Seminar, G. Addis and R. Y. Komai, Eds. Report No. EPRI-EL-3581 (Palo Alto, CA: Electric Power Research Institute, 1984).

Williams, C. H., Jr., C. L. Prescott, P. B. Stewart, and G. Choudhary. "Formation of Polychlorinated Dibenzofurans and Other Potentially Toxic Chlorinated Pyrolysis Products in PCB Fires," in Chlorinated Dioxins and Dibenzofurans in the Total Environment II, L. H. Keith, C. Rappe, and G. Choudhary, Eds., (Boston: Butterworth Publishers, 1985). pp. 457-468.

Williams, D. T. and B. J. Blanchfield. "Thin Layer Chromatographic Separation of Two Chlorodibenzo-p-dioxins from Some Polychlorinated Biphenyl and Organochlorine Pesticides," J. Assoc. Offic. Anal. Chem. 54(6):1429-1431 (1971).

Williams, D. T. and B. J. Blanchfield. "Screening Method for the Detection of Chlorodibenzo-p-dioxins in the Presence of Chlorobiphenyls, Chloronaphthalenes, and Chlorodibenzofurans," J. Assoc. Offic. Anal. Chem. 55(1):93-95 (1972).

Williams, D. T. and F. M. Benoit. "The Determination of Polychlorinated Biphenyls in Selected Household Products," Bull. Environ. Contam. Toxicol. 21:179-184 (1979).

Williams, D. T., G. L. LeBel and T. Furmanczyk. "Polychlorinated Biphenyl Contamination of Laboratory Air," Chemosphere 9:45-50 (1980).

Willis, D. E. and R. F. Addison. "Identification and Estimation of the Major Components of a Commercial Polychlorinated Biphenyl Mixture, Aroclor 1221," J. Fish. Res. Board Can. 29(5):592-595 (1972).

Willmott, F. W. and R. J. Dolphin. "A Novel Combination of Liquid Chromatography and Electron Capture Detecton in the Analysis of Pesticides," J. Chromatogr. Sci. 12:695-700 (1974).

Wilson, N. K. and M. Anderson. "Carbon-13 and Proton Magnetic Resonance Studies of Chlorinated Biphenyls," in Mass Spectrometry and NMR Spectroscopy in Pesticide Chemistry, R. Haque and F. J. Biros, Eds. (New York, NY: Plenum Press, 1973), pp. 197-218.

Wingender, R. J. and R. M. Williams. "Evidence for the Long-Distance Atmospheric Transport of Polychlorinated Terphenyl," Environ. Sci. Technol., 18:625-628 (1984).

MONS 005674

Winslow, S. G. and H. B. Gerstner (Eds.), Polychlorinated Biphenyls, Polybrominated Biphenyls, and Their Contaminants: A Literature Compilation 1965-1977, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1978).

Wolbach, C. D., W. F. Fitch, N. Flynn and B. Markoja, "Analytical Results of a PCB Test Incineration," in Second Symposium on Process Measurements for Environmental Assessment (February 1980, Atlanta), J. C. Harris (Ed.), Environmental Protection Agency, Report No. EPA-600/9-81-018 (1981).

Wolff, M. S., J. Thornton, A. Fischbein, R. Lilis and I. J. Selikoff, "Disposition of Polychlorinated Biphenyl Congeners in Occupationally Exposed Persons," Toxicol. Appl. Pharmacol. 62:294-306 (1982a).

Wolff, M. S., A. Fischbein, J. Thornton, C. Rice, R. Lahs and I. J. Selikoff, "Body Burden of Polychlorinated Biphenyls Among Persons Employed in Capacitor Manufacturing," Int. Arch. Occup. Environ. Health 49:199-203 (1982b).

Wolff, M. S., H. A. Anderson, I. J. Selikoff, "Human Tissue Burdens of Halogenated Aromatic Chemicals in Michigan," J. Am. Med. Assoc. 247(15):2112-2116 (1982c).

Wong, P. T. S. and K. L. E. Kaiser, "Bacterial Degradation of Polychlorinated Biphenyls II. Rate Studies," Bull. Environ. Contam. Toxicol. 13(2):249-255 (1975).

World Health Organization, "Polychlorinated Biphenyls and Terphenyls, Environmental Health Criteria 2," Geneva: World Health Organization (1976) 85 pp.

Yakushiji, T., I. Watanabe, K. Kuwabara and S. Yoshida, "Identification of Low Chlorinated Biphenyls in Human Milk by Gas Chromatography-Mass Spectrometry," J. Chromatogr. 154: 203-210 (1978).

Yakushiji, T., I. Watanabe, S. Yoshida, R. Tanaka, T. Kashimoto and N. Kunita, "Analytical Methods for Organochlorine Compounds in Human Milk," Osaka-furitsu Koshu Eisei Kenkyusho Kenkyu Hokoku, Shokuhin Eisei Hen 11:87-91 (1980); Chem. Abstr. 96: 137221z (1982).

Yakushiji, T., I. Watanabe, K. Kuwabara, R. Tanaka, T. Kashimoto, N. Kunita, and I. Hara, "Rate of Decrease and Half-Life of Polychlorinated Biphenyls (PCBs) in the Blood of Mothers and Their Children Occupationally Exposed to PCBs," Arch. Environ. Contam. Toxicol. 13(3):341-345 (1984); Chem. Abst. 101:42857u (1984).

Yalkowsky, S. H., S. C. Valvani, and D. Mackay. "Estimation of the Aqueous Solubility of Some Aromatic Compounds." Residue Reviews 85:43-55 (1983).

Yarbrough, J. D. and M. R. Wells. "Vertebrate Insecticide Resistance: The in vitro Endrin Effect on Succinic Dehydrogenase Activity on Endrin-Resistant and Susceptible Mosquitofish," Bull. Environ. Contam. Toxicol. 6(2):171-176 (1971).

Yezzi, J., J. Brugger, I. Wilder, F. Freestone, R. Miller, C. Pfrommer, and R. Lovell. "Results of the Initial Trial Burn of the EPA-ORD Mobile Incineration System," Environmental Protection Agency, Municipal Environmental Research Laboratory--Cincinnati, OH, EPA-600/D-84-088 (1984).

Yobs, A. R. "Levels of Polychlorinated Biphenyls in Adipose Tissue of the General Population of the Nation," Environ. Health Perspec. 1:79-81 (1972).

Yoshimura, H., N. Ozawa, and S. Saeki. "Inductive Effect of Polychlorinated Biphenyls Mixture and Individual Isomers on the Hepatic Microsomal Enzymes," Chem. Pharm. Bull., 26:1215-1221 (1978).

Yoshimura, H., S. Yoshihara, N. Ozawa and M. Miki. "Possible Correlation Between Induction Modes of Hepatic Enzymes by PCBs and Their Toxicity in Rats," Ann. N. Y. Acad. Sci. 320: 179-192 (1979).

Yost, R. A. and C. G. Enke. "Triple Quadrupole Mass Spectrometry for Direct Mixture Analysis and Structure Elucidation," Anal. Chem. 51(12):1251A-1264A (1979).

Yost, R. W., L. S. Ettre and R. D. Conlon (Eds). Practical Liquid Chromatography - An Introduction (Norwalk, CT Perkin-Elmer, 1980).

Youden, W. J. and E. H. Steiner. Statistical Manual of the Association of Official Analytical Chemists (Arlington, VA: Association of Official Analytical Chemists, 1975), 88 pp.

Young, S. J. V. and J. A. Burke. "Micro Scale Alkali Treatment for Use in Pesticide Residue Confirmation and Sample Cleanup," Bull. Environ. Contam. Toxicol. 7(2/3):160-167 (1972).

Young, S. J., C. Finsterwalder and J. A. Burke. "Extraction and Cleanup for Determination of Polychlorinated Biphenyls in Paper and Paperboard," J. Assoc. Off. Anal. Chem. 56:957-961 (1973).

Young, S. J. V. and L. R. Kamps. "Gas-Liquid Chromatographic Determination of Nonpolar Organochlorine Pesticide Residues in a Crude Vegetable Oil and Its Refinery By-Products," J. Assoc. Off. Anal. Chem. 65(4):916-920 (1982).

Young, S., M. Clower, Jr., J. A. G. Roach. "Method for Determinination of Organohalogen Pesticide Residues in Vegetable Oil Refinery By-Products," J. Assoc. Off. Anal. Chem. 67(1): 95-106 (1984).

Zabik, M. J. "The Photochemistry of PCBs," in PCBs: Human and Environmental Hazards, F. M. D'Itri and M. A. Kamrin, Eds. (Boston: Butterworth Publishers, 1983), pp. 141-164.

Zelenski, S. G., J. Tashiro and L. R. Worthen. "A Gas Chromatographic Method of Quantitating DDT in the Presence of Interferring Polychlorinated Biphenyl," J. Chromatogr. 84: 67-73 (1973).

Zelenski, S. G., J. Hall and S. E. Haupt. "Applying for a Permit to Destroy PCB Waste Oil; Vol. I. Summary," U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, EPA-600/2-81-033a; NTIS No. PB81-173 346, 85 pp. (March 1981a).

Zelenski, S. G., J. Hall and S. E. Haupt. "Applying for a Permit to Destroy PCB Waste Oil; Vol. II. Documentation," U.S. Environmental Protection Agency, Office of Research and Development, Research Triangle Park, NC, EPA-600/2-81-033b; NTIS No. PB81-234874, 220 pp. (March 1981b).

Zell, M., H. J. Neu and K. Ballschmiter. "Identifizierung der PCB-Komponenten durch Retentionsindexvergleich nach Kapillar-Gaschromatographie," Chemosphere 6:69-76 (1977).

Zell, M., H. J. Neu and K. Ballschmiter. "Single Component Analysis of Polychlorinated Biphenyl (PCB)- and Chlorinated Pesticide Residues in Marine Fish Samples," Fresenius' Z. Anal. Chem. 292:97-107 (1978).

Zell, M. and K. Ballschmiter. "Baseline Study of the Global Pollution. III. Trace Analysis of Polychlorinated Biphenyls (PCB) by ECD Glass Capillary Gas Chromatography in Environmental Samples of Different Trophic Levels," Fresenius' Z. Anal. Chem. 304:337-349 (1980).

Zhang, T., T. Gu, and X. Xu. "Determination of Polychlorinated Biphenyls in Seawater," Haiyang Yu Huzhao 14(4):353-356 (1983); Chem. Abst. 101:11919m (1984).

MONS 005677

Zimmerli, B. "Beitrag zur Bestimmung von Umweltkontaminantien Mittels der Hydrierenden Reaktionsgaschromatographie," J. Chromatogr. 88:65-75 (1974).

Zimmerli, B., B. Marek and H. Sulser. "Determination of Chlorinated Biphenyls and Chloride Pesticides," Mitt. Geb. Lebensmittelunters. Hyg. 64(1):70-79 (1973); Chem. Abst. 79: 124762a (1973).

Zitko, V. "Polychlorinated Biphenyls and Organochlorine Pesticides in Some Freshwater and Marine Fishes," Bull. Environ. Contam. Toxicol. 6(5):464-470 (1971a).

Zitko, V. "Effects of Pesticide-grade Hexanes on the Silicic Acid Chromatography of Polychlorinated Biphenyls and Organochlorine Pesticides," J. Chromatogr. 59:444-445 (1971b).

Zitko, V. "Problems in the Determination of Polychlorinated Biphenyls," Intern. J. Environ. Anal. Chem. 1:221-231 (1972).

Zitko, V. "Chromatography of Chlorinated Paraffins on Alumina and Silica Columns," J. Chromatogr. 81:152-155 (1973).

Zitko, V. "The Detection of Aromatic and Chlorinated Hydrocarbons in Marine Lipids," J. Am. Oil Chemists' Soc. 52:131A (1975).

Zitko, V. "Levels of Chlorinated Hydrocarbons in Eggs of Double-Crested Cormorants from 1971 to 1975," Bull. Environ. Contam. Toxicol. 16(4):399-405 (1976).

Zitko, V "The Interference of Aromatic Hydrocarbons in the Determination of PCB's," in Proceedings of the Joint Conference on Sensing of Environmental Pollutants, 4th, New Orleans (1977). pp. 757-760.

Zitko, V. "'Shorthand' Numbering of Chlorobiphenyls," Chemosphere 12(6):835-836 (1983).

Zitko, V. and P. M. K. Choi. "PCB and Other Industrial Halogenated Hydrocarbons in the Environment." Technical Report No. 272. St. Andrews, New Brunswick, Canada: Fisheries Research Board of Canada (1971).

Zitko, V., O. Hutzinger and S. Safe. "Retention Times and Electron-Capture Detector Responses of Some Individual Chlorobiphenyls," Bull. Environ. Contam. Toxicol. 6(2):160-163 (1971).

Zitko, V. and P. M. K. Choi. "PCB and p,p'-DDE in Eggs of Cormorants, Gulls, and Ducks from the Bay of Fundy, Canada," Bull. Environ. Contam. Toxicol. 7(1):63-64 (1972).

MONS 005678

Zitko, V., O. Hutzinger, and P. M. K. Choi, "Determination of Pentachlorophenol and Chlorobiphenylols in Biological Samples," Bull. Environ. Contam. Toxicol. 12(6):649-653 (1974a).

Zitko, V. P. M. K. Choi, O. J. Wildish, C. F. Monaghan and N. A. Lister. "Distribution of PCB and p,p'-DDE Residues in Atlantic Herring (Clupea harengus harengus) and Yellow Perch (Perca flavescens) in Eastern Canada-1972," Pestic. Mon. J., 8(2): 105-109 (1974b).

Zobel, M. G. R. "Quantitative Determination of Polychlorinated Biphenyls--A Computer Approach," J. Assoc. Offic. Anal. Chem. 57(4) 791-795 (1974).

Zoll, D. F., G. V. Cox, R. J. Fensterheim and E. W. Warren. "Comments in Response to Proposed Rule on Manufacture, Processing, Distribution and Use of Polychlorinated Biphenyls in Closed and Controlled Waste Manufacturing Processes," Submitted to the U.S. Environmental Protection Agency by the Chemical Manufacturers Association Special Program Panel on PCBs, EPA Docket No. OPTS-62017A, July 8, 1982, 80 pp.

Zweig, G. and J. Sherma. CRC Handbook of Chromatography, (Cleveland, OH: CRC Press, 1972).

MONS 005679

APPENDIX A

NOMENCLATURE AND PHYSICAL CONSTANTS OF POLYCHLORINATED BIPHENYLS

MONS 005680

Table A-1. Nomenclature and Physical Constants of Polychlorinated Biphenyls

IUPAC No.[a]	Compound	CAS No.	Melting Point (°C)[b]	Solubility in H_2O (ppm)[b]
	Biphenyl	92-52-4	71[c]	7.2[d]
	Monochlorobiphenyl	27323-18-8		
1	2	2051-60-7	34	5.9
2	3	2051-61-8	16.5	3.5
3	4	2051-62-9	77.7	1.19
	Dichlorobiphenyl	25512-42-9		
4	2,2'	13029-08-8	60.5	1.50
5	2,3	16605-91-7	27.7-28.2	
6	2,3'	25569-80-6	oil	
7	2,4	33284-50-3	24.1-24.4	1.40
8	2,4'	34883-43-7	46	1.88
9	2,5	34883-39-1	22-23?	0.59[d]
10	2,6	33146-45-1	35-36	
11	3,3'	2050-67-1	29	
12	3,4	2974-92-7	49-50	
13	3,4'	2974-90-5	oil	
14	3,5	34883-41-5	31-32	
15	4,4'	2050-68-2	148-149	0.08
	Trichlorobiphenyl	25323-68-6		
16	2,2',3	38444-78-9	28.1-28.8	
17	2,2',4	37680-66-3		
18	2,2',5	37680-65-2	43-44	0.14[d]
19	2,2',6	38444-73-4		
20	2,3,3'	38444-84-7		
21	2,3,4	55702-46-0	101-102	
22	2,3,4'	38444-85-8	73-73.2	
23	2,3,5	55720-44-0	41	
24	2,3,6	58702-45-9		
25	2,3',4	55712-37-3		
26	2,3',5	38444-81-4	40-40.5	
27	2,3',6	38444-76-7		
28	2,4,4'	7012-37-5	57-58	0.085
29	2,4,5	15862-07-4	78-79	0.092[d]
30	2,4,6	35693-92-6	62.5	
31	2,4',5	16606-02-3	67	

MONS 005681

Table A-1 (Continued)

IUPAC No.[a]	Compound	CAS No.	Melting Point (°C)[b]	Solubility in H_2O[b] (ppm)
32	2,4',6	38444-77-8		
33	2',3,4	38444-86-9	60	0.078
34	2',3,5	37680-68-5	58	
35	3,3',4	37680-69-6		
36	3,3',5	38444-87-0		
37	3,4,4'	38444-90-5	86.8-87.8	0.015[d]
38	3,4,5	53555-66-1		
39	3,4',5	38444-88-1	88	
	Tetrachlorobiphenyl	26914-33-0		
40	2,2',3,3'	38444-93-8	119.5-121.5	0.034
41	2,2',3,4	52663-59-9		
42	2,2',3,4'	36559-22-5	68-70	
43	2,2',3,5	70362-46-8		
44	2,2',3,5'	41464-39-5	46.5-47	0.170
45	2,2',3,6	70362-45-7		
46	2,2',3,6'	41464-47-5	125.5-127	
47	2,2',4,4'	2437-79-8	41, 83	0.068
48	2,2',4,5	70362-47-9		
49	2,2',4,5'	41464-40-8	64-66	
50	2,2',4,6	62796-65-8		
51	2,2',4,6'	65194-04-7		
52	2,2',5,5'	35693-99-3	87-89	0.046
53	2,2',5,6'	41464-41-9	103-104.5	
54	2,2',6,6'	15968-05-5	198	
55	2,3,3',4	74338-24-2		
56	2,3,3',4'	41464-43-1	96-97	
57	2,3,3',5	70424-67-8		
58	2,3,3',5'	41464-49-7	127.5-129	
59	2,3,3',6	74472-33-6		
60	2,3,4,4'	33025-41-1	142	0.058
61	2,3,4,5	33284-53-6	92-92.5	0.019[d]
62	2,3,4,6	54230-23-7		
63	2,3,4',5	74472-35-8	104	
64	2,3,4',6	52663-58-8		
65	2,3,5,6	33284-54-7	79	
66	2,3',4,4'	32598-10-0	124	0.058
67	2,3',4,5	73575-53-8		
68	2,3',4,5'	73575-52-7		
69	2,3',4,6	60233-24-1		
70	2,3',4',5	32598-11-1	104	0.041
71	2,3',4',6	41464-46-4		

MONS 005682

Table A-I (Continued)

IUPAC[a] No.	Compound	CAS No.	Melting Point (°C)[b]	Solubility in H_2O (ppm)[b]
72	2,3',5,5'	41464-42-0	105.5-106.5	
73	2,3',5',6	74338-23-1		
74	2,4,4',5	32690-93-0	125	
75	2,4,4',6	32598-12-2		
76	2',3,4,5	70362-48-0		
77	3,3',4,4'	32598-13-3	173	0.175
78	3,3',4,5	70362-49-1		
79	3,3',4,5'	41464-48-6	119-120	
80	3,3',5,5'	33284-52-5	164	
81	3,4,4',5	70362-50-4		
	Pentachlorobiphenyl	25429-29-2		
82	2,2',3,3',4	52663-62-4	119-120.5	
83	2,2',3,3',5	60145-20-2		
84	2,2',3,3',6	52663-60-2		
85	2,2',3,4,4'	65510-45-4		
86	2,2',3,4,5	55312-69-1		0.0098[c]
87	2,2',3,4,5'	38380-02-8	111.5-113	0.022 0.012[d]
88	2,2',3,4,6	55215-17-3		
89	2,2',3,4,6'	73575-57-2		
90	2,2',3,4',5	68194-07-0		
91	2,2',3,4',6	58194-05-8		
92	2,2',3,5,5'	52663-61-3		
93	2,2',3,5,6	73575-56-1		
94	2,2',3,5,6'	73575-55-0		
95	2,2',3,5',6	38379-99-6	98.5-100	
96	2,2',3,6,6'	73575-54-9		
97	2,2',3',4,5	41464-51-1	81-82	
98	2,2',3',4,6	60233-25-2		
99	2,2',4,4',5	38380-01-7		
100	2,2',4,4',6	39485-83-1		
101	2,2',4,5,5'	37680-73-2	76.5-77.5	0.031
102	2,2',4,5,6'	68194-06-9		
103	2,2',4,5',6	60145-21-3		
104	2,2',4,6,6'	56558-16-8		
105	2,3,3',4,4'	32598-14-4	101-105	
106	2,3,3',4,5	70424-69-0		
107	2,3,3',4',5	70424-68-9		
108	2,3,3',4,5'	70362-41-3		
109	2,3,3',4,6	74472-35-8		
110	2,3,3',4',6	38380-03-9		
111	2,3,3',5,5'	39635-32-0		

Table A-I (Continued)

IUPAC[a] No.	Compound	CAS No.	Melting Point (°C)[b]	Solubility in H_2O[b] (ppm)
112	2,3,3',5,6	74472-36-9		
113	2,3,3',5',6	68194-10-5		
114	2,3,4,4',5	74472-37-0	98-99	
115	2,3,4,4',6	74472-38-1		
116	2,3,4,5,6	18259-05-7	123	0.0068[d]
117	2,3,4',5,6	68194-11-6		
118	2,3',4,4',5	31508-00-6	105-107	
119	2,3',4,4',6	56558-17-9		
120	2,3',4,5,5'	68194-12-7		
121	2,3',4,5',6	56558-18-0		
122	2',3,3',4,5	76842-07-4		
123	2',3,4,4',5	65510-44-3		
124	2',3,4,5,5'	70424-70-3		
125	2',3,4,5,6'	74472-39-2		
126	3,3',4,4',5	57465-28-8		
127	3,3',4,5,5'	39635-33-1		
	Hexachlorobiphenyl	26601-64-9		
128	2,2',3,3',4,4'	38380-07-3	145.5-146.6	0.00044[d]
129	2,2',3,3',4,5	55215-18-4		0.00085[d]
130	2,2',3,3',4,5'	52663-66-8		
131	2,2',3,3',4,6	61798-70-7		
132	2,2',3,3',4,6'	38380-05-1		
133	2,2',3,3',5,5'	35694-04-3	128-129	
134	2,2',3,3',5,6	52704-70-8		0.00091[d]
135	2,2',3,3',5,6'	52744-13-5		
136	2,2',3,3',6,6'	38411-22-2	114-114.5	
137	2,2',3,4,4',5	35694-06-5	77-78	
138	2,2',3,4,4',5'	35065-28-2	78.5-80	
139	2,2',3,4,4',6	56030-56-9		
140	2,2',3,4,4',6'	59291-64-4	69.5-71	
141	2,2',3,4,5,5'	52712-04-6		
142	2,2',3,4,5,6	41411-61-4	134-137	
143	2,2',3,4,5,6'	68194-15-0		
144	2,2',3,4,5',6	68194-14-9		
145	2,2',3,4,6,6'	74472-40-5		
146	2,2',3,4',5,5'	51908-16-8		
147	2,2',3,4',5,6	68194-13-8		
148	2,2',3,4',5,6'	74472-42-7		
149	2,2',3,4',5',6	38380-04-0	oil	
150	2,2',3,4',6,6'	68194-08-1		
151	2,2',3,5,5',6	52663-63-5	100-101	

MONS 005684

Table A-1 (Continued)

IUPAC[a] No.	Compound	CAS No.	Melting Point (°C)[b]	Solubility in H_2O (ppm)[b]
152	2,2',3,5,6,6'	68194-09-2		
153	2,2',4,4',5,5'	35065-27-1	103-104	0.0013[d]
154	2,2',4,4',5,6'	60145-22-4	oil	
155	2,2',4,4',6,6'	33979-03-2	112.5	0.00091[d]
156	2,3,3',4,4',5	38380-08-4		
157	2,3,3',4,4',5'	69782-90-7		
158	2,3,3',4,4',6	74472-42-7		
159	2,3,3',4,5,5'	39635-35-3		
160	2,3,3',4,5,6	41411-62-5	97-100	
161	2,3,3',4,5',6	74472-43-8		
162	2,3,3',4',5,5'	39635-34-2		
163	2,3,3',4',5,6	74472-44-9		
164	2,3,3',4',5',6	74472-45-0		
165	2,3,3',5,5',6	74472-46-1		
166	2,3,4,4',5,6	41411-63-6	160-165	
167	2,3',4,4',5,5'	52663-72-6		
168	2,3',4,4',5',6	59291-65-5	110-111	
169	3,3',4,4',5,5'	32774-16-6	201-202	
	Heptachlorobiphenyl	28655-71-2		
170	2,2',3,3',4,4',5	35065-30-6	134.5-135.5	
171	2,2',3,3',4,4',6	52663-71-5		
172	2,2',3,3',4,5,5'	52663-74-8		
173	2,2',3,3',4,5,6	68194-16-1	—	
174	2,2',3,3',4,5,6'	38411-25-5	130.5-130.7	
175	2,2',3,3',4,5',6	40186-70-7		
176	2,2',3,3',4,6,6'	52663-65-7		
177	2,2',3,3',4',5,6	52663-70-4		
178	2,2',3,3',5,5',6	52663-67-9		
179	2,2',3,3',5,6,6'	52663-64-6		
180	2,2',3,4,4',5,5'	35065-29-3	109-110	
181	2,2',3,4,4',5,6	74472-47-2		
182	2,2',3,4,4',5,6'	60145-23-5	152-153	
183	2,2',3,4,4',5',6	52663-69-1		
184	2,2',3,4,4',6,6'	74472-48-3		
185	2,2',3,4,5,5',6	52712-05-7	147-150	0.00048[d]
186	2,2',3,4,5,6,6'	74472-49-4		
187	2,2',3,4',5,5',6	52663-68-0		
188	2,2',3,4',5,6,6'	74487-85-7		
189	2,3,3',4,4',5,5'	39635-31-9	162-163	
190	2,3,3',4,4',5,6	41411-64-7	116-118	
191	2,3,3',4,4',5',6	74472-50-7		

Table A-I (Continued)

IUPAC No.[a]	Compound	CAS No.	Melting Point (°C)[b]	Solubility in H_2O (ppm)[b]
192	2,3,3',4,5,5',6	74472-51-8		
193	2,3,3',4',5,5',6	69782-91-8		
	Octachlorobiphenyl	31472-83-0[f]		
194	2,2',3,3',4,4',5,5'	35694-08-7	156-157	0.0014[d]
195	2,2',3,3',4,4',5,6	52663-78-2		
196	2,2',3,3',4,4',5,6'	42740-50-1		
197	2,2',3,3',4,4',6,6'	33091-17-7	132	
198	2,2',3,3',4,5,5',6	68194-17-2		
199	2,2',3,3',4,5,5',6[g]	52663-75-9		
200	2,2',3,3',4,5,6,6'[g]	52663-73-7		
201	2,2',3,3',4,5',6,6'[g]	40186-71-8		
202	2,2',3,3',5,5',6,6'	2136-99-4	161	0.00018[d]
203	2,2',3,4,4',5,5',6	52663-76-0		
204	2,2',3,4,4',5,6,6'	74472-52-9		
205	2,3,3',4,4',5,5',6	74472-53-0		
	Nonachlorobiphenyl	53742-07-7		
206	2,2',3,3',4,4',5,5',6	40186-72-9	204.5-206.5	0.00011[d]
207	2,2',3,3',4,4',5,6,6'	52663-79-3		
208	2,2',3,3',4,5,5',6,6'	52663-77-1		
	Decachlorobiphenyl	2051-24-3		
209	2,2',3,3',4,4',5,5',6,6'	2051-24-3	305-306	0.00049[d]

a Ballschmiter, K., and M. Zell (1980).
b All melting point and water solubility data from Hutzinger, et al. (1974a) unless otherwise noted. Other experimental values were often reported; where major discrepancies exist, extreme values are separated by a comma. The other references report conflicting values for many of the congeners. Do not compare values from different citations without consulting primary reference.
c CRC Handbook of Chemistry and Physics (57th ed.).
d Yalkowsky et al. (1983).
e Mackay et al. (1980).
f Four chlorines on each ring at unspecified locations.
g Revised numbering sequence as noted by Schulte and Malisch (1983).

MONS 005686

APPENDIX B

COMPOSITION OF SOME COMMERCIAL PCB MIXTURES

MONS 005687

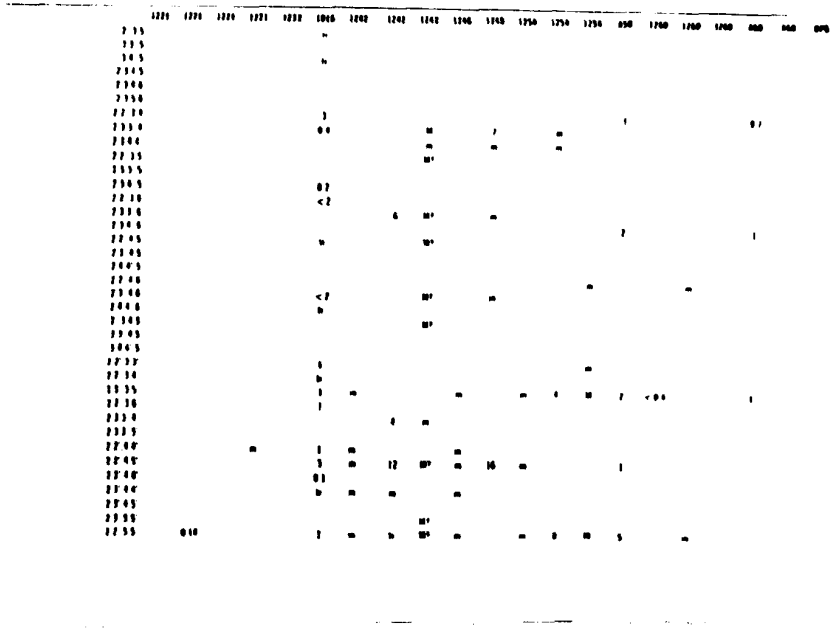
Table B-1. Qualitative and Percent Chlorobiphenyl and Biphenyl Compositions of Commercial PCB Preparations

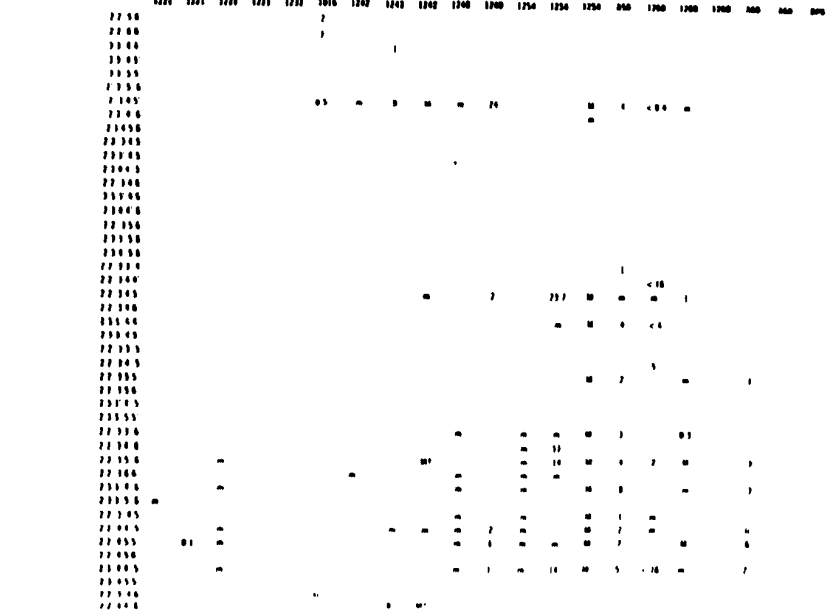
Cl. Substituted Positions	Commercial Preparation Designations (trade names omitted)																		
	1221	1232	1016	1242	1248	1254	1260	1262	1268										
0	12	16	15	0.5	tr			tr	tr				tr						
1	28	32	35	1	tr	0.8		tr	tr				tr			tr			
2		3	3																
3	19	19	20	7									tr			tr			
4				0.6															
5	5	5	7	1		<0.1	tr	<0.1					tr			tr			
6		0.7	1			tr	tr												
7		0.3	0.4		tr	tr													
8	9	5	5	tr	7	tr	<1.0	tr	tr				tr			tr			
9		1	2	tr	1	tr	tr	tr	tr				tr			tr			
10	10	10	11	tr	11	tr	<1	tr	tr	0.5			tr			tr			
11		1	tr				tr												
12					tr														
13			1				tr			<1									
14	5	4	4	tr	2		1	tr		<1			tr			tr			
15																			
16																			
17				tr	5	tr		tr*	tr										
18		0.1			tr			tr*											
19					tr														
20																			
21																			
22		0.1	tr	tr	1	tr	1.1	tr	tr	0			tr			tr			
23				tr	1	tr	<.15	tr	tr	<.11			tr			tr			
24		0.2		tr	1	tr	2	tr*	tr	1									
25		0.6		0.6	tr	tr	2	tr	tr	0.1			tr			tr			
26		0.2				tr		tr	tr	<.11									
27		0.2		tr	tr	tr		tr	tr				tr			tr			
28					tr	tr		tr	tr				tr			tr			
29					0.1			tr*											
30					2			tr					tr			tr			
31		0.1			tr	tr	1.6	tr	tr	2		0.1	tr			tr			
32					tr			tr											
33					2			tr											

Table B-1 (Continued)

MONS 005688

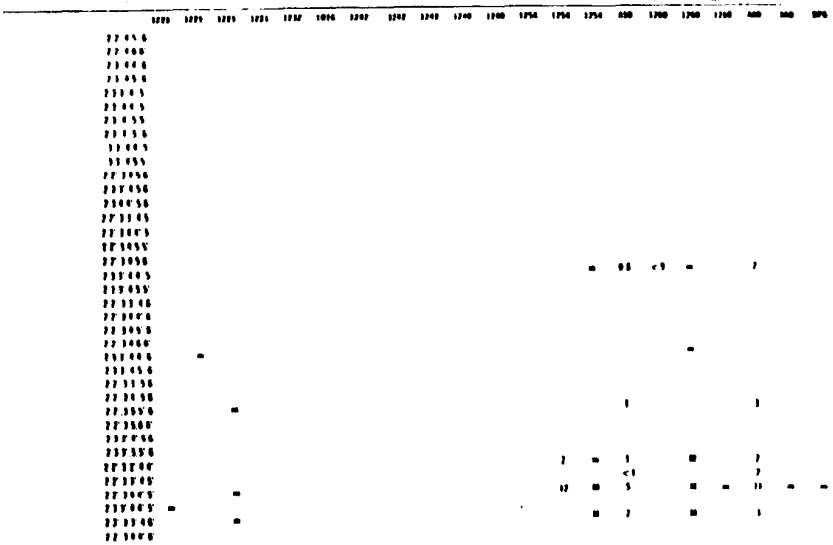
Table B-1 (Continued)





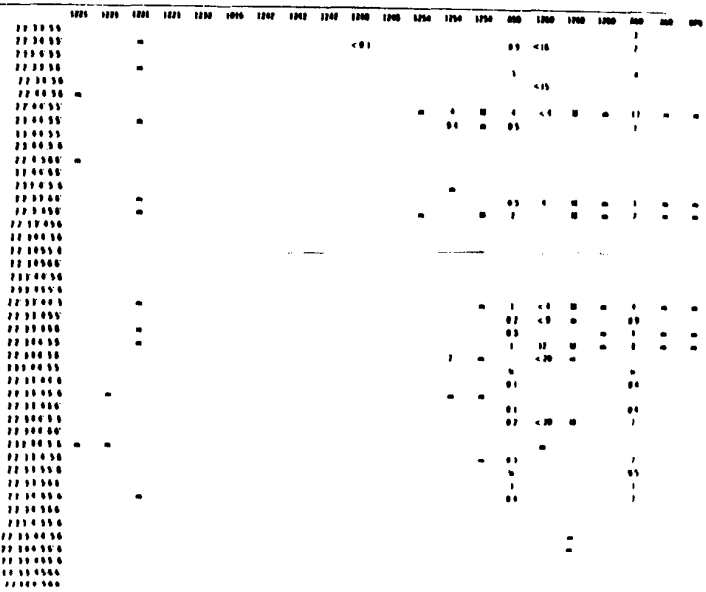
MONS 005690

Table 8-1 (Continued)



MONS 005691

Table B-1 (Continued)



MONS 005692



Table 8-1 (Concluded)

Reference	a	b	c	b	c	b	c	b	d	c	b	c	b	d	e	b	d	f	e	c	f
77-33-00-55-6																					
77-33-00-55															04	7	m		07		
77-33-00-56		m															m				
77-33-055-6															01	5	m		07		
77-33-00-66															h	m					
77-33-05-66															h		m				
77-33-55-66															h		m				
77-33-00-566																00	m		h		
77-33-055-66		m															m				
77-33-00-55-6																m	m				
77-33-00-55-66																	m				

Note: Qualitatively major peaks = M, minor peaks = m, ambiguous identities = ?, quantitatively, percentages rounded.

a Nagayama et al (1976).
b Albro, P.W., NIEHS, Research Triangle Park, North Carolina, written communication (November 1976).
c Willis and Addison (1972).
d Sissons and Welti (1971).
e Jensen and Sundström (1974).
f Tas and deVos (1971).

Source: NIOSH (1977c).

MONS 005693

APPENDIX C

MASS SPECTRAL CHARACTERISTICS OF PCBs

MONS 005694

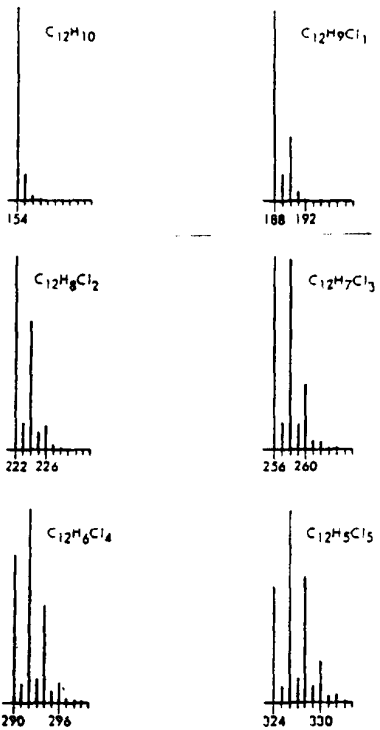


Figure C-1. Mass Spectral Patterns of PCBs a Mono- Through Pentachlorobiphenyls

The molecular ion clusters were calculated using natural abundance ratios of carbon, hydrogen, and chlorine.

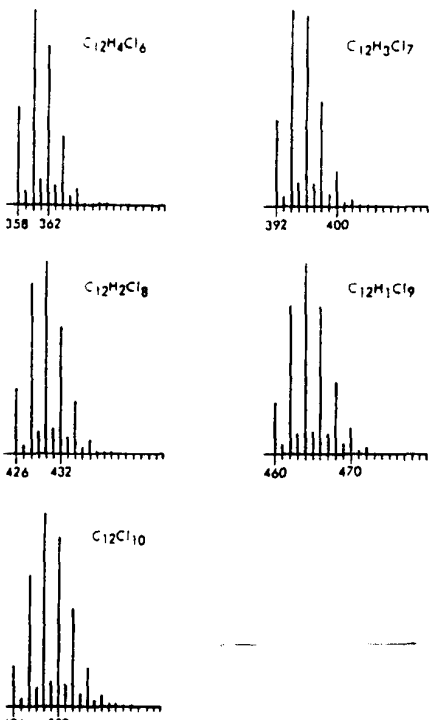


Figure C-1 (concluded). Mass Spectral Patterns of PCBs Hexa- Through Decachlorobiphenyl

The molecular ion clusters were calculated using natural abundance ratios of carbon, hydrogen, and chlorine.

Table C-1 Major Molecular Cluster Ions for Common Chlorinated Aromatics[1]

No. of Chlorines (n)	PCBs $C_{12}H_{10-n}Cl_n$		PCNs $C_{10}H_{8-n}Cl_n$		PCBFs $C_{12}H_{9-n}Cl_nO$		PCDFs $C_{12}H_{8-n}Cl_nO$	
	Exact Mass	Relative Abundance	Exact Mass	Relative Abundance	Exact Mass	Relative Abundance	Exact Mass	Relative Abundance
0	154.0783		128.0626		170.0575		168.0575	
1	188.0393	100.00	162.0237	100.00	218.0135	100.00	202.0186	100.00
	190.0363	31.92	164.0207	33.10	220.0105	31.92	204.0156	33.07
2	222.0003	100.00	195.9847	100.00	251.9745	100.00	235.9796	100.00
	223.9974	14.84	197.9817	65.19	253.9716	64.45	237.9766	64.74
	225.9944	11.15	199.9788	10.99	255.9686	11.47	239.9737	11.29
3	255.9614	100.00	229.9457	100.00	285.9355	100.00	269.9406	100.00
	257.9584	98.66	231.9428	96.61	287.9326	96.07	271.9377	96.87
	259.9555	32.78	233.9398	32.68	289.9296	33.10	273.9347	32.98
	261.9525	3.72	235.9369	3.64	291.9267	3.86	275.9318	3.79
4	289.9226	76.17	263.9067	76.31	319.8965	75.93	303.9016	76.35
	291.9196	100.00	265.9038	100.00	321.8936	100.00	305.8987	100.00
	293.9165	44.43	267.9008	43.77	323.8906	43.48	307.8957	43.55
	295.9135	10.36	269.8979	10.06	325.8877	11.13	309.8928	11.05
	297.9106	1.04	271.8949	0.93	327.8847	0.99	311.8898	0.97
5	323.8836	61.01	297.8677	61.10	353.8575	56.86	337.8627	60.93
	325.8805	100.00	299.8648	100.00	355.8546	100.00	339.8597	100.00
	327.8775	65.72	301.8618	65.57	357.8517	63.96	341.8568	65.64
	329.8746	21.69	303.8588	21.57	359.8487	21.91	343.8538	21.88
	331.8716	3.62	305.8559	3.57	361.8458	3.78	345.8509	3.66
6	357.8446	30.88	331.8288	30.95	387.8185	30.78	371.8237	30.81
	359.8415	100.00	333.8258	100.00	389.8156	100.00	373.8207	100.00
	361.8385	82.82	335.8229	81.87	391.8127	82.25	375.8178	82.14
	363.8356	35.97	337.8199	35.82	393.8097	36.23	377.8148	36.10
	365.8326	6.92	339.8170	6.85	395.8068	6.95	379.8119	6.90
7	391.8056	43.54	365.7898	43.69	421.7795	43.36	405.7847	43.58
	393.8025	100.00	367.7868	100.00	423.7767	100.00	407.7817	100.00
	395.7995	98.32	369.7839	98.18	425.7737	98.58	409.7788	98.44
	397.7966	53.08	371.7809	53.51	427.7708	54.10	411.7758	53.95
	399.7936	17.72	373.7780	17.68	429.7678	17.98	413.7729	17.83
8	425.7665	33.73	399.7508	33.48	455.7405	33.21	439.7457	33.27
	427.7635	87.74	401.7478	87.35	457.7377	87.07	441.7428	87.15
	429.7606	100.00	403.7449	100.00	459.7347	100.00	443.7398	100.00
	431.7576	65.58	405.7419	65.60	461.7318	65.76	445.7369	65.67
	433.7547	21.93	407.7390	21.83	463.7288	21.98	447.7339	21.92
9	459.7275	21.14						
	461.7245	54.28						
	463.7216	54.20						
	465.7186	21.65						
	467.7157	3.67						
10	493.6885	21.11						
	495.6856	34.32						
	497.6826	33.24						
	499.6797	21.33						
	501.6767	5.48						

Table C-1 (continued)

No. of Chlorines (n)	PCBs $C_{12}H_{10-n}Cl_n$		PCNBs $C_{12}H_{9-n}Cl_{n+1}N$		CT Isomers $C_{14}H_{10-n}Cl_n$		CT-Phenyl $C_{20}H_{14-n}Cl_n$	
	Exact Mass	Relative Abundance	Exact Mass	Relative Abundance	Exact Mass	Relative Abundance	Exact Mass	Relative Abundance
0	152 0626		170 0732	-	178 0670	-	94 0313	-
1	186 0227	100 00	204 0342	100 00	212 0280	100 00	128 0629	100 00
	188 0207	33 41	206 0313	33 02	214 0251	32 01	130 0600	33 01
2	219 9847	100 00	237 9953	100 00	245 9890	100 00	161 9635	100 00
	221 9817	64 04	239 9923	64 78	247 9861	65 43	163 9630	65 93
	223 9788	12 16	241 9894	11 29	249 9831	10 76	165 9580	10 09
3	253 9457	100 00	271 9563	100 00	279 9500	100 00	195 9250	100 00
	255 9428	96 66	273 9533	96 87	281 9777	96 86	197 9220	96 25
	257 9398	32 78	275 9504	32 08	283 9281	32 13	199 9191	32 33
	259 9369	3 17	277 9474	3 19	285 9252	3 53	201 9161	3 59
4	287 9067	76 17	305 9173	76 06	313 9111	76 52	229 8860	76 40
	289 9038	100 00	307 9143	100 00	315 8881	100 00	231 8830	100 00
	291 9008	49 43	309 9114	49 55	317 8852	49 05	233 8801	49 18
	293 8979	10 96	311 9084	11 05	319 8822	10 72	235 8771	10 80
	295 8949	0 95	313 9055	0 97	321 8793	0 89	237 8742	0 91
5	321 8677	61 01	339 8783	60 93	347 8521	61 23	263 8470	61 15
	323 8648	100 00	341 8754	100 00	349 8491	100 00	265 8440	100 00
	325 8618	49 72	343 8724	49 84	351 8462	49 96	267 8411	49 48
	327 8589	11 69	345 8695	11 80	353 8432	11 80	269 8381	11 49
	329 8559	1 62	347 8665	1 66	355 8403	1 51	271 8352	1 55
6	355 8288	50 08	373 8393	50 03	381 8131	51 04		
	357 8258	100 00	375 8364	100 00	383 8102	100 00		
	359 8229	47 32	377 8334	47 14	385 8072	47 37		
	361 8199	14 97	379 8305	14 10	387 8043	15 10		
	363 8170	1 97	381 8275	1 99	389 8013	1 74		
7	389 7898	43 64	407 8004	43 60				
	391 7868	100 00	409 7974	100 00				
	393 7839	90 32	411 7945	90 46				
	395 7809	53 00	413 7915	53 15				
	397 7780	17 72	415 7886	17 81				
8	423 7488	33 33	441 7614	33 27				
	425 7478	87 26	443 7584	87 15				
	427 7449	100 00	445 7555	100 00				
	429 7420	55 58	447 7525	55 67				
	431 7390	26 93	449 7496	27 02				
9			475 7224	25 00				
			477 7194	76 31				
			479 7165	100 00				
			481 7135	76 53				
			483 7106	17 72				

a PCBs = polychlorinated biphenyls; PCNs = polychlorinated naphthalenes; PCDEs = polychlorinated diphenylethers; PCDFs = polychlorinated dibenzofurans; PCBPs = polychlorinated biphenylenes; and PCNBs = polychlorinated nitrobenzobiphenyls.

MONS 005698

APPENDIX D

PGC/ECD CHROMATOGRAMS OF AROCLOR MIXTURES

Hexane solutions were chromatographed on a 180 x 0.2 cm ID glass column, packed with 1.5% SP 2250/1.95% SP 2401 on 100/120 mesh Supelcoport. The nitrogen carrier gas flow rate was 30 mL/min. The injector and detector temperatures were 250°C and 300°C, respectively. The column temperatures are noted on each figure.

MONS 005699

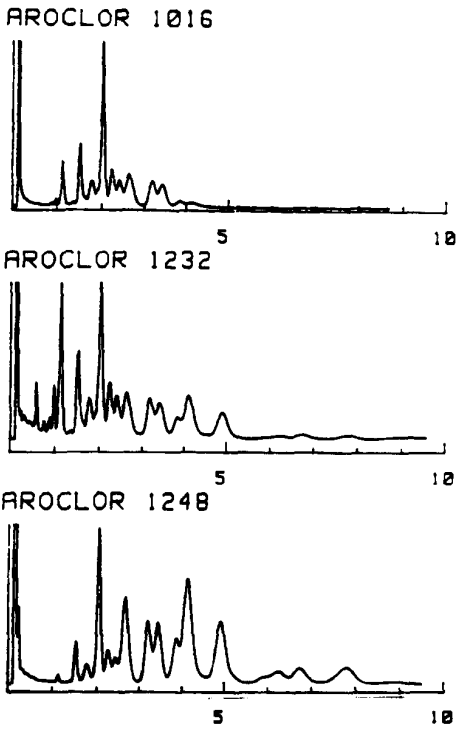


Figure D-1. Isothermal Chromatograms of Aroclors 1016, 1232, and 1248

The column temperature was 180°C.

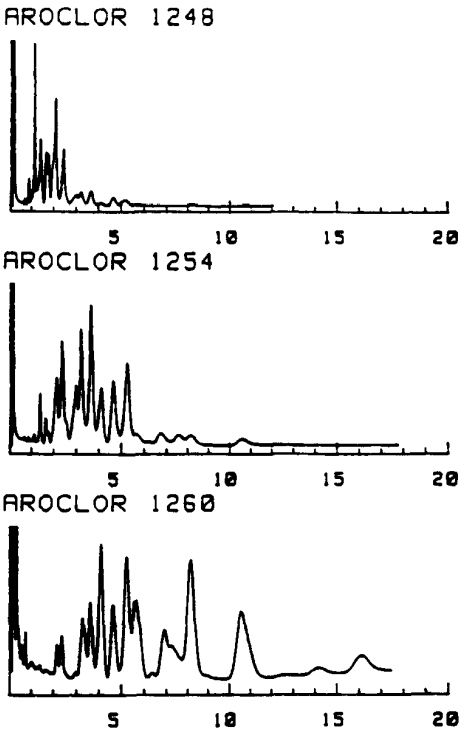


Figure D-2. Isothermal Chromatograms of Aroclors 1248, 1254, and 1260

The column temperature was 200°C.

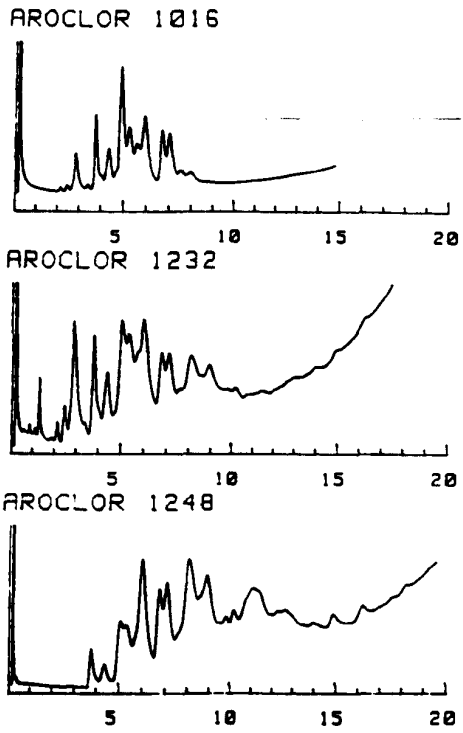


Figure D-3. Temperature-Programmed Chromatogram of Aroclors 1016, 1232, and 1248

The column temperature was programmed from 150°C to 250°C at 10°C/min.

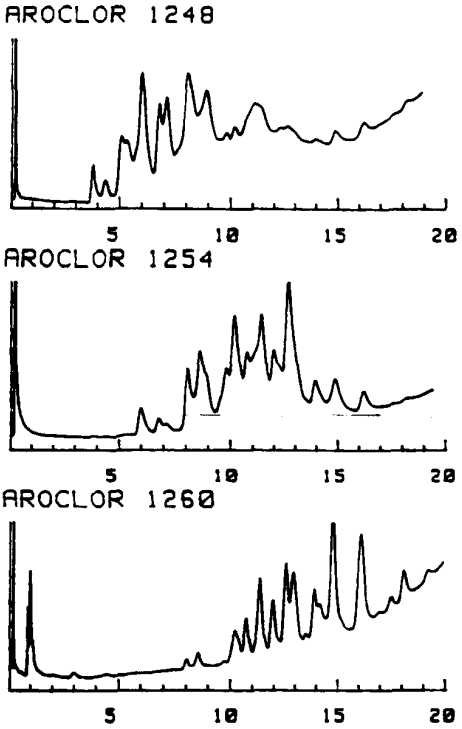


Figure D-4. Temperature-Programmed Chromatogram of Aroclors 1248, 1254, and 1260

The column temperature was programmed from 150°C to 250°C at 10°C/min.

APPENDIX E

TERMS AND ABBREVIATIONS

MONS 005704

Table E-1. Glossary of Terms

Accuracy: Closeness of the analytical result to the "true" value.

Analysis: The ascertainment of the identity and/or the concentration of the constituents or components of a sample. Analysis is often used incorrectly in place of determination. Only samples can be analyzed; constituents or components are determined (see below). Examples of correct usage are: Analysis of fish for PCBs, determination of PCBs in fish.]

Analyte: Chemical compound or element which is the subject of an analysis.

Aroclor: Trade name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the United States.

Askarel: A general term for a group of nonflammable synthetic chlorinated aromatic hydrocarbons used as electrical insulating media. See ASTM 1978a, b.

Brockmann Activity: Amount of water added to alumina to control its adsorbent activity (Activity I = 0% water; Activity V = 15% water).

By-product PCBs: PCBs unintentionally generated as impurities in synthesis of other products (as opposed to commercial PCBs).

CAS Registry Number: Unique number assigned by Chemical Abstracts Service to each chemical compound (see Appendix A).

Chlophen: Trade name (Bayer, GFR) for a series of PCB mixtures.

Congener: One of 209 PCBs or other group of compounds, not necessarily the same homolog.

Destruction and removal efficiency (DRE): A measure of an incinerator's (or alternative method of destruction) performance in removing or destroying PCBs (or another compound). DRE is expressed as percent efficiency:

$$\frac{\text{mass}_{in} - \text{mass}_{out}}{\text{mass}_{in}} \times 100$$

Table E-1 (Continued)

Determination: The ascertainment of the quantity or concentration of a specific substance in a sample. See analysis.

Electron impact mass spectrometry (EIMS): Low resolution mass spectrometry operated in the electron impact ionization mode.

Equivalent method: Any method, certified against the primary method, which can be used for routine analysis of samples.

External standard: Standards for calibration which are not added to the sample extract.

Florisil: Trade name (Floridin Company) for a synthetic magnesium silicate used for liquid chromatographic cleanup and also for air sampling.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column including WCOT, SCOT, fused silica, glass, and metal.

Homolog: One of the 10 degrees of chlorination of PCBs ($C_{12}H_9Cl$ through $C_{12}Cl_{10}$) or other group of compounds varying by systematic addition of a substituent.

Internal standard: Standards used expressly for quantitation added to sample extract immediately prior to the analytical determination.

Isomer: Any PCB or other compound which has the same molecular formula, but different positional substitutions. 2,2'-Dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

Limit of detection (also MDL): Lowest concentration at which an analyte can be identified as present in the sample at a stated statistical confidence level.

Lower limit of quantitation: Lowest concentration to which a value can be assigned at a stated statistical confidence level.

MONS 005706

Table E-1 (Continued)

Mean: Arithmetic mean.

Method: A series of techniques which form a specific, well-defined sampling or chemical analysis for a specified compound(s)/matrix(ces) combination. A distinct adaptation of a technique for a selected measurement purpose (e.g., a specific GC/ECD operating mode for analysis of PCBs, including column specifications and sample preparation.

Method detection limit: See limit of detection.

Mineral oil: Liquid mixture of hydrocarbons obtained from petroleum.

Packed column gas chromatography (PGC): Gas-liquid chromatography performed using a column, typically 180 cm long x 2 mm ID, packed with a liquid phase on a granular solid support material.

Part per million (ppm): One part in 10^6. For gaseous mixtures, a volume/volume (v/v) basis is typically used and:

$$1 \text{ ppm} = \text{mg/m}^3 \times \frac{RT}{MW}$$

where RT = 22.4 L/g-mole at 0°C and 1 atm
= 24.5 L/g-mole at 25°C and 1 atm
and MW = molecular weight of compound, i.e., g/g-mole

For low concentration aqueous samples, a weight/volume (w/v) basis is most commonly used and 1 ppm = 1 mg/L (~ 1 mg/kg for liquids with density ~ 1). For nonaqueous liquids and solid materials, a weight/weight (w/w) basis is most commonly used and 1 ppm = 1 mg/kg.

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula $C_{12}H_nCl_{10-n}$, where n = 0-9. 4-Chlorobiphenyl and 3,4,3',4'-tetrachlorobiphenyl are examples. This definition includes monochlorobiphenyls, but not biphenyl.

Polychlorinated dibenzo-p-dioxin (PCDD): One of 75 individual compounds having the molecular formula $C_{12}H_nCl_{8-n}O_2$, where n = 0-7. This definition includes monochlorodibenzo-p-dioxins.

MONS 005707

Table E-1 (Continued)

Polychlorinated dibenzofuran (PCDF). One of 135 individual compounds having the molecular formula $C_{12}H_{8-n}Cl_nO$, where n = 0-7. This definition includes monochlorodibenzofurans.

Procedure: The written directions necessary to use a method or series of methods and techniques.

Protocol: A sampling or analysis procedure which is highly specific and from which few or no deviations are allowed.

Qualitative: Having to do with establishing the presence or identity of a compound.

Quantitative: Having to do with measuring the amount or concentration of a compound in a sample.

Relative retention time: Retention time of a compound on a chromatographic system, relative to an internal standard; unitless number.

Response factor: Instrumental response of an analyte measured against an internal standard.

Retention index: Systematic, unitless measure of a compound's chromatographic retention as compared to an homologous series of standards, usually the n-alkanes.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

Saponification: Chemical reaction of a fat with strong base to form a glycerol and an acid salt.

Sensitivity: The slope of instrument response with respect to the amount of analyte. Also used colloquially in reference to lowest detectable amount of analyte.

Silica gel: Granular form of silicic acid (H_2SiO_3).

Standard operating procedure: A written QA document which describes the way an organization typically conducts a routine activity. May address instrumental operation, instrumental maintenance, application of a laboratory technique, data review, or management oversight.

MONS 005708

Table E-1 (Continued)

Surrogate: Nonanalyte compounds added to the sample prior to any analytical manipulations for the express purpose of measuring recovery through extraction, cleanup, etc.

Technique: Scientific principle or specific operation (e.g., GC/ECD, Florisil column cleanup, or Webb and McCall quantitation).

Yusho: A mass food poisoning incident caused by ingestion of a commercial rice oil contaminated with PCBs and other haloaromatics

MONS 005709

Table E-2. List of Abbreviations

ASME	American Society of Mechanical Engineers
ANSI	American National Standards Institute
AOAC	Association of Official Analytical Chemists
ASTM	American Society for Testing and Materials
BHC	Benzene hexachloride (hexachlorocyclohexane); several possible isomers
CI	Chemical ionization (mass spectrometry)
CIMS	Positive chemical ionization mass spectrometry
CLE	Continuous liquid-liquid extraction
DCMA	Dry Color Manufacturer's Association
DDE	1,1-Dichloro-2,2-bis(p-chlorophenyl)ethylene
DDT	1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane
ECD	Electron capture detector
EI	Electron impact ionization (mass spectrometry)
EICP	Extracted ion current plot
EIMS	Electron impact ionization mass spectrometry
EPA	(U.S.) Environmental Protection Agency
EPRI	Electric Power Research Institute
FDA	(U.S.) Food and Drug Administration
FFAP	Free fatty acid phase
FID	Flame ionization detector
FTIR	Fourier transform infrared spectrometry
GC	Gas-liquid chromatography (column type unspecified)
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)

MONS 005710

Table E-2 (Continued)

GPC	Gel permeation chromatography
HECD	Hall electrolytic conductivity detector (other similar detectors such as the Coulson are included)
HPLC	High performance liquid chromatography
HREIMS	High resolution electron impact mass spectrometry
HRGC	High resolution gas-liquid chromatography
ID	Inside diameter
IR	Infrared spectrometry
IUPAC	International Union of Pure and Applied Chemistry
K	Partition coefficient
K_{ow}	Octanol-water partition coefficient
KD	Kuderna-Danish evaporator
KOH	Potassium hydroxide
LMS	Limited mass scanning (mass spectrometry)
LOD	Limit of detection. Lowest concentration at which an analyte can be identified as present in the sample at a stated statistical confidence level
LOQ	Limit of quantitation.
M	Parent m/z ion in a mass spectrum (equivalent to molecular weight)
MDL	Method detection limit
MOG	Mills-Onley-Gaither procedure for analysis of fatty foods and related matrices (Mills et al., 1963)
MS/MS	Mass spectrometry/mass spectrometry

Table E-2 (Continued)

m/z	Mass-to-charge ratio in mass spectrometry; m/e, amu, and dalton also describe the mass units in mass spectrometry
NAA	Neutron activation analysis
NBS	(U.S.) National Bureau of Standards
NCI	Negative chemical ionization (mass spectrometry)
NCIMS	Negative chemical ionization mass spectrometry
NIOSH	(U.S.) National Institute for Occupational Safety and Health
NMR	Nuclear magnetic resonance spectrometry
NRC	National Research Council
NTIS	(U.S.) National Technical Information Service
OECD	Organization for Economic Cooperation and Development
PAM	Pesticide Analytical Manual (FDA)
PBB	Polybrominated biphenyl
PCB	Polychlorinated biphenyl
PCBP	Polychlorinated biphenylene
PCCY	Polychlorinated chrysene
PCDD	Polychlorinated dibenzo-*p*-dioxin
PCDF	Polychlorinated dibenzofuran
PCN	Polychlorinated naphthalene
PCPY	Polychlorinated pyrenes
PCQ	Polychlorinated quaterphenyl
PCQE	Polychlorinated quaterphenyl ether
PCT	Polychlorinated terphenyl
PGC	Packed column gas-liquid chromatography

MONS 005712

Table E-2 (Continued)

PID	Photoionization detector
ppb	Parts per billion (10^{-9}; American system)
ppm	Parts per million (10^{-6})
Precision	Reproducibility of an analysis, measured by SD of replicates
PUF	Polyurethane foam
QA	Quality assurance. An organization's program for assuring the integrity of data it produces or uses
QC	Quality control. The specific activities and procedures designed and implemented to measure and control the quality of data being produced
R_f	Movement of a TLC spot, measured as a fraction of the solvent front. Also used with column chromatography to measure the fraction of the total column length a band moves.
RF	Response factor
RI	Retention index
RIA	Radioimmunoassay or radioisotope dilution assay
RIC	Reconstructed ion chromatogram (in GC/MS)
RMR	Relative molar response
RP	Reverse phase (liquid chromatography)
RRF	Relative response factor
RRT	Relative retention time
RSD	Percent relative standard deviation (SD/mean x 100)
RT	Retention time
SASS	Source Assessment Sampling System
SCOT	Support coated open tubular (HRGC column)

MONS 005713

Table E-2 (Continued)

SIM	Selected ion monitoring (also multiple ion detection, MID, or mass fragmentography; in GC/MS)
SIMCA	SIMple Classification by Analogy (principal components modeling technique)
TCD	Thermal conductivity detector
TCDD	Tetrachlorodibenzo-p-dioxin
TCDF	Tetrachlorodibenzofuran
TIC	Total ion current chromatogram (in GC/MS)
TLC	Thin-layer chromatography
TOCl	Total organic chlorine
TOX	Total organic halogen
TSCA	Toxic Substances Control Act, PL 94-469 (1976)
USWAG	Utilities Solid Waste Activities Group of the Edison Electric Institute
UV	Ultraviolet (spectroscopy)
WHO	World Health Organization
XAD-2	Polystyrene-divinylbenzene copolymer; also marketed with different numerical suffices. Trade mark, Rohm and Haas
XRF	X-ray fluorescence

MONS 005714

Acetonitrile back-partition, 58-60, 62, 101, 106, 109, 122, 154-156, 167 (also see liquid-liquid partition)
Acid digestion, 101, 107, 109, 156-158, 167 (also see sulfuric acid)
Adipose tissue (also see animal tissues, humans, and lipids)
  Analysis of, 56, 59, 99-103, 106, 120, 121, 126, 127, 131, 136, 143, 150, 152, 153, 155, 157, 161, 166, 186, 313, 326
  Occurrence in, 24, 25, 33, 34, 258
Adsorptive losses, 68-69, 71, 114, 115
Air (also see source sampling)
  Analysis of, 56-59, 95-97, 122, 127, 131-133, 321, 329
  Contamination by, 115, 123
  Occurrence in, 24, 27, 28, 35, 51-53
  Sampling of, 63, 71-84
Alcoholic KOH (see base, cleanup)
Alumina, 100, 102, 107, 108, 118, 119, 122, 126, 130-134, 141, 145, 148, 163, 168
Animal tissue (also see adipose tissue, blood, eggs, food, humans, milk)
  Analysis of, 100-108, 119, 121, 122, 127, 131, 141-143, 161, 168
  Occurrence in, 24-26, 32, 35
Apiezon L, 176, 182, 186, 188, 189, 195
Aqueous solubility, 10, 461-467
Aroclor composition, 17-19, 136-138, 140, 145, 175, 179-180, 290, 469-475
Aroclor, 1, 15, 16, 490 (also see Aroclor composition)
Askarel, 17, 490
Automated quantitation, 299-300
Azulene, 118-120, 124, 169
Ballschmiter numbers (see IUPAC numbers)
Base, cleanup, 57-60, 89, 99, 104, 106, 120, 131, 161, 162, 165
Bioconcentration, 9, 24-26, 34
Biological properties, 37-40, 45-51
Biphenyl, 5, 177, 190, 242, 462
Birds (also see animal tissue)
  Analysis of, 108, 148, 320-322 (also see food)
  Occurrence in, 24-26
Blood (also see animal tissue, and humans)
  Analysis of, 56, 59, 87, 97-100, 119, 121, 127, 131, 154, 155, 313, 322, 336
  Occurrence in, 24, 25, 51-53
Bodman bottle, 64
Boiling points, 10-12
Brockmann activity, 130, 490
By-product PCBs, 3, 490 (also see pigments)
  Analysis of, 60-62, 74, 121, 156, 314, 318, 331-336
  Sources and regulations, 22-23

MONS 005715

Calibration (GC), 230, 279-281 (also see response factors)
Capacitor fluids, 60, 112, 157, 162-163, 211, 311-312 (also see oil)
Capillary GC, 174 (also see high resolution gas chromatography)
Carbon (adsorbent), 113, 118, 131, 134-142, 148, 166
CAS registry number, 6, 461-467, 490
Celite, 60, 67, 90, 124, 136
Charcoal (see carbon)
Chemical ionization mass spectrometry, 61, 77, 85, 222, 231, 299, 495
Chemical properties, 14-23, 36-44 (also see physical properties)
Chlor-N-Oil , 263
Chlorinated benzenes, 17, 60
Chromic acid (see chromium trioxide)
Chromium trioxide, 148, 158-161, 167
CIMS (see chemical ionization mass spectrometery)
Coeluting congeners, 188-194
Collaborative studies, 67, 93, 99, 267, 293, 319-337
Colorimetric detection, 260, 263
Commercial mixture properties, 15-22
Commercial use, 15-17, 22
Computerized quantitation (see automated quantitation)
Confirmation, 161, 257-259, 308, 317, 318
Congener, 6, 490
Continuous liquid-liquid extraction, 63, 67, 88, 89, 91, 92
Cooking oil (see Yusho)
Cyanide, 164-165
DDE, 119, 121, 123-126, 130, 131, 134, 136, 148, 150, 158-161, 167, 197, 236, 243, 244, 495
DDT, 34, 102, 121, 124, 126, 130, 131, 134, 136, 147, 148, 150, 160, 161, 242, 244, 246, 249, 254, 495
Decachlorobiphenyl, 5, 12, 15, 16, 22, 240-242, 467
Degradation, 36-45, 156, 159
Detection limit (general), 61, 65, 89-91, 194, 209, 248, 259, 302, 307-309 (also see limit of detection and method detection limit)
Diagnostic peaks, 272, 289, 293-294
Disposal, 3, 35-37
Distillation, 89, 102, 145 (also see steam distillation)
Dowtherm G, 22
Dry deposition, 68, 76, 77, 97
Dual column GC, 257-258, 295-296
Earthworms, 108
Eggs (also see birds, animal tissue)
  Analysis of, 107, 119, 121, 130, 131, 148, 155
  Occurrence in, 24, 25, 32
EIMS (see electron impact mass spectrometry)

MONS 005716

Electrochemical properties, 13
Electrolytic conductivity detector, 210-211, 260-262, 265
Electron capture detection (see high resolution gas chromatography and packed column gas chromatography)
Electron impact mass spectrometry, 217-230, 275-277, 295, 297 (also see high resolution gas chromatography, packed column gas chromatography, and response factors)
Environmental persistence, 37-39 (also see weathering)
Environmental transport, 34-36 (also see weathering)
Fat (see adipose tissue)
Feed (animal), 108, 148 (also see food, analysis of)
Fenclor DK, 22
Fish (also see shellfish)
  Analysis of, 103-105, 121, 124, 126, 127, 130, 131, 134, 138, 141, 147, 150, 154, 158, 160, 161, 320-322, 336 (also see food, analysis of)
  Occurrence in, 1, 24-26, 32
Florisil, 491
  Air sampling, 58, 59, 74-75, 80-84, 96-97
  Column cleanup, 55, 57-60, 62, 99, 119-124, 126-128, 131, 134, 135, 143, 153, 155, 157, 159, 161, 167, 168, 337, 330
  Slurry cleanup, 61, 148-149, 163
Fluorescence spectra, 13
Fluorescent light ballasts, 16, 28
Food (also see animal tissue, feed, fish, milk, oil, plant tissue, and shellfish)
  Analysis of, 56, 60, 62, 100-110, 113-114, 120, 127, 131, 153, 155, 159, 161
  Occurrence in, 24, 32
Formation, 23
Fourier transform infrared spectrometry (see infrared spectrometry)
Freeze-dried samples, 107
FTIR (see infrared spectrometry)
Fugacity, 13
Fuming sulfuric acid, 158, 165 (also see sulfuric acid and acid digestion)
Fused silica capillary GC (see high resolution gas chromatography)
GC (unspecified), 57-60, 171-243, 255, 275, 495 (also see high resolution gas chromatography and packed column gas chromatography)
GC/MS (unspecified), 57, 58, 60, 240, 242, 277-280, 284, 495 (also see high resolution gas chromatography and packed column gas chromatography)
Gel permeation chromatography, 149-154, 167
Glass capillary GC (see high resolution gas chromatography)
Glass fiber filter, 76, 78-80

MONS 005717

Grain, 108 (also see feed and food, analysis of)
Half-lives, 37-39
Half-retention indices, 175, 177-179, 271 (also see retention index)
Hall detector (see electrolytic conductivity detector)
Henry's Law constants, 13
Hi-Vol sampler, 76
High performance liquid chromatography, 141-147, 247-254, 299, 496
High resolution electron impact mass spectrometry, 200, 236-237, 254, 258-259, 265
High resolution gas chromatography, 174, 182, 186-188, 270-273, 491 (also see packed column gas chromatography)
  Electron capture detection, 184, 188-196, 204, 273, 288-296, 301-302, 329
  Electron impact mass spectrometry, 3, 44, 57-60, 186, 212-230, 258, 275-277, 295-98, 315-316, 322, 331, 333 (also see electron impact mass spectrometry)
  Flame ionization detection, 249
  Negative chemical ionization mass spectrometry, 201, 231-234, 258 (also see NCIMS)
Homolog, 6, 491
HRGC (see high resolution gas chromatography)
Humans (also see adipose tissue, blood, milk)
  Analysis of, 56, 59, 97-103, 121, 313
  Occurrence in, 1, 24-32
Hydraulic fluids, 16, 112, 157, 163, 209, 211, 312
Ice coring, 77
Impingers, 75, 83 (also see Modified Method 5)
Inadvertently generated PCBs (see by-product PCBs)
Incidental PCBs (see by-product PCBs)
Incineration, 3, 36, 56, 59, 78-84, 314-315
Infrared spectra, 13, 14
Infrared spectrometry, 197, 255-256
Injection (GC), 196-197
Interlaboratory studies (see collaborative studies)
Ion-specific electrode, 260
Isomer, 6, 491
IUPAC numbers, 6, 461-467
Lauric acid, 120
Limit of detection (instrumental), 56, 198, 199, 211, 233, 239, 253, 254, 256, 257, 297, 492 (also see detection limit and method detection limit)
Lipids, 100-103, 106-110, 122, 124, 130, 134, 149-155, 159, 161, 165-168 (also see adipose tissue, acetonitrile back-partitioning, Florisil, food, milk, and gel permeation chromatography)
Liquid-liquid partition, 154-156, 159 (also see acetonitrile back-partition)
Low temperature luminescence, 257
Low temperature precipitation, 102

MONS 005718

Mammals (occurrence in), 24-26 (also see animals, humans)
Mass spectra, 215-216, 275-277, 478-481
Mass spectrometry, 212-238, 295-299 (also see high resolution gas chromatography, mass spectra, and packed column chromatography)
Mass, exact, 10, 480-481 (also see molecular weight)
Melting point, 10, 461-467
Mercury, 164
Method detection limit, 55-60, 72, 77, 80, 85, 94, 102, 138, 198, 200, 201, 231, 236, 244, 247, 254, 327, 492 (also see detection limit and limit of detection)
Microcoulometry, 260
Milk
  Analysis of, 56, 59, 102, 106, 107, 119, 121, 122, 127, 256, 313, 315-316, 321, 324-326 (also see food, analysis of)
  Occurrence in, 1, 24, 25, 32
Mills-Onley-Gaither (see Florisil)
Mineral oil (see oil, mineral)
Mobile mass spectrometer, 75, 85, 231 (also see portable instrument)
Modified Method 5 sampling train, 61, 78-84 (also see source sampling)
Molecular weight, 7, 9, 10 (also see mass, exact)
Monochlorobiphenyl, 5, 22, 39, 462
MS/MS, 94, 236-238, 254, 259, 265, 496
Natural gas, 56, 59, 84
NCIMS, 231-236, 258, 259, 265, 497 (also see high resolution gas chromatography)
Neutron activation analysis, 257
Nuclear magnetic resonance spectrometry, 14, 255
Octanol-water partition coefficient, 10-13, 244
Oil, 85, 122, 133, 153, 154, 157, 253 (also see capacitor fluids, hydraulic fluids)
  Cooking (see Yusho)
  Insulating, 322, 330
  Lubricating, 323, 337-338
  Mineral, 60, 77, 111-112, 145, 148, 155, 202, 209-211, 256, 330, 492 (also see transformer oil)
  Motor, 292, 311
  Rice, 32-33 (also see Yusho)
  Silicone, 75, 111, 113, 155, 253
  Transformer, 60, 61, 85, 111-113, 117, 122, 127, 133, 145-148, 154, 155, 158, 162, 163, 186, 202, 209-211, 247, 253, 255-256, 259, 263, 264, 270, 273, 274, 281, 287, 292, 293, 300, 301, 311-312, 315, 317, 330
  Vegetable, 113-114, 155, 157
  Waste, 60, 61, 85, 112, 157, 163, 186, 211, 281, 287, 300, 317

MONS 005719

Packed column gas chromatography (also see high resolution gas chromatography)
  Electron capture detection, 56-60, 74, 200, 203, 247, 254, 268-270, 282-288, 293, 295, 296, 301-302, 320-331, 337, 483-488
  Electron impact mass spectrometry, 59-61, 200, 295 (also see electron impact mass spectromectrometry)
  Flame ionization, 205, 238-239
  Hall electrolytic conductivity detection, 200, 210-211, 269, 320
  Photoionization detection, 329
  Thermal conductivity detection, 239
Paper and paper products, 56, 60, 110, 120, 122, 127, 143, 144, 158, 320, 321, 325, 327
Partition coefficients, 10, 13, 88 (also see octanol-water partition cofficients)
Pattern recognition, 268-270, 273-274
PCB nomenclature, 5, 6
PCBs as by-products (see by-product PCBs)
Percent chlorine in PCBs, 7, 18
Perchlorination, 240-242, 253, 257
PGC (see packed column gas chromatography)
Phosphorescence, 13, 253, 258
Photolysis, 37
Physical properties, 9-14, 461-467, 480, 481 (also see chemical properties)
Pigments, 22, 23, 56, 60, 121, 123, 157, 207, 314, 321, 330
Plant tissue, 24, 35, 108-109, 143, 148 (also see feed, food, and grain)
Plasma chromatography, 257
Polychlorinated biphenylenes, 41, 42, 481, 497
Polychlorinated dibenzo-p-dioxins, 32, 41, 42, 126, 131, 138, 141, 142, 145, 186, 236, 237, 480, 492, 497
Polychlorinated dibenzofurans, 2, 17, 21, 32, 33, 39, 41, 42, 45, 131, 138, 141, 142, 145, 186, 480, 493, 497
Polychlorinated naphthalenes, 141, 142, 159, 480, 497
Polychlorinated quaterphenyls, 17, 42
Polychlorinated terphenyls, 16, 42, 183
Polyurethane foam
  Air sampling, 71-75, 96, 131
  Column cleanup (with carbon), 134, 135, 138, 140, 141
  Water sampling, 63, 65-66, 68
Portable instrument, 75, 85, 210, 231
Preservation (see sample storage)
Properties (see chemical properties, commercial mixture properties, and physical properties)
Purge and trap, 90
Quality assurance, 305-318, 498
Quality control, 56-61, 305, 307-310, 314-318, 498
Radioimmunoassay, 256

MONS 005720

Rainwater, 29, 68 (also see dry disposition)
RCl (see total organic halide)
Reference materials (see standards)
Registry number (see CAS registry number)
Regulatory analyses, 293-294 (also see diagnostic peaks)
Relative retention times (see retention time)
Response factors, 278-279, 493, 498 (also see calibration)
  ECD, 188, 190-192, 202, 205, 209
  FID, 205
  EIMS, 222-229
  NCIMS, 231, 232
Retention index, 175, 179-180, 270-271, 493, 498 (also see half-retention index and retention time)
Retention time, 174, 175, 176, 179, 186, 187, 190-194, 268-273, 276, 493, 498 (also see retention index)
Rice oil (see oil, rice)
Sample storage, 68-71
Saponification, 493 (see base, cleanup)
SASS train, 80 (also see source sampling)
Screening for interferences, 264
Screening for PCBs, 240-242, 259-264
Sediment, 311-312
  Analysis of, 56-58, 92-5, 120, 130, 133, 135, 161, 164, 168, 321, 324, 327-329
  Occurrence in, 24, 31, 33-35
  Sampling of, 85
Sewage sludge (see sludge)
Shellfish and other macroinvertabrates (also see fish), 119, 121, 130, 148
Silica gel, 57-60, 62, 119, 123-130, 143, 145, 147, 148, 157-158, 245, 246, 249, 250, 252, 325, 329, 413
Silicone oil (see oil, silicone)
SIMCA, 273-274, 499 (also see pattern recognition)
Size-exclusion chromatography (see gel permeation chromatography)
Sludge, 33, 37, 56-58, 91-92, 127, 154, 158, 164, 165, 168
Soap, 113
Soil
  Analysis of, 56-58, 92-95, 120, 127, 130, 133, 134, 161, 313
  Occurrence in, 24, 31, 35
  Sampling of, 85
Solid waste, 58
Sorbents (see alumina, carbon, Florisil, polyurethane foam, Tenax, and XAD)
Source sampling, 58, 59, 61, 62, 78-84, 96-97, 127, 158, 186, 260-261
Spills, 61
Stack gas (see source sampling)
Standards, 14-15, 289, 292, 310-312

MONS 005721

Steam distillation, 88, 95, 104, 105 (also see distillation)
Sulfuric acid, 57-60, 101, 109, 110, 122, 141, 147, 148, 155-158, 163, 167 (also see acid digestion)
Surface samples, 41, 85
Surrogate, 300-301, 494
Synthesis, 14-15
Tenax
  Air sampling, 72, 73, 75, 81
  Water sampling, 67, 68, 90
Thermal desorption, 93-94
Thin-layer chromatography, 59, 147-148, 242-247, 259, 265, 269, 299
TOCl (see total organic halide)
Total areas (quantitation), 57-60, 283, 287-288, 324-327
Total organic chlorine (see total organic halide)
Total organic halide, 260-262
TOX (see total organic halide)
Toxic Substances Control Act, 2, 45, 499
Transformer oil (see oil, transformer)
Ultraviolet spectra, 13, 299
Unintentionally generated PCBs (see by-product PCBs)
Vapor pressures, 10-13, 77-78
Vegetable oil (see oil, vegetable)
Voltametry, 257 (also see electrochemical properties)
Waste oil (see oil, waste)
Water
  Analysis of, 56, 57, 61, 88-90, 121, 122, 127, 131, 133, 154, 161, 293, 294, 321-322, 325-327
  Occurrence in, 24, 29-30, 35
  Sampling of, 63-71 (also see rainwater sampling)
Water solubility, 10, 461-468
Weathering, 272, 293-295 (also see environmental persistence and environmental transport)
Webb-McCall, 57-60, 282-286, 293, 324-327
Wipe samples (see surface samples)
X-Ray fluorescence, 264
XAD
  Air sampling, 71-75, 78, 80-84, 96, 97
  Water samling, 63, 66-68, 90-91
Yusho, 2, 25, 32-33, 39, 40, 42, 46, 48, 111, 113-114, 131, 494

MONS 005722

CRC

PCBs
and the
ENVIRONMENT

Volume I

John S. Waid

CRC PRESS

MONS 005723

PCBs and the Environment

Volume I

Editor

John S. Waid, D. Phil.(Oxford), F.I.Biol., M.A.S.M.
Chairman and Head
Department of Microbiology
La Trobe University
Bundoora, Victoria, Australia



CRC Press, Inc.
Boca Raton, Florida

MONS 005724

Library of Congress Cataloging-in-Publication Data

PCBs and the environment.

Includes bibliographies and indexes.
1. Polychlorinated biphenyls--Environmental aspects.
I. Waid, John S.
QH545.P6P236 1986 363.1'79 86-17549
ISBN 0-8493-5923-6 (v. 1)
0-8493-5924-4 (v. 2)
0-8493-5925-2 (v. 3)

This book represents information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Every reasonable effort has been made to give reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431

© 1986 by CRC Press, Inc.

International Standard Book Number 0-8493-5923-6 (v. 1)
International Standard Book Number 0-8493-5924-4 (v. 2)
International Standard Book Number 0-8493-5925-2 (v. 3)
International Standard Book Number 0-8493-5929-5 (set)

Library of Congress Card Number 86-17549
Printed in the United States

MONS 005725

THE EDITOR

John S. Waid, D.Phil.(Oxford), F.I.Biol., M.A.S.M., is Chairman and Head, Department of Microbiology, La Trobe University, Bundoora, Victoria, Australia, a position he has held since 1974. He also served as Dean of the School of Biological Sciences from 1977-1979.

Prior to his offices at La Trobe University, Professor Waid served in various capacities at the Grassland Research Institute; the Nature Conservancy; Levington Research Station, Fissons, Ltd.; University of New England, New South Wales; Cornell University; Reading University; and the University of Canterbury, New Zealand.

His experimental experience includes the post as joint editor of the proceedings and a convenor of an international symposium on the ecology of soil fungi held in Liverpool in 1968; initiator and Executive Editor of *Soil Biology and Biochemistry* from 1969 to the present; New Zealand delegate to the Committee on Microbial Ecology, International Association of Microbiology Societies (1972-1974); leader of the advisory team from New Zealand under the auspices of the Colombo Plan to review and report on science teaching at Khon Kaen University in northeast Thailand (1974); Victorian representative on the Standing Committee for Environmental Community Problems (SCENCOP) of the Australian Society for Microbiology (1975-1977); and the national representative for the Australian Society for Microbiology on the International Committee of Microbial Ecology (1979-present).

Professor Waid's research interests at present are root biology (in particular the decomposition of grass and legume roots and release of legume-nitrogen to the soil, a study which has been supported by ARGC grants since 1977) and polychlorinated biphenyls in the environment and their degradation. The PCB work has been supported by grants from the Rural Credits Development Fund (1976-1978), the Victoria Ministry for Conservation (1979-1989), and the Australian Marine Sciences and Technologies Advisory Committee (1980-1981). He has also had contracts with the Victoria Ministry for Conservation, and the Federal Department of Science and the Environment to review problems associated with PCBs and the monitoring of hazardous chemicals in the environment. He has made surveys of PCBs in soils and waterways on behalf of a government department, an urban authority, and a large industrial organization (all unnamed), and is consulted regularly on matters pertaining to PCBs by the Victoria Environment Protection Authority.

MONS 005726

CONTRIBUTORS

Elliot Atlas, Ph.D.
Associate Research Scientist
Department of Oceanography
Texas A & M University
College Station, Texas

Terry Bidleman, Ph.D.
Associate Professor
Department of Chemistry
Marine Science Program/Belle W
Baruch Institute for Marine Biology
and Coastal Research
University of South Carolina
Columbia, South Carolina

Thomas Cairns, Ph.D.
Department of Health and Human
Services
Food and Drug Administration
Office of Regulatory Affairs
Los Angeles, California

Sheng-Fu Chou, Ph.D.
Associate Organic Chemist
Geochemistry Section
Illinois State Geological Survey
Champaign, Illinois

D. W. Connell, M.Sc., Ph.D.
Reader
School of Australian Environmental
Studies
Griffith University
Nathan, Queensland, Australia

Gregory M. Doose
Department of Health and Human
Services
Food and Drug Administration
Office of Regulatory Affairs
Los Angeles, California

Jerry E. Froberg
Department of Health and Human
Services
Food and Drug Administration
Office of Regulatory Affairs
Los Angeles, California

C. S. Giam, Ph.D.
Professor
Department of Chemistry
Graduate School of Public Health
Department of Industrial
Environmental Health Sciences
University of Pittsburgh
Pittsburgh, Pennsylvania

R. A. Griffin, Ph.D.
Geochemist and Head
Geochemistry Section
Illinois State Geological Survey
Champaign, Illinois

Alan V. Holden
Manse Road
Moulin, Pitlochry, Scotland

Robert A. Jacobson
Department of Health and Human
Servies
Food and Drug Administration
Office of Regulatory Affairs
Los Angeles, California

John A. G. Roach
Mass Spectrometrist
CFSAN
Food and Drug Administration
Washington, D.C.

Brij L. Sawhney, Ph.D.
Soil Chemist
The Connecticut Agricultural
Experiment Station
New Haven, Connecticut

Glen R. Shaw, B. App. Sci.
Senior Chemist
Government Chemical Laboratory
Brisbane, Queensland, Australia

MONS 005727

Emil G. Siegmund
Department of Health and Human Services
Food and Drug Administration
Office of Regulatory Affairs
Los Angeles, California

Virginia F. Stout, Ph.D.
Research Chemist
Utilization Research Division
Northwest & Alaska Fisheries Center
National Oceanic and Atmospheric Administration
U.S. Department of Commerce
Seattle, Washington

Shinsuku Tanabe, Ph.D.(Agric.)
Assistant Professor
Department of Environment Conservation
Ehime University
Matsuyama, Japan

Ryo Tatsukawa, Ph.D.(Agric.)
Professor
Department of Environment Conservation
Ehime University
Matsuyama, Japan

MONS 005728

TABLE OF CONTENTS

Volume I

Chapter 1
Analytical Chemistry of PCBs 1
Thomas Cairns, Gregory M. Doose, Jerry E. Froberg, Robert A. Jacobson, and Emil G. Siegmund

Chapter 2
Chemistry and Properties of PCBs in Relation to Environmental Effects 47
B.L. Sawhney

Chapter 3
The Reliability of PCB Analysis 65
A.V. Holden

Chapter 4
Atmospheric Transport of PCB to the Oceans 79
E. Atlas, T. Bidleman, and C.S. Giam

Chapter 5
Solubility and Soil Mobility of Polychlorinated Biphenyls 101
S.F.J. Chou and R.A. Griffin

Chapter 6
Factors Controlling Bioaccumulation of PCBs 121
Glen R. Shaw and D.W. Connell

Chapter 7
Factors Controlling Bioaccumulation in Food Chains 135
G.R. Shaw and D.W. Connell

Chapter 8
Distribution, Behavior, and Load of PCBs in the Oceans 143
Shinsuke Tanabe and Ryo Tatsukawa

Chapter 9
What is Happening to PCBs? Elements of Environmental Monitoring as Illustrated by an Analysis of PCB Trends in Terrestrial and Aquatic Organisms 163
Virginia F. Stout

Chapter 10
Nonmetabolic Alteration of PCBs 207
John A.G. Roach

Index 215

MONS 005729

Volume II

Chapter 1
Polychlorinated Biphenyls: Accumulation and Effects Upon Plants ... 1
H.K. Mahanty

Chapter 2
Accumulation and Effects of PCBs in Marine Invertebrates and Vertebrates ... 9
G.C. Harding and R.F. Addison

Chapter 3
Accumulation and Effects on Birds ... 31
D.B. Peakall

Chapter 4
PCBs and the Environment: Perturbations of Biochemical Systems ... 49
Wilbert Gamble

Chapter 5
Uptake, Retention, Biodegradation, and Depuration of PCBs by Organisms ... 63
M.K. Hamdy and J.A. Gooch

Chapter 6
Modification of PCBs by Bacteria and Other Microorganisms ... 89
Kensuke Furukawa

Chapter 7
Effect of PCBs on Reproduction in Mammals ... 101
Gene B. Fuller and William C. Hobson

Chapter 8
Use of Organisms to Quantify PCBs in Marine and Estuarine Environments ... 127
David J.H. Phillips

Index ... 183

Volume III

Chapter 1
Differences Between Yusho and Other Kinds of Poisoning Involving Only PCBs ...
Takashi Kashimoto and Hideaki Miyata

Chapter 2
PCB Poisoning from Toxic Rice-Bran Oil in Taiwan ...
Paul H. Chen and Shu-Tao Hsu

Chapter 3
PCBs in Human Populations ...
Jos Mes

MONS 005730

Chapter 4
Polychlorinated Biphenyls in the Workplace
Alexander B. Smith and David P. Brown

Chapter 5
Disposal and Destruction of Waste PCBs
Jack D. Lauber

Chapter 6
The Great Lakes Ecosystem — Modeling of the Fate of PCBs
Robert V. Thomann, John P. Connelly, and Nelson A. Thomas

Chapter 7
PCBs in the Baltic Environment
Mats Olsson

Chapter 8
PCBs and the Environment: The Mediterranean Marine Ecosystem
Scott W. Fowler

Chapter 9
Case Study: The Australian Ecosystem
Bruce J. Richardson, Robert H. Smillie, and John S. Waid

Index

MONS 005731

Chapter 1

ANALYTICAL CHEMISTRY OF PCBs

Thomas Cairns, Gregory M. Doose, Jerry E. Froberg, Robert A. Jacobson, and Emil G. Siegmund

TABLE OF CONTENTS

I. Global Uses and Contamination 2
A. Industrial Applications 2
B. Need for Regulatory Controls 2
C. Implications in Trace Analysis 5
1. Composition 5
2. Analytical Sensitivity 5
3. Incurred Residues 5

II. Extraction and Sample Cleanup 5
A. Separation 5
B. Weathering and Metabolism 6

III. Chemical Characterization 7
A. Gas Chromatography 7
B. Gas Chromatography/Mass Spectrometry 14
C. Liquid Chromatography 17
D. Nuclear Magnetic Resonance 21

IV. Approaches to Quantitation 34

Acknowledgments 41

References 45

MONS 005732

I. GLOBAL USES AND CONTAMINATION

A. Industrial Applications

Although the synthesis of polychlorinated biphenyls (PCBs) was first described in 1881 by Schmidt and Schultz,[1] the potential industrial applications were not fully realized until about 1930. The increased use of PCBs as important industrial chemicals for use as nonflammable oils in a host of products gave birth to a series of commercially available raw materials marketed under various trade names: e.g., Aroclor® (Monsanto, U.S.), Clophen® (Bayer, West Germany), Phenoclor® (Caffaro, Italy), Kanechlor® (Kanegafuchi, Japan), Pyralene® (Prodelec, France), and Sovol® (U.S.S.R.) — to name a few. These mixtures of PCBs quickly gained wide acceptance in industrial products where nonflammability and heat-resistant properties were highly desired. For reference purposes, the Aroclor® series manufactured in the U.S. can be taken as representative of the range of PCB mixtures available on the world marketplace. Foreign counterparts had different names but their PCB content was very similar to an existing member of the Aroclor® series. This series of Aroclors® was sold under various Arabic number designations which reflected their relative compositions and physical properties (Table 1). In theory, the total number of possible compounds resulting from chlorination of the biphenyl nucleus is 209 (Figure 1). Molecular structural type was defined by the first two digits: 12 for PCBs, 25 and 44 for blends of PCBs and polychlorinated terphenyls (PCTs), and 54 for PCTs. The last two digits were an approximate estimate for the wt% of chlorine. Popularity in industrial applications of such materials as constituents of heat transfer systems, hydraulics/lubricants, transformers, capacitors, plasticizer applications, and petroleum additives catapulted U.S. domestic sales[1] of Aroclors® (1221 to 1268) from 32 million lb (14,515 t) in 1957 to almost 80 million lb (36,287 t) in 1970. The most popular blend was Aroclor® 1242 (18 million lb [8,165 t] in 1957 to almost 50 million lb [22,680 t] in 1970). Industrial applications involving transformers and capacitors were the leaders in usage pattern (29 million lb [13,154 t] in 1957 to almost 40 million lb [18,182 t] in 1969). This quantitative historical data has been deliberately limited to pre-1970 to provide a suitable backdrop for the environmental consequences that were to follow this intense growth in production and uses of PCBs.

B. Need for Regulatory Controls

Grave concerns about the environmental fate of such vast quantities of PCBs and their resultant toxicological effects were alerted by the first reported findings of PCBs in fish and wildlife by Jensen[4] in 1966. Soon it became glaringly obvious that the widespread popularity of PCBs in a somewhat uncontrolled fashion had eventually led to their environmental incorporation as persistent and ubiquitous contaminants on a global scale.[5-8] In the ecosystem, PCBs had become the most abundant of the chlorinated aromatic pollutants,[9] rivaling DDE. Sadly, indirect contamination by PCBs had eventually led to their presence in the food chain.[10-12]

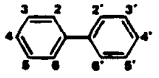
Shortly after Jensen's report of PCBs in 200 pike,[4] an unfortunate accident in Japan[13] in 1968 was a preview of similar events that would occur in the U.S. during the next decade. PCBs had accidentally leaked from a heat exchanger used in the production of rice oil. Resultant levels of PCBs in the rice oil, when ingested, produced a spectrum of adverse symptoms: chloracne, discoloration of the gums and nailbeds, swelling of the joints, waxy secretions of the glands in the eyelids, as well as more general manifestations such as lethargy and joint pain. Perhaps it was this single historical event rather than the widespread environmental contamination reported in the scientific literature that prompted regulatory intervention. The U.S. Food and Drug Administration (FDA) initiated a national survey to determine the exact extent and levels to which PCBs might have made their way into the food chain by indirect use of PCB contaminated animal feed, industrial and environmental

MONS 005733

Table 1
GENERAL PHYSICAL AND TOXICOLOGICAL PROPERTIES OF VARIOUS AROCLORS[a,b]

Aroclor[a] no.	Form	Sp. gravity	Distillation range (°C)	Rats oral LD_{50} (mg/kg)	Rabbits skin MLD (mg/kg)
1221	Clear, mobile oil	1.182—1.192	275—320	3.980	>2.000
1232	Clear, mobile oil	1.270—1.280	290—325	4.470	>1.260
1242	Clear, mobile oil	1.381—1.392	325—366	8.650	>794
1248	Clear, mobile oil	1.405—1.415	340—375	11.000	>794
1254	Light yellow viscous oil	1.495—1.505	365—390	11.900	>1.260
1260	Light yellow, soft sticky resin	1.555—1.566	385—420	10.000[c]	>1.260[c]
1262	Light yellow sticky viscous resin	1.572—1.583	395—425	11.300[c]	>1.260[c]
1268	White to off-white powder	1.804—1.811	435—450	10.900[c]	>2.510[c]

[a] Administered as 50% solution in corn oil.
[b] 10% solution in corn oil.



Chlorine Substitution	Number of Possible Isomers
Mono-	3
Di-	12
Tri-	24
Tetra-	42
Penta-	46
Hexa-	42
Hepta-	24
Octa-	12
Nona-	3
Deca-	1
Total:	209

FIGURE 1. Number of possible isomers of PCBs.

sources, and the use of PCB-containing paper food-packaging materials. This extensive survey finally resulted in a "Notice of Proposed Rule Making"[14] to limit the level of PCBs in foods containing unavoidable residues from environmental and industrial sources. It was interesting to note that of the animal feed samples analyzed less than 5% contained PCBs (0 to 0.6 ppm). Several accidents similar to the "Yusho" incident had, however, directly

MONS 005734

Table 2
FDA TOLERANCES FOR PCBs IN SEVERAL CLASSES OF FOOD

Product	Concentration (ppm) 1973	1979
Milk & dairy products (fat basis)	2.5	1.5
Poultry (fat basis)	5.0	3.0
Eggs	0.5	0.3
Fish & shellfish (edible portion)	5.0	5.0*
Infant & junior foods	0.2	0.2
Feed for food producing animals	0.5	0.2
Animal feed components including fishmeal & other by-products of marine origin	5.0	2.0
Paper food packaging materials intended for or used with human food	10.0	10.0

* A regulation establishing a new level of 2 ppm was promulgated but was stayed on October 5, 1979 until further notice.

contaminated animal feed and subsequently the poultry and eggs intended for human consumption. Other parts of the survey indicated that the use of PCB-containing coatings on the inner walls of grain silos had been responsible for PCB residues in milk[15] derived from dairy cows who fed on the grain stored in such silos. Results on food packagings were revealing; 67% of the samples tested contained PCBs with the highest value found being 338 ppm, and of these samples only 19% of the actual food contained in such packages contained PCBs at the maximum level of 0.1 ppm. A parallel survey of infant food packaged cereals found PCBs in 75% of the samples tested with an average concentration of 0.3 ppm and a maximum concentration of 1 ppm. In spite of the scanty quantitative knowledge of the toxicological effects of PCBs in 1973, the FDA concluded that it would be in the interest of the public health to reduce human low-level exposure to PCBs by limiting the ways in which PCBs might enter the food chain as well as limit the levels of PCBs in food containing unavoidable residues from environmental or industrial sources by the establishment of temporary tolerances (Table 2) until such time as additional toxicological data might cause reconsideration.[16] In this interim period, domestic production of PCBs in the U.S. declined drastically to below 10 million lb (4535 t). The age of unpopularity of PCBs as industrial chemicals had arrived. However, their popularity for scientific inquiry was spectacular. Seemingly, the concern about the ubiquitous distribution of PCBs in the ecosystem prompted a multitude of additional evidence to emphasize their prevalence as global contaminants.[17-26] Uppermost in this massive scientific probe was the need to increase awareness of the potential toxicity of PCBs. By 1975, the EPA responded to this new wealth of data by sponsoring a "National Conference on PCBs"[27] at which the FDA announced it had initiated a review of the appropriateness of the 1973 temporary tolerances. After such a review the FDA proposed to reduce the temporary tolerances[28] for unavoidable residues of PCBs in several classes of food. Interested parties likewise responded with over 100 comments being received for consideration before final disposition. The FDA Commissioner then issued a final order reducing PCB tolerances (Table 2) through publication of his responses and reasons for adoption of these new reduced tolerances.[29]

Since part of the problem with PCBs was the vulnerability of food and feed commodities to direct contamination through accidental causes, the EPA issued rules governing the continued deployment of PCBs in certain industrial applications. These regulatory controls

MONS 005735

were made under the Toxic Substances Control Act of 1976 and proposed the discontinued use of PCBs in heat transfer systems in plants manufacturing or processing food, drugs, and cosmetics. An interagency alert notice[10] was then issued by the EPA to urge voluntary compliance in removal of equipment containing PCBs and replacement with non-PCB units to prevent food contamination.[11]

C. Implications in Trace Analysis

In any attempt to extract, separate, and identify trace levels of PCBs from a wide variety of matrices several major problem areas must first be fully understood. The analytical problems encountered in dealing with PCBs have recently been reviewed by Cairns and Siegmund.[12]

1. Composition

The complications induced by analyzing mixtures of PCBs rather than any single specific isomer have probably contributed the most serious impediment to both identification and quantification. Although the theoretical calculations establish 209 possible congeners, the actual number of major components in Aroclor® 1254, for example, by capillary GC[13] was only 19 (69 eluting peaks, 50 represented minor constituents). Parallel studies using packed columns[14] have demonstrated elution profiles with less than 20 discernible peaks.[15] In analytical terms, this problem can be summed up as having to deal with a potential group of compounds within the mol wt range 188 to 494 daltons possessing vastly different chemical and physical properties.

2. Analytical Sensitivity

Halogen-sensitive chromatographic detectors such as the Hall electrolytic conductivity detector (HECD) and the electron capture detector (EC) are now capable of detection in the subnanogram range and offer the residue chemist a convenient analytical approach[16] when dealing with trace levels of PCBs (below 1 ppm). Added confirmation of residue levels by gas chromatography/mass spectrometry (GC/MS) often must employ multiple ion detection (MID) techniques[17] to achieve the necessary and parallel level of sensitivity of such GC detectors. Other analytical techniques such as nuclear magnetic resonance (NMR)[18] and liquid chromatography with UV detection[19] do offer alternative methods for analysis but can only be successfully applied where the suspected concentration level of PCBs is in excess of 1000 ppm.

3. Incurred Residues

Perhaps the most serious problem in identifying PCB residues from environmental samples is the inability to correlate the results with a known reference standard.[46] In spite of the availability of a wide range of reference materials, the EC/GC elution profiles obtained from samples containing PCBs do not always match directly. Although a number of reasons have been advanced (see Section III) for this phenomenon, the challenge experienced by the analytical chemist is often met by employing an auxiliary technique such as GC/MS or HE/CD which can assist in the judicious choice as to which reference standard most closely resembles the elution profile detected in the actual sample. The analyst in this arena must clearly develop a high degree of skill in the application of these types of methodologies by acquiring an ability to interpret elution profiles correctly, particularly if quantitation is required.

II. EXTRACTION AND SAMPLE CLEANUP

A. Separation

Jensen's historical breakthrough in 1966 of the first confirmed report[4] of PCBs in fish

MONS 005736

and wildlife was made after repeated and somewhat frequent encounters of similar GC elution patterns while routinely analyzing for DDT and other chlorinated pesticides. Indeed, the earlier failures to properly recognize this PCB presence must surely have contributed to the overestimation of DDT and TDE in the environment. The noticeable shift in emphasis to PCBs after 1966 reversed the roles almost overnight and PCB residues were then described to have interferences from a wide variety of organochlorine pesticides. Use of a halogen-sensitive GC detector such as EC in conjunction with a nonpolar stationary phase such as OV-101 or SE-30 had resulted in interferences with DDT, DDD, and DDE as well as early eluting pesticides such as BHC isomers, aldrin, heptachlor, and heptachlor epoxide because of similar retention times. Dependent upon the matrix selected for analysis, three distinct analytical protocols emerged involving either no prior separation, separation via column chromatography, or separation with destruction or conversion of interfering compounds.

In the case of fatty foods (milk, cheese, fish), the officially adopted method by the regulatory agencies[41] involved petroleum ether extraction of the fat (3 g) followed by residue partitioning into acetonitrile, dilution with water, re-extraction into petroleum ether, and finally column chromatography on Florisil® with 6% ethyl ether in petroleum ether. Additional cleanup procedures have also been devised to permit separation of DDT and its analogues from some of the PCBs.[42] Masumoto[43] has pointed out, however, that such procedures can be flawed by various experimental factors which cause variability in column preparation and hence recoveries. Additionally, those congeners with the lowest chlorination were held on the silicic acid column and could only be eluted by a more polar solvent than petroleum ether.

Lower recoveries with the less chlorinated residues were demonstrated. This methodology has also been miniaturized to analyze PCBs in fish.[44] Similar approaches have been developed to efficiently separate PCBs from such organochlorine pesticides as DDT and toxaphene,[45] heptachlor epoxide, lindane, and dieldrin.[46] In the analysis of paper and packaging, advantage of the chemical stability of PCBs to treatment with alkali[47] was optimized in devising a procedure based on extraction by refluxing with alcoholic KOH followed by an abbreviated cleanup. Sequential use of the alkaline hydrolysis and oxidation with chromic acid/acetic acid converted DDE and DDT to the respective dichlorobenzoquinones[48-50] and left the PCBs unchanged for analysis by EC/GC. Various other techniques have been described in the literature for the separation of PCBs from DDT and its analogues by similar approaches involving chemical derivatization and column chromatography.[51-54] Thin layer chromatographic procedures[55,56] were also developed to analyze PCBs in the presence of DDT, but lacked the specificity to distinguish the source of contamination.

B. Weathering and Metabolism

Previous mention has already been made to the fact that GC elution profiles observed experimentally by EC for PCB residues in biological samples[57-59] very often do not resemble in any recognizable way the profile for one of the many standard reference materials. This observation could be due to two main processes, metabolism and/or degradation. Dechlorination, arene oxide formation, and hydroxylation have already been identified as metabolic pathways for PCBs.[60-61] The main ramification of dechlorination to lesser chlorinated congeners is that it will tend to contribute to the production of an elution profile suggestive of a lower chlorinated reference standard and lead to confusion in the choice of the most suitable standard. However, the more serious consequence is the preferential removal from the PCB GC profile of certain congeners which have undergone metabolic hydroxylation. Such chlorobiphenylols do not exhibit the same chemical characteristics as their parent moieties and therefore do not co-extract and/or co-elute with the sample preparation and cleanup techniques adopted for routine analysis. Metabolic processes in biological samples can therefore complicate the assignment of PCB residues to contamination by a primary commercial product.

MONS 005737

Additionally, the extraction and cleanup procedures might introduce a minor complication in that the attempt to solvent partition the various congeners as a single chemical entity is regarded as a compromise.

III. CHEMICAL CHARACTERIZATION

Because of the large number of standard reference materials available throughout the world, the following subsections are the first attempt in the scientific literature to provide a comprehensive library of elution profiles and patterns obtained by those analytical techniques both in common use as well as practiced by specialized laboratories. It must be stressed that not all these techniques can be employed for trace analysis work. However, the range and sensitivity of the analytical methods exhibited here should assist the reader in selecting a suitable reference standard and an analytical approach relative to their current problem. The wealth of data to be presented is somewhat overwhelming but serves to emphasize the magnitude of the problems of analyzing for PCB residues. Although the relative sensitivity of the various techniques are illustrated, the information offered is to be considered qualitative. A full discussion of the experimental approaches to quantitation will be presented in Section IV.

A. Gas Chromatography

Three GC detectors have been extensively employed in the analysis of PCBs in environmental and biological samples: namely, electron capture (EC), Hall electrolytic conductivity detector (HECD), and flame ionization detection (FID).[57] While the first two are sensitive to chlorine and are used mainly for trace work, the continued use of FID is still in practice where samples have a high concentration of PCBs. Clearly the advantages of both EC and HECD are that they are halogen sensitive and essentially ignore the majority of other sample components that have been co-extracted provided they are nonhalogen-containing entities. In the case of EC, sample cleanup is usually required to avoid detection of other electron capturing species present from the sample matrix. This is not the case with FID and sample extracts require extensive cleanup before analysis to avoid possible interferences from endogeneous components of the sample matrix. However, with EC as the detecting system for chlorinated aromatic samples such as PCBs, the main disadvantage is that of differences in response, i.e., highly dependent on the degree and location of chlorination. Detector responses have been shown to vary as much as two to four orders of magnitude between mono- and polychlorinated species.[58] The EC responses to 1 ng injected on the same GC column of five selected dichlorobiphenyls is illustrated in Figure 2. Dependent on the relative location of the two chlorine atoms on the biphenyl nucleus, a wide range of detector responses were obtained illustrating the marked differences within the same molecular weight group. This situation is disturbing because the reference standards are employed as standards for quantitation and the proper selection is dependent on the closest match to the incurred sample profile. Disproportionality of response with EC has been the main feature of criticism concerning analysis of several homologous series such as toxaphene,[59] strobane,[60] chlordane,[61] dibenzodioxins and dibenzofurans,[61] PCTs,[62] and PCBs.[63] Whereas EC responds to all electron capturing species, the HECD in the case of PCBs offers a direct measure of the HCl produced by the various congeners as they elute, i.e., proportional to Cl content. Therefore, it is not surprising that the elution profiles produced by EC and HECD for the same sample will be different. Both these detectors, however, offer high sensitivity and are capable of providing routine and reliable results. On the other hand, the responses of the FID are directly related to thermally excited ions produced in a hydrogen-air flame, i.e., a function of the number and type of burnable carbon atoms in the molecule. Response differences are most noticeable for the lowest members of a homologous series such as the

MONS 005738

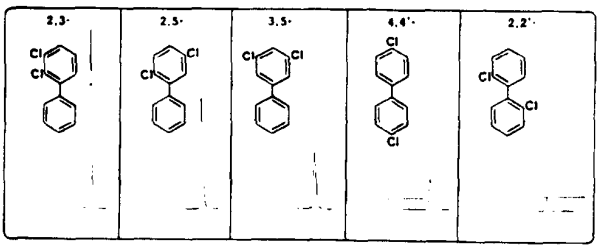


FIGURE 2. EC responses for 1 ng injected on column of selected PCBs. 2% OV-101, 125 cm × 2 mm I.D. 180°C, attenuation 16 ×

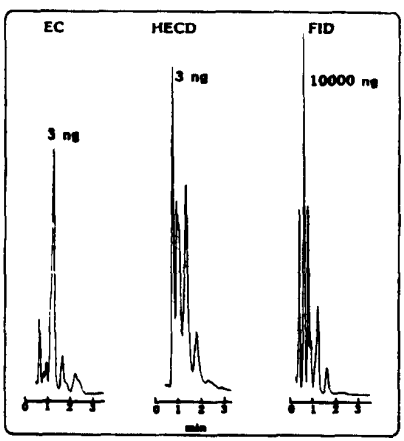


FIGURE 3. GC detector response profiles for Aroclor® 1221 together with amounts injected on-column.

PCBs. In terms of relative sensitivity, both EC and HECD demonstrate a level usually three orders of magnitude greater than that observed with FID.

With this informational background as to the utility of these various GC detectors, a tripartite graphical approach has been adopted to convey the various elution profiles obtained from 15 PCB standard reference materials and three PCTs (Figures 3 to 20). Standard operating conditions were employed throughout this series of experiments to provide comparative data: 2% OV-101, 120 cm × 2 mm I.D., 200°C isothermal, 40 mℓ/min argon/methane. To permit reproduction and/or extrapolation to other systems the elution times

MONS 005739

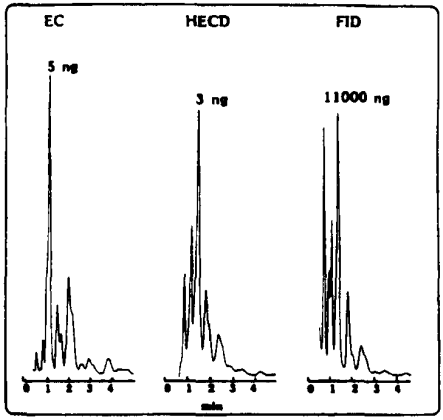


FIGURE 4. GC detector response profiles for Aroclor® 1232 together with amounts injected on-column.

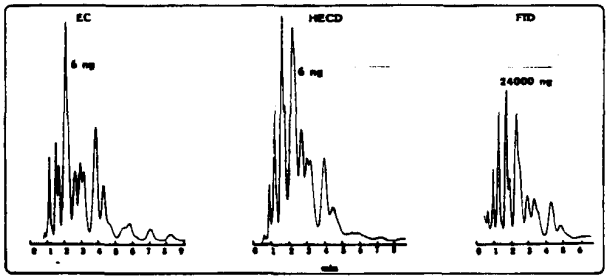


FIGURE 5. GC detector response profiles for Aroclor® 1242 together with amounts injected on-column.

under these selected conditions for aldrin, *p,p*-DDE, and *p,p*-DDT were 6.5, 8, and 13.5 min, respectively. Furthermore, standard reference materials from different manufacturing sources which resemble each other have been conveniently grouped together for discussion purposes. It is hoped that the illustration of all three elution profiles to describe each reference material (Table 3) will facilitate the choice of the most suitable one to describe the incurred residue.

In viewing this data base, it is clear that each detector has provided a response pattern entirely different from its two companion detectors. As previously stated, this experimental

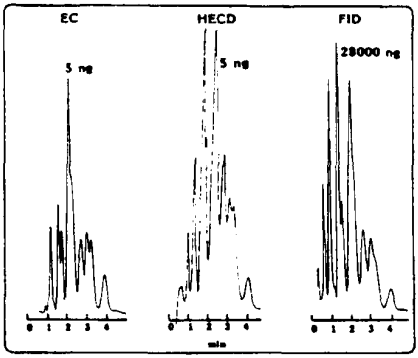


FIGURE 6. GC detector response profiles for Aroclor® 1016 together with amounts injected on-column.

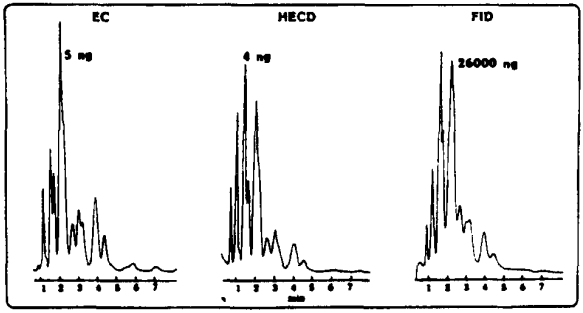


FIGURE 7. GC detector response profiles for Clophen® A-30 together with amounts injected on-column.

evidence is not that surprising since each detector has a different criterion for detection. However, it is reassuring to know that from an examination of these profiles we can conclude which reference materials are equivalents. While it might be difficult to select a suitable standard from a single detector elution profile, the additional information from a second and even third detector should make the task easier. Another factor in the posidetermination of the nature of the PCB residue is the retention time of the elution profile. As the retention time increases so does the degree of chlorination encountered.

A number of additional observations are worthy of mention. While the three GC detector profiles are distinctly different at low levels of %Cl, the responses recorded for HECD and

MONS 005741

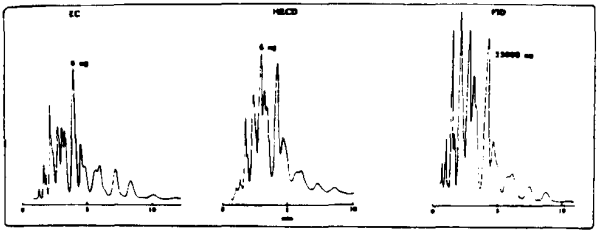


FIGURE 8. GC detector response profiles for Aroclor® 1248 together with amounts injected on-column.

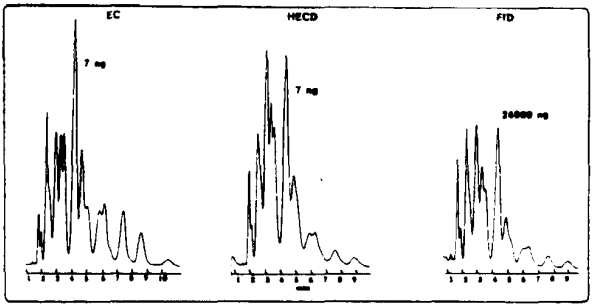


FIGURE 9. GC detector response profiles for Clophen® A-40 together with amounts injected on-column.

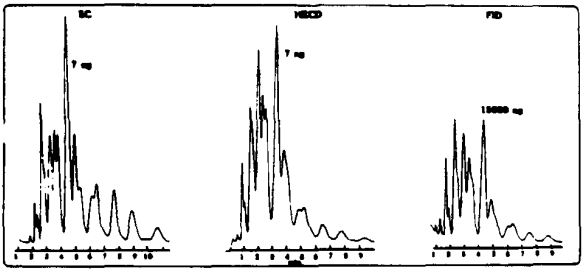


FIGURE 10. GC detector response profiles for Kanechlor® 400 together with amounts injected on-column.

MONS 005742

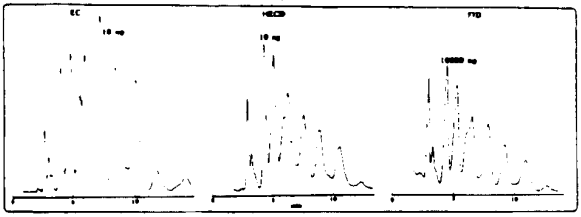


FIGURE 11. GC detector response profiles for Aroclor® 1254 together with amounts injected on-column.

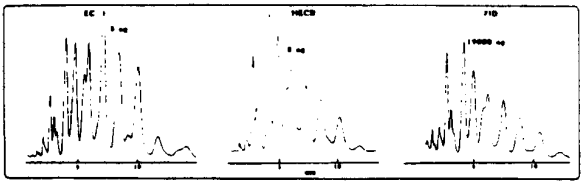


FIGURE 12. GC detector response profiles for Clophen® A-50 together with amounts injected on-column.

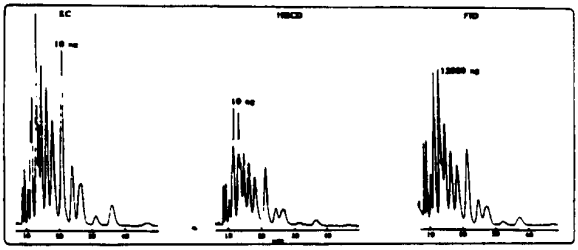


FIGURE 13. GC detector response profiles for Aroclor® 1260 together with amounts injected on-column.

FID begin to look similar at %Cl values greater than 48 (Figures 11 to 17). In only one case (Aroclor® 1268, Figure 17) did all three elution profiles match. This observation might not be that significant in that at this level of chlorination, only a few congeners are possible and with the high degree of chlorine substitution, disproportionality of response, etc., becomes a relatively unimportant matter to consider. The remaining Aroclors® (Figures 18 to 20) were PCTs and elution profiles varied little between detectors because of the high degree of chlorination. Perhaps the most enlightening value of this data base is the amount of material injected under FID conditions to match the responses recorded for both EC and HECD.

MONS 005743

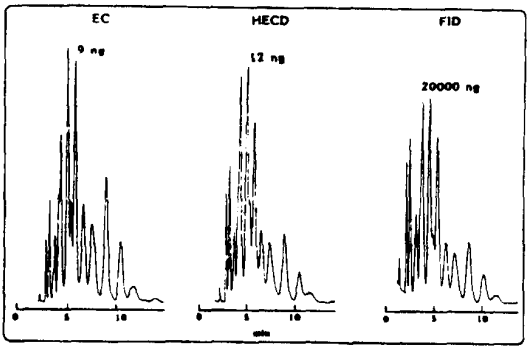


FIGURE 14 GC detector response profiles for Clophen® A-60 together with amounts injected on-column.

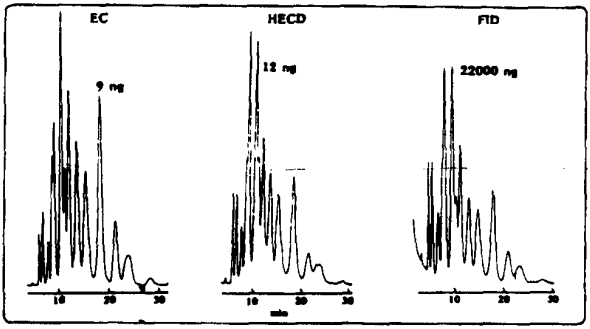


FIGURE 15. GC detector response profiles for Pyralene® 6000 together with amounts injected on-column.

In summary, the potential value of all three detectors for identifying PCBs in residue work as well as a description of the possible source of origin is now documented. This data base in graphical format should assist the analytical chemist to make the proper choice of a suitable standard reference material when quantitation is required. Where the incurred residue is in the low parts per million range, only EC and HECD can provide the necessary level of sensitivity required for detection. While the incurred residue profiles may not always bear an exact resemblance to one of the standard reference materials presented here, a choice can be made as to which is the most appropriate.

MONS 005744

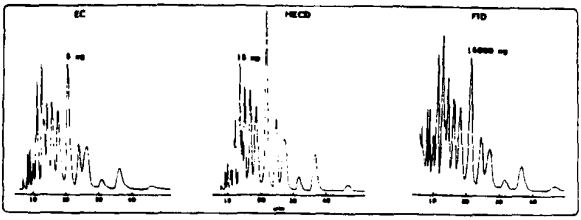


FIGURE 16. GC detector response profiles for Aroclor® 1262 together with amounts injected on-column.

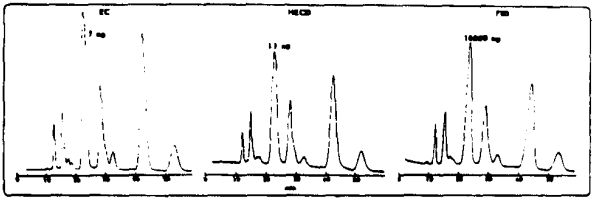


FIGURE 17. GC detector response profiles for Aroclor® 1268 together with amounts injected on-column.

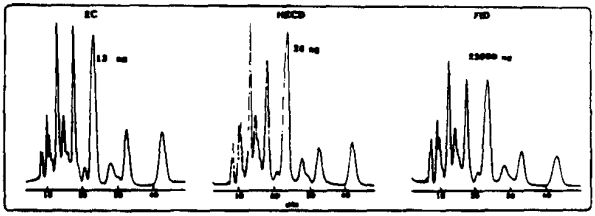


FIGURE 18. GC detector response profiles for Aroclor® 4465 together with amounts injected on-column.

B. Gas Chromatography/Mass Spectrometry

The analytical pitfalls or difficulties that can arise when using GC with one of the detectors mentioned above have led to the increased application of mass spectrometry to help resolve difficult identification problems. In particular, confirmation of incurred residues[67-69] has often been provided by GC/MS where full use is made of the isotopic distribution of chlorine (75.53% ^{35}Cl and 24.47% ^{37}Cl) in identifying ion clusters corresponding to certain degrees of chlorination.[70]

The electron impact (EI) spectra of PCBs have been previously studied in detail by Safe and Hutzinger[68,69] who concluded that the fragmentation scheme of the PCB congeners

MONS 005745

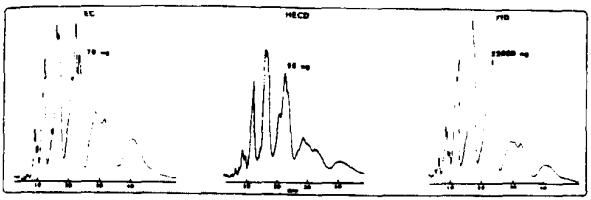


FIGURE 19 GC detector response profiles for Aroclor® 5432 together with amounts injected on-column

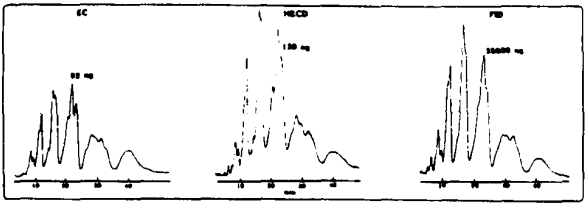


FIGURE 20. GC detector response profiles for Aroclor® 5442 together with amounts injected on-column.

was predominantly successive expulsion of chlorine atoms. This fragmentation pattern of PCBs made it difficult to distinguish the various molecular weight groups that might occur within an eluting peak. A recent study of the methane (CH_4) chemical ionization (CI) spectra of PCBs by Cairns and Siegmund[43] indicated that very little fragmentation took place (Figure 21). There was some evidence to suggest a minor population (less than 2%) of ions corresponding to the loss of HCl from the protonated molecular species which might be misinterpreted as belonging to the next lower homolog. Since the protonated molecular ions (MH^+) were the most abundant in the spectra whatever the degree of chlorination, a method of analysis involving the ions corresponding to chlorine content (in essence, molecular weight plus 1 dalton) was possible. It was found that responses from individual members of each molecular weight group were identical (within 5%) but decreased between molecular weight groups with increasing molecular weight, i.e., sensitivity of detection decreased with increasing molecular weight. This decrease in sensitivity of detection on going from mono- to hexachlorobiphenyl (1:0.4) was rationalized in terms of the availability of additional sites of protonation on the aromatic nucleus when only one or two chlorines were present. Since PCBs on CI produced almost entirely molecular ion clusters, an experimental approach was then devised involving monitoring only those ions corresponding to the different levels of chlorination. The resulting ion profiles obtained were found to be highly characteristic in providing differentiation for the various Aroclors®.

In keeping with the format established above for EC/HECD/FID (Figures 7 to 20), the necessary GC/MS information obtained under CI conditions has been compiled to add to that library of data. To provide a perspective view of the GC/MS data all the total ion current (TIC) profiles were obtained under identical conditions (Figures 22 to 24): 3% SP2100, 120 cm × 2 mm I.D., 190 to 250°C at 20°C/min, 30 mℓ/min methane. These elution profiles

Table 3
LOCATION OF GC ELUTION PROFILES ON REFERENCE STANDARDS

Reference standard	%Cl content	GC data* (EC/HECD/FID)
Aroclor® 1221	21	Figure 3
Aroclor® 1232	32	Figure 4
Aroclor® 1242	42	Figure 5
Aroclor® 1016		Figure 6
Clophen® A-30		Figure 7
Aroclor® 1248	48	Figure 8
Clophen® A-40		Figure 9
Kanechlor® 400		Figure 10
Aroclor® 1254	54	Figure 11
Clophen® A-50		Figure 12
Aroclor® 1260	60	Figure 13
Clophen® A-60		Figure 14
Pyralene® 6000		Figure 15
Aroclor® 1262	62	Figure 16
Aroclor® 1268	68	Figure 17
Aroclor® 4465 (PCBs + PCTs)	65	Figure 18
Aroclor® 5432 (PCTs only)	32	Figure 19
Aroclor® 5442 (PCTs only)	42	Figure 20

* All data generated under standard recording conditions to permit direct comparisons: electron capture (EC), Hall electroconductivity detector (HECD), and flame ionization detector (FID). The amount injected on column is displayed in each figure at the same attenuation factor of the recorder.

when compared to the GC data do not bear any strong resemblance to the previous elution patterns obtained by EC or HECD. However, the resemblance between FID and GC/MS-CI-CH_4 is established. Presumably the criterion for detection in both these cases runs parallel. Once again, the ability to group certain standards as equivalents (Table 3) has been demonstrated by observing similar elution profiles. The close similarity between Aroclor® 1262 and Aroclor® 1260 (Figure 22) is a reflection of the inability of GC/MS-CI-CH_4 to distinguish between such a small %Cl difference. As with the EC/HECD/FID data for Aroclor® 1268 (Figure 17) the GC/MS data (Figure 22) are a perfect profile match to all three detectors for the same reasons previously outlined. Besides this ability to distinguish standards via TIC profiles, the retention time ranges involved must not be totally forgotten as an additional criterion for identification. The higher chlorinated Aroclors® have larger ranges of retention time. While the GC data previously presented were based on a column temperature of 190°C, a temperature programming approach had to be adopted for GC/MS to provide the necessary peak widths (time for about 10 scans) for total ion detection (*m/z* 80 to 500) as well as completing the analysis within 10 min. To achieve these profiles illustrated in Figures 22 to 24, the amount injected on column was in the range of 3 to 7 μg, i.e., two orders of magnitude greater than that employed for EC or HECD. While it is not anticipated that this particular mode of detection (i.e., TIC over *m/z* 80 to 500) will be used in actual sample analysis, these basic profiles do serve as the primary data source in understanding the mass chromatograms that can be extracted from the data collected. In simple terms, a mass chromatogram is a computer-assisted technique that searches the total data collected and plots out only the responses recorded for the particular single *m/z* value requested. In the case of PCBs, this is a very useful technique since CI conditions produce only protonated molecular ions. Therefore, by specification of the *m/z* values corresponding to protonated

MONS 005747

molecular ions of biphenyl, monochlorobiphenyl, dichlorobiphenyl, trichlorobiphenyl, tetrachlorobiphenyl, pentachlorobiphenyl, hexachlorobiphenyl, heptachlorobiphenyl, and octachlorobiphenyl (155, 189, 223, 257, 293, 327, 361, 395, and 431, respectively) the total ion current can be subdivided to give maps of the composition of each eluting peak by molecular weight or chlorine content (Figures 25 to 33). This process can be considered as providing a second dimensional analysis of the TIC. Such mass chromatograms are very revealing in that they provide an instant visual representation of the composition of each Aroclor® by molecular weight. The ability to perform such mass chromatograms has increased the power of the GC/MS-CI-CH_4 data to the extent of providing unambiguous proof of identification as well as possible origin of contamination. In actual analysis of residue samples, however, the technique employed is to scan only for those ions of interest thereby achieving the level of sensitivity equivalent to that of EC or HECD.

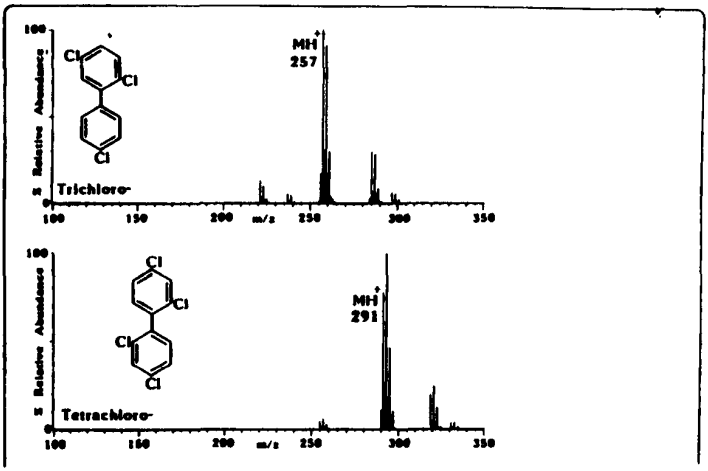
C. Liquid Chromatography

While liquid chromatography (LC) has been demonstrated to be particularly useful in the analysis of thermally labile compounds, its potential utility in PCB analysis has been reported by only a few investigators.[9,71,72] At the present time, two LC techniques have been used to analyze PCB samples — adsorption liquid solid chromatography (LSC) and reversed-phase liquid liquid chromatography (RPLC). Aitzetmuller,[73] Brinkman et al.,[74] and Chiosi et al.[75] all favored the application of LSC since the observed elution patterns of PCBs were the reverse order of that observed both in GC with nonpolar stationary phases and RPLC, i.e., order of elution was according to decreasing chlorine content. With this technique, DDT and its analogues were separated from PCBs and hence removed the need for chemical separation before analysis. However, the resultant elution profiles illustrated poor separation of the congeners making assignment of the possible source of contamination difficult. Dry hexane[76] was used to increase resolution of the elution profile requiring additional analysis time and at the same time destroying the advantage of DDT separation from PCBs. On the other hand, Kirkland[78] favored RPLC for the nonpolar congeners. Sieber[72] has shown that RPLC can be used to assign individual chlorinated biphenyls to the certain reference standards.

In the continuing effort to provide extensive graphical documentation on elution profiles, the solvent system (5% water in methanol with ODS column) was deliberately chosen for direct transfer to liquid chromatography/mass spectrometry (LC/MS) using a moving belt interface.[79] Elution patterns obtained in this manner are illustrated in Figures 34 to 37 and can be considered similar to the GC elution profiles illustrated in the previous sections. Such elution patterns are in general agreement with those obtained by Sieber[72] and demonstrate decreased solubility in the mobile phase solvent for increasing molecular weight. As with GC/MS, deployment of SIM techniques (Figures 38 and 39) can be useful in determining the composition by degree of chlorination, thereby assisting in the proper assignment of source of contamination whenever possible. Additionally, the use of SIM is able to selectively ignore the presence of DDT and its analogues eliminating the disadvantage reported by those workers favoring LSC. The most widely used ultraviolet (UV) detector unfortunately requires extensive sample cleanup before analysis. Cairns et al.[79] have already demonstrated that LC/MS-SIM can eliminate the need for sample cleanup prior to quantitative analysis. However, one disadvantage continues to plague LC and LC/MS. Operating sensitivity is often two orders of magnitude lower than that experienced with EC or HECD. With the advent of modern detectors such as the photoconductivity detector (PCD), some of these sensitivity problems should begin to disappear.

In conclusion, LC has the potential to become an additional powerful analytical tool in the hands of the residue chemist. It is already established as a confirmatory technique in the absence of MS, but lacks sufficient sensitivity to compete with EC or HECD in residue analysis.

MONS 005748


100
% Relative Abundance
Cl
Cl
Cl
MH+
257
Trichloro-
0
100
150
200
m/z
250
300
350
100
% Relative Abundance
Cl
Cl
Cl
Cl
MH+
291
Tetrachloro-
0
100
150
200
m/z
250
300
350

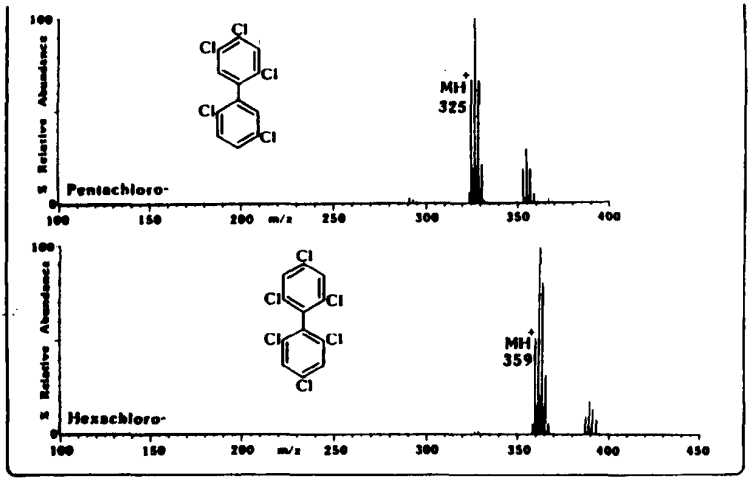


FIGURE 21 Chemical ionization mass spectra (CI/MS) of selected PCB isomers.

MONS 005750

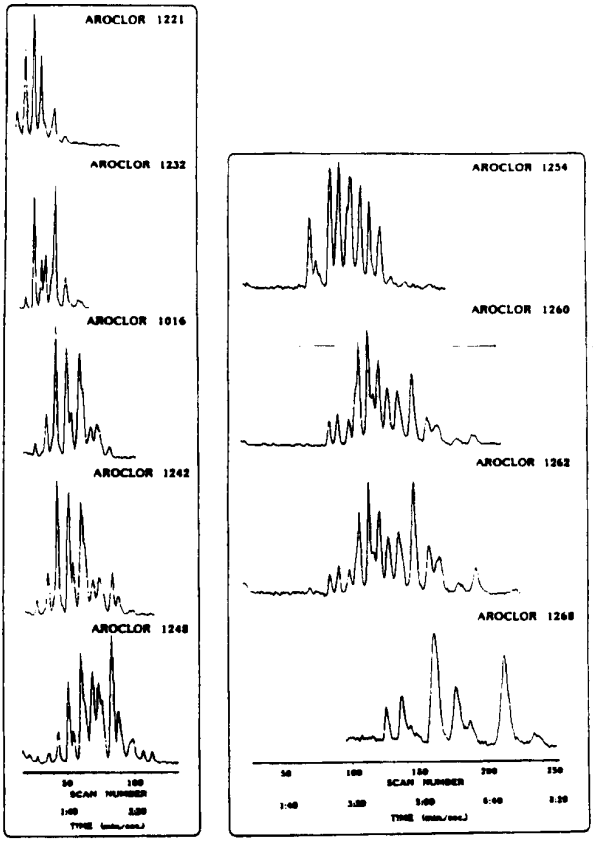


FIGURE 22. Total ion current profiles for Aroclors® under GC/MS-CI-CH_4.

MONS 005751

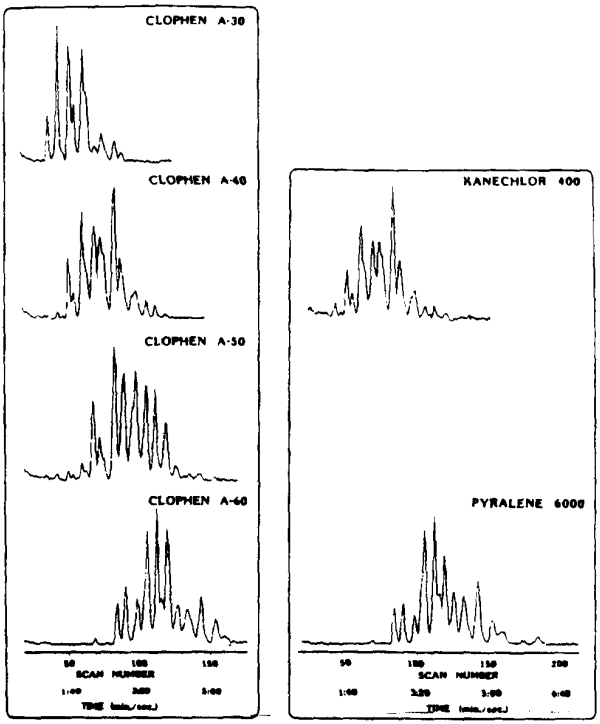


FIGURE 23. Total ion current profiles for commercial PCBs manufactured outside the U.S.

D. Nuclear Magnetic Resonance

Although the acknowledged sensitivity of nuclear magnetic resonance (NMR) is much less than that demonstrated for chromatographic and mass spectrometric methods, it can function as a powerful analytical tool in providing data on molecular structure, electronic charge distribution, and molecular interactions. The first report of an attempted identification of PCBs by proton NMR was conducted at 60 MHz.[80] This study concluded that in the absence of reference standards of the individual congeners, identification of certain specific isomers belonging to the PCB family was possible based on a priori arguments involving chemical shifts and coupling constants. In fact, the higher chlorinated congeners were the simplest to identify based on the small number of coupled protons expected in such structures. Welti and Sissons[81] then reported proton NMR data at 220 MHz for a large number of PCBs

MONS 005752

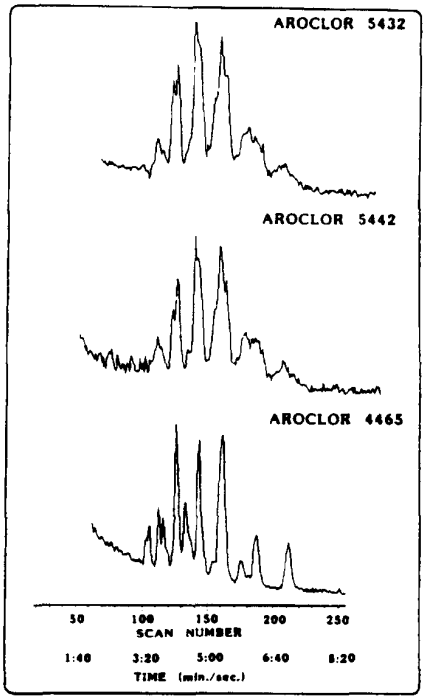


FIGURE 24. Total ion current profiles for polychlorinated terphenyls.

isolated from commercial standards such as the Aroclors®. This work fortified the preliminary studies by Bartle[80] and permitted less complicated spectral analysis. Symmetrically substituted dihalobiphenyls were extensively studied by Tarpley and Goldstein[82] who were able to account for chemical shifts in 2,2'-dichlorobiphenyl by application of an additivity scheme based on chlorobenzene and biphenyl. With technological advancements in instrumentation and the availability of Fourier transform (FT), studies were naturally then extended to the application of ^{13}C NMR to PCBs. Wilson and Anderson[83] reported the ^{13}C and ^{1}H NMR spectra for ten symmetrically substituted chlorinated biphenyls. These authors were able to predict the ^{13}C shieldings with reasonable precision from additive substituent parameters on benzene. Additional data on ^{13}C shieldings was then measured by Wilson[84] for 25 chlorinated biphenyls. Assignment of the protonated carbon atoms in 13 compounds was confirmed by selective proton coupling. Using additive procedures derived from data on chlorobenzene

MONS 005753

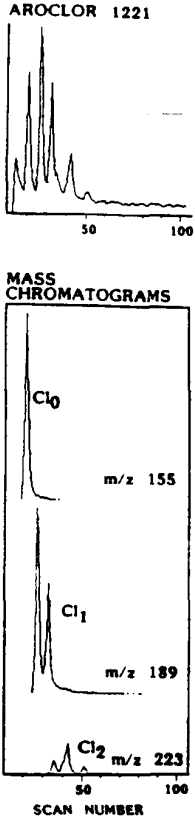


FIGURE 25. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1221.

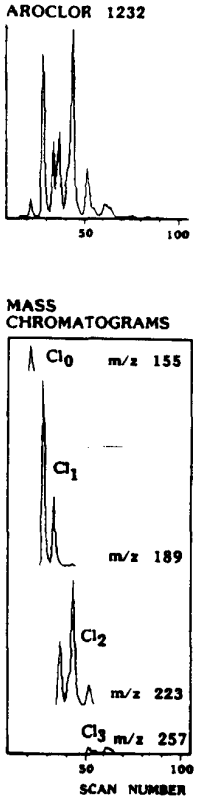


FIGURE 26. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1232.

and 2-, 3-, and 4-chlorobiphenyl, the author was able to predict in an approximate fashion the effect of chlorine substitution on the ^{13}C shieldings. An interesting conclusion concerning the effects of a chlorine substituent was the discovery of their significant transmission through eight covalent bonds. The most significant finding, however, was the gross correlation of ^{13}C shieldings with total charge density which in turn permitted the division of the spectrum

MONS 005755

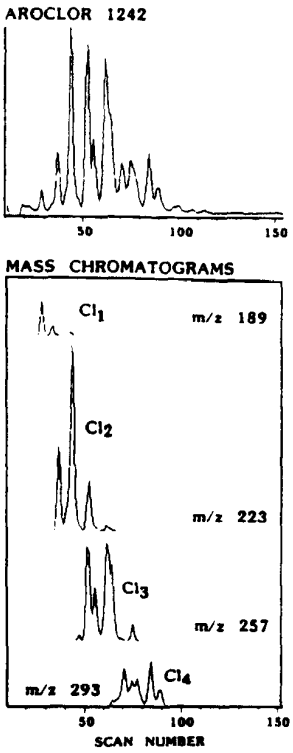


FIGURE 27. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1242.

into three distinct sections: 135 to 144 ppm for C-1 carbons, 130 to 135 ppm for C-Cl carbons, and 120 to 130 ppm for C-H carbons. Levy and Hewitt[85] employed this analytical approach in the semiquantitative analysis by ^{13}C NMR (69.7 MHz) of Aroclor® 1221. The total chlorine content obtained by NMR was 1.4 atoms of chlorine per molecule. Based on GC/MS and EC/GC studies the quantitative value obtained was 1.2 atoms per molecule (i.e., 21% Cl by weight).

Rather than attempt to illustrate typical spectra obtained for certain individual congeners with tables of chemical shifts and coupling constants, four Aroclors® have been selected as

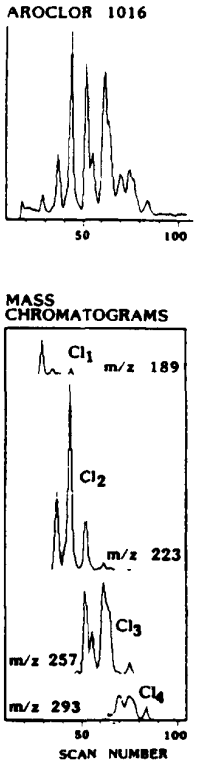


FIGURE 28. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1016.

representative reference materials and their ^1H (270 MHz) and ^{13}C (69.7 MHz) NMR spectra are presented in Figures 40 and 41. These spectra were obtained on a Bruker WH270 spectrometer. Samples were dissolved in chloroform-d, (270 mg/mℓ) for the ^{13}C measurements and in methylene chloride-d_2 (280 mg/mℓ) for the ^1H measurements. ^{13}C spectra were recorded with proton broad band decoupling. In addition, the spin relaxation reagent chromium acetylacetonate (0.052 *M*) was present for all the ^{13}C measurements. The concentration of the relaxation reagent and the ^{13}C data acquisition parameters were selected so that

MONS 005757

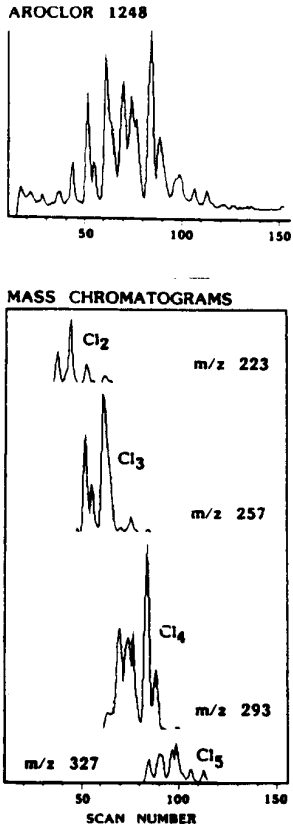


FIGURE 29. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1248.

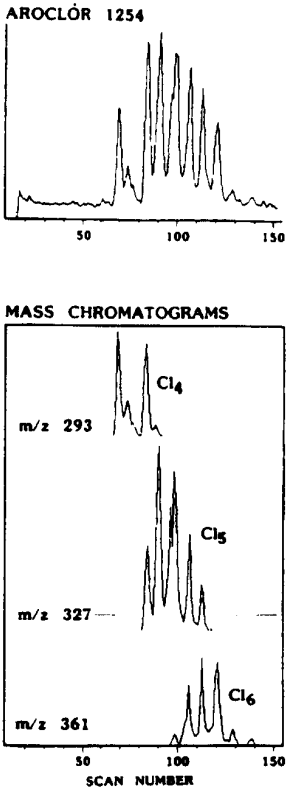


FIGURE 30. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1254.

sensitivity was optimized under conditions where quantitative data was obtained. The ^1H data was recorded under quantitative conditions simply by using a long relaxation time. Chemical shifts were reported in ppm downfield from internal TMS for both ^{13}C and ^1H spectra.

These spectra of selected Aroclors® have been presented to characterize or fingerprint rather than provide a detailed structural analysis of the data. In the case of ^1H NMR spectra

MONS 005759

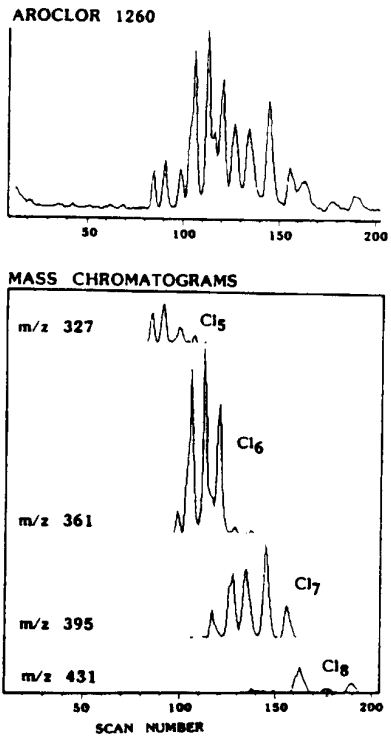


FIGURE 31. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1260.

(Figure 40) the trend in chemical shift of the various protons *(ortho* to *para)* is downfield as the %Cl by weight increases. Chlorine substituents have the expected deshielding effect on the protons in adjacent positions. Application of these fingerprints might well serve to indicate the degree of chlorination in the sample and hence provide proof for the absence or presence of particular congeners.

In the case of the ^{13}C NMR spectra (Figure 41) the gross correlation of charge density and ^{13}C shielding established by Wilson has been applied to differentiate the different types of carbon atoms present within the complex mixtures. The approach to semiquantitative analysis used by Levy and Hewitt[25] has also been applied to these spectra. Results from this

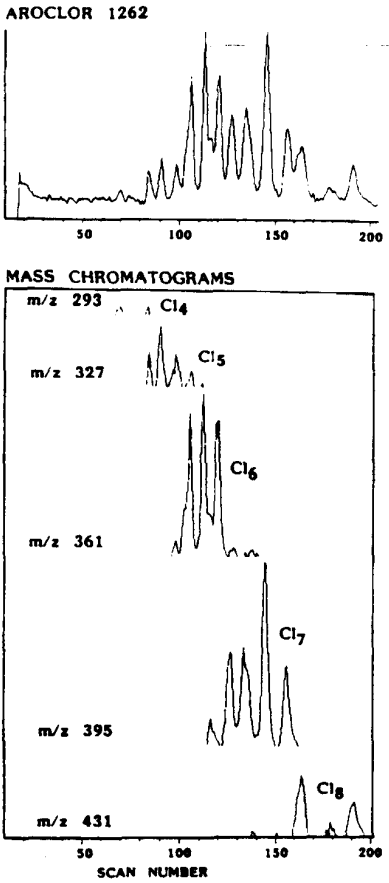


FIGURE 32. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1262.

MONS 005761

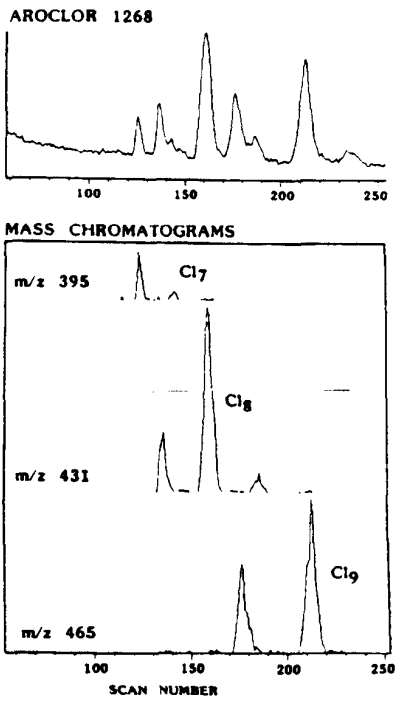


FIGURE 33. Total ion current with relevant mass chromatograms to illustrate the composition of Aroclor® 1268.

approach are listed in Table 4. The semiquantitative agreement is somewhat discouraging. When the range for the C-Cl was reduced to 131.5 to 135.5 ppm then the results all came within 1% of the theoretical values for %Cl by weight. While there are good reasons to support reducing the range, the uncertainty in deciding the true boundary still exists. Chemical shift values to substantiate both boundaries have been published and for this reason the quantitative analysis by ^{13}C NMR of PCBs is not recommended. Closer examination of the spectra, however, do give a vast amount of information concerning the nature of the carbon atoms in the samples studied. The reduction in the type of C-1 carbon atoms observed (135 to 140 ppm) as %Cl increased reflected the reduction in the number of congeners present and hence a resultant increase in the population of certain other congeners with common C-1 carbons. Conversely, the spectra demonstrated the clear trend in the disappearance of

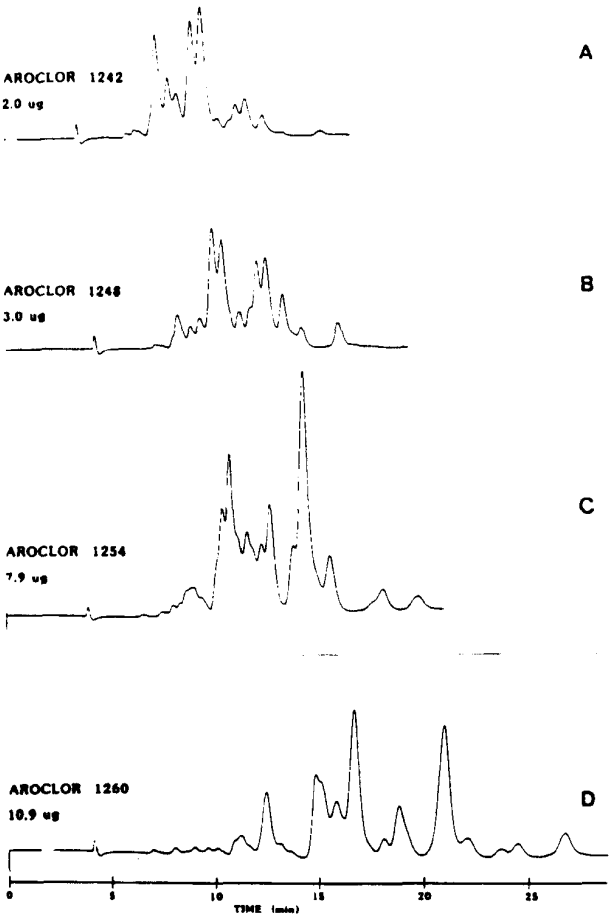


FIGURE 34 Reversed-phase LC elution patterns observed for various Aroclors®: mobile phase, 5% water in methanol, 0.5 mℓ/min; Altex ultrasphere ODS 5 μm; 254 nm fixed wavelength detector.

MONS 005763

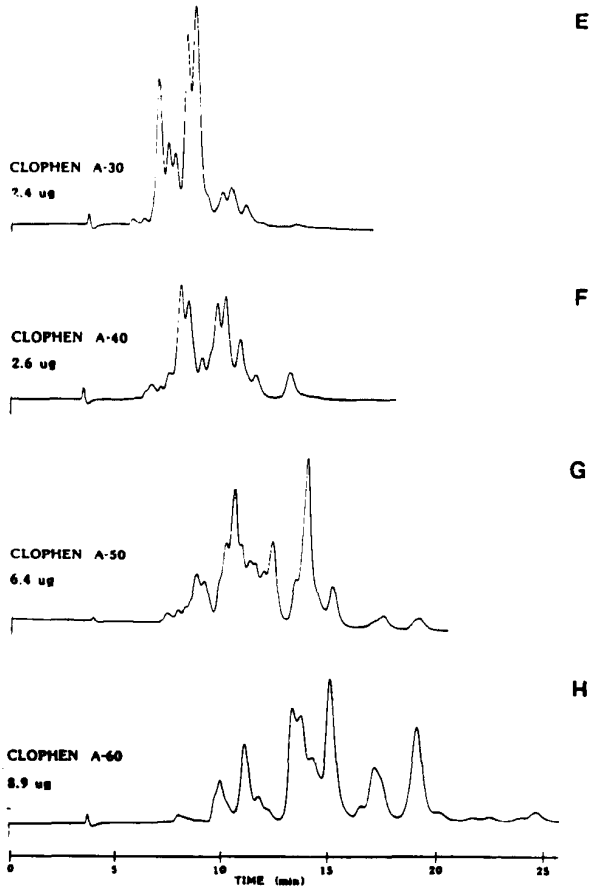


FIGURE 35. Reversed-phase LC elution patterns observed for various Clophens® mobile phase, 5% water in methanol, 0.5 ml/min; Altex ultrasphere ODS 5 μm; 254 nm fixed wavelength detector.

MONS 005764

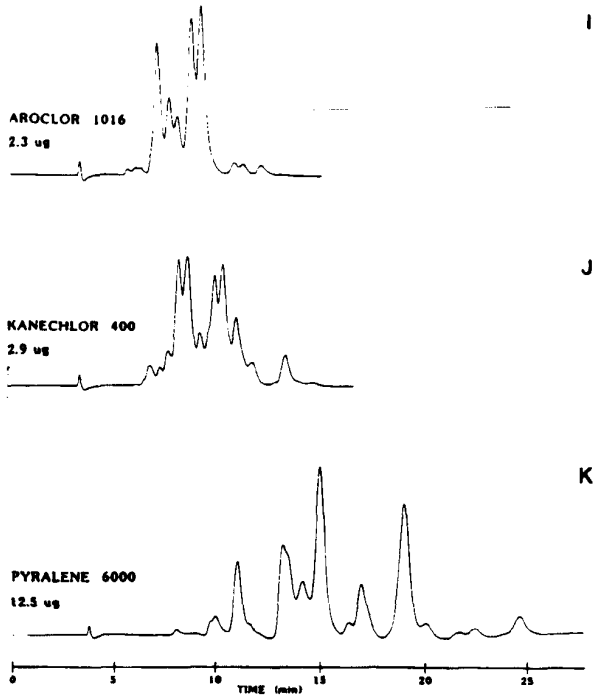


FIGURE 36. Reversed-phase LC elution patterns observed for various other commercial PCB mixtures. mobile phase, 5% water in methanol, 0.5 ml/min; Altex ultrasphere ODS 5 μm; 254 nm fixed wavelength detector.

carbons bearing a proton as %Cl increased. However, the chemical shift zone for carbon atoms bearing a chlorine (130 to 135 ppm) was so complex as to discourage interpretation. At best these spectra can be a useful addition to the library of spectral data on PCBs for use in qualitative identification only.

IV. APPROACHES TO QUANTITATION

With the widespread availability of EC as the most cost-effective detector for incurred PCB residues at the parts per million level, quantitation becomes a complex issue.[86] Unfortunately, the majority of PCBs found in environmental samples only resemble certain Aroclors® in chromatographic pattern but do not match them exactly (Section III.A). Because

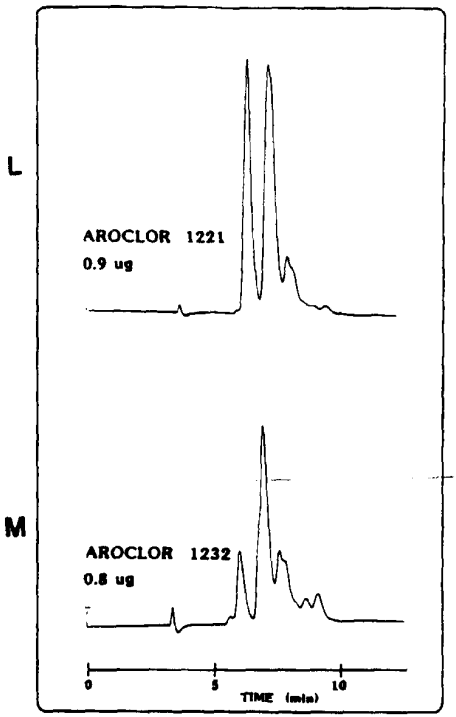


FIGURE 37. Reversed-phase LC elution patterns observed for various other Aroclors®; mobile phase, 5% water in methanol, 0.5 ml/min; Altex ultrasphere ODS 5 μm; 254 nm fixed wavelength detector.

of the disproportionality of detector response, the choice of a suitable reference standard can significantly affect the final analytical result. Having made the necessary judgmental decision as to the most suitable standard, quantitation by comparison of profile areas can be executed. Very often, however, the PCB residue may be a composite of two or more reference standards, and a mixture of reference materials may be required. Considerable improvement in the reliability of results obtained by EC was provided through an interlaboratory study[87,88] utilizing a peak-by-peak area comparison (retention times) procedure rather than a total pattern concept. This approach originally suggested by Webb and McCall[86] was highly dependent on properly characterized reference materials (i.e., weight percentage by peak) and illustrated the improved precision and accuracy over existing methods.

MONS 005766

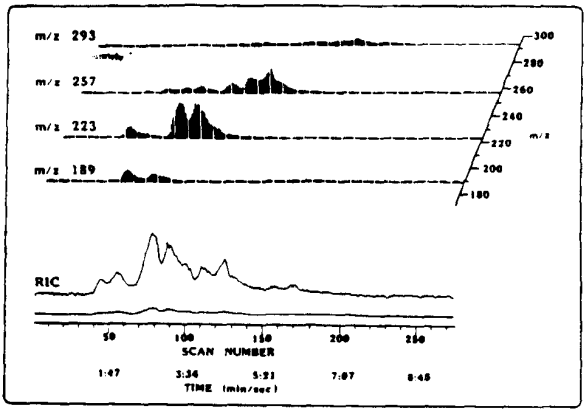


FIGURE 38. Total ion current profile and relevant mass chromatograms for Aroclor® 1242 by LC/MS.

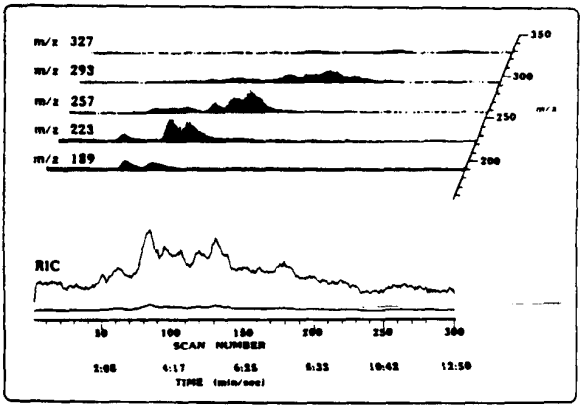


FIGURE 39. Total ion current profile and relevant mass chromatograms for Aroclor® 1248 by LC/MS.

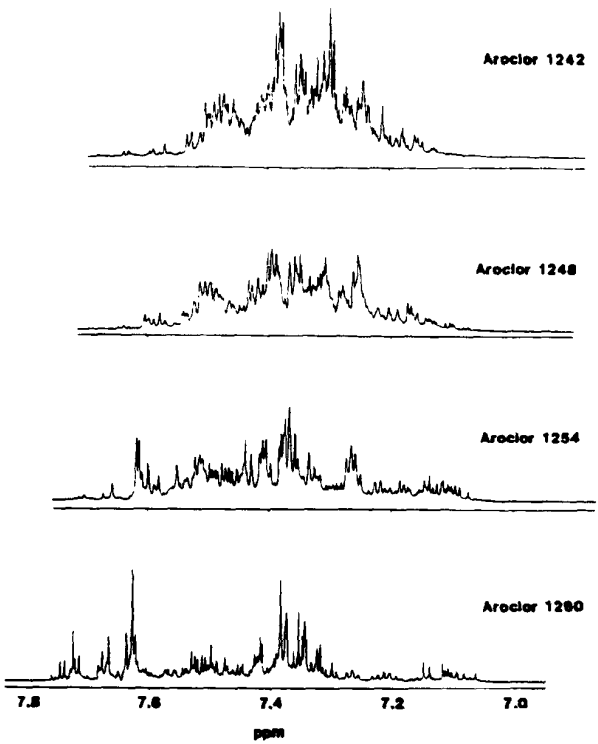
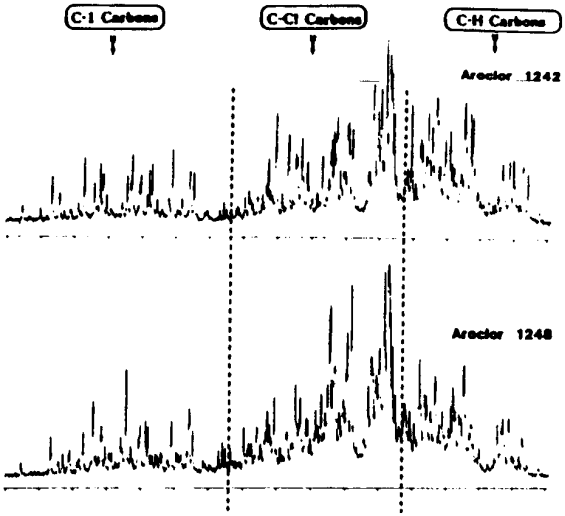


FIGURE 40. Proton magnetic resonance (270 MHz) spectra of various Aroclors®

Use of halogen-specific detectors such as HECD greatly reduces the potential error of disproportionality of response between reference standard and sample. However, their lack of availability in many laboratories has precluded their use in quantitative analysis. HECD has contributed to the vital characterization of Aroclors® fundamental to the analytical approach adopted for quantitation by EC via peak-by-peak comparisons. Additionally, the use of GC/MS-CI with representative congeners of PCBs has also assisted in providing quantitative analysis[43] of five Aroclor® standards (Figure 42) recommended for use in quantitation via EC.

To assess the relative merits of these techniques, the composition of Aroclor® 1248 was


C-I Carbons
C-Cl Carbons
C-H Carbons
Aroclor 1242
Aroclor 1248

MONS 005769

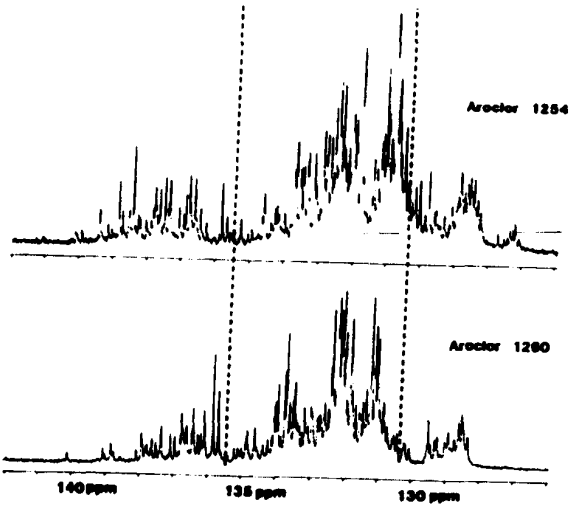


FIGURE 41. ^{13}C magnetic resonance (69.7 MHz) of various Aroclors*

MONS 005770

Table 4
SEMIQUANTITATIVE ANALYSIS OF AROCLORS® BY ^{13}C NMR

	Area measurements (integration range in ppm)				
				%Cl	
Aroclor®	C-I (135.5—142)	C-Cl (135.5—130.25)	C-H (130.25—126)	Calc. theor.	Actual found
1242	2.1	5.6	4.3	57	42
1248	2.0	6.8	3.2	62	48
1254	1.9	7.8	2.3	65	54
1260	1.9	8.3	1.8	66	60

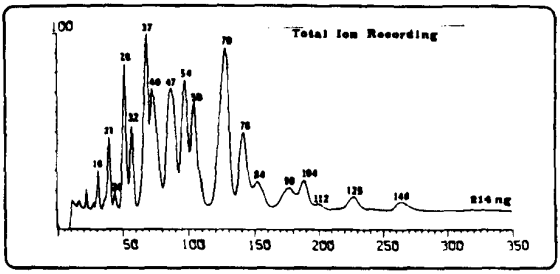
determined by EC, HECD, and GC/MS-CI (Table 5).[83] The peak identification system employed by Sawyer[87] has been used to provide a numerical value for each of the elution peaks in the profile (retention values for *p,p'*-DDE = 100, *p,p'*-DDT = 168, and aldrin = 54 constitute a reference system). It is recognized that both EC and HECD share the same basic principle of detection, i.e., increased sensitivity to the total number of chlorines in the molecule. Therefore, it is not surprising that a peak-by-peak quantitation of Aroclor® 1248 by both these methods provided good overall agreement. In several instances, however, the correlation must be considered as poor (peaks 21, 28, 37, and 40). These results are experimental evidence of disproportionality in spite of similar sensitivity to molar chlorine. In the case of results via GC/MS-CI, the inability to properly quantitate the last five peaks separately due to their low intensity elution profiles was evident. In general, however, the agreement between GC/MS-CI and/or EC and HECD was poor. In the case of peaks containing Cl_5 to Cl_8, the values by GC/MS were much larger. This was an indication of the greater sensitivity of MS to lower molecular weight compounds while for EC and HECD the reverse was true. Irrespective of the factors governing the mechanism of detection, all three methods did provide a total chlorine content extremely close to that injected on column. A conclusion to be gathered from this example is that the summation of individual area measurements usually results in an averaging of the disproportionality factors experienced by each method.

The variety of problems encountered in quantitation of PCB residues has focused attention on developing alternate approaches involving measurement of a single species rather than a mixture. Such brave attempts have included carbon-skeleton GC where PCBs are reduced on-column (5% Pt at 180°C with H_2 as carrier gas) to biphenyl,[89] perchlorination of PCBs by antimony pentachloride to give decachlorobiphenyl,[90] and microcoulometric determination of total chlorine as HCl.[91]

Perhaps the most innovative approach to quantitation has been provided by GC/MS where representative congeners from each molecular weight class are utilized as single standards to quantitate all members of their respective families.[92] In the analysis of a fish sample contaminated by PCBs and DDE (Figure 43), the ability to manipulate the recorded total ion current data base into various mass chromatograms (Figure 44) provided a clear separation of PCBs from DDE without further chemical treatment.[92] This ability to assign the observed PCB residue to Aroclor® 1254 was then easily established and the quantitation carried out with a high degree of confidence. This key determinative step performed by GC/MS seems to be free from previously encountered difficulties.

In conclusion, the routine use of EC for primary determination of PCBs and a whole host of other organochlorine-containing pesticides is still mandatory based on sensitivity. The gross differences in sample residue composition from that of a recognized standard can often contribute to the complexity of an analysis. Such incidences result in other novel approaches

MONS 005771



Peak Identification R_{996} (x 100)	Biphenyls (ng) Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	chlorine (ng)
10	0·1	1·6				0·62
21		4·3				1·35
24			1·0			0·41
28		1·4	18·0			7·82
32		0·3	8·1			3·42
37			21·6			8·96
40			13·1	0·2		5·3
47			3·9	35·3		18·5
54			3·6	21·6		11·82
58			1·9	18·0		9·4
70				29·4	3·3	15·86
78				9·0		4·65
84					5·6	2·7
98					0·5	3·5
104						
112						
126					1·8	0·97
140						
Totals =	0·1	7·6	73·4	121·5	10·6	99·36
	Polychlorinated Biphenyls = 217·2 ng					

FIGURE 42. Total ion current by GC/MS of Aroclor® 1248 with quantitative results calculated as chlorinated biphenyls and chlorine.[52]

to quantitation which avoid these complexities. Whatever the analytical approach adopted, it should be clearly understood that good judgment on the part of the performing analyst is still required to ensure reliable reporting of PCBs in the literature.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Dr. Fred Evans of the National Center for Toxicological Research for providing the high field strength NMR data.

MONS 005772

Table 5
QUANTITATIVE COMPARISON OF CHLORINE DETERMINATIONS FOR AROCLOR® 1248 REFERENCE STANDARD BY EC, HECD, AND GC/MS-CI[a,b]

Peak ident. R_{mass} × 100	No. Cl.	%Cl via EC	%Cl via HECD	Quantitative analysis (ng) EC	HECD	GC/MS
18	2 3	0 3	0 2	0 31	0 21	0 52
21	2	1 1	0 7	1 14	0 73	1 35
24	3	0 2	0 2	0 21	0 21	0 41
28	2 3	6 0	5 1	6 21	5 28	7 82
32	2 3	2 6	2 2	2 69	2 28	3 42
37	3	8 7	7 6	9 00	7 87	8 94
40	3 4	7 4	6 8	7 66	7 04	9 30
47	3 4	15 7	15 8	16 24	16 37	18 50
54	3 4	9 3	9 3	9 62	9 62	11 82
58	3 4	8 3	8 4	8 59	8 70	9 40
70	4 5	18 2	18 9	18 83	19 58	15 86
78	4	6 4	6 6	6 62	6 84	4 85
84	5	4 6	5 3	4 76	5 49	2 70
98	5	3 4	3 9	3 52	4 04	3 50
104	5	3 3	3 8	3 42	3 94	
112	5	1 0	1 1	1 04	1 14	
125	5	2 3	2 6	2 38	2 69	0 97
146	5	1 2	1 4	1 24	1 45	
Total (ng)				103 48	103 49	99 36

[a] 214 ng Aroclor® 1248 injected in each case; 48 4% Cl; 103.5 ng Cl injected.

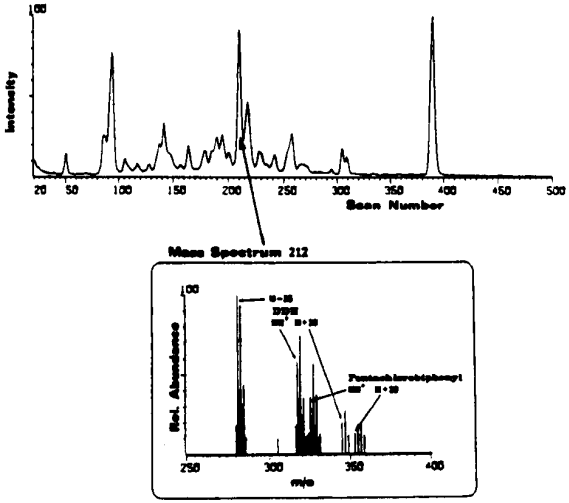


FIGURE 43. GC/MS-CI analysis of an extract of salmon illustrating the co-elution of DDE with pentachlorobiphenyl.[a]

MONS 005773

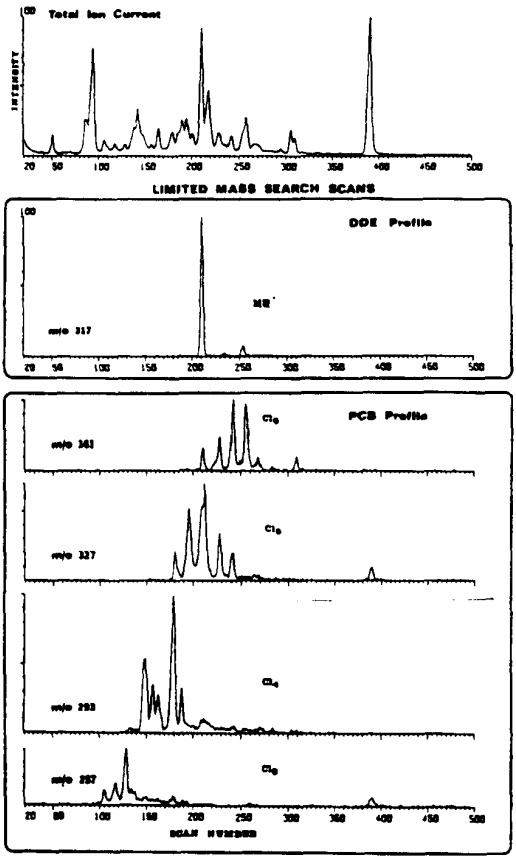


FIGURE 44. GC/MS-CI analysis of an extract of salmon and subsequent mass chromatograms for profile of the PCB content.[44]

REFERENCES

1. Schmidt, H. and Schultz, G., *Ann. Chem.*, 207, 338, 1881
2. Aroclor Plasticizers. Technical Bulletin O/PL-306A. Monsanto Chemical Co. St. Louis, 1981
3. Nisbet, I. C. T. and Sarofim, A. E., *Environ. Health Perspect.*, 1, 21, 1972
4. Jensen, S., *New Sci.*, 32, 612, 1966
5. Holmes, D. C., Simmens, J. M., and Tatton, J. O. G., *Nature (London)*, 216, 227, 1967
6. Risebrough, R. W., Reichle, P., and Olcott, H. S., *Bull. Environ. Contam. Toxicol.*, 4, 192, 1969
7. Koeman, J. H., Debrauw, M. C., and DeVos, R. H., *Nature (London)*, 221, 1126, 1969
8. Richardson, B. J. and Waid, J. S., *Search*, 13, 17, 1982.
9. Risebrough, R. W., Reichle, P., Herman, S. G., Peakall, D. B., and Kirven, M. N., *Nature (London)*, 220, 1098, 1968.
10. Westoo, G., Noren, K., and Anderson, M., *Var Foda*, 2—3, 10, 1970
11. Biros, F. J., Walker, A. C., and Medbury, A., *Bull. Environ. Contam. Toxicol.*, 5, 317, 1970.
12. Risebrough, R. W. and Brodine, V., *Environment*, 12, 958, 1970.
13. Soeki, S., Tsutsui, A., Oguri, K., Yoshimura, H., and Hamano, M., *Fukuoka Acta Med.*, 62, 20, 1971.
14. *Fed. Reg.*, 37(No. 54), March 18, 1972.
15. Skrentny, R. F., Hemken, R. W., and Dorough, H. W., *Bull. Environ. Contam. Toxicol.*, 6, 409, 1971
16. *Fed. Reg.*, 38, 18096, July 6, 1973
17. Winston, S. G. and Gerstner, H. B., Polychlorinated Biphenyls, Polybrominated Biphenyls and Their Contaminants — A Literature Compilation, 1965—1977, ORNL/TIRC-78/2, National Library of Medicine, March 1978
18. Polychlorinated Biphenyls and the Environment, Interdepartmental Task Force on PCBs, Washington, D.C., COM-72-10419, National Technical Information Services, Springfield, Va., 1972.
19. Bird, F. H., Chawan, C. B., and Genty, R. W., *Poult. Sci.*, 57, 538, 1978.
20. Fukano, S. and Doguchi, M., *Bull. Environ. Contam. Toxicol.*, 17, 613, 1977.
21. Greenlee, W. F. and Poland, A., *J. Biol. Chem.*, 254, 9814, 1979.
22. Ghiasuddin, A. M., Menzer, R. E., and Nelson, J. O., *Toxicol. Appl. Pharmacol.*, 36, 187, 1976.
23. Dymerski, P., Kennedy, M., and Kaminsky, L., Trace origins in analysis: new frontier, *Anal. Chem.* 519, 685, 1979.
24. Norback, D. H., Britt, J., Hain, M. T., and Allen, J. R., *Fed. Proc.*, 37, 299, 1978.
25. Gardner, A. M., Righter, H. F., and Roach, J. A., *J. Assoc. Off. Anal. Chem.*, 59, 273, 1976.
26. Jensen, S. and Jansson, B., *Ambio*, 5, 257, 1976.
27. National Conference on PCBs, EPA-560/6-75-004, U.S. Environmental Protection Agency, Washington, D.C., March 1976.
28. *Fed. Reg.*, 42, 17487, April 1, 1977
29. *Fed. Reg.*, 44, 38330, June 29, 1979.
30. PCBs: An Alert for Food and Feed Facilities, U.S. Environmental Protection Agency, Washington, D.C., December 1979.
31. *Fed. Reg.*, 45, 30980, May 9, 1980.
32. Cairns, T. and Siegmund, E. G., *Anal. Chem.*, 53, 1183A, 1981.
33. Simons, D. and Welti, D., *J. Chromatogr.*, 60, 15, 1971.
34. Fishbein, L., *J. Chromatogr.*, 68, 345, 1972.
35. Cook, J. W., *Environ. Health Perspect.*, 1, 3, 1972.
36. Fishbein, L., *J. Chromatogr.*, 68, 345, 1972.
37. Cairns, T., *Bull. Assoc. Food Drug Off.*, 42, 3, 1978.
38. Wilson, N. K., *J. Am. Chem. Soc.*, 97(13), 3573, 1975.
39. Brinkman, U. A. Th., Soets, J. W. F. L., and Reymer, H. G. M., *J. Chromatogr.*, 116, 353, 1976.
40. Zitko, V., *Int. J. Environ. Anal. Chem.*, 1, 221, 1972.
41. Sawyer, L. D., *J. Assoc. Off. Anal. Chem.*, 61, 282, 1978
42. Ameur, J. and Burke, J., *J. Assoc. Off. Anal. Chem.*, 53, 761, 1970.
43. Mazumdar, H. T., *J. Assoc. Off. Anal. Chem.*, 55, 1092, 1972.
44. Erney, D. R., *J. Assoc. Off. Anal. Chem.*, 57, 5576, 1974.
45. Bidleman, T. F., Matthews, J. R., Olney, C. E., and Rice, C. P., *J. Assoc. Off. Anal. Chem.*, 61, 820, 1978.
46. Park, C. K., Lee, C. Y., and Park, R. D., *Han'guk Sikmul Poho Hakhoe Chi*, 16, 221, 1977.
47. Young, S. J. V., Flusterwalder, C., and Burke, J. A., *J. Assoc. Off. Anal. Chem.*, 56, 957, 1973.
48. Mulhern, B. M., Cromartie, E., Reichel, W. L., and Bellatti, A. A., *J. Assoc. Off. Anal. Chem.*, 54, 548, 1970.
49. Trotter, W. J., *J. Assoc. Off. Anal. Chem.*, 58, 461, 1975.

MONS 005775

50 **Miles, J. R. W.,** *J. Assoc. Off. Anal. Chem.*, 55, 1039, 1972.
51 **Mitsutani, T., Matsumoto, M., and Kaguka, E.,** *J. Hyg. Chem.*, 19, 287, 1973.
52 **Gothe, R.,** *Bull. Environ. Contam. Toxicol.*, 11, 451, 1974.
53 **Westöo, G. and Noren, K.,** *Acta Chem. Scand.*, 24, 1639, 1970.
54 **Jensen, S. and Sundstrom, G.,** *Ambio*, 3, 70, 1974.
55 **Fehringer, N. V. and Westfall, J. E.,** *J. Chromatogr.*, 57, 397, 1971.
56 **deVos, R. H. and Peet, E. W.,** *Bull. Environ. Contam. Toxicol.*, 6, 1164, 1971.
57 **Natusch, D. F. S. and Thrope, T. M.,** *Anal. Chem.*, 45, 1184A, 1973.
58 **Rote, J. W. and Murphy, P. G.,** *Bull. Environ. Contam. Toxicol.*, 6, 377, 1971.
59 **Cairns, T. and Siegmund, E. G.,** *Biomed. Mass Spectrom.*, 8, 569, 1981.
60 **Casida, J. E. and Saleh, M. A.,** Toxaphene Composition and Toxicology, EPA-600/1-78-060, U.S. Environmental Protection Agency, Washington, D.C., September 1978.
61 **Cochrane, W. P., Lawrence, J. F., Lee, T. W., Maybury, R. B., and Wilson, B. P.,** *J. Assoc. Off. Anal. Chem.*, 58, 1051, 1975.
62 **William, D. T. and Blanchfield, B. J.,** *J. Assoc. Off. Anal. Chem.*, 55, 93, 1972.
63. **Cairns, T. and Siegmund, E. G.,** *Anal. Chem.*, 53, 1599, 1981.
64. **Hutzinger, O., Jamieson, J., and Zitko, V.,** *Nature (London)*, 226, 664, 1970.
65. **Webb, R. S. and McCall, A.,** *J. Assoc. Off. Anal. Chem.*, 55, 746, 1972.
66. **Stalling, D. and Huckins, J.,** *J. Assoc. Off. Anal. Chem.*, 54, 801, 1971.
67. **Safe, S. and Hutzinger, O.,** *Nature (London)*, 232, 641, 1971.
68. **Safe, S. and Hutzinger, O.,** *Chem. Commun.*, 446, 1971.
69 **Safe, S. and Hutzinger, O.,** *J. Chem. Soc. Perkin Trans. 1*:, 5, 686, 1972.
70. **Rote, J. W. and Morris, W. J.,** *J. Assoc. Off. Anal. Chem.*, 56, 188, 1973.
71. **Byrne, S. H., Schmidt, J. A., and Johnson, P. E.,** *J. Chromatogr. Sci.*, 9, 592, 1971.
72. **Eisenbeis, F. and Sieper, H.,** *J. Chromatogr.*, 83, 439, 1973.
73 **Selber, J. N.,** *J. Chromatogr.*, 94, 151, 1974.
74. **Willmott, F. W. and Dolphin, R. J.,** *J. Chromatogr. Sci.*, 12, 695, 1974.
75 **Altnetmuller, K.,** *J. Chromatogr.*, 107, 411, 1975.
76. **Frei, R. W., Lawrence, J. F., Hope, J., and Cassidy, R. M.,** *J. Chromatogr. Sci.*, 12, 40, 1974.
77. **Chiesi, S., Evidente, A., Randazzo, G., and Scalorbi, O.,** *J. Liquid Chromatogr.*, 5, 1653, 1982.
78. **Kirkland, J. J.,** *Modern Practice of Liquid Chromatography*, Wiley Interscience, New York, 1971, chap. 5.
79. **Cairns, T., Siegmund, E. G., and Deese, G. M.,** *Anal. Chem.*, 54, 953, 1982.
80. **Bartle, K. D.,** *J. Assoc. Off. Anal. Chem.*, 55, 1101, 1972.
81. **Wehtl, D. and Sinoms, D.,** *Org. Magnetic Reson.*, 4, 309, 1972.
82. **Tarpley, A. R. and Goldstein, J. H.,** *J. Phys. Chem.*, 75, 421, 1971.
83. **Wilson, N. K. and Anderson, M.,** *Mass Spectrometry and NMR Spectroscopy in Pesticide Chemistry*, Haque, R. and Biros, F. J., Eds., Plenum Press, New York, 1974, 197.
84 **Wilson, N. K.,** *J. Am. Chem. Soc.*, 3573, 1975.
85. **Levy, G. C. and Hewitt, J. M.,** *J. Assoc. Off. Anal. Chem.*, 60, 241, 1977.
86. **Webb, R. G. and McCall, A. C.,** *J. Chromatogr. Sci.*, 11, 366, 1973.
87. **Sawyer, L. D.,** *J. Assoc. Off. Anal. Chem.*, 61, 282, 1978.
88. **Sawyer, L. D.,** *J. Assoc. Off. Anal. Chem.*, 61, 272, 1978.
89. **Cooke, M., Nicklass, G., Prescott, A. M., and Roberts, J. D.,** *J. Chromatogr.*, 156, 293, 1978.
90. **Robbins, A. L. and Wilhite, C. B.,** *Bull. Environ. Contam. Toxicol.*, 21, 428, 1979.
91. **Donkin, P., Mann, S. V., and Hamilton, E. I.,** *Anal. Chim. Acta*, 88, 289, 1977.

MONS 005776

Chapter 2

CHEMISTRY AND PROPERTIES OF PCBs IN RELATION TO ENVIRONMENTAL EFFECTS

B. L. Sawhney

TABLE OF CONTENTS

I. Structure and Preparation of PCBs 48
A. Nomenclature 48
B. Synthesis of Individual Chlorobiphenyls 48
C. Commercial PCBs 49

II. Properties of PCBs 49
A. General Physical Properties 49
B. Solubility 49
C. Vapor Pressure and Vaporization 54
D. Sorption Reactions 55

III. Processes and Products of PCBs Degradation 56
A. Photochemical Degradation 56
B. Biodegradation 58
C. Thermal Degradation 59

References 61

MONS 005777

I. STRUCTURE AND PREPARATION OF PCBs

A. Nomenclature

PCBs are a class of synthetic chlorinated organic compounds with biphenyl as the basic structural unit. Chlorination of the group can produce 209 possible chlorobiphenyls (congeners) substituted with 1 to 10 chlorine atoms. Systematic numbering and structures of these chlorobiphenyls from Ballschmiter and Zell[1] are given in Table 1. According to the IUPAC definitive rules for nomenclature of organic chemistry, one ring system in the biphenyl ring assembly is assigned unprimed numbers and the other primed numbers as illustrated in Figure 1.

The order for assigning priorities to the substituents in the ring assembly, as Cl in PCBs is (1) unprimed number is assigned lower order than the corresponding primed number, as 2 vs. 2'; (2) lower number is assigned to a point of attachment in equivalent position, as 2 vs. 6, for a substituent in one of the *ortho* positions; (3) when the number of substituents in the two ring systems is the same, unprimed numbers are assigned to the ring system with smaller numbered substituents. These rules are illustrated in Figure 2 for pentachlorobiphenyl. Nomenclatures of chlorinated biphenyls containing additional substituents as hydroxyl, amino, and carboxyl groups are further described in a comprehensive account of the chemistry of PCBs by Hutzinger et al.[2] These principal functions are cited as the suffix, chlorobiphenylol, chlorobiphenyl amine, chlorobiphenyl carboxylic acid and so on.

B. Synthesis of Individual Chlorobiphenyls

Synthesis of most of the 209 chlorobiphenyls has been accomplished and many of these are now available. Methods used for the preparation of individual chlorobiphenyls include (1) phenylation or arylation of aromatic compounds, (2) condensation reactions, and (3) chlorination of biphenyl.

Arylation of a number of aromatic compounds as aroyl peroxides, carboxylic acids, diazonium salts, nitrosoamines, aryltriazenes, phenylhydrazines, and others has been attained. The reactions between the selected aromatic compounds and the substrate, benzene, usually involve free radicals provided either by the aromatic compound or the free radical precursors used in the reaction. Examples of arylation in the presence of benzene and chlorinated benzene are given in Figures 3A and B.

A number of condensation reactions involving aromatic halides, phenylsulfinates, aryl peroxides and acid anhydrides, chlorobenzenes, and other aromatic compounds have been described by Hutzinger et al.[2] Condensation of two aromatic halides in the presence of finely divided Cu is probably the most widely used procedure for the preparation of symmetrical chlorobiphenyls. Figure 4A illustrates formation of hexachlorobiphenyl from trichloroiodobenzene. Copper is usually mixed with the halide and heated for several hours. Mixtures of symmetrical and asymmetrical chlorobiphenyls are produced by this reaction when two different halides are used (Figure 4B).

Chlorination of biphenyl can occur either by substitution of Cl for H (H-Cl) to form chlorobiphenyls or by addition



to form hexachlorocyclohexyl benzenes ($C_{12}H_6Cl_6$). The products formed by the addition of Cl are, however, thermally unstable and decompose to produce chlorobiphenyls during the chlorination process. Direct chlorination produces mixtures of chlorobiphenyls, depending upon the chlorine to biphenyl ratio, the catalyst used, and the temperature of the ex-

MONS 005778

periment. For example, in the presence of iron filings, equivalent proportions of biphenyl and chlorine produced about 32% 2-chlorobiphenyl, 26% 4-chlorobiphenyl, and 2% dichlorobiphenyl.[3] In the presence of bentonite clay as catalyst, 70% of the product was *o*-chlorobiphenyl.[4] Chlorination of biphenyl with liquid chlorine in the presence of $FeCl_3$ produced a mixture of nona- and decachlorobiphenyls,[5] while at high temperatures, in the presence of $SbCl_5$[6] or $TiCl_4$,[7] decachlorobiphenyl was produced. Replacements of amino, hydroxyl, nitro, sulfonic acid, and others by chlorine also produce chlorinated biphenyls.

C. Commercial PCBs

Chlorination of biphenyl in the presence of a catalyst, such as iron filings or iron chloride is used for industrial preparations of PCBs. The chlorination process produces mixtures of chlorobiphenyls which are influenced by the ratio of chlorine to biphenyl. The crude product resulting from chlorination of biphenyls is purified to remove color, catalyst, and traces of HCl by alkali treatment and distillation. The purified PCB preparations are generally viscous liquids. In the U.S., PCBs have been manufactured by Monsanto under the trade name Aroclors®. The most common Aroclor® preparations include 1242, 1248, 1254, and 1260. The first two digits are the number of carbon atoms in the biphenyl group and the last two digits give approximate %Cl content in the PCB preparation. GC analysis of the Aroclors® (and other commercial preparations sold under different trade names around the world (see Chapter 1), show that they are complex mixtures of different chlorobiphenyls. Gas chromatograms of each preparation show a number of peaks. Use of glass capillary columns in GC has permitted better resolution of the peaks, resulting in over 60 peaks from Aroclor® 1248 and over 90 peaks from Aroclors® 1254 and 1260.[8] Using high-resolution thin-film glass capillary GC, Ballschmiter and Zell[9] have identified about 200 chlorobiphenyls in a commercial PCB preparation, Clophen®. Determinations of the composition of different peaks using a conductivity detector show that Aroclors® with lower chlorine content contain less chlorinated biphenyls with peaks having smaller retention times.[8,10] Aroclor® 1242 gave peaks corresponding to compounds containing 1 to 5 chlorine atoms, while peaks from Aroclor® 1254 contained 3 to 6 chlorine atoms and those from Aroclor® 1260 contained 5, 6, and 7 chlorine atoms.

Analyses of chlorobiphenyls in commercial preparations using capillary GC/MS,[11] based on retention times and molecular ions permit definitive identification and quantitative estimation of different chlorobiphenyls in the sample. Relative percentages of about 100 different PCBs in the Aroclors®, thus determined, can be used as secondary standards for environmental samples.

II. PROPERTIES OF PCBs

A. General Physical Properties

PCBs are among the most stable organic compounds known. They have a low dielectric constant and high heat capacity which render them ideal for use in electrical capacitors and transformers. While most individual chlorobiphenyls are solids at room temperature, commercial preparations are generally resins or viscous liquids of density greater than water. Table 2 shows some selected properties of four common Aroclors® and Table 3 gives amounts of chlorobiphenyls of different chlorine contents in the Aroclors®. Other properties of PCBs, solubility, vaporization, and sorption, which are important in controlling their transport and distribution in the environment are discussed in detail below.

B. Solubility

Solubility of PCBs in water and in organic solvents, as lipids, greatly influences their transport and persistence in the environment. Solubilities of a number of individual chlo-

MONS 005779

Table 1
SYSTEMATIC NUMBERING OF PCB COMPOUNDS

No.	Structure	No.	Structure	No.	Structure	No.	Structure
	Monochlorobiphenyls		**Tetrachlorobiphenyls**		**Pentachlorobiphenyls**		**Hexachlorobiphenyls**
1	2	52	2,2',5,5'	105	2,3,3',4,4'	151	2,2',3,5',6
2	3	51	2,2',5,6'	106	2,3,5',4,5	152	2,2',3,6,6'
3	4	50	2,2',6,6'	107	2,3,3',4',5	153	2,2',4,4',5,5'
		55	2,3,3',4	108	2,3,3',4,5'	154	2,2',4,4',5,6
	Dichlorobiphenyls	56	2,3,3',4'	109	2,3,3',4,6	155	2,2',4,4',6,6'
4	2,2'	57	2,3,3',5	110	2,3,3',4',6	156	2,3,3',4,4',5
5	2,3	58	2,3,3',5'	111	2,3,3',5,5'	157	2,3',4,4',5,5'
6	2,3'	59	2,3,3',6	112	2,3,3',5,6	158	2,3',4,4',5',6
7	2,4	60	2,3,4,4'	113	2,3,3',5',6	159	3,3',4,4',5,5'
8	2,4'	61	2,3,4,5	114	2,3,4,4',5		
9	2,5	62	2,3,4,6	115	2,3,4,4',6		**Heptachlorobiphenyls**
10	2,6	63	2,3,4',5	116	2,3,4,5,6	170	2,2',3,3',4,4',5
11	3,3'	64	2,3,4',6	117	2,3,4',5,6	171	2,2',3,3',4,4',6
12	3,4	65	2,3,5,6	118	2,3',4,4',5	172	2,2',3,3',4,5,5'
13	3,4'	66	2,3',4,4'	119	2,3',4,4',6	173	2,2',3,3',4,5,6
14	3,5	67	2,3',4,5	120	2,3',4,5,5'	174	2,2',3,3',4,5,6'
15	4,4'	68	2,3',4,5'	121	2,3',4,5',6	175	2,2',3,3',4,5',6
		69	2,3',4,6	122	2',3,3',4,5	176	2,2',3,3',4,6,6'
	Trichlorobiphenyls	70	2,3',4',5	123	2',3,4,4',5	177	2,2',3,3',4',5,6
16	2,2',3	71	2,3',4',6	124	2',3,4,5,5'	178	2,2',3,3',5,5',6
17	2,2',4	72	2,3',5,5'	125	2',3,4,5,6'	179	2,2',3,3',5,6,6'
18	2,2',5	73	2,3',5',6	126	3,3',4,4',5	180	2,2',3,4,4',5,5'
19	2,2',6	74	2,4,4',5	127	3,3',4,5,5'	181	2,2',3,4,4',5,6
20	2,3,3'	75	2,4,4',6			182	2,2',3,4,4',5,6
21	2,3,4	76	2',3,4,5		**Hexachlorobiphenyls**	183	2,2',3,4,4',5',6
22	2,3,4'	77	3,3',4,4'	128	2,2',3,3',4,4'	184	2,2',3,4,4',6,6'
23	2,3,5	78	3,3',4,5	129	2,2',3,3',4,5	185	2,2',3,4,5,5',6
24	2,3,6	79	3,3',4,5'	130	2,2',3,3',4,5'	186	2,2',3,4,5,6,6'
25	2,3',4	80	3,3',5,5'	131	2,2',3,3',4,6	187	2,2',3,4',5,5',6
26	2,3',5	81	3,4,4',5	132	2,2',3,3',4,6'	188	2,2',3,4',5,6,6'

MONS 005780

27	2,3',6			131	2,2',3,3',5,5'	189	2,3,3',4,4',5,5
28	2,4,4'		Pentachlorobiphenyls	132	2,2',3,3',5,6	190	2,3,3',4,4',5,6
29	2,4,5	82	2,2',3,3',4	133	2,2',3,3',5,6'	191	2,3,3',4,4',5',6
30	2,4,6	83	2,2',3,3',5	134	2,2',3,3',6,6'	192	2,3,3',4,5,5',6
31	2,4',5	84	2,2',3,3',6	135	2,2',3,4,4',5	193	2,3,3',4',5,5',6
32	2,4',6	85	2,2',3,4,4'	136	2,2',3,4,4',5'		
33	2',3,4	86	2,2',3,4,5	137	2,2',3,4,4',6		Octachlorobiphenyls
34	2',3,5	87	2,2',3,4,5'	138	2,2',3,4,4',6'	194	2,2',3,3',4,4',5,5'
35	3,3',4	88	2,2',3,4,6	139	2,2',3,4,5,5'	195	2,2',3,3',4,4',5,6
36	3,3',5	89	2,2',3,4,6	140	2,2',3,4,5,6	196	2,2',3,3',4,4',5',6
37	3,4,4'	90	2,2',3,4',5	141	2,2',3,4,5,6'	197	2,2',3,3',4,4',6,6'
38	3,4,5	91	2,2',3,4',6	142	2,2',3,4,5',6	198	2,2',3,3',4,5,5',6
39	3,4',5	92	2,2',3,5,5'	143	2,2',3,4,6,6'	199	2,2',3,3',4,5,6,6'
		93	2,2',3,5,6	144	2,2',3,4',5,5'	200	2,2',3,3',4,5',6,6'
	Tetrachlorobiphenyls	94	2,2',3,5,6'	145	2,2',3,4',5,6	201	2,2',3,3',4',5,5',6
40	2,2',3,3'	95	2,2',3,5',6	146	2,2',3,4',5,6'	202	2,2',3,3',5,5',6,6'
41	2,2',3,4	96	2,2',3,6,6'	147	2,2',3,4',5',6	203	2,2',3,4,4',5,5',6
42	2,2',3,4'	97	2,2',3',4,5	148	2,2',3,4',6,6'	204	2,2',3,4,4',5,6,6'
43	2,2',3,5	98	2,2',3',4,6	149	2,2',3,4',5',6	205	2,3,3',4,4',5,5',6
44	2,2',3,5'	99	2,2',4,4',5	150	2,2',3,4',6,6'		
45	2,2',3,6	100	2,2',4,4',6	151	2,2',3,5,5',6		Nonachlorobiphenyls
46	2,2',3,6'	101	2,2',4,5,5'	152	2,2',3,5,6,6'	206	2,2',3,3',4,4',5,5',6
47	2,2',4,4'	102	2,2',4,5,6'	153	2,2',4,4',5,5'	207	2,2',3,3',4,4',5,6,6'
48	2,2',4,5	103	2,2',4,5',6	154	2,2',4,4',6,6'	208	2,2',3,3',4,5,5',6,6'
49	2,2',4,5'	104	2,2',4,6,6'	155	2,2',4,4',6,6'		
50	2,2',4,6			156	2,3,3',4,4',5		Decachlorobiphenyl
51	2,2',4,6'			157	2,3,3',4,4',5	209	2,2',3,3',4,4',5,5',6,6'
				158	2,3,3',4,4',6		
				159	2,3,3',4,5,5'		
				160	2,3,3',4,5,6		

From Ballschmiter, K. and Zell, M., *Fresenius' Z. Anal. Chem.*, 302, 20, 1980. With permission.

MONS 005781

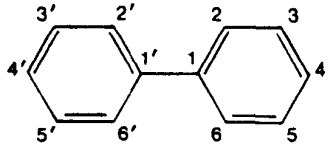


FIGURE 1 Numbering in the biphenyl ring system

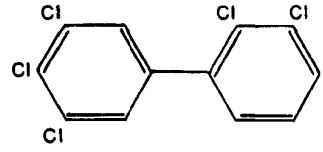
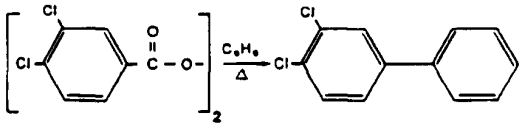
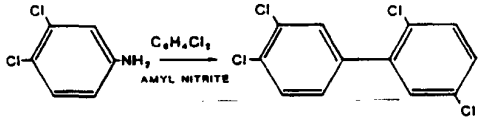


FIGURE 2. Structure of 2,3,3′,4′,5′-pentachlorobiphenyl.



A



B

FIGURE 3. (A) Arylation of 3,3′,4,4′-tetrachlorobenzoyl peroxide to 3,4-dichlorobiphenyl.[2] (B) Arylation of 3,4-dichloroaniline to 2,3′,4′,5-tetrachlorobiphenyl.[2]

MONS 005782

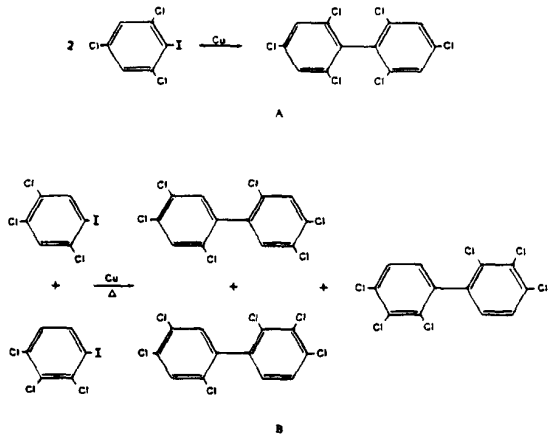


FIGURE 4. (A) Condensation of 2,4,6-trichloroiodobenzene to 2,2',4,4',6,6'-hexachlorobiphenyl.[1] (B) Condensation of trichloroiodobenzenes to hexachlorobiphenyls.[2]

Table 2
PHYSICAL CHARACTERISTICS OF FOUR COMMON AROCLORS[a,2]

Aroclor[a]	Dielectric constant (at 1000 c) 25°C	100°C	Distillation range (°C)	Density
1242	5.8	4.9	325—366	1.38
1248	5.6	4.6	340—375	1.44
1254	5.0	4.3	365—390	1.53
1260	4.3	3.7	385—420	1.62

robiphenyls as well as of commercial preparations have been tabulated by Hutzinger et al.[3] Because of very low solubility of PCBs in water, a common method used for solubility determination involves placing a quantity of the chlorobiphenyl in a large quantity of water which is continuously stirred. Aliquots are then withdrawn periodically, centrifuged, and chlorobiphenyl in the supernatant estimated. This procedure is continued until an equilibrium is attained, which is a slow process.[12]

Solubility of PCBs in water generally decreases with increase in the degree of chlorination. Individual chlorobiphenyls vary in their solubility from about 6 ppm for monochlorobiphenyl to as low as 0.007 ppm for octachlorobiphenyl.[2] Decachlorobiphenyl, despite its higher chlorine content, is about twice as soluble as the octachlorobiphenyl. The solubilities also vary among chlorobiphenyls with the same number of chlorines; for example, solubilities

MONS 005783

Table 3
MOLECULAR WEIGHT, Cl CONTENT, AND AMOUNTS OF CHLOROBIPHENYLS IN FOUR COMMON AROCLORS®[3]

Chlorobiphenyl	Mol wt	%Cl	% in Aroclors®			
			1242	1248	1254	1260
Monochlorobiphenyl	188.65	18.79	3	—	—	—
Dichlorobiphenyl	223.10	31.77	13	2	—	—
Trichlorobiphenyl	257.54	41.30	28	18	—	—
Tetrachlorobiphenyl	291.99	48.56	30	40	11	—
Pentachlorobiphenyl	326.43	54.30	22	36	49	12
Hexachlorobiphenyl	360.88	58.93	4	4	34	38
Heptachlorobiphenyl	395.32	62.77	—	—	6	41
Octachlorobiphenyl	429.77	65.98	—	—	—	8
Nonachlorobiphenyl	464.21	68.73	—	—	—	1

of 2,4-, 2,2'-, and 2,4'-dichlorobiphenyls are 1.40, 1.50, and 1.88 ppm, respectively, while that of 4,4'-dichlorobiphenyl is only 0.08 ppm.[2] Chlorine substitutions in different positions of the biphenyl ring system are apparently responsible for the differences in solubilities of chlorobiphenyls with same chlorine content.

Solubilities of chlorobiphenyls reported by different workers are similar in most instances. For example, solubility of 2,4,5,2',5'-pentachlorobiphenyl is 10,[13] 20,[14] and 31 ppb.[2] Solubility of 2,4,5,2',4',5'-hexachlorobiphenyl, on the other hand, differed by an order of magnitude in two reports — Hutzinger et al.[2] reported a solubility of 8.8 ppb while Haque and Schmedding[15] reported 0.9 ppb.

Solubilities of various Aroclors® reported by Hutzinger et al.[2] are Aroclors® 1242 = 200 ppb, 1248 = 100 ppb, 1254 = 40 ppb, and 1260 = 25 ppb. Solubility of Aroclor® 1254 determined by Haque et al.[12] was about 56 ppb, similar to 40 ppb above. Because less chlorinated biphenyls are generally more soluble than more chlorinated biphenyls, aqueous solutions of Aroclors® show greater proportions of the lower chlorinated biphenyls than the standard Aroclors® from which the solutions are made.[2,12] However, some anomalies are observed because of differential solubilities of certain PCB congeners, as noted above. Ratios of GC peak heights from saturated aqueous solution of Aroclor® 1254 at 26°C to the corresponding peaks from the standard Aroclor® 1254 varied from about 5 for the first two peaks to less than 1 for peaks 8 through 13. Peak number 4 had a value of 14 for this ratio, presumably because of high solubility of the isomer corresponding to the peak.[2]

Solubilities of PCBs are greatly influenced by the environment. For example, aqueous phases in the environment generally contain dissolved organic substances which probably enhance the concentration of PCBs in solution. Zitko[16] obtained solubilities of Aroclor® 1254 in "fresh water" in the range of 0.3 to 3 ppm, which are much higher than 0.012 ppm reported by MacKay and Wolkoff,[17] and 0.056 ppm by Haque et al.[12] and were attributed by these authors to the presence of organic material in water. Conversely, sorption of PCBs on soil or sediment surfaces in the aquatic environment would decrease their solution concentration. A recent study shows that the movement of PCBs from dialysis membrane bags suspended in water was much less from bags with particles than from those without particles.[18]

C. Vapor Pressure and Vaporization

PCBs have very low vapor pressures which, like their solubility in water, decrease with increased chlorination. Vaporization rates for six common Aroclors® (Table 4) show that the vaporization rates decrease about 200-fold from Aroclor® 1221 which consists primarily of mono- and dichlorobiphenyls, to 1260 which consists essentially of penta-, hexa-,

MONS 005784

Table 4
VAPORIZATION RATES OF SIX AROCLORS® MEASURED AT 100°C[3]

Aroclor® (12.28 cm² surface)	Vaporization rate (g/cm²/hr)
1221	0.00174
1232	0.000874
1242	0.000338
1248	0.000152
1254	0.000053
1260	0.000009

hepta-, and octachlorobiphenyls. Haque et al.[12] observed a vaporization rate of 0.0000036 g/cm²/hr for Aroclor® 1254 at 60°C as compared to 0.000053 g/cm²/hr at 100°C (Table 4).

In environmental samples where PCBs are sorbed on soil or sediment surfaces, the rate of vaporization of PCBs is greatly reduced. The vaporization rate depends upon the sorption surface. Haque et al.[12] observed that about 60% of Aroclor® 1254 sorbed by Ottawa sand was lost by vaporization in a 4-week period, while no significant loss occurred from Woodburn soil in the same period. Also, the less chlorinated biphenyls in the Aroclor® showed the most loss and the more chlorinated biphenyls the least loss in accordance with their vapor pressures. The role of the various components of soils or sediments in affecting the vaporization of PCBs from their surfaces is not well understood. However, characteristics such as surface area, organic matter content, type of clay, and pH of the medium which are important in considerations of environmental samples, would likely influence the vaporization of sorbed PCBs.

While vaporization of PCBs sorbed on soil and sediment surfaces is reduced, their vaporization from aqueous solutions is anomalously high, given their low vapor pressure and high molecular weight. Mechanism of this high vaporization rate is not known. However, the losses from aqueous solutions of PCBs and other chlorinated hydrocarbons of very low solubility have been described in terms of fugacity, the escaping tendency of the solute, by MacKay.[19] Fugacity appears to be a useful concept in considering losses of organic materials from aqueous solutions. Based on this approach, the half-life of PCBs in a well-mixed 1-m deep body of water such as a fast-flowing river was calculated to be about 10 hr.[20] Evaporation of PCBs from contaminated rivers and lakes may, thus, represent a major means of their transport into the environment.

D. Sorption Reactions

Transport and fate of PCBs in aquatic systems and their partitioning in different compartments of the environment depend to a large degree on the sorption reactions. These reactions have received considerable attention and sorption-desorption of a number of individual chlorobiphenyls as well as of commercial PCB preparations with sorbents of different characteristics have been studied. Generally, sorption increases with increase in chlorine content of the chlorobiphenyl, and with surface area and organic carbon of the sorbent.

Haque and Schmedding,[13] using individual chlorobiphenyls, found that sorption by four different sorbents, a sand, a soil, a clay, and a humic acid sample occurred in the order: hexachlorobiphenyl > tetrachlorobiphenyl > dichlorobiphenyl. Not only are the chlorobiphenyls with higher chlorine content sorbed in larger quantity but they are also held more tightly on sorbent surfaces. In experiments on desorption of Aroclor® 1254, Haque et al.[12] observed that vapor loss of individual chlorobiphenyls in Aroclor® 1254 decreased with increased chlorination in accordance with their vapor pressures.

MONS 005785

Hiraizumi et al.[21] using a number of adsorbents, observed that the sorption of PCBs was linearly related to the specific surface areas of the adsorbents. The relationships between the PCBs sorbed and their concentrations in solutions have generally been described in terms of equilibrium models such as the Freundlich model:

$$C_w = K \cdot Co^{1/n}$$

where C_w is the amount adsorbed (microgram per gram), Co is the equilibrium solution concentration (microgram per liter), and K and 1/n are constants. For the adsorption and desorption of PCBs, however, the observed isotherms are nonsingular, with desorption showing marked hysteresis. Horzempa and Toro[22] found values of K for desorption of hexachlorobiphenyl to be two to three times the value for adsorption by a lake sediment and two clay minerals, montmorillonite and kaolinite. The sorption appeared to be correlated both with the surface area and the organic matter content. The nonsingular behavior which may result from lack of attainment of equilibrium,[23] besides other poorly understood factors, clearly demonstrates that PCBs are strongly held on the surfaces of the sorbents. Indeed, experiments show that PCBs sorbed by soils remain immobile against leaching with water[24,25] or landfill leachate.[26] Similarly, PCBs are strongly sorbed on sediment surfaces and are thus transported downstream in river systems.[26,27]

A number of investigations show that sorption of PCBs by sediments and soils is related to their total organic carbon.[28-31] These correlations have led to the suggestion that sorption of PCBs and other nonionic organic compounds of low aqueous solubility is due to solute partitioning in the organic matter.[31,32] Consequently, partitioning of an organic compound, as PCBs, between organic matter of soils and sediments and water should correlate well with its partition coefficient between water and an immiscible solvent, as *n*-octanol. Octanol/water partition coefficients and water solubilities of a number of organic compounds, including PCBs, covering more than eight orders of magnitude in solubility (10^{-3} to 10^{4}) and six orders of magnitude in partition coefficient (10 to 10^{7}) have been demonstrated.[32] Thus, estimates of distribution coefficient or sorption of these organic compounds by environmental samples as soils and sediments can be obtained either from their aqueous solubilities or *n*-octanol/water partition coefficients. Although these relationships apply to sorbents with appreciable organic surface coatings, in sorbents with little or no organic matter present, sorption must proceed through other mechanisms.

III. PROCESSES AND PRODUCTS OF PCBs DEGRADATION

A. Photochemical Degradation

One possible route of environmental breakdown of PCBs is photochemical degradation. Early laboratory experiments on photolysis of PCBs were conducted with mercury lamps as UV sources, emitting radiations at a wavelength of about 254 nm. These photodegradations resulted in dechlorination of PCBs. PCBs do absorb in the 280 to 300 nm range,[26] which is the high energy end of the solar spectrum reaching the earth's surface. Many experiments have been performed with the high energy UV radiation and UV fluorescent lamps simulating sunlight, producing less chlorinated PCBs than the starting material. Safe and Hutzinger[33] observed that 2,2',4,4',6,6'-hexachlorobiphenyl photolyses readily at 310 nm, with stepwise loss of chlorine, producing molecular ions corresponding to di-, tri-, tetra-, and pentachlorobiphenyls. Photolysis of 3,3',4,4'-tetrachlorobiphenyl at 300 nm produced 3,4,3'-trichlorobiphenyl and 4,4'-dichlorobiphenyl, while that of 4,4'-dichlorobiphenyl produced 4-chlorobiphenyl. No further dechlorination of 4-chlorobiphenyl occurred because of its lack of absorption of the wavelength used.[26] Although photolysis results mainly in dechlorination of PCBs, examples of photo-induced isomerization and of condensation of the individual chlorobiphenyls have been reported.

MONS 005786

Photochemical degradation of PCBs is influenced by the degree of chlorination, position of chlorine substitution in the ring, and the solvent used for PCB dissolution. Photolysis of PCBs has been studied in the gaseous, solution, and solid phases. In the solution phase, most photolysis experiments have been done with PCBs dissolved in organic solvents or in aqueous organic mixtures because of very low solubility of PCBs in water. In solid phase, PCBs have been photolyzed as thin films on glass plates or as layers adsorbed on silica.

Chlorobiphenyls with higher chlorine content undergo photolysis faster than those with lower chlorine content.[1,37] For example, irradiation at 310 nm wavelength of 0.1% solutions of tetra-, hexa-, and octachlorobiphenyls in hexane for 24 hr under N_2 degraded about 70% of tetra-, 96% of hexa-, and more than 99% of octachlorobiphenyl.[2] Bunce et al.[38] observed increased photodecomposition with increased chlorine content and with increased irradiation time. Ruzo et al.[39] studied photodecomposition of six tetrachlorobiphenyls at 300 nm in cyclohexane and found di- and trichlorinated biphenyls as the major products. They further observed that in 20 hr, all *o*-chlorines produced dechlorinated products. In the absence of *o*-chlorines, *m*-chlorines were cleaved; but when an *o*-chlorine was present, less than 1% of the altered product arose from loss of *m*-chlorine. No cleavage of the *p*-chlorine occurred during this time period.

The primary process in photoreaction is reductive dechlorination, which appears to occur by C–Cl bond cleavage, producing a biphenyl free radical species which abstracts H from the solvent as:

$$ArCl \rightarrow Ar\cdot + Cl\cdot \rightarrow ArH$$

Consequently, photolysis occurs readily in solvents as hexane and isopropyl alcohol whose hydrogens are lost easily by free radical attack.

Ruzo et al.[39] suggested the following scheme to illustrate the photochemical mechanism where excited triplet is considered responsible for the photoreaction and abstraction of hydrogen from the solvent.

$$\underset{\text{PCB in ground state}}{{}^0[P\text{-}Cl]} \rightarrow \underset{\text{Excited singlet}}{{}^1[P\text{-}Cl^*]} \rightarrow \underset{\text{Excited reactive triplet}}{{}^3[P\text{-}Cl]^*}$$

In accordance with this mechanism, photolysis of 2,2',4,4'-tetrachlorobiphenyl in methanol and cyclohexane solutions is illustrated in Figure 5. As expected, formation of HCl was detected during photolysis in both solvents. Although dechlorination was the major reaction in both solvents, small quantities (<3%) of methoxylated products were observed in methanol solution.

The greater photolysis of the *o*-chlorine[4,39] is probably due to steric hindrance to the preferred excited state geometry. Wagner[40] inferred a planar structure for the excited triplet from its inefficiency in quenching ketones. The "crowding" by the *o*-substituents causes greater twisting of the inter-ring bond that decreases its double bond character. Thus, *o*-chlorines are easily lost, relieving the strain on the bond and producing greater quantum yields of the products.

As with individual chlorobiphenyls, the more highly chlorinated commercial PCBs also photolyze preferentially in the environmental samples.[39] These authors estimated that in natural waters, the loss of PCBs may be of the order of 10 to 1000 $g/Km^{-2}/year$. Their estimates also show that in shallow waters, at least one chlorine from chlorobiphenyls of high chlorine content is photolyzed annually; apparently photolysis plays a significant role in PCB chemistry in the environment. These predictions are based upon concentrations of PCBs dissolved in water. It is generally contended, however, that nonpolar compounds, as PCBs, form surface films where concentrations of the compound are much greater and can

MONS 005787

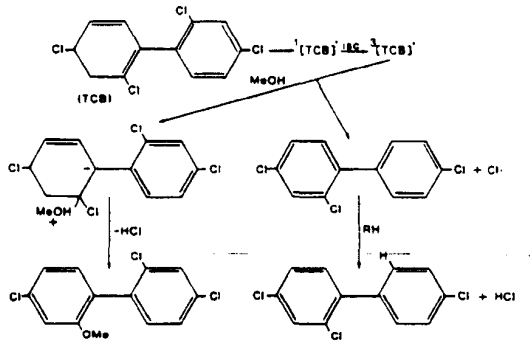


FIGURE 5. Photolysis of 2,2',4,4'-tetrachlorobiphenyl in methanol and cyclohexane solutions [39]

be as high as 10^6 times the concentration in the bulk solution.[38] Consequently, much larger amounts of PCBs can be photolyzed from water bodies.

Environmental photodegradation of PCBs can also increase in the presence of organic compounds that sensitize the photoreaction. Zepp et al.[41] reported that natural substances as humic or other suspended materials can induce or accelerate photolysis of various types of synthetic chemicals, including PCB. Occhiucci and Patachiola[42] have recently observed that photodegradation of PCBs adsorbed on silica gel or montmorillonite clay was considerably enhanced by the addition of triethylamine to the system. The sensitization has been attributed to the formation of an excited charge-transfer complex. Sensitization of the photoreaction in PCBs has also been observed in the presence of aliphatic and aromatic amines,[43,44] and titanium oxide.[45]

B. Biodegradation

Investigations of biodegradation of PCBs in soils, sediments, and lakes and rivers show that both aerobic and anaerobic microorganisms decompose and metabolize PCBs. Pal et al.[46] reviewed biodegradation of PCBs in soil-plant systems and compiled microorganism sources and products of biodegradation of a number of chlorinated biphenyls and commercial PCB preparations. Experiments by Wong and Kaiser[47] show stimulation of bacterial growth in moderate concentration (500 ppm) of Aroclors® 1221, 1242, and 1254 as carbon and energy sources, demonstrating PCBs metabolization by the bacteria. Similarly, growth of *Escherichia coli* was stimulated in the presence of Aroclor® 1242 at the low concentrations of 0.01 and 0.1 ppm. At high concentration, 10,000 ppm Aroclor® 1254, soil microbial activity as measured by CO_2 evolution was inhibited and no degradation of the Aroclor® was observed during a 60-day period.[48] Likewise, Moein et al.[49] detected no degradation of Aroclor® 1254 in a soil during a 2-year period following a spill of transformer fluid. Clearly, while small concentration of PCBs can stimulate bacterial growth by providing carbon, large concentrations are toxic to microorganisms.

A number of reports show that microbial degradation of the lower chlorinated biphenyls occurs at a faster rate than the higher chlorinated biphenyls. Furukawa and Matsumura,[50] using a microbial strain *Alkaligenes* sp. from a lake sediment, found that 2-, 3-, and 4-

MONS 005788

monochlorobiphenyls, 2,3'-, 2,4'-, 3,3'-, 2,4-, 2,6-, and 3,4-dichlorobiphenyls, and 2,4,5- and 2,4,4'-trichlorobiphenyls degraded completely within 20 hr. In contrast, tetra- and pentachlorobiphenyls degraded very slowly. Using different and mixed microbial strains, Metcalf et al.,[31] Baxter et al.,[32] Clark et al.,[33] Liu,[34] and Hankin and Sawhney,[35] also observed increased degradation in lower chlorinated biphenyls.

It has also been observed that some chlorobiphenyls that do not degrade easily when present alone in a culture medium do so when present in a mixture or when biphenyl is added to the substrate.[32] The enhanced degradation is likely due to co-metabolism, which is commonly observed in microbial processes.[36]

Not only does the degree of chlorination influence biodegradation, but the environment also affects biodegradation. For example, Iwata et al.,[37] studied PCB degradation in six different soils and found no degradation of Aroclor® 1254 in two soils, little degradation in two, and significant degradation in the remaining two soils. In a recent study of PCBs degradation in eight soil cultures, Hankin and Sawhney[35] observed that all soils but one degraded at least 70% of Aroclor® 1248 in 14 days, while only three soils degraded 1254. In a 112-day incubation period, over 90% of Aroclor® 1248 and about 40% of Aroclor® 1254 were degraded in some soils, while no Aroclor® 1260 degraded in any soil. Growth of aerobic organisms increased with time as did degradation of the Aroclors®.

Although hydroxylation and ring cleavage are the main mechanisms in biodegradation of PCBs, producing less chlorinated chlorobiphenyls than in the starting materials, other products of PCB biodegradation have also been identified. Degradation of mono- and dichlorobiphenyls by two *Achromobacter* cultures produced *p*-chlorobenzoic acid.[38] Degradation of 4-chlorobiphenyl by a Gram negative bacterium in the presence of nitrate produced four compounds, 2- and 4-hydroxy-4'-chlorobiphenyl and 2- and 4-hydroxymononitro-4'-chlorobiphenyl.[39] The mechanism for the formation of these compounds is illustrated in Figure 6. The proposed mechanism involves the formation of arene oxide intermediates which have high reactivity with biological materials.

Incubation of commercial PCB preparation Aroclor® 1242 with a bacterial culture from a harbor produced a number of alkenes and alkyl benzenes.[40] Under anaerobic conditions, bacterial dehalogenation of halobenzoates, the degradation products of PCBs, proceeded to give CH_4 + CO_2.[41] Clearly, biological degradation of PCBs proceeds via different, as yet not well understood mechanisms depending upon the environmental conditions.

As PCBs are soluble in lipids, they are accumulated by a number of organisms, following lipid/water partition coefficients. Chlorobiphenyls show selective bioaccumulation and degradation, which are affected by both the chlorobiphenyl and the animal species. Hansen[42] has reviewed various factors, including animal species, size of adipose compartments, enzyme activity etc., that affect bioaccumulation and biodegradation by animals. Accumulation ratios of chlorobiphenyls vary among different animals as well as in lipids from different parts of an animal.[43]

While the biodegradation of PCBs has been studied extensively, no information on the fate of PCBs sorbed or taken up by plants is available. Indeed, controversy persists as to whether PCBs are translocated through the plants or are merely sorbed on plant surfaces from PCB vapors or PCB-bearing dust particles. Although long-term alteration in PCBs sorbed by perennial plants or trees is not known, the PCBs in plants growing on contaminated soils increases as the chlorine content of the chlorobiphenyl decreases[44-46] (Figure 7).

C. Thermal Degradation

Because of the stability and potential toxicity of PCBs, numerous laboratory experiments have been conducted for the combustion and complete destruction of these compounds for safe disposal of industrial wastes and used products. While pyrolysis at below 700°C produces various toxic materials, higher temperatures decompose PCBs completely. Buser and Rappe[47]

MONS 005789

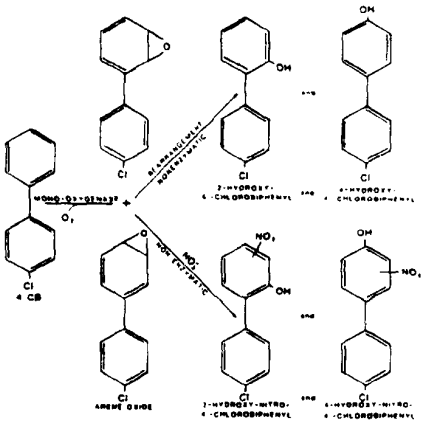


FIGURE 6. Biodegradation of 4-chlorobiphenyl by a Gram negative bacterium in presence of nitrate.[99]

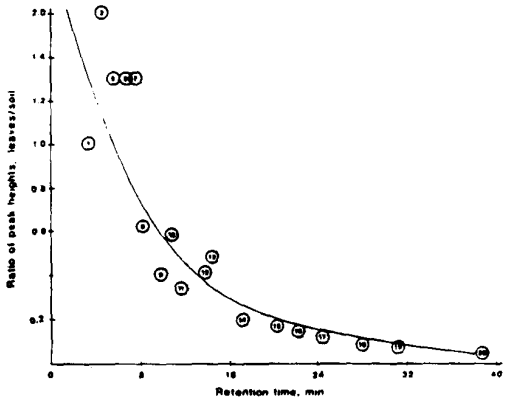


FIGURE 7 Ratios of GC peak heights from extracts of beet leaves grown on a soil contaminated with PCBs to the corresponding peaks from soil extracts. Peak numbers are given in circles. (From Sawhney, B. L. and Hankin, L., *J. Food Protect.*, 47, 232, 1984. With permission.)

MONS 005790

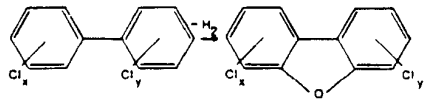


FIGURE 8 Thermal conversion of PCBs to polychlorinated dibenzofurans

conducted pyrolysis of 18 individual chlorobiphenyls including tetra-, penta-, hexa-, hepta-, octa-, nona-, and decachlorobiphenyls at 600°C. Using high resolution GC/MS for their separation and identification, they identified several highly toxic polychlorinated dibenzofurans (PCDFs) in the products and discussed different schemes for their formation. The yield of PCDFs ranged from 0.1 to several percent of the starting PCBs. The conversion of PCBs to PCDFs involves intramolecular cyclization with loss of H_2 (as shown in Figure 8) or HCl and loss or rearrangement of chlorine.

Pyrolysis of commercial PCBs, Aroclor® 1248 by Morita et al.[66] at 300°C and Aroclor® 1254 by Buser et al.[69] at 550 to 650°C formed PCDFs, while above 700°C, the PCBs were completely destroyed. PCDFs as well as chlorobenzenes and *p*-dioxins in municipal incinerator wastes[70-72] have been attributed to chlorophenols and thermal synthesis from phenols and chlorine, and they are not necessarily formed from pyrolysis of PCBs. Mechanisms for their formation are discussed by Choudhry et al.[73] Many chemical procedures of complete dechlorination of PCBs using catalysts have also been developed. Examples are 5% platinum or paladium,[74] nickel boride in alcohol with excess sodium borohydride,[75] and $LiAlH_4$.[76]

Yamasaki et al.[77] reported complete destruction of PCBs in the presence of a methanol and sodium hydroxide solution at 300 to 320°C and 180 kg/cm² pressure. They suggested that the method can be adopted on an industrial scale, using continuous pipeline capillary system. Based upon PCBs incineration in accordance with the EPA test protocols in high efficiency boilers with a thermal destruction efficiency of >99%, Hunt et al.[78] have recently concluded that the method provides a satisfactory means of disposing waste oil contaminated with 50 to 500 ppm PCBs. Thermal destruction, as well as other physicochemical and biological methods, for low and high level PCB contamination have recently been discussed by Ackerman et al.[79]

REFERENCES

1. **Ballschmiter, K. and Zell, M.**, Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography, *Fresenius' Z. Anal. Chem.*, 302, 20, 1980.
2. **Hutzinger, O., Safe, S., and Zitko, V.**, *The Chemistry of PCBs*, CRC Press, Cleveland, 1974.
3. **Jenkins, R. L., McCullough, R., and Booth, C. F.**, Synthesis in the biphenyl series, *Ind. Eng. Chem.*, 22, 31, 1931.
4. **Schmidt, F. M.**, Selective monochlorination of biphenyl with clay catalysts, German Patent 2,056,441, 1971, *Chem. Abstr.*, 75, 35379, 1971.
5. **Lawler, F. E.**, Substitution chlorination of aromatic compounds with liquid chlorine, U.S. Patent 2,608,532, 1952, *Chem. Abstr.*, 48, 3390, 1954.
6. **Webb, R. G. and McCall, A. C.**, Identities of polychlorinated biphenyl isomers in Aroclors, *J. Assoc. Off. Anal. Chem.*, 55, 746, 1972.
7. **Sandoz Ltd., Halogenated vat dyes**, Belgian Patent 665,732, 1965, *Chem. Abstr.*, 64, 19847, 1966.
8. **Albro, P. W., Corbett, J. T., and Schroeder, J. L.**, Quantitative characterization of polychlorinated biphenyl mixtures (Aroclors 1248, 1254 and 1260) by gas chromatography using capillary columns, *J. Chromatogr.*, 205, 103, 1981.
9. **Webb, R. G. and McCall, A. C.**, Quantitative PCB standards for electron capture gas chromatography, *J. Chromatogr. Sci.*, 11, 366, 1973.

MONS 005791

10. **Sawyer, L. D.**, Quantitation of polychlorinated biphenyl residues by electron capture gas-liquid chromatography: reference material characterization and preliminary study. *J. Assoc. Off. Anal. Chem.*, 61, 272, 1978.
11. **Tuinstra, L. G. M. Th. and Traag, W. A.**, Capillary gas chromatographic-mass spectrometric determination of individual chlorobiphenyls in technical Aroclors. *J. Assoc. Off. Anal. Chem.*, 66, 1708, 1983.
12. **Haque, R., Schmedding, D. W., and Freed, V. H.**, Aqueous solubility, adsorption, and vapor behavior of polychlorinated biphenyl Aroclor 1254. *Environ. Sci. Technol.*, 8, 139, 1974.
13. **Chiou, C. T., Freed, V. H., Schmedding, D. W., and Kohnert, R. L.**, Partition coefficient and bioaccumulation of selected organic chemicals. *Environ. Sci. Technol.*, 11, 475, 1977.
14. **Metcalf, R. L., Sanborn, J. R., Lu, P., and Nye, D.**, Laboratory model ecosystem studies of the degradation and fate of radiolabeled tri-, tetra-, and pentachlorobiphenyl compared with DDE. *Arch. Environ. Contam. Toxicol.*, 3, 151, 1975.
15. **Haque, R. and Schmedding, D.**, Studies on the adsorption of selected polychlorinated biphenyl isomers on several surfaces. *J. Environ. Sci. Health.*, B11, 129, 1979.
16. **Zitko, V.**, Polychlorinated biphenyls (PCB) solubilized in water by nonionic surfactants (or studies of toxicity to aquatic animals. *Bull. Environ. Contam. Toxicol.*, 5, 279, 1970.
17. **Mackay, D. and Wolkoff, A. W.**, Rate of evaporation of low solubility contaminants from water bodies to atmosphere. *Curr. Res.*, 7, 611, 1973.
18. **Neu-Ritter, G. M. and Wurster, C. F.**, Sorption of polychlorinated biphenyls (PCB) to clay particulates and effects of desorption on phytoplankton. *Water Res.*, 17, 383, 1983.
19. **Mackay, D.**, Finding fugacity feasible. *Environ. Sci. Technol.*, 13, 1218, 1979.
20. **Mackay, D. and Leinonen, P. J.**, Rate of evaporation of low solubility contaminants from water bodies to atmosphere. *Environ. Sci. Technol.*, 9, 1178, 1975.
21. **Hiraizumi, Y., Takahashi, M., and Nishimura, H.**, Adsorption of polychlorinated biphenyl onto sea bed sediment, marine plankton, and other adsorbing agents. *Environ. Sci. Technol.*, 13, 580, 1979.
22. **Hornsmpa, L. M. and Di Toro, D. M.**, The extent of reversibility of polychlorinated biphenyl adsorption. *Water Res.*, 17, 851, 1983.
23. **Rao, P. S. C. and Davidson, J. M.**, Estimation of pesticide retention and transformation parameters required in nonpoint source pollutant models, in *Environmental Impact of Nonpoint Source Pollution*, Sect. 1, Overcash, M. R. and Davidson, J. M., Eds., Ann Arbor Scientific Publications, Ann Arbor, Mich., 1980, chap. 1.
24. **Fliessow, A. B., Jacobs, L. W., and Mortland, M. M.**, Fate of polybrominated biphenyls (PBB's) in soils. Retention of hexabromobiphenyl in four Michigan soils. *J. Agric. Food Chem.*, 24, 1201, 1976.
25. **Griffin, R. A. and Chou, S. F. J.**, Movement of PCB's and other persistent compounds through soil. *Water Sci. Technol.*, 13, 1153, 1981.
26. **Sawhney, B. L., Frink, C. R., and Glowa, W.**, PCBs in the Housatonic River: determination and distribution. *J. Environ. Qual.*, 10, 444, 1981.
27. **Frink, C. R., Sawhney, B. L., Kulp, K. R., and Frederte, C. G.**, Polychlorinated biphenyls in Housatonic River sediments in Massachusetts and Connecticut: determination, distribution and transport. *Conn. Agric. Exp. Sta. Bull.*, 800, 20, 1982.
28. **Karickhoff, S. W., Brown, D. S., and Scott, T. A.**, Sorption of hydrophobic pollutants on natural sediments. *Water Res.*, 13, 241, 1979.
29. **Sawhney, B. L.**, Sorption of PCBs by soils. *Abstr. 12th Int. Soil Sci. Congr.*, New Delhi, 1982, 33.
30. **Weber, W. J., Voice, T. C., Pirbazari, M., Hunt, G. E., and Ulanoff, D. M.**, Sorption of hydrophobic compounds by sediments, soils and suspended solids. II. Sorbent evaluation studies. *Water Res.*, 17, 1443, 1983.
31. **Lambert, S.M.**, Omega (Ω) a useful index of soil sorption equilibria. *J. Agric. Food Chem.*, 16, 340, 1968.
32. **Chiou, C. T., Peters, L. J., and Freed, V. H.**, A physical concept of soil-water equilibria for non ionic organic compounds. *Science*, 206, 831, 1979.
33. **Pavlou, S. P. and Dexter, R. N.**, Distribution of polychlorinated biphenyls (PCB) in estuarine ecosystems. Testing the concept of equilibrium partitioning in the marine environment. *Environ. Sci. Technol.*, 13(1), 65, 1979.
34. **MacNeil, J. D., Safe, S., and Hutzinger, O.**, The ultraviolet absorption spectra of some chlorinated biphenyls. *Bull. Environ. Contam. Toxicol.*, 15, 66, 1976.
35. **Safe, S. and Hutzinger, O.**, Polychlorinated biphenyls: photolysis of 2,4,6,2',4',6'-hexachlorobiphenyl. *Nature (London)*, 232, 641, 1971.
36. **Ruse, L. O., Zavit, M. J., and Schuetz, R. D.**, Polychlorinated biphenyls: photolysis of 3,4,3',4'-tetrachlorobiphenyl and 4,4'-dichlorobiphenyl in solution. *Bull. Environ. Contam. Toxicol.*, 8, 217, 1972.
37. **Hannan, E. J., Bills, D. D., and Herring, J. L.**, Analysis of polychlorinated biphenyls by gas chromatography and ultraviolet irradiation. *J. Agric. Food Chem.*, 21, 87, 1973.

MONS 005792

38. **Bunce, N. J., Kumar, Y., and Brownlee, B. G.,** An assessment of the impact of solar degradation of polychlorinated biphenyls in the aquatic environment. *Chemosphere*. 7. 155. 1978.
39. **Ruzo, L. O., Zabik, M. J., and Schuetz, R. D.,** Photochemistry of bioactive compounds. Photochemical processes of polychlorinated biphenyls. *J. Am. Chem. Soc.*, 96, 3809, 1974.
40. **Wagner, P. J.,** Conformational changes involved in the singlet-triplet transitions of biphenyl. *J. Am. Chem. Soc.*, 89, 2820, 1967.
41. **Zepp, R. G., Baughman, G. L., and Schlotzhauer, P. F.,** Comparison of photochemical behavior of various humic substances in water: sunlight induced reactions of aquatic pollutants photosensitized by humic substances. *Chemosphere*. 10. 109. 1981.
42. **Oechsner, G. and Patacchiola, A.,** Sensitized photodegradation of adsorbed polychlorobiphenyls (PCB's). *Chemosphere*. 11. 255. 1982.
43. **Ohashi, M., Tsujimoto, K., and Seki, K.,** Photoreduction of 4-chlorobiphenyl by aliphatic amines. *J. Chem. Soc. Chem. Commun.* 384. 1973.
44. **Nordblom, G. D. and Miller, L. L.,** Photoreduction of 4,4'-dichlorobiphenyl. *J. Agric. Food Chem.* 22. 37. 1974.
45. **Carey, J. H., Lawrence, J., and Tosine, H. M.,** Photodechlorination of PCB's in the presence of titanium dioxide in aqueous suspensions. *Bull. Environ. Contam. Toxicol.*, 16, 697, 1976.
46. **Pal, D., Weber, J. B., and Overcash, M. R.,** Fate of polychlorinated biphenyls (PCBs) in soil-plant systems. *Residue Rev.*, 74, 45, 1980.
47. **Wong, P. T. S. and Kaiser, K. L. E.,** Bacterial degradation of polychlorinated biphenyls. II. Rate studies. *Bull. Environ. Contam. Toxicol.*, 13, 249, 1975.
48. **Nissen, T. V.,** Stability of PCB in the soil. *Tidsskr. Planteavl*, 77, 533, 1973.
49. **Moore, G. J., Smith, A. J., Jr., and Stewart, P. L.,** Follow-up study of the distribution and fate of PCBs and benzenes in soil and ground water samples after an accidental spill of transformer fluid. *Proc. Natl. Conf. on Control of Hazardous Material Spills*. Information Transfer, Rockville, Md., 1976, 368.
50. **Furukawa, K. and Matsumura, F.,** Microbial metabolism of polychlorinated biphenyls. Studies on the relative degradability of polychlorinated biphenyl components by *Alkaligenes* sp. *J. Agric. Food Chem.*, 24, 251, 1976.
51. **Metcalf, R. L., Sanborn, J. R., Lu, P.-Y., and Nye, D.,** Laboratory model ecosystem studies of the degradation and fate of radiolabeled tri-, tetra-, and pentachlorobiphenyl compared with DDE. *Arch. Environ. Contam. Toxicol.*, 3, 151, 1975.
52. **Bauer, R. A., Gilbert, P. E., Lidgett, R. A., Malmprise, J. H., and Vedden, H. A.,** The degradation of polychlorinated biphenyls by micro-organisms. *Sci. Total Environ.*, 4, 53, 1975.
53. **Clark, R. R., Chian, E. S. K., and Griffin, R. A.,** Degradation of polychlorinated biphenyls by mixed microbial cultures. *Appl. Environ. Microbiol.*, 37, 680, 1979.
54. **Liu, D.,** Assessment of continuous biodegradation of commercial PCB formulations. *Bull. Environ. Contam. Toxicol.*, 29, 200, 1982.
55. **Hankin, L. and Sawhney, B. L.,** Microbial degradation of PCBs in soil. *Soil Sci.*, 137, 401, 1984.
56. **Jacobson, S. N. and Alexander, M.,** Enhancement of the microbial dehalogenation of a model chlorinated compound. *Appl. Environ. Microbiol.*, 42, 1062, 1981.
57. **Iwata, Y., Westlake, W. E., and Gunther, F. A.,** Varying persistence of polychlorinated biphenyls in six California soils under laboratory conditions. *Bull. Environ. Contam. Toxicol.*, 9, 204, 1973.
58. **Ahmed, M. and Focht, D. D.,** Degradation of polychlorinated biphenyls by two species of *Achromobacter*. *Can. J. Microbiol.*, 19, 47, 1973.
59. **Sylvestre, M., Masse, R., Messier, F., Fauteux, J., Blouillon, J.-G., and Beaudet, R.,** Bacterial nitration of 4-chlorobiphenyl. *Appl. Environ. Microbiol.*, 44, 871, 1982.
60. **Kaiser, K. L. E. and Wong, P. T. S.,** Bacterial degradation of polychlorinated biphenyls--I. Identification of some metabolic products from Aroclor 1242. *Bull. Environ. Contam. Toxicol.*, 11, 291, 1974.
61. **Suflita, J. M., Horowitz, A., Shelton, D. R., and Tiedje, J. M.,** Dehalogenation: a novel pathway for the anaerobic biodegradation of haloaromatic compounds. *Science*. 218. 1115. 1982.
62. **Hansen, L. G.,** Selective accumulation and depletion of polychlorinated biphenyl components: food animal implications. *Ann. N.Y. Acad. Sci.*, 320, 238, 1979.
63. **Hansen, L. G., Tuinstra, L. G. M. Th., Kan, C. A., Stirk, J. J. T. W. A., and Koerman, J. H.,** Accumulation of chlorobiphenyls in chicken fat and liver after feeding Aroclor 1254 directly or fat from swine fed Aroclor 1254. *J. Agric. Food. Chem.*, 31, 254, 1983.
64. **Iwata, Y. and Gunther, F. A.,** Translocation of the polychlorinated biphenyl Aroclor 1254 from soil into carrots under field conditions. *Arch. Environ. Contam. Toxicol.*, 4, 44, 1976.
65. **Suzuki, M., Aizawa, N., Ohsawa, G., and Takahashi, T.,** Translocation of polychlorobiphenyls in soil into plants: a study by a method of culture of soybean sprouts. *Arch. Environ. Contam. Toxicol.*, 5, 343, 1977.

MONS 005793

66. **Sawhney, B. L. and Hankin, L.**, Plant contamination by PCBs from amended soils. *J. Food Protect.* 47, 232, 1984.
67. **Buser, H. R. and Rappe, C.**, Formation of polychlorinated dibenzofurans (PCDFs) from the pyrolysis of individual PCB isomers. *Chemosphere*, 3, 157, 1979.
68. **Morita, M., Nakagawa, J., and Rappe, C.**, Polychlorinated dibenzofuran (PCDF) formation from PCB mixture by heat and oxygen. *Bull. Environ. Contam. Toxicol.*, 19, 665, 1978.
69. **Buser, H. R., Bosshardt, H.-P., and Rappe, C.**, Formation of polychlorinated dibenzofurans (PCDFs) from the pyrolysis of PCBs. *Chemosphere*, 1, 109, 1978.
70. **Olie, K., Lustenhouwer, J. W. A., and Hutzinger, O.**, Polychlorinated dibenzo-p-dioxins and related compounds in incinerator effluents, in *Chlorinated Dioxins and Related Compounds*, Hutzinger, O., Frei, R. W., Merian, E., and Pocchiari, F., Eds., Pergamon Press, New York, 1980, 227.
71. **Liberti, A. and Brocco, D.**, Formation of polychlorodibenzodioxins and polychlorodibenzofurans in urban incinerators emissions, in *Chlorinated Dioxins and Related Compounds*, Hutzinger, O., Frei, R. W., Merian, E., and Pocchiari, F., Eds., Pergamon Press, New York, 1980, 245.
72. **Cavallaro, A., Luciani, L., Cerone, G., Rocchi, I., Invernizzi, G., and Gorni, A.**, Summary of results of PCDDs analyses from incinerator effluents, *Chemosphere*, 11, 859, 1982.
73. **Choudhry, G. G., Olie, K., and Hutzinger, O.**, Mechanisms in the thermal formation of chlorinated compounds including polychlorinated dibenzo-p-dioxins, in *Chlorinated Dioxins and Related Compounds*, Hutzinger, O., Frei, R. W., Merian, E., and Pocchiari, F., Eds., Pergamon Press, New York, 1980, 275.
74. **Berg, O. W., Dinnady, P. L., and Reus, G. A. V.**, Column chromatographic separation of polychlorinated biphenyls from chlorinated hydrocarbon pesticides and their subsequent gas chromatographic quantitation in terms of derivatives, *Bull. Environ. Contam. Toxicol.*, 7, 338, 1972.
75. **Dennis, W. H., Jr., Chang, Y. H., and Cooper, W. J.**, Catalytic dechlorination of organochlorine compounds. V. Polychlorinated biphenyls — Aroclors 1254, *Bull. Environ. Contam. Toxicol.*, 22, 750, 1979.
76. **De Kok, A., Geerdink, R. B., Frei, R. W., and Brinkman, U. A. Th.**, The use of dechlorination in the analysis of polychlorinated biphenyls and related classes of compounds, *Int. J. Environ. Anal. Chem.*, 9, 301, 1981.
77. **Yamasaki, N., Yasui, T., and Matsuoka, K.**, Hydrothermal decomposition of polychlorinated biphenyls, *Environ. Sci. Technol.*, 14, 550, 1980.
78. **Hunt, G. T., Wolf, P., and Fennelly, P. F.**, Incineration of polychlorinated biphenyls in high-efficiency boilers: a viable disposal option, *Environ. Sci. Technol.*, 18, 171, 1984.
79. **Ackerman, D. G., Sciota, L. L., Bakshi, P. S., Delonyea, R. G., Johnson, R. J., Richard, G., Takata, A. M., and Sworzyn, E. M.**, *Destruction and Disposal of PCBs by Thermal and Non-Thermal Methods*, Noyes Data Corp., Park Ridge, Ill., 1983.

MONS 005794

Chapter 3

THE RELIABILITY OF PCB ANALYSIS

A. V. Holden

TABLE OF CONTENTS

I. Introduction 66

II. Composition of PCB Residues 66

III. Analytical Procedures for Environmental Samples 68
- A. Levels of Determination 68
- B. Separation from Interfering Residues 69
- C. Gas Liquid Chromatography 69

IV. Analytical Intercomparison Studies 73

V. Future Developments 75

References 77

MONS 005795

I. INTRODUCTION

Chemical analysis for polychlorinated biphenyls (PCBs), since their identification in environmental samples by Jensen[1] in 1966, has been almost exclusively performed by gas liquid chromatography (GLC), with the aid of the electron capture (EC) detector which is particularly sensitive to organochlorine compounds. This detector, developed by Lovelock,[2] proved very effective in detecting and quantifying organochlorine pesticides such as hexachlorocyclohexane (HCH), aldrin, dieldrin, and DDT and its breakdown products. Each individual compound, as it emerges from the GC column, produces a signal from the EC detector, the magnitude of which is proportional to the amount of the compound present, and hence is related to the concentration in the solution injected. The time elapsing between injection and elution, for a particular temperature of operation, is characteristic of the compound present.

PCBs however, normally occur in mixtures of many individual isomers and homologs, each mixture in GLC analysis producing a pattern of serially eluted peaks emerging from the electron capture detector. Although analyses for PCBs are commonly reported as single values, such values are only obtained by comparing the peak pattern with that from a standard PCB mixture (normally a commercial product), and no information is given of the relative proportions of the different components in the mixture. For various reasons the single value can only be regarded as a compromise, and in many situations it may be both inaccurate and misleading. This chapter discusses the problems of accurate PCB analysis (hardly attainable at the present time) and indicates the developments likely to lead to both improved accuracy and more detailed information regarding individual PCB compounds.

II. COMPOSITION OF PCB RESIDUES

The mixtures of PCB residues which may be subjected to chemical analysis can vary widely, depending on several factors. The commercially produced mixtures intended for a wide variety of uses, according to the physical and chemical properties of these mixtures, vary with the degree of chlorination to which the parent biphenyl has been subjected. Some change in the composition of a commercial product may occur during use, e.g., in heat exchangers or as hydraulic fluids. On discharge to the environment, the mixtures, whether used or not, can undergo further modification in respect of the proportions of individual compounds present, as a result of photodegradation or hydrolysis, preferential solubility, absorption or evaporation, or mixing with other PCB products manufactured at a different level of chlorination. Finally, the group of PCB residues extracted from an environmental sample will usually be mixed with coextracted organochlorine compounds such as pesticides which can interfere in GLC analysis unless steps are taken to avoid this.

A total of 209 chlorinated biphenyl isomers and homologs is theoretically possible. This total consists of

3 Monochloro-
12 Dichloro-
24 Trichloro-
42 Tetrachloro-
46 Pentachloro-
42 Hexachloro-
24 Heptachloro-
12 Octachloro-
3 Nonachloro-
1 Decachloro-

MONS 005796

Commercial producers have manufactured mixtures which have generally resulted from the chlorination of biphenyl to give products containing approximately 20, 30, 40, 50, 60, and 70% of chlorine by weight. The actual percentage of chlorine varies to some extent between manufacturers, and to a smaller degree between batches from an individual manufacturer. Monsanto Ltd. (U.S.), who marketed a series of products under the trade name Aroclor®, listed nine separate products based on PCBs with 21, 32, 42, 48, 54, 60, 62, and 68% by weight of chlorine. (Other products were wholly or partly based on polychlorinated terphenyls). Other manufacturers produced similar mixtures, for example, a 50% chlorinated product which bore a fairly close resemblance to the 48 or 54% chlorinated Aroclor®, but a detailed chemical analysis would almost certainly have revealed some differences in the proportions of different individual PCBs.

Several studies have been made to determine the identities of the individual PCBs in commercial products. Webb and McCall[3] examined the Aroclor® series 1221, 1232, 1242, 1248, and 1254, in which the first two digits denote biphenyls and the last two the degree of chlorination. Aroclor® 1221 contained mainly mono- and dichlorophenyls, 1232 mostly trichlorophenyls with some mono- and dichlorophenyls; 1242 contained most of the compounds present in 1232 but also several tetra- and pentachlorobiphenyls. Aroclor® 1248 extended the mixture to include more pentachloro compounds and a few hexachloro compounds, while Aroclor® 1254 consisted primarily of tetra-, penta-, and hexachlorobiphenyls. A more recent study by Ballschmiter and Zell,[4] using the Clophen® series of products (Bayer, Federal Republic of Germany), demonstrated the presence of the following compounds in the 30, 50, and 60% chlorinated products.

	Clophen® A-30	Clophen® A-50	Clophen® A-60
1 Chloro-	1	0	0
2 Chloro-	9	1	4
3 Chloro-	16	14	7
4 Chloro-	18	13	4
5 Chloro-	10	19	14
6 Chloro-	1	22	22
7 Chloro-	0	0	10
8 Chloro-	0	0	1

As the individual compounds listed were those separated on a particular GLC stationary phase, and a few could not be identified from their specific retention indexes, the true numbers of compounds present will be somewhat greater. It is clear, however, that the 50 to 60% chlorinated preparations will contain at least 60 to 70 different compounds although some will be present only in very small proportions. Improvements in the ability to separate the individual PCBs over a decade are demonstrated by the fact that Webb and McCall[3] in 1971 recorded 33 compounds in Aroclor® 1242, whereas Ballschmiter and Zell[4] in 1980 presented a chromatogram of the same product in which at least 74 peaks could be distinguished.

It is clear that, even in the analysis of a mixture of PCBs in an unused commercial product, the complete separation, identification, and quantification of the individual compounds will be difficult, but the comparison of a chromatogram from a sample with that from a standard solution of the identical commercial product will normally provide a sufficient basis for quantification in terms of total PCB, expressed on the basis of the reference product. When, however, the product has undergone some form of degradation, selective removal of compounds, or mixing with other organochlorines, the analysis by GLC becomes more difficult. Comparison of a chromatogram from a sample with that of a standard commercial product can only provide a crude assessment of the total quantity of PCBs present, information which is often of doubtful value, and may be misleading. In particular, it must be emphasized that quantification in terms of a particular product does not imply that contamination by that product has necessarily occurred.

MONS 005797

The analysis of organochlorine residues by packed column GLC, which has been used by the majority of analysts since the electron capture detector became available over 20 years ago is, in the hands of most analysts, capable of separating at best only some 15 to 20 peaks on the chromatogram resulting from the injection of a PCB sample. As stated above the PCB products most commonly manufactured are likely to contain at least 60 to 70 individual compounds and packed column chromatography is thus inadequate for accurate analysis. However, at the present time the number of individual PCB compounds available as standards for quantification is much smaller than the number which can be separated by capillary column chromatography, so that the latter technique, while a considerable improvement, cannot yet be fully exploited.

Although chromatograms from the most efficient packed columns may show the presence of 15 to 20 separate peaks, many of these are very small and not measurable with sufficient accuracy. Consequently, quantification of the PCB complex using such chromatograms is based usually on the measurement of the heights or areas of at most five or six peaks (some of which may be produced by more than one individual PCB compound). Care must be taken, with environmental samples, to avoid the use of any PCB peak which coincides or overlaps with the *p,p'*-DDT degradation product *p,p'*-DDE, usually coextracted with PCBs. If the analytical technique used fails to separate or eliminate DDT and TDE (another degradation product of DDT) these too may interfere with the PCB chromatogram.

III. ANALYTICAL PROCEDURES FOR ENVIRONMENTAL SAMPLES

Although there are circumstances when the analysis of commercial PCB products is required, either in their original or used form (as in heat exchangers), most analysts are likely to be confronted with the task of determining PCBs in environmental samples following contamination resulting from some form of discharge. The organochlorine residues extracted will usually be a mixture of PCBs and various pesticidal compounds, many of which have chemical properties similar to those of PCBs. This section is therefore directed primarily toward the problems arising from the analysis of environmental samples, or of agricultural or marine products for human consumption.

A. Levels of Determination

Concentrations of total PCB in environmental materials can range from several thousand milligrams per kilogram in lipid samples to the order of about 1 ng/kg in sea water and perhaps 0.1 ng/m^3 in clean air. All materials, whatever their origin, must be extracted, and the final extracts concentrated or diluted to provide concentrations sufficient for analysis at levels easily determinable by GLC techniques. The minimum acceptable response produced by most electron capture detectors occurs with the injection of about 100 pg of total PCB (e.g., 5 $\mu\ell$ of a solution containing 0.02 μg/mℓ), but only four or five of the largest peaks will be measurable. If individual isomers are to be determined, the EC detector may require up to 10 pg of each for an adequate response, and the quantity of a mixture of PCBs required will thus be a minimum of several nanograms. With the smaller volumes (1 to 2 $\mu\ell$) injected for splitless capillary column GLC analysis the total PCB concentration required in the extract for injection may be at least 5 μg/mℓ, if a large number of individual PCBs are to be quantified.

Some environmental samples, e.g., the organs of birds or fish, will limit the quantity of PCBs available for analysis, and hence the concentration in the final extract. With other materials, e.g., air and water, the quantity of samples may be unlimited, but difficulties can arise in handling large volumes for extraction. (Both air and water samples can be extracted by passage through suitable adsorbents in specially designed apparatus.)

Irrespective of the nature of the sample material, when low concentrations of PCBs are

MONS 005798

to be determined adequate precautions must be taken to ensure that no extraneous contamination occurs either in the sampling or subsequent handling. Plastic materials (except PTFE), paints and lubricants, or hydraulic fluids must be avoided, and all solvents and adsorbents used in the analyses must be free of detectable contaminants likely to interfere in the determination of PCBs. Aliquots of all solvents used should give no measurable response on GLC analysis after 100-fold concentration. Dummy runs through the entire extraction, separation, and concentration procedures should provide residue-free chromatograms from the analysis of the final concentrate.

Extraction of biological sample material is usually achieved using Soxhlet extractors and a boiling solvent such as *n*-hexane. It is essential that the solvent penetrates the sample on each cycle, and to ensure this the biological material is often ground to a powder with pure dry sodium sulfate beforehand. However, even with such precautions, some samples such as animal fats, may require periods of extraction up to 16 hr to achieve complete removal of organochlorines and lipids.

Some sample materials containing appreciable quantities of water, if not dried beforehand, will require extraction with a polar solvent such as acetone or diethyl ether, perhaps mixed with hexane. After extraction the polar solvent is removed by evaporation, or washing with residue-free distilled water, until a final extract in hexane is obtained.

B. Separation from Interfering Residues

The initial extract will normally contain organochlorines together with pigments, fats, and other co-extractives which must be eliminated prior to GLC analysis. Three procedures have been developed and widely used over the past 25 years — solvent partition, sulfuric acid or alkaline treatment, and adsorption chromatography.

Solvent partition involves dispersion of the organochlorine residues and fats in a mixture of hexane and either dimethylformamide[3] or acetonitrile,[4] the organochlorines remaining largely in the hexane fraction. The method was developed for pesticide analysis, and it is doubtful whether it is now sufficiently efficient to ensure complete extraction of PCBs and some other organochlorines.

Sulfuric acid treatment[5] of the hexane extract results in the destruction of fats and pigments, usually forming water soluble compounds which can be removed by shaking with distilled water, although many analysts remove aliquots of the hexane layer without such washing. Hydrolysis of fats with alcoholic potassium hydroxide is sometimes used, the alkali and hydrolysis products being removed by an aqueous wash. Both procedures will destroy certain pesticides, but PCBs are unaffected.

Adsorption chromatography employs columns of either Florisil[6] or alumina,[7] through which a volume of the hexane extract is passed to remove the lipids and pigments. Separation of the various organochlorines into several fractions can also be achieved on columns of Florisil[8] or silica[9,10] by the use of solvents of different polarity, the PCB group usually being separated from most interfering organochlorine pesticides except *p,p'*-DDE. However, in the presence of chlorinated naphthalenes, chlordane, and toxaphene more elaborate techniques are required.

Adsorption chromatography with fractionation is perhaps the most widely used technique, but a somewhat similar procedure using gel permeation chromatography[11,12] deserves more attention, as it can be automated. It can remove lipids and separate organochlorines in the same process.

C. Gas Liquid Chromatography

In this section only an outline can be given of the main procedures used for GLC analysis. Most analysts over the past 20 years have employed packed glass columns up to 2 m in length and 2- to 6-mm bore. As indicated earlier, injections of PCB extracts using such

MONS 005799

columns produce chromatograms showing a maximum of about 20 peaks but often only 6 or 7 peaks. The resolution of individual peaks can be expressed in terms of the number of equivalent theoretical plates calculated from the width and elution time of a specified peak, the higher number denoting greater separation efficiency. Uthe and Musial[13] compared the results submitted by 23 analysts in an international comparative study, and found that the GLC columns used produced plate counts ranging from 320 to 3600. (Capillary columns achieve separations equivalent to plate counts exceeding 10,000 and often up to 100,000.)

The stationary phases used in packed GLC columns, all stable at the high operating temperatures, have different compound separation characteristics, but with the large number of organochlorine compounds likely to be present in any environmental sample it is inevitable that several compounds will elute at the same times as others. However, for the determination of total PCB little difference in the final measurement is evident from the use of the various stationary phases available. The degree of resolution achieved depends primarily on the care taken in preparing and coating the solid support used for packing the columns, rather than on the selection of the stationary phase.

In recent years capillary column chromatography has been developed, using glass or silica columns 25 to 50 m in length with a bore of 0.2 to 0.3 mm. The column temperature is usually programmed to improve the separation of the various organochlorine compounds, particularly those which are more volatile. With such columns it is possible to separate over 100 different peaks from an injection of a mixture of commercial PCB products.[13] Approximately half of the peaks are quantifiable by peak height, but electronic area integration would probably enable most peaks to be measured.

Although the separation of individual PCB compounds is much more effective with capillary columns than with packed columns, some overlapping or coincidence of peaks will still occur, irrespective of the particular stationary phase chosen. If other organochlorine compounds are present, and a few pesticide residues may be eluted from adsorption columns with PCBs despite the use of different solvents, the possibility of confusion between peaks emerging from the capillary column at the same time is increased.[14]

The identification of individual PCB compounds on capillary GC chromatograms has been studied by several workers,[4,14-18] using mass spectrometric and NMR spectroscopic techniques to establish the molecular structure of individual PCB components, and confirming the identity of some by comparison with the injection of known synthetically prepared compounds.

Ballschmiter and Zell[4] state that retention indexes, which they measured using a series of *n*-alkyltrichloroacetates as reference homologs, depend strongly on the separation characteristics of the individual glass capillary column used, involving both the type of stationary phase and the nature of the glass surface on which it is coated. No standard PCB retention indexes can be defined at present, but the matching of peaks with those from reference compounds enables other unknown peaks to be identified through retention indexes on a particular column. Examples of capillary chromatograms are shown in Figures 1 and 2.

The 209 possible PCB compounds are systematically numbered,[4] and their positions calculated in the form of retention indexes. The precision of these calculations, which serve to identify individual compounds not available as reference compounds, is high. Ballschmiter and Zell[4] measured the retention indexes of 43 available compounds, which agreed well with those measured as PCB components of three commercial (Clophen®) products. A further 66 retention indexes were calculated, and were in good agreement with those measured from other components of the Clophen® mixtures.

Chromatograms obtained by Ballschmiter and Zell[4] on capillary columns coated with Apiezon L show a number of examples of coincidence (or possible coincidence) of individual PCB components despite the generally good separation of peaks (see also examples in Figures 1 and 2). For Aroclor® 1254, ten peaks combining two different components and one

MONS 005800

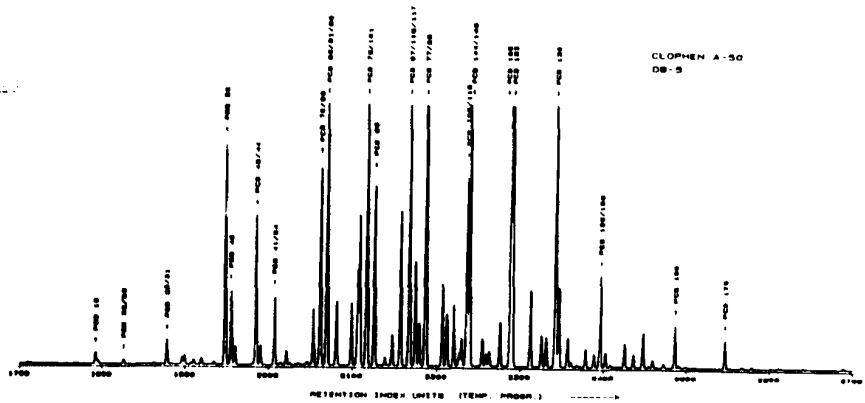


FIGURE 1. Capillary column chromatogram of Clophen® A-50. Instrument: Hewlett-Packard 5880A. Column: 60 m x 0.33 mm bore, fused silica. Stationary phase: DB-5, polymethyl-5% phenyl-siloxane; temperature programmed. (Courtesy of Prof. K. Ballschmiter.)

MONS 005801

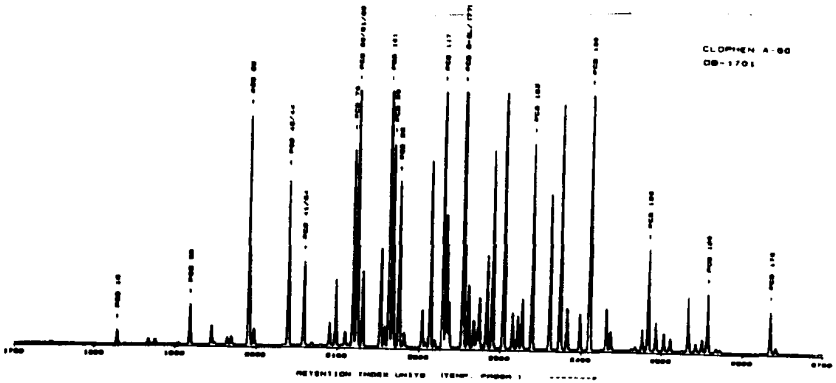


FIGURE 2 Capillary column chromatogram of Clophen® A-50. Instrument: Hewlett-Packard 5880A. Column: 30 m × 0.23 mm bore, fused silica. Stationary phase: DB-1701, 7% phenyl, 7% cyanopropyl, 86% methyl silicones, temperature programmed. (Courtesy of Prof. K. Ballschmiter.)

MONS 005802

combining four components occur. In the latter case two are pentachloro- and two hexachlorobiphenyls, the grouping also appearing in the chromatographs of Aroclor® 1242 and 1260. Employing a different stationary phase (SE 30), other examples of coincidence of different components in the Clophen® series of products were found by the same authors. It is thus evident that even the improved techniques of capillary chromatography are not yet able to achieve complete separation of all PCB components, and thus full quantification of PCB mixtures.

There is ample evidence that the pattern of PCB peaks isolated from environmental samples usually differs in detail from those of commercial mixtures, although a rough matching with the 54 to 60% chlorinated types is sometimes possible. For approximate quantification of total PCB this level of agreement may be sufficient, but if the question of toxicity is important it will become necessary to know both the concentrations of individual PCB components and their relative toxicities. At the present time too few have been synthesized, and the quantities available are too small for sufficient research on toxicity to be undertaken. Yet, with the recognition that the proportions of PCB components in environmental samples differ in detail from those found in commercial mixtures, it is unwise to assume that the toxicity of any mixture of residues found in the environment would be similar to that of a concentration of a commercial product calculated on a total PCB basis. More information is required on the mechanism of toxic action of PCBs, perhaps leading to an indication of the molecular structures most likely to be toxic. This in turn would enable analysts to confine their measurements to the compounds of greatest interest. (The toxicity of impurities in commercial products, particularly the chlorinated dibenzofurans, must also be considered.[17,18])

IV. ANALYTICAL INTERCOMPARISON STUDIES

In the foregoing section the ultimate need for the determination of individual PCB compounds has been stressed. At present, however, too few laboratories are equipped with the essential instrumentation, and our knowledge of the techniques of separation and identification is inadequate. For the past 15 years laboratories in different countries have been developing their expertise in the general field of organochlorine analysis, primarily for the ubiquitous types of organochlorine pesticide residues, and total PCB determinations have been attempted as part of such analyses. The degree of variability experienced among analysts in respect of total PCB determinations is, not surprisingly, rather greater than can be achieved for certain easily separated and determinable pesticides using the same analytical procedure.

Holden[19] reviewed the results of a number of international organochlorine intercomparison exercises conducted on behalf of OECD (Organisation for Economic Co-operation and Development) up to 1972. In these studies the analysts were asked to use their customary analytical procedures, and their own reference standards, no attempt being made to specify any common procedure. In 1969 a solution of a commercial PCB mixture in hexane, sealed in glass ampoules, was distributed and 14 laboratories reported their analytical results. A 60% chlorinated mixture (similar to that in the sample) was used by 12 laboratories as reference, obtaining a mean value of 10.17 mg total PCB per liter, as compared with the true value of 9.8 mg/ℓ. Two laboratories using a reference identical to that of the sample obtained values of 10.0 mg/ℓ, and the coefficient of variation for the 16 laboratories was ± 10.2%. Two other laboratories employing a 50% chlorinated reference mixture reported a concentration of 8.0 mg/ℓ, an underestimate of only about 20%.

When an environmental sample of cormorant tissue heavily contaminated by PCBs was analyzed by the laboratories, the reference solutions chosen included 50, 54, and 60% chlorinated mixtures. Fourteen laboratories reported concentrations of PCBs between 240 and 525 mg/kg, but eight basing their calculations on a 60% chlorinated reference found 279 to 462 mg/kg. At this early period of PCB analysis, and for such high concentrations, the agreement was reasonably good.

MONS 005803

In 1972, a sample of fish oil spiked with organochlorines including PCBs was distributed, and on this occasion 14 laboratories reported concentrations averaging 9.23 mg/kg, with a coefficient of variation of ± 12.0%. Unlike the solution in hexane, both the fish oil and earlier cormorant tissue required a full clean-up and separation procedure. The methods of measuring PCB concentrations were varied, using peak heights or peak areas of from one to nine peaks.

One criticism made of the exercise using spiked fish oil was that the concentrations present were unrealistically high by comparison with those the analysts were accustomed to expect from environmental samples. (This situation arose because the spike levels were intentionally an order of magnitude greater than the residue levels in the matrix oil, to ensure that the difference from the matrix could be estimated with reasonable accuracy). In 1974 a vegetable oil virtually free of organochlorine contamination was used as a matrix and spiked with lower concentrations of organochlorines. This sample was distributed both among OECD laboratories and to several laboratories representing countries belonging to the International Council for the Exploration of the Sea (ICES).

The results of the PCB determinations by 24 analysts in the OECD exercise[20] gave a mean concentration of 1.100 mg/kg, with a mean percentage recovery of 97.3% and a coefficient of variation of 15.4%. (Individual pesticide residues were also determined with coefficients of variation in the range 10.3 to 28.1%.) The ICES analysts,[21] reporting from eight laboratories, found a mean concentration of 1.100 mg/kg with a mean percentage recovery of 96.3% and a coefficient of variation of 9.0%. (The range of coefficients of variation for other organochlorine residues in this smaller group of analysts was 6.5 to 40.6%.)

The agreement between analysts was considered to be lower than desirable, when organochlorine residue determinations are made in the interests of acceptability of the source material for human consumption. A coefficient of variation of ± 40% implies that the results from 19 out of 20 analysts may span a range covering an order of magnitude. Even a coefficient of variation of ± 20% could lead to substantial disagreement as to whether a commodity was unfit for consumption. Further intercomparison exercises have therefore been considered essential to examine whether improved analytical techniques and greater experience would increase the level of agreement among analysts.

In 1978, samples of a fish oil, considered to contain a relatively low level of organochlorine contamination and not spiked with additional residues, were distributed to 43 laboratories in 18 ICES countries. Many analysts had difficulty in conducting the analysis of this sample, and over a period of 10 months 30 laboratories reported,[22] 2 of them attempting the analysis by each of 2 methods. A total of 28 values were reported for the total PCB content, but it was found that those analysts using a sulfuric acid clean-up technique obtained results significantly different from those using other methods. The 13 values from sulfuric acid treatment averaged 863.15 μg/kg, with a coefficient of variation of ± 50.0%, while the 15 values obtained by other methods averaged 451.40 μg/kg, with a coefficient of variation of ± 45.3%. The coefficients of variation for seven pesticidal residues reported ranged from 32.7 to 71.1%. This exercise demonstrated the difficulties presented by the analysis of an environmental sample containing a relatively low level of contamination.

Six laboratories had used capillary GC columns in the 1978 exercise, but one could not quantify the PCBs, and the other five reported results averaging 472.75 μg/kg with a coefficient of variation of ± 42.6%. Nevertheless, many analysts considered that progress would only be achieved in the direction of capillary GC analysis. In 1980, a further ICES exercise was conducted, again using a marine fish oil, in both spiked and unspiked form.[23] For the unspiked oil, 23 results (excluding one outlier) averaged 1.07 mg/kg of PCB, with a coefficient of variation of ± 31%. The spiked oil results averaged 1.93 mg/kg with a coefficient of variation of ± 21%. Uthe and Musial,[23] reporting on this exercise, were not able to confirm that sulfuric acid treatment gave higher values for PCB as only two analysts

MONS 005804

used the method, but they identified a difference in the means of the PCBs reported by laboratories using Florisil for sample clean-up as compared with alumina.

This exercise also established that neither the use of a common PCB standard solution nor a common method of calculation of the PCB concentration gave any significant improvement in agreement among analysts. The determination of PCB concentrations was influenced by the stationary phase of the GLC column used, and the use of peak heights rather than peak areas on the same chromatogram also gave somewhat different results.

One further intercomparison exercise conducted among ICES analysts was confined to those using capillary GC.[23] Five laboratories analyzed the spiked and unspiked herring oil used in the 1980 ICES exercise, and reported the individual PCB isomers, identified by their IUPAC numbers, found in both samples and in Aroclor® 1254. A total of 35 different PCB compounds was reported, but individual laboratories reported different compounds, between 15 and 22 compounds being listed by each analyst. Of the 35 isomers, 32 were found in the Aroclor® sample, 15 to 20 again being reported by any one laboratory. The total amount of PCB isomers reported in the Aroclor® sample represented 52.2 to 88.1% by weight of the total Aroclor® present.

Only six isomers were reported by all five analysts, three of them coeluting with other isomers. Four analysts reported on a further four isomers. Uthe et al.[22] concluded that some analysts (or suppliers of reference isomers) wrongly identified some isomers, and that coelution of isomers on capillary columns was a source of error. It is possible that some isomers available commercially may not be pure, and the quantities available are often insufficient for the preparation of accurate reference standards.

Other intercomparison exercises conducted by the International Atomic Energy Agency (IAEA) on oyster and sea plant tissue,[24] and by the Intergovernmental Oceanographic Commission[25] on sea water have confirmed the current difficulty in approaching a satisfactory level of agreement among analysts undertaking organochlorine analysis including PCBs in environmental materials. For the reasons stated earlier, it will be necessary to move in the direction of more accurate techniques using capillary GLC, but it is essential that sufficient quantities of several of the more common isomers in pure form are made available at a reasonable cost for both standardization and toxicity testing.

V. FUTURE DEVELOPMENTS

The accuracy of the determination of individual organochlorine compounds, as in the case of any trace contaminant, decreases with the level of contamination. Horwitz et al.[26] showed that the interlaboratory coefficient of variation increases exponentially with decreasing concentration, and suggested that at the microgram per kilogram level of contamination it might be at least ±50%. Before analysts are asked to determine very low concentrations of PCBs in any samples, and attempt to achieve levels of precision and accuracy which may well be unattainable, those requiring the information should consider seriously whether less stringent demands would be sufficient. If toxicological data indicate that concentrations of total PCB below 5 mg/kg in material for human consumption are acceptable, screening at a 1 mg/kg limit of detection should be adequate, and the added difficulties presented by attempts to determine concentrations down to 0.1 mg/kg can be avoided.

However, if future research indicates that certain individual PCBs, perhaps minor components in commercial mixtures, are particularly toxic to life in some form, these compounds will require determination at significantly lower concentrations than are calculated for total PCB. Both the separation and measurement techniques necessary to achieve this will demand greater care in operation, with an associated increase in the cost of analysis.

It will also be necessary, for the better understanding of the processes which determine the movement of PCBs within our environment and the ultimate fate of individual com-

MONS 005805

ponents, to measure very low concentrations of some isomers (or possibly their degradation products) in air, water, soil, sediments, and biological material. It is not always essential that a high level of interlaboratory agreement is achieved, but within the individual laboratory undertaking such research, regular monitoring of the analytical precision and accuracy is necessary to ensure that the data produced are always comparable, particularly when the analysts change or the techniques are modified. Suggestions for the improvement of routine analytical techniques for organochlorines including PCBs have been made by Holden et al.[7] and are repeated in the following paragraphs.

Regular testing by intercalibration or intercomparison is highly desirable to ensure that the quality of analytical data is maintained. This should involve the analysis of appropriate matrixes containing PCBs, e.g., soil or biological samples, or aliquots of suitable absorbents such as resins which have been used to extract contaminants from air or water. For biological materials vegetable or fish oils provide a suitable matrix, particularly if spiking with known amounts of selected compounds is required, as effective mixing can be achieved using oils.

A number of sources of potential error in organochlorine analysis are possible including impure solvents, inadequate clean-up of sample extracts to remove lipids pigments and other interfering material, lack of separation of PCB residues from other organochlorine compounds, poor resolution of peaks or sensitivity in GLC analysis, failure to concentrate extracts accurately or sufficiently, and variability in the volume of extract injected into the chromatograph.

Improvements in techniques used for routine analysis which will help to eliminate or at least reduce the degree of error include:

1. The use of solvents of the highest quality. No significant GLC peaks which could interfere with the measurement or identification of PCB compounds should be present after 100-fold concentration of the solvent.
2. Extraction of biological tissues (suitably ground and in dried form) should be carried out in Soxhlet extractors for a minimum of 40 c.
3. Extracts should be cleaned up with absorbent columns, using Florisil or alumina.
4. Organochlorine residues in extracts must be subdivided into at least two fractions, PCB residues being separated from other compounds as completely as possible.
5. The PCB fraction (or fractions) must be concentrated to not less than 1 ml accurately measured (unless techniques are developed for the reduction to smaller volumes precisely measured).
6. Internal standards (e.g., the series of *n*-alkyltrichloroacetates) should be used to correct for errors at the GLC injection stage.
7. For the determination of individual PCB compounds, glass capillary columns with a resolving power equivalent to at least 50,000 theoretical plates should be used.
8. The sensitivity of the GLC detector should be sufficient to give a peak height response of five times the recorder baseline width for 10 pg of dieldrin or *p,p'*-DDE, or the equivalent area response for automatic integration.
9. The detector response should be within the linear range with frequent calibration.
10. Standard reference solutions should be renewed regularly, and solvent evaporation from these solutions minimized by refrigeration.

It is essential that each individual laboratory carries out regular calibration checks on the analytical procedure used, including the clean-up and pre-GLC separation stages. The international standardization of techniques is an unlikely prospect, but differences between laboratories in respect of performance, which currently give rise to coefficients of variation in PCB intercomparison studies of 30 to 50%, should be reduced significantly by better control in individual laboratories. The wider use of capillary columns, and the increased

MONS 005806

availability of individual PCB compounds as reference material, together with automated integration and data recording, are essential for the complete analysis of the spectrum of PCB residues in a sample. The conditions under which the analytical procedures are conducted, whether at the clean-up and separation stages before GLC analysis, at the GLC injection stage, or in temperature-programmed GLC analysis, must all be clearly specified and rigidly adhered to, if quantification at acceptable levels of accuracy and precision is to be achieved.

REFERENCES

1. **Jensen, S.**, The PCB story. *Ambio* 1, 123, 1972.
2. **Lovelock, J. E. and Lipsky, S. R.**, Electron affinity spectroscopy — a new method for the identification of functional groups in chemical compounds separated by gas chromatography. *J. Am. Chem. Soc.* 82, 431, 1960.
3. **Webb, R. G. and McCall, A. C.**, Quantitative PCB standards for electron capture gas chromatography. *J. Chromatogr. Sci.*, 11, 366, 1973.
4. **Ballschmiter, K. and Zell, M.**, Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius Z. Anal. Chem.*, 302, 20, 1980.
5. **de Faubert Maunder, M. J., Egan, H., Godley, E. W., Hammond, E. W., Roberts, J., and Thomson, J.**, Clean-up of animal fats and dairy products for the analysis of chlorinated pesticide residues. *Analyst* 89, 168, 1964.
6. **Jones, L. R. and Riddick, J. A.**, Separation of organic insecticides from plant and animal tissues. *Anal. Chem.*, 24, 569, 1952.
7. **Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G.**, DDT and PCB in herring and cod from the Baltic, the Kattegat and the Skagerrak. *Ambio Special Report*, No. 1, 71, 1972.
8. Pesticide Analytical Manual, Vol. 2, U.S. Department of Health, Education and Welfare, Food and Drug Administration, Washington, D.C., 1975.
9. **Holden, A. V. and Marsden, K.**, Single-stage clean-up of animal tissue extracts for organochlorine residue analysis. *J. Chromatogr.*, 44, 481, 1969.
10. **Wells, D. E. and Johnstone, S. J.**, Method for the separation of organochlorine residues before gas-liquid chromatographic analysis. *J. Chromatogr.*, 140, 17, 1977.
11. **Tindle, R. C. and Stalling, D. L.**, Apparatus for automated gel permeation clean-up for pesticide residue analysis. *Anal. Chem.*, 44, 1768, 1972.
12. **Krahl, D. W. and Leonard, E. N.**, Isolation of xenobiotic chemicals from tissue samples by gel permeation chromatography. *Anal. Chem.*, 50, 182, 1978.
13. **Uthe, J. F. and Musial, C. J.**, Report on the fourth ICES intercalibration study of PCBs in biological material, Cooperative Research Report No. 115, International Council for the Exploration of the Sea, Copenhagen, 1982.
14. **Zell, M. and Ballschmiter, K.**, Baseline studies of the global pollution. III. Trace analysis of polychlorinated biphenyls (PCB) by ECD glass capillary gas chromatography in environmental samples of different trophic levels. *Fresenius' Z. Anal. Chem.*, 304, 337, 1980.
15. **Sissons, D. and Welti, D.**, Structural identification of polychlorinated biphenyls in commercial mixtures by gas-liquid chromatography, nuclear magnetic resonance and mass spectrometry. *J. Chromatogr.*, 60, 15, 1971.
16. **Zell, M., Neu, H. J., and Ballschmiter, K.**, Single component analysis of polychlorinated biphenyl (PCB) — and chlorinated pesticide residues in marine fish samples. *Fresenius' Z. Anal. Chem.*, 292, 97, 1978.
17. **Vos, J. G. and Beems, R. B.**, Dermal toxicity studies of technical polychlorinated biphenyls and fractions thereof in rabbits. *Toxicol. Appl. Pharmacol.*, 19, 617, 1971.
18. **Bowes, G. W., Mulvihill, M. J., Simoneit, B. R. T., Burlingame, A. L., and Risebrough, R. W.**, Identification of chlorinated dibenzofurans in American polychlorinated biphenyls. *Nature (London)*, 256, 305, 1975.
19. **Holden, A. V.**, The OECD international co-operative studies of organochlorine residues in wildlife. in *Environmental Quality and Safety*, Vol. 3, Coulston, F. and Korte, F., Eds., Georg Thieme, Stuttgart, 1975, 40.
20. Chemical Trends in Wildlife, An International Cooperative Study, Organisation for Economic Co-operation and Development, Paris, 1980, 26.

MONS 005807

21. **Topping, G. and Holden, A. V.**, Report on intercalibration analyses in ICES North Sea and North Atlantic baseline studies. Co-operative Research Report No. 80. International Council for the Exploration of the Sea, Copenhagen, 1978.
22. **Holden, A. V. and Topping, G.**, Report on further intercalibration analysis in ICES pollution monitoring and baseline studies. Co-operative Research Report No. 108. International Council for the Exploration of the Sea, Copenhagen, 1981.
23. **Uthe, J. F., Musial, C. J., and Palmork, K. H.**, A report on an intercomparison study of the determination of chlorinated biphenyl (PCB) isomers in fish oil. Paper C.M. 1981/E:49. International Council for the Exploration of the Sea, Copenhagen, 1981.
24. **Anon.**, Activities of the International Laboratory of Marine Radioactivity. Report No. IAEA-187. International Atomic Energy Agency, Vienna, 1976.
25. **Andersen, N., Bowers, J. M., Duinker, J., Knap, A., Palmork, J., and Villeneuve, J.-P.**, Scientific report of the intercalibration exercise. The IOC-WMO/UNEP pilot project on monitoring background levels of selected pollutants in open ocean waters. Intergovernmental Oceanographic Commission Tech. Ser. 22. UNESCO, Paris, 1982.
26. **Horwitz, W., Kamps, L. R., and Boyer, K. W.**, Quality assurance in the analysis of foods for trace constituents. *J. Assoc. Off. Anal. Chem.* 63, 1344, 1980.
27. **Holden, A. V., Topping, G., and Uthe, J. F.**, The use and relevance of analytical intercomparison exercises in monitoring the marine environment. *Can. J. Fish. Aquat. Sci.*, 1985, in press.

MONS 005808

Chapter 4

ATMOSPHERIC TRANSPORT OF PCBs TO THE OCEANS

E. Atlas, T. Bidleman, and C. S. Giam

TABLE OF CONTENTS

I. Introduction 80

II. PCBs in the Atmosphere 80
- A. Collection Methods for PCBs in the Air 80
- B. PCB Concentrations in the Air 83
- C. The Atmospheric Reservoir of PCBs 83
- D. Vapor-Particle Partitioning of PCBs 85

III. Atmospheric Removal Processes for PCBs 86
- A. Collection Methods for Aerial Deposition 86
- B. PCB Levels in Precipitation and Dry Deposition 88

IV. Atmospheric Inputs of PCBs to the Ocean 89
- A. Dry Deposition of Particles 89
- B. Wet Deposition of Particles 91
- C. Dry Deposition of Gases 91
- D. Wet Deposition of Gases 93
- E. Comparison of PCB Inputs to the Ocean 94

V. Summary 96

References 96

MONS 005809

I. INTRODUCTION

The atmosphere is increasingly being recognized as a significant pathway for the movement of chemicals in the environment.[1,2] Once airborne, stable chemicals such as polychlorinated biphenyls (PCBs) can be transported thousands of kilometers from their original sources, contaminating even remote regions of the earth. For example, PCB and other organochlorines have been detected in air from Enewetak Atoll[3] and Antarctica,[4] marine mammals from Antarctica,[5] and surface water from the major oceans and seas.[6,7] This chapter will discuss several aspects of aerial PCB transport to the oceans. First we will review sampling procedures for PCB in ambient air and atmospheric deposition, and will summarize some recent measurements of airborne PCB around the globe. This will provide data to estimate the atmospheric reservoir of PCB. Then we will examine rates and mechanisms of air-to-sea PCB transfer.

II. PCBs IN THE ATMOSPHERE

A. Collection Methods for PCBs in the Air

PCBs are found in the atmosphere as vapors or associated with particulate matter. As will be discussed later, the gaseous form predominates, typically comprising >90% of the total PCB concentration. PCB levels in ambient air are on the order of a few picograms per cubic meter to nanograms per cubic meter, and hundreds or even thousands of cubic meters of air must be sampled to obtain enough material for analysis. With a high volume (hi-vol) sampling system, particulate PCBs are collected on a precombusted glass- or quartz-fiber filter and an adsorbent column behind the filter is used to retain gaseous PCBs.

Within the last decade solid adsorbents have become popular for collecting organic vapors in ambient and workplace air. References to some of these applications for sampling PCB vapors in a variety of situations are given in Table 1. The list emphasizes the literature since 1977, and is not intended to be comprehensive but illustrative of the widespread usage of these sampling systems. Adsorbents are also useful for collecting many other types of high molecular weight organic vapors, including pesticides, phthalate esters, and polycyclic aromatic hydrocarbons (PAH). References to these applications and to earlier work can be found in the Table 1 citations and in several reviews on organic vapor sampling.[10-14]

An important consideration for an adsorbent is its blank value. Polymeric adsorbents are usually precleaned by Soxhlet extraction with chromatographic quality solvents followed by drying under vacuum or in organic-free air. Florisil has the advantage of being cleaned up easily by baking in a muffle furnace at 320°C.[32,33] With care it is possible to reduce electron-capturing impurities to a few nanograms, quantified as PCB. Some reported PCB blanks for different adsorbents are listed in Table 2. These generally range from <10 to 30 ng total PCBs for the polymeric materials and less for Florisil. A blank of 20 ng total PCBs corresponds to a detection limit of 0.03 to 0.04 ng/m for a 500 to 700 m^3 sample, a typical volume for a 24-hr air monitoring period. This is about two orders of magnitude below urban air PCB concentrations. In remote and oceanic regions, air volumes can be increased to raise the sample/blank ratio if collection efficiency can be maintained.

The ability of an adsorbent bed to quantitatively collect vapors can be determined in several ways. One approach to measuring collection efficiency is to vaporize a known quantity of chemical into an airstream which is passed through an adsorbent bed. The fraction collected is calculated by mass balance from the residues found in the sampling train. Sometimes retention efficiencies are measured instead by spiking the adsorbent with a known quantity of chemical and determining the percent retained after clean air has been pulled through the trap. Collection efficiencies in field work are often estimated by separately analyzing front and backup adsorbent traps. If the second trap contains much less material than the first

MONS 005810

Table 1
SOLID ADSORBENTS USED FOR PCB VAPOR SAMPLING

Adsorbent	Air volume range (m^3)	Application	Ref.
Polyurethane foam	100—1600	Collection studies	10—14
	800—1600	Urban air	15—17
	400—4000	Ocean air	3, 4, 18—21
	8—16	Collection study	22
	1	Collection study	23, 24
	1	Home and workplace air	24, 25
XAD-2	70—3000	Collection studies	22, 26
	500—1800	Urban air	16, 27
	400—1100	Lake Michigan air	27
	200—400	Lake Superior air	28—30
	6—18	Collection study	22
	0.005—0.01	Collection study	31
Tenax-GC	300—1600	Urban air	15, 16
Florisil	8—20	Collection studies	22, 32
		Incinerator/capacitor mfg	33
	10—15	Urban air	34
	75—150	Ocean air	3
	400—1500	Ocean air	35
Chromasorb® 102		Urban air, stack gases	36
Mixed adsorbent cartridges	300	Collection study	11

Table 2
PCB BLANK VALUES (ng) FOR SOLID ADSORBENTS

Adsorbent	Aroclor® 1016/1242	Aroclor® 1254	Total PCB	Cleanup*	Remarks	Ref.
PUF	9	5	14	A, H_2SO_4	Immediately after cleanup	16
	19	10	29	A, H_2SO_4	3—35 mo storage	16
		6		F		19
			<32	None		10
			<10	None		18
			≤2	H_2SO_4		4
			<3†	HPLC, S		20
XAD-2	8	7	15	A, H_2SO_4	Immediately after cleanup	16
	11	14	25	A, H_2SO_4	8—11 mo storage	16
Tenax-GC	15	9	24	A, H_2SO_4	Immediately after cleanup	16
	15	14	29	A, H_2SO_4	8—11 mo storage	16
Florisil			0.1	F		32
			<5	F		34

* Cleanup: A = alumina, F = Florisil, S = silica, H_2SO_4 = concentrated or 7% fuming sulfuric acid.
† Hexa- and heptachlorobiphenyls.

trap, it is assumed that breakthrough beyond the backup trap has not occurred. However, as the quantities on the two traps become similar, it is apparent that a certain fraction of the sample has also passed through the entire adsorbent bed. This uncollected fraction cannot be calculated simply from the trap-1/trap-2 ratio; a more detailed knowledge of the vapor front movement is needed, as will be discussed later.

Most workers include some estimate of collection efficiency in their reports. Sampling conditions and adsorbent quantities differ greatly among studies, so while quantitative vapor trapping is usually documented for a particular investigation, it is difficult to generalize

MONS 005811

Table 3
BREAKTHROUGH VOLUMES (V_a) FOR PCB CONGENERS AND HEXACHLOROBENZENE (HCB) ON PUF AND SAMPLING VOLUMES (V_s) CORRESPONDING TO DESIGNATED COLLECTION EFFICIENCIES*

Compound	V_a, m³	V_s, m³ at collection efficiency 90%	V_s, m³ at collection efficiency 95%
HCB	125	103	78
3,3'-DCB	720	590	446
2,4',5-TCB	1440	1180	893

* PUF column 7.6 cm diameter × 7.5 cm thick (N = 7.5), 20°C.

collection efficiencies from this literature. Several collection studies are listed in Table 1. Among these, solute volatility stands out as a major factor influencing collection. Several investigators have shown that the ability of adsorbents to trap PCB vapors increases with the number of chlorines on a homolog. Under the conditions usually employed for hi-vol sampling, the later-eluting components of Aroclor® 1242 and all the Aroclor® 1254 components are quantitatively trapped by polyurethane foam (PUF). Some of the dichlorobiphenyls may be lost, depending on the sampling temperature and total air volume. Tenax-GC, XAD-2, and Florisil collect the lower molecular weight PCBs more effectively than PUF.

Recently, some work has been done to express PCB vapor collection in a way that has some predictive capability for designing sampling systems. Senum[11] pointed out that the collection efficiency of an adsorbent bed is a function of the solute retention volume (V_a) and the number of theoretical plates (N) in the bed. The first measurements of V_a for PCB congeners in a hi-vol system were reported by Simon and Bidleman.[12] A PCB spike was introduced to a column of 15 1-cm thick × 7.6-cm diameter PUF slices and eluted with clean air. The PCB moved through the column as chromatographic bands, with the band penetration linearly related to air volume. Subsequently Burdick and Bidleman[13] extended this work to a frontal chromatography system, where vapors were continuously introduced to the PUF bed while sampling at 20°C. Breakthrough volumes (V_a) were obtained for two PCB congeners and hexachlorobenzene (HCB). In a separate study[14] V_a for four PAH as well as values of N for a PUF hi-vol sampler were determined.

Knowing V_a for the PCB homologs and N for the adsorbent bed, V_s can be calculated for desired collection efficiencies.[11,14] This is seen in Table 3 for a PUF column 7.6-cm diameter × 7.5-cm thick (7.6 g), the approximate dimensions of a PUF plug used in several field investigations.[9,15,16,18,19] These V_s apply to 20°C sampling temperature only. PCB vapor pressures increase by a factor of 1.8 to 1.9 for a 5°C rise in temperature,[20] and sampling at 25°C rather than 20°C should have nearly the same effect on breakthrough as doubling the air volume. In field studies, breakthrough of Aroclor® 1016 from front to backup PUF traps was better correlated with a temperature-weighted air volume than with air volume alone.[19]

In practice, the choice of adsorbent used for PCB sampling depends on the application.

MONS 005812

concentrations to be determined, necessary sampling times, and available equipment. Simultaneous collection of PCBs using two or three sampling systems has been carried out to test the comparability of different adsorbents.[15,16] Side-by-side collections in three cities using PUF, Tenax-GC, and XAD-2 showed that concentrations of Aroclor® 1016, Aroclor® 1254, and the pesticides chlordane and toxaphene measured with the three adsorbents agreed excellently. Average relative standard deviations for organochlorine levels measured with the different adsorbents ranged from 10 to 15% in most cases, and were within the precision of the analytical method. HCB concentrations measured with Tenax-GC and XAD-2 agreed well, and were several times higher than those obtained using PUF. HCB was not quantitatively collected by PUF in the air volume range studied (300 to 1600 m³), since its V_g on PUF is only 125 m³ (Table 3).

B. PCB Concentrations in the Air

Concentrations of airborne PCB depend on numerous factors, including proximity to local sources, source emission strengths, and meteorological variables. Levels as high as 57 μg/m³ have been reported in air directly over a PCB spill in North Carolina.[44] Air in homes and offices typically contains several hundred ng/m³ PCB.[39,53,54] By comparison, the NIOSH proposed criterion for PCB in workplace air over an 8 to 10 hr workday is 1.0 μg/m³.[55] Other areas where elevated PCB levels have been measured are landfills,[14,16,46,47] capacitor and transformer manufacturers,[33,44,46,48] and incinerators.[39] Away from direct sources, PCB concentrations are highest near urban centers, 1 to 10 ng/m³ representing the usual range for cities in the U.S. (Table 4). As expected, PCB levels decrease away from cities. Values from nonurban continental areas are typically in the range of 0.1 to 0.5 ng/m³. In remote marine areas concentrations of Aroclor® 1254 are usually 0.01 to 0.02 ng/m³ (Table 4).

C. The Atmospheric Reservoir of PCBs

Computation of the total amount of PCBs in the atmosphere is complicated by several factors. Relatively few data for atmospheric PCBs are available outside the U.S., and even less data have been collected in the Southern Hemisphere. In addition, the vertical distribution of PCBs in the atmosphere has not been measured. Finally, since the ban on open use of PCBs, there is some evidence for a decrease in environmental PCB concentrations,[31] though insufficient data are available to evaluate any decline in atmospheric PCB concentrations. Therefore, some simplifying assumptions and extrapolations are required to obtain a reasonable estimate of the total atmospheric reservoir of PCB.

Most data on atmospheric concentrations of PCB have been presented in terms of the commercial Aroclor® mixtures 1016/1242 and/or 1254, rather than as single congeners. Generally, in atmospheric samples, especially at low PCB concentrations, very light PCBs (monochloro) and very heavy (hepta- through decachloro-) PCBs are not included in the calculation of total atmospheric PCB. By including PCBs only as 1242 and 1254 in our calculation we may slightly underestimate the total PCB reservoir, but given the approximate nature of the calculation this should not lead to serious error.

Table 4 illustrates the high degree of variability in the reported PCB concentrations between urban, rural, and remote marine locations. Furthermore, examination of the original data sets reveals concentration variations which depend on meteorological factors and proximity to sources. Thus, calculation of the atmospheric PCB reservoir can be only approximate, perhaps within a factor of two or three. Also, there is variability in the apparent composition of atmospheric PCBs. Relative proportions of Aroclor® 1242 to Aroclor® 1254 range from 1:1 to 6:1. For the purposes of these subsequent calculations, we will use the proportions of 2:1 to represent the relative amounts of Aroclors® 1242 and 1254 in the atmosphere and to calculate total PCB when only concentrations of Aroclor® 1254 are given. Using this approximation to calculate total atmospheric PCBs from data in Table 4, we find that total

MONS 005813

Table 4
CONCENTRATION OF PCBs IN THE AMBIENT ATMOSPHERE

	Av. conc. (ng/m³) as Aroclor®			
	Total	1242	1254	Ref.
Urban				
Denver, Colo. (1980)	2.25	1.80	0.45	16
Columbia, S.C. (1977—80)	4.70	3.20	1.50	15, 16
Houston, Tex.	—	—	3.00	49
Minneapolis, Minn. (1978—79)	7.10	5.60	1.36	28, 29
Chicago, Ill. (1975—76)	8.00	6.70	1.28	17
Madison, Wisc. (1978)	7.50	6.50	1.05	27
Milwaukee, Wisc. (1977)	2.25	1.64	0.61	27
Ontario, several cities				
1979	5.90	—	—	34
1980	0.21	—	—	34
Stockholm, Sweden (1983—84)	0.34	0.23	0.11	50
Jacksonville, Fla. (1975)	4.70	—	—	14
Gainesville, Fla. (1977)	20.00	—	—	14
Rural/suburban/coastal				
Pigeon Key, Fla. (1978)	—	—	0.41	49
North Inlet Estuary, S.C. (1977—79)	0.44	0.25	0.19	51
Texas Gulf Coast (1976)	—	—	0.52	19
Texas Gulf Coast (1980)	—	—	0.067	35
College Station, Tex. (1979)	—	—	0.29	49
White Sands, N.M. (1981)	—	—	0.11	49
Ontario Province				
1979	5.40	—	—	34
1980	0.19	—	—	34
Rural Sweden (1984)	0.07	0.04	0.03	49
Rural Norway (1982)	—	—	0.02*	20, 21
Great Lakes				
Lake Michigan (1977)	0.87	0.65	0.22	27
Lake Superior (1978—80)	1.20	0.86	0.34	28, 29
Marine				
Gulf of Mexico (1976)	—	—	0.16	19
Newfoundland (1977)	—	—	0.096	18
Barbados (1977—78)	—	—	0.065	18
Enewetak Atoll (1979)	0.11	0.061	0.049	3, 49
American Samoa (1981)	—	—	0.012	49
Peruvian Coast (1981)	—	—	0.012	49
Bermuda (1976—77)	—	—	0.075	7
E. Indian Ocean (1980—81)	0.15	—	—	9
W. Pacific	0.34	—	—	9
Antarctic/Southern Ocean	0.11	—	—	4, 9
Arctic Ocean (1982—83)	—	—	0.02*	21

Note: —, Not measured or not reported.

* Pentachlorobiphenyls.

MONS 005814

atmospheric PCBs for urban, rural, and marine areas is 6.0, 0.63, and 0.19 ng/m³, respectively. An overall weighted average of continental (30%) and marine (70%) air yields a global average PCB concentration of 0.25 ng/m³.

This average computed from reported data probably overestimates the "true average" concentration for several reasons. Data from rural areas are biased toward higher values because of proximity to industrialized areas of the U.S. and Europe. Concentrations of PCBs in large areas of the Asian, African, and South American continents are potentially lower than 0.6 ng/m³, and are probably nearer "background" concentrations. Similarly, the data reported in the marine atmosphere are influenced by coastal population centers. From close examination of the data in Table 4, we subjectively estimate concentrations typical of open ocean regions to be ~100 pg/m³ in the Northern Hemisphere and 30 pg/m³ in the Southern Hemisphere. The average, 65 pg/m³, is approximately 1/3 of the marine average reported above. A modified average computed from only 10% "rural" contribution (0.6 ng/m³) and 90% "marine/remote" (0.065 ng/m³) contribution is 0.12 ng/m³, which may be closer to representing the PCB load currently in the global atmosphere. In any event, this more subjective average is within a factor of two of the earlier estimate based on all reported data.

To calculate the atmospheric reservoir of PCB, we will assume a uniform concentration of PCBs in the troposphere up to 6 km over the earth's surface. If PCB vapors behave as other stable halocarbons in the atmosphere, such as the freons, then this is a reasonable assumption. Using an area of 5.1×10^{14} m² for the earth's surface and the "high" average of 0.25 ng/m³, we calculate a total PCB burden in the atmosphere of 7.7×10^5 kg. There is obviously some uncertainty in this calculation; however, the actual PCB burden in the atmosphere should lie in the range of 1 to 10×10^5 kg. This amount represents a small percentage of the total "mobile environmental reservoir" of U.S.-derived PCB estimated by the National Academy of Sciences (820×10^5 kg) in 1979.[7] This result is somewhat surprising considering the important role of atmospheric transport to the widespread distribution of PCBs in remote regions and suggests several features of the atmospheric reservoir of PCB. First, the atmosphere appears to be a relatively rapid conduit for transport of PCBs to remote areas. If the atmosphere slowly accumulated and retained PCBs we would expect a larger fraction of "mobile" PCBs to reside in the atmosphere. Second, we expect that the atmospheric reservoir must have been larger in the past, e.g., prior to 1970, to account for the accumulated PCBs in ocean water and sediments. This aspect is discussed more completely in a later section.

D. Vapor-Particle Partitioning of PCBs

The vapor/particle (V/P) ratio of airborne PCBs is operationally defined by the quantities retained in the adsorbent trap and on the filter. How closely adsorbent/filter (A/F) ratios found with hi-vol samplers approximate the true V/P distribution in the atmosphere is unknown, but is an active area of investigation since the V/P ratio is important in assessing the various mechanisms of deposition. Some A/F ratios for PCBs in various cities and over the ocean are given in Table 5.

Many investigators feel that A/F overestimates V/P because of the "blow-off effect" — stripping of organics from particles on the filter by the flowing airstream.[9,10] On the other hand, it is possible that the particle mass on the filter acts as an adsorbent and scavenges vapors, which leads to an underestimation of V/P.[9] Experiments in Atlas' laboratory suggest that airflow alone has little effect on PCB vapor adsorption or stripping during hi-vol sampling. In the experiments air samples collected at different face velocities showed the same PCB A/F ratios. Changes in temperatures, aerial concentrations, and particle chemistry probably have the greatest effect on A/F, and whether blow-off losses or adsorption gains are observed will depend on how and when these variables change during a collection period.

MONS 005815

Table 5
AVERAGE A/F RATIOS FOR ATMOSPHERIC PCBs

Location and PCB	A/F	% Vapor	Ref.
Columbia, S.C. (Aroclor® 1254)	17.00	94	15, 16
Denver, Colo. (Aroclor® 1254)	0.56	36	16
New Bedford, Mass. (Aroclor® 1254)	6.00	86	16
Toronto, Ont.	1.3—6.3	56—86	60
Chicago, Ill. (Total PCB)	33.00	97	17
Milwaukee, Wisc. (Total PCB)	6.30	86	27
Madison, Wisc. (Total PCB)	0.33	97	27
Lake Michigan	8.30	89	27
North Atlantic (Aroclor® 1254)	>10.0*	90	1
North Atlantic (Aroclor® 1254)	>99.0*	99	61
Gulf of Mexico (Aroclor® 1254)	>99.0*	99	9

* Filter-retained PCB less than detection limit.

For example, what is deposited on the filter at night may be blown off again in the heat of day.

Despite these problems, some attempts have been made to correlate A/F ratios with temperature and airborne particle concentrations. Yamasaki et al.[62] demonstrated that the A/F ratio for PAH could be described by an equation derived from Langmuir adsorption theory:

$$\log(A/F) = mT^{-1} + b - \log(TSP) \quad (1)$$

where m and b are empirical constants, TSP is the total suspended particle concentration ($\mu g/m^3$), and T is the average absolute sampling temperature. In an attempt to correlate PCB A/F ratios with temperature, a plot of Equation 1 was made for Aroclor® 1254 in Columbia, S.C., New Bedford, Mass., Denver, Colo., and Stockholm, Sweden.[30] Data from the 4 cities represented A/F ratios from 0.2 to 190 and average temperatures for the sampling periods of −10 to 26°C. For 34 data points, linear regression gave: $m = -4686$, $b = 19.428$, and $r^2 = 0.885$. Using this relationship, the apparent percentage of particulate Aroclor® 1254 in a city with TSP = 60 $\mu g/m^3$ would be estimated as 2.1% at 20°C and 25% at 0°C. Because of the lower TSP levels in the marine atmosphere, even lower particulate PCB fractions over the oceans would be expected. For example, if oceanic TSP is 7 $\mu g/m^3$ (mineral and sea salt),[63] at 0°C, 3.7% of the Aroclor® 1254 would be on particles. (This percentage is expected to be an upper limit because of the difference in particle size distributions and chemical characteristics of urban vs. marine aerosols.) At 20°C this percentage would fall to ~0.3%. Since Aroclor® 1242 has a vapor pressure ~5 times higher than Aroclor® 1254, the particle-bound Aroclor® 1242 should be ~1/5 of the above values. Thus, the low percentage of particulate PCB measured in the marine atmosphere is consistent with theoretical estimates.

III. ATMOSPHERIC REMOVAL PROCESSES FOR PCBs

A. Collection Methods for Aerial Deposition

Wet and dry deposition are two important processes for transferring PCBs from the atmosphere to the ocean surface. Precipitation sampling methods can be classified as "bulk" or "wet", depending on whether they collect dry deposition in addition to rain or snow. "Event" sampling refers to collections made during a single precipitation period. These and other terms associated with precipitation monitoring have been defined.[64]

MONS 005816

One advantage of bulk collectors is that they are cheap, often consisting of nothing more than a jug and a funnel. Bulk collectors require no power, an important consideration for sampling at remote sites, and they provide an integrated measure of atmospheric input per unit area. A serious drawback is that these collectors are easily contaminated by bird droppings and insects. Moreover, they do not differentiate between input by precipitation and by dry deposition. An interesting way to measure total aerially derived pollutants is to analyze snow or ice cores. This bulk collection method, subject to the same contamination problems as mentioned above, has been used by several workers.

Wet samples are taken only during precipitation periods by manually exposing a collector, or by using an automated collector with a rain-tripped sensor.[64,67] Sample containers are usually made of glass or metal. Plastics other than polytetrafluoroethylene are not suitable for trace organic work because they may introduce contamination into the sample or cause losses by adsorption to the plastic surface.

Organic compounds deposited into precipitation collectors are subject to revolatilization losses and to chemical and microbial breakdown. Problems with transportation also discourage the collection of large water volumes. Some investigators have tried to circumvent these difficulties by drawing the collected rain sample through a plug of PUF,[68] a glass fiber filter-PUF combination,[17] or an XAD resin column.[66]

Dry deposition of trace organics occurs by gravitational settling, turbulent impaction of aerosol-bound materials, and adsorption of vapors to the deposition surface. Södergren[69,70] and Bengtsson and Södergren[71] coated a nylon mesh screen with silicone oil and exposed the nets for 2 to 3 months at a time to determine total aerial fluxes per unit area. The nets probably collected particles by filtration as well as impaction. McClure and LaGrange[72,73] collected dry deposition on mineral oil-coated glass plates, a technique that was also used by Young et al.[74,75] to collect DDT and PCB fallout samples in southern California. Heesen et al.[76] exposed sets of these collection plates over several days and found that the collection efficiency decreased over an 8-day period; i.e., residues on plates exposed for 8 days were less than the sum of residues recovered from plates exposed for 1-, 2-, or 4-day intervals over the same time period.

Murphy[77] criticized the use of oil-coated surfaces to sample organic dry deposition because of the possibility that the oil might scavenge vapors as well as particles. Murphy recommended the use of a polar fluid, and has used glass fiber filters coated with diols to collect PCB dry deposition.[78] Eisenreich et al.[79] collected PCB dry deposition on glass plates coated with glycerol. Christensen et al.[79] evaluated three surfaces for sampling PCB, DDT, and chlordane fallout. Pans filled with water or ethylene glycol-water to simulate a natural water surface were compared to glycerol-sprayed and dry pans of the same geometry. On the average, the wet surface pans collected 1.5 to 3 times as much organochlorine dry deposition as did the dry surface pans with no differences among the types of wet surfaces.

How well any of these surrogate surfaces approximate dry deposition to the surface of environmental interest (ocean, lake, plant foliage) is unknown. Removal of particles is strongly influenced by their size, meteorological factors, and surface properties of the collector. Reviews of dry deposition[80,81] reveal an incredible number of field experiments carried out over the last 25 years. Particle deposition velocities, V_g, vary by three orders of magnitude. A discussion of all factors affecting washout and dry deposition is beyond the scope of this chapter and the reader is referred to several articles on the subject.[80-82] For trace organics, deposition processes are further complicated by their fractionation between the particle and vapor phases.

A workshop held at Argonne National Laboratory in November 1979 evaluated methods to measure dry deposition.[80] A conclusion of the workshop was that surrogate surfaces are not accurate enough estimators of fallout fluxes to use in monitoring networks. Instead, research was recommended on using micrometeorological parameters to calculate dry dep-

MONS 005817

Table 6
PCBs IN RAIN AND SNOW

Location and year	Collection method	Range (ng/ℓ)	Mean (ng/ℓ)	Ref.
Norway, 1973—76	Bulk rain and snow	1.2—7.6	3.7	89
Chicago and Lake Michigan, 1975—76	Event rain and snow, PUF extraction		193.0 119.0(P)*	17
British East Coast, 1975—76	Bulk rain, PUF	1.80—74.0	14.9	68
Great Lakes Eastern Canada, 1975—77	Event rain, snow cores→		21—29	90,91
South Carolina coast, 1976—78	Bulk and event rain	<1.0—27.0	1.6	88
Lakes Michigan and Huron, 1977—79	Bulk and event rain, snow and ice cores		14—65(P)	78
Southern Ontario, 1975—77	Bulk rain		100	92
Lake Superior, South, Isle Royal, 1976—76	Snow cores		50—230	93
Ontario cities, 1979	Bulk rain and snow	<20.0—50.0	21—35	94
Pigeon Key, Fla., 1978	Event rain	7.1—8.3	7.7	49
Enewetak Atoll, North Pacific, 1979	Event rain		<0.6	3
Hamilton, Ontario	Rain, wet only	9.0—61.0	27.0	66
Sault St. Marie, Ontario (remote)	Rain, wet only	1.0—8.0	3.0	66
Antarctica, Mt. Olympus Washington, 1975	Snow cores	0.03—1.2	0.3(median)	95
Antarctica, 1981	Snow and ice cores	0.16—1.0	0.4	4

* P = precipitation volume-weighted mean. No symbol = arithmetic mean of concentrations, or method of mean computation, not specified.

osition fluxes from atmospheric concentrations. These techniques are summarized in reports.[86,87] Other workers disagree (the present authors included), and feel that more emphasis should be placed on field comparisons of fallout fluxes to surrogate and "real" surfaces.

B. PCB Levels in Precipitation and Dry Deposition

Compared to the number of studies on wet and dry deposition of inorganic substances, relatively little has been done to investigate removal processes for organic compounds. PCB concentrations in rain and snow are presented in Table 6, with an emphasis on recent literature. Higher PCB concentrations are found in rain near urban areas. Murphy and Rzeszutko[17] reported a precipitation-weighted mean PCB concentration of 119 ng/ℓ in Chicago and on Beaver Island, Lake Michigan. By comparison, only 11 out of 51 rain samples taken at a South Carolina estuary showed detectable PCB residues; the mean concentration in these 11 samples was 7.5 ng/ℓ.[88] Strachan and Huneault[66] collected rain 10 km downwind from a heavily industrialized area near Hamilton, Ontario and at a "remote" site 50 km from Sault St. Marie, Ontario. Average PCB concentrations were 27 ng/ℓ near Hamilton and 3 ng/ℓ at the remote site.

The few fluxes and deposition parameters that have been measured for PCBs are summarized in Tables 7 and 8. Table 7 shows that deposition fluxes to the Great Lakes are in the range of 10 to 100 μg/m²/year, while marine deposition may be somewhat lower. Removal parameters tend to be higher for the less volatile compounds. For example, washout ratios (W) and V_g are higher for Aroclor® 1254 than for Aroclors® 1016 and 1242 (Table 8). The same trend has been found for chlordane and the less volatile DDT.[96] A likely explanation is that a greater proportion of the heavier organics are particle-bound and are removed more efficiently by wet and dry processes. This behavior is modeled in the next sections.

MONS 005818

Table 7
PRECIPITATION AND DRY DEPOSITION INPUTS OF PCBs TO WATER BODIES

Location and year	Input mode	Area (km^2)	Flux kg (months)	$\mu g/m^2/year$	Ref.
S. California Bight, 1973—1974	Dry deposition	—	1,000 (12)	—	76
Lake Michigan, 1975—1976	Precipitation and dry deposition	5.80×10^4	2,500—5,000 (12)	43.0—86	17,78
Lake Huron, 1977—1978	Precipitation and dry deposition	6.00×10^4	1,100 (12)	18.0	78
Lake Superior, 1974—1977	Precipitation and dry deposition	8.20×10^4	6,600—8,400 (12)	80.0—102	28
Saginaw Bay, Lake Huron, 1977—78	Precipitation and dry deposition	1.50×10^3	6.5—8 (2—3)	17.0—23	96
North Sea, 1975—1976	Precipitation and dry deposition	5.75×10^5	1,900 (12)	3.3	68
Five Great Lakes	Precipitation and dry deposition	2.40×10^5	29,000 (12)	121.0	2
Lake Michigan (calculated)	Total	—	—	5.4—10	97
Lake Superior (calculated)	Total	—	—	7.3—73	30

IV. ATMOSPHERIC INPUTS ON PCBs TO THE OCEAN

In this section we will attempt to model the deposition of PCBs to the ocean surface. Similar attempts at modeling the air/water flux of PCBs to the Great Lakes have been reported.[75,96] In a broad sense our approach here will be similar to other models, but some of the deposition parameters and assumptions necessarily will be modified for application to the marine environment. Also, where possible, our estimates will conform with data recently acquired for deposition of other substances, such as various trace metals to the ocean surface.[97] The main results from this model will be a comparison of the fluxes due to different deposition mechanisms of PCB and an estimate of the overall flux of PCB to the ocean.

Substances can be transferred from the atmosphere to the ocean by deposition of both particles and gases. Since PCB is partitioned between a vapor and particle phase, both mechanisms must be considered. Furthermore, both wet and dry deposition processes for each phase must be considered. Each process is considered separately below.

A. Dry Deposition of Particles

Particle deposition to a natural water surface is a highly complicated process. In a very simple mathematical form which masks many complexities, the flux of particles may be calculated from:

$$F_D = V_D C_p \tag{2}$$

where F_D = dry flux of particle-bound compound, V_D = particle deposition velocity, and C_p = concentration of the compound bound to particles. Large differences in particle deposition rates are expected as a function of particle size.[82] Measurements of V_D (total) described earlier (Table 8) may not be applicable to open-ocean areas. Data of Bidleman and Christensen[31] and Murphy et al.[19] suggest that dry deposition rates of PCB measured in continental areas may be dominated by a small percentage of PCB which is associated with large particles. Rapid deposition of these continentally derived large particles near the

MONS 005819

Table 8
ATMOSPHERIC REMOVAL RATES AND DEPOSITION PARAMETERS FOR PCB

Compound	Location	Dry flux, ng/m²/day Range	Mean	V_d, cm/sec[a]	W[b]	Ref.
Aroclor® 1242/1016	Columbia, S.C.	11—119	29	<0.04		51, 79
	North Inlet Estuary, S.C.		<11	<0.046		51, 79
	Kingston, R.I.	<29—325	159	0.07		51, 79
	Enewetak Atoll				<1	3
	Chicago, Beaver Island, Lake Michigan				14	17
Aroclor® 1254	Columbia, S.C.	<24—368	118	0.41		51, 79
	North Inlet Estuary, S.C.	<2—74	21	0.16	94	51, 79
	Kingston, R.I.	61—360	237	0.11		51, 79
	La Jolla, Calif.			1.20		72
	Chicago; Beaver Island, Lake Michigan				193	17
	Pigeon Key, Fla.		2.4		18—32	49
Clophen® A50	Sweden[c]	20—350	110			69, 98
	Iceland[c]	<0.4—35	7			71
	Czechoslovakia[c]	4—113				70
	Kenya[c]	<0.4—0.7				70
Total (as unspecified)	Minneapolis, Minn.		630	0.13		28
	Chicago, Ill.					78
PCB	Waukegan, Ill.		121			78
	Lake Huron (towns)		17			78

[a] Deposition velocity for total PCB (particle and vapor)
[b] W = pAg rain + pAg air
[c] May include precipitation-derived residues

MONS 005820

source will lessen the effective deposition rate of PCB over most ocean areas. Since any particulate PCB present in the ocean atmosphere is mainly on small particles, it may behave similarly to other atmospheric compounds associated with small particles, such as Pb. A recent analysis of Pb deposition in the marine atmosphere[99] suggests a net dry deposition velocity of small-particle Pb on the order of 0.1 cm/sec.

Recent measurements of particle-borne PCBs in the marine atmosphere suggest that < 1% is associated with particles. This result may be biased toward low values because measurements have typically been made near sea level, in temperate or tropical climates, and in relatively warm weather. As discussed earlier, temperature can affect the amount of PCB on atmospheric particles. For the purposes of our calculation we will assume that 2% of Aroclor® 1254 and 0.4% of Aroclors® 1016 and 1242 in the atmosphere are associated with particles. These percentages correspond to a temperature of ~4°C and should provide an upper limit of particulate PCBs for clean air conditions in the marine boundary layer.

B. Wet Deposition of Particles

Particles are efficiently scavenged from the atmosphere by precipitation. Data on particulate organics in precipitation[100,101] and on trace metal scavenging[102] suggest a value of 300 to 700 [ng/kg (rain)/ng/kg (air)]. For our calculation we will use a value of 500. The flux due to wet deposition of particulate PCB then is given by:

$$F_w = 500RC_p \qquad (3)$$

where R = annual rainfall rate over the ocean (~1 m/year).

C. Dry Deposition of Gases

The magnitude (and direction) of the gas exchange of PCBs across the air/water boundary has been a subject of controversy in recent years, particularly with reference to the Great Lakes.[103,104] It has been shown from mass balance estimates and from water column measurements that the atmosphere must be an important source of PCB to the Great Lakes. However, physicochemical data on PCB vapor pressure, solubility, and Henry's Law constants suggest that the Great Lakes are supersaturated with respect to atmospheric PCB. Therefore, surface water should volatilize excess PCB and be a source, rather than a sink, of PCB. Some have suggested that the physical data are incorrect[105] or have pointed to assumptions regarding mass transfer rates and sorption of PCB as potential sources of miscalculation.[97]

A similar dilemma exists for gas transfer of PCB to the ocean surface. Direct measurements are not available to determine the net flux of vapor-phase PCB across the air/water interface. However, some indirect data are available to suggest the magnitude of the gas exchange flux. First, we will examine the equations and parameters used to estimate gas exchange.

The two-film resistance model of Whitman has been widely used to examine gas exchange in natural water systems.[106] In this model, the transfer of a gas is limited by diffusion across thin stagnant films of air and water adjacent to the interface. The overall transfer coefficient, K_{OL}, is based on the individual transfer coefficients across the liquid and gas films and on the Henry's Law constant of the compound. Thus:

$$1/K_{OL} = 1/K_L + RT/HK_G \qquad (4)$$

where K_L and K_G are the individual mass transfer coefficients in the liquid (L) and gas (G) film, and (H/RT) = dimensionless air/water partition coefficient, H = Henry's Law constant (atm − m³/mol), R = gas constant, and T = temperature. Depending on the magnitude of (RT/H), one of the two terms in Equation 4 may become large compared to the other

MONS 005821

and the exchange will be designated as either "liquid-phase" or "gas phase" controlled. K_l and K_g are based on estimates of oxygen and water vapor mass transfer rates in the ocean. Typical values of 3000 and 20 cm/hr have been suggested for K_g and K_l, respectively.[106] These rates need to be corrected for the smaller diffusivity of PCB. Theoretical estimates[107,108] and laboratory experiments[109] suggest a correction factor of approximately 0.2. Thus, K_g ~600 cm/hr and K_l ~8 cm/hr for PCB.

Recent experiments by Atlas et al.[109,110] have shown that (H/RT) at 23°C for various PCBs in sea water is approximately 0.028 for Aroclor® 1242 and 0.014 for Aroclor® 1254. Using these values yields a K_{OL} of 5.4 cm/hr and 4.1 cm/hr for Aroclors® 1242 and 1254, respectively. These transfer coefficients show that both gas and liquid phase resistances are significant in the transfer of PCBs across the air/water interface.[111]

Given the mass transfer rate K_{OL}, the net flux F_D^G depends on the disequilibrium between air and water concentrations, or

$$F_D^G = K_{OL}(C_{eq} - C) \tag{5}$$

where C = the concentration of dissolved PCBs in water, and C_{eq} the aqueous concentration of PCBs in equilibrium with atmospheric PCB. If $C > C_{eq}$, the flux is from the water to the air, and vice versa. One assumption in prior estimates of gaseous PCB flux is that the ocean surface acts as a perfect sink for PCB, i.e., C = 0. Under this assumption the flux to the ocean is maximum and is given by $F = K_{OL} * C_{eq}$, where $C_{eq} = C_w/(H/RT)$. Using appropriate parameters yields a maximum air-sea flux of 5.0×10^{-6}g PCB/m²/year (12.9×10^{-6}g 1242 + 2.1×10^{-6}g 1254).

Reported concentrations of PCBs in the oceans are not zero, however. Aqueous concentrations of "dissolved" PCB of 50 to 500 pg/ℓ in surface ocean waters are at least 10 times the equilibrium concentration expected from Henry's Law calculations. The compilation of environmental air/water concentration ratios vs. theoretical estimates (Table 9) clearly illustrates this point. The data in Table 9 show that PCB partitions at least 10 times more into the aqueous phase (in marine and fresh water systems and in rain water) than is predicted from merely equilibrium with atmospheric PCB. Apparent supersaturation is evidently a generally widespread phenomenon in natural waters.

If we assume that the oceans are a sink rather than a source of atmospheric PCB, these observations suggest that the practical differentiation of particulate and dissolved PCBs in rain and other natural waters may not accurately reflect the actual physical state and chemical behavior of PCBs in solution. For example, PCBs sorbed to microparticulate material, which passes through glass-fiber filters, would be considered "dissolved"; consequently, the solution would appear supersaturated with respect to atmospheric PCB. There is little data available to test this hypothesis, however. Voice et al.[112] suggested the effect of microparticulate (= colloidal) PCB in laboratory experiments of PCB adsorption of sediments. Recently, Gschwend and Wu demonstrated this effect in a laboratory system.[114] Other studies have demonstrated the strong binding of synthetic organics to natural colloid material.[115,116] Available data on PCB distribution between air and water would be more easily explained if PCBs in natural waters were not in true solution, but rather associated with colloidal or microparticulate material. This does not suggest, though, that gas-phase PCB does not transfer to aqueous solution. Laboratory studies[109,110] on gas exchange of PCBs have demonstrated that gas-phase PCBs will reach equilibrium with aqueous solutions and subsequently can be purged from solution with clean air. Thus, gas deposition and volatilization of PCBs can occur; however, in natural systems this process may be masked by the presence of PCBs sorbed to very small particles. Data are presently unavailable to determine the extent to which the pool of particulate PCBs is involved in the equilibration of gas-phase PCBs with surface waters. Further work is required to determine the various mechanisms which control the air/water exchange processes in natural waters.

MONS 005822

Table 9
MEASURED AND THEORETICAL AIR/WATER CONC. RATIOS OF PCBs [ng/m³ (air)/ng/ℓ (water)]

Location	PCB mixture (Aroclors®) 1242	1254	Ref.
Marine			
Antarctica*	3.4	3.4	9
Tropical Pacific*	1.7	1.8	9
Coastal China*	1.3	(14)	9
North Atlantic	—	2—6	6
Gulf of Mexico	—	1.2	19
Fresh water			
Lake Michigan surface water (total)	2.0	1.0	112
Microlayer	0.7	0.24	112
Lake Superior	1.6	0.4	28, 104
Average			
Marine	2.3	2.1	—
Fresh	1.8—2.3	0.7—0.9	—
Rainwater	0.13	0.03—0.17	Table 8
Theoretical			
Marine	28.5	14.1	110
Fresh	13.6	6.7	110

* Calculated from individual PCB isomer distributions.

Because of the uncertainty in the magnitude of "dissolved" PCBs, the actual saturation state of surface sea water with respect to atmospheric PCBs cannot be calculated directly and assumptions regarding the saturation state must be made. Two scenarios are considered. The first case assumes that processes removing PCBs from the "dissolved" form to colloidal or particulate matter are rapid compared to the gas exchange rate. This case (discussed above) suggests the ocean absorbs gaseous PCBs at the maximum rate. In the second case, gas exchange is rapid compared to other processes influencing aqueous PCB concentration. Since measurements of anthropogenic gases, such as freons, indicate that surface ocean waters are in near equilibrium with the atmosphere, it is probable that "dissolved" PCBs are also in equilibrium with atmospheric PCBs. If the ocean surface were stagnant there would be no net flux of PCBs from the atmosphere to the oceans. However, surface waters are being mixed constantly with old, deeper waters which are presumably undersaturated with respect to atmospheric PCBs. Thus, gas exchange of PCBs may be limited by the residence time of water in the mixed layer rather than by a diffusion-limited transfer across thin interfacial films. If, for example, we assume the 100 m surface layer of the ocean has a residence time, τ, of 2 to 4 years and is being mixed with water undersaturated in PCB, then the gas exchange flux becomes $100\ m \times C_w/\tau$. This calculation results in a gas-exchange PCB flux of only 5% of the maximum rate.

D. Wet Deposition of Gases

This process involves equilibrium of rain with vapor phase PCBs in the atmosphere. Essentially, this mechanism has been discussed in the last section. The flux from wet deposition of gaseous PCBs is

$$F_w^g = RC_{wg} \qquad (6)$$

MONS 005823

Table 10
PARAMETERS FOR PCB FLUX CALCULATION

Parameters	PCB Aroclor® mixture	
	1242	1254
Vapor conc. (pg/m³)	126.0	63.0
Particulate conc. (pg/m³)	0.5	1.3
Partition coefficient, m³(air)/ℓ(water)		
Sea water	28.0	14.0
Fresh water	14.0	7.0
V_D (particles) cm/sec	0.1	0.1
Particle washout factor		
W_p	500.0	500.0
Rain rate (m/year)	1.0	1.0
Ocean area (m²)	3.6×10^{14}	3.6×10^{14}

Table 11
FLUX OF PCBs TO THE OCEAN SURFACE

	Flux (ng/m²/year)		
	Aroclor® 1242	Aroclor® 1254	Total
Particles			
Dry	16.0	41.0	57.0
Wet	250.0	650.0	900.0
Gas Phase			
Dry maximum	2,100.0	1,600.0	3,700.0
minimum	100.0	100.0	200.0[a]
Wet	9.0	9.5	19.0
Total	2375.0	2301.0	4676.0
Total flux to oceans ($\times 10^6$ g/year)	8.6	8.3	16.9

[a] Based on sea water composition = 0.5 Aroclors® 1242 and 0.5 1254.

where the symbols used are those already described (Equation 5). As shown in Table 8 field measurements of PCB washout ratios are one to two orders of magnitude higher than those predicted based solely on dissolution of gas-phase PCBs in precipitation (Table 9). This suggests that PCBs in rainfall is obtained primarily from particulate matter and that gas-phase dissolution of PCBs is a relatively minor contribution.

E. Comparison of PCB Inputs to the Ocean

A summary of flux estimates is given in Tables 10 and 11. Under assumptions of maximum gas exchange, the flux of atmospheric PCB to the ocean is dominated by gas exchange processes (79%). Precipitation scavenging of the relatively small reservoir of particulate PCB is the second major mechanism for air/sea transfer of PCB (19%). On the other hand a smaller gas transfer flux would make these two processes comparable. Wet deposition of gaseous PCB and dry deposition of particulate PCB are less important processes in the marine environment. These estimates can be compared to other calculations of PCB input to the ocean. For example, "total" dry deposition velocity (particles and gas) have been measured for atmospheric PCB (see Table 8). A simple measure of "total dry deposition" is calculated from:

$$F^T = V_D^T C_A^T \quad (7)$$

MONS 005824

where F = total dry deposition (gas and particle) flux, V_D^t = "total" dry deposition velocity, and C_A^t = total atmospheric PCB concentration. Using data from a pristine coastal area (Table 8), an estimated V_D for the marine environment is 0.15 cm/sec (Aroclor® 1254) and 0.03 cm/sec (Aroclor® 1242). Use of these factors yields a total PCB flux of 4.2 $\mu g/m^2$/year (71% Aroclor® 1254, 29% Aroclor® 1242). This compares favorably with 3.8 $\mu g/m^2$/year calculated in the maximum exchange model.

An independent measure of particulate PCB flux to the ocean may be obtained from recent measurements of dust flux to the ocean. Using an average flux of 50 $\mu g/cm^2$/year of dust to the central Pacific[117,118] and a particulate PCB concentration of 0.25 $\mu g/g$ (Table 10) and 7 $\mu g/m^3$ particulate matter in marine air we calculate a net flux (not including gas exchange) of 0.125 $\mu g/m^2$/year. This also agrees well with model calculations above (Table 11).

These calculations suggest an *upper limit* of PCB flux to the oceans is ~5 $\mu g/m^2$/year, or a total annual flux of 1700 t. There are, of course, relatively large uncertainties in this estimate. The degree of gas exchange of PCBs between the atmosphere and ocean surface waters is the largest uncertainty. Effects of storms, wind speed, and temperature on air/sea exchange of PCB have been ignored in this model. Also, potentially important regional variations in particle size and concentration of atmospheric PCB have been ignored. A more refined model of PCB flux will require additional laboratory and field measurements of PCBs. In spite of the uncertainties, the flux calculated above is probably a reasonable upper limit of PCB input to the oceans over the last 10 to 15 years.

Calculations below will illustrate the importance of atmospheric inputs of PCBs by comparing the atmosphere-ocean input fluxes with other main inputs of PCBs to the ocean and with the size of the ocean reservoir of PCBs.

The second potential major input of PCBs to the ocean will be from rivers. We are aware of no data on PCBs in rivers with the largest flow, i.e., the Amazon, Congo, and Yangtze, which drain nonindustrialized regions. Mean PCB concentrations in the Mississippi River Delta area were reported as 2.5 ng/ℓ[6] and some rivers draining highly industrialized areas of Europe report PCB concentrations on the order of 10 to 20 ng/ℓ,[119] though much of this is associated with particulate material which will be deposited near the river mouth. Considering that the largest rivers drain rural or undeveloped lands, a reasonable upper limit for PCBs in "average" river water is 1 ng/ℓ. Using an annual runoff to the ocean of 3×10^{13} m^3, we calculate an annual riverine flux of PCBs to the ocean of 30 t. This amounts to only 2% of the estimated atmospheric flux of PCBs to the ocean.

The ocean reservoir of PCBs is discussed in detail elsewhere in this volume,[120] and thus it will be considered only briefly here. The concentration of PCBs in ocean water is still relatively poorly defined. Data suggest PCBs are distributed relatively uniformly throughout the water column;[120] they are present even in very deep water. If we assume a uniform concentration of 0.1 $\mu g/m^3$ (100 pg/ℓ)[121] to 4000 m depth in the world ocean (3.6×10^{14} m^2), the amount of PCBs in the ocean is 1.4×10^{11} g. This does not include the ocean-sediment reservoir. This amount seems slightly high compared to the mobile environmental reservoir of 0.8×10^{11} g of U.S.-derived PCBs, but it is not unreasonable. At the *maximum* rate of atmospheric and riverine input, it would take approximately 82 years for the ocean reservoir to reach its present size. However, PCBs have only been produced in significant quantities over the last 40 to 50 years. Thus, even maximum estimated fluxes of PCBs cannot account for the size of the oceanic PCB reservoir. This suggests that atmospheric fluxes of PCBs to the ocean in the past (prior to 1970) may have been greater than present rates to account for PCBs accumulated in the ocean, or that there are still errors in estimating the reservoir sizes and exchange rates of PCBs in the environment. Indeed, some recent measurements of surface water PCB concentrations in the Pacific Ocean[8] are less than 100 pg/ℓ used in the above calculation, which would indicate a smaller oceanic PCB reservoir. A smaller reservoir of oceanic PCB would be more consistent with estimated rates of atmospheric inputs of PCB to the ocean.

MONS 005825

V. SUMMARY

This chapter has examined the collection techniques, concentration, and deposition of PCBs from the atmosphere. Suitable collection and analytical techniques are available to measure low concentrations of PCBs in the ambient atmosphere. Direct determinations of wet deposition of PCB are rare, and there is still controversy concerning measurement and interpretation of dry deposition of atmospheric PCBs. Available data of PCB concentrations indicate an atmospheric reservoir size of approximately 7.7×10^5 kg. This reservoir is small compared to other reservoirs of "mobile" PCBs in the environment. However, the atmosphere is still a major transport mechanism for distributing PCBs throughout the environment. It is estimated here that up to 98% of the PCBs entering the oceans is currently being deposited from the atmosphere. A maximum atmospheric input of 1700 t/year of PCB is calculated.

The most important mechanisms for depositing PCBs from the atmosphere to the ocean surface are gas exchange and washout of particulate PCBs. Washout of gas-phase PCB is negligible. Dry deposition of particulate PCBs is only 5 to 10% of the wet deposition. However, there are still numerous uncertainties in the picture of PCB exchange with the ocean. The magnitude of PCB gas exchange with ocean surface waters is largely uncertain. Also, the model presented here is based on average properties and ignores temporal and regional differences in PCB transfer. Factors such as air temperature, wind speed, storm frequency, rainfall rate, and other meteorological factors will exert an important influence on the pattern and rates of PCB movement over the oceans and need to be considered in a detailed picture of PCB cycling between the oceans and the atmosphere. However, such a model will require more measurements of PCBs in the marine environment than are presently available. Finally, mass balance considerations should be applied to models of PCB cycling to set limits on observed and estimated concentrations and transport rates in the oceans.

REFERENCES

1. *Tropospheric Transport of Pollutants and Other Substances to the Oceans*. National Academy of Sciences, Washington, D.C., 1978.
2. **Eisenreich, S. J., Looney, B. B., and Thornton, J. D.**, Airborne organic contaminants in Great Lakes ecosystem, *Environ. Sci. Technol.*, 15, 30, 1981.
3. **Atlas, E. L. and Glam, C. S.**, Global transport of organic pollutants: ambient concentrations in the remote marine atmosphere, *Science*, 211, 163, 1981.
4. **Tanabe, S., Hidaka, H., and Tatsukawa, R.**, PCBs and chlorinated hydrocarbon pesticides in Antarctic atmosphere and hydrosphere, *Chemosphere*, 12, 277, 1983.
5. **Tanabe, S., Mori, T., Tatsukawa, R., and Miyazaki, N.**, Global pollution of marine mammals by PCBs, DDTs, and HCHs (BHCs), *Chemosphere*, 12, 1269, 1983.
6. **Glam, C. S., Chan, H. S., Neff, G. S., and Atlas, E. L.**, Phthalate esters plasticizers: a new class of marine pollutant, *Science*, 199, 419, 1978.
7. *Polychlorinated Biphenyls*, prepared by the Committee on the Assessment of Polychlorinated Biphenyls in the Environment, National Academy of Sciences, Washington, D.C., 1979.
8. **deLappe, B. W., Risebrough, R. W., and Walker, W., II**, A large-volume sampling assembly for the determination of synthetic organic and petroleum compounds in the dissolved and particulate phases of seawater, *Can. J. Fish. Aquat. Sci.*, 40(Suppl. 2), 322, 1983.
9. **Tanabe, S., Kawano, M., and Tatsukawa, R.**, Chlorinated hydrocarbons in the Antarctic, Western Pacific, and Indian oceans, *Trans. Tokyo Univ. Fish.*, 5, 97, 1982.
10. **Lewis, R. G., Brown, A. R., and Jackson, M. D.**, Evaluation of polyurethane foam for sampling of pesticides, PCB, and PCN in ambient air, *Anal. Chem.*, 49, 1668, 1977.
11. **Lewis, R. G. and Jackson, M. D.**, Modification and evaluation of a high volume air sampler for pesticides and semivolatile industrial organic chemicals, *Anal. Chem.*, 54, 592, 1982.

MONS 005826

12. **Simon, C. G. and Bidleman, T. F.**, Sampling airborne PCB with polyurethane foam, a chromatographic approach to determining retention efficiencies, *Anal. Chem.*, 51, 1110, 1979.
13. **Burdick, N. F. and Bidleman, T. F.**, Frontal movement of PCB and HCB vapors through polyurethane foam, *Anal. Chem.*, 53, 1926, 1981.
14. **Stratton, C. L., Whitlock, S. A., and Allan, J. M.**, A Method for the Sampling and Analysis of PCBs in Ambient Air, EPA-600/4-78-048, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1978.
15. **Billings, W. N. and Bidleman, T. F.**, Field comparison of polyurethane foam and Tenax-GC resin for high volume air sampling of chlorinated hydrocarbons, *Environ. Sci. Technol.*, 14, 679, 1980.
16. **Billings, W. N. and Bidleman, T. F.**, High volume collection of chlorinated hydrocarbons in urban air using three solid adsorbents, *Atmos. Environ.*, 17, 383, 1983.
17. **Murphy, T. J. and Rzeszutko, C. P.**, Precipitation inputs of PCBs to Lake Michigan, *J. Great Lakes Res.*, 3, 305, 1977.
18. **Bidleman, T. F., Christensen, E. J., Billings, W. N., and Leonard, R.**, Atmospheric transport of organochlorines in the North Atlantic gyre, *J. Mar. Res.*, 39, 443, 1981.
19. **Glam, C. S., Atlas, E. L., Chan, H. S., and Neff, G. S.**, Phthalate esters, PCB and DDT residues in the Gulf of Mexico atmosphere, *Atmos. Environ.*, 14, 65, 1980.
20. **Oehme, M. and Stray, H.**, Quantitative determination of ultra-traces of chlorinated compounds in high volume air samples from the Arctic using polyurethane foam as a collection medium, *Fresenius Z. Anal. Chem.*, 311, 665, 1982.
21. **Oehme, M. and Mano, S.**, The long-range transport of organic pollutants to the Arctic, *Fresenius Z. Anal. Chem.*, 319, 141, 1984.
22. **Doskey, P. V. and Andren, A. W.**, High volume sampling of airborne PCB with Amberlite XAD-2 resin, *Anal. Chim. Acta*, 110, 129, 1979.
23. **Lewis, R. G. and MacLeod, K. E.**, Portable sampler for pesticides and semivolatile industrial organic chemicals in air, *Anal. Chem.*, 54, 310, 1982.
24. **MacLeod, K. E.**, Polychlorinated biphenyls in indoor air, *Environ. Sci. Technol.*, 15, 926, 1981.
25. **Vannucchi, C. and Bertincioni, M.**, Sampling and analytical method to determine PCB concentrations in the air of the working areas of an electrical industry, *Am. Ind. Hyg. Assoc. J.*, 41, 352, 1980.
26. **Holled, G. J. and Eisenreich, S. J.**, Collection of atmospheric PCB on Amberlite XAD-2 resin, *Anal Chim. Acta*, 124, 31, 1981.
27. **Doskey, P. V. and Andren, A. W.**, Concentrations of PCB over Lake Michigan, *J. Great Lakes Res.*, 7, 15, 1981.
28. **Eisenreich, S. J., Holled, G. J., and Johnson, T. C.**, Atmospheric concentrations and deposition of PCB to Lake Superior, in *Atmospheric Pollutants in Natural Waters*, Eisenreich, S. J., Ed., Ann Arbor Science, Ann Arbor, Mich., 1981, 425.
29. **Eisenreich, S. J., Looney, B. B., and Holled, G. J.**, PCBs in the Lake Superior atmosphere 1978-1980, in *Physical Behavior of PCBs in the Great Lakes*, MacKay, D., Paterson, S., Eisenreich, S. J., and Simmons, M., Eds., Ann Arbor Science, Ann Arbor, Mich., 1983, 115.
30. **Eisenreich, S. J. and Looney, B. B.**, Evidence for the atmospheric flux of PCBs to Lake Superior, in *Physical Behavior of PCBs in the Great Lakes*, MacKay, D., Paterson, S., Eisenreich, S. J., and Simmons, M., Eds., Ann Arbor Science, Ann Arbor, Mich., 1983, 141.
31. **Andersson, K., Levin, J. O., and Nilsson, C. A.**, Sampling of polychlorinated aromatics in workroom air using Amberlite XAD-2 resin, *Chemosphere*, 10, 137, 1981.
32. **Glam, C. S., Chan, H. S., and Neff, G. S.**, Rapid and inexpensive method for detection of PCB and phthalates in air, *Anal. Chem.*, 47, 2319, 1975.
33. **Helle, C. L. and Baladi, E.**, Methods for Determining the Total PCB Emissions from Incinerators and Capacitor and Transformer Filling Plants, EPA-600/4-77-048, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1977.
34. **Singer, E., Jarv, T., and Sega, M.**, Survey of PCB in ambient air across the province of Ontario, in *Physical Behavior of PCBs in the Great Lakes*, MacKay, D., Paterson, S., Eisenreich, S. J., and Simmons, M., Eds., Ann Arbor Science, Ann Arbor, Mich., 1983, 367.
35. **Chang, L. W., Atlas, E., and Glam, C. S.**, Chromatographic separation and analysis of chlorinated hydrocarbons and phthalate esters from ambient air samples, *J. Int. Environ. Anal. Chem.*, 19, 145, 1985.
36. **Jackson, J. W. and Chang, D. P. Y.**, PCB recovery efficiency from stack gases and ambient air, *Air Pollut. Control Assoc. J.*, 27, 1008, 1977.
37. **Van Dyk, L. P. and Viswesweriah, K.**, Pesticides in air: sampling methods, in *Residue Reviews*, Vol. 55, Gunther, F. A. and Gunther, J. D., Eds., Springer-Verlag, Basel, 1975, 92.
38. **Lewis, R. G., Sampling and analysis of airborne pesticides**, in *Air Pollution from Pesticides and Agricultural Processes*, Lewis, R. G. and Lee, R. E., Eds., CRC Press, Cleveland, 1976, 51.

MONS 005827

39. **Lamb, S. I., Petrowski, C., Kaplan, I. R., and Simoneit, B. R. T.**, Organic compounds in urban atmospheres: a review of distribution, collection and analysis, *Air Pollut. Control Assoc. J.*, 30, 1098, 1980.
40. **Simoneit, B. R. T. and Mazurek, M. A.**, Air pollution: the organic components, *CRC Crit. Rev. Environ. Control*, 11, 219, 1981.
41. **Senum, G. I.**, Theoretical collection efficiencies of adsorbent samplers, *Environ. Sci. Technol.*, 15, 1073, 1981.
42. **Feng, Y. and Bidleman, T. F.**, Influence of volatility on the collection of PAH vapors with polyurethane foam, *Environ. Sci. Technol.*, 18, 330, 1984.
43. **Westcott, J. W. and Bidleman, T. F.**, Determination of PCB vapor pressures by capillary gas chromatography, *J. Chromatogr.*, 210, 331, 1981.
44. **MacLeod, K. E. and Lewis, R. G.**, Measurement of contamination from PCB sources, in *Sampling And Analysis of Toxic Organics in the Atmosphere*, STP-721, Wheeler, J. B., Huersch, H. M., Mahy, H. P. and Kleinburg, A. S., Eds., American Society for Testing and Materials, Philadelphia, 1980, 56.
45. National Institute for Occupational Safety and Health (NIOSH), Recommended Criteria for Occupational Exposure to PCB, Publ. No. 77-225, U.S. Department of Health, Education, and Welfare, Washington, D.C., 1977.
46. **Weaver, G.**, PCBs in the area of New Bedford, MA, *Environ. Sci. Technol.*, 18, 22A, 1984.
47. **Hetling, L., Horn, E., and Tofflemire, J.**, Summary of Hudson River PCB Results, New York State Department of Environmental Conservation, Albany, N.Y., 1978.
48. **MacLeod, K.**, Sources of PCB Emissions into the Ambient Atmosphere and Indoor Air, EPA-600/4-79-022, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1979.
49. **Glass, C. S. and Atlas, E.**, Unpublished data.
50. **Bidleman, T. F., Billings, W. N., and Foreman, W. T.**, Vapor-particle partitioning of semivolatile organic compounds: estimates from field collections, *Environ. Sci. Technol.*, in press.
51. **Bidleman, T. F. and Christensen, E. J.**, Atmospheric removal processes for high-molecular weight organochlorines, *J. Geophys. Res.*, 84, 7857, 1979.
52. **Addison, R. F., Zinck, M. E., and Smith, T. G.**, PCBs have declined more than DDT group residues in Arctic ringed seals (*Phoca hispida*) between 1972 and 1981, *Environ. Sci. Technol.*, 20, 253, 1986.
53. **Cautreels, W. and Van Cauwenberghe, K.**, Experiments on the distribution of organic pollutants between airborne particulate matter and the corresponding gas phase, *Atmos. Environ.*, 12, 1133, 1978.
54. **König, J., Funcke, W., Balfanz, E., Grosch, B., and Pott, F.**, Testing a high volume air sampler for quantitative collection of PAH, *Atmos. Environ.*, 14, 609, 1980.
55. **Broddin, G., Cautreels, W., and Van Cauwenberghe, K.**, On the aliphatic and polyaromatic hydrocarbon levels in urban and background aerosols from Belgium and the Netherlands, *Atmos. Environ.*, 14, 895, 1980.
56. **Grosjean, D.**, PAH in Los Angeles from samples collected on teflon, glass, and quartz fiber filters, *Atmos. Environ.*, 14, 895, 1980.
57. **Spitzer, T. and Dannecker, W.**, Membrane filters as adsorbents for PAH during high volume sampling of air particulate matter, *Anal. Chem.*, 55, 2226, 1983.
58. **Van Vaeck, L., Van Cauwenberghe, K., and Janssens, J.**, The gas-particle distribution of organic aerosol constituents: measurement of the volatilization artifact, *Atmos. Environ.*, 18, 417, 1984.
59. **Schwartz, G. P., Daisey, J. M., and Lioy, P. J.**, Effect of sampling duration on the concentration of particulate organics collected on glass fiber filters, *Am. Ind. Hyg. Assoc. J.*, 42, 258, 1981.
60. **Gilbertson, M.**, Background to the Regulation of PCB in Canada, Task Force on PCB, Report to the Environmental Contamination Committee of Environment Canada and Health and Welfare Canada, Toronto, Ontario, Canada, 1976.
61. **Harvey, G. R. and Steinhauer, W. G.**, Atmospheric transport of polychlorobiphenyls to the North Atlantic, *Atmos. Environ.*, 8, 777, 1974.
62. **Yamasaki, H., Kuwata, K., and Miyamoto, H.**, Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.*, 16, 189, 1982.
63. **Prospero, J. M.**, Mineral and sea salt aerosol concentrations in various ocean regions, *J. Geophys. Res.*, 84, 725, 1979.
64. **Miller, J. and Summers, P. W.**, United States-Canada Memorandum of Intent on Transboundary Air Pollution, Report 2F-I, Atmospheric Sciences Review Subgroup, Work Group 2, 1982.
65. **Bogen, D. C., Nagourney, S. J., and Torquato, C.**, A field evaluation of the HASL wet-dry deposition collector, *Water Air Soil Pollut.*, 13, 453, 1980.
66. **Strachan, W. M. J. and Huneault, H.**, Automated rain sampler for trace organic substances, *Environ. Sci. Technol.*, 18, 127, 1984.
67. **Pankow, J. F., Isabelle, L. M., and Asher, W. E.**, Trace organic compounds in rain. I. Sampler design and analysis by adsorption/thermal desorption (ATD), *Environ. Sci. Technol.*, 18, 310, 1984.

MONS 005828

68 **Wells, D. E. and Johnstone, S. J.**, The occurrence of organochlorine residues in rainwater. *Water Air Soil Pollut.*, 9, 271, 1978.

69 **Sodergren, A.**, Chlorinated hydrocarbon residues in airborne fallout. *Nature (London)*, 236, 395, 1972.

70 **Sodergren, A.**, Monitoring DDT and PCB in airborne fallout. *Environ. Qual. Saf.*, 3, 803, 1975.

71 **Bengston, S. A. and Sodergren, A.**, DDT and PCB residues in airborne fallout and animals in Iceland. *Ambio.*, 3, 84, 1974.

72 **McClure, V. E.**, Transport of heavy chlorinated hydrocarbons in the atmosphere. *Environ. Sci. Technol.*, 10, 1223, 1976.

73 **McClure, V. E. and LaGrange, J.**, Deposition of heavy chlorinated hydrocarbons from the atmosphere. *Bull. Environ. Contam. Toxicol.*, 17, 219, 1977.

74 **Young, D. R., McDermott, D. J., Heesen, T. C., and Jan, T. K.**, Pollutant inputs and distributions off Southern California, in *Marine Chemistry in the Coastal Environment*, Vol. 18, Church, T., Ed., ACS Symposium Series American Chemical Society, Washington, D.C., 1975, 424.

75 **Young, D. R., McDermott, D. J., and Heesen, T. C.**, Aerial fallout of DDT in Southern California. *Bull. Environ. Contam. Toxicol.*, 16, 604, 1976.

76 **Heesen, T. C., Young, D. R., and McDermott-Ehrlich, D.**, Evaluation of a technique for measuring dry aerial deposition rates of DDT and PCB residues. *Atmos. Environ.*, 13, 1677, 1979.

77 **Murphy, T. J.**, Evaluation of a technique for measuring dry aerial deposition rates of DDT and PCB — discussion. *Atmos. Environ.*, 15, 206, 1981.

78 **Murphy, T. J., Schinsky, A., Poulucci, G., and Rzeszutko, C. P.**, Inputs of polychlorinated biphenyls from the atmosphere to lakes Huron and Michigan, in *Atmospheric Pollutants in Natural Waters*, Eisenreich, S. J., Eds., Ann Arbor Science, Ann Arbor, Mich., 1981, 445.

79 **Christensen, E. J., Olney, C. E., and Bidleman, T. F.**, Comparison of dry and wet surfaces for collecting organochlorine dry deposition. *Bull. Environ. Contam. Toxicol.*, 23, 196, 1979.

80 **Sehmel, G. A.**, Particle and gas dry deposition: a review. *Atmos. Environ.*, 14, 983, 1980.

81 **Lunde, G., Gether, J., Gjos, N., and Stobet Lunde, M. B.**, Organic micropollutants in precipitation in Norway. *Atmos. Environ.*, 11, 1007, 1977.

82 **Slinn, W. G. N., Hasse, L., Hicks, B. B., Hogan, A. W., Lal, D., Liss, P. S., Munnich, K. O., Sehmel, G. A., and Vittori, O.**, Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. *Atmos. Environ.*, 12, 2055, 1978.

83 **Slinn, S. A. and Slinn, W. G. N.**, Predictions for particle deposition on natural waters. *Atmos. Environ.*, 14, 1013, 1980.

84 **Slinn, S. A. and Slinn, W. G. N.**, Modeling of atmospheric particulate deposition to natural waters, in *Atmospheric Pollutants in Natural Waters*, Eisenreich, S. J., Ed., Ann Arbor Science, Ann Arbor, Mich., 1981, 23.

85 **Scott, B. C.**, Modeling of atmospheric wet deposition, in *Atmospheric Pollutants in Natural Waters*, Eisenreich, S. J., Ed., Ann Arbor Science, Ann Arbor, Mich., 1981, 3.

86 **Hicks, B. B., Wesely, M. L., and Durham, J. L.**, Critique of Methods to Measure Dry Deposition — Workshop Summary, Report 600/9-80-050, U.S. Environmental Protection Agency, Washington, D.C., 1980.

87 **Deinke, D. A. and Getz, D. F.**, A field intercomparison of methods for the measurement of particle and gas dry deposition. *J. Geophys. Res.*, 90, 2075, 1985.

88 **Hardee, H. W., Christensen, E. J., Matthews, J., and Bidleman, T. F.**, Rainfall input of toxaphene to a South Carolina estuary. *Estuaries*, 3, 142, 1980.

89 **Lunde, G., Gether, J., Gjos, N., and Stobet Lunde, M. B.**, Organic micropollutants in precipitation in Norway. *Atmos. Environ.*, 11, 1007, 1977.

90 **Strachan, W. M. J., Huneault, H., Schertzer, W. M., and Elder, F. C.**, Organochlorines in precipitation in the Great Lakes region, in *Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment*, Afghan, B. K. and Mackay, D., Eds., Plenum Press, New York, 1980, 387.

91 **Strachan, W. M. J. and Huneault, H.**, PCB and organochlorine pesticides in Great Lakes precipitation. *J. Great Lakes Res.*, 5, 61, 1979.

92 **Sanderson, M. and LaValle, P. D.**, Surface loading from pollutants in precipitation in Southern Ontario: some climatic and statistical aspects. *J. Great Lakes Res.*, 5, 52, 1979.

93 **Swain, W. R.**, Chlorinated organic residues in fish, water, and precipitation from the vicinity of Isle Royale, Lake Superior. *J. Great Lakes Res.*, 4, 398, 1978.

94 **Davis, A. B.**, The Canadian Network for Sampling Organic Compounds in Precipitation. Inland Waters Directorate, Ottawa, Ontario, Canada, 1980.

95 **Risebrough, R. W., deLappe, B. W., and Walker, W.**, Transfer of higher molecular weight chlorinated hydrocarbons to the marine environment, in Marine Pollutant Transfer, Windom, H. and Duce, R. A., Eds., Lexington Books/D.C. Heath & Co., Lexington, Mass., 1976, 261.

96 **Murphy, T. J. and Schinsky, A. W.**, Net atmospheric inputs of PCBs to the ice cover on Lake Huron. *J. Great Lakes Res.*, 9, 92, 1983.

MONS 005829

97 **Andren, A. W.**, Processes determining the flux of PCBs across air-water interfaces, in *Physical Behavior of PCBs in the Great Lakes*, MacKay, D., Paterson, S., Eisenreich, S. J., and Simmons, M., Eds., Ann Arbor Science, Ann Arbor, Mich., 1983, 127.

98 **Sodergren, A.**, Transport, distribution, and degradation of organochlorine residues in a South Swedish lake ecosystem, *Vatten*, 2, 90, 1973.

99 **Settle, D. M. and Patterson, C. C.**, Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewetak, *J. Geophys. Res.*, 87, 8857, 1982.

100 **Zafiriou, O. C., Gagosian, R. B., Peltzer, E. T., Alford, J. B., and Loder, T.**, Air-to-sea fluxes of lipids at Enewetak Atoll, *J. Geophys. Res.*, 90, 2409, 1985.

101 **Atlas, E., Sullivan, K., Madero, M., and Glam, C. S.**, Trace organic compounds in rural air and rainfall, in preparation.

102 **Arimoto, R., Duce, R. A., Ray, B. J., and Unni, C. K.**, Atmospheric trace and dry deposition, *J. Geophys. Res.*, 90, 2391, 1985.

103 *MacKay, D., Paterson, S., Eisenreich, S. J., and Simmons, M. S., Eds., Physical Behavior of PCBs in the Great Lakes*, Ann Arbor Science, Ann Arbor, Mich., 1983.

104 **Eisenreich, S., Ed.**, *Atmospheric Pollutants in Natural Waters*, Ann Arbor Science, Ann Arbor, Mich., 1981.

105 **Doskey, P. V. and Andren, A. W.**, Modeling the flux of atmospheric PCB across the air-water interface, *Environ. Sci. Technol.*, 15, 705, 1981.

106. **Liss, P. S. and Slater, P. G.**, Fluxes of gases across the air-sea interface, *Nature (London)*, 247, 181, 1974.

107 **Smith, J. H., Bomberger, D. C., Jr., and Haynes, D. L.**, Prediction of the volatilization rates of high-volatility chemicals from natural water bodies, *Environ. Sci. Technol.*, 14, 1332, 1980.

108 **Reid, R. C., Prausnitz, J. M., and Sherwood, T. K.**, *The Properties of Gases and Liquids*, 3rd ed., McGraw-Hill, New York, 1977.

109 **Atlas, E., Foster, R., and Glam, C. S.**, Air-sea exchange of high molecular weight organic pollutants: laboratory studies, *Environ. Sci. Technol.*, 16, 283, 1982.

110 **Atlas, E., Velasco, A., Sullivan, K., and Glam, C. S.**, A radiotracer study of air-water exchange of synthetic organic compounds, *Chemosphere*, 12, 1251, 1983.

111 **MacKay, D. and Wolkoff, A. W.**, Rate of evaporation of low-solubility contaminants from water bodies to atmosphere, *Environ. Sci. Technol.*, 7, 611, 1973.

112. **Rice, C. P., Eadie, B. J., and Erstfeld, K. M.**, Enrichment of PCBs in Lake Michigan surface films, *J. Great Lakes Res.*, 8, 265, 1982.

113. **Voice, T. C., Rice, C. P., and Weber, J. R.**, The effect of solids concentration on the sediment/water partitioning of hydrophobic pollutants, *Environ. Sci. Technol.*, 17, 513, 1983.

114 **Gschwend, P. M. and Wu, S.**, On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants, *Environ. Sci. Technol.*, 19, 90, 1985.

115 **Means, J. C., Wijayaratne, R. D., and Boynton, W. R.**, Fate and transport of selected herbicides in an estuarine environment, *Can. J. Fish. Aquat. Sci.*, 40(Suppl. 2), 337, 1983.

116. **Means, J. C. and Wijayaratne, R.**, Role of natural colloids in transport of hydrophobic pollutants, *Science*, 215, 968, 1982.

117 **Uematsu, M., Duce, R. A., Prospero, J. M., Chen, L., Merrill, J. T., and Donald, R. L.**, The transport of mineral aerosol from Asia over the North Pacific Ocean, *J. Geophys. Res.*, 88, 5343, 1983.

118. **Honjo, S., Manganini, S. J., and Cole, J. J.**, Sedimentation of biogenic matter in the deep ocean, *Deep-Sea Res.*, 29, 609, 1982.

119 **Duinker, J. C. and Hillebrand, M. T. J.**, Behavior of PCB, pentachlorobenzene, hexachlorobenzene, α-HCH, β-HCH, γ-HCH, dieldrin, endrin, and p,p'-DDD in the Rhine-Meuse estuary and the adjacent coastal area, *Neth. J. Sea Res.*, 13, 256, 1979.

120. **Tanabe, S. and Tatsukawa, R.**, Distribution, behavior, and load of PCBs in the ocean, in *PCBs and the Environment*, Vol. 1, Waid, J. S., Ed., CRC Press, Boca Raton, Fla., 1986, chap. 8.

121. **Tanabe, S. and Tatsukawa, R.**, Vertical transport and residence time of chlorinated hydrocarbons in the open ocean water column, *J. Oceanogr. Soc. Jpn.*, 39, 53, 1983.

MONS 005830

Chapter 5

SOLUBILITY AND SOIL MOBILITY OF POLYCHLORINATED BIPHENYLS

S. F. J. Chou and R. A. Griffin

TABLE OF CONTENTS

I. Abstract 102

II. Introduction 102

III. Aqueous Solubility 102

IV. Sorption of PCBs by Earth Materials 105

V. Mechanism of Sorption 110

VI. Correlation of K Values with Earth Material and Compound Properties 111

VII. Mobility of PCBs in Soils 113

VIII. Surface Runoff 115

IX. Plant Uptake 117

X. Summary and Conclusions 117

References 118

MONS 005831

I. ABSTRACT

Aqueous solubilities of polychlorinated biphenyls (PCBs) are low, ranging from 2.7 ppb for Aroclor® 1260 to 3500 ppb for Aroclor® 1221. Water-soluble PCBs are reported to be richer in lower chlorinated isomers than were the original PCB fluids.

PCBs are strongly sorbed by earth materials. There is a very high direct correlation between the total organic carbon content of the soil and the amount sorbed. The sorption and retention of PCBs by soils and soil constituents are influenced by the number of chlorine atoms in the molecule, the more highly chlorinated derivatives being more tenaciously held. A linear regression relation for sorption of PCBs expressed on a unit carbon basis as a function of water solubility is presented. The correlation of sorption with compound *n*-octanol/water partition coefficients is also examined.

PCBs are not readily mobile in soils when leached with aqueous solutions such as water or sanitary landfill leachates but are highly mobile when leached with organic solvents. Mobility of PCBs is proportional to their solubility in the leaching solvent and to the soil organic matter content.

II. INTRODUCTION

PCBs are a class of chlorinated aromatic hydrocarbons that are thermally and chemically stable. They have been widely used as a dielectric fluid in transformers and as an impregnating agent for capacitors and condensers. The occurrence of PCBs in the environment and their consequences on environmental quality have been well emphasized.[1-4] The Toxic Substances Control Act (TSCA), Public Law 94-469, specifically prohibits production of PCBs within the U.S., regulates disposal of materials contaminated by PCBs, and restricts the use of any such materials already in service. The effect of these measures should be to eliminate further releases into the environment and eventually, to reduce quantities existing in the environment. However, because of the extreme stability of PCBs, environmental levels will not be reduced substantially for many years, and the problem of dealing with existing reservoirs of mobile PCBs will remain.

The disposal of PCBs and related materials in landfills is of great concern[5,6] because of the possibility of ground water contamination if these compounds are leached from landfills. The limited amount of available information indicates that PCBs have a strong affinity for soil[7-9] and are not readily leached by percolating water.[10] Briggs[11] reported that adsorption of nonionic organic compounds by soils was related to the organic matter content of soils and to their octanol/water partition coefficient. He predicted that PCBs would be immobile in soils. The water solubility, sorption, mobility, translocation, and plant uptake of PCBs will be discussed in this review. The correlation of the sorption constant of PCBs with soil and compound properties will also be examined.

III. AQUEOUS SOLUBILITY

The aqueous solubility of hydrophobic compounds such as PCBs is a valuable indictor of its environmental fate, for example, its tendency to sorb to soil or to bioaccumulate in organisms. A considerable volume of data has been published on PCB solubilities,[10,12-27] but discrepancies exist because of the experimental difficulty of generating and handling such dilute solutions. The aqueous solubilities of some individual PCB isomers and commercially available mixtures of PCBs are listed in Table 1. The soil sorption constant (K_{oc}) is also listed in Table 1. Aqueous solubilities of PCBs are very low ranging from 0.95 ppb for 2,4,5,2',4',5'-hexachlorobiphenyl to 5900 ppb for 2-chlorobiphenyl and 2.7 ppb for Aroclor® 1260 to 3500 ppb for Aroclor® 1221. The composition of Aroclors® is given in

MONS 005832

Table 1
SOLUBILITY, K_{ow}, AND K_{oc} OF SEVERAL PCBs

Compound	Solubility (ppb)	log S	Ref.	K_{ow}	log K_{ow}*	Ref.	K_{oc}	log K_{oc}*	Ref.
Biphenyl	7,500	3 88	43	2,512	(3 40)		7,540	3 88	18
Monochlorobiphenyls									
2-	5,900	3 77	27	2,951	(3 47)		14,790	(4 17)	
3-	3,500	3 54	27	4,168	(3 62)		21,877	(4 34)	
4-	1,190	3 08	26, 27	7,943	(3 90)		79,400	4 90	50
Dichlorobiphenyls									
2,4-	1,400	3 15	27	7,244	(3 86)		41,686	(4 62)	
2,2'-	1,500	3 18	27	6,918	(3 84)		39,810	(4 60)	
2,4'-	1,260	3 10	23, 27	8,000	3 90	8	45,708	14 66)	
4,4'-	80	1 90	27	42,658	(4 63)		346,736	(5 54)	
Trichlorobiphenyls									
2,4,4'-	85	1 93	27	40,738	(4 61)		323,593	(5 51)	
2',3,4-	78	1 89	27	43,652	(4 64)		346,336	(5 54)	
Tetrachlorobiphenyls									
2,2',5,5'-	36	1 56	23, 27	47,000	4 67	8	602,559	(5 78)	
2,2',3,3'-	34	1 53	27	72,443	(4 86)		645,654	(5 81)	
2,2',3,5'-	170	2 23	27	26,915	(4 43)		194,984	(5 29)	
2,2',4,4'-	66	1 82	24, 25, 27	47,863	(4 68)		158,400	5 20	49
2,3',4,4'-	58	1 76	27	52,480	(4 72)		436,555	(5 64)	
2,3',4,5'-	41	1 61	27	64,565	(4 81)		562,341	(5 75)	
3,3',4,4'-	180	2 26	27	25,033	(4 41)		186,208	(5 27)	
Pentachlorobiphenyls									
2,2',3,4,5'-	22	1 34	27	95,324	(4 98)		870,693	(5 94)	
2,2',4,5,5'-	31	1 49	27	76,948	(4 89)		691,830	(5 84)	
Hexachlorobiphenyl									
2,4,5,2',4',5'-	0 95	− 0 02	23	1,200,000	6 08	43	5,248,000	6 72	15
Aroclors									
1221	3,500	3 54	19	4,123	(3 62)		12,300	4 09	25
1232	1,450	3 16	12	7,092	(3 85)		41,686	(4 62)	
1242 (Aroclor 1242)	698	2 84	19	10,725	4 03		70,794	(4 85)	
1016	332	2 52	10, 12, 14	17,684	(4 25)		202,000	5 31	14, 18

MONS 005833

Table 1 (continued)
SOLUBILITY, K_{ol}, AND K_{ow} OF SEVERAL PCBs

Compound	Solubility (ppb)	log S	Ref.	K_{ow}	log K_{ow}*	Ref.	K_{ow}	log K_{ow}*	Ref.
1242	288	2.46	12, 13, 16, 17, 20	12,600	4.09	44	190,500	5.29	14, 18
1248	54	1.73	27	54,676	(4.74)		562,000	5.75	12
1254	42	1.62	15, 20, 21, 22	63,914	(4.81)		1,288,000	6.11	15
1260	2.7	0.43	12	349,462	(5.54)		4,073,800	6.61	

* Data in parentheses were estimated using the method of Hansch et al.[44]
* Data in parentheses were estimated using Equation 9

MONS 005834

Table 2
APPROXIMATE MOLECULAR COMPOSITION (%) OF AROCLORS[9,14]

Empirical formula	Aroclor® no. 1221	1232	1016	1242	1248	1254	1260
$C_{12}H_{10}$	11	<0.1	<0.1	<0.1	ND	<0.1	ND
$C_{12}H_9Cl$	51	31	1	1	ND	<0.1	ND
$C_{12}H_8Cl_2$	32	24	20	16	2	0.5	ND
$C_{12}H_7Cl_3$	4	28	57	49	18	1	ND
$C_{12}H_6Cl_4$	2	12	21	25	40	21	1
$C_{12}H_5Cl_5$	<0.5	4	1	8	36	48	12
$C_{12}H_4Cl_6$	ND	<0.1	<0.1	1	4	23	38
$C_{12}H_3Cl_7$	ND	ND	ND	<0.1	ND	6	41
$C_{12}H_2Cl_8$	ND	ND	ND	ND	ND	ND	8
$C_{12}HCl_9$	ND	ND	ND	ND	ND	ND	ND
Average mol wt	200.7	232.2	257.9	266.5	299.5	328.4	375.7

Note: ND means none detected

Table 3
SUMMARY OF ISOMER COMPOSITION (%) OF WATER-SOLUBLE AROCLORS® [19]

Empirical formula	Aroclor® no. 1221	1016	1242	Capacitor fluid	1254
$C_{12}H_9Cl$	92	12	19	18	ND
$C_{12}H_8Cl_2$	7	34	35	32	ND
$C_{12}H_7Cl_3$	1	35	31	36	20
$C_{12}H_6Cl_4$	<0.1	19	14	13	56
$C_{12}H_5Cl_5$	ND	ND	1	1	24
$C_{12}H_4Cl_6$	ND	ND	ND	ND	<0.1
$C_{12}H_3Cl_7$	ND	ND	ND	ND	<0.1

Note: ND means none detected.

Table 2. The overall compositions of chlorobiphenyl isomers in the water-soluble fraction of these Aroclors® are listed in Table 3. Representative GC chromatograms of water-soluble Aroclors®[19] are shown in Figure 1. In comparing the composition of the water-soluble Aroclors® reported by Thurston[20] and Lee et al.,[19] the water-soluble fractions were found to be richer in the lower-chlorinated isomers than were the original PCBs. Aroclor® 1254 is reported to contain isomers from tetra- to heptachlorobiphenyl in the original fluid. The GC traces of hexane-soluble Aroclor® 1254 reported by several researchers[19,20] show some small peaks in the position of trichlorobiphenyl; this has also been confirmed by Lee et al.[19] Because trichlorobiphenyls are more water-soluble than the more highly chlorinated biphenyls, detection of trace amounts in water is reasonable. The hexa- and heptachlorobiphenyls are enriched in the Aroclor® 1254 fluid and do not dissolve readily in water. The low solubility of these highly chlorinated isomers in water is apparently the reason.

IV. SORPTION OF PCBs BY EARTH MATERIALS

Sorption of PCBs by earth materials is the major nondestructive physicochemical process

MONS 005835

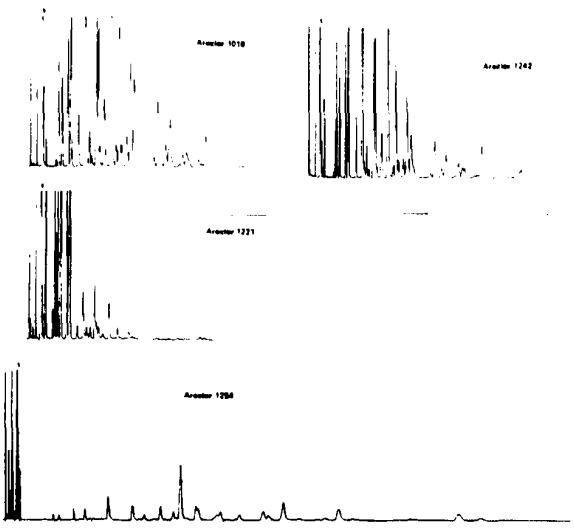


FIGURE 1. GC chromatograms of water-soluble Aroclors® [4] (IS means internal standard)

affecting PCB concentrations after introduction into the aquatic environment. The combination of low water solubility and high octanol/water partition coefficients (see Table 1) indicates that PCBs have a high affinity for suspended solids, especially those high in organic carbon.[31] This has been confirmed by a number of experiments which have shown that PCBs are rapidly sorbed and that the greatest amounts of PCBs are usually associated with the soils or sediments in soil-water systems.[7,14,32,33] Griffin and Chou[34] reported adsorption of water soluble PCBs by soil materials and coal chars. Data for PCB sorption by various earth materials are given in Table 4. Representative sorption isotherms are shown in Figures 2 and 3. The amount of PCBs sorbed by the earth materials was related to the equilibrium solution concentration of PCBs, and could be described by the simple linear relation[35]

$$x/m = KC \qquad (1)$$

where x = micrograms of compound sorbed, m = weight of adsorbent (g), C = the equilibrium concentration of the PCBs in solution ($\mu g/m\ell$), and K = the sorption constant ($m\ell/g$).

The PCB sorption data reported here are a special case of the Freundlich equation where $1/n = 1$. K_f and K are thus identical and Freundlich K_f values reported in the literature for other compounds can be compared with the K values for PCBs reported in Table 4. The data presented in Table 4 illustrate the wide differences in sorption by the various earth materials. Sorption of PCBs followed the series Medium Temperature Coal Char > High

MONS 005836

Table 4
EARTH MATERIALS USED IN SORPTION STUDIES, THEIR SORPTION CONSTANT (K), THEIR TOTAL ORGANIC CARBON (TOC) CONTENT, AND SURFACE AREA (SA)[35]

Sorbent	K	TOC (%)	SA (m^2/g)
Ottawa silica sand	22	0.01	0.4
Montmorillonite clay	172	0.93	20.1
Montmorillonite clay (LTA)	145	0.13	20.2
Catlin silt loam	532	4.73	26.5
Catlin, 6 hr (LTA)	472	4.37	25.4
Catlin, 12 hr (LTA)	310	3.64	24.5
Catlin, 336 hr (LTA)	239	1.84	23.8
Medium temp. coal char 650°C	1,938	74.04	253
Medium temp. coal char 650°C (LTA)	1,432	64.00	214
High temp. coal char 980°C	1,220	76.62	44
High temp. coal char 980°C (LTA)	1,174	32.14	120

Note: LTA denotes low temperature ashed samples.

Temperature Coal Char > Catlin Soil > Montmorillonite Clay > Ottawa Silica Sand. Low-temperature ashing reduced the amounts of PCBs sorbed by all samples. For the samples of Catlin soil (CS), PCB sorption decreased as ashing time increased; this corroborates the observations of Briggs[11] that there is a relationship between organic matter content and sorption.

The sorption of isomers from water-soluble Aroclor® 1242 solutions by different sorbents was investigated by Lee et al.[9] They found that higher chlorinated isomers were sorbed more than the lower chlorinated isomers. Haque and Schmedding[4] indicated that the extent of sorption for the surfaces they studied followed the sequence hexachloro- > tetrachloro- > dichlorobiphenyl for the isomers studied. The sorption of the water-soluble isomers of Aroclor® 1242 by coal char was reported by Griffin and Chian.[35] The average sorption of all isomers in groups such as monochloro- or dichloro-isomers were considered together. Griffin and Chian[35] concluded that the higher chlorinated were preferentially sorbed over the lower-chlorinated isomers which agreed with the sequence found by Haque and Schmedding.[4]

The relationship between total organic carbon (TOC) content, surface area, and PCB sorption were investigated by Lee et al.[9] A highly significant ($p = 0.001$ level) correlation was found with a linear regression relation of the PCB sorption constant (K) and TOC of:

$$K = 255 + 18.5\ TOC \qquad r^2 = 0.87 \qquad (2)$$

Thus, the PCB sorption constant (K) can be estimated from a knowledge of the TOC content of the earth material. A highly significant ($p = 0.001$ level) correlation was also found with a linear regression relation of the PCB sorption constant (K) with surface area (SA, measured by using CO_2 gas adsorption):

$$K = 230 + 6.64\ SA \qquad r^2 = 0.82 \qquad (3)$$

MONS 005837

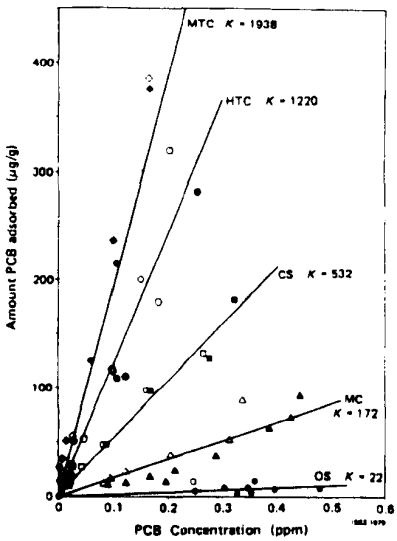


FIGURE 2. PCB adsorption by earth materials.[4] Solid symbols represent data for capacitor fluid, open symbols represent data for Aroclor® 1242, and Xs in open symbols indicate analysis using capillary column.

A three-variable regression analysis of the PCB sorption constant (K), TOC, and SA was investigated by Lee et al.[9] A very highly significant ($p = 0.001$ level) correlation was obtained with a linear regression relation of:

$$K = 188 + 3.36\,SA + 11.4\,TOC$$
$$r^2 = 0.94 \qquad (4)$$

The magnitude of the coefficients for SA and TOC indicate that TOC is the dominant factor in sorption. The best estimates of K were obtained by incorporating both SA and TOC; however, if only one earth material property must be chosen to estimate K, and TOC would be the most useful property.

The relation between the Aroclor® 1242 sorption constant, K, and the TOC content of the seven soil materials in Table 4 is illustrated in Figure 4. A linear relation was obtained and the slope of the line was used to estimate the K_{oc} value for Aroclor® 1242. The K_{oc} is the sorption constant normalized for the organic carbon content of soil and was found to have a value of 10,725. A three-variable regression analysis of the Aroclor® 1242 sorption constant, K, TOC, and SA was investigated using the data for soil materials (i.e., excluding coal chars) reported in Table 4 and is shown in Figure 5. A very highly significant correlation was obtained with a linear regression relation of:

MONS 005838

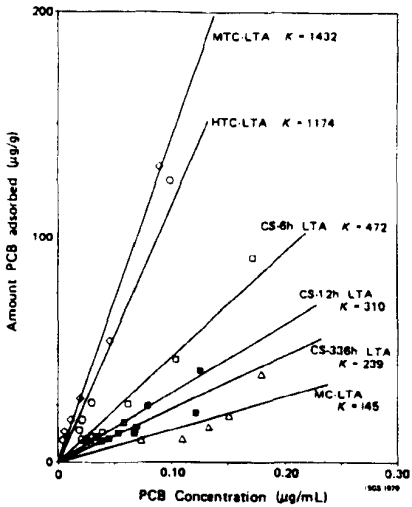


FIGURE 3 PCB adsorption by low temperature ashes of earth materials [4]

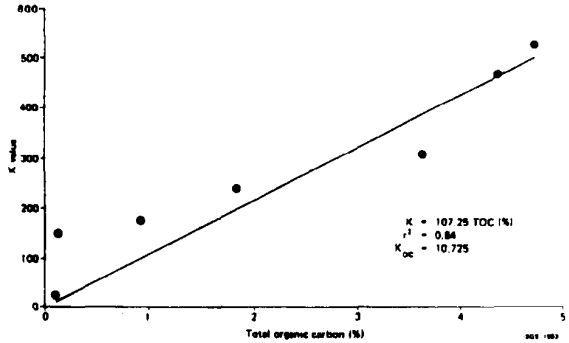


FIGURE 4. Aroclor® 1242 soil sorption constant (K) vs. soil material TOC content

MONS 005839

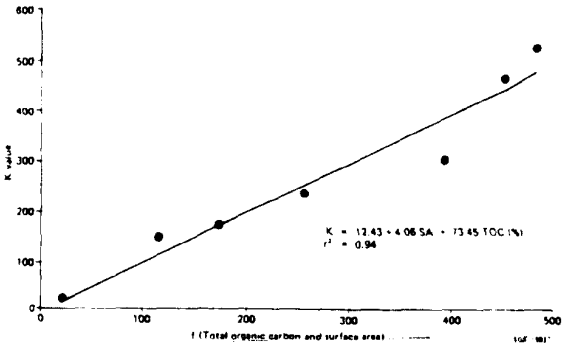


FIGURE 5 Multiple variable regression analysis of the Aroclor® 1242 soil sorption constant (K) plotted as a function of the TOC content and SA of 7 soil materials.

$$K = 12.43 + 4.06\,SA + 73.45\,TOC$$
$$r^2 = 0.94 \qquad (5)$$

The magnitude of the coefficients for SA and TOC indicates that TOC is the dominant soil property in sorption. The best estimates of K are obtained by a knowledge of both S and TOC; however, TOC is again, the single most important property controlling PCB sorption. When the PCB contamination level of soils or sediments becomes large, these materials may serve as a reservoir for desorption.[36] This is illustrated by Equation 1 which indicates that K is a ratio of x/m to C and as x/m becomes large, C also grows in relation to K. This fact has important ramifications to situations where PCBs are spilled or disposed in high concentrations because release of PCBs by soil materials can cause long-term pollution. For example, oysters still contained measurable levels of PCBs 7 years after a spill, even though the concentrations in the water were below detection limits.[37]

V. MECHANISM OF SORPTION

The sorption of PCBs by earth materials is suggested to be a hydrophobic sorption, which is the partitioning of the nonpolar solute out of the polar aqueous phase onto hydrophobic surfaces on the earth materials. The hydrophobic surfaces are primarily associated with soil organic matter but may also include ≡Si–O–Si≡ bonds at mineral surfaces.[38] The primary feature of hydrophobic sorption is the very weak interaction between the solute and the solvent. As the term hydrophobic suggests, the solvent water plays a major role in the interaction. Although not strictly the case, the interaction may be so weak as to acquire the nature of a repulsion of the PCB molecule from the water. The more hydrophobic the PCB molecule (lower in water solubility), the greater the repulsion from the water phase and the greater the sorption on a hydrophobic surface. In a stricter treatment, hydrophobic sorption is thought to be an entropy driven process governed by the basic thermodynamic relation:

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

MONS 005840

where ΔG is the change in free energy of the system, ΔH is the heat of sorption (enthalpy), T is temperature, and ΔS is the change in entropy of the system. Sorption results when there is a negative free energy change. The primary driving force in hydrophobic sorption appears to be the large entropy change resulting from the removal of the organic molecule from solution and sorption onto a hydrophobic surface.[39,40] The entropy change is the primary driving force due to the destruction of the cavity occupied by the PCB molecule in the solvent and the destruction of the highly structured water shell surrounding the solvated PCB molecule.[40,41]

The role of the solute-solvent interaction in determining the degree of sorption of hydrophobic compounds was demonstrated by a soil thin-layer chromatography study using solutes and solvents (mobile phase) of different polarities.[42] When the mobile phase was 100% water, the polar compounds were weakly sorbed and moved with the solvent front, and the less polar compounds were strongly sorbed and showed little movement. As the mobile phase was made less polar by additions of ethanol, it became a better solvent for the nonpolar compounds and their sorption decreased. With ethanol additions, the mobile phase became a poorer solvent for the polar compound and its sorption increased and movement decreased. Similar results for Aroclors® 1242, 1254, and dicamba have also been reported.[43]

VI. CORRELATION OF K VALUES WITH EARTH MATERIAL AND COMPOUND PROPERTIES

Sorption experiments with nonpolar organic compounds and different earth materials produce a different K value for each earth material and organic compound. Hydrophobic sorption has been highly correlated with the organic carbon content of the earth material while at the same time being relatively independent of other sorbent properties.[43-46] When sorption of a hydrophobically sorbed compound is examined relative to the organic carbon content of the earth material, a constant, K_{oc}, is generated which is a unique property of the compound being sorbed. The K_{oc} can be determined graphically as shown in Figure 4 or computed as follows:

$$K_{oc} = K_f \times 100/(\%)TOC \quad (7)$$

where K_f is the Freundlich constant and TOC is the percent organic carbon in the respective soil material. K_{oc} values are compound properties, not soil properties, and have been related to other compound properties such as water solubility (S) and *n*-octanol/water partition coefficients (K_{ow}). Figure 6 shows the $\overline{K}_{oc}$-S relation for the PCBs for which data are tabulated in Table 1. The linear regression equation obtained was

$$\log K_{oc} = 5.85 - 0.64 \log S \text{ (ppb)} \quad (8)$$

The data indicate that a good approximation of sorption of PCBs by soil materials can be made based on their water solubility. Water solubilities have been also shown to predict the K_{oc} values of a wide range of other hydrophobic compounds.[43,44,47]

The octanol/water partition coefficient (K_{ow}) measures the tendency of a compound to partition between an organic solvent and water. The octanol/water partition coefficient is usually obtained by measuring the concentration of the compound in equilibrium with *n*-octanol and water.[48] However, a satisfactory linear relationship is also observed between the log K_{ow} and log S, which extends over more than eight orders of magnitude in solubility (10^{-4} to 10^{3} ppm) and four orders of magnitude in partition coefficient (10^{3} to 10^{7}). The *n*-octanol/water partition coefficients of several PCBs are listed in Table 1. A plot of log

MONS 005841

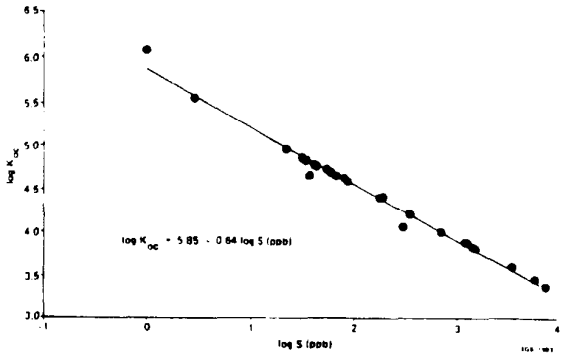


FIGURE 6. PCB soil sorption vs. water solubility.

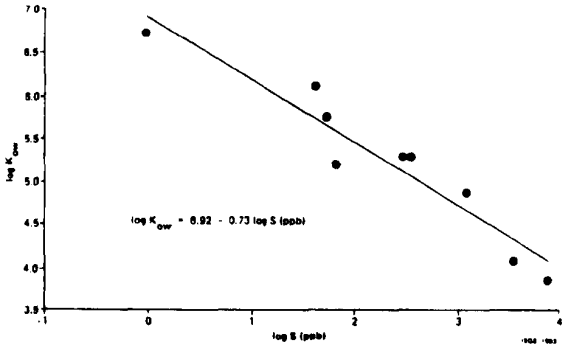


FIGURE 7. Relation of K_{ow} and the water solubility (S) of several PCBs.

K_{ow} vs. log S using the values cited in Table 1 is shown in Figure 7. The regression equation is

$$\log K_{ow} = 6.923 - 0.730 \log S \text{ (ppb)}$$
$$r^2 = 0.91 \qquad (9)$$

Equation 9 allows an estimation of the partition coefficient of a given compound from its aqueous solubility. The reliability of these relationships suggests that they may be very

MONS 005842

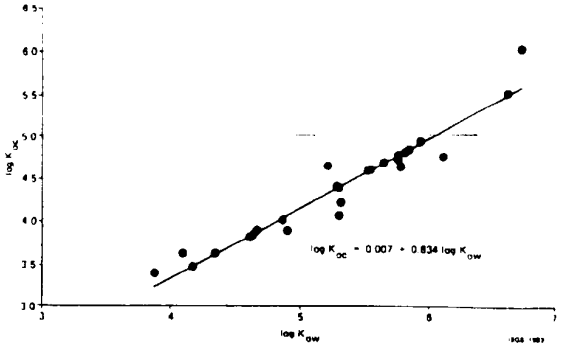


FIGURE 8 PCB K_{oc} vs. the K_{ow}

useful in estimating the sorption of PCBs under many circumstances of soil and sediment conditions as well as bioaccumulation potential.

The sorption of nonionic organics has been related to the partitioning of an organic compound between an organic solvent (*n*-octanol) and water.[11,18,43,44,49] It follows therefore, that K_{oc} should be related to the tendency of the same compound to partition between water and soil organic matter. Figure 8 illustrates the relationship between K_{oc} and K_{ow} for PCBs. There is a high linear correlation between the two yielding the regression equation:

$$\log K_{oc} = 0.007 + 0.834 \log K_{ow} \quad (10)$$

VII. MOBILITY OF PCBs IN SOILS

The migration and vertical distribution of PCBs in soil profiles is a topic of much interest. A soil thin-layer chromatography (TLC) technique has been used to measure mobility of PCBs.[51] Soil TLC is a laboratory method of measuring the migration of a particular compound or element through a soil by using the soil as the sorbent phase and a developing solvent (water, landfill leachate, organic solvent, etc.) in a TLC system. The results are reported as R_f values, defined as the ratio of the distance the compound moved relative to the distance the solvent moved. The R_f value is a quantitative indication of the movement of a given compound in a soil-solvent system and a reproducible index of mobility.[52] The mobility of Aroclor® 1242 and Aroclor® 1254 in several earth materials was studied by Griffin and Chian[53] and expressed as frontal R_f values which are given in Table 5. The data indicate that under the conditions tested, Aroclor® 1242 and Aroclor® 1254 stayed immobile in these soil materials when leached with water and sanitary landfill leachates, but were highly mobile when leached with carbon tetrachloride. Similar results for polybrominated biphenyls (PBBs) and hexachlorobenzene (HCB) were also reported by Griffin and Chou.[53]

PCBs are nonpolar and are only very slightly soluble in polar solvents like water. Solubilities of Aroclor® 1242 and Aroclor® 1254 in distilled water have been determined to be approximately 288 and 42 ppb (see Table 1), respectively. However, PCBs are much more

MONS 005843

Table 5
MOBILITY OF AROCLORS® 1242 AND 1254 IN SEVERAL SOIL MATERIALS LEACHED WITH VARIOUS SOLVENTS AS MEASURED BY SOIL-THIN-LAYER CHROMATOGRAPHY[33]

	R_f values					
	Water		Landfill leachate		Carbon tetrachloride	
Soil materials	1242	1254	1242	1254	1242	1254
Ava silty clay loam	0.02	0.02	0.02	0.02	1.00	0.95
Bloomfield loamy sand	0.03	0.03				
Catlin silt loam	0.02	0.02	0.04	0.04	1.00	1.00
Catlin loam	0.02	0.02	0.03	0.03	1.00	1.00
Cisne silt loam	0.03	0.02	0.03	0.02	1.00	1.00
Coal char (650°C)	0.03	0.03	0.04	0.04	1.00	1.00
Drummer silt loam	0.03	0.03			1.00	1.00
Flanagan silt loam	0.02	0.02	0.06	0.05	1.00	1.00
Ottawa silica sand	0.03	0.03	0.03	0.03	1.00	1.00

soluble in organic solvents such as acetone, methanol, benzene, or carbon tetrachloride. Griffin et al.[33] also tested the mobility of Aroclor® 1242 and Aroclor® 1254 in silica gel leached with acetone, methanol, benzene, carbon tetrachloride, and mixtures of water-acetone and water-methanol. They found the data consistent with the soil TLC data obtained by leaching with carbon tetrachloride; R_f values of 1.00 were obtained using the organic solvents. It is quite clear that mobility of PCBs in soil materials and silica gel is highly related to the solubility of PCBs in the solvent with which the TLC plates were being leached. In a soil column leaching study, Griffin and Chou[33] found that related compounds such as PBBs and HCB were not retained in the columns when ethanol was percolated through the soil columns. These data confirmed previous findings from soil TLC studies.

Leaching of water through soil containing PCBs may lead to the downward movement of PCBs, depending on the soil type and clay content. Moza et al.[34] incorporated ^{14}C-labeled 2,2'-dichlorobiphenyl in the top centimeter of a loamy sand at a concentration of approximately 1 ppm under field conditions. They found that the PCB dispersed to a depth of 30 cm during the first year and no radioactivity was detectable in the 30- to 40-cm layer. At the end of 1 year, when carrots grown on the test plots were harvested, concentrations of PCBs and their metabolites were highest in the 0- to 10-cm layer (0.24 ppm), intermediate in the 10- to 20-cm layer (0.17 ppm), and lowest in the 20- to 30-cm layer (0.03 ppm). Below 30 cm, the concentration of PCB and metabolites were less than 0.001 ppm. At the end of the second year, when sugar beets had been harvested, total PCB concentrations in the soil were 0.15 ppm in the top 10-cm layer, 0.04 ppm in the 10- to 20-cm layer, 0.02 ppm in the 20- to 30-cm layer, 0.008 ppm in the 30- to 40-cm layer, and 0.002 ppm in the leached water below the 40-cm depth. This study indicates that very small amounts of dichlorobiphenyls (or quite possibly a metabolite) moved below 40 cm in the soil; only 0.2% of the PCB-radioactivity applied to the soil appeared in leached water at the 40-cm depth over a period of 2 years.

Tucker et al.[18] studied the migration of PCBs in soil columns treated with Aroclor® 1016 and subjected to water percolation. The PCB application rate was 2.5% of soil weight, a very high rate for a land application system but more representative of landfill operations. The soils used were Norfolk sandy loam, Ray silty loam, and Drummer silty loam; the water application rates for each soil were 0.26, 0.53, and 0.32 ℓ/day, creating an essentially saturated flow. They concluded that soils containing more clay retained larger amounts of

MONS 005844

Table 6
AROCLOR® 1016 FOUND IN PERCOLATING WATER FROM SOIL COLUMNS[10]

Norfolk sandy loam		Ray silty loam		Drummer silty clay loam	
Effluent vol. (ℓ)	PCBs (ppb)	Effluent vol. (ℓ)	PCBs (ppb)	Effluent vol. (ℓ)	PCBs (ppb)
1.3—8.1	ND	2.7—16.4	ND	1.6—9.9	ND
10.1	ND	20.7	65	12.5	ND
13.5	23	27.6	92	31.4	ND
48.1	63	51.9	153	59.2	ND

Note: ND means none detected

Table 7
CLASSIFICATION OF SOIL MOBILITY POTENTIAL OF PCBs BY R_f, K_{oc}, OR K_{ow}[11,56]

Class	R_f	K_{oc}	K_{ow}
Very mobile	0.90—1.00	<1.2	0—50
Mobile	0.65—0.89	1.2—23	50—150
Medium	0.35—0.64	23—245	150—500
Low	0.10—0.34	245—6000	500—2000
Slight	—	—	2000—5000
Immobile	0.0—0.09	>6000	>5000

PCBs. The ease of leaching of Aroclor® 1016 from the different soil types (Table 6) was in the order: Norfolk sandy loam > Ray silty loam > Drummer silty clay loam. It should also be noted that this order of retention follows the organic matter content of these soils, as well as their clay content; the conclusion of the authors may be in error regarding the active fraction of the soil that caused the observed retention. Regardless of the mechanism involved, approximately 0.05% of total Aroclor® 1016 in the soil column was leached from the soil during the 4-month period when 50 to 100 ℓ of water had passed through the soil. This high percolation rate is equivalent to 15 to 30 m of rainfall, assuming no runoff or evaporation. Tucker et al.[10] also observed that the less chlorinated and more degradable species leached from soils more readily than highly chlorinated and more resistant PCBs. This was later confirmed by Suzuki.[55] Thus, the more resistant PCBs are retained in the surface soil layers.

The vapor loss of PCBs from soils depends strongly upon their adsorption characteristics by soils. Haque et al.[7] have shown that the vapor loss of Aroclor® 1254 from a sand surface was significant which could have been due to the poor sorption capacity of sand. When, similar experiments were carried out with a soil, the loss was very low.

The relative mobility of PCBs in soils can be classified using the parameters of R_f, K_{oc}, and K_{ow} discussed above. The soil mobility classes assigned to the various values of these three parameters are given in Table 7. The values of the various parameters assigned to each mobility class are somewhat arbitrary, but have been chosen from experience based on the relative mobility of these compounds in the environment.[11,56]

VIII. SURFACE RUNOFF

There are several ways by which PCBs get into the environment. One of these is by

MONS 005845

runoff from industrial wastes, dumps, and spills. Other sources are the points of manufacture and the plants where PCBs are processed into other products. PCBs can escape through the plant ventilation and exhaust system into the atmosphere and through its waste treatment system into sewers or directly into waterways. PCB input into fresh water by industries has been high in the past, and PCBs have accumulated in sediments.[57,58] Even if PCB input were stopped today, these sediments could continue to release PCBs into freshwater systems for years to come.

Nisbet and Sarofim[59] estimated that 4000 to 5000 tons/year of PCB were discharged into fresh and coastal waters in the peak year of PCB use. This estimate was based upon figures and industrial and disposal practices in effect at that time. Of the total PCBs, about 1000 tons may be assumed to have consisted of pentachlorobiphenyls. Analysis of waste waters and of surface water runoff entering the Southern California Bight since 1971 has shown that trichlorobiphenyls have constituted the majority of the total PCB residues. In this area, PCB input into the sea from waste waters is considerably higher than the input from surface runoff.

Martel et al.[60] reported that PCBs were found in the suburban watershed of Reston, Va. PCB concentrations in the Lake Anne basin increased going from water (<0.05 to 0.2 ppb), to bed sediment (<2.5 to 105 ppb), to fish (140 to 700 ppb) in an average ratio of 1:500:3000. The highest concentrations were observed in the lake itself, which is 10 years old, and receives no sewage or industrial waste discharges. Evidence indicates that the PCBs originated from diffuse sources associated with urban development and urban living and entered the hydrologic system through storm-water runoff. They also found that the PCB concentrations in sediment samples from two areas which were receiving rainfall runoff from two active construction sites were much higher than those from other streams feeding the lake. In the early 1970s, PCBs were commonly used in the formulation of plasticizers, adhesives, surface coatings, sealants, and fire-retardant compositions.[4,27] This suggests that building materials would be one possible source of PCBs.

In the summer of 1976, a serious spill of PCBs and chlorobenzenes was detected in Regina, Saskatchewan, Canada.[61] Approximately 6800 to 9100 ℓ of transformer oil containing PCBs (Aroclor® 1254) and chlorobenzene were spilled when an underground pipe broke at a transformer manufacturing plant. Large quantities of PCBs were found to have migrated both vertically and horizontally at the site. There was also strong evidence that the contaminants were being redistributed by surface processes. At the plant site, Roberts et al.[61] reported that PCB levels were up to 1000 ppm along some of the routes of surface drainage and zones of sediment accumulation after rainstorms. The sludge obtained from the catch basin in the street, which received the runoff, contained 20 ppm PCBs. The PCB levels at the surface in one area, which received the runoff from the highly contaminated area of the plant site ranged from less than 2 to 250 ppm.

A similar incident of a PCB spill occurred in a rural area near Kingston, Tenn. in 1973.[62] The spill resulted in the environmental contamination of two watersheds because the spill site was situated on the crest of a hill. Through the influence of rainfall, geological factors, and characteristics of the overlying stratum of soil, the chemical was subsequently dispersed through the soil both horizontally and vertically. The spread of the Askarel (a commercial mixture of Aroclor® and chlorinated benzenes) was also affected by the movement of contaminated surface water resulting from mass rainfall in the weeks immediately following the spill.

There are two potential means for PCBs to be transported at the surface: as a dissolved phase in water or as a sorbed phase on sediments. In the above cases of chemical spills, chlorobenzenes may play an important role in the movement of PCBs through soils. In previous soil-thin-layer chromatography studies,[34,35] it has been demonstrated that the mobilities of PCBs, PBBs, and HCB in soils were directly proportional to the solubility of the compounds in the leaching solvents.

MONS 005846

Horn et al.[18] reported that measurable quantities of PCBs were leaching or eroding from some landfills and dredge spoil sites in the Upper Hudson River Basin. PCB losses to groundwater at the dredge spoil sites and at the landfills and dumps were approximately 44.4 kg/year and 172 kg/year, respectively. The results indicated that the landfills and dumps appeared to be larger contributors to the surrounding environment than the dredge spoil areas. The erosion losses of PCBs from the same sites were 32.2 kg/year and 172 kg/year, respectively. The upper Hudson Basin delivered approximately 2.6 t of PCBs to the estuary in 1977.[19]

IX. PLANT UPTAKE

Since PCBs are strongly sorbed on carbonaceous materials and sediments, it is not surprising to observe that they are sorbed onto plant roots as well. Using Aroclors® 1242 and 1254, Suzuki[35] observed that soybean sprouts accumulated more lower chlorinated biphenyls than the higher chlorinated isomers during the first 2 weeks of exposure from a sandy soil containing 100 ppm PCBs. This may be due to the higher solubility and mobility of these isomers, thus allowing them to move to the plant root. A few gardeners in Indiana who used PCB contaminated sludge found that their vegetables had also picked up PCBs. Beets contained 0.6 ppm PCBs when grown in soil containing 4 ppm PCBs.[3] Grass clipped from a field with 8.5 ppm in the soil contained 1.16 ppm PCBs.[3]

Moza et al.[36] applied radioactive 2,2-dichlorobiphenyl to soils at a concentration of approximately 1 ppm. Carrot roots contained 0.24 ppm of 2,2'-dichlorobiphenyl while the phenolic metabolites from this PCB were found at a concentration of 0.012 ppm. In a similar study, Iwata et al.[63] found that 97% of the total absorbed Aroclor® 1254 remained on the carrot peel and very little was translocated into the plant tissue. Fries and Marrow[64] also reported that soybean plants grown on PCB contaminated soil would not be contaminated by root uptake and translocation, but some foliar contamination could occur from vapor sorption.

X. SUMMARY AND CONCLUSIONS

The aqueous solubility of PCBs is very low, ranging from 2.7 ppb for Aroclor® 1260 to 3500 ppb for Aroclor® 1221. Water-soluble PCBs were found to be richer in the lower-chlorinated isomers than were the original PCB fluids.

PCBs are strongly sorbed by soil materials. There is a very high direct correlation between the TOC content of the soils and the amount sorbed. The sorption and retention of PCBs by soils and soil constituents are influenced by the number of chlorine atoms in the molecule; the more highly chlorinated derivatives are more tenaciously held. The K_{oc} can be estimated from the water solubility of a PCB.

The higher-chlorinated isomers are preferentially sorbed to the organic matter of soils and suspended solids. Significant amounts of PCBs have been redistributed in the environment by surface-water runoff containing PCB contaminated soil particles. Sorption of PCBs onto suspended solids and their subsequent incorporation into sediments is considered the major mechanism for their immobilization in aquatic systems. However, the persistence of PCBs in sediments makes desorption a possibility for years after incorporation.

The vapor loss of PCBs from soils depends strongly upon their sorption to soils. The vapor loss of PCBs from a soil surface was very low but was significant from sand. The sorption of PCBs greatly influences their dynamics in soils. The diffusion, leaching, and vapor loss of PCBs in soils is retarded as the extent of sorption increases. The degree of sorption increases directly with an increase in organic matter content of a soil.

Highly chlorinated PCBs are not degraded or leached through soil by water to any sig-

MONS 005847

nificant extent. They are also apparently not taken up by plants and are thus not readily mobile in surface soil systems. However, PCBs do have a moderate vapor pressure and a likely path for redistribution or migration in soils may be by vapor phase transport through the unsaturated pores.

The above findings are significant to the land disposal of PCBs and related wastes. To prevent potential migration of PCBs from a landfill, PCB wastes and organic solvents should not be disposed of in the same landfill location, and should not be allowed to come in contact with leaching organic solvents.

REFERENCES

1. **Nelson, N., Hammond, P. B., Nisbet, L. C. T., Sarofim, A. F., and Drury, W. H.**, Polychlorinated biphenyls — environmental impact, *Environ. Res.*, 5, 249, 1972.
2. **Gustafson, C. G.**, PCBs — prevalent and persistent, *Environ. Sci. Technol.*, 4, 814, 1970.
3. **Gustafson, C. G., Ed.**, Proc. Symp. on PCBs — Still Prevalent — Still Persistent, 164th American Chemical Society Meeting, New York, September 1972.
4. **Peakall, D. B. and Lincer, J. L.**, Polychlorinated biphenyls: another long-life widespread chemical in the environment, *Biosphere*, 20, 958, 1970.
5. **Jordan, D.**, The town dilemma, *Environment*, 19, 6, 1977.
6. **Henderson, H.**, The dilemma of Wilsonville, *Ill. Times*, 4, 4, 1978.
7. **Haque, R., Schmedding, D. W., and Freed, V. H.**, Aqueous solubility, adsorption, and vapor behavior of polychlorinated biphenyl Aroclor 1254, *Environ. Sci. Technol.*, 8, 139, 1974.
8. **Haque, R. and Schmedding, D.**, Studies on the adsorption of selected polychlorinated biphenyl and isomers on several surfaces, *J. Environ. Sci. Health*, B11, 129, 1976.
9. **Lee, M. C., Griffin, R. A., Miller, M. L., and Chian, E. S. K.**, Adsorption of water-soluble polychlorinated biphenyl Aroclor 1242 and used capacitor fluid by soil materials and coal chars, *J. Environ Sci. Health*, A14, 415, 1979.
10. **Tucker, E. S., Litschgi, W. J., and Moss, W. M.**, Migration of polychlorinated biphenyls in soil induced by percolating water, *Bull. Environ. Contam. Toxicol.*, 13, 86, 1975.
11. **Briggs, G. G.**, A simple relationship between soil adsorption of organic chemicals and their octanol/water partition coefficients, in *Proc. 7th British Insecticide and Fungicide Conf.*, British Crop Protection Council, London, 1973, 83.
12. Versar Inc., Water Related Environmental Fate of 129 Priority Pollutants, A Literature Search, V Polycyclic Aromatic Hydrocarbons, PCBs, and Related Compounds, Office of Water and Waste Management, U S Environmental Protection Agency, Washington, D.C., 1979, 36-1.
13. Monsanto Co., Presentation to the Interdepartmental Task Force on PCB, Washington, D.C., May 15, 1972.
14. **Paris, D. F., Steen W. C., and Baughman, G. L.**, Role of the physicochemical properties of Aroclor 1016 and 1242 in determining their fate and transport in aquatic environments, *Chemosphere*, 7, 319, 1978.
15. **Chiou, C. T., Freed, U. H., Schmedding, D. W., and Kohnert, R. L.**, Partition coefficient and bioaccumulation of selected organic chemicals, *Environ. Sci. Technol.*, 11, 475, 1977.
16. **Wiese, C. S. and Griffin, D. A.**, The solubility of Aroclor 1254 in seawater, *Bull. Environ. Contam. Toxicol.*, 19, 403, 1978.
17. **Mackay, D., Mascarenhas, R., Shiu, W. Y., Valvani, S. C., and Yalkowsky, S. H.**, Aqueous solubility of polychlorinated biphenyls, *Chemosphere*, 9, 257, 1980.
18. **Kenaga, E. E. and Goring, C. A. I.**, Relationship between water solubility, soil sorption, octanol/water partitioning, and concentration of chemicals in biota, *Aquatic Toxicology*, ASTM STP 707, Eaton, J. G., Parrish, P., and Hendricks, A. C., Eds., American Society for Testing and Materials, Philadelphia, 1980, 78.
19. **Lee, M. C., Chian, E. S. K., and Griffin, R. A.**, Solubility of polychlorinated biphenyls and capacitor fluid in water, *Water Res.*, 13, 1249, 1979.
20. **Chou, S. F. J. and Griffin, R. A.**, Adsorption of PCBs by cellulose fiber filteraids and carbonaceous adsorbents used for water treatment, *4th Annu. Conf. of Applied Research and Practice on Municipal and Industrial Waste*, University of Wisconsin-Extension, Madison, Wisc., 1981, 238.
21. **Lawrence, J. and Roshe, H. M.**, Adsorption of polychlorinated biphenyls from aqueous solution and sewage, *Environ. Sci. Technol.*, 10, 381, 1976.

MONS 005848

22. **Nisbet, L. C. T. and Sarofim, A. F.**, Rates and routes of transport of PCBs in the environment. *Environ. Health Perspect.*, 1, 21, 1972.
23. **Haque, R. and Schmedding, D.**, A method of measuring the water solubility of hydrophobic chemicals: solubility of five polychlorinated biphenyls. *Bull. Environ. Contamin. Toxicol.*, 14, 13, 1975.
24. **Hutzinger, O., Safe, S., and Zitko, V.**, *The Chemistry of PCBs*, CRC Press, Boca Raton, Fla., 1980, 23.
25. **Tulp, M. M. and Hutzinger, O.**, Some thoughts on aqueous solubility and partition coefficients of PCB and the mathematical correlation between bioaccumulations and physico-chemical properties. *Chemosphere*, 7, 849, 1978.
26. **Mackay, D. and Wolkoff, A. W.**, Rate of evaporation of low solubility contaminants from water bodies to the atmosphere. *Environ. Sci. Technol.*, 7, 611, 1973.
27. **Beeton, A. M. et al.**, *Polychlorinated Biphenyls*. Report of Committee on the Assessment of Polychlorinated Biphenyls in the Environment, National Academy of Sciences, Washington, D.C., 1979.
28. **Thurston, A.**, Quantitative analysis of PCBs. *PCB Newslett.*, July, No. 3, p. 4, 1971.
29. **Stalling, D. L. and Huckins, J. N.**, Gas-liquid chromatography mass-spectrometry characterization of polychlorinated biphenyls (Aroclors) and ^{36}Cl-labeling of Aroclor 1248 and 1254. *J. Assoc. Off. Anal. Chem.*, 54, 801, 1971.
30. **Sissons, D. and Welti, D.**, Structural identification of polychlorinated biphenyls in commercial mixtures by gas-liquid chromatography, nuclear magnetic resonance, and mass spectrometry. *J. Chromatogr.*, 60, 16, 1971.
31. **Hamelink, J. L., Waybrant, R. C., and Ball, R. C.**, A proposal: exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. *Trans. Am. Fish. Soc.*, 100, 207, 1971.
32. **Oloffs, P. C., Albright, L. J., and Szeto, S. Y.**, Fate and behavior of five chlorinated hydrocarbons in three natural waters. *Can. J. Microbiol.*, 18, 1393, 1972.
33. **Mocio, G. J.**, Study of Distribution and Fate of PCBs and Benzenes after Spill of Transformer Fluid. EPA 904/9-76-014, U.S. Environmental Protection Agency, Washington, D.C., 1976, 128.
34. **Griffin, R. A. and Chou, S. F. J.**, Movement of PCBs and other persistent compounds through soil. *Water Sci. Technol.*, 13, 1153, 1981.
35. **Griffin, R. A. and Chiou, E. S. K.**, *Attenuation of Water Soluble Polychlorinated Biphenyls by Earth Materials*. EGN 86, Illinois State Geological Survey, Champaign, 1979, 98.
36. **Veith, G. D. and Comstock, V. M.**, Sediments as a PCB source to aquatic systems. *J. Fish. Res. Bd. Can.*, 32, 1849, 1974.
37. **Wilson, A. J. and Forester, J.**, Persistence of Aroclor 1254 in a contaminated estuary. *Bull. Environ. Contam. Toxicol.*, 19, 637, 1978.
38. **Chou, N. Y.**, Hydrophobic properties of zeolites. *J. Phys. Chem.*, 80, 60, 1976.
39. **Nemethy, G. and Scheraga, H. A.**, The structure of water and hydrophobic bonding in proteins. III. The thermodynamic properties of hydrophobic bonds in proteins. *J. Phys. Chem.*, 66, 1773, 1962.
40. **Horvath, C. and Melander, W.**, Reversed-phase chromatography and the hydrophobic effect. *Am. Lab.*, 10, 17, 1978.
41. **Frank, H. S. and Evans, M. W.**, Free volume and entropy in condensed systems. III. Entropy in binary liquid mixtures; partial molar entropy in dilute solutions; structure and thermodynamics vs. aqueous electrolytes. *J. Chem. Phys.*, 13, 507, 1945.
42. **Hassett, J. J., Banwart, W. L., Wood, S. G., and Means, J. C.**, Sorption of alpha-naphthol: implications concerning the limits of hydrophobic sorption. *Soil Sci. Soc. Am. J.*, 45, 38, 1981.
43. **Karickhoff, S. W., Brown, D. S., and Scott, T. A.**, Sorption of hydrophobic pollutants on natural sediments. *Water Res.*, 13, 241, 1979.
44. **Hassett, J. J., Banwart, W. L., and Griffin, R. A.**, Correlation of compound properties with sorption characteristics of nonpolar compounds by soils and sediments: concepts and limitations. in *Environment and Solid Wastes: Characterization, Treatment, and Disposal*, Francis, C. W. and Auerback, S. I., Eds., Butterworths, Reading, Mass., 1983, 161.
45. **Hassett, J. J., Means, J. C., Banwart, W. L., Wood, S. G., Ali, S., and Khan, A.**, Sorption of dibenzothiophene by soils and sediments. *J. Environ. Qual.*, 9, 184, 1980.
46. **Khan, A., Hassett, J. J., Banwart, W. L., Means, J. C., and Wood, S. C.**, Sorption of acetophenone by sediments and soils. *Soil Sci.*, 128, 287, 1979.
47. **Chiou, C. T., Peters, L. J., and Freed, V. H.**, A physical concept of soil-water equilibrium for nonionic organic compounds. *Science*, 206, 831, 1979.
48. **Means, J. C., Hassett, J. J., Wood, S. G., and Banwart, W. L.**, Sorption properties of energy-related pollutants and sediments. Polynuclear aromatic hydrocarbons. *3rd Int. Symp. on Chemistry and Biology: Carcinogenesis and Mutagenesis*, Jones, P. L. and Leber, P., Eds., Ann Arbor Science, Ann Arbor, Mich., 1979, 327.

MONS 005849

49. **McDuffie, B.**, Estimation of octanol/water partition coefficients for organic pollutants using reverse phase HPLC, *Chemosphere*, 10, 73, 1981.
50. **Branson, D. R.**, A new capacitor fluid, a case study in product stewardship, in *Aquatic Toxicology and Hazard Calculation*, ASTM STP 634, American Society for Testing and Materials, Philadelphia, 1977, 44.
51. **Griffin, R. A., Au, A. K., and Chian, E. S. K.**, Mobility of polychlorinated biphenyls and dicamba in soil materials: determination by soil thin-layer chromatography, Proc. 8th Natl. Conf. and Exhibit on Municipal Sludge Management, 1979, 183.
52. **Helling, C. S.**, Pesticide mobility in soils. I. Parameters of thin-layer chromatography, *Soil Sci. Soc. Am. Proc.*, 35, 732, 1971.
53. **Griffin, R. A. and Chou, S. F. J.**, *Attenuation of Polybrominated Biphenyls and Hexachlorobenzene by Earth Materials*, EGN 87, Illinois State Geological Survey, Champaign, 1980.
54. **Moza, P., Weisgerber, I., and Klein, W.**, Fate of 2,2'-dichlorobiphenyl-^{14}C in carrots, sugarbeets, and soil under outdoor conditions, *J. Agric. Food Chem.*, 24, 881, 1976.
55. **Suzuki, M.**, Translocation of polychlorobiphenyls in soil into plants, *Arch. Environ. Contam. Toxicol.*, 5, 343, 1977.
56. **McCall, P. J., Swann, R. L., Laskowski, D. A., Unger, S. M., Vrona, S. A., and Dishburger, H. J.**, Estimation of chemical mobility in soil from liquid chromatographic retention times, *Bull. Environ. Contam. Toxicol.*, 24, 190, 1980.
57. **Hetling, L., Horn, E., and Tofflemire, J.**, Summary of Hudson River PCB Study Results, New York State Department of Environmental Conservation, Bureau of Water Research, Albany, 1978.
58. **Horn, E. G., Hetling, L. L., and Tofflemire, T. J.**, The problem of PCBs in the Hudson River system, *Ann. N.Y. Acad. Sci.*, 1979, 591.
59. **Nisbet, L. C. T. and Sarofim, A. F.**, Rates and routes of transport of PCBs in the environment, *Environ. Health Perspect.*, 1, 21, 1972.
60. **Martell, J. M., Rickert, D. A., and Siegel, F. R.**, PCBs in suburban watershed, Reston, Va., *Environ. Sci. Technol.*, 9, 872, 1975.
61. **Roberts, J. R., Cherry, J. A., and Schwartz, F. W.**, A case study of a chemical spill: polychlorinated biphenyls (PCBs). I. History, distribution, and surface translocation, *Water Resources Res.*, 18, 525, 1982.
62. **Moore, G. J., Smith, A. J., Jr., Bigiane, K. E., Loy, B., and Bennett, T.**, Follow-up Study of the Distribution and Fate of Polychlorinated Biphenyls and Benzene in Soil and Ground Water Samples after an Accidental Spill of Transformer Fluid, EPA 904/9-76-014, U.S. Environmental Protection Agency, Washington, D.C., 1976.
63. **Iwata, Y., Gunther, F. A., and Westlake, W. E.**, Uptake of a PCB (Aroclor 1254) from soil by carrots under field conditions, *Bull. Environ. Contam. Toxicol.*, 11, 523, 1974.
64. **Fries, G. F. and Marrow, G. S.**, Chlorobiphenyl movement from soil to soybean plants, *J. Agric. Food Chem.*, 29, 575, 1981.

MONS 005850

Chapter 6

FACTORS CONTROLLING BIOACCUMULATION OF PCBs

G. R. Shaw and D. W. Connell

TABLE OF CONTENTS

I. Introduction 122

II. Mechanisms and Routes of Bioaccumulation 122

III. Physicochemical Properties Controlling Bioaccumulation 123
A. Degree of Chlorination 123
B. Water Solubility and Partition Coefficients 123
C. PCB Stereochemistry 125

IV. Thermodynamic Aspects of Bioaccumulation 127

V. Models for Bioaccumulation 129

VI. Conclusions 130

References 131

MONS 005851

I. INTRODUCTION

In recent years, there has been considerable interest in developing an understanding of the mechanisms leading to the distribution of contaminant chemicals in the environment. Such an understanding would not only improve our scientific knowledge of environmental processes but could be used in a variety of management situations.

An important segment of the environmental distribution process is the uptake of contaminant chemicals from the environment by biota. Persistent lipophilic chemicals, including PCBs have been shown to exhibit somewhat similar control mechanisms. A picture is gradually emerging of the influence of the physicochemical properties of lipophilic contaminants on their biotic behavior.

Before discussing the nature of mechanisms of transfer of chemicals from the environment to biota it is important to briefly consider the terminology used. A variety of descriptive terms are used in the literature for the various processes. In this discussion bioaccumulation or accumulation is used to describe uptake and retention of a chemical by any mechanism or pathway. Bioconcentration is used in a more restricted sense to represent uptake and retention of chemicals from the water mass through such tissues as gills or epithelial tissues.

II. MECHANISMS AND ROUTES OF BIOACCUMULATION

Biota could potentially acquire PCBs from three sectors of the environment — atmosphere, water, and food. With terrestrial organisms, uptake could occur by three mechanisms:

1. Absorption of PCBs in the atmosphere through the lung walls
2. Similar uptake from the atmosphere but through the epidermis
3. Consumption of food containing PCBs and passage through the stomach walls

The atmosphere route through the lungs and epidermis is of little significance due principally to the very low concentrations of PCBs in the atmosphere. The major route of acquisition of PCBs by terrestrial organisms is through contaminated food. Aquatic birds and mammals are also included in this category.

A similar set of potential uptake mechanisms could be visualized from aquatic organisms

1. Absorption of PCBs in the water mass through the gills
2. Similar uptake through the epidermis
3. Consumption of contaminated food

There is no significant information indicating that uptake through the epidermis is of general importance and the structure of the epidermis does not facilitate such a mechanism. On the other hand, there is sound evidence that all aquatic organisms studied in aquaria, can absorb PCBs directly from water.[1-7] Also, bioconcentration of PCBs by fish from water in natural systems has also been shown to occur.[8,9]

In fact, the main route of uptake by aquatic organisms has been shown to be absorption by the gills since the gills represent the active membrane surface for water exchange.[10-14] The gill membrane permeability for PCBs can be estimated by the calculation of their efficiency transfer coefficients, E.[15] The E values are estimated using uptake rate constants for PCBs, oxygen concentration in the water, the E value for oxygen, and the metabolic rate constant for the organism involved. Once absorbed by the gills, the PCBs are then partitioned into the blood and then from blood to tissues.[12,16]

An informative study of PCB levels in various organisms in Puget Sound, Wash. by Clayton et al.[17] demonstrated that all biota in that ecosystem had similar PCB levels nor-

MONS 005852

Table 1
BIOCONCENTRATION FACTORS FOR INDIVIDUAL CHLOROBIPHENYLS

Compound	BCF
Trichlorobiphenyl	54
Tetrachlorobiphenyl	460
Pentachlorobiphenyl	1510

From Sanborn, J. R., Childers, W F., and Metcalf, R. L., *Bull. Environ. Contam. Toxicol.*, 13, 209, 1975. With permission.

malized to lipid content. This indicates that food content was not the controlling factor. It has been suggested that the accumulation of PCBs by aquatic organisms is a physicochemical process and that uptake is predominantly governed by equilibrium partitioning of the PCBs between the organism and ambient water.[7,18,19] Nevertheless, the assimilation of PCBs from ingested food organisms occurs by partition across the lipoprotein membranes lining the gut into the bloodstream[18] but is usually of much less quantitative significance.

The uptake of PCBs by some benthic organisms may be controlled by different mechanisms to those associated with free swimming aquatic organisms. The association of PCBs with bottom sediments leads to contamination of the organisms[19-22] and the resultant concentration of PCBs are directly related to the concentrations in the sediment.[23-25]

III. PHYSICOCHEMICAL PROPERTIES CONTROLLING BIOACCUMULATION

Most information is available on the bioaccumulation of PCBs by aquatic organisms. It is usually measured as the ratio between the concentration in the animal to concentration in water, i.e., BCF (bioaccumulation factor = C animal/C water). A variety of factors have been shown to influence bioaccumulation as outlined below.

A. Degree of Chlorination

The degree of chlorination of the PCB molecule is known to have an effect on bioaccumulation of PCBs with the penta- and hexachloro isomers being accumulated to the greatest extent.[19,26] Table 1 lists bioconcentration factors for PCBs from water by the green sunfish (*Lepomis cyanellus*) as determined by Sanborn et al.[27] In addition, the halflives of various PCBs in organisms have been shown to be related exponentially to their degree of chlorination by weight.[28]

B. Water Solubility and Partition Coefficients

With lipophilic compounds in general, a linear inverse relationship has been shown to exist between water solubility and BCF such that log BCF = $-A$ log (water solubility) + C, where A and C are constants.[29-31] The use of water solubility as a simple and rapid measure of a PCBs potential for bioaccumulation has great appeal. However, some chemicals with low water solubility, including PCBs, deviate significantly from this relationship.[29] Also, the numerous conflicting solubility values in the literature[19,31] and the lack of solubility data for many chemicals have led to the use of another parameter, the *n*-octanol/water partition coefficient (P_{ow}) for estimation of bioconcentration factors.[32] The approximately

MONS 005853

Table 2
RELATIONSHIP BETWEEN LOG BCF AND LOG P_{ow}

Relationship	Ref.
$\log BCF = 0.56 \log P_{ow} + 0.124$	34
$\log BCF = 0.85 \log P_{ow} - 0.70$	38
$\log BCF = 1.119 \log P_{ow} - 1.579$	54
$\log BCF = 0.76 \log P_{ow} - 0.23$	9

inverse relationship between water solubility and P_{ow} has been known for some time [33] It has been shown that bioaccumulation from water by aquatic organisms is correlated with lipophilicity for PCBs and other chemicals.[9,34-39] Table 2 presents relationships between BCF and P_{ow} for a wide variety of lipophilic compounds, including PCBs. However, PCBs exhibit some significant deviations from this relationship as outlined in the section on the effects of molecular stereochemistry.

The values of P_{ow} are usually not determined directly from a simple partition between *n*-octanol and water because the concentrations in water at the extremely low concentrations involved are difficult to measure accurately.[31] A variety of methods can be used as outlined below.

The Hansch et al.[40] method involves the calculation of P_{ow} using substituent π constants, where the substituent constant is defined as: $\pi = \log P_X - \log P_H$ where P_X is the partition coefficient of the derivative group and P_H that of the parent molecule. Rearranging the equation gives:

$$\log P_X = \text{substituent constants} + \log P_H$$

A large number of substituent constant values and log P_H values have been tabulated by Lee et al.[41] The substituent constant π is a free energy related constant and is a measure of the relative free energy change resulting from moving a derivative from one phase to another.[42] A different method of calculating partition coefficients using the hydrophobic fragmental constant, f, introduced by Rekker[43] is based on the same approach. However, with PCBs there are 209 possible compounds, varying in number and position of chlorine atoms and neither the Hansch or Rekker system offers an acceptable approach to calculate log P values, since in these calculations the π or f values used are the same for each chlorine atom in the molecule, regardless of its position.

Another approach to predicting BCFs is the use of i* and o* characters as described by Matsuo[44] and utilizing the following relationships:

$$\log BCF = -0.016\, i^* + 0.014\, o^*$$

$$\log BCF = -6.3 \frac{i^*}{o^*} + 5.4$$

The i* character is both additional and proportional to the strength of a polar group unit (e.g., -OH; -COOH) with polar interactions such as H-bonding or u-u interaction. Similarly, o* is associated with nonpolar interactions such as Van der Waals or dispersion forces. Matsuo[44] concludes that bioaccumulation of chemicals in fish is caused by the total interactions at polar and nonpolar areas between the PCB molecule and fish tissues. Similar shortcomings to those observed with the Hansch and Rekker systems are found when predicting bioaccumulation factors using this method.

The most widely used method involves high performance liquid chromatography using

MONS 005854

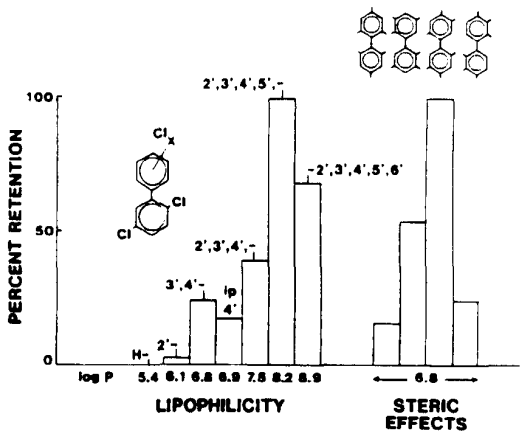


FIGURE 1 Relative retention of substituted biphenyls in abdominal fat of rats 2 weeks after single dose administration by stomach tube. Values are relative to the compound which is retained in highest amounts (= 100). Calculated log P values indicated at baseline. (From Hutzinger, et al. in *Aquatic Pollutants: Transformation and Biological Effects*, Hutzinger, O. et al., Eds., Pergamon Press, Oxford, 1978, 13. With permission.)

an aqueous phase, resembling water, and a permanently bonded C_{18} reversed phase, resembling *n*-octanol. With this system log retention time of lipophilic compounds has been shown to be linearly related to log P_{ow}.[38] This procedure is recognized as being the most appropriate because of the difficulties and inaccuracies in direct and calculation methods.[37,38,46,47]

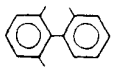
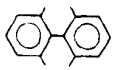
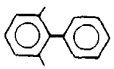
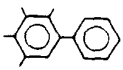
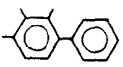
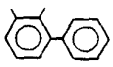
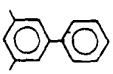
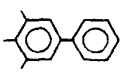
C. PCB Stereochemistry

The correlation between BCF and log P_{ow} indicates that with increasing log P_{ow}, i.e., increasing lipophilicity of PCB molecules, there will be a greater tendency to bioaccumulate. However, there are some exceptions to this generalization as shown in Figure 1[37] which indicates the retention of PCBs in rat abdominal fat as influenced by lipophilicity and steric factors. The left part of Figure 1 indicates that there is not a linear relationship between lipophilicity and bioaccumulation (expressed as retention). The right part shows the different degrees of bioaccumulation exhibited by symmetrical hexachlorobiphenyls which have the same calculated log P_{ow} value (6.8). Similarly, this is consistent with the observations of Tulp and Hutzinger[31] who found that PCBs with comparable lipophilicities may exhibit different bioaccumulation factors. They concluded that there is an optimal steric configuration and molecular size for processes such as membrane passage, thereby affecting bioaccumulation. Similar results for PCBs have been found by other authors.[37,44,47-49]

More recent investigations have been conducted by Shaw and Connell[25,50,51] using polychaetes (*Capitella capitata*) and sea mullet (*Mugil cephalus*) in aquaria together with field investigations. A number of steric factors were found to influence the bioaccumulation of PCBs. A steric effect coefficient (SEC) was developed[50] and later revised[25] as shown in Table 3. These authors have suggested that bioaccumulation is controlled by both lipophilicity

MONS 005855

Table 3
REVISED COEFFICIENTS FOR DIFFERENT CHLORINE SUBSTITUTION PATTERNS USED TO CALCULATE THE STERIC EFFECT COEFFICIENT (SEC)

Description	Structure	Coefficient
Three chlorines in the 2,2',6,6' positions		0.80
Four chlorines in the 2,2',6,6' positions		0.60
Two chlorines in the 2,6 or 2',6' positions		0.85
Four chlorines adjacent		0.80 (1 ring) 0.60 (2 rings)
Three chlorines adjacent		0.95 (1 ring) 0.90 (2 rings)
Chlorines in 3 or 5 positions if adjacent to chlorine in 2 or 6 positions		0.95 (1 in molecule) 0.90 (2 in molecule) 0.85 (3 in molecule) 0.80 (4 in molecule)
Chlorines in 3 or 5 positions not adjacent to chlorine		Subtract 0.02 from SEC for each chlorine in this configuration
No chlorines in the 2,2',6,6' positions		SEC is one irrespective of substitution pattern

From Shaw, G. R. and Connell, D. W., *Aust. J. Mar. Freshwater Res.*, p. 1057, 1982. With permission.

(P_{oct}) and steric effects (SEC) and a combination of these has a direct relationship to bioaccumulation (see Figure 2).

The stereochemistry of the PCB molecules affects the strength of adsorption of these compounds onto surfaces. Huckins et al.[32,33] have demonstrated that PCB molecules can be separated by chromatography on charcoal. The most planar molecules are most strongly absorbed and those with more irregular shapes, particularly the two aromatic rings out of plane, are comparatively weakly adsorbed. Chlorine substituents in the *ortho* positions give

MONS 005856

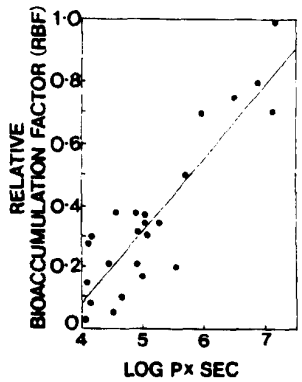


FIGURE 2. Relationship between relative bioaccumulation factor and the product of log P_{oct} and SEC. (From Shaw, G. R. and Connell, D. W., *Aust. J. Mar. Freshwater Res.*, p. 1057, 1982. With permission.)

this latter effect while chlorines in adjacent positions cause distortion of the aromatic rings (see Table 3). Consistent with these observations, the SEC developed by Shaw and Connell[51] is closely correlated with the elution time on charcoal and found that this combined with log P_{oct} provides a more accurate prediction for bioaccumulation (see Figure 3).

Thus, it has been shown that bioaccumulation of PCBs by aquatic organisms is influenced by both lipophilicity and adsorption characteristics of the PCB molecules. The adsorption of PCBs can be measured as elution volumes by chromatography on charcoal or by the SEC. The combination of lipophilicity and adsorption expressed as (log P × elution time) or (log P × SEC) is highly correlated with uptake. Shaw and Connell[51] have suggested that the bioaccumulation of PCBs by aquatic organisms involves adsorption of these substances onto membranes, such as the gills or stomach lining, and subsequent passage into the organism's lipid tissues.

IV. THERMODYNAMIC ASPECTS OF BIOACCUMULATION

In the process of bioconcentration, the organic molecules leaving the aqueous phase are adsorbed onto the membrane surface of the organism before penetration into the organism occurs.[42,54] Adsorption processes involve a decrease in free energy. Since the entropy change for adsorption must be negative, the system becoming more ordered with the surface binding, the enthalpy change must be positive. The heat of adsorption can thus give some index of the strength of binding. Smaller heats of adsorption (less than 10 kcal/mol) usually denote physical adsorption and involve Van der Waals interactions.[39]

The free energy related substituent constant, π, the hydrophobic fragmental constant, f, and the Hammett function, δ, used in structure activity relationships, are all measures of the relative free energy change resulting from moving a PCB molecule from one phase to another.[42,43] Matsuo[36] has calculated the free energy of accumulation of PCBs by fish from water as 2 to 6 kcal/mol using this expression:

MONS 005857

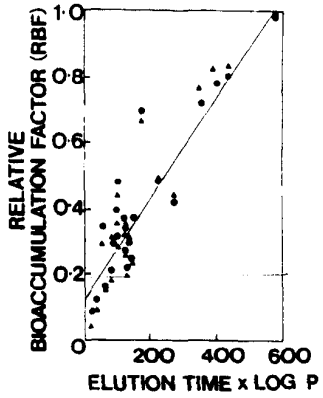


FIGURE 3. Relationship of relative bioaccumulation factor to the product of elution time (on charcoal chromatography) and log P_{oct}. (From Shaw, G. R. and Connell, D. W., *Aust. J. Mar. Freshwater Res.*, p. 1057, 1982. With permission.)

$$-\Delta\mu^{\circ} = 2.303RT \log (BCF)$$

where: $-\Delta\mu^{\circ}$ is the free energy of accumulation, R, the universal gas constant, and T, temperature. From the low values obtained, Matsuo[36] concluded that the driving force for accumulation originated in an energetic head drop corresponding to one hydrogen bonding or two or three Van der Waals forces.

When a nonpolar PCB molecule leaves the aqueous phase for the lipid phase an increase in entropy results.[40] The enthalpy and entrophy of bioaccumulation of PCB 1254 by fathead minnows *(Pimephales promelas)*, green sunfish *(Lepomis cyanellus)*, and rainbow trout *(Salmo gairdneri)* have been calculated.[36] To obtain enthalpy, ΔH°, and entrophy, ΔS°, R ln BCF was plotted against inverse absolute temperature change and the gradient and intercept on the ordinate were calculated by the method of least squares. These values were assigned to $-\Delta H^{\circ}$ and ΔS° respectively, according to the following equation:

$$R \ln (BCF) = -H^{\circ}/T + S^{\circ}$$

where; R is the universal gas constant; ΔH°, the enthalpy; S° the entrophy and T, temperature Free energy is related to enthalpy and entrophy by the following expression:

$$\Delta\mu^{\circ} = \Delta H^{\circ} - T \cdot \Delta S^{\circ}$$

In the uptake of PCBs by fish, Matsuo[36] found that both ΔH° and ΔS° are positive. The positive enthalpy change means that the process of bioaccumulation is endothermic and requires heat. The positive and very large values of ΔS° obtained imply that the transfer of the PCB from water to fish increases the randomness of the PCB molecules to a large extent.

MONS 005858

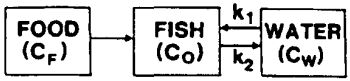


FIGURE 4 A model for the bioaccumulation of PCBs by fish from food and water

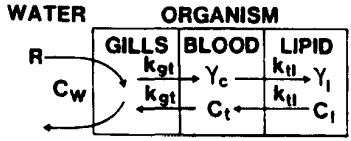


FIGURE 5 A compartmental model for the bioaccumulation of PCBs by an aquatic organism. (From Bruggerman, W. A. et al., *Chemosphere*, 10, 811, 1981. With permission.)

Matsuo[36] concluded that a large increase in entropy occurs because the water molecules in the vicinity of PCB molecules are arranged in a quasi-crystalline structure. Therefore, bioaccumulation of PCBs by fish is controlled by a large positive entropy change.

V. MODELS FOR BIOACCUMULATION

A variety of models have been developed to simulate uptake of lipophilic compounds by organisms. For example, Kerr and Vass[37] assumed that in fish and the larger more complex invertebrates, uptake occurs primarily through ingestion of contaminated food and direct absorption from water through the gills. Losses occur to the water through excretion in a chemically unchanged or a modified form. Figure 4 can be seen in accordance with this, the processes, and the following expression obtained assuming first order kinetics:[15,38]

$$\frac{dC_o}{dt} = \epsilon f C_F + k_1 C_w - k_2 C_o$$

where C_o is the concentration in the organism; ϵ is the absorption efficiency for the ingested chemical; f is the feeding rate; C_F is concentration in food; k_1 is the uptake rate constant; k_2 is the loss rate constant; and C_w is the concentration in water.

A more comprehensive model by Bruggerman et al.[15] assumes the body lipids are the storage compartment; the blood, the transport compartment, and the gills are the exchange or gate compartment, through which water is pumped. All compartments are considered homogeneous in relation to the concentration of the bioaccumulating chemical. The transfer rate from one compartment to another is proportional to the difference in thermodynamic activities, γ, and is dependent on the surface properties and area of the exchange barrier (such as a biomembrane), expressed together as the transfer coefficient, k. This model is diagrammatically represented in Figure 5 and is characterized by the equations below:

Net uptake in fish:

$$F\left(\frac{dC_f}{dt}\right) = R\,(C_w - C_a)$$

MONS 005859

Net increase in the gate compartment:

$$G\left(\frac{dC_g}{dt}\right) = R\,(C_w - C_g) - k_{gt}\,(\gamma_w C_g - \gamma_t C_t)$$

Net increase in the transport compartment:

$$T\left(\frac{dC_t}{dt}\right) = k_{gt}\,(\gamma_w C_g - \gamma_t C_t) - k_{tl}\,(\gamma_t C_t - \gamma_l C_l)$$

Increase in lipid compartment:

$$L\left(\frac{dC_l}{dt}\right) = k_{tl}\,(\gamma_t C_t - \gamma_l C_l)$$

where C_g, C_t, and C_l are the concentrations of the chemical in each compartment; C_w is the concentration in ambient water; C_f is the concentration in fish; γ_w, γ_t, γ_l are activity coefficients of the chemical in the different compartments; F, G, T, and L are the mass of the different compartments; and k_{gt} and k_{tl} are transfer coefficients for exchange between compartments; and R is ventilation rate.

The capacity of the transport compartment plays an important role after a sudden change in the aqueous concentration, e.g., at the start of an experiment. In this case, the unloading of the transport compartment will initially dominate the depuration kinetics, followed later by the partitioning between the lipid and transport compartments, producing a two-phase clearance curve.[13] Other authors have found that clearance rate constants tend to decrease during clearance experiments if two or more compartments are involved which are cleared at different rates.[39] Some authors however, have attempted to describe this phenomenon by the use of concentration dependent rate constants and second order kinetics.[46] This implies that a lower dose of the chemical would result in a smaller clearance rate constant. However, assuming passive transport mechanisms for persistent, nonpolar lipophilic chemicals, first order kinetics are probably most accurate.[13]

VI. CONCLUSIONS

The most important routes of uptake of PCBs are via contaminated foods and contaminated foods with terrestrial organisms through the gills by aquatic organisms. With aquatic organisms the gill route is generally the most significant.

The physicochemical properties of the individual PCBs are the major factors controlling bioaccumulation. Two factors have been identified as of principal significance. First, is the P_{ow} which is a measure of the equilibrium partition between organism lipids, the site of PCB deposition, and the ambient water mass. Second, are the surface adsorption properties, which can be measured by chromatographic techniques. This is believed to represent the strength of adsorption of the PCBs on the gill membrane surface before uptake. A combination of these factors has a direct relationship to bioaccumulation of individual PCBs.

A number of models have been developed which provide a reasonably accurate representation of the bioaccumulation mechanism. The use of first order kinetics with a variety of different compartments within the organism probably provides the most accurate model.

MONS 005860

REFERENCES

1. World Health Organization. *Polychlorinated Biphenyls and Terphenyls*, WHO, Geneva, 1976.
2. **Herbst, L., Scheuvert, I., Klein, W., and Korte, F.,** Uptake and conversion of 2,5,4'-trichlorobiphenyl-^{14}C, 2,4,6,2',4'-pentachlorobiphenyl-^{14}C and chloroalkylene-9-^{14}C by goldfish after a single water treatment, *Chemosphere*, 3, 221, 1978.
3. **Mayer, F. L., Mehle, P. M., and Sanders, H. O.,** Residue dynamics and biological effects of polychlorinated biphenyls in aquatic organisms, *Arch. Environ. Contam. Toxicol.*, 5, 501, 1977.
4. **Stalling, D. L. and Mayer, F. L., Jr.,** Toxicities of PCB's to fish, and environmental residues, *Environ. Health Perspect.*, 1, 159, 1972.
5. **Sanders, H. O. and Chandler, J. H.,** Biological magnification of a polychlorinated biphenyl (Aroclor 1254) from water by aquatic invertebrates, *Bull. Environ. Contam. Toxicol.*, 7, 257, 1972.
6. **Hansen, D. J., Parrish, P. R., Lowe, J. L., Wilson, A. J., Jr., and Wilson, P. D.,** Chronic toxicity, uptake and retention of Aroclor 1254 in two estuarine fishes, *Bull. Environ. Contam. Toxicol.*, 6, 113, 1971.
7. **Keil, J. E., Priester, L. E., and Sandifer, S. H.,** Polychlorinated biphenyl (Aroclor 1254) effects on uptake on growth, nucleic acids and chlorophyll of a marine diatom, *Bull. Environ. Contam. Toxicol.*, 6, 156, 1971.
8. **Shea, J. C., Simonin, H. A., Dean, H. J., Colquhoun, J. R., Spagnoli, J. J., and Veith, G. D.,** Bioaccumulation of Aroclor 1016 in Hudson River fish, *Bull. Environ. Contam. Toxicol.*, 22, 332, 1979.
9. **Veith, G. C., Macek, K. J., Petrocelli, S. R., and Carroll, J.,** An evaluation of using partition coefficients and water solubility to estimate bioconcentration factors for organic chemicals in fish, *Aquatic Toxicol.*, 707, 116, 1980.
10. **Phillips, D. J. H.,** *Quantitative Aquatic Biological Indicators — Their Use to Monitor Trace Metal and Organochlorine Pollution*, Applied Science, London, 1980.
11. **Nadeau, R. J. and Davis, R. A.,** Polychlorinated biphenyls in the Hudson River (Hudson Falls-Fort Edward, New York State), *Bull. Environ. Contam. Toxicol.*, 16, 436, 1976.
12. **Kenaga, E. E.,** Transport of insecticides by blood and body fluids, in *Toxicology of Insecticides*, Matsumura, F., Ed., Plenum Press, New York, 1975, 92.
13. **Gunkel, G. and Streit, B.,** Mechanisms of bioaccumulation of a herbicide (atrazine, S-triazine) in a freshwater mollusc (*Anevlus fluviatilis*) and a fish (*Coregonus fera jurine*), *Water Res.*, 14, 1573, 1980.
14. **Addicott, R. F.,** Organochlorine compounds in aquatic organisms, their distribution, transport and physiological significance, in *Effects of Organic Pollutions on Aquatic Organisms*, Lockwood, A. P. M., Ed., Cambridge University Press, Cambridge, England, 1976, 126.
15. **Bruggerman, W. A., Martron, L. B. J. M., Koolman, O., and Hutzinger, O.,** Accumulation and elimination kinetics of di-, tri-, and tetrachlorobiphenyls by goldfish after dietary and aqueous exposure, *Chemosphere*, 10, 811, 1981.
16. **Walker, C. H.,** Variations in the intake and elimination of pollutants, in *Organochlorine Insecticides Persistent Organic Pollutants*, Moriarity, F., Ed., Academic Press, New York, 1975, 77.
17. **Clayton, J. R., Pavlou, S. P., and Breitner, N. F.,** Polychlorinated biphenyls in coastal marine zooplankton, Bioaccumulation by equilibrium partitioning, *Environ. Sci. Technol.*, 11, 676, 1977.
18. **Pavlou, S. P. and Dexter, R. M.,** Distribution of polychlorinated biphenyls (PCB) in estuarine ecosystems, Testing the concept of equilibrium partitioning in the marine environment, *Environ. Sci. Technol.*, 13, 65, 1979.
19. **Kahnna, E. V. and Kahnna, G. D.,** Transport, distribution and toxic effects of polychlorinated biphenyls in ecosystems: review, *Ecol. Model.*, 6, 223, 1979.
20. **Langston, W. J.,** Accumulation of polychlorinated biphenyls in the cockle *Cerastoderma edule* and the tellin *Macoma balthica*, *Mar. Biol.*, 45, 265, 1978.
21. **Sodergren, A. and Larsson, P.,** Transport of PCB's in aquatic laboratory model ecosystems from sediment to the atmosphere via the surface microlayer, *Ambio.*, 11, 41, 1982.
22. **Halter, M. T. and Johnson, H. E.,** A model system to study the desorption and biological availability of PCB in hydrosols, in *Aquatic Toxicology and Hazard Evaluation*, Mayer, F. L. and Hamelink, J. L., Eds., ASTM/STP 634, American Society for Testing and Materials, Philadelphia, 1977, 178.
23. **Nimmo, D. R., Wilson, P. D., Blackman, R. R., and Wilson, A. J., Jr.,** Polychlorinated biphenyl absorbed from sediments by fiddler crabs and pink shrimp, *Nature (London)*, 231, 50, 1971.
24. **Murray, H. E., Ray, L. E., and Grain, C. S.,** Analysis of marine sediment, water and biota for selected organic pollutants, *Chemosphere*, 10, 1327, 1981.
25. **Shaw, G. R. and Connell, D. W.,** Factors influencing concentrations of polychlorinated biphenyls in organisms from an estuarine ecosystem, *Aust. J. Mar. Freshwater Res.*, P. 1057, 1982.
26. **Gruger, E. H., Karrick, N. L., Davidson, A. I., and Kruby, T.,** Accumulation of 3,4,3',4'-tetrachlorobiphenyl and 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl in juvenile coho salmon, *Environ. Sci. Technol.*, 9, 121, 1975.

MONS 005861

27. **Sanborn, J. R., Childers, W. F., and Metcalf, R. L.**, Uptake of three polychlorinated biphenyls, DDT and DDE by the green sunfish *Lepomis cyanellus*. *Bull. Environ. Contam. Toxicol.*, 13, 209, 1975.
28. **Matthews, H. B. and Anderson, M. W.**, The effects of chlorination on the distribution and excretion of PCB's. *Toxicol. Appl. Pharmacol.*, 33, 183, 1975.
29. **Geyer, H., Viswanathan, R., Freitag, D., and Korte, F.**, Relationship between water solubility of organic chemicals and their bioaccumulation by the alga *Chlorella*. *Chemosphere*, 10, 1307, 1981.
30. **Haque, R. and Schmedding, D.**, A method of measuring the water solubility of hydrophobic chemicals: solubility of five polychlorinated biphenyls. *Bull. Environ. Contam. Toxicol.*, 14, 13, 1975.
31. **Tulp, M. Th. M. and Hutzinger, O.**, Some thoughts on aqueous solubilities and partition coefficients of PCB and the mathematical correlation between bioaccumulation and physicochemical properties. *Chemosphere*, 10, 849, 1978.
32. **Hollifield, H. C.**, Rapid nephelometric estimate of water solubility of highly insoluble organic chemicals of environmental interest. *Bull. Environ. Contam. Toxicol.*, 23, 579, 1979.
33. **Hansch, C., Quinlan, J. E., and Lawrence, G. L.**, Relationship of n-octanol/water coefficient to water solubility. *J. Org. Chem.*, 33, 347, 1967.
34. **Neely, W. B., Branson, D. R., and Blau, G. E.**, Partition coefficient to measure bioconcentration potential of organic chemicals in fish. *Environ. Sci. Technol.*, 8, 1113, 1974.
35. **Chiou, C. T., Freed, V. H., Schmedding, D. W., and Kohnert, R. L.**, Relationship between bioaccumulation and partition coefficient. *Environ. Sci. Technol.*, 11, 475, 1977.
36. **Mackay, D., Bobra, A., and Shiu, W. Y.**, Relationship between aqueous solubility and octanol-water partition coefficients. *Chemosphere*, 9, 701, 1980.
37. **Hutzinger, O., Tulp, M. Th. M., and Zitko, V.**, Chemicals with pollution potential, in *Aquatic Pollutants Transformation and Biological Effects*. Hutzinger, O., Van Lelyveland, I. H., and Zoeteman, B. C. J., Eds., Pergamon Press, Oxford, 1978, 13.
38. **Veith, G. D., De Foe, D. L., and Bergstedt, B. V.**, Measuring and estimating the bioconcentration factor of chemicals in fish. *J. Fish. Res. Bd. Can.*, 36, 1040, 1979.
39. **Koeman, H. and Van Leeuwen, K.**, Toxicokinetics in fish. Accumulation and elimination of six chlorobenzenes by guppies. *Chemosphere*, 9, 3, 1980.
40. **Hansch, C., Leo, A., and Nikaitani, D.**, On the additive-constitutive character of partition coefficients. *J. Org. Chem.*, 37, 3090, 1972.
41. **Lee, A., Hansch, C., and Elkins, D.**, Partition coefficients and their uses. *Chem. Rev.*, 71, 525, 1971.
42. **Hansch, C. and Fujita, T.**, p-σ-π Analysis: method for the correlation of biological activity and chemical structure. *J. Am. Chem. Soc.*, 86, 1616, 1964.
43. **Rekker, R. F.**, *The Hydrophobic Fragmental Constant*, Elsevier, Amsterdam, 1977.
44. **Matsuo, M.**, The 1*/0 — characters to relate accumulation facors of some halogenated biphenyls in fish. *Chemosphere*, 9, 61, 1980.
45. **Matsuo, M.**, The 1*/o — characters to describe ecological magnification of some organophosphorus insecticides in fish. *Chemosphere*, 7, 477, 1979.
46. **Ellgehausen, H., Girth, J. A., and Esser, H. O.**, Factors determining the bioaccumulation potential of pesticides in the individual compartments of aquatic food chains. *Ecotoxicol. Environ. Safety*, 4, 134, 1980.
47. **McDuffie, B.**, Estimation of octanol/water partition coefficients for organic pollutants using reverse phase HPLC. *Chemosphere*, 10, 73, 1981.
48. **Vreeland, V.**, Uptake of chlorobiphenyls by oysters (*Crassostrea virginica*). *Environ. Pollut.*, 6, 135, 1974.
49. **Mizutani, T., Hidaka, K., Obe, T., Matsumoto, M., Yamamoto, K., and Tajima, K.**, Comparative study on accumulation and elimination of hexachlorobiphenyls and decachlorobiphenyl in mice. *Bull. Environ. Contam. Toxicol.*, 25, 181, 1980.
50. **Shaw, G. R. and Connell, D. W.**, Relationships between steric factors and bioconcentration of polychlorinated biphenyls (PCB's) by the sea mullet (*Mugil cephalus*). *Chemosphere*, 9, 731, 1980.
51. **Shaw, G. R. and Connell, D. W.**, Physicochemical properties controlling PCB concentrations in aquatic organisms. *Environ. Sci. Technol.*, in press, 1985.
52. **Huckins, J. N., Stalling, D. L., and Smith, W. A.**, Foam-charcoal chromatography for analysis of polychlorinated dibenzodioxins in herbicide orange. *J. Off. Anal. Chem.*, 61, 32, 1978.
53. **Huckins, J. N., Stalling, D. L., and Petty, J. D.**, Carbon-foam chromatographic separation of non-o'chlorine substituted PCBs from Arochlor mixtures. *J. Assoc. Off. Anal. Chem.*, 63, 750, 1980.
54. **Kenaga, E. E.**, Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. *Ecotoxicol. Environ. Safety*, 4, 26, 1980.
55. **Tinsley, J.**, *Chemical Concepts in Pollution Behaviour*, Wiley Interscience, New York, 1979, 86.
56. **Matsuo, M.**, A thermodynamic interpretation of bioaccumulation of Arocior 1254 (PCB) in fish. *Chemosphere*, 9, 671, 1980.

MUNS 005862

57 **Kerr, S. R. and Vass, W. P.**, Pesticide residues in aquatic invertebrates, in *Environmental Pollution by Pesticides*, Edwards, C. A., Eds., Plenum Press, New York, 1973.

58 **Branson, D. R., Blau, G. E., Alexander, I. S., and Neely, W. B.**, Partition coefficient to measure bioaccumulation of organic chemicals, *Trans. Am. Fish. Soc.*, 104, 785, 1975.

59 **Konemann, H. and Van Leeuwen, K. V.**, Toxicokinetics in fish: accumulation and elimination of six chlorobenzenes by guppies, *Chemosphere*, 9, 3, 1980.

MONS 005863

Chapter 7

FACTORS CONTROLLING PCBs IN FOOD CHAINS

G.R. Shaw and D.W. Connell

TABLE OF CONTENTS

I. Introduction 136

II. Theoretical Considerations 136

III. Occurrence of PCB Biomagnification in Natural Ecosystems 139
A. Terrestrial Ecosystems 139
B. Aquatic Ecosystems 139

IV. Conclusions 140

References 140

MONS 005864

I. INTRODUCTION

Early in the investigations of persistent chemicals in the environment it was recognized that often top predators may exhibit comparatively high concentrations of these substances. The process leading to this phenomenon has been described as "food chain magnification", "ecological magnification", "bioamplification", "bioaccumulation along food chains", "trophic contamination", and "trophic magnification". However, "biomagnification" is currently the most widely accepted descriptive term. Biomagnification can be described as:

1. The transfer of a chemical through a food chain to produce a high concentration in top predators
2. An increase of a given material at successive trophic levels within an ecosystem[1]
3. A process by which the tissue concentrations of bioaccumulated chemical residues increase as these materials pass up the food chain through two or more trophic levels[2]

The most convincing evidence for the occurrence of this process is provided by the chlorinated hydrocarbon insecticides, particularly DDT and related compounds.[3] The process can be seen as a series of bioaccumulation steps through a food chain and thus a compound which does not bioaccumulate would not be expected to be biomagnified. The PCBs have octanol to water partition coefficients and bioaccumulation factors higher than DDT[4] and thus have a greater tendency to bioaccumulate in individual organisms. The biomagnification process, being a series of bioaccumulation steps, takes a considerably longer period to develop and thus comparatively high persistence in organisms is necessary. The PCBs are generally more persistent than DDT and related compounds.

Thus, the PCBs have somewhat similar environmental properties to DDT and related compounds but with a greater tendency to bioaccumulate and persist. By analogy, biomagnification could be expected with the PCBs in natural ecosystems.

II. THEORETICAL CONSIDERATIONS

The biomagnification mechanism described above results from uptake of PCBs in the food of organisms. Of course, an alternative uptake route of considerable importance is directly from the environment, e.g., from water through the gills with fish. With bioaccumulation and biomagnification the individual organisms do not differentiate between PCBs and other food contaminants on uptake but on depuration the organism retains the PCBs due to its resistance to degradation compared to normal food components. Energy is lost at each level of a trophic pyramid as a result of respiration and nonassimilated energy, and the energy content at any level is approximately 90% less than the level below it.[5] It follows then that a persistent compound that enters one trophic level will be concentrated approximately ten times in the next trophic level. In fact, organisms can remove foreign compounds taken up and food is not the only route through which an organism can take up a persistent chemical, especially in the case of aquatic organisms.

A mathematical model can be developed for the transport of PCBs through different trophic levels.[3] The basic principle of mass conservation criteria can be applied at each trophic level, n, equating the inflow of PCBs to a level to the rate of ingestion of organisms from lower levels, i, and equating the outflow of PCBs to the rates of death and excretion. Using the conditions that biomass at any level is in a steady-state condition then the concentration of PCBs in the nth predator level as a function of time can be written as:

$$\left[\frac{M_n}{M_{d,n}}\right]\frac{dC_n}{dt} + C_n = \left[\frac{1}{M_{d,n}}\sum_{i=1}^{n-1} \sigma_i M_i C_i - (M_r)_{n,n} - C_n M_{r,n}\right]$$

MONS 005865

where M is the biomass at the trophic level, M_d is the biomass death rate due to natural death or ingestion, $(M_r)_R$ is the rate of metabolism of the PCBs, M_r is the rate of excretion, C_r is the concentration of PCBs in the nth predator level, C_e is the concentration of PCBs in the excretions, and σ is an efficiency factor relating to the percent of ingested material which is retained in the trophic level.[7]

If it is assumed that the input of PCBs to the system is zero and the degradation rates are negligible then the equilibrium concentration for PCBs at the nth level can be written as

$$C_n \text{ equilibrium} = \frac{T_n}{M_n}\left[\sum_{n-1}^{n-1} \sigma_r M_r C_r - C_e C_{n-1}\right]$$

where T_n is the life span of trophic level, n. This equation indicates that the equilibrium concentration of PCBs at any trophic level varies directly with the life span and inversely with the total mass, M_n, of the level.

Another approach[8] takes into account uptake from both food and water and assumes first order kinetics. Thus, for an individual organism consisting of a single homogeneous compartment the rate of uptake is

$$\frac{dQ}{dt} = C_e k_u$$

where Q is the amount of substance in the organism, C_e is the concentration of the substance in the external environment, and k_u is the uptake rate constant.

The loss of the substance by metabolism or excretion also follows first order kinetics; thus, overall the rate of bioaccumulation is

$$\frac{dQ}{dt} = C_e k_u - Qk$$

where k is the rate loss constant.

Differentiation and rearrangement of this expression give for the amount of substance in the organism at time t:

$$Q = \frac{C_e k_u}{k}(1 - e^{-kt})$$

thus:

$$C_s W = \frac{C_e k_u}{k}(1 - e^{-kt}) \qquad (1)$$

where C_s is the concentration in the organism and W is its body weight.

This expression applies for uptake of the substance from the surrounding stable environment. However, with the biomagnification mechanism uptake will occur through contaminated food. Thus, taking both food and the external environment into account:

$$C_e k_u = Ck(\text{food}) + Ck(\text{water})$$

The intake from food with animals takes the general form of a W^{-b} where a and b are constants and W is its body weight. The intake from food can be written:

$$Ck(\text{food}) = a_i W^{-bi} r_i C_i$$

MONS 005866

where a_1 and b_1 are constants, W is body weight, C is the concentration in food, and r_1 is the proportion of the concentration taken up. Since the volume of water passing over the gills is proportional to body weight a similar expression can be derived for uptake from water:

$$Ck(water) = a_2 W^{-b_2} r_2 C_2$$

where C_2 is the concentration of the substance in water and r_2 is the proportion taken up. Excretion may also be considered to vary with body size such that:

$$k = a_3 W^{\gamma - 1}$$

where a_3 and γ are constants.

Substituting the expressions above for Ck (food), Ck (water), and k in Equation 1 the following expression can be obtained for an organism at constant weight:

$$C_e = \frac{a_1 W^{-b_1} r_1 C_1 + a_2 W^{-b_2} r_2 C_2}{a_3 W^{\gamma}} \left(1 - e^{-a_3 W^{\gamma - 1}}\right)$$

This equation indicates a number of different aspects of biomagnification. The relative size of the coefficients preceding C_1 and C_2 is the principal factor indicating whether biomagnification is operating. If $C_1 \gg C_2$ then transfer in food is the major factor influencing the concentration of a substance in the organism and biomagnification is in operation.

Biomagnification can also be considered to result from the partition process.[8] At equilibrium the following relationship exists:

$$K_a = \frac{C_a}{C_w}$$

where K_a is the bioaccumulation factor, C_a is the concentration in the organism, and C_w is the concentration in the surrounding environment.

At the lowest trophic level, phytoplankton take up a pollutant in equilibrium with water according to the following relationship derived from the equation above:

$$C_{pp} = K_a C_w \qquad (2)$$

where C_{pp} is the concentration of pollutant in phytoplankton (or detritus), K_a is the bioaccumulation factor, and C_w is the pollutant concentration in water. When the phytoplankton are consumed by a herbivore the following relationship applies if (1) the food (phytoplankton) is the only source of pollutant; (2) the pollutant has not been chemically modified; (3) sufficient time has elapsed for equilibrium to be attained; and (4) K_a is constant and applicable to the herbivore to phytoplankton relationship:

$$C_H = K_a C_{pp} \qquad (3)$$

where C_H is the concentration in the herbivore.

Since food is the only source of pollutant, the equilibrium in this case will be between the stomach contents of the organism and the organism itself rather than the organism and the surrounding environment.

Substituting Equation 2 in Equation 3 the following is obtained:

MONS 005867

$$C_n = (K_B)^2 C_w$$

Similarly, the following general relationship can be established for the conditions outlined above:

$$C_{TR} = (K_B)^{TR} C_w$$

where C_{TR} is the concentration in organisms at a particular trophic level and TR is the number of transfers of the pollutant in the food web. It would be expected that concentrations would be somewhat lower than this due to losses from the organism by equilibrium establishment between the organism and the water mass.

Thus, a sequential increase in concentration could be expected in a food chain with organisms at the highest levels exhibiting the highest concentrations. However, in many natural food chains the conditions necessary for this to occur may not exist.

IV. OCCURRENCE OF PCB BIOMAGNIFICATION IN NATURAL ECOSYSTEMS

It is convenient to consider ecosystems in two classes: terrestrial and aquatic. Organisms in terrestrial ecosystems have only one significant source of PCBs, contaminated food, whereas in aquatic ecosystems both food and water are significant potential sources.

A. Terrestrial Ecosystems

It is generally accepted that biomagnification can occur with terrestrial ecosystems where food is the main source of PCBs for organisms.[9-11] For example, fish-eating birds and predatory raptors at the top of the food web are often found to contain high levels of PCBs.[4,12] In addition, Presst et al.[13] have established a correlation between PCBs in the livers of wild birds and their diets. Less than 1 mg/kg PCB was found with insectivorous birds while more than 70 mg/kg was found in the sparrow hawk, a top carnivore.

B. Aquatic Ecosystems

The significance of biomagnification of persistent residues as compared to direct uptake from water has been the subject of a considerable debate. Addison[14] has concluded that in invertebrates, both ingestion and contamination from water contribute to uptake but ingestion appears to predominate with increasing size, and is the main uptake route in fish.

A variety of other investigations have indicated that biomagnification of PCBs can occur in aquatic ecosystems. In a study of pollutant levels in marine ecosystems in southern California, Young et al.[15] found that increases in PCB 1254 concentrations were related to increases in the trophic level. The clearest relationship between PCB concentration and trophic position was usually obtained when the concentrations in wet weight were converted to a lipid basis. The authors attributed the biomagnification effect to the relatively long biological halflives of the PCBs. As a result of studies on the PCB levels of organisms in the Hudson River, Nadeau and Davis[16] have reported that a possible pathway for bioaccumulation exists between snails and larger game fish.

A comprehensive review of the literature information available on PCBs in diverse aquatic food chains has been carried out by Thomann[27] using a model food chain transfer number, f:

$$f = \alpha C/K + G$$

where α is the chemical absorption efficiency; C is the specific consumption; K is the

MONS 005868

excretion rate, and G is the net organism growth. Thomann[17] found that PCB levels in top predators are almost entirely due to biomagnification. In accord with this, the World Health Organization[4] has evaluated levels of PCBs found in marine ecosystems which concluded that the top predators in polluted areas generally exhibit the highest concentrations. This suggests that biomagnification may be generally occurring with the top predators. With fish Butler et al.[17] concluded that pollutant levels do not represent levels in the marine environment but are probably the result of storage and recycling in different links of the food web.

The alternative view proposed by Hamelink et al.[18] is that organochlorine levels in organisms depend on the physicochemical properties of the organochlorine and particularly those properties which control its tendency to distribute itself between lipoid and aqueous phases.

In an analysis of literature data, Moriarty[19] found that phytoplankton and zooplankton, at the lowest trophic levels, often contain PCB residues at higher levels than higher trophic level predators. Direct contamination from water and PCB-rich surface microlayers have been suggested as the most important uptake route.[7,20] Similarly, Shaw and Connell[20] found no evidence of biomagnification at lower trophic levels but carnivorous birds exhibited this phenomenon.

After extensive research into factors determining the bioaccumulation potential of chemicals in aquatic food chains, Ellgehausen et al.[21] concluded that biomagnification was of lesser importance than direct uptake from water. A similar conclusion has been reported by Bruggerman et al.[2] from studies with the goldfish. Investigations into ecosystems in the Baltic Sea[22] and an Oklahoma stream[23] did not reveal any relationship between trophic level and PCB concentration.

This and other data have led several authors[24] to conclude that, for pelagic biota at the lower trophic levels, food chain biomagnification is not a controlling factor in attaining observed PCB levels. Bioaccumulation is predominantly controlled by equilibrium partitioning of the chemical between the internal lipids of the biota and ambient water. In addition, Gruger et al.[25] have postulated that no matter how high the PCB concentrations in food are, the equilibrium level in the aquatic organism will be controlled by partitioning back into the water.

IV. CONCLUSIONS

The available evidence indicates that, as a general rule, biomagnification and food chain transfer are the major mechanisms for deposition of PCBs in the top carnivore members of terrestrial ecosystems. However, the overall significance of biomagnification in aquatic ecosystems is less certain. Direct uptake from water and sediments appears to be the dominant process for many persistent pollutants including PCBs in unstructured food webs and at lower trophic levels. Thus, equilibrium mechanisms between individual organisms and the water mass are the controlling factors. However, at higher trophic levels the information available suggests that biomagnification is generally the major mechanism of PCB deposition.

REFERENCES

1 **Rudd, R. L.,** *Pesticides and the Living Landscape*, University of Wisconsin Press, Madison, 1964.
2 **Bruggerman, W. A., Martron, L. B. J. M., Kooiman, D., and Hutzinger, O.,** Accumulation and elimination kinetics of di-, tri- and tetra-chlorobiphenyls by goldfish after dietary and aqueous exposure, *Chemosphere*, 10, 811, 1981.

MONS 005869

3. GESAMP. Impact of Oil on the Marine Environment. No. 7. Joint Groups of Experts on the Scientific Aspects of Marine Pollution. Reports and Studies. GESAMP. 1977.
4. *World Health Organization. Polychlorinated Biphenyls and Terphenyls.* WHO. Geneva. 1976.
5. Mackay, D., Correlation of bioconcentration factors. *Environ. Sci. Technol.*, 16, 274, 1982.
6. FAO/SIDA. Lectures presented at the Fifth FAO/SIDA Workshop on Aquatic Pollution in Relation to Protection of Living Resources. Food and Agricultural Organization. Rome. 1978. 268.
7. **Kalmaz, E. V. and Kalmaz, G. D.**, Transport, distribution and toxic effects of polychlorinated biphenyls in ecosystems (review). *Ecol. Model.*, 6, 223, 1979.
8. **Connell, D. W. and Miller, G. J.**, *Chemistry and Ecotoxicology of Pollution.* John Wiley & Sons. New York. in press. 1985.
9. **Peakall, D. B.**, PCB's and their environmental effects. *CRC Crit. Rev. Environ. Control*, 5, 469, 1975.
10. **Tinsley, J.**, *Chemical Concepts in Pollution Behaviour.* Wiley Interscience. New York. 1979. 86.
11. **Vermeer, K. and Peakall, D. B.**, Toxic chemicals in Canadian fish-eating birds. *Mar. Pollut. Bull.*, 9, 205, 1977.
12. **Bourne, W. R. P. and Bogan, W. A.**, Polychlorinated biphenyls in North Atlantic sea-birds. *Mar. Pollut. Bull.*, 3, 171, 1972.
13. **Presat, I., Jeffries, D. J., and Moore, N. W.**, Polychlorinated biphenyls in wild birds in Britain and their avian toxicity. *Environ. Pollut.*, 1, 3, 1970.
14. **Addison, R. F.**, Organochlorine compounds in aquatic organisms, their distribution, transport and physiological significance, in *Effects of Organic Pollutants on Aquatic Organisms.* Lockwood, A. P. M., Eds., Cambridge University Press. Cambridge. England. 1976. 126.
15. **Young, D. R., Mearns, A. J., Jan, T., Heesen, T. C., Moore, M. D., Eganhouse, R. P., Hershelman, G. P., and Gossett, R. W.**, Trophic structure and pollutant concentrations in marine ecosystems of Southern California. *Cal. COFI Rep.*, 21, 197, 1980.
16. **Nadeau, R. J. and Davis, R. A.**, Polychlorinated biphenyls in the Hudson River (Hudson Falls-Fort Edward, New York State). *Bull. Environ. Contam. Toxicol.*, 16, 436, 1976.
17. **Butler, P. A., Kennedy, C. D., and Schutzmann, R. L.**, Pesticide residues in estuarine molluscs, 1977 versus 1972 — National Pesticide Monitoring Program. *Pest. Monit. J.*, 12, 99, 1978.
18. **Hamelink, J. L., Waybrant, R. C., and Ball, R. C.**, A proposal exchange equilibria to control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. *Trans. Am. Fish. Soc.*, 100, 207, 1971.
19. **Moriarty, F.**, *Organochlorine Insecticides: Persistent Organic Pollutants.* Academic Press. New York. 1975.
20. **Nisbit, I. C. T. and Sarofim, A. F.**, Rates and routes of transport of PCB's in the environment. *Environ. Health Perspect.*, 1, 21, 1972.
21. **Ellgehausen, G., Guth, J. A., and Esser, H. O.**, Factors determining the bioaccumulation potential of pesticides in the individual compartments of aquatic food chains. *Ecotoxicol. Environ. Safety*, 4, 134, 1980.
22. **Clayton, J. R., Pavlou, S. P., and Breitaer, N. F.**, Polychlorinated biphenyls in coastal marine zooplankton. Bioaccumulation by equilibrium partitioning. *Environ. Sci. Technol.*, 11, 676, 1977.
23. **Hunter, R. G., Randolph, J. C., and Carroll, J. H.**, Polychlorinated biphenyls in the sediments and fish of an Oklahoma stream. *Environ. Pollut. B*, 1, 233, 1980.
24. **Mauck, K. J., Petrocelli, S. R., and Sleight, B. H.**, Consideration in assessing the potential for and significance of biomagnification of chemical residues in aquatic food chains. *Aquatic Toxicology.* ASTM/STP 667. American Society for Testing and Materials. Philadelphia. 1979. 251.
25. **Gruger, E. H., Karrick, N. L., Davidson, A. I., and Kruby, J.**, Accumulation of 3,4,3',4'-tetrachlorobiphenyl and 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl in juvenile coho salmon. *Environ. Sci. Technol.*, 9, 121, 1975.
26. **Shaw, G. R. and Connell, D. W.**, Factors influencing concentrations of PCB's in organisms from an estuarine ecosystem. *Aust. J. Mar. Freshwater Res.*, 33, 1057, 1983.
27. **Thomann, R. V.**, *Equilibrium fate of micronutrients in diverse aquatic food webs. Can. J. Fish. Aquat. Sci.*, 38, 280, 1981.

MONS 005870

Chapter 8

DISTRIBUTION, BEHAVIOR, AND LOAD OF PCBs IN THE OCEANS

Shinsuke Tanabe and Ryo Tatsukawa

TABLE OF CONTENTS

I. Introduction 144

II. Distribution and Behavior of PCBs in the Open Ocean Environment 144
A. PCBs in the Atmosphere 144
B. PCBs in Water 146
C. PCBs in Organisms 150

III. General Concentration Levels and Estimated Load of PCBs in the Oceans 155

IV. Prospects and Ultimate Fate of PCBs in the Ocean Reservoir 158

References 159

MONS 005871

I. INTRODUCTION

Polychlorinated biphenyls (PCBs) as well as DDT are the cause of much concern as manmade organic pollutants and many studies have been made of them in a wide range of environmental media and biota. The first indication of worldwide dispersion of PCBs was made in Antarctic birds.[1] Since then, the global distribution of PCBs has been demonstrated by their detection in the open ocean atmosphere,[2-7] water,[3,4,7-9] and marine organisms.[5,10-13]

In the early 1970s, Woodwell et al.[14] and the National Academy of Sciences[15] predicted that the open ocean environment serves as a vast reservoir for the persistent organochlorines. A recent report of the National Academy of Sciences[16] documented that the major portion of PCBs present in the environment of the United States was contained in North Atlantic waters, accounting for 50 to 80% of the total. This estimate suggests that open ocean water acts as a major sink for PCBs. There are some estimates of the PCB loads in terrestrial and coastal environments.[17-20] However, comprehensive and reasonable estimates regarding the PCB load in the open ocean environment have not been made. This seems to be due to the lack of PCB measurement data covering all the oceans, especially the Southern Hemisphere. In 1978, the National Academy of Sciences recommended that a major effort should be made to obtain monitoring data of organochlorines in the Southern Hemisphere.[21]

Since 1975, we have been surveying the Pacific, Indian, and Antarctic Oceans, and have measured PCBs and organochlorine insecticides in air, water, and biological samples.[4,7,11,16,22,23] In this chapter, our main concern is to estimate the PCB load in the open ocean environment. To understand the geochemical circulation and ultimate fate of PCBs, it is essential to estimate the PCB load in the ocean. Thus, we first describe the distribution and behavior of PCBs in open ocean environments including the atmosphere, hydrosphere, and biosphere. Based on our data and those of other workers, we attempt to estimate the general concentration level and load of PCBs in all environmental media and biota in the ocean. Finally, the prospects and ultimate fate of PCBs are discussed.

II. DISTRIBUTION AND BEHAVIOR OF PCBs IN THE OPEN OCEAN ENVIRONMENT

A. PCBs in the Atmosphere

There is not enough data about PCBs in the open ocean atmosphere. This is because the atmospheric concentrations are very low and therefore novel sampling devices and more accurate and sensitive analytical methods were not available. In the late 1970s, a suitable collection method using polyurethane foam was developed[24] and made it possible to isolate PCBs from large volumes of air. In addition, the introduction of capillary gas chromatography[3,9] and mass fragmentography[7] enabled us to determine the respective PCB isomers and congeners and to separate them from various interfering materials contained in environmental samples. Most of the recent studies have been carried out using these techniques and have enabled more detailed considerations of atmospheric transport processes, behavior, and flux of PCBs in the open ocean environment.

PCB concentrations in the open ocean atmosphere reported so far are summarized in Table 1. PCBs are widely distributed in the atmosphere over the oceans worldwide and atmospheric concentrations are mostly below 1 ng/m^3. A most interesting fact is their presence in the Southern Ocean and Antarctica, indicating that the impacts of industrial and human activities extend all over the world. The aerial concentrations of PCBs over the mid-latitudes of the Northern Hemisphere were found to be rather high, which is accounted for by their extensive use on land in this region. By contrast, relatively lower concentrations were observed in the Southern Ocean and the northern North Atlantic and Pacific Oceans. The atmospheric PCB levels over the North Pacific seem to be somewhat lower than those over the North Atlantic.

MONS 005872

Table 1
PCB CONCENTRATIONS IN THE OPEN OCEAN ATMOSPHERE

Location	Year	N	PCB conc. (ng/m³) Range	Mean	Ref.
North Atlantic					
Bermuda	1973	4	0.15—0.50	0.30	2
Bermuda	1973	8	0.21—0.65	0.51	3
Bermuda, U.S.	1973	4	0.72—1.6	0.99	3
Grand Banks (45°N, 52°W)	1973	5	0.05—0.16	0.086	2
Newfoundland	1977	6	0.042—0.15	0.12	6
Gulf of Mexico	1977	10	0.17—0.79	0.35	25
Barbados	1977-1978	17	<0.005—0.37	0.057	6
North Pacific					
Enewetak Atoll (12°N, 162°E)	1979	14	0.35—1.0	0.54	5
Western Pacific (3-35°N, 105-151°E)	1980-1981	7	0.089—0.74	0.25	7
Western Pacific (43-53°N, 154-172°E)	1981	2	0.041—0.061	0.051	26
Western Pacific (41-46°N, 144-174°E)	1982	5	0.022—0.095	0.043	26
Bering Sea	1981	3	0.026—0.059	0.041	26
South Pacific					
Western Pacific (1-46°S, 151-157°E)	1981	5	0.083—0.50[a]	0.27	7
Indian					
Eastern Indian (1-44°S, 104-125°E)	1980	5	0.066—0.33[a]	0.15	7
Western Indian (20-54°S, 48-57°E)	1982	4	0.060—0.24	0.16	27
Antarctic					
53-65°S, 125-161°E	1980-1981	5	0.056—0.18	0.091	7
54-68°S, 38-58°E	1982	4	0.076—0.11	0.091	27
Syowa Station (69°00'S, 39°35'E)	1981-1982	11	0.017—0.17	0.061	27

[a] Excluding the coastal regions.

This difference might be because smaller amounts of PCBs are used in Asian countries than in the U.S. and European countries. According to our recent survey in the western Pacific and eastern Indian Oceans,[7] rather high concentrations of aerial PCBs were found in the low latitudes of both the hemispheres. In another survey ranging from Syowa Station, Antarctica (69°00'S, 39°55'E) to Mauritius in the western Indian Ocean (21°10'S, 57°30'E),[27] an apparent increase of aerial PCB concentrations was observed towards the low latitudes. These observations may suggest that low latitude countries currently act as one of the PCB sources, as well as the developed countries. A recent rice bran oil incident in Taiwan[28] emphasizes the current use of PCBs without any restriction in low latitude countries.

Besides such geographical variations, seasonal variations have also been recognized in the aerial concentrations of PCBs. Figure 1 shows the atmospheric concentrations of PCBs and organochlorine insecticides at Syowa Station, Antarctica.[27] Although the seasonal variation was slightly different according to the variety of chemicals, rather high concentrations were generally found during the austral summer. Recently, Bidleman et al.[6] measured airborne organochlorines in the North Atlantic gyre. PCB concentrations in the Barbados atmosphere were apparently higher in summer than in winter, but organochlorine insecticides did not vary between the two seasons. Oehme and Stray[29] also noted seasonal variations of aerial organochlorines in the Arctic where higher concentrations of HCHs were found in summer. In Antarctica, snowfall prevails during the autumn and winter when relatively lower concentrations of atmospheric organochlorines were observed (Figure 1). Snowfall may assist the removal of atmospheric organochlorines in Antarctica. The seasonal usage of chemicals in countries located to the north of Antarctica may also contribute to such seasonal variations. The application of organochlorine insecticides on land most frequently occurs in

MONS 005873

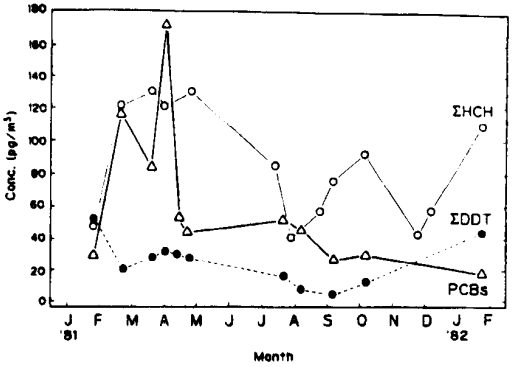


FIGURE 1 Seasonal variations of ΣDDT, ΣHCH, and PCB concentrations in the Antarctic atmosphere (Syowa Station, Antarctica; 69° 00'S, 39°35'E).[27]

summer. The dispersion of insecticides applied on land extends all over the world through the atmosphere, which may account for the high concentrations of HCHs and DDTs in the Antarctic atmosphere in the summer season. However, PCBs are unlikely to be used during a limited season, even though higher concentrations were found in summer. This might be a result of the active evaporation from various PCB sources on land due to high temperatures in the summer. The relatively high concentration levels of PCBs in the Antarctic atmosphere persisted during a short period of only two or three months. This fact suggests that the atmospheric lifetime of PCBs is rather short, probably less than 80 days.

Recent studies made clear the composition of PCBs in the open ocean atmosphere. Atlas and Giam[3] measured the aerial PCB concentrations at a land station on Enewetak Atoll and identified 30 PCB isomers and congeners which excellently matched the Aroclor® 1242 pattern. Bidleman et al.[6] also noted many lower chlorinated biphenyls in the Newfoundland and Barbados atmospheres by capillary gas chromatography. We also identified and quantified 53 PCB isomers and congeners ranging from di- to heptachlorobiphenyls using a gas chromatograph-mass spectrometer, and recognized relatively larger amounts of lower chlorinated biphenyls in the atmosphere over the western Pacific, eastern Indian, and Antarctic Oceans.[7] The enrichment of lower chlorinated biphenyls in the open ocean atmosphere is the result of their comparatively active evaporation and consequent preferential long distance transport. The behavior and lifetime of PCBs in the open ocean atmosphere are supposed to vary according to the isomers and congeners but this possibility remains to be studied.

B. PCBs in Water

A method to collect trace organics from a large volume of water has been developed using macroreticular resins.[30,31] This technique has also been applied to the isolation of PCBs and other organochlorines from open ocean water.[4,7,9,23,28,33] However, less information is available for PCBs in open ocean water as well as the overlying atmosphere. This is attributed to several difficulties such as sample storage, chemical analysis, contamination and so on. Some of these problems have not yet been examined sufficiently.

MONS 005874

Table 2
PCB CONCENTRATIONS IN OPEN OCEAN SURFACE WATERS

Location	Year	N	PCB conc. (ng/ℓ) Range	Mean	Ref.
North Atlantic					
Sargasso Sea	1973	8	<0.9—3.6	1.0	3
Sargasso Sea, New York	1973	9		0.8	24
9—55°N, 9—73°W	1973-1975	39	0.4—8.0	2.9	9
North Sea and Scottish coast	1974	5	<0.15—4.52	0.23	33
South Atlantic					
11—36°S, 2—33°W	1975	8	0.3—3.7	1.0	9
North Pacific					
Western Pacific (22—35°N, 141—154°E)	1975	13	0.25—0.56	0.41	4
Western Pacific (32—42°N, 133—143°E)	1976	8	0.29—1.1	0.54	4
Western Pacific (12—33°N, 129—138°E)	1978	6	0.23—0.59	0.35	4
Western Pacific (29—34°N, 137—146°E)	1979	5	0.27—0.38	0.33	4
Western Pacific (5—31°N, 107—152°E)	1980-1981	9	0.039—0.15	0.089	7
Bering Sea	1981	3	0.073—0.13	0.10	26
South Pacific					
Western Pacific (2—41°S, 152—156°E)	1981	5	0.081—0.21	0.12	7
Indian					
Eastern Indian (4—45°S, 104—123°E)	1980	6	0.057—0.25	0.14	7
Antarctic					
48—65°S, 124—163°E	1980-1981	7	0.042—0.072	0.058	7
Syowa Station (69°00'S, 39°35'E)	1981-1982	3	0.035—0.069	0.053	27

PCB concentrations in open ocean surface waters reported so far are summarized in Table 2. There are some other reports on PCBs in North Atlantic water between 1971 and 1972,[12,35,36] but PCB concentrations are one or two orders of magnitude higher compared to those made since 1973 as shown in Table 2. No satisfactory and reasonable explanation has been made for this rapid decrease.

Concentration levels of PCBs in open ocean water are generally in the few nanograms per liter range or less. North Atlantic waters revealed relatively higher concentrations of PCBs than the other oceans. This seems to be due to the extensive use of PCBs in the U.S. and European countries. Much lower concentrations of PCBs were found in the Southern Ocean, ranging from 0.035 to 0.072 ng/ℓ. This concentration level is probably the lowest among the monitoring data on PCBs reported so far. According to our survey of the western Pacific and eastern Indian Oceans from 1975 to 1982,[4,7,26] PCB levels in surface waters were found to be apparently lower in the Southern Hemisphere than in the Northern Hemisphere and much higher concentrations were observed in the mid-latitudes of the Northern Hemisphere (Figure 2). Harvey and Steinhauer[9] reported higher levels of PCBs in North Atlantic surface waters than in the South Atlantic. Both observations strongly suggest progressive contamination by PCBs in the Northern Hemisphere. Harvey and Steinhauer further noted that higher PCB concentrations in the low (10°N to 20°N) and mid-latitudes (45°N to 55°N) of the North Atlantic might be caused by evaporation-precipitation processes. In the case of western Pacific and eastern Indian waters, we could not find any correlation between the latitudinal variation of PCBs and net annual precipitation. It seems that the extensive use of PCBs in the Northern Hemisphere, particularly in mid-latitude countries, is a major factor in this geographical distribution of PCBs.

The vertical transport of PCBs and DDTs in open ocean waters has been also demonstrated by their detection in deep sea fish,[12] sediments,[17] and subsurface water itself.[9,37-39] We also noted the presence of PCBs and organochlorine insecticides in North Pacific, eastern Indian,

MONS 005875

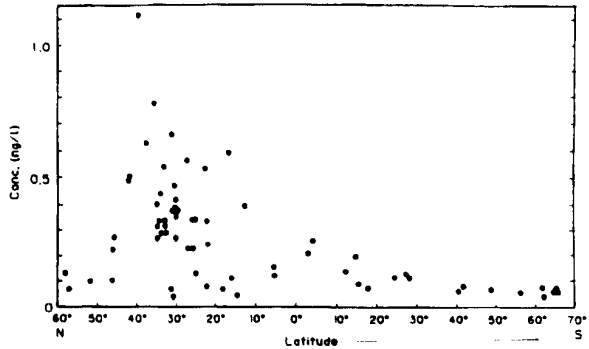


FIGURE 2. Latitudinal distribution of PCBs in open ocean surface waters from the western Pacific and eastern Indian Oceans during 1975 to 1982.

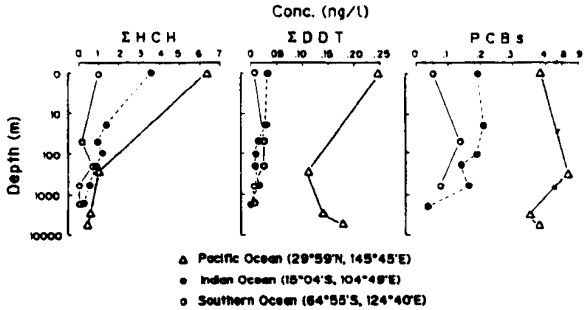


FIGURE 3. Vertical profiles of PCBs and organochlorine insecticides in open ocean water columns.

and Southern Ocean deep waters (Figure 3).[40] According to this report, vertical profiles of PCBs and ΣDDT (sum of p,p'-DDT, p,p'-DDE, and o,p'-DDT) concentrations were found to have small variations throughout the water column, whereas ΣHCH (sum of α, β, and γ isomers) concentrations decreased systematically with depth. PCB and organochlorine insecticide residues in deep water cannot be explained by the convectional and diffusional mixing of water, because it takes a long time for the surface and deep waters to mix and no more than 50 years has passed since PCB production and use began. The vertical transport of these chemicals seems to be strongly associated with sinking particles in the water column. Elder and Fowler[41] reported that fecal pellets from natural populations of euphausiids contained high concentrations of PCBs and also noted that such biogenic particles make a significant contribution to the vertical deposition of PCBs.

MONS 005876

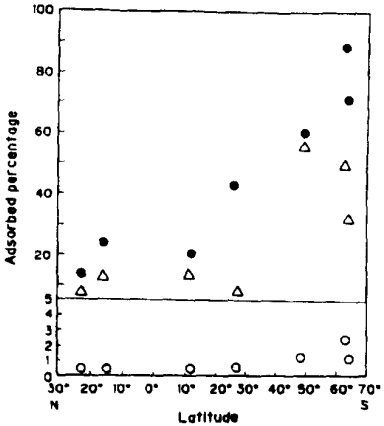


FIGURE 4. Latitudinal variations of the percentage of PCBs (△), ΣDDT (●), and ΣHCH (○) adsorbed on suspended solids in open ocean surface water.[40]

In order to elucidate the transport mechanism of organochlorines, it is necessary to know the forms in which they are present in open ocean water. Thus, we filtered large volumes of surface water and separated the organochlorines into dissolved and adsorbed fractions. Consequently, it became clear that a large portion of PCBs and DDTs was retained on particulate matter, while a major fraction of HCHs was present in filtered water (Figure 4). It was also apparent that there were prominent negative correlations in the relationships between the water solubilities of organochlorines and the concentration ratios of adsorbed to dissolved fractions (Figure 5). These observations strongly suggest that less water soluble organochlorines such as PCBs and DDTs are rapidly transported into deeper layers of water columns by sinking particles. By contrast, relatively water soluble organochlorines such as HCHs are slowly scavenged from surface to deeper layers. The different vertical profiles of organochlorines in open ocean water columns (Figure 3) are most likely because of their different affinity to particulate matter resulting from their water solubilities. Furthermore, the percentage of adsorbed fractions of organochlorines increased toward the high latitudes (Figure 4). It is well known that primary production and particle concentration in the oceans generally increase toward the high latitudes.[42,43] The latitudinal variations for the adsorbed percentage of organochlorines (Figure 4) appear to be related to particle concentrations in surface waters. According to the laboratory experiment by Biggs et al.[44] who examined the partition of ^{14}C-PCB between water and particles, 19 to 22% of ^{14}C-PCB were retained on particles at a particle concentration of 25 ppm, while at 100 ppm, 66 to 69% of ^{14}C-PCB were adsorbed on particles. This fact favorably accounts for the latitudinal variations of organochlorines in adsorbed fractions as shown in Figure 4.

PCB compositions in open ocean water consist mainly of lower chlorinated biphenyls and closely resemble those in the open ocean atmosphere.[7] Higher chlorinated biphenyls are also

MONS 005877

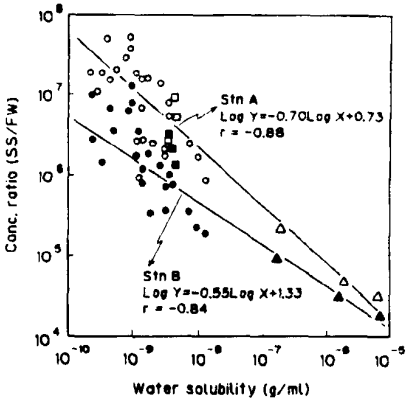


FIGURE 5. Relationship between the water solubilities of PCBs (○,●), DDT compounds (□,■), and HCH isomers (△,▲) and their concentration ratios in suspended solids to filtered water.[48] Stations A and B are located at 22°05'N, 145°02'E and 48°59'S, 127°31'E, respectively. The open and solid symbols indicate Stations A and B, respectively.

present in water, but in much smaller amounts. Such PCBs are mostly retained on particulate matter because of their relatively low water solubilities and high particle affinities, whereas the dissolved fraction mainly consists of lower chlorinated biphenyls (Figure 6). This discrepancy leads to the assumption that PCB compositions in deeper layers are relatively enriched with higher chlorinated biphenyls due to their comparable rapid deposition rates by sinking particles. Although no one has yet demonstrated this, studies of the PCB compositions in Antarctic[46] bottom living fish showed a relatively greater proportion of higher chlorinated biphenyls than surface living fish, may support the selective deposition of PCB isomers and congeners from surface to deeper layers in the water column.

C. PCBs in Organisms

Despite extensive literature on PCB concentrations in estuarine and coastal organisms, relatively few studies are available on open ocean organisms as shown in Tables 3 to 5. Among these organisms, marine mammals have been comparatively well studied all over the world (Table 5). This is due to the facility of PCB detection because of higher accumulation levels of PCBs in marine mammals than in other organisms. PCBs in open ocean fish have also been well monitored, but the portion of the fish body analyzed has been variable (Table 4). This makes it somewhat difficult to compare the PCB concentration levels in fish from different oceans. There is much less information on PCB monitoring data in open ocean plankton (Table 3). It is, therefore, most difficult to discuss the global viewpoint of PCB contamination in plankton samples.

In general, PCB concentrations in open ocean fish and mammals living in the Northern Hemisphere were found to be higher than those in the Southern Hemisphere. The highest range of PCB concentration was observed in the mid-latitudes of the Northern Hemisphere.

MONS 005878

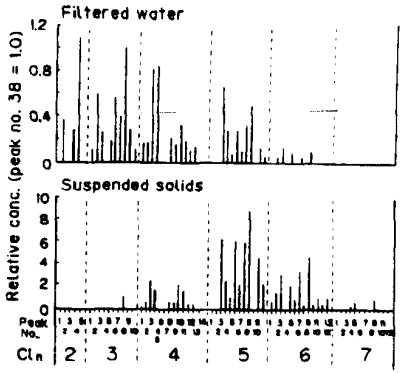


FIGURE 6. PCB compositions in filtered water and suspended solids from open ocean surface water (48°59'S, 127°31'E).[49] The notation Cl, indicates the number of chlorine atoms substituted in biphenyls. Peak no. shows the order of retention time on the mass fragmentogram for PCBs with respect to substituted chlorine number. Each bar shows the relative concentration of individual PCB isomers and congeners measured by mass fragmentography. Details of each peak and its chemical structure are given in our previous report.[49] Mono-, octa-, nona-, and decachlorobiphenyls were below detection levels.

Table 3
PCB CONCENTRATIONS IN OPEN OCEAN PLANKTON

Location	Year	N	PCB conc (ng/g wet wt.) Range	Mean	Ref.
North Atlantic	1970		300—450	380	48
Northeast Atlantic	Before 1972	22	10—110		47
North and South Atlantic	1970-1972	53		200	11
South Atlantic	1971	4	18—640	200	48
Western North Pacific	1981	1		1.1	49
Bering Sea	1982	3	1.0—1.6	1.3	49
Western South Pacific	1981	3	1.2—2.3	1.7	49
Antarctic (Ross Sea)	1972	1		<3	50
Antarctic (50-65°S, 124°-126°E)	1981	3	0.2—1.0	0.5	49

By contrast, fish and mammalian samples from the northern North Pacific and the northern North Atlantic revealed rather low levels of PCBs. The Arctic and Antarctic mammals accumulated even less amounts of PCBs. The lowest concentration of PCBs in marine mammals was found in the Antarctic Weddell seal. The geographical distribution of PCBs in open ocean fish and mammals almost agreed with those in open ocean surface waters (Table 2). This suggests that the bioaccumulation of PCBs in open ocean organisms is strongly affected by their ambient water.

MONS 005879

Table 4
PCB CONCENTRATIONS IN OPEN OCEAN FISHES

Location/species	Year	N	Analyzed portion	PCB conc. (ng/g fresh wt.) Range	Mean	Ref.
North Atlantic						
Flying fish	1970—1971		Whole		50	11
Flying fish (*Cypselurus exsilens*)	1970—1971		Muscle		1.4	11
Flying fish (*Pterynichthys cinderella*)	1970—1971		Muscle		4	11
Trigger fish (*Canthidermis maculatus*)	1970—1971		Muscle		1.9	11
Western North Pacific (off Japan)						
Emmelichthys struhsakeri	1980	3	Whole	12-75	44	49
Trachinotus ameiensis	1979	3	Whole	17-71	35	49
Priacanthus hiwis	1979	3	Whole	12-73	45	49
Bering Sea						
Herring (*Clupea pallasi*)	1973	1	Muscle		80	51
Walleye pollock (*Theragra chalcogramma*)	1973	2	Muscle	40-40	40	51
Flatfish (*Limanda aspera*)	1973—1974	7	Muscle	20-130	50	52
Chum salmon (*Oncorynchus keta*)	1980	1	Whole		5.0	53
Sockeye salmon (*Oncorynchus nerka*)	1980	1	Whole		15	53
Chum salmon (*Oncorynchus keta*)	1982	3	Whole	5.3-9.8	7.3	49
Walleye pollock (*Theragra chalcogramma*)	1982	4	Whole	9.8-13	11	49
Eastern South Pacific (off Chile)						
Cheilodactylus sp.	1978	5	Muscle	1.2-2.2	1.5	13
Merluccius australis	1977	5	Muscle	0.3-0.6	0.4	13
Brama sp.	1978	5	Muscle	0.6-1.6	0.9	13
Neophrynichthys marmoratus	1978	4	Muscle	0.2-0.3	0.2	13
Cyclorhynchus fasciatus	1978	5	Muscle	<0.1-0.2	0.2	13
Micromesistius australis	1977	3	Whole	0.11-0.33	0.19	49
Cyclorhynchus fasciatus	1978	4	Whole	0.06-0.11	0.09	49
North Indian (Arabian Sea)						
Argyrops spinifer	1976	2	Whole	0.74-1.4	1.1	49
Thryssa vitirostris	1976	3	Whole	0.93-2.0	1.6	49
South Indian (off Australia)						
Caryphaena hippurus	1980	5	Whole	0.02-0.05	0.03	49
Antarctic						
Two whole fish	1972				2.0	50
Pagothenia borchgrevinki	1981	21	Whole	0.18-0.77	0.31	46
Trematomus berenacchii	1981	5	Whole	0.12-0.24	0.17	46
Trematomus hansoni	1981	4	Whole	0.28-0.59	0.48	46
Trematomus newnesi	1981	2	Whole	0.08-0.33	0.21	46

There was a marked variation of PCB concentrations in plankton samples taken from different oceans (Table 3). PCB concentrations in Atlantic plankton were one or two orders of magnitude higher than those in Pacific samples. All the PCB data on Atlantic plankton had been measured before 1972. Although no recent PCB data on Atlantic plankton could be found, the much higher concentrations before 1972 can probably be attributed to the same reasons as for the North Atlantic surface waters where an immediate decrease of PCB concentrations has been noted since 1973. As the monitoring data show that the discrepancy of PCB concentration levels between Atlantic and Pacific samples in respect of atmosphere, surface water, fish, and mammals were less than tenfold, the current PCB concentration in

MONS 005880

Table 5
PCB CONCENTRATIONS IN THE BLUBBER OF MALE PINNIPEDS AND CETACEANS

Location	Species	Year	PCB conc. (μg/g fresh wt.) N	Range	Mean	Ref.
Arctic						
Canada	Ringed seal	1972	4	0.05—1.5	0.58	13
	Ringed seal	1972	15	1—6	4.1	54
North Greenland	Atlantic walrus	1975—1977	8	0.16—1.1	0.36	55
North Atlantic						
Newfoundland	Harp seal	1970	1		26	56
Gulf of St. Lawrence	Harp seal	1971	7	6—22	13	57
Nova Scotia	Atlantic white-sided dolphin	1972	1		37	58
Rhode Island	Striped dolphin	1972	1		39	58
Caribbean	Long-snouted dolphin	1972	1		5.0	59
South Atlantic						
Uruguay	Franciscana dolphin	1974	5	3.2—18	6.8	15
North Pacific						
Bering Sea	Dall's porpoise	1980	4	1.5—6.8	5.2	60
Japan	Striped dolphin	1978	3	22—23	22	61
	Finless porpoise	1968—1975	2	64—96	80	15
	Pilot whale		1		2.0	15
California	Common dolphin	1974—1976	10	80—300	120	15
	Pilot whale		1		14	15
Hawaii	Rough-toothed dolphin	1976	3	7.0—14	9.4	15
Eastern tropical	Striped dolphin	1973—1976	3	2.6—7.6	5.7	15
South Pacific						
Eastern tropical	Fraser's dolphin	1973—1976	1		3.2	15
	Striped dolphin		1		5.0	15
New Zealand	Dusky dolphin	1980	1		1.4	60
Antarctic						
Syowa Station	Weddell seal	1981	1		0.038	62

Atlantic plankton is assumed to be in the few nanogram per gram range on a wet weight basis.

PCB concentrations in open ocean organisms tend to be greater in the higher trophic levels. Open ocean plankton generally have concentrations of a few nanograms per gram or less. Fish samples accumulate nearly the same or one order of magnitude higher than this, while PCB concenerations in marine mammals are a further one or three orders of magnitude higher than those in fish. Such an amplification with trophic levels has been demonstrated in terrestrial and coastal aquatic environments.[63-65] We also found PCB amplification in open ocean ecosystems from the northwestern Pacific where bioconcentration factors (ratio of PCB concentrations in organisms to ambient water) were 10^3 for plankton, 10^4 to 10^5 for squid and mycotophid, and 10^7 for striped dolphin.[66] In addition to the quantitative variation of PCBs with trophic level, qualitative variation regarding PCB isomers and congeners has also become a major interest recently.

According to detailed PCB determinations in various organisms taken from the Bering Sea,[33] apparent variations were recognized in their PCB compositions (Figure 7). Although the major fractions of PCBs in surface waters were lower chlorinated biphenyls with two and three chlorine atoms, plankton and fish samples retained not only the lower chlorinated biphenyls but also fairly large amounts of penta- and hexachlorobiphenyls. Furthermore, PCBs in Dall's porpoise were composed mainly of higher chlorinated biphenyls with more

MONS 005881

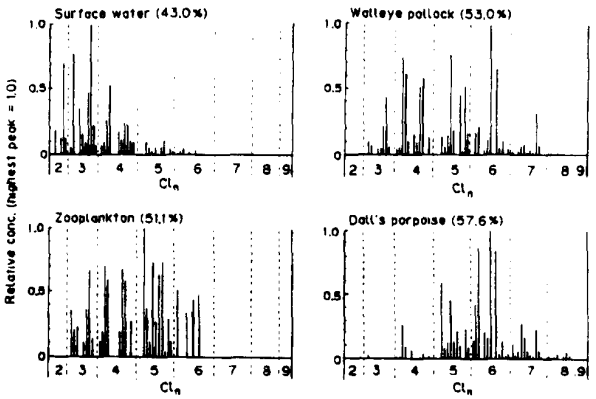


FIGURE 7. PCB compositions in surface water and organisms from the Bering Sea.[11] Parentheses show the chlorine contents. Details of each bar and Cl_n are the same as Figure 6. Dichlorobiphenyls in zooplankton could not be measured due to interfering materials.

than five chlorine atoms and a much lesser amount of lower chlorinated biphenyls. Jansson et al.[67] and Zell and Ballschmiter[68] also noted different PCB compositions in various biological samples such as fish, bird, seal, and human and they suggested that the metabolic potential inherent in organisms is a major factor for the variation of PCB compositions in different trophic levels. The PCB composition of Dall's porpoise (Figure 7) is most likely affected by a biological factor such as metabolism. However, plankton do not seem to have such an active metabolic potential. The different compositions of PCBs in plankton and surface water in the Bering Sea probably depend upon physicochemical factors. In fact, many authors support lipid/water partitioning and cell/water adsorption mechanisms as major uptake routes of PCBs by plankton,[69-72] while PCBs in those fish that are mesotrophic animals in marine food chains appear to be affected by both physicochemical and biochemical factors. It is known that the uptake of PCBs through the gills and digestive tracts in fish depends principally on lipid/water partitioning and molecular size,[73-76] whereas higher chlorinated biphenyls are accumulated more readily through gills but lesser amounts are absorbed through digestive tracts. Moreover, it is also noted that fish certainly have a potential to metabolize PCBs, but this is limited to lower chlorinated members.[76-78] The PCB composition of Bering fish (Figure 7) seems to basically reflect a result of physicochemical factors, but the relatively smaller proportion of lower chlorinated biphenyls in comparison with plankton is probably due to metabolism.

The ocean contains many species of organisms and their life spans vary considerably. These organisms more or less function as effective integrators of persistent organochlorines. The residues of these chemicals in plankton and fish which have rather short life spans reflect the present state or short-term contamination in the marine environment. By contrast, mammals, long-living animals, provide historical evidence of marine pollution in their bodies. Presently, we have no available information to trace the historical contamination by PCBs of the oceans. Organisms with long life spans may provide useful clues to the elu-

MONS 005882

cidation of the time course of PCB pollution in the ocean environment in the past and also probably in the future.

III. GENERAL CONCENTRATION LEVELS AND ESTIMATED LOAD OF PCBs IN THE OCEANS

Based on the measured data of PCB concentrations in various open ocean environments so far reported (Tables 1 to 5), PCB concentrations and loads in the world oceans were estimated and are shown in Table 6.

PCB monitoring data are not sufficient for the estimation of PCB concentration and load in the open ocean environment. In particular, there is much less data available for all environmental media and biota in the South Atlantic. Thus, we applied the PCB data of the South Pacific to the South Atlantic. Current data could not be found for North Atlantic waters. Thus, a median value of PCB data in the North Sea[33] and Sargasso Sea[34] was adopted as a general concentration level of PCBs in North Atlantic waters. There is only one paper available for estimating the PCB concentration and load in open ocean sediment, which was reported by Harvey and Steinhauer[17] and dealt with the North Atlantic Ocean. PCB concentrations in other oceanic sediments were estimated from this data and concentration levels in surface waters of the respective oceans. PCB monitoring data for plankton are extremely scarce for all oceans. Fish and mammalian data are also insufficient for the Southern Hemisphere. Moreover, we could not find any biomass data for the respective oceans, thus, there was no other way to estimate the PCB loads in organisms in each of the oceans but to describe them as a single or whole ocean.

Despite these limitations, this estimate (Table 6) provides sufficient information to understand the fate of PCBs. The total PCB load in the open ocean environment was estimated to be about 230,000 t. The major fraction of PCBs in the open ocean environment is in water, accounting for more than 99% of the total load. In spite of the fact that open ocean organisms accumulate PCBs in concentrations three to seven orders of magnitude higher than water, their PCB loads were extremely small. This is due to the relatively much smaller volume of biomass compared to the water mass. The open ocean environment in the Northern Hemisphere contains about 150,000 t of PCBs, accounting for nearly two thirds of the total load. The largest load was in the North Atlantic waters, which contained 90,000 t of PCBs. Recent estimates by the National Academy of Sciences[19] indicated that oceanic water over the North American Basin contained a maximum of 66,000 t of PCBs. This value compares favorably to our estimate of 90,000 t in the whole North Atlantic waters. Worldwide statistics regarding PCB production and use are not available. The total cumulative use of PCBs in the U.S. was estimated to be 61,000 t up to 1975.[19] Assuming the world PCB production to be twice this amount (1.2 million t), about 20% of the cumulative world production is retained in the open ocean environment. According to our estimate of PCB loads conducted in the Seto-Inland Area, Japan,[20] 12% of the total amount of the PCB used in this region was contained in the terrestrial and coastal environments. If this percentage is representative for all global terrestrial and coastal environments, it can be estimated that about 30% of the total PCB production in the world, an amount of approximately 400,000 t, has escaped into the open environment. Miller[42] noted that of the PCBs produced in the U.S., 3.6% has been degraded or incinerated. Thus, the destroyed portion of PCBs is negligible in any estimate of the world PCB load. Overall, it is estimated that about 800,000 t of PCBs are still in service, including the amounts used for electrical equipment and other products or deposited in landfills and dumps.

The open ocean atmosphere contains 790 t of PCBs at present (Table 6). If the following assumptions are allowed, (1) the land-stocked PCBs (800,000 t) disappear only through volatilization, (2) PCB concentrations in the atmosphere remain at their present level, (3)

MONS 005883

Table 6
ESTIMATED CONCENTRATION AND LOAD OF PCBs IN THE OPEN OCEAN ENVIRONMENT

Compartment mass PCB conc., load	North Pacific	South Pacific	North Atlantic	South Atlantic	Indian	Antarctic	Total load
Compartment mass							
Air (× 10^{20} m^3)[a]	70	76	38	55	56	46	
Water (× 10^{20} l)[a]	92	33	15	14	23	19	
Sediment (dry, × 10^{21} g)[a]	70	76	38	55	56	46	
Plankton (wet, × 10^{15} g)[b]			48 (whole ocean)				
Fish (fresh, × 10^{15} g)[b]			26 (whole ocean)				
Mammals (fresh, × 10^{12} g)[b]			85 (whole ocean)				
PCB conc							
Air (ng/m^3)	0.3	0.2	0.5	0.2	0.2	0.1	
Water (ng/l)	0.2	0.1	0.6	0.1	0.1	0.05	
Sediment (dry, ng/g)	0.6	0.2	1.0	0.2	0.2	0.1	
Plankton (wet, ng/g)	2.0	1.0	5.0	1.0	1.0	0.5	
Fish (fresh whole, ng/g)	10	2.0	50	2.0	2.0	0.2	
Mammals (fresh whole, μg/g)[c]	2.0	0.5	5.0	0.5	0.5	0.05	
PCB load (t)							
Air	210	150	190	70	120	50	790
Water[d]	61,000	33,000	90,000	14,000	23,000	10,000	230,000
Sediment	20	15	10	7	12	5	105
Plankton[e]							1 MP
Fish[e]			20—240 (whole ocean)				30
Mammals[e]			1—10 (whole ocean)				100
			2—200 (whole ocean)				
Total							231,165

[a] Data on the surface area and mean depth in respective oceans employed for the calculation of air mass, water mass, and sediments mass were adapted from Sugawara [9].

[b] Calculated in troposphere (10 km height).

[c] Calculated on upper 1 mm sediment layer. Sediments was assumed to contain about 50% water and have a mass density of 2.

[d] Modified from Duursma[10] in consideration of the following measured contents: plankton 95%, fish 75%, and mammals 65%.

[e] Values show the PCB concentrations regarding male specimens. PCB concentrations on whole body basis were calculated following the relationship of PCB concentrations between bladder and whole body obtained from the striped dolphin [7].

[f] PCB loads in water were estimated on the assumption of their having vertically uniform concentrations in the water column as shown by their vertical profiles in the literature [7,11].

[g] PCB loads in these organisms were estimated from the following probable concentrations: plankton 0.5—5 ng/g (wet), fish 0.2—20 ng/g, and mammals (male) 0.05—5 μg/g. The PCB load in mammals took into account that female specimens generally have lower concentrations of PCBs in their bodies than males because of parturitional and lactational losses [12,13].

[h] Median values.

MONS 005884

Table 7
ESTIMATED RESIDENCE TIME OF PCBs IN THE OPEN OCEAN MIXING LAYER (UPPER 100 m OF WATER COLUMN)[40]

Ocean	Carbon productivity (g/m²/year)[42]	Residence time (day)
Oligotrophic		
Pacific Ocean (22°05'N, 145°02'E)	50—100	130—280
Eutrophic		
Southern Ocean (64°42'S, 124°15'E)	150—250	26—44

the atmospheric residence time of PCBs is 60 days, and (4) atmospheric PCBs can become irreversibly transferred into open ocean water, then it is estimated that about 4800 t of PCBs are annually released from land-stocked PCBs and transferred into open ocean waters. This estimate suggests that, if further regulation is not enforced to ensure PCB disposal, more than 150 years are required for the complete disappearance of land-stocked PCBs and the contamination of PCBs in open ocean environments will continue during the same period. It should be noted that strict measures to prevent leakage or volatilization from land-stocked PCBs are needed and an effective technology to incinerate or destruct PCBs must be developed.

IV. PROSPECTS AND ULTIMATE FATE OF PCBs IN THE OCEAN RESERVOIR

Undoubtedly, open ocean water serves as a vast reservoir of PCBs. To predict the long-term contamination and ultimate fate of PCBs in the open ocean environment, it is necessary to know the removal rates of PCBs from the open ocean atmosphere and water. Bidleman et al.[6] reported that the atmospheric residence times of PCBs in the North Atlantic were in the range of 46 to 70 days. Recently, we reported PCB residence times in the open ocean mixing layer (upper 100 m of water column), based on our measured data of PCBs[40] and using an equation on the relationship between the organic carbon flux and the primary production rate in the world oceans reported by Suess.[43] The results are summarized in Table 7 and the detailed procedure used in the estimation is given elsewhere.[40]

The residence time of PCBs in the open ocean mixing layer was estimated to be in the range of 26 to 44 days in eutrophic oceans and 130 to 280 days in oligotrophic oceans. Supposing that the atmospheric residence time of PCBs is nearly the same over all oceans, ranging from 46 to 70 days, the residence time of PCBs in the eutrophic waters is shorter than in the atmosphere, while in oligotrophic waters it is rather longer. The different residence times between the atmosphere and the mixing layers indicate that, if the airborne PCB flux could be completely stopped, PCB concentrations in the mixing layers of both the eutrophic and oligotrophic oceans would rapidly decrease and eventually fall to zero within a rather short period. However, if the atmospheric flux of PCBs were to be kept in its present state, PCB contamination in the eutrophic ocean would be preserved at the present level, while in the oligotrophic ocean a gradual increase of PCB concentrations may occur according to the residual amounts of PCBs in the atmosphere and mixing layer. Mathematical simulation and more accurate monitoring surveys are required to validate this forecast.

Although the deposition rate of PCBs in the open ocean water column under the mixing layer is unknown, PCBs are certainly contained in deep waters and bottom sediments.[9,34,37,38,40] PCBs deposited into these environments are most unlikely to contribute to their geochemical and biochemical circulation, because the vertical mixing of deep water is extremely slow and the biomass there is very small. Thus, it can be concluded that open ocean deep water or bottom sediment serve as a final sink for PCBs.

MONS 005885

The commercial production of PCBs has now ceased in most developed countries. However, as a rough estimate, we still use about 800,000 t of PCBs on land. This amount corresponds to more than three times the total PCB load in the open ocean environment. It is, therefore, justifiable to say that the large amount of land-stocked PCBs holds a crucial key for the future trend of PCB contamination in the open ocean environment as well as in the terrestrial and coastal environments. A major effort must be made to control the discharge of land-stocked PCBs and continuous surveillance is needed to pursue the trend of PCB pollution in the open ocean environment.

REFERENCES

1. **Risebrough, R. W. and Carmignani, G. M.**, Chlorinated hydrocarbons in Antarctic birds. in *Proc. Colloq. Conserv. Problems in Antarctica*, Lawrence, P. B. C., Ed., Allen Press, Lawrence, Kan., 1972, 63.
2. **Harvey, G. R. and Steinhauer, W. G.**, Atmospheric transport of polychlorobiphenyls to the North Atlantic, *Atmos. Environ.*, 8, 777, 1974.
3. **Bidleman, T. F. and Olney, C. E.**, Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water, *Science*, 183, 516, 1974.
4. **Tanabe, S. and Tatsukawa, R.**, Chlorinated hydrocarbons in the North Pacific and Indian Oceans, *J. Oceanogr. Soc. Jpn.*, 36, 217, 1980.
5. **Atlas, E. and Giam, C. S.**, Global transport of organic pollutants: ambient concentrations in the remote marine atmosphere, *Science*, 211, 163, 1981.
6. **Bidleman, T. F., Christensen, E. J., Billings, W. N., and Leonard, R.**, Atmospheric transport of organochlorines in the North Atlantic Gyre, *J. Mar. Res.*, 39, 443, 1981.
7. **Tanabe, S., Kawano, M., and Tatsukawa, R.**, Chlorinated hydrocarbons in the Antarctic, western Pacific and eastern Indian Oceans, *Trans. Tokyo Univ. Fish.*, 5, 97, 1982.
8. **Williams, P. M. and Robertson, K. J.**, Chlorinated hydrocarbons in sea-surface films and subsurface waters at nearshore stations and in the north central Pacific Gyre, *U. S. NOAA Fish. Bull.*, 73, 445, 1975.
9. **Harvey, G. R. and Steinhauer, W. G.**, Transport pathways of polychlorinated biphenyls in Atlantic water, *J. Mar. Res.*, 34, 561, 1976.
10. **Giam, C. S., Richardson, R. L., and Weng, M. G.**, Polychlorinated biphenyls in Antarctic biota, *Antarctic J. U. S.*, 8, 303, 1973.
11. **Harvey, G. R., Miklas, H. P., Bowen, V. T., and Steinhauer, W. G.**, Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms, *J. Mar. Res.*, 32, 103, 1974.
12. **Barber, R. T. and Warten, S. M.**, Organochlorine insecticide residues in deep sea fish from 2500 m in the Atlantic Ocean, *Environ. Sci. Technol.*, 13, 1146, 1979.
13. **Tanabe, S., Tanaka, H., Tatsukawa, R., and Nakamura, J.**, Organochlorine compound residues in several species of fishes caught off Chile, *Bull. Jpn. Soc. Sci. Fish.*, 46, 763, 1980.
14. **Bowen, G. W. and Jeuhel, C. J.**, Presence and distribution of polychlorinated biphenyls (PCB) in arctic and subarctic marine food chains, *J. Fish. Res. Bd. Can.*, 32, 2111, 1975.
15. **O'Shea, T. J., Brownell, R. L., Jr., Clark, D. R., Jr., Walker, W. A., Gay, M. L., and Lamont, T. G.**, Organochlorine pollutants in small cetaceans from the Pacific and South Atlantic Oceans, November 1968—June 1976, *Pest. Monit. J.*, 14, 35, 1980.
16. **Tanabe, S., Tatsukawa, R., Tanaka, H., Maruyama, K., Miyazaki, N., and Fukiyama, T.**, Distribution and total burdens of chlorinated hydrocarbons in bodies of striped dolphins (*Stenella coeruleoalba*), *Agric Biol. Chem.*, 45, 2569, 1981.
17. **Woodwell, G. M., Craig, P. P., and Johnson, H. A.**, DDT in the biosphere: where does it go?, *Science*, 174, 1101, 1971.
18. **Ocean Affairs Board, The ultimate fate of substances that relate to the quality of the marine environment**, in *Marine Environmental Quality*, National Academy of Sciences, Washington, D.C., 1971, chap. 6.
19. **Environmental Studies Board, PCB transport throughout the environment**, in *Polychlorinated Biphenyls*, National Academy of Sciences, Washington, D.C., 1979, chap. 1.
20. **Tanabe, S. and Tatsukawa, R.**, Behavior of man-made organics in the coastal and estuarine environment, *Bull. Coast. Oceanogr.*, 19, 9, 1981.
21. **Ocean Sciences Board, Halogenated hydrocarbons**, in *The Tropospheric Transport of Pollutants and Other Substances to the Oceans*, National Academy of Sciences, Washington, D.C., 1978, chap. 6.

MONS 005886

22. **Tanabe, S., Tatsukawa, R., Maruyama, K., and Miyazaki, N.**, Transplacental transfer of PCBs and chlorinated hydrocarbon pesticides from the pregnant striped dolphin (*Stenella coeruleoalba*) to her fetus. *Agric. Biol. Chem.*, 46, 1249, 1982.
23. **Tanabe, S., Tatsukawa, R., Kawano, M., and Hidaka, H.**, Global distribution and atmospheric transport of chlorinated hydrocarbons: HCH (BHC) isomers and DDT compounds in the western Pacific, eastern Indian and Antarctic Oceans. *J. Oceanogr. Soc. Jpn.*, 38, 137, 1982.
24. **Simon, C. G. and Bidleman, T. F.**, Sampling airborne polychlorinated biphenyls with polyurethane foam — chromatographic approach to determining retention efficiencies. *Anal. Chem.*, 51, 1110, 1979.
25. **Giam, C. S., Atlas, E., Chan, H. S., and Neff, G. S.**, Phthalate esters, PCB, and DDT residues in the Gulf of Mexico atmosphere. *Atmos. Environ.*, 14, 65, 1980.
26. **Tanabe, S., Tanaka, H., and Tatsukawa, R.**, Unpublished data, 1983.
27. **Tanabe, S., Hidaka, H., and Tatsukawa, R.**, PCBs and chlorinated hydrocarbon pesticides in Antarctic atmosphere and hydrosphere. *Chemosphere*, 12, 277, 1983.
28. **Chen, P. H., Gaw, J. M., Wong, C. K., and Chen, C. J.**, Levels and gas chromatographic patterns of polychlorinated biphenyls in the blood of patients after PCB poisoning in Taiwan. *Bull. Environ. Contam. Toxicol.*, 25, 325, 1980.
29. **Oehme, M. and Stray, H.**, Quantitative determination of ultratraces of chlorinated compounds in high-volume air samples from the Arctic using polyurethane foam as collection medium. *Fresenius Z. Anal. Chem.*, 31, 665, 1982.
30. **Burnham, A. K., Calder, G. V., Fritz, J. S., Junk, G. A., Svec, H. J., and Wills, R.**, Identification and estimation of neutral organic contaminants in potable water. *Anal. Chem.* 44, 139, 1972.
31. **Junk, G. A., Richard, J. J., Greiser, M. D., Fritz, J. S., and Calder, G. V.**, Use of macroreticular resins in the analysis of water for trace organic contaminants. *J. Chromatogr.*, 99, 745, 1974.
32. **Harvey, G. R., Steinhauer, W. G., and Teal, J. M.**, Polychlorobiphenyls in North Atlantic ocean water. *Science*, 180, 643, 1973.
33. **Dawson, R. and Riley, J. P.**, Chlorine-containing pesticides and polychlorinated biphenyls in British coastal waters. *Estuarine Coast. Mar. Sci.*, 4, 55, 1977.
34. **Harvey, G. R., Steinhauer, W. G., and Miklas, H. P.**, Decline of PCB concentrations in North Atlantic surface water. *Nature (London)*, 252, 387, 1974.
35. **Olney, C. E. and Wade, T. L.**, Chlorinated hydrocarbon in the marine atmosphere and sea surface microlayer. IDOE Workshop on Baseline Measurement, May 22, 1972, Brookhaven, N Y.
36. **Bidleman, T. F., Rice, C. P., and Olney, C. E.**, High molecular weight chlorinated hydrocarbons in the air and sea: rates and mechanism of airsea transfer, in *Marine Pollution Transfer*, Windom, H. L. and Duce, R. A., Eds., Heath & Co., Lexington, Mass., 1976, 323.
37. **Harvey, G. R. and Steinhauer, W. G.**, Biochemistry of PCB and DDT in the North Atlantic, in *Environmental Biochemistry*, Vol. 1, Niagu, J. O., Ed., Ann Arbor Science, Ann Arbor, Mich., 1976, 203.
38. **Seura, E. D. and McClure, V. E.**, Chlorinated hydrocarbons in sea water: analytical method and levels in the northeastern Pacific, *Mar. Chem.*, 3, 337, 1975.
39. **Jonas, R. B. and Pfaender, F. K.**, Chlorinated hydrocarbon pesticides in western North Atlantic Ocean. *Environ. Sci. Technol.*, 10, 770, 1976.
40. **Tanabe, S. and Tatsukawa, R.**, Vertical transport and residence time of chlorinated hydrocarbons in the open ocean water column. *J. Oceanogr. Soc. Jpn.*, 39, 46, 1983.
41. **Elder, D. L. and Fowler, S. W.**, Polychlorinated biphenyls: penetration into the deep ocean by zooplankton fecal pellet transport. *Science*, 197, 459, 1977.
42. **Koblents-Mishke, O. J., Volkovinsky, V. V., and Kabanova, J. G.**, Plankton primary production of the world ocean, in *Scientific Exploration of the South Pacific*, National Academy of Sciences, Washington, D.C., 1970, 183.
43. **Lal, D.**, The oceanic macrocosm of particles. *Science*, 198, 997, 1977.
44. **Biggs, D. C., Powers, C. D., Lowland, R. G., O'Connors, H. B., Jr., and Warster, C. F.**, Uptake of polychlorinated biphenyls by natural phytoplankton assemblages: field and laboratory determination of ^{14}C-PCB particulate-water index of sorption. *Environ. Pollut.*, 22, 101, 1980.
45. **Tanabe, S., Nakagawa, Y., and Tatsukawa, R.**, Absorption efficiency and biological half-life of individual chlorobiphenyls in rats treated with Kanechlor products. *Agric. Biol. Chem.*, 45, 717, 1981.
46. **Subramanian, B. R., Tanabe, S., Hidaka, H., and Tatsukawa, R.**, DDTs and PCB isomers and congeners in Antarctic fishes. *Arch. Environ. Contam. Toxicol.*, 12, 621, 1983.
47. **Goldberg, E. D.**, Halogenated hydrocarbons, in *The Health of the Oceans*, UNESCO Press, Paris, 1976, chap. 3.
48. **Risebrough, R. W. and Vreeland, V.**, PCB residues in Atlantic Zooplankton. *Bull. Environ. Contam. Toxicol.*, 8, 345, 1972.
49. **Tanabe, S., Maruyama, K., Hiranaga, U., Matsumoto, M., and Tatsukawa, R.**, Unpublished data, 1983.

MONS 005887

50. **Glam, C. S., Richardson, R. L., Wong, M. K., and Sackett, W. M.**, Polychlorinated biphenyls in antarctic biota, *Antarctic J. U. S.* 8, 303, 1973.
51. **Muravama, H., Soma, S., Iida, A., and Takagi, M.**, PCB contents in several fish obtained in the Okhotsk Sea and the Bering Sea, *Proc. Hakodate Jr. Coll.* 17, 1, 1974.
52. **Takagi, M., Muravama, H., and Soma, S.**, PCB contents in several species of flatfish collected in the eastern Bering Sea, *Bull. Jpn. Soc. Sci. Fish.* 41, 685, 1975.
53. **Tanaka, H.**, Bioaccumulation of Chlorinated Hydrocarbons in Open Ocean Ecosystems, Master's thesis, Ehime University, Matsuyama, 1982.
54. **Addison, R. F. and Smith, T. G.**, Organochlorine residue levels in Arctic ringed seals: variation with age and sex, *Oikos*, 25, 335, 1974.
55. **Born, E. W., Kraul, I., and Kristensen, T.**, Mercury, DDT and PCB in the Atlantic walrus (*Odobenus rosmarus rosmarus*) from the Thule district, North Greenland, *Arctic*, 34, 255, 1981.
56. **Frank, R., Ronald, K., and Braun, H. E.**, Organochlorine residues in harp seal (*Pagophilus groenlandicus*) caught in eastern Canadian waters, *J. Fish. Res. Bd. Can.*, 30, 1053, 1973.
57. **Addison, R. F., Kerr, S. R., Dale, J., and Sergeant, D. E.**, Variation of organochlorine residue levels with age in Gulf of St. Lawrence harp seals (*Pagophilus groenlandicus*), *J. Fish. Res. Bd. Can.*, 30, 595, 1973.
58. **Taruski, A. G., Olney, C. E., and Winn, H. E.**, Chlorinated hydrocarbons in cetaceans, *J. Fish. Res. Bd. Can.*, 32, 2205, 1975.
59. **Gaskin, D. E., Smith, G. J. D., Arnold, P. W., Louisy, M. V., Frank, R., Holdrinet, M., and McWade, J. W.**, Mercury, DDT, Dieldrin and PCB in two species of odontoceti (cetacea) from St. Lucia, Lesser Antilles, *J. Fish. Res. Bd. Can.*, 31, 1235, 1974.
60. **Tanabe, S., Mori, T., Maruyama, K., and Tatsukawa, R.**, Unpublished data, 1983.
61. **Tanabe, S., Tanaka, H., Maruyama, K., and Tatsukawa, R.**, Ecology and bioaccumulation of *Stenella coeruleoalba*: elimination of chlorinated hydrocarbons from mother striped dolphins (Stenella coeruleoalba) through parturition and lactation, in *Studies on the Levels of Organochlorine Compounds and Heavy Metals in the Marine Organisms*, Fujiyama, T., Ed., Report for the Fiscal Year of 1980, Grant-in-Aid for Scientific Research, University of Ryukyus, Taiwan, 1980, 115.
62. **Hidaka, H., Tanabe, S., and Tatsukawa, R.**, DDT compounds and PCB isomers and congeners in Weddell seals and their fate in the Antarctic marine ecosystem, *Agric. Biol. Chem.*, 47, 2009, 1983.
63. **Woodwell, G. M., Wurster, C. F., and Isaacson, P. A.**, DDT residues in an east coast estuary: a case of biological concentration of a persistent insecticide, *Science*, 156, 821, 1967.
64. **Robinson, J., Richardson, A., Crabtree, A. N., Coulson, J. C., and Potts, G. R.**, Organochlorine residues in marine organisms, *Nature (London)*, 214, 1307, 1967.
65. **Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G.**, DDT and PCB in marine animals from Swedish waters, *Nature (London)*, 224, 247, 1969.
66. **Tanabe, S., Tanaka, H., and Tatsukawa, R.**, Polychlorobiphenyls, ΣDDT, and hexachlorocyclohexane isomers in the western North Pacific ecosystem, *Arch. Environ. Contam. Toxicol.*, 13, 731, 1984.
67. **Jansson, B., Jensen, S., Olsson, M., Renberg, L., Sundström, G., and Vaz, R.**, Identification by GC-MS of phenolic metabolites of PCB and *p,p'*-DDE isolated from Baltic guillmot and seal, *Ambio*, 4, 93, 1975.
68. **Zell, M. and Ballschmiter, K.**, Baseline studies of the global pollution. III. Trace analysis of polychlorinated biphenyls (PCB) by ECD glass capillary gas chromatography in environmental samples of different trophic levels, *Fresenius' Z. Anal. Chem.*, 304, 337, 1980.
69. **Clayton, J. R., Jr., Pavlou, S. P., and Breitner, N. F.**, Polychlorinated biphenyls in coastal marine zooplankton: bioaccumulation by equilibrium partitioning, *Environ. Sci. Technol.*, 11, 676, 1977.
70. **Pavlou, S. P. and Dexter, R. N.**, Distribution of polychlorinated biphenyls (PCB) in estuarine ecosystems: Testing the concept of equilibrium partitioning in the marine environment, *Environ. Sci. Technol.*, 13, 65, 1979.
71. **Harding, L. W., Jr. and Phillips, J. H., Jr.**, Polychlorinated biphenyls (PCB) uptake by marine phytoplankton, *Mar. Biol.*, 49, 103, 1978.
72. **Hirakawa, Y., Takahashi, M., and Nishimura, H.**, Adsorption of polychlorinated biphenyl onto sea bed sediment, marine plankton and other adsorbing agents, *Environ. Sci. Technol.*, 13, 580, 1979.
73. **Neely, W. B., Branson, D. R., and Blau, G. E.**, Partition coefficient to measure bioconcentration potential of organic chemicals in fish, *Environ. Sci. Technol.*, 8, 1113, 1974.
74. **Chiou, C. T., Freed, V. H., Schmedding, D. W., and Kohnert, R. L.**, Partition coefficient and bioaccumulation of selected organic chemicals, *Environ. Sci. Technol.*, 11, 475, 1977.
75. **Veith, G. D., DeFoe, D. L., and Bergstedt, B. V.**, Measuring and estimating the bioaccumulation factor of chemicals in fish, *J. Fish. Res. Bd. Can.*, 36, 1040, 1979.
76. **Tanabe, S., Maruyama, K., and Tatsukawa, R.**, Absorption efficiency and biological half-life of individual chlorobiphenyls in carp (Cyprinus carpio) orally exposed to Kanechlor products, *Agric. Biol. Chem.*, 46, 891, 1982.

MONS 005888

77. **Hinz, R. and Matsumura, F.**, Comparative metabolism of PCB isomers by three species of fish and the rat, *Bull. Environ. Contam. Toxicol.*, 18, 631, 1977.
78. **Melancon, M. J. and Lech, J. J.**, Isolation and identification of a polar metabolite of tetrachlorobiphenyl from bile of rainbow trout exposed to ^{14}C tetrachlorobiphenyl, *Bull. Environ. Contam. Toxicol.*, 15, 181, 1976.
79. **Sugimura, Y.**, Personal communication, 1983.
80. **Bowen, H. J. M.**, Living organisms and elementary cycles, in *Trace Elements in Biochemistry*, Academic Press, New York, 1966, chap. 4.
81. **Gaskin, D. E., Frank, R., Holdrinet, M., Ishida, K., Walton, C. J., and Smith, L. M.**, Mercury, DDT and PCB in harbour seals (*Phoca vitulina*) from the Bay of Fundy and Gulf of Maine, *J. Fish. Res. Bd. Can.*, 30, 471, 1973.
82. **Miller, S.**, The persistent PCB problem, *Environ. Sci. Technol.*, 16, 98A, 1982.
83. **Suess, E.**, Particle organic carbon flux in the oceans — surface productivity and oxygen utilization, *Nature (London)*, 288, 260, 1980.

MONS 005889

Chapter 9

WHAT IS HAPPENING TO PCBs?

Elements of Effective Environmental Monitoring as Illustrated by an Analysis of PCB Trends in Terrestrial and Aquatic Organisms

Virginia F. Stout

TABLE OF CONTENTS

I. Introduction 164
- A. Experimental Design for Trend Assessment 165
- B. Chemical Analyses for Measuring Trends 165
  - 1. The Art of PCB Analysis 165
  - 2. New Developments 166
  - 3. The Reality of PCB Data 167
- C. Issues in Biological Sampling 167
  - 1. Species 167
  - 2. Age and Size of Specimens 169
  - 3. Timing of Collection 169
  - 4. Sex 170
  - 5. Collection Site 170
  - 6. Natural Biological Fluctuations 171
  - 7. Tissues Sampled 171
  - 8. Number of Specimens and Pooling 171
  - 9. New Approaches 172
- D. Statistical Aspects of Trend Assessment 173

II. Findings 175
- A. Small Projects 175
- B. Extensive Monitoring Programs 179
  - 1. Great Lakes — Overall Region 179
  - 2. Southern California Bight 182
  - 3. Hudson River 185
  - 4. California Mussel Watch 188
  - 5. National Mussel Watch 189
  - 6. Brown Pelicans 190
  - 7. NPMP: Estuarine Organisms 191
  - 8. NPMP: Starlings 192
  - 9. NPMP: Ducks 193
  - 10. NPMP: Fresh Water Fishes 194

III. Conclusions 195

IV. Outlook 197

V. Needs 198

Acknowledgments 198

MONS 005890

References 199

ABSTRACT

Since voluntary restriction of PCB usage began in 1970, PCB levels have fallen in some areas where they were previously highest but are increasing in previously clean areas and remaining more or less constant where low levels were already noted. These findings reflect the gradual spread of PCBs from earlier hot spots such as dumps, spills, estuarine disposal sites, and waste water discharges. Biological variability, environmental fluctuation, and evolving analytical techniques obscure the detection of PCB trends. Nonetheless, until the 680,000 t reservoir of PCBs produced worldwide since 1929 is destroyed or immobilized, PCB residues will continue to accumulate in aquatic and terrestrial organisms. Complexities of PCB analysis in trend assessment and issues in biological sampling are detailed. Studies of PCB trends in gulls, ducks, starlings, pelicans, mussels, and freshwater and marine fishes are reviewed.

The presence and danger of polychlorinated biphenyls (PCBs) in the environment is not yet a dead issue, but it is one that appears to be dying quite rapidly — Thomas Maugh II, 1972[1]

22,000 kg of PCB have been burned at the [New Bedford municipal] landfill ... airborne PCB were 400–1300 ng/m³ in June 1977.[2]

In 1977, there were individual goldfish.... [in the Hudson River].... which had 40,000 to 99,000 ppm PCB per gram of lipid...[3]

...between 32 and 54 metric tons of PCBs will be transported into the [New York] estuary during the next 20 years if no remedial action is taken.[4]

I. INTRODUCTION

Since polychlorinated biphenyls (PCBs) were first identified in Swedish fish in 1966,[5] they have been found throughout the world,[6,7] even in Antarctica.[8] * Initially they were observed as contaminants interfering with the quantification of *DDT*.[9,10] By the early 1970s, they were recognized as widespread problems in their own right. Before long, PCBs in high concentrations had been isolated from numerous lakes and rivers. Marine birds and fishes also contained amounts of PCBs quantifiable by early methods.[7,11] High levels in goatfish[11,12] (*Mulloidichthys auriflamma*)** confirmed that tropical islands such as Hawaii were not free of this new environmental pollutant.

* In this review, the term PCB is used to include all polychlorinated biphenyls regardless of the extent of chlorination. A specific degree of chlorination is indicated by the last two digits; thus, PCB 1242 contains 42% chlorine by weight. As PCBs weather, a residue which initially derived from a commercial mixture such as the Monsanto Company product Aroclor® 1221, 1242, or 1248 will come to resemble a more highly chlorinated substance such as Aroclor® 1254, 1260, or even 1268. As a reminder that no implication is intended that the higher chlorinated substances were ever used in any large amounts, I prefer the terms PCB 1254 and PCB 1260 to indicate the degree of chlorination observed in environmental samples. I have used the manufacturer's designation only in the case of Aroclor® 1016 which was intentionally dumped into the Hudson River. In this case, using the term PCB 1242 would be less accurate. Residues in the Hudson River are more appropriately related to Aroclor® 1016, a special formulation containing 42% chlorine but lacking the highly chlorinated components of Aroclor® 1242 itself. This chapter concerns PCBs, but not polar metabolites. Monitoring programs up to now have only considered the hydrophobic parent chlorinated hydrocarbons.

** Scientific names are included the first time each species is mentioned.

MONS 005891

This chapter will discuss the issues involved in determining PCB trends over time. More than a decade has passed since quantitation of PCBs became routine. Techniques suitable for long-term assessment will be defined. Data from diverse laboratories will be summarized. These findings will be integrated into an overall picture of past and present PCB pollution. The prognosis for the future and recommendations for further research will be described.

A voluminous literature on PCBs has developed over the past 15 years. I have made an intensive and extensive search to find records suitable for this chapter. Numerous scientists have been generous in providing unpublished manuscripts and even raw data. Some reports are not readily available, while others may have been overlooked. Even with these limitations, distinct patterns have emerged that provide a clear picture of the present status of PCBs.

A. Experimental Design for Trend Assessment

Holden[13] described some of the parameters for an early international environmental monitoring program. These included determining the extent to which collaborating laboratories could both identify and quantify organochlorine residues. Protocols were also designed to assure representative samplings of marine, freshwater, and terrestrial ecosystems. Exact species were listed, although even within individual countries, no species was universally available. As far as possible, annual samples were to include 25 specimens of the same age, size, and sex, with the animals to be analyzed individually. Fishes were to be collected before spawning and birds before fledging. Holden even noted the importance of government support in mounting an effective monitoring program. Although sampling requirements were explicitly detailed, in practice the described protocol often was not followed exactly.

These early specifications are the foundation of modern monitoring programs, and they contain hints of difficulties in their implementation. General requirements for designing and implementing environmental studies were defined in 1980.[153] This subject still merits reflection, for again in 1981 Veith et al.[14] reiterated the need for stringent requirements in trend-monitoring programs including "precise methods for measuring small differences in concentration, and, to minimize biological variability, a fairly rigid procotol with respect to species and size". In the following section, some of the problems will be described in greater detail.

B. Chemical Analyses for Measuring Trends

1. The Art of PCB Analysis

Quantitation of PCBs will be discussed only insofar as it relates to trend assessment. Electron-capture gas chromatography (GC) has remained the standard tool for quantitation despite operational difficulties. PCB analysis started as an art with the analyst deciding how and what to quantify, e.g., how to draw baselines, what to eliminate because of interference, and what standard to use as a reference.

The complexity of PCBs challenged even the choice of standards and quantitation techniques. Commercial mixtures used as standards yielded numerous chromatographic peaks, from one to ten of which were chosen for quantitation. Either the height or area of peaks was measured. The PCB content would vary widely depending on the choice of peaks, baselines, and standards,[11] especially in weathered samples. Furthermore, patterns of peaks might differ from one gas chromatograph to another, environmental samples by no means provided consistent patterns, and the choice of peaks was changed sometimes in order to quantify unusual samples more accurately.

As computers were introduced, a more exact regimen was established. Arbitrary use of automation has not been a panacea, however, since it can also lead to inaccurate results when samples do not conform to a pre-established pattern. Capillary-column GC introduced another degree of sophistication, which gives hope of improved accuracy. Quantitation has not yet improved, however, according to an interlaboratory collaborative study. Even more

MONS 005892

discouraging, some components were *not identified correctly*.[15] After more than a decade, basic identification of pollutants in environmental samples is not assured.

In addition, both the proportion and quantity of components in an extract vary with extraction procedures. Diverse techniques are used for extracting PCBs from environmental samples because each type of sample presents its own specific analytical challenges. Methods have evolved also when standard procedures designed for surveillance of food products proved impractical for large-scale monitoring programs.[16]

International cooperative studies have measured the real effect of such analytical problems. An early study[17] reported a ± 30 to 60% coefficient of variation (C.V.) for wildlife samples requiring complex processing. In a subsequent study, 14 laboratories in 10 nations provided a total of 18 analyses on the same sample from a dead cormorant (*Phalacrocorax carbo*) found in the Netherlands in 1970. Seven standards were used for quantitation: PCB 1250, 1254, 1260, and 1264, mixtures of PCB 1250 and 1260, as well as DDE and dieldrin.[18] The wide variety of standards reflected early attempts to quantify complex mixtures and also batch variations of PCB formulations, sold by chlorine content rather than exact structure. Analysts chose the standard corresponding most closely to each sample, but matching of chromatographic profiles was a time-consuming process, sometimes compromised in routine monitoring. The C.V. for all results on the cormorant sample was ± 20.7%. This figure probably represents the best outcome up to that time since participants in such a study may well have been more skilled than other analysts, and collaborative study data reflect optimum performance resulting from extra care. A later oyster homogenate containing 0.3 ppm dry weight PCB 1254 showed a 55% C.V. among 14 laboratories,[18] even though data from 12 other laboratories were excluded because the levels were reported as below the detection limit or different, unknown, or mixed standards were used.

More recently, agreement between laboratories seems to have improved, though data may still vary up to 100-fold between laboratories.[19] Goldberg et al.[20] found a mean C.V. of 8.8% (range of 0 to 15%) for three samples. By 1980, C.V.s[21] for six samples had declined to 5.7% (range 1.5 to 9.7%). In contrast, an interlaboratory calibration of two urban air *extracts* showed C.V.s among nine participants ranging from 26 to 39%, even though the use of extracts had already eliminated one source of variability,[22] the extraction process itself. Improvement is selflimiting, however, since as analyte concentration decreases, the C.V. increases.[23] Perhaps quality assurance will benefit from the statistical evaluation described by Schmitt.[24]

2. New Developments

Chlorinated hydrocarbon studies at a remote site uncovered another problem in the late 1970s. Lake trout (*Salvelinus namaycush*), fat lake trout (*S. namaycush siscowet*), and lake whitefish (*Coregonus clupeaformis*) from Isle Royale contained elevated levels of several chlorinated hydrocarbon pollutants, compared to other Lake Superior sites closer to urban development. Initially, Isle Royale, located in the northern apex of Lake Superior, was chosen as a control site for environmental studies of Lake Superior because the island has been a national park since 1940[25] and it had never been logged nor contaminated by motor vehicles. Pollution of this supposedly clean site was attributed to atmospheric fallout until a better explanation surfaced. Extracts contaminated with toxaphene had been quantified inaccurately, perhaps as the result of automated analyses without careful examination of GC patterns.

This finding signaled a soon-to-be-discovered widespread difficulty, interference by multicomponent pollutants, including chlordane as well as toxaphene. (Although chlordane is a single compound, the commercial formulation contains several byproducts.) Once toxaphene and chlordane were rather uncommon pesticides, but more recently they have substituted for the banned DDT. Use of these compounds, which mimic PCBs in the usual

MONS 005893

separation procedures expanded without being noticed by analysts, because like PCBs they are mixtures appearing as a mass of mainly small peaks in GC traces. Ironically, PCBs themselves were identified in environmental samples because they interfered with DDT quantification. Now other interferences put a cloud on PCB trend assessment. The extent of interference, which undoubtedly varies from region to region has yet to be assessed. In the late 1970s, analysts were still searching for separation methods suitable for routine analysis. As PCB analysis was already expensive, each additional step would further constrain the already limited number of analyses that could be funded.

Another problem is the issue of evolving methodology. Capillary column GC brought indication of decreasing PCB levels in Lake Superior, but further study showed that the reduction was an artifact of a new technique, which resolved components previously assumed to be entirely PCBs.[26] Although it is impossible to freeze techniques for contaminant analysis, nonetheless it is difficult to compare current data to those obtained by older methods.

3. The Reality of PCB Data

In assessing trends, one must remember that PCB residues are complex mixtures. In the first place, PCBs are not exact substances, because the composition of each formulation varies with manufacturing conditions. Moreover, individual PCBs behave in different ways. For example, the lower molecular weight compounds evaporate more rapidly and also tend to react and degrade more readily. Even among the more highly chlorinated components, individual compounds do not behave and react uniformly.

To compare residue levels over the years is, in a sense, like asking whether we now have as many Winesap apples as we previously had MacIntosh apples. Numbers can be compared, but what do the answers mean?

As new methods are implemented, efforts are made to assure the comparability of data. Ideally we should be comparing the level of specific components today with levels in past years. Frequently that is not feasible, because most PCB data represent sums of several components. Even the purported identities of individual compounds have evolved with the development of techniques.

Assuming all the data are correct, interpretation is still an issue. If PCB 1260 starts appearing in fish somewhere, does it announce yet another PCB dump or a carefully hidden spill? Or does it mean that an old source of PCB 1242 or 1254 is slowly dissipating, leaving in its wake a tattletale, the high-boiling components which resemble PCB 1260?

I have described these analytical difficulties in order to support the restrictions I have placed on samples chosen for this review and to acknowledge imprecision in the process. It is vital to take stock of progress in an effort to rid the world of PCB pollution, but it is also important to spell out the limitations of trend assessment. Comparison between laboratories is usually a questionable process,[27] except in special cases where interlaboratory collaborative studies assure comparability.[28] Comparison between years within a single laboratory is more practical as long as a single quantitation technique is used and quality assurance programs are maintained.[27]

C. Issues in Biological Sampling

Over the years, numerous laboratories have analyzed for chlorinated hydrocarbons including PCBs. Many authors compare their data with published reports. Unfortunately, as Willford[29] has noted, "results frequently contradicted each other and sampling programs lacked the intensity, the uniformity of sampling procedures, and the continuity that permitted evaluation with time...." In this section, I shall address aspects of biological variability that affect the suitability of data for trend assessment.

1. Species

Organisms differ in the rate and extent of accumulation of chlorinated hydrocarbons.

MONS 005894

Feeding habits, longevity, lipid content, metabolism, and migratory patterns are the kinds of factors that can contribute to marked intra- and interspecies differences. Twenty-year-old fish, for example, may reflect pollution over the entirety of their lives. Birds may migrate thousands of miles and accumulate pollutants wherever they live. Juvenile salmon, born from pea-sized lipid-filled eggs, carry forth a small contaminant burden from their mothers, while sole, born from tiny eggs, are nourished from their surroundings at a much earlier stage of development. Marine mammal pups receive a large dose of chlorinated hydrocarbons[31] in the fat-rich milk. Preening birds lose PCBs through the uropygial gland[31] but can also ingest PCBs from their feathers.

Over the years, a number of species have been chosen as indicator organisms. Butler[32] used mollusks, especially oysters, as sentinels of general pollution in estuaries. Oysters contain concentrations of organic contaminants as much as 50,000 times as high as those in the surrounding water, in which such compounds are nearly insoluble. Bioaccumulation expedites identification and quantification just because the higher levels can be measured so much more easily.

Mussels[20,28,33,34] have become common monitoring organisms because they are readily available in adequate numbers over a wide geographical range. Such sessile organisms have the advantage that they stay in one place. Perhaps for this reason sampling variance was considerably lower than analytical variance in the California Mussel Watch.[35] Compared to PCB determinations in water or sediment, PCB levels in mussels indicate bioavailability directly since contaminants are already in the living organism.[36] Mussels absorb and eliminate chlorinated hydrocarbons at known rates.[37,38] They reflect exposure over a distinct time interval. In contrast to fishes and crustaceans, mussels possess minimal enzymatic capability to metabolize contaminants. Perhaps for that reason, they can survive even in highly polluted environments. They can be transplanted readily and can be retained in bags or cages when suitable support is lacking.[39] They tolerate depths of at least 60 m.[40] These properties favor the use of mussels to monitor around sewer outfalls and in highly polluted harbors. Furthermore, consumers are directly concerned about the wholesomeness of wild and cultivated mussels, because these popular sport and commercial species live in potentially contaminated environments.

Estuarine contaminant data must be interpreted carefully. Intertidal animals sometimes are exposed to contaminant levels much higher than those present throughout the whole water column. Chlorinated hydrocarbons concentrate at the air/water interface in a lipid-rich monolayer.[41] Furthermore, at times of high runoff, organic compounds bound to particulate matter are carried in the surface layers where salinity is lowest. Consequently, mussels held below the surface may provide a more representative picture of PCB contamination. On the other hand, Richardson and Waid[21] found larger mussels collected 5 to 7 m below the surface contained much higher levels of PCBs than very small surficial specimens (0.12 to 0.21 ppm dry weight vs. <0.010 ppm). They suggested that size and rate of accumulation may have contributed to these differences. In the vicinity of a sewer outfall, however, PCB levels were highest at the greatest depth, i.e., closest to the point of their release.[42]

PCBs also concentrate in organic-rich sediment, which accumulates at the water/sediment interface. As a result, animals which live and feed on the bottom will receive greater exposure than animals living or foraging even a small distance above the sediment.

Numerous species of fishes have been chosen for monitoring free-ranging aquatic organisms. Often practical considerations are decisive, such as the sampling of commercially important species to ascertain their wholesomeness. Wide ranging species which are readily available in adequate numbers are taken in preference to more sedentary, but elusive or uncommon fishes. Several species classified only as bottom dwellers or predators[43] were selected for the U.S. National Pesticide Monitoring Program, because no single species is available at all 109 freshwater stations surveyed.

MONS 005895

Fishes accumulate PCBs rapidly[44,45] but do not depurate them in measurable amounts.[46] Any apparent loss results from spawning or dilution through growth. Thus, the total body burden of PCBs reflects a time-averaged composite of exposure throughout life. To lessen the influence of long-past exposure, Butler and Schutzman[47] chose juvenile estuarine fish as indicator organisms. Fish less than 1-year-old contain contaminants from two possible sources, carry-over from parents and exposure during at most 1 year of life. For the most part, they reflect current exposure. One exception is juvenile dogfish (*Squalus acanthias*); this ovoviviparous species transfers a substantial burden to the next generation from its large eggs.[48]

Among terrestrial organisms, herring gulls (*Larus argentatus*), starlings (*Sturnus vulgaris*), and ducks were chosen because of availability and widespread distribution. Variability between specimens reflects individual feeding habits as well as the obvious ability of birds to travel. The gulls were also studied because they experienced reproductive difficulties on Lake Ontario.[49]

Brown pelicans were monitored in several areas mainly because they were disappearing in the late 1960s and early 1970s. The extent of sampling was, however, limited by the necessity of maintaining the dwindling stocks.

2. Age and Size of Specimens

The ideal sample would include specimens within specific size and age distributions. Unfortunately such samples rarely exist. Variations in weather, food supply,[50] pressure from predators, to name just a few factors, can contribute to fluctuations in size and abundance of animals. Aging in the field is not practical and analyzing enough specimens to assure the correct age distribution is too expensive. Samples of fishes have been restricted to fish less than 1 year old[47] and to a limited size range.[29] Alternatively, fish from a broad range of sizes and age have been compared[51,52] and size and age included in data comparison. Organic contaminants generally increase with age in fish[53] by a multiplicative factor.[54] Holden[13] suggested nestling birds as suitable indicators of terrestrial contamination. Alternatively, adult birds or their eggs have been studied.

Mussels are usually selected from a narrow range of shell lengths; aging is not currently possible.[20] In early mussel studies, no effects on contaminant levels were noted from divergent growth rates. Perhaps flow rate, water temperature, salinity, and available nutrients influenced growth only to a minor extent or canceled each other enough that they were not detected initially.

3. Timing of Collection

Farrington et al.[28] recently reported a two- to fourfold uncertainty in contaminant levels in mussels resulting from seasonal variability. Mussels from Narragansett Bay, R.I., and Bodega Head, Calif., exhibited different periodicities and magnitudes in contaminant levels. What causes these fluctuations? Changing biological and biochemical activities of mussels themselves or associated organisms, as well as changing concentrations and bioavailability of pollutants in the environment, contribute to seasonal fluctuation.

Weather can affect organisms in several ways. Some species reproduce only at specific light intensities or at critical temperatures. Climatic conditions alter the availability of food supplies. Heavy precipitation and rapid thawing alter water flow, salinity, and contaminant burden. Since the weather is not controllable, researchers can only remain mindful of its influences.

The life history of individual species determines the optimum period of collection. Both breeding status and weather influence PCB levels.[55] Regular sampling at the same stage of reproductive development increases the consistency of samples. Organisms which increase lipid stores preparatory to breeding transfer PCB-laden lipids to their spawn. The seasonal

MONS 005896

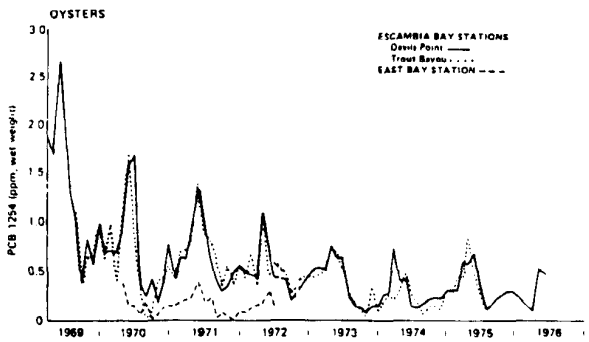


FIGURE 1. Annual fluctuation in PCB content associated with oyster (*Crassostrea gigas*) reproduction. In the spring, oysters accumulate lipid and lipophilic PCBs which are excreted again with the spawn. (Modified from Wilson and Forester [36])

fluctuation associated with oyster reproduction[36] is shown in Figure 1. Because fishes eliminate chlorinated hydrocarbons mainly through reproduction, collection at different reproductive stages would reflect different types of contamination. Correcting for order of egg laying in common terns (*Sterna hirundo*) is necessary since the PCB content decreased 20% from the first to the third egg in a clutch.[37] Similarly, repeated spawning could alter PCB levels in fishes.

Beyond the more obvious factors which influence the consistency of sampling, the well-being of endangered species must also be considered. Brown pelicans and marine mammals along the California coast often abandon their young when disturbed. Only after the young have become independent are the rookeries approached to collect dead specimens. Thus, fresh eggs from the eastern brown pelican (*Pelecanus occidentalis carolinensis*) can be taken throughout the breeding season without ill effects on the young. In Texas[38] and in California, however, pelican (*P. o. californicus*) eggs are collected after the young have left the nest.[39] These samples are obviously atypical because they are confined to eggs which failed to hatch for lack of fertility, viability, or suitable incubation. Such specimens introduce further variability because loss of water and metabolic processes during incubation influence residue levels.

4. Sex

The sex of specimens frequently influences data.[40,41] Females of several species eliminate PCBs through reproduction. Salmon, pelicans, gulls, and terns lose chlorinated hydrocarbons through egg production. Marine mammals lose them by lactation.[30] Each species is unique, however, since chlorinated hydrocarbon levels in the roach (*Leuciscus rutilus*) showed no correlation with sex, age, or size in a set of 95 specimens.[35] The choice of sex, then, depends on the aim of individual projects.

5. Collection Site

Both pristine and polluted sites contribute useful data for trend assessment. Presumed "clean" sites in developed countries often receive unsuspected pollutants via aerial transport,

MONS 005897

runoff, clandestine dumping, or accidental spills. Cities, harbors, and in-shore areas contain high concentrations of PCBs from direct and indirect sources. Agricultural, sylvan, and open water areas reflect average burdens from numerous diffuse sources. Estuaries may be expected to receive contaminants in proportion to the intensity of human habitation.[62] They are monitored as nurseries for aquatic species[63] and as popular sports fishing areas.[64] Analyses of samples from truly pristine sites provide baseline data to be related to more polluted areas and to signal future increases in pollution. Data from highly polluted sites reflect the response of the environment to high levels of contamination, while studies at sites without intense or direct pollution are useful for predicting long-term progress.

Furthermore, the foraging and migratory habits of animals must be considered in choosing sampling sites and evaluating data. Only stationary plants[64] and sedentary or caged animals reflect pollutant levels at unique locations. Diurnal movement, for example, can expose organisms to significantly different levels of contaminants, and animals collected at different times of day or year may represent different populations. Tides and currents may disperse pollutants in unforeseen ways.[1,32] This brief discussion is intended to suggest the efforts necessary to obtain consistent samples — and to acknowledge that sometimes even these are unavailing.

6. Natural Biological Fluctuations

Short- and long-term fluctuations in fishery stocks and other wildlife populations[65] influence the levels of contaminants in complex but unpredictable ways.[66] For instance, the oil content of menhaden decreased markedly in recent years.[67] Chlorinated hydrocarbon concentrations in an organism may depend on lipid content,[35] partition equilibria, or extent of exposure. Assuming a specific total PCB content or burden, a change from 8 to 2% oil would quadruple the PCB concentration in the contained oil. Unless the mode of accumulation is defined, monitoring oil or individual tissues may not reflect environmental levels accurately. Even more of a problem, when animals disappear completely from their usual haunts, sampling fails and a prescribed sampling pattern is disrupted. The intrinsic variability of biological samples can be allowed for, but not entirely eliminated by appropriate design of monitoring programs. Biological variability is one of the main factors obscuring detection of new trends.

7. Tissues Sampled

The purpose of a study often dictates the type of sample. The National Pesticide Monitoring Program analyzed whole fish to assess the effect of contaminants on wildlife which consumed them.[68] Other studies[39,69] used muscle or fillets with skin in an effort to determine the safety to human consumers. Stout et al.[70] included whole fish and fish meal and oil to evaluate the impact of contaminants throughout the menhaden (*Brevoortia tyrannus* and *B. patronus*) fishery. Though sometimes done, comparing data from different tissues is not meaningful, unless the relationship for accumulation of contaminants in the various tissues has been documented. Preliminary data for fish muscle and liver suggested a complex relationship.[71]

8. Number of Specimens and Pooling

The number of specimens is dependent on the variability and the desired level of discrimination. Individuals in a single collection sometimes show nearly a 100-fold range in PCB content.[12,72] Furthermore, the distribution of organochlorine residues among individual specimens is often skewed.[17] To detect a 75% difference between residue levels, 10 specimens would suffice, but to detect a 25% difference, 50 specimens are necessary. Holden[13] recommended 25 specimens as an appropriate sample size. Gordon et al.[73] detailed the number of specimens required for varying degrees of resolution of several trace metal pollutants, data that can enhance the understanding of sampling problems for trace organic analysis as

MONS 005898

well. Butler[68] documented the combined variability of individual organisms and a river environment to have a standard error of 15 to 30%.

Jensen and Lassen[74] investigated problems of sample size and stratification of critical sample parameters. They calculated the effect of length stratification, i.e., choosing specific numbers of specimens in several length intervals, as compared to random sampling on the number of specimens required in a single sample. They did not advocate keeping biological variables constant because the influence of various parameters is not thoroughly documented. Instead they recommended continuing surveillance of the relationship between biological variable and contaminant levels. They determined that variance in chlorinated hydrocarbon values in one set of herring data contributed a 1.07- to 1.14-fold increase in the number of specimens needed in a random sample compared to one which took into account variations in length. In a sample of cod, the factor increased to 1.56 for PCBs in liver. Using these calculations, Jensen and Lassen[74] suggested that annual samples of 20 fish analyzed individually would detect a 10 to 20% annual change over a 5-year period. If the ratio for random vs. stratified-length variability increases substantially, the sample size would also need to increase to detect the specified trend. Likewise, if the trend is smaller, a larger sample size would be necessary to observe a statistically significant trend.

Not only statistical considerations, but also availability of specimens and cost of analyses influence the choice of these sampling parameters. Limited numbers of specimens of endangered species are available. Mussels, on the other hand, are plentiful in many regions of the world and easy to collect and handle in large numbers. Analysis of individual specimens, however, escalates the cost of monitoring. When limitations in funding restrict the number of analyses, compositing specimens becomes a necessary compromise. Nonetheless, the variability of individual specimens and their environment must be determined as frequently as practical at every site[73] to assure the accuracy of trend assessment. Where it is not practical to determine the variability of individuals, replicate pools at least provide pool variances. Whatever the experimental design, a consistent pattern of sampling and analysis simplifies statistical treatment of data.

9. New Approaches

Kaiser[73] has developed a new approach to trend assessment. He used interspecies contaminant quotients to compensate for background residue levels previously in biota.

$$\text{Quotient} = \frac{\text{PCB concentration in host}}{\text{DDT concentration in host}} - \frac{\text{PCB concentration in parasite}}{\text{DDT concentration in parasite}}$$

He evaluated chlorinated hydrocarbon data from sea lamprey (*Petromyzon marinus*) and the associated host lake whitefish from Lakes Huron and Michigan. Trends in the original data were obscured because residue levels of individual specimens within a single catch varied widely (0.24 to 14 ppm* PCBs in whole fish) with a mean and standard deviation of 0.50 ± 0.30 in lake whitefish and 2.2 ± 4.2 ppm in lamprey. For the PCB:DDT ratio, the variation was much reduced to 1.9 ± 0.65 in lamprey. Kaiser[73] considered the use of ratios as a kind of normalization, akin to an internal standard. Using the new technique, he found that DDE and PCBs were both increasing in the two Great Lakes, while several other chlorinated hydrocarbons appeared to be decreasing.

* PCB concentration is reported on the basis of the tissue as received or wet weight, unless otherwise indicated. Dry weight means related to the weight after drying to remove water. Fat basis or lipid weight relates PCB residues to the fat content of the tissues. It is not meaningful to compare data reported on different bases. At the same time, data are not always available to convert to a common basis. Consequently, all data are reported as originally published. (See Section II.)

MONS 005899

This concept requires further validation. All chlorinated hydrocarbon levels are not necessarily related to each other; the correlations of ratios may be a mere coincidence. Furthermore, since lampreys parasitize several species with as yet undefined organochlorine uptake ratios and interactions, interspecies ratios may not be as consistent as in this initial investigation. Nonetheless, data for lake trout and lake whitefish collected at nine sites in Lake Superior[5] did support the thesis. If validated, this technique will allow trends assessment with many fewer specimens by compensating for variability. Another application of contaminant ratios compared PCB levels of several species of plants at polluted sites with corresponding background PCB levels.[64] Perhaps this could be applied to stationary animals as well.

D. Statistical Aspects of Trend Assessment

What is the appropriate measure of central tendency? Some authors choose to report means based only on quantifiable values. Any or all values below either the quantitation limit or the detection level are ignored. Such a system overestimates the mean and to my mind misrepresents the picture, even when footnotes describe the methods of handling data. When this practice exaggerates the situation grossly, it leads to misinterpretation by the general public and does a disservice to environmental scientists.

A greater issue arises from assessing trends from averaged incidence rates alone. After collecting 38,000 fish and analyzing 1524 composites, the National Pesticide Monitoring Survey of estuarine fishes combined data for 144 estuaries into brief summaries for each state. New York State was reported to have a 63% incidence of quantifiable PCB residues based on sampling of three estuaries, while North Carolina had a 9% incidence based on 19 estuaries. Washington State reputedly had PCBs in 17% of its samples, even though none of the 128 samples from five estuaries contained PCBs and all 27 from one highly polluted river contained quantifiable levels. By the same logic, Washington State ranked highest in PCB level with a mean of 1.67 ppm, while *83% of all samples contained <0.05 ppm* PCBs.[47] Estuary-by-estuary analysis would be a more appropriate method of evaluating this massive body of data. Naming polluted estuaries and tallying the number in each state would be more meaningful than impugning whole states on the basis of single hot spots. In place of simple inspection, analysis of variance or some other statistical test is needed to determine any trend in this body of data.

Lassen[18] proposed substituting half the detection limit for observations below the detection level as long as they represent no more than 5% of the total number of values. When a major proportion of values was zero, he felt it was not meaningful to compute contaminant relationships. Alternatively, the National Pesticide Monitoring Program fresh water fishes study normalized lipid values by an angular transformation and concentration values by log transformation of the residue value + 1.0,[48] i.e., log (x + 1).

In their studies of pollutants in herring gull eggs from the Great Lakes, Gilman et al.[49] found not only skewed distributions of residue levels, but also a variation in direction of the skew for different contaminants. Consequently, they found the use of either arithmetic mean and confidence intervals or the assumption of log normality and geometric mean inappropriate as descriptions of central tendency. Furthermore, they avoided assigning absolute values to trace amounts because of the bias introduced by this process. They concluded that the median and range were accurate descriptive statistics regardless of the shape of the residue distribution and allowed direct inclusion of trace values. Nisbet and Reynolds[37] observed that the extent of the positive skew is not consistent as is evident from a comparison of the geometric and arithmetic means of tern eggs (Table 1). Individual data sets may determine the best descriptors, but lack of standardization then precludes comparison with other data.

Beyond these descriptive statistics, how have yearly data been evaluated? Schmitt[43] sum-

MONS 005900

Table 1
COMPARISON OF GEOMETRIC AND ARITHMETRIC MEANS OF PCB RESIDUES IN COMMON TERN EGGS AT DIFFERENT SITES[37]

		Conc. in ppm. fresh weight			
Year	No. of eggs	Geometric mean	Arithmetric mean	SD	Range
1973	10	5.3	5.4	1.3	4.0—8.5
1975	11	19	20	7.9	12—40
1976[a]	8	15	22	17	2.1—53
1976[b]	8	4.0	8.9	15	1.5—45

Note: ppm: μg/g fresh weight; PCB 1254 + PCB 1260.

[a] Same station as 1975 data.
[b] Different station from preceding entry.

marized problems in applying statistical tests to contaminant residue data. He reminded the reader that no statistical approach is automatically correct. The objectives of a program and perspectives of those conducting the research influence the choice of statistical techniques. The National Pesticide Monitoring Program duck wing survey used *t*-tests for each "data pair", presumably each state, in a single flyway. Only pairs with detectable levels in 50% of all pools were compared.[77] Dropping data is a questionable procedure. Conclusions based on 40% of a data base cannot assess the whole picture.[77] The *t*-test is seldom applicable for trend assessment. With numerous stations and years, analysis of variance is preferable.

Nonparametric statistics allow testing of unequally sized samples and skewed data. Nisbet and Reynolds[37] and Gossett et al.[78] used the Spearman rank correlation coefficient to assess temporal trends in their data. The Mann-Whitney U-test,[79,80] the Kruskal-Wallis analysis of variance of ranks,[78] the Wilcoxon matched-pair signed-rank test,[81] the Friedman two-way analysis of variance,[82] and the Kramer multiple range test[83] have also been used for evaluating PCB trends. Scientists involved in trend assessment do not always understand the subtleties of statistical tests. For example, destructive analytical techniques such as PCB analysis cannot meet the requirements of the Wilcoxon test. It was designed for testing a single system under different conditions rather than similar populations in different years.

Schmitt[43] detailed a procedure for applying a partially nested factorial analysis of variance technique. He tested this method with 6 years of data from the National Pesticide Monitoring Program for fresh water fishes. He chose 15 stations which were sampled in each year and were consistently analyzed by a single method. Two- and three-way factorial techniques were compared with the partially nested factorial scheme. The effects of uneven replication and random vs. fixed location effects on a nationwide monitoring program were considered. Location and temporal differences were shown for PCB 1254 by all techniques, but were changing in a similar fashion at all 15 stations. Partially nested factorial analysis resolved species differences, but three-way factorial did not distinguish between predators and bottom-dwellers. These findings suggest differences between species at a single location, but not between species types.

This study[43] showed the complexities in analyzing a seemingly simple set of data. These included non-normality, unequal sample numbers, broad-ranging variance, multiple species, and inconsistent patterns at each site. The resolution of trends probably was enhanced by compositing specimens because individuals vary considerably and composites unavoidably underestimate variability. The data set used by Schmitt[43] comprised samples from sites with a history of pollution. To the extent that the data were influenced by point-source discharge,

MONS 005901

the detailed conclusions may not relate to sites with diffuse contamination. The method has also been applied to the whole 1976 to 1979 data set.[24] Partially nested factorial analysis represents a significant development in pollution assessment.

Multivariable linear regression (MLR) is another recent technique for evaluating contaminants in fishes. This procedure takes into account parameters such as length, weight, age, sex, season, area, and year as well as interactive effects such as season-year and length-season-year. A brief description of findings for metals will warn about the pitfalls of extrapolating data. A log-linear model appeared to yield a more normal distribution than a simple MLR model.[76] For cadmium, copper, and zinc in three species of fishes from the vicinity of a Greenland lead and zinc mine,[64] significant effects from year to year were observed, but no temporal trend was evident. Length, season, and year interacted but not consistently. Since interactive effects were difficult to quantify, time trends were hard to prove. Mercury from industrial pollution seemed to affect flounders differently near a point source than at greater remove. Near a former pesticide factory, no relationship between biological parameters and mercury levels in fish was observed, but year, length, and age relationships were evident further away.[93]

Scott et al.[66] compared rectilinear and interactive MLR with analysis of covariance. They were looking for less costly ways of determining time trends in resident fish. They tested predictor variables as a way to reduce variance. MLR was somewhat effective for metals but not for PCBs. Individual cod (*Gadus morhua*) did not respond to environmental contaminants in a consistent manner. MLR substantiated rather than eliminated the need for a range of sample sizes for effective monitoring.

These findings confirm the difficulties in extrapolating contaminant data from species to species, site to site, or substance to substance. They also show that statistical evaluation for trend assessment still needs refining.

II. FINDINGS

A. Small Projects

Studies limited in scope will be discussed first followed by more extensive programs. Comparison between laboratories remains uncertain and will not be attempted. Some reports depended on data from more than one laboratory. Such studies will help illustrate pitfalls and limitations of such interlaboratory comparisons.

A New Jersey salt marsh provides unusually early data. Clapper rails (*Rallus longirostris*) killed during a hurricane and contemporary samples of fishes and invertebrates were frozen until they were analyzed with samples collected 6 years later. Moisture determinations showed no dehydration during storage. Fauna in this salt marsh exhibited no PCB trend in the whole ecosystem. Instead, PCB levels in the rails increased 160% between 1967 and 1973, whereas levels decreased more than 86% in three species of fishes. In all three sets $p < 0.05$, according to two-tailed Wilcoxon two-sample tests.[67] The changes in both directions are large enough that discounting them would seem unjustified. They may result from transfer of PCBs from lower to higher trophic levels. Whatever the cause, these findings emphasize the complex characteristics of any natural site.

The presumption in discussing trends in PCBs in biota is that, eventually, as PCB usage and disposal cease, the levels in biota will decline. Often wildlife respond variously to PCB pollution. Three species of seabirds from eastern Canada showed no clear trend from 1972 to 1976. Only three of seven sets of egg data showed changes ($p < 0.01$): two decreases and one increase, one for each species.[69]

Wilson and Forester[26] studied the fate of Aroclor® 1254 after an accidental leak from an industrial site along the Escambia River in 1969. The PCBs dispersed more than 20 km downstream into Escambia Bay near Pensacola, Fla., where they accumulated up to 2.7

MONS 005902

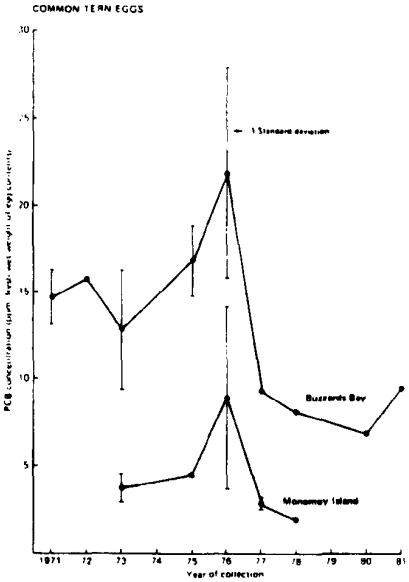


FIGURE 2. PCBs in common tern (*Sterna hirundo*) eggs from Buzzards Bay and Monomoy Island, a site relatively remote from known contamination. (From the data of Nisbet and Reynolds.[11])

ppm in oysters (*Crassostrea virginica*). Monthly monitoring for 7 years showed that when the leak was stemmed, PCB levels declined initially. Although PCBs nearly disappeared from the water at the spill site by 1974, in Escambia Bay, oysters still contained up to 0.5 ppm Aroclor® 1254 in May 1976. The levels fluctuated annually; they increase during the spawning season when lipid contents increase temporarily (Figure 1). Presumably, the contaminated sediments provide a persistent reservoir for continuing pollution of the bay.

In Massachusetts, New Bedford Harbor and nearby Buzzards Bay have attracted attention because of the high levels of PCBs found in sediments, fishes, and shellfishes.[37,39] PCBs declined significantly between 1971 and 1981 in eggs of common terns from Buzzards Bay.[11] The Spearman rank correlation coefficient was -0.67 ($p < 0.05$). At Monomoy Island, 80 km eastward and relatively remote from known sources of contamination, PCB concentrations were lower but followed a similar temporal trend. In both areas, maximum levels were observed in 1976 (Figure 2). The authors noted that samples collected in that year were analyzed by a different laboratory than in other years. They did not eliminate the possibility of analytical variability between the laboratories. Assuming the maxima are not artifacts, these sets of data provide a vivid example of long-range aerial transport from the urban, industrial center of New Bedford to the eastern shore of Cape Cod, 80 km away.

MONS 005903

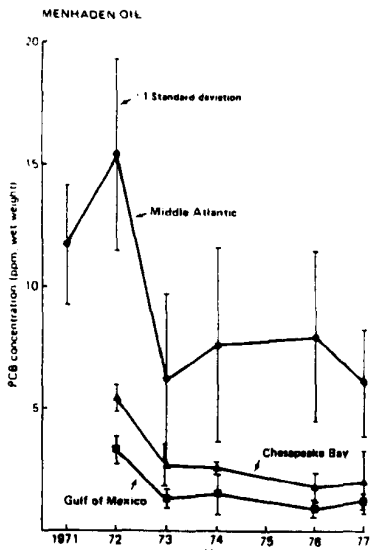


FIGURE 3. PCBs in menhaden (*Brevoortia tyrannus* and *B. patronus*) oil from three areas of the fishery. (From the data of Stout et al.[70])

PCB levels from fishes in Lake Simcoe, Ontario, Canada, decreased between 1970 and 1976. Ten species were sampled during two or more years. Because weights of the 367 specimens varied from year to year, a subset of 196 fish in comparable weight groups was selected for analysis of variance. PCBs declined significantly ($p < 0.05$ in the F-test) except in larger yellow perch (*Perca flavescens*) and smaller walleye (*Stizostedion vitreum vitreum*). Significant decreases in fat content of several species over the time studied complicated interpretation of the data.[69] As will be seen again and again, the decline was greater when the initial chlorinated hydrocarbon level was higher. Levels change much less dramatically when the initial levels are low.

PCB levels decreased in the menhaden fishery over the years 1969 to 1977.[70] Whole fish and the commercially important products meal and oil were analyzed. Menhaden is the largest fishery in the U.S. in weight of fish. PCBs were measured in 314 samples collected from the Atlantic and Gulf Coasts and Chesapeake Bay. For statistical studies, 132 samples of menhaden oil were chosen. The null hypothesis of equality could be rejected for three areas of the fishery, but the differences between years were significant ($p < 0.05$) only in a few cases. Unequal numbers of samples and wide variations in PCB levels within years contributed to this situation. Coefficients of variation were as large as 86% (Figure 3).

Holden[71] found no change in PCBs in the blubber of gray seals (*Halichoerus grypus*) from

MONS 005904

the east coast of Scotland between 1968 and 1974. For a total of 108 specimens collected in 5 different years, the mean level in blubber was 36 ± 1.6 ppm.

Jones et al.[92] compared concentrations of PCBs in the liver, blubber, and brain of young harp seals *(Pagophilus groenlandicus)* collected from the ice in the Gulf of St. Lawrence in 1971 and 1973. Blubber contained 2.4 ± 1.4 ppm in the earlier year and 1.08 ± 0.53 ppm 2 years later. The level also decreased significantly ($p = 0.05$) in brain but not in liver. The 37% decrease in fat content in the liver may have masked any change in PCB content during this period. Neither the relationship between lipid and chlorinated hydrocarbon content nor the reason for the decline in lipid content has been established. PCBs as well as total DDT and dieldrin varied widely between individuals and without any correlation between compounds. The authors held that differences in lipid content of specimens and body burden in the mothers accounted for the variation. Not mentioned was the limited sample size, 16 animals in 1973 and 11 in 1971. With a sample of four adults, the PCB content in 1973 was higher in young than in older specimens. In a larger sample collected in 1970, the PCB concentration in females increased from birth to 5 to 6 years and then leveled off.[93]

Cod from the Gulf of St. Lawrence were analyzed in 1977, 1978, and 1979. Data from 122 specimens of liver were subjected to intensive statistical tests. Rectilinear MLR showed that PCBs were increasing while interactive MLR showed the opposite.[94] The authors felt that 3 years was a short interval for trend assessment.

Schneider[95] found no change in PCBs in cod from Kiel Bay, West Germany, between 1974/75 and 1977. He used a regression to calculate the value of 4.8 ppm in livers for the earlier time period, to compare with the 2.9 ± 1.0 ppm found in fish of the same length in 1977. Luckas and Lorenzen[95] reported that limitations in data made trend assessment in the North Sea and Ostsee (Kiel Bight) difficult. They cited earlier observations of a temporary increase, a period without change, or a slight decrease in PCBs in the area, as resulting from an inadequate data base.

In Finland, PCBs decreased in the marine ecosystem but stayed the same or increased in lakes. Paasivirta and Linko[96] found a significant decrease in PCB levels ($p < 0.001$) at two sites in the northern Baltic Sea. Between 1973 and 1978, the concentration in Baltic herring *(Clupea harengus)* fillets fell from 0.60 to 0.24 ppm and from 0.51 to 0.14 ppm at the two sites. Data for 1982 suggest that PCBs continued to disappear at the same rate.[96] From 1973 to 1978, PCB levels in perch *(Perca fluviatilis)* increased ($p < 0.01$) in one lake and showed no trend in another. The actual levels were low in both cases: reportedly increasing from 0.052 ± 0.020 to 0.078 ± 0.031 ppm in white lateral muscle in one case, and ranging between 0.056 and 0.098 ppm in the other.[96] The conclusions are based on stepwise multiple linear regression. Independent evaluation questioned the appropriateness of the statistical treatment.[97] Nonetheless, this small study may reflect as accurate a picture of PCBs as we are likely to obtain. In areas with high initial PCB contamination, reductions were seen, perhaps at the cost of low-level pollution spreading more widely. The reported decrease of PCBs in the muscle and liver of pike *(Esox lucius)* from the Turku Archipelago is based on an inadequate sample of 23 fish.[98] PCB levels in pike from Lake Päijänne have increased significantly ($p < 0.001$) from 1972 to 1980. The levels were some of the lowest in the world, 0.015 to 0.049 ppm in muscle. Because of the correlation between PCB level and fat content, the effect of fat content was eliminated by covariance analysis. The authors[98] did not believe local pollution was the cause, for PCBs had been banned in Sweden and were essentially never used in Finland. Instead they suggested that atmospheric transport apparently was averaging global pollution.

Although this chapter concerns animals in the wild, brief comment on beef and pork for human consumption may interest the reader. In these instances, the change in PCB levels reflects direct official action rather than environmental trends, as contamination levels in

MONS 005905

feedstuffs are regulated. In Ontario, Canada, the PCB concentrations of beef abdominal fat fell from 0.25 ± 0.058 ppm (fat basis) in 1969/70 to 0.0095 ± 0.022 ppm in 1981. In pork, the corresponding values were 0.33 ± 0.14 ppm and 0.003 ± 0.005 ppm.[99] Residues disappeared at a first order rate; the halflife was 3.2 years for beef and 1.8 years for pork. The levels in bovine milk decreased at about the same rate in southern Ontario. Between 1973 and 1977, the concentration in milk fat fell from 0.11 to 0.033 ppm.[100] Such a trend reflects the pattern of usage and disposal in an agricultural area. These data show the changes possible in agricultural commodities subject to direct intervention in contrast to the less direct control of environmental exposure of wildlife and fish.

These few studies from a number of sites in the Northern Hemisphere convey some of the challenge in assessing PCB trends. What is reported to be happening depends on location, type of sample, and adequacy of data.

B. Extensive Monitoring Programs

In some of the more intensive studies, I will cover the diverse species included in each regional program in order to evaluate contaminant trends in specific geographical areas. Then I shall describe integrated fish or wildlife monitoring programs which cover wider expanses.

1. Great Lakes — Overall Region

The Great Lakes of North America exemplify an aquatic environment surrounded by intense agricultural, industrial, urban, and recreational activities. The downstream course toward the sea provides a living model for studying the flow of contaminants through a complex system. Increasing population and pollution density[24] along Lake Huron and Lake Erie tend to obscure measurement of the PCB flux. Persistent chemicals remain for long periods, because outflow from the lakes is limited. Since 1978, the International Joint Commission[101] representing both Canada and the U.S. has coordinated monitoring of pollutants in the Great Lakes Basin ecosystem.

Lake Superior is farthest from the Atlantic Ocean and least densely populated. Between 1971 and 1975, PCBs in headless, eviscerated lake trout declined from 1.8 to 0.4 ppm.[102] For fish weighing 1.0 to 1.5 kg, the same trend was observed, from 1.9 to 0.49 ppm, although the authors[102] claimed PCBs had not decreased significantly. After stating that PCB values before 1970 were estimates, they apparently included both 1968 and 1969 data in concluding that there was no significant decline in PCB level in fish of a specific size. A smaller decrease, 0.8 to 0.3 ppm was observed for lake whitefish. The increase, 0.6 to 1.0 ppm for blooters *(Coregonus hoyi)* may relate to the inclusion of one or more large fatty specimens in the data for 1975. All these conclusions are based on limited specimen numbers. According to another report,[27] PCB levels in lake trout were 2.3, 1.8, and 2.0 ppm in the edible portion in the years 1972, 1973, and 1977. The level fell to 0.85 ppm in *whole* trout near Thunder Bay in 1980. However, the exact status of Lake Superior has been clouded by the confounding of PCBs with toxaphene, mentioned earlier.

Only in three species in the main waters of Lake Huron did PCBs decrease between 1970 and 1976: alewives *(Alosa pseudoharengus)*, rainbow smelt *(Osmerus mordax)*, and walleye. PCBs in four other species increased at least at one location.[102] Not surprisingly the areas with least circulation are represented: cisco *(Coregonus artedii)* from Georgian Bay and yellow perch from North Channel. PCB levels in splake (hybrid between *Salvelinus fontinalis* and *S. namaycush)* and coho salmon *(Oncorhynchus kisutch)* (introduced in 1966) also increased in the main part of Lake Huron. For other locations of the above species and for other species, the PCB levels remained static. The reported increases were confounded by limited sample number and changes in size distribution or fat content from year to year. For instance, grouping splake by weight class showed that PCBs in headless, eviscerated fish

MONS 005906

actually decreased substantially from 1970 to 1974. Residues in the 1.0 to 1.5 kg weight class, for instance, fell from 1.5 to 0.3 ppm.

Lake St. Clair lies downstream from Lake Huron, upstream from Lake Erie. Frank et al.[103] reported that PCB levels in smallmouth bass (*Micropterus dolomieui*) in Lake St. Clair increased between 1968 and 1975. Before 1970, PCBs were only estimated, so this conclusion may be unwarranted. PCB levels in headless, eviscerated freshwater drum (*Aplodinotus grunniens*) were low and did not change substantially: 0.22 ppm for 0.25 to 0.50 kg specimens in 1971 and 0.17 ppm in 1976.

PCB levels in Lake Erie, the next downstream toward the Atlantic Ocean, appear to have declined somewhat over the period 1971 to 1975.[103] Data were limited, however, and reported increases between 1968 and later years may have been unwarranted. As stated above, the analytical technique in 1968 only allowed estimation of PCB content. Furthermore, in that procedure, TDE often obscures certain PCB components. Finally, the PCB standard (Aroclor® 1254 and 1260 in the ratio of 5:1 to 4:1) undoubtedly appropriate for later samples (for which it was designed presumably) may have undervalued the Aroclor® 1242 and 1254 that were often more typical in earlier years.

More recently PCB levels in spottail shiners (*Notropis hudsonius*) have reflected declining contamination in the nearshore environment of Lake Erie. Fish less than 1 year old have been sampled to monitor trends in this planktivorous species.[27,101] At Point Pelee, the most polluted site, PCB levels fell 82% from 840 ± 400 ppm in 1975 to 150 ± 37 ppm in 1980. Starting at a similar level in 1978, 157 ± 28 ppm, Lake Erie's Thunder Bay shiners reached 95 ± 29 ppm by 1980, i.e., a 40% decline in 2 years.

Although levels in coho salmon, rainbow smelt, and walleye (or yellow pickerel) were reported to have decreased in the main body of Lake Erie,[27] I found no trend in whole fish between 1977 and 1980. Only in the edible tissue of coho salmon did they decline from 3.2 ppm in 1972 and 2.8 ppm in 1973 to 0.91 ppm in 1977. The paucity of detail precludes real evaluation. Armstrong and Sloan[33] reported a 33% decline in six species of fishes after 1975.

The 1980 samples of top level predators from Lake Ontario showed a "minimal increase in PCB levels" over 1979.[27,101] Still, PCB pollution was not necessarily increasing. Instead the figures may reflect the usual fluctuations in contaminant data. For both lake trout and rainbow smelt, the levels were slightly lower than in 1977. In coho salmon the level declined 24% from 1977 to 1980, though the trend may not be statistically significant. These data may reflect the delayed response of top level predators to changing pollution levels. The data for the planktivorous spottail shiner reinforce this supposition. PCB levels decreased 58 to 82% at four locations in 2- to 5-year periods ending in 1980. The increase at one site from 153 ± 23 ppm in 1979 to 270 ± 51 ppm in 1980 is attributed to year-to-year variation, not increasing input. Both difficulties in obtaining representative samples and the complexities of the Great Lakes ecosystem contribute to such fluctuations.

All these studies underscore the variability of contaminant data and the hazards in attributing change with limited information. The above studies often lacked the intensity of sampling requisite for rigorous statistical evaluation. The Great Lakes Fisheries Laboratory designed a systematic assessment of three species of fish from Lake Michigan.[104] Large adult fish were collected in the fall at a specific location. The size was carefully regulated to give consistent samples suitable for yearly trend analysis.

Lake Michigan, which connects with Lake Huron, is the one Great Lake wholly within the U.S. Much of this lake is surrounded by intensive human activity. About 80 to 90% of the PCBs enter the region from the atmosphere vaporized either during incineration or directly from landfills.[101] The highly polluted sediments of Waukegan Harbor also contribute PCBs to the lake.

After 5 years of careful sampling, neither lake trout nor coho salmon showed a significant

MONS 005907

Table 2
PCBs IN FISHES FROM LAKE MICHIGAN[106,107]

Year	PCBs (ppm)		
	Lake trout	Coho salmon	Bloaters
1972	13 (4.8)	11 (2.1)	5.7 (0.95)
1973	19 (2.1)	12 (0.8)	5.2 (0.37)
1974	23 (3.7)	10 (0.9)	5.6 (0.31)
1975	22 (2.9)	11 (0.6)	4.5 (0.36)
1976	19 (2.7)	9 (0.5)	4.1 (0.22)
1978			3.1 (0.28)
1980			2.2 (0.27)

Note: ppm: μg/g wet weight whole fish; arithmetic mean (95% confidence interval). Bloaters and lake trout were collected off Saugatuck, Mich., in southeastern Lake Michigan; Coho salmon were taken from east-central Lake Michigan. All fishes collected in the fall. Number of specimens: salmon and trout — 9 or 10 in 1972, 29 or 30 in other years, analyzed individually; bloaters — 100 to 170 analyzed as composites of 10 fish per sample.

PCB trend. The variability of PCB levels in 1972 (note the large 95% confidence intervals) remind the reader that the small number of specimens in 1972, nine or ten fish, do not comprise a representative sample (Table 2). Furthermore, the specimens were larger that year than later: 648 vs. 602 to 616 mm for trout and 693 vs. 620 to 665 mm for salmon. Unknown factors such as abundance of food, stress from adverse weather, or predation may have altered both the size and the contaminant distributions. The PCB level in lake trout showed no obvious trend, even when 1972 data were omitted. PCBs did decline 24% in coho salmon from 1973 to 1976. Lake trout live 10 to 20 years[105] and like dogfish in the marine environment,[40] they reflect long-term pollution in a top predator. Coho salmon spend about 18 months in Lake Michigan before returning to spawn.[106] They should respond more rapidly to declining contamination of the ecosystem because they are shorter lived.

The third species in the study, bloaters, was sampled more intensively. An important commercial species, bloaters are readily available and easy to catch. Seven samples of 100 to 170 fish each were collected between 1972 and 1980. Bloaters, like lake trout, are nonmigratory. Both reflect local conditions in contrast to coho salmon, which range widely and reflect lakewide pollution.[107] PCB levels in bloaters declined 27% by 1976 and 61% by 1980 (Table 2). Bloaters caught commercially at about 6 years of age[105] should respond to changing pollution more rapidly than long-living lake trout, but not as promptly as coho salmon.

Herring gull eggs monitored throughout the five Great Lakes provide an integrated approach to assessing a complex ecosystem. Herring gulls are advantageous as indicator organisms because they occur widely throughout the Northern Hemisphere, eat mainly fishes, bioaccumulate to high concentrations, and, as adults, are year-round residents.[108] The PCB concentration in eggs from Lake Superior colonies did not change significantly from 1974 to 1979. Interference by toxaphene, found in increasing concentrations in Lake Superior specimens, may have obscured any trend. PCBs declined in a log-normal fashion on Lakes Ontario, Erie, and Huron. The "average population half-life" for the first-order model was 3.6 years for Lake Ontario, 8.4 years for Lake Erie, and 5.2 years for Lake Huron.[108] The average population half-life is a summation of dynamic factors in both the herring gull and

MONS 005908

its food. The actual half-life of PCBs in the gulls was assumed to be similar to the 250 days measured for ^{14}C-DDE.[108] Preliminary summaries of egg data for 1980[27] showed little change from the preceding year, except on Lake Ontario. In this area at the beginning of the study, levels were approximately twice as high as on Lakes Superior, Huron, and Erie. As the PCB levels for Lake Ontario herring gulls decline, the pattern may imitate the other lakes: initial dramatic declines followed by leveling off or at best gradual disappearance. The latter stage is difficult to discriminate from yearly variability.

Mineau et al.[108] were surprised that PCBs in herring gulls fell so rapidly following restriction in usage of these chlorinated hydrocarbons. They claim that reduced bioavailability stemmed from flushing, decreases in atmospheric contamination, or "irreversible" sedimentation. They predicted that contaminants would remain in the upper lakes, i.e., Superior and Huron, longer because of lower sedimentation rates, slower flushing, and greater input from the atmosphere onto the larger lake surface areas. Continued release of PCBs would explain the long average population half-life for Lake Erie (8.4 years). Extensive resuspension of sediments in the western part of Lake Erie may also play some role. As the diet of herring gulls is identified more exactly and the dynamics of PCB distribution are described, the relation between the food chain and the egg residue levels can be defined.

Herring gulls from Lake Michigan were monitored separately from birds on the lakes bordering both Canada and the U.S. PCB contamination in eggs decreased more than 50% from 1971 to 1980. The variability dropped at the same time. Specific data for one site are 129 ± 63 ppm in 1971, 151 ± 51 ppm in 1973, 110 ± 26 ppm in 1976, and 53 ± 10 ppm in 1980. Statistical interpretation of these data was not included.[27] The values are similar to those for Lake Ontario, which contained the highest levels of all.[27]

An intensive study of waterfowl nesting at the mouth of Green Bay in Lake Michigan shows the difficulty in detecting trends in environmental samples quickly. Mean PCB levels in red-breasted merganser (*Mergus serrator*) eggs did not change ($p > 0.05$) from 1977 to 1978, even though more than 200 eggs from a limited area were analyzed. PCB pollution in Green Bay still may have decreased, because the range dropped from 4.9 to 230 ppm in 1977 to 6.6 to 36 ppm in 1978.[79]

2. Southern California Bight

Perhaps the most intensely studied area in the world is the Southern California Bight. In 1969, Ventura County, the cities of San Diego and Los Angeles, and the county sanitation districts of Los Angeles and Orange County joined forces to found the Southern California Coastal Water Research Project (SCCWRP). They pooled scientific resources to acquire integrated regionwide data on the coastal waters from Point Conception to the Mexican border. All too frequently environmental research is short-term, narrow scope, point source problem oriented. From the beginning, SCCWRP chose instead "to understand the overall effects of man on the biology and chemistry of southern California's coastal waters".[109]

This more integrated approach to pollution assessment provides an opportunity to understand the flux of contaminants in a complex marine ecosystem adjacent to a metropolitan area. Eleven million persons, 5% of the total U.S. population, inhabit this coastal plain,[110] where intense agricultural and industrial activities present ample sources of pollutants. The Los Angeles city outfall into Santa Monica Bay and the county outfalls into the waters of the neighboring Palos Verdes Peninsula are the major "rivers" of Southern California. Formerly, they received industrial wastes directly. They continue to transport toxic substances concentrated by runoff from precipitation, aerial fallout, and agricultural drainage. They provide the main sources of fresh water entering the Southern California Bight. In 1979, the five largest dischargers of the region released 4×10^9 ℓ/day of municipal waste water, the predominant source of contaminants reaching Southern California coastal waters.[111] In 1979, for instance, waste water discharge contributed 0.8 t of PCBs compared to about 0.1

MONS 005909

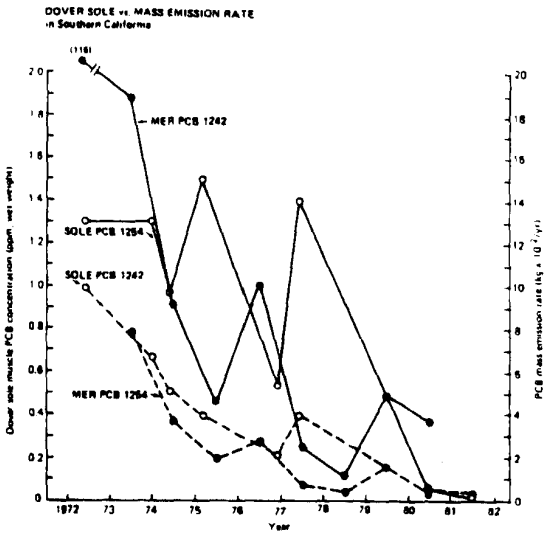


FIGURE 4 The relationship between PCB components in Southern California effluents and Dover sole (*Microstomus pacificus*) muscle. (From the data of Gossett;[116] see also Young and Heesen.[117])

t via storm runoff from the drainages of three major rivers of the Los Angeles Basin, the Los Angeles River, the San Gabriel River, and Ballona Creek.[112] As soon as the sewer outfalls were identified as the largest source of marine pollution in the bight, this influx was promptly restricted. Manufacturers and processors were prohibited from dumping industrial wastes into the sewer system.

The intensive studies by SCCWRP provide data for a comprehensive description of the many facets of pollution abatement. I am talking here about the complex combination of natural decomposition and dispersion and human efforts to limit use and release of toxic substances, and the observed responses of various components of the marine ecosystem.

SCCWRP has been monitoring chlorinated hydrocarbons off the coast of Southern California for the past decade. According to dated sediments from the Santa Barbara Basin (west of Santa Barbara and southeast of Point Conception), PCB deposition in the region began about 1945[112-114] the same time it occurred elsewhere in the U.S.[115] As the result of improved sewage treatment during the past decade, PCB emission from waste water in the Los Angeles County Sanitation District decreased 97% between 1972 and 1980 (Figure 4).[116] In the surface sediment near the outfall, PCB 1254 concentration decreased nearly 99% from 1972 to 1982; at the outfall site itself, the PCB 1242 and 1254 concentration decreased 94% from 1975 to 1981.[116]

What effects have these decreases in the amount of PCBs entering and residing in the marine ecosystem had on organisms? PCB levels in mollusks decreased much more rapidly

than in flatfish. According to Bight-wide surveys of the open-coast mussel (*Mytilus californianus*) during 1971 and 1974, PCB contamination decreased significantly. The median decrease was 54%.[76] In contrast, PCB levels in the benthic flatfish, Dover sole (*Microstomus pacificus*), showed no statistically significant decrease over a similar period. In the regions of highest contamination, however, the maximum values did fall. Thus, at Palos Verdes, the highest value in the 1971/72 survey was 6.3 ppm in muscle compared to 2.5 ppm in the 1974/75 survey.[76] By 1981, PCBs had nearly disappeared from Dover sole muscle,[116,117] even at the most contaminated site. The PCB 1242 mean value had declined from 0.99 ± 0.15 ppm in 1972 to 0.028 ± 0.006 ppm, and PCB 1254 from 1.3 ± 0.2 ppm to 0.10 ± 0.02 ppm.

Although the level of PCB 1242 decreased in a fairly regular fashion, that of PCB 1254 fluctuated dramatically, as shown in Figure 4. The mass emission rate (MER) of PCB 1254 from the Los Angeles County Sanitation District outfalls at Palos Verdes showed only modest fluctuations, but the MER for PCB 1242 was more variable. The PCB 1254 level in Dover sole may be influenced by the MER for PCB 1242 because as the latter mixture weathers, many of the lower molecular weight components disappear, leaving behind residues resembling more closely PCB 1254. As early as 1975, McDermott et al.[81] noted that the proportions of PCB 1242 and 1254 in Dover sole did not bear a direct relationship to the proportions in municipal waste water discharges. They found 29% PCB 1254 in the discharges contrasted with 67% in Dover sole muscle. They suggested that factors such as volatility of individual components of the PCBs, sediment burden, and presence of other substances (e.g., metals, DDT, hydrogen sulfide) also influence the biological absorption processes, which are reflected in the ultimate levels in organisms. Furthermore, they found that proportions of PCB 1242 and 1254 in wild crab and mussels were similar to those in Dover sole.

In contrast, mussels from an uncontaminated source, exposed to the waste water plume at Palos Verdes for 3 months contained a decreased proportion of PCB 1254, namely 58%.[81] The marked decrease in PCB 1254 in mussels exposed higher above the bottom suggests that these PCBs derive from sediment and/or settling components of effluents. Closest to the bottom sediments, the PCB 1254 concentration approached 0.4 ppm, tenfold more than 35 m above at the surface.

Santa Monica Bay is a major sports fishing ground for the popular white croaker (*Genyonemus lineatus*). This species has been studied recently because one out of every three fish landed in Southern California is white croaker, and most are consumed by humans. PCB data were collected out of concern for the wholesomeness of these fish, which swim somewhat off the bottom, but feed on or in sandy bottom.[118] Between 1975 and 1980,[78,119] the mean PCB levels in edible tissue of white croaker collected at the nearby Los Angeles County Sewer outfall declined from 2.8 ppm total PCBs (PCB 1242 and PCB 1254) to 0.38 ppm. In 1980, PCB 1254 constituted 87% of these residues, a much higher proportion than found in Dover sole.

Waste water from sanitary treatment plants influences the behavior of PCBs in water and sediment. In the New York area, plankton blooms caused by the nutrient load absorb PCBs,[53] and remove them from the water. Moreover, particulate matter in sewage effluent buries PCB and DDT-contaminated sediments. Such processes may serve to scavenge the area around the Los Angeles County sewer outfalls, since PCBs in fish decreased much more rapidly than originally predicted.[120] Ironically, improved waste water treatment can have a detrimental effect on buried PCB deposits. As improved treatment reduces the particulate content of the effluent, currents and wave action erode the overlying sediment. In fact, the Hendricks DDT model[121,122] suggests that zero discharge from the Los Angeles sewer outfalls would enable vast quantities of PCBs to be remobilized starting around 1990 (Figure 5). On the other hand, record storms in 1983 may have completely dissipated the contaminated sediment.

MONS 005911

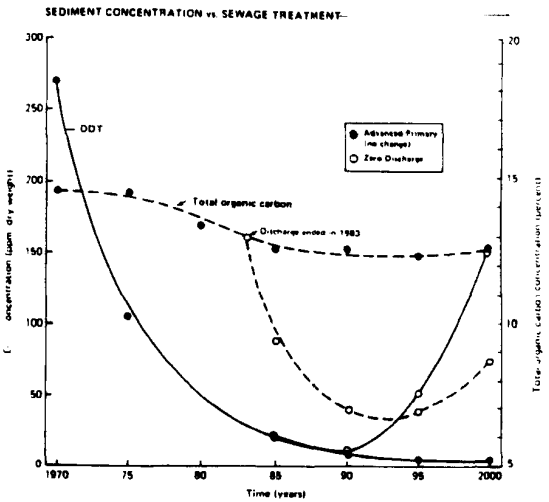


FIGURE 5. The influence of improved sewage treatment on the DDT concentration in sediment at the Los Angeles County sewer outfalls. Total organic carbon is related to the amount of particulate matter in sewage effluent. (After the model of T. Hendricks.[121,122])

3. Hudson River

Most of the studies described up to now have concerned areas with relatively diffuse sources of PCB contamination. The Los Angeles County sewer outfalls were considered point sources, but they discharged wastes from many sources. No direct disposal of pure PCBs was described. In contrast, the Hudson River in New York State was the site of massive intentional PCB dumping at a General Electric capacitor manufacturing plant. More than 200 t of PCBs were found in the river.[123] Dumping was reduced in 1976 and stopped in mid-1977. A monitoring program was established as part of the settlement agreement between New York State and General Electric after extensive pollution of the river was discovered. Monitoring involved both resident/fresh water and migratory/anadromous species (the authors' terminology).[32] For each species, specimens (30 per sample) were collected within 2 weeks of the target date each year.

PCB concentrations in mature resident/fresh water fishes from this heavily polluted area were directly proportional to lipid content from 1975 through 1980. This relationship applied to each collection site, and included specimens ranging over a number of age classes for sites downstream from the PCB source. No correlation was found between length or weight and PCB concentration.[32]

The behavior of PCBs depended on chlorine content. Overall, PCBs declined substantially in all species at all locations, the result of massive losses of Aroclor® 1016, the PCBs involved in the last years of discharge. Like Aroclor® 1242, Aroclor® 1016 contains 42% chlorine, but with reduced amounts of higher chlorinated components. While the components

MONS 005912

corresponding to 21 and 42% chlorination were decreasing, material resembling PCB 1254 generally remained constant or actually rose. The case of brown bullhead (*Ictalurus nebulosus*) shows an extreme of complexity in assessing PCB contamination. While Aroclor® 1016 decreased from 1900 ± 800 ppm lipid weight in skinless fillets to 700 ± 190 ppm between 1977 and 1980 and total PCBs from 2500 ± 1060 to 1480 ± 460 ppm, PCB 1254 increased from 390 ± 250 to 750 ± 290 ppm. (On a wet weight basis, the total PCBs dropped from 107 ± 49 to 12.3 ± 6.6 ppm.)

Aroclor® 1016 decreased significantly in yearling pumpkinseed (*Lepomis gibbosus*) from 1979 to 1980 at two sites. At a third site further downstream, it increased slightly but significantly. Since the correlation between PCB and lipid content was significant as well, outside sources of PCB apparently contributed to the PCB burden at this site.[32]

PCB 1254 levels in these fish varied much more. At Stillwater, 25 mi south of the industrial discharge, they decreased 51% from 1979 to 1980; farther south at Albany, they increased 157%, and farther downstream at Newburgh they remained constant. These results were attributed to resuspension of PCB-contaminated sediment during routine dredging. According to the ratios of PCB components in successive years, PCB 1254 had been more prevalent in previous years.

The mean annual decline of total PCB for all species was 34 ± 13%/year; Aroclor® 1016 decreased more rapidly, 47 ± 10%/year. Although not discussed in the paper,[32] PCBs disappeared more rapidly as the distance downstream from the source increased. In a 60-mi space, the rate of disappearance from all species increased 10%/year from 42 to 52%/year. Nonetheless, for three species taken individually, the rate increased 17.1%/year.

The declines in Aroclor® 1016 levels appear to be first order, i.e., disappearance rates in recent years were not different from previous years. The apparent "population" half-life for Aroclor® 1016 was 1.2 ± 0.4 years and for total PCBs, 2.3 ± 2.1 years. These are not true half lives for PCBs in a specific fish because they include both uptake and loss by all mechanisms. Instead, they compare lipid-based PCB levels in different years from similar populations at specific sites.

PCB levels in migratory/marine species were also studied to determine whether these species responded to the point source in the same way as resident/freshwater species. Aside from American shad (*Alosa sapidissima*), 83% of 30 sample sets showed correlations $p < 0.05$) between PCB content and lipid content. Only 24% of 50 data sets showed correlations of PCB content with fish length including one inverse relationship.

The lipid-based (see third footnote of chapter) PCB concentration of four species related inversely to body size. These species enter the river to spawn, but apparently do not feed there. Both large and small fishes (e.g., American shad averaging 1948 g and rainbow smelt averaging 9 g) followed this pattern. The smaller the fish the higher the PCB concentration, in quasiequilibrium with respect to PCB concentration in the local environment. The authors[3] suggest that PCBs accumulate passively showing a relationship to body size, i.e., the ratio of surface area to volume. Absorption may be through the gills, skin, and gut (only to the extent contaminated sediment was ingested). Smaller fish may accumulate more PCBs by filtering more water. If PCBs accumulate according to an equilibrium process, what is the maximum possible PCB concentration near the PCB source? In 1977, the lipid of resident goldfish (*Carassius auratus*) contained up to 10% PCBs, or 99,000 ppm.

PCBs in American shad dropped substantially between 1977 and 1979, and then leveled off or increased in 1980. The total PCB concentration in both sexes was 1.17 to 1.9 ppm in 1979/80. The increase of 0.3-0.4 ppm near the Tappan Zee Bridge was comprised of PCB 1221 which had been below the detectable limit in 1979. No explanation was available for the reappearance of the mainly monochlorinated PCB component, which had never had wide application and had virtually disappeared. Here is an example of the continuing problem of PCB pollution: often it goes undetected except in a chance case such as the shad data.[3]

MONS 005913

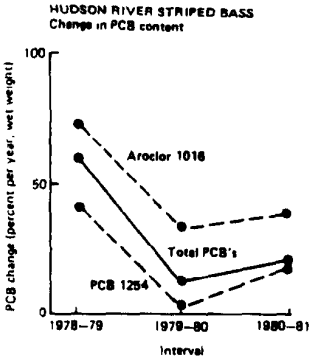


FIGURE 6. Rate of disappearance of PCBs from striped bass (*Morone saxatilis*) in the Hudson River after intentional dumping ceased. (From the data of Sloan and Armstrong [1])

The 1978 PCB level in American eel (*Anguilla rostrata*) was so high (74 ± 67 ppm total PCBs in 42 specimens) that further monitoring did not seem worthwhile. Two years later, the level in six specimens had decreased to 9.1 ± 8.6 ppm PCBs, a value substantiated in 1981 by a mean of 10.8 ± 6.2 ppm in 30 eels. Even more dramatic was the virtual disappearance of Aroclor® 1016: from 40 ppm in 1978 to 0.46 to 0.49 ppm in 1980/81, a 76% annual decline, confirmed by similar findings at several other sites. Even closer to the dumpsite at the capacitor plant, Aroclor® 1016 only amounted to 0.93 ± 0.56 ppm and PCB 1254 to 12.2 ± 11.5 ppm in 1981. On a lipid basis, similar trends occurred. Thus, PCB 1254 became the predominant contaminant, more so than in any other species of fish.

Striped bass residues showed a marked decline from 18 ± 28 ppm total PCBs for 375 specimens in 1978 to 7.0 ± 6.1 ppm for 29 specimens in 1979 and 4.8 ± 5.0 ppm for 205 specimens in 1981. Aroclor® 1016 declined nearly 90% in that interval to 1.0 ± 2.2 ppm, but PCB 1254 declined only 55%. The average *annual* decline was 53% for Aroclor® 1016, but only 23% for PCB 1254. These average rates, however, obscure the true picture. Both components disappeared rapidly from 1978 to 1979 and then declined modestly at a more constant rate in the next 2 years (Figure 6).

Overall in the Hudson River between 1978 and 1981, Sloan and Armstrong[1] found the annual rate of decline of PCBs in migratory/anadromous fishes to be 42% for Aroclor® 1016 and 5% for PCB 1254. Elevated levels had been found before the study began, but the high values in resident/fresh water as well as migratory/anadromous species in 1978 may reflect elevated levels in the water column resulting from mobilization of sediments during the record spring floods of 1976 and 1977. Low levels in later years may result from stable water flow more recently. Under these conditions, burial can temporarily immobilize contaminated sediment. Further declines in PCB levels in the Hudson River will be less dramatic. Aroclor® 1016 levels are already quite low and residues resembling PCB 1254, now the preponderant component, seem to be much more persistent or are still being introduced into the river from diverse, seemingly stable sources.

MONS 005914

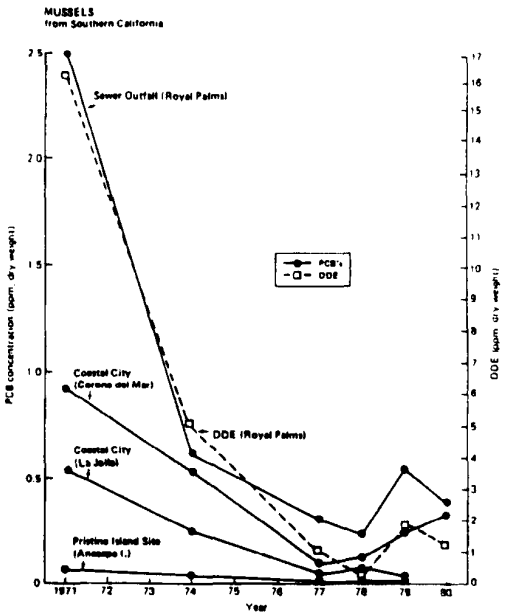


FIGURE 7. PCB and DDE levels in mussels (*Mytilus californianus*) at the Los Angeles County sewer outfall and PCB levels at three site on the coast of Southern California. (From the data of the Southern California Coastal Water Research Project,[151] Martin et al.,[34,126] and Risebrough et al.[35])

4. *California Mussel Watch*

Regional studies on the Hudson River provided an introduction to statewide and national monitoring programs. The California Mussel Watch, an outgrowth of the SCCWRP studies, was established for the purpose of monitoring pollutant levels in coastal waters throughout California. Mussels of the species *Mytilus edulis* or *M. californianus* were sampled depending on availability. Residue levels reflect the wide differences in the extent of pollution at individual sites. Mussels from Royal Palms State Beach, inshore from the sewer outfall of the Los Angeles County Sanitation Districts (LACSD), historically contained exceptionally high levels of both DDT and PCBs. They underwent a tenfold decrease in PCB content in the 7 years from 1971, when the focus of marine pollution was first identified, until 1978. The level fell from 2.5 ppm dry weight to 0.24 ppm. In 1979, however, the trend reversed and mussels contained 0.56 ppm PCBs.[124] In 1980, the content appeared to level off again at 0.39 ppm (Figure 7).[34]

What was the cause of the increase in PCB levels between 1978 and 1979? After a

MONS 005915

dramatic decline from 1971 to 1978, perhaps dumping regulations were being ignored. Or an old transformer may have fallen and spewed out PCBs, as occurred in the Duwamish River in the harbor of Seattle, Wash.[125] Perhaps the increase was only an artifact of the change in analytical techniques between 1978 and 1979. Other alternatives include residues mobilized by repairing or cleaning sewer lines or disturbing the sediment in the vicinity of the sewer outfall. In 1971, a 300 t reservoir of DDT[126] and 6 t of PCBs[127] surrounded the Los Angeles County sewer outfalls. Improved waste treatment, dredging, or unusual wind and wave action can increase the recirculation of pollutants normally buried progressively deeper by constant sedimentation. Examination of the concurrent trends for PCB and DDT suggests mobilization of previously deposited materials as a likely source of the slight increase in chlorinated hydrocarbon pollution levels noted above.

PCB levels in mussels from Corona del Mar, about 45 km southeast of Royal Palms, decreased ninefold from 0.92 ppm (dry weight) in 1971 to 0.102 ppm in 1977. Note that the level in 1977 was nine times as high as that found at the "pristine" site on Anacapa Island (see below).[124] What was the source of PCB pollution at Corona del Mar? If not a local spill, perhaps dispersion from the Los Angeles County sewer outfalls and surrounding sediments. The influence of this repository spread at least 100 km for DDT,[128] though mainly to the northwest. After 1977, the PCB level in California mussels from Corona del Mar increased each year to 0.25 ppm in 1979 and 0.33 ppm in 1980, a smaller but similar trend to that of Royal Palms (see Figure 7). This increase may be insignificant, because a five- to tenfold difference was considered minimal for significance[34] until a suitable data base for mussels was established and the statistical evaluation refined.

In 1980, resident mussels in Anaheim Bay south of Corona del Mar contained 2.4 ppm (dry weight) PCBs. This value equals the highest level found at Royal Palms in 1971. Elevated PCB levels in transplanted mussels at Port Hueneme (2.0 ppm) and Marina del Mar (1.8 ppm), a short distance north of Royal Palms, also suggest continuing widespread release of these compounds into the marine ecosystem of Southern California. The early dramatic decline in residue levels has not led to the complete disappearance of this pollutant.

In La Jolla, 100 km further southeast of Corona del Mar, the initial PCB level was only 20% of the level at Royal Palms. The disappearance of PCBs from this area has been even more profound, a 15-fold decline from 1971 to 1979. An early substantial decline was followed by a more gradual, but consistent decrease: 0.54 to 0.037 ppm dry weight over the 8-year period (Figure 7).

At Anacapa Island, a pristine site 110 km offshore and to the northwest of Royal Palms, PCB levels in California mussels decreased from 0.067 in 1971 to 0.010 ppm dry weight in 1979.[124] In contrast, the west part of San Miguel Island, another seemingly pristine site, twice as far from the sewer outfalls as Anacapa Island, contained an order of magnitude higher concentrations of PCBs (0.16 ppm) in 1978.[35] The levels at Ano Nuevo Island off the coast south of San Francisco were also higher (0.28 ppm) than at Royal Palms State Beach (0.24 ppm). The PCBs probably do not result from a spill or dumping since elevated levels of DDT also occur. Both San Miguel and Ano Nuevo Island contain extensive rookeries for marine mammals, such as California sea lions *(Zalophus californianus)* and northern elephant seals *(Mirounga angusterostris)*. Risebrough et al.[35] suggested PCBs and DDT are recycled into the food webs after excretion from marine mammals, which accumulate high levels of both substances. No data on fecal concentrations of DDT or PCBs are available. Flegal et al.[129] did find similar patterns of elevated mercury concentrations in California mussels adjacent to these pinniped and marine bird rookeries and in excrement from California sea lions on Ano Nuevo Island. Thus, PCBs ingested throughout the entire feeding range of the pinnipeds eventually are deposited at the remote seemingly pristine hauling out areas.

5. National Mussel Watch

Starting from Butler's oyster surveillance[32] and the SCCWRP mussel monitoring program,

MONS 005916

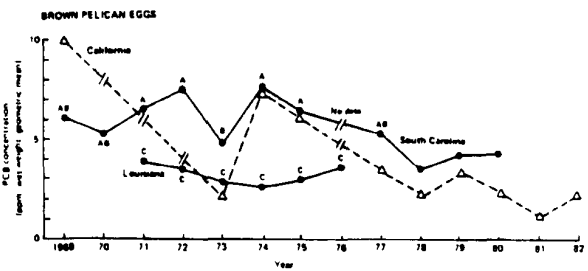


FIGURE 8. PCBs in brown pelicans (*Pelecanus occidentalis carolinensis* and *P. o. californicus*) Means which share a common letter do not differ significantly ($p > 0.05$). Data from California have not been evaluated statistically. (From the data of Blus,[82] Blus and Bunck,[113] Mendenhall and Prouty,[151] Blus et al.,[152] Anderson et al.,[39] and Gress.[153])

a national Mussel Watch was established in 1976 to monitor PCBs as well as DDT, heavy metals, radionuclides, and petroleum in coastal areas throughout the U.S. Part of an international program, Mussel Watch[38] employs mussels (*Mytilus* sp.) and oysters (*Ostrea* or *Crassostrea* sp.) to assay the marine environment. To eliminate differences in sampling, one scientist in a mobile laboratory collected all specimens at stations along the Atlantic, Gulf, and Pacific Coasts of the U.S. Interlaboratory comparisons with control samples were carried out in an attempt to improve consistency and accuracy of analyses.

Mussel Watch found no decrease in PCB levels in East Coast mussels during the years 1976 through 1978; these areas may be in the slowly changing phase of a decreasing exponential type curve,[28] such as has been noted for the DDT metabolite, DDE, in Southern California.[130] During the initial part of a seemingly bimodal loss process, about 85% of the original DDE disappeared with a half-life of 11 days. The remaining material had nearly a 200-day half-life. It is also possible that the initial restrictions on PCB usage had only limited effect on the primary sources of PCBs to the marine environment. Continuing study will help describe the results of the more recent near ban on PCBs. Assuming the changes are subtle, meticulous sampling design and statistical analysis will be needed to describe the process accurately.[38] A similar mussel watch has begun in Port Phillip Bay in Australia.[33]

6. *Brown Pelicans*

The U.S. Fish and Wildlife Service began monitoring PCBs in brown pelican eggs because of the massive decline in populations of this popular waterbird. In Louisiana, for instance, the estimated 50,000 to 85,000 birds before 1920 had disappeared by 1963,[39] apparently the result of DDE intoxication. Pelicans are an endangered species and people enjoy watching them. Their status is relevant to human beings in other ways, as well. Pelicans feed along the coasts where two thirds of all marine fishes and shellfishes spawn or spend their early lives.[131] Thus, pollutant levels in pelicans reflect the health of the nursery grounds of the seas. PCBs flow through estuaries and coastal waters on their way to the oceans. Controlling PCBs throughout the world helps protect 90 to 100 million t of foods potentially harvestable from the oceans each year.[131]

From 1969 to 1977, the levels of four chlorinated hydrocarbon insecticides declined significantly ($p < 0.05$) in brown pelican eggs in South Carolina, but PCB levels varied erratically without obvious trend (Figure 8).[82] Means for 1978 to 1980 were lower than in

MONS 005917

previous years;[132] the data await statistical evaluation. The geometric mean at two sites sampled extensively between 1969 and 1975 ranged from 4.8 to 7.63 ppm.[30] Interestingly, the level of PCBs in fresh eggs from nests which produced young successfully increased significantly from 4.3 ppm in 1971/72 to 12.0 ppm in 1975, whereas those from fresh eggs from nests which failed to produce viable young varied significantly but erratically. Taken together, fresh and embryonated pelican eggs, whether successful or unsuccessful, showed no temporal trend for PCBs that would suggest any effect from PCBs on the outcome of breeding.[31] Rather than pollution, anchovy (*Engraulis mordax*) biomass appears to be the main factor related to breeding success in California.[154]

In Florida, the trends in brown pelican eggs were not consistent. Along the Atlantic Coast, levels increased significantly ($p < 0.05$) from 2.7 ppm in 1969/70 to 6.1 ppm in 1974.[30] Specimens from Florida Bay and the Gulf Coast, however, showed little change, the former containing 0.75 ppm in 1969/70 and 0.62 ppm in 1974, the latter 0.70 and 1.18 ppm in the corresponding years. Characteristically, when chlorinated hydrocarbon levels were lower initially, significant changes occurred less frequently.

In Louisiana, PCB levels remained essentially unchanged from 1971 through 1976 (Figure 8). The geometric means varied only from 2.6 to 3.9 ppm,[133] while individual levels ranged from 0.69 to 8.9 ppm.

In Texas, King et al.[28] reported a significant ($p < 0.001$ *t*-test) decrease from 10 ± 5 ppm arithmetic (?) mean in 1970 to 3.0 ± 1.4 ppm in 1974. Because of the catastrophic decline in the brown pelican population in Texas, sampling was restricted to abandoned eggs. The number was quite limited; 11 eggs in 1970 and 5 eggs in 1974. Furthermore, the accuracy of analysis was vitiated by several factors. PCBs were not separated from other chlorinated hydrocarbons before analysis, and the analytical method became more precise in 1974. The individual values were not corrected for loss of moisture associated with incubation[134] or abandonment. For these reasons, Texas data are not conclusive. They were included only for general information.

PCB levels in brown pelican from Anacapa Island, Calif. probably decreased between 1969 and 1973 to 1975,[29] a trend confirmed by recent data.[135] Because the California pelicans are readily disturbed, eggs were collected only after the breeding season. In several years, only a few eggs were available. The limited sample sizes and changes in methodology precluded statistical evaluation of the data, which are shown in Figure 8.

7. NPMP: Estuarine Organisms

The National Pesticide Monitoring Program (NPMP) began evaluating organochlorine contaminants and toxic trace metals in 1967. A network of stations was established to sample fishes and wildlife throughout the U.S. Fresh water fishes, ducks, starlings, oysters, mollusks, and estuarine fishes have been analyzed on a regular basis for 15 years to determine present and potential future threats to the well-being of fishes and wildlife. PCBs were included in 1969, but accurate quantitation became practical only in 1971.

Butler's monumental report on estuarine mollusks, part of the National Pesticide Monitoring Program, noted the presence of PCBs in a few samples. Quantitation was not, however, routine in the early years of 1965 to 1972.[72] The follow-up survey in 1977 found no PCBs in oysters (<0.05) in the 87 estuaries sampled.[136]

The NPMP survey of estuarine fishes was designed to collect specimens less than 1 year old in both the spring and fall in 144 estuaries. To represent a broad spectrum of the food web, both carnivores and particle feeders were selected. Overall, 154 species representing 30% of the families of North American marine fishes were included. Every year the same species were chosen in each estuary to allow comparison between years. In all, from 1972 to 1976, 1524 samples composited from 38,000 whole fish were analyzed.

As detailed in Section I.D, this ambitious program has not been evaluated effectively.

MONS 005918

Table 3
PCBs IN STARLINGS[71,130,139]

Year	No of pools	PCB incidence (%)	PCBs (ppm, wet weight) Geometric	Geometric (residue + 1)	Arithmetic	SE
1970	125	(100)	(0.36)		(0.66)	0.20
1972	130	(100)	(0.22)		(0.42)	0.15
1974	126	100	0.068	0.100/0.10	0.11	0.016
1976	125	21	0.24/0.003[a,b]	0.28/0.053	0.29/0.061	0.036
1979	112	83	0.082/0.039[c]	0.13/0.11	0.15/0.13	0.030
			Stations Sampled in Both 1976 and 1979			
1976	106	23	0.24/0.003	0.28/0.058	0.29[d]	0.039
1979	106	83	0.079/0.038	0.13/0.10	0.15[d]	0.031

Note: ppm: μg/g wet weight; each sample consisted of 10 whole starlings with skin, wing tips, feet, and beak removed. Parentheses indicate the means in 1970 and 1972 cannot be compared to later data because the method of analysis changed in 1974.

[a] Mean of quantifiable values only/mean with 0.001 used arbitrarily for not detected values (quantitation limit was 0.01 ppm).
[b] Cain and Bunck[139] reported 0.01 ppm.
[c] Cain and Bunck[139] reported 0.05 ppm.
[d] Not calculated.

Butler and Schutzmann[47] concluded from statewide and grand total means that both maximum and average residue levels declined gradually. The means, however, are very sensitive to the extent of sampling at each site, because the residue levels varied widely between estuaries. For instance, whole fish contained less than 0.05 ppm PCBs in some estuaries and as much as 4.9 ppm in others. Butler,[32] in an earlier paper, had warned against comparison between states because of different sample sizes. Inspection is not an appropriate method of assessing trends for such a body of data. Two-way analyses of variance[57] or partially nested factorial analysis of variance[58] might be effective. The PCB incidence in estuarine fishes could not be compared with that in molluscs because PCBs are not found where shellfishes are commercially harvested.[47]

8. NPMP: Starlings

The starling survey covering the contiguous 48 states sampled 139 sites initially and after the inevitable falloff still included 112 sites in 1979. Starlings, introduced from Europe, range throughout the U.S. Common to the point of being pests, these birds are readily available for analysis. Their omnivorous diet includes insects, wild fruits, domestic crops, and other items. They reflect terrestrial levels in diverse foods.[137] Because starlings sometimes migrate, all data are considered on an integrated national basis.

Assessing the starling study is extremely difficult because of the statistical methods employed. Means included only quantifiable values without expressly noting the approach. Thus, the data exaggerated the actual levels, especially in 1976.[138] The levels are reported to have increased from 1976 to 1979, according to comparison of the geometric means.[139] My calculations[71] from the raw data did not confirm the means as calculated by Cain and Bunck.[139] PCB levels did increase when 0.001 ppm (one tenth the quantitation limit) was used for not detected values. On the other hand, the geometric mean, the geometric mean of PCB residue + 1, and the arithmetic mean of 1979 data were similar to the levels in 1974 (0.068 vs. 0.082 ppm, 0.103 vs. 0.130 ppm, and 0.113 vs. 0.150 ppm) (Table 3).

MONS 005919

PCBs may have decreased from 1974 to 1976 and then increased again. Alternatively, these data may be an example of natural biological variation. In fact, I found that two-way analysis of variance rejected the null hypothesis between years ($p < 0.05$).[71] Scheffe's multiple comparison procedure indicated that both 1974 and 1979 differed from 1976. Beyond the issue of interpreting the data, it is still not clear that 1000 animals per year present an accurate picture of PCB contamination throughout the whole U.S.

9 *NPMP: Ducks*

The National Pesticide Monitoring Program selected ducks as representative of terrestrial pollution. Mallards *(Anas platyrhynchos)* occur throughout most of the U.S. The closely related black duck *(A. rubripes)* lives in certain areas of the Atlantic Flyway, where mallards are not found. Together these two species afford extensive coverage of a cross section of environmental exposure. Since black ducks feed more extensively on aquatic animals which concentrate chlorinated hydrocarbons, analysis of both species of ducks in the Atlantic Flyway expands the realm monitored.

A vast pool of samples otherwise to be discarded was available without effort.[140] Hunters throughout the U.S. were already submitting tens of thousands[141] of duck wings for an annual census of waterfowl productivity. Since DDT residues in mallard wings correlated ($p < 0.01$) with levels in breast muscle,[142] discarded wings could easily provide an indication of residue levels in the edible portion of prized waterfowl, which hunters would not readily donate for monitoring. The survey of duck wings aimed at detecting trends in continental populations not only of mallards and black ducks but also other waterfowls and the terrestrial environment more generally. As ducks are highly mobile, PCB levels reflect the status of the whole flyway in which they reside rather than in the specific state where they are shot.

Trends in PCB levels in duck wings are somewhat difficult to assess because of changes in methodology. It is only possible to compare the year 1969 to 1972 and separately 1976 to 1979. The early years cannot be compared to the later years. During the earlier period,[143] PCBs remained constant in the Atlantic Flyway and decreased 48 to 50% in the Central and Pacific Flyways ($p < 0.01$). In the Mississippi River Flyway, the apparent increase in 1972 resulted from skewed data. The mean level in four samples from Alabama was 6.3 ppm. Eliminating these data drops the flyway mean for 57 samples from 0.66 to 0.26 ppm, well below 0.44 ppm found in 1969. This example shows how a few data can bias the overall picture. The Alabama data may very well have been inaccurate. Gross industrial contamination near the Wheeler National Wildlife Refuge[144] caused high levels of DDE, TDE, and DDT. These may have interfered with PCB quantitation by the technique in use at that time. White[145] reported in his abstract that PCBs decreased significantly from 1972 to 1976 in the Atlantic Flyway (from 1.36 ± 0.15 to 0.52 ± 0.08 ppm). In the text, however, he stated that differences in quantitation precluded comparison between years.

From 1976 to 1979, the incidence of quantitatable levels of PCBs increased ($p < 0.05$) in all flyways but the Atlantic, where all samples contained PCBs in both years.[77] Incidences in earlier years were not reported. Declines in PCB levels were reported for mallards from all flyways, but $p > 0.05$. Furthermore, the comparison used only samples with detectable levels of residues. Data pairs were compared only if 50% of the pools had detectable PCB levels. Thus, all "zero" values were ignored.[77] The effect of this procedure depends on the distribution of zero values, but could be substantial. Means using 0.00 for all not-detected values[71] are shown in Table 4, along with published duck wing data. Partially nested factorial analysis[62] might be a better statistical approach than the *t*-test. The duck wing survey, containing results from 891 pools of 25 wings per sample, is one of the largest contaminant data sets in the world. Further statistical evaluation is certainly warranted at the earliest practical date.

Table 4
PCB LEVELS IN DUCK WINGS (1969—79)[77,143,171]

Species	Flyway	Year	No. of pools	PCBs mean (ppm) Incidence	Detect./all	SE
Black	Atlantic	1969	42		(1.4)	0.16
		1972	44		(1.4)	0.15
		1976	32	100a	0.52	0.08
		1979	24	100a	0.63	0.09
Mallard	Atlantic	1969	19		(1.3)	0.46
		1972	21		(1.2)	0.23
		1976	20	100a	0.52	0.18
		1979	29	100a	0.45	0.07
	Mississippi	1969	51		(0.44)	0.061
		1972	61		(0.66)	0.30
		1976	69	61a	0.23/0.14	0.03
		1979	64	98b	0.11/0.11	0.02
	Central	1969	49		(0.20)	0.039
		1972	56		(0.10)*	0.013
		1976	56	13a	0.15/0.02	0.01
		1979	54	90b	0.06/0.05	0.01
	Pacific	1969	51		(0.20)	0.014
		1972	55		(0.11)*	0.009
		1976	50	14a	0.16/0.02	0.04
		1979	44	93b	0.07/0.07	0.02

Note: ppm: μg/g wet weight; each sample consisted of 25 wings.

* Arithmetic means; for 1976 and 1979 "Detect." values include only samples with detectable PCB levels; "all" values are means using 0.00 for undetected values. Parentheses indicate means for 1969 and 1972 not comparable to later years because of differences in analysis. a,b: Incidences differ ($p < 0.05$) within a flyway when letters (a,b) differ.

* 1972 mean differed ($p < 0.05$) from 1969 mean in same flyway; means of detectable levels in 1976 and 1979 not significantly different ($p > 0.05$).

10. NPMP: Fresh Water Fishes

The fresh water fish program included 113 survey stations on major lakes and rivers. Three samples each composed of 3 to 5 whole fish were collected at each site. Adult specimens were to represent two bottom feeding and one predator species.[24] Five species were collected most frequently: common carp *(Cyprinus carpio)*, channel catfish *(Ictalurus punctatus)*, largemouth bass *(Micropterus salmoides)*, white sucker *(Catostomus commersoni)*, and yellow perch. They represent 45 to 50% of all the samples, and the incidence of each varied little over the years of study.

This monitoring effort considered both the incidence and the level of PCB contamination. PCBs seemed to be spreading, for by 1978/79, PCBs were found at 98% of the stations, up from 93% in 1974. Dispersal of contaminated sediments and atmospheric fallout seemed to be responsible. The characteristics of PCB residues shifted over the years. As the less chlorinated components disappeared, the more highly chlorinated ones came to predominate. Residues resembling PCB 1242 were missing after 1974. Intermediate components resembling PCB 1248 were present at about 40% of the stations from 1976 to 1979. The more highly chlorinated fraction resembling PCB 1254 was present most frequently at 84% of the stations in 1976/77 and at 98% in 1978/79. The most highly chlorinated fraction monitored (resembling PCB 1260) occurred at 84 to 88% of the stations in these years.

Comparisons of the 74 stations sampled in both early periods of the study, 1970 to 1972

MONS 005921

vs. 1973 to 1974, suggested a decline of 26% on a wet basis and 48% on a lipid basis. The change may reflect major developments in methodology rather than environmental differences.

Mean PCB levels changed little between 1976 and 1979. Only the total PCBs based on lipid weight showed a significant difference between 1976/77 and 1978/79. The mean wet weight total PCBs and component PCBs on both wet and lipid bases did not differ significantly during this period. Data for 1974 contained analytical inconsistencies which clouded meaningful comparison. Data corrected for differences due to changed quantitative techniques suggested that PCB residue levels in fresh water fishes did not change from 1974 through 1979.

It is extremely difficult to portray adequately the findings of such a massive study. The maxima, means, and incidence of total PCBs and several components give only a brief review of the total effort. Data for the years 1973 through 1979 are summarized in Table 5.

The mixed nested-crossed model used for statistical calculations[41] allowed comparison of the trends at individual stations over time (i.e., year-station interactions). From this process, it was suggested that some stations still received fresh, unweathered PCBs like PCB 1242 or 1248. Most others were either no longer receiving any PCBs or alternatively were exposed only to PCB mixtures resembling the more chlorinated formulations, probably the products of weathering.

At individual stations, the concentrations of PCBs changed little. At 4 of the 78 sites, the lipid-weight levels increased, while at 5 of 78 stations, PCB levels declined ($p \leq 0.05$). Decreases occurred at sites where the initial levels were above 1 ppm. The components resembling PCB 1254 decreased at 14 stations and increased at 4, but did not exceed 1.5 ppm at any of these stations. The highest total PCB concentrations between 1973 and 1979 ranged from 71 to 93 ppm. At some highly contaminated stations, the levels may have decreased slightly but at the expense of spreading to natural sinks like the Great Lakes.[24]

A small subset of the National Pesticide Monitoring Program samples provided a more consistent data base for studying trends.[42] These cross-check samples were re-analyzed by the Columbia National Fisheries Research Laboratory for the quality assurance program. Methodology, though intended to be more consistent, nonetheless changed at intervals throughout the course of these studies. Furthermore, the cross-check program selected samples (1) known to have high residue levels or (2) caught at stations previously polluted with PCBs.[68] Obviously, they represent a biased sample from the point of view of trend assessment. Comparison of 92 cross-check samples from the early years, 1970 to 1972 vs. 1973/74, suggested differences ($p < 0.01$). Values declined more than 65%, part of which may have been an artifact of a rapidly changing quantitation technique. Again at these point sources, the pattern of pollution contrasted with that observed in areas distant from direct PCB contamination. Data based on lipid weight exhibited greater relative precision than those based on wet weight, similar to findings for the Hudson River. The overall picture at the 15 polluted sites between 1970 and 1976/77 is shown in Figure 9.

III. CONCLUSIONS

Despite years of concern about PCB pollution, PCB levels in terrestrial and aquatic organisms have declined mainly in the most polluted areas. PCB levels have remained stable or actually increased where they were previously low or absent. PCB levels have dropped substantially in the Hudson River, the site of intentional massive dumping of Aroclor® 1016. Total PCBs in striped bass dropped from 18.1 ppm in 1978 to 4.8 ppm in 1981. Aroclor® 1016, containing 42% chlorine declined 90% and PCB 1254 55%. By comparison, levels in fresh water fishes sampled throughout the U.S. for the National Pesticide Monitoring Program followed a pattern typical of lower levels of pollution. PCB levels ranged up and

MONS 005922

Table 5
INCIDENCE AND CONCENTRATION OF PCBs IN NATIONAL PESTICIDE MONITORING PROGRAM SAMPLES OF FRESH WATER FISHES[34,60]

	Total PCBs (ppm)				PCB 1242 (ppm)			PCB 1248 (ppm)		PCB 1254 (ppm)			
	73*	74	76—77	78—79	73	74	76—77	76—77	78—79	73	74	76—77	78—79
No. of stations	**	87	106	108									
No. of samples	**	335	305	315									
Lipid content (%)	5 5	5 8	6 8	6 5									
Length (cm)	**	**	33 6	33 0									
Residue incidence (%)	70	93	92	98	14	5 4	0	39	42	62	86	84	98
Residue content (ppm)													
Wet weight basis													
Mean (all)	0.78	0 95	0 87	0 84	0.11	0.01	0	0 15	0 14	0 58	0 82	0 47	0 46
Mean (78)		1 1	0 97	0 97							0 96	0 53	0 50
Maximum	25.0	75	71	93	15	4 5	0	52	67	25	75	16	22
Lipid weight basis													
Mean	5.7	9 7	8 0	8 8	0 3	0.1	0	0 64	0 73	3 7	7 0	4 0	4 7
Mean (78)		10	9 7	11							7 8	5 0	5 4
Maximum	812	1060	740	480	180	95.5	0	470	350	710	1060	280	110

Note: ppm: µg/g whole fish; mean: "geometric" mean using $\log_{10}$ (PCB residue + 1). Mean (78): geometric mean for 78 stations represented in all years 1974 to 1979; no data for PCB 1242 or PCB 1248. *First year PCB 1242, 1254, and 1260 were determined separately. No data for PCB 1242 in 78—79. No data for PCB 1248 in 73 or 74. **Unknown.

MONS 005923

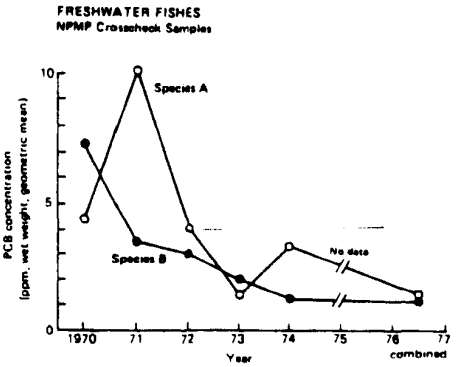


FIGURE 9 PCBs in cross check samples from the National Pesticide Monitoring Program survey of freshwater fishes. Specimens from 13 polluted sites were analyzed by a single laboratory in the years 1970—1977. (From the data of Schmitt.[71])

down from year to year without showing distinct trends: from 0.78 to 0.95 to 0.84 ppm total PCBs in the years 1973, 1974, and 1978/79.

Other data are similarly variable. Declines in PCB levels were noted in ten species of fishes from Lake Simcoe, Canada, in young harp seals from the Gulf of St. Lawrence, and in herring from the Baltic Sea. On the other hand, no significant change in PCB levels was observed in gray seals from the east coast of Scotland, brown pelicans from South Carolina (U.S.) or mallard ducks throughout the U.S. Thus, the specific trend of PCB contamination depends on the exact location and species.

Why have we seen no clear worldwide PCB trend? Biological variation and environmental fluctuation contribute to the variability of PCB data, but more important still, a vast reservoir remains from the estimated 680,000 t of PCBs produced worldwide starting in 1929.[33] Recent human poisonings in Taiwan witness the continuing use of PCBs in open systems.[146] Even in the U.S. a ruptured transformer contaminated poultry and eggs in several states in 1979.[147]

Beyond these episodes of essentially direct contamination of human and animal feed, polluted landfills and sediment continue to release PCBs, which are recycled starting with worms[148] and detritivores,[149] and continuing for decades in at least marine mammals[64] and sharks.[68]

Once PCBs cease to be released, they will still continue to dissipate slowly. Their disappearance from organisms presumably follows an exponential curve. After an initial rapid decline, further loss will be much more gradual,[29,130] until PCBs degrade or reach the ocean depths,[150] where remobilization occurs more slowly.

IV. OUTLOOK

The purpose of this paper has been to assess the status of PCB pollution. Readers undoubtedly hoped to see some change, preferably a substantial decrease, in environmental levels of PCBs. They assumed that heightened awareness of the problem and subsequent

MONS 005924

restrictions in use would limit the amount dispersing throughout the world. They may have assumed that with all the developments in analytical techniques, trends could be determined easily, rapidly, and accurately.

As we have seen, these hopes have not yet been fulfilled. Measuring trends of these complex, refractory mixtures is extremely complicated. Gradual dissipation and degradation of PCB residues can be discerned only after an extended period. Even then the evolution of analytical techniques has introduced elements of doubt.

With all these limitations, why bother to monitor at all? If we cannot detect small changes rapidly, we can at least see gradual shifts downward or upward after extended periods of surveillance. Such changes serve as an early warning that desired trends may not be achieved, that feared increases in pollution may actually occur, that further action may be necessary. Even more important, we have gained some insights. While we cannot quantitatively compare specific data, we can still apply our knowledge in general terms to predicting the future of pollution.

V. NEEDS

This chapter would not be complete without a brief statement on future needs. We must accept the intrinsic imprecision of environmental data until discrete individual compounds are being monitored. As long as analytical techniques for complex mixtures continue to be refined, we must recognize the uncertainty of comparing data over time. We must also recognize the need for patience, for even in this era of microprocessors and space travel, trend assesesment will never be an instantaneous process.

A more concrete issue is appropriate statistical methods for assessment of PCB (and other pollutant) data. Chemists and biologists need to join with statisticians in an intensive examination of the nature of our data and effective statistical approaches. Chemists and biologists seldom have the expertise to devise statistically valid analyses, while statisticians need the experience and insights of biologists and chemists.

We also need to continue sampling on a regular basis. As we have seen, residue levels vary widely. Occasional samples at long intervals will not provide the substantive information only available from intensive monitoring.

Finally, we must realize that ultimately all the inhabitants of planet Earth pay for quick "free" disposal of toxic wastes. "Disposal" in landfills and sanitary sewers is only the beginning of long-term pollution. Real control of toxic substances requires confinement and destruction at the source. Toxic substances already in landfills and sediment require special attention, including new methods for immobilization or removal. Since new processes such as advanced sanitary waste water treatment can be detrimental rather than beneficial, we need to evaluate the long-range impact of techniques before introducing them in polluted areas.

ACKNOWLEDGMENTS

Many of the scientists noted in this chapter generously shared their insights and recent research even before publication. I wish to thank specifically T. F. Bidleman, L. J. Blus, C. M. Bunck, J. W. Farrington, R. Frank, F. Gress, S. D. Haseltine, A. V. Holden, E. G. Horn, A. Jensen, A. J. Mearns, H. A. Schafer, C. J. Schmitt, W. R. Swain, J. F. Uthe, W. A. Willford, and D. R. Young.

J. A. Dassow, E. J. Gauglitz, Jr., C. R. Houle, M. M. Krahn, A. J. Mearns, R. Miller, G. H. Stout, and especially W. D. MacLeod, Jr. provided critical review of the manuscript. R. F. Kappenman provided guidance for the statistical evaluation. D. A. DeWitt prepared the manuscript with great skill and endless patience. G. H. Stout proofed the final copy.

I wish to thank J. Spinelli and W. Aron for their continuing support throughout the writing of this chapter.

MONS 005925

REFERENCES

1. Maugh, T. H., II. Polychlorinated biphenyls: still prevalent, but less of a problem. *Science*. 178, 388, 1972.
2. Stratton, C. L., Whitlock, S. A., and Allan, J. M., A method for the sampling and analysis of polychlorinated biphenyls (PCBs) in ambient air. EPA-600/4-78-048, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1978, as quoted in **Billings, W. N. and Bideman, T. F.**, High volume collection of chlorinated hydrocarbons in urban air using three solid adsorbents. *Atmos Environ*., 17, 383, 1983.
3. **Sloan, R. J. and Armstrong, R. W.**, PCB patterns in Hudson River fish. II. Migrant/marine species. *Proc. Hudson River Environ. Soc.*, Norrie Point, N.Y., September 1981, in press, 1985.
4. **Lawler, Matusky, and Skelly Engineers**, Upper Hudson River PCB no action alternative study: final report, Pearl River, N.Y., 1978, as quoted in **Horn, E. G., Hetling, L. J., and Tofflemire, T. J.**, The problem of PCBs in the Hudson River system, in *Health Effects of Halogenated Aromatic Hydrocarbons*, Nicholson, W. J. and Moore, J. A., Eds., *Ann. N.Y. Acad. Sci.*, 320, 591, 1979.
5. **Jensen, S.**, Report of a new chemical hazard, *New Sci.*, 32, 612, 1966.
6. **Risebrough, R. W., Riecke, P., Peakall, D. B., Herman, S. G., and Kirven, M. N.**, Polychlorinated biphenyls in the global ecosystem, *Nature (London)*, 220, 1098, 1968.
7. **Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G.**, DDT and PCB in marine animals from Swedish waters, *Nature (London)*, 224, 247, 1969.
8. **Risebrough, R. W., Walker, W., II, Schmidt, T. T., de Lappe, B. W., and Connors, C. W.**, Transfer of chlorinated biphenyls to Antarctica, *Nature (London)*, 264, 738, 1976.
9. **Holden, D. C., Simmons, J. H., and Tatton, J. O'G.**, Chlorinated hydrocarbons in British wildlife, *Nature (London)*, 216, 227, 1967.
10. **Stout, V. F.**, Pesticide levels in fish of the Northeast Pacific, *Bull. Environ. Contam. Toxicol.*, 3, 240, 1968.
11. **Beesheld, F. L. and Stout, V. F.**, The use and effect of mixed standards on the quantitation of polychlorinated biphenyls, *Bull. Environ. Contam. Toxicol.*, 10, 10, 1973.
12. **Stout, V. F. and Beesheld, F. L.**, Chlorinated hydrocarbon levels in fishes and shellfishes of the northeastern Pacific Ocean, including the Hawaiian Islands, *Mar. Fish. Rev.*, 43(1), 1, 1981.
13. **Holden, A. V.**, International cooperative study of organochlorine and mercury residues in wildlife, 1969—71, *Pest. Monit. J.*, 7, 37, 1973.
14. **Veith, G. D., Kuehl, D. W., Leonard, E. N., Welch, K., and Pratt, G.**, Polychlorinated biphenyls and other organic chemical residues in fish from major United States watersheds near the Great Lakes, 1978, *Pest. Monit. J.*, 15, 1, 1981.
15. **Uthe, J. F., Musial, C. J., and Palmork, K. H.**, A report on an intercomparison study of the determination of chlorinated biphenyl (PCB) isomers in fish oil, *Int. Council Expl. Sea Mar. Environ Qual. Comm. C. M.*, E 49, 1981.
16. **Stout, V. F. and Beesheld, F. L.**, Analysis of chlorinated hydrocarbon pollutants: a simplified extraction and cleanup procedure for fishery products, *Fish. Bull.*, 76, 880, 1979.
17. **Holden, A. V.**, International cooperative study of organochlorine pesticide residues in terrestrial and aquatic wildlife, 1967/1968, *Pest. Monit. J.*, 4, 117, 1970.
18. **Villeneuve, J. P., Marchand, M., Elder, D., Fowler, S. W., LaRosa, J., Deursens, E. K., Vas, D., and Parsi, P.**, Intercalibration measurements for non-nuclear pollutants, Organochlorine compounds: progress and results to date, in *Activities of the International Laboratory of Marine Radioactivity 1976 Report*, IAEA-187, International Atomic Energy Agency, Vienna, 1976, 99.
19. **Holden, A. V.**, personal communication, 1982.
20. **Goldberg, E. D., Bowen, V. T., Farrington, J. W., Harvey, G., Martin, J. H., Parker, P. L., Risebrough, R. W., Robertson, W., Schneider, E., and Gamble, E.**, The mussel watch, *Environ. Conserv.*, 5, 101, 1978.
21. **Richardson, B. J. and Wald, J. S.**, PCBs in the Port Phillip Region. Survey of Polychlorinated Biphenyls (PCBs) in Port Phillip Bay, Environmental Studies Program Task No. POS-802, Ministry for Conservation, Victoria, Australia, 1980.
22. **Bidleman, T. F.**, Interlaboratory analysis of high molecular weight organochlorines in ambient air, *Atmos. Environ.*, 15, 619, 1981.
23. **Horwitz, W., Kamps, L. R., and Boyer, K. W.**, Quality assurance in the analysis of foods for trace constituents, *J. Assoc. Off. Anal. Chem.*, 63, 1344, 1980.
24. **Schmitt, C. J., Ribick, M. A., Ludke, J. L., and May, T. W.**, National Pesticide Monitoring Program: Organochlorine Residues in Freshwater Fish, 1976—79, Resource Publ. 152, U.S. Department of the Interior, Fish and Wildlife Service, Washington, D.C., 1983.
25. **Swain, W. R.**, Chlorinated organic residues in fish, water, and precipitation from the vicinity of Isle Royale, Lake Superior, *J. Great Lakes Res.*, 4, 398, 1978.

MONS 005926

26. **Swain, W. R. and Mullin, M. D.**, Refined Analysis of Residue Forming Organic Substances in Lake Trout from the Vicinity of Isle Royale, Lake Superior, Absract, 25th Annu. Meet., Int. Assoc Great Lakes Res., *Sault Ste. Marie, Ontario, 1982.*
27. Great Lakes Water Quality Board, 1981 Report on Great Lakes Water Quality, Appendix, Great Lakes Surveillance, Report to the International Joint Commission, November 1981.
28. **Farrington, J. W., Goldberg, E. D., Risebrough, R. W., Martin, J. H., and Bowen, V. T.**, U.S. "Mussel watch" 1976—1978: an overview of the trace metal, DDE, PCB, hydrocarbon and artificial radionuclide data, *Environ. Sci. Technol.*, 17, 490, 1983.
29. **Willford, W. A.**, The Role of the Great Lakes Fishery Laboratory (USFWS) in Surveillance of Contaminants in Great Lakes Fishes, Agenda Item 20, Interim Meeting, Great Lakes Fishery Commission, Ann Arbor, Mich., November 29, 1978.
30. **Addison, R. F. and Brodie, P. F.**, Organochlorine residues in maternal blubber, milk, and pup blubber from grey seals (*Halichoerus grypus*) from Sable Island, Nova Scotia, *J. Fish. Res. Bd. Can.*, 34, 937, 1977.
31. **Frank, R., Lumsden, H., Barr, J. F., and Braun, H. E.**, Residues of organochlorine insecticides, industrial chemicals, and mercury in eggs and in tissues taken from healthy and emaciated common loons Ontario, Canada, 1968—1980, *Arch. Environ. Contam. Toxicol.*, 12, 641, 1983.
32. **Butler, P. A.**, Organochlorine residues in estuarine mollusks, 1965—72 — National Pesticide Monitoring Program, *Pest. Monit. J.*, 6, 238, 1973.
33. **Richardson, B. J. and Wade, J. S.**, Polychlorinated biphenyls (PCBs): an Australian viewpoint on a global problem, *Search*, 13, 17, 1982.
34. **Martin, M., Crane, D., Lew, T., and Seto, W.**, Synthetic organic compound in mussels, *M. californianus* and *M. edulis*, from California's coast, bays, and estuaries, in *California Mussel Watch, 1980—1981*, Part III, State Water Resources Control Board, Sacramento, 1982.
35. **Risebrough, R. W., de Lappe, B. W., Lettermann, E. F., Lane, J. L., Firestone-Gillis, M., Springer, A. M., and Walker, W., II**, Organic pollutants in mussels, *Mytilus californianus* and *M. edulis*, along the California coast, in *California Mussel Watch: 1977—1978*, Vol. 3, Water Quality Monitoring Report No. 79—22, State Water Resources Control Board, Sacramento, 1980.
36. **Ballschmiter, K., Buchert, H., Bihler, S., and Zell, M.**, Baseline studies of the global pollution. IV. The pattern of pollution by organo-chlorine compounds in the North Atlantic as accumulated by fish, *Fresenius' Z. Anal. Chem.*, 306, 323, 1981.
37. **Parrish, P. R., Lowe, J. I., Wilson, A. J., Jr., and Patrick, J. M., Jr.**, Effects of Aroclor® 1254 a PCB, on oysters, *Crassostrea virginica* (bivalvia: prosobranchia: Ostreidae), *Assoc. Southeast Biol. Bull.*, 19, 90, 1972.
38. **Parrish, P. R., Hansen, D. J., Couch, J. N., Patrick, J. M., Jr., and Cook, G. H.**, Effects of the polychlorinated biphenyl Aroclor® 1016, on estuarine animals, *Assoc. Southeast Biol. Bull.*, 21, 74, 1974.
39. **McDermott, D. J., Young, D. R., and Heesen, T. C.**, PCB contamination of southern California marine organisms, in Proc. Natl. Conf. on Polychlorinated Biphenyls, Buckley, J. L., Ed., U.S. Environmental Protection Agency, Washington, D.C., 1976, 209.
40. **Stout, V. F. and Lewis, L. G.**, Role of disposal of PCB-contaminated sediment in the accumulation of PCB's by marine animals, in Aquatic Disposal Field Investigations Duwamish Waterway Disposal Site Puget Sound, Washington, Tech. Rep. D-77-24, Appendix B., U.S. Army Engineer Waterways Experiment Station, Vicksburg, November, 1977.
41. **Phillips, D. J. H.**, *Quantitative Aquatic Biological Indicators, Their Use to Monitor Trace Metal and Organochlorine Pollution*, Applied Science Publishers, London, 1980, 290.
42. **Young, D. R., Heesen, T. C., and McDermott, D. J.**, An offshore biomonitoring system for chlorinated hydrocarbons, *Mar. Pollut. Bull.*, 7, 156, 1976.
43. **Schmitt, C. J.**, Analysis of variance as a method for examining contaminant residues in fish: National Pesticide Monitoring Program, in *Aquatic Toxicology and Hazard Assessment, Fourth Conference*, American Society for Testing and Materials Spec. Tech. Publ. No. 737, Branson, D. R. and Dickson, K. L., Eds., ASTM, Philadelphia, 1981, 270.
44. **Skea, J. C., Simonin, H. A., Deas, H. J., Colquhoun, J. R., Spagnoli, J. J., and Veith, G. D.**, Bioaccumulation of Aroclor 1016 in Hudson River fish, *Bull. Environ. Contam. Toxicol.*, 22, 332, 1979.
45. **Zitko, V.**, Uptake of chlorinated paraffins and PCB from suspended solids and food by juvenile Atlantic salmon, *Bull. Environ. Contam. Toxicol.*, 12, 406, 1974.
46. **Lieb, A. J., Bills, D. D., and Sinnhuber, R. O.**, Accumulation of dietary polychlorinated biphenyls (Aroclor 1254) by rainbow trout (*Salmo gairdneri*), *J. Agric. Food. Chem.*, 22, 638, 1974.
47. **Butler, P. A. and Schutzmann, R. L.**, Residues of pesticides and PCBs in estuarine fish, 1972—76 National Pesticide Monitoring Program, *Pest. Monit. J.*, 12, 51, 1978.
48. **Butler, P. A. and Schutzmann, R. L.**, Bioaccumulation of DDT and PCB in tissues of marine fishes, *Aquatic Toxicology*, American Society for Testing and Materials Spec. Tech. Publ. No. 667, Marking, L. L. and Kimerle, R. A., Eds., ASTM, Philadelphia, 1979, 212.

MONS 005927

49. **Gilman, A. P., Fox, G. A., Peakall, D. B., Teeple, S. M., Carroll, T. R., and Haymes, G. T.,** Reproductive parameters and egg contaminant levels of Great Lakes herring gulls, *J. Wildl. Manage.*, 41, 458, 1977.
50. **Blus, L. J., Lamont, T. C., and Neely, B. S., Jr.,** Effects of organochlorine residues on eggshell thickness, reproduction, and population status of brown pelicans *(Pelecanus occidentalis)* in South Carolina and Florida, 1969—76, *Pest. Monit. J.*, 12, 172, 1979.
51. **Bache, C. A., Serum, J. W., Youngs, W. D., and Lisk, D. J.,** Polychlorinated biphenyl residues accumulation in Cayuga Lake trout with age, *Science*, 177, 1191, 1972.
52. **Armstrong, R. W. and Sloan, R. J.,** PCB patterns in Hudson River fish. I. Resident/freshwater species, *Proc. Hudson River Environ. Soc.*, Norrie Point, N.Y., September 1981, in press, 1985.
53. **Armstrong, R. W. and Sloan, R. J.,** *Trends in Levels of Several Known Chemical Contaminants in Fish from New York State Waters*, Tech. Rep. 80-2, New York State Department of Environmental Conservation, Albany, 1980.
54. **Hansen, M. M., Jensen, A., and Lassen, H.,** Trend monitoring. I. Problems in the interpretation of contaminant concentrations using fish as indicator organisms, *Int. Council Expl. Sea Mar. Environ. Qual. Comm.*, C.M., E 25, 1982.
55. **Olsson, M., Jensen, S., and Reutergard, L.,** Seasonal variation of PCB levels in fish — An important factor in planning aquatic monitoring programs, *Ambio*, 7, 66, 1978.
56. **Wilson, A. J. and Forester, J.,** Persistence of Aroclor 1254 in a contaminated estuary, *Bull. Environ. Contam. Toxicol.*, 19, 637, 1978.
57. **Nisbet, I. C. T. and Reynolds, L. M.,** Organochlorine residues in common terns and associated estuarine organisms, Massachusetts, 1971—81, *Mar. Environ. Res.*, 11, 33, 1984.
58. **King, K. A., Flickinger, E. L., and Hildebrand, H. H.,** The decline of brown pelicans on the Louisiana and Texas Gulf Coast, *Southwest Nat.*, 21, 417, 1977.
59. **Anderson, D. W., Jurek, R. M., and Keith, J. O.,** The status of brown pelicans at Anacapa Island in 1975, *Calif. Fish Game*, 63, 4, 1977.
60. **Holden, A. V.,** Organochlorine residues in blubber of grey seals *(Halichoerus grypus)* from the Farne Islands, *Int. Council Expl. Sea Mar. Environ. Qual. Comm. Ref. Mar. Mammals Comm.*, C.M., E 41, 1978.
61. **Addison, R. F. and Smith, R. G.,** Organochlorine residue levels in Arctic ringed seals: variation with age and sex, *Oikos*, 25, 335, 1974, as cited in **Holden, A. V.,** Pollutants and seals — a review, *Mammal Rev.*, 8, 53, 1978.
62. **Allbright, L. J., Northcote, T. G., Oloffs, P. C., and Saeto, S. Y.,** Chlorinated hydrocarbon residues in fish, crabs, and shellfish of the lower Fraser River, its estuary, and selected locations in Georgia Strait, British Columbia — 1972—3, *Pest. Monit. J.*, 9, 134, 1975.
63. **Gahler, A. R., Cummins, J. M., Blazevich, J. N., Riech, R. H., Arp, R. L., Gangmark, C. E., Pope, S. V. W., and Filip, S.,** Chemical Contaminants in Edible, Non-Salmonid Fish and Crabs from Commencement Bay, Washington, EPA-910/9-82-093, U.S. Environmental Protection Agency, Seattle, 1982.
64. **Buckley, E. H.,** Accumulation of airborne polychlorinated biphenyls in foliage, *Science*, 216, 520, 1982.
65. **Mearns, A. J.,** Responses of coastal fishes and invertebrates to wastewater discharges, *Prog. Water Technol.*, 4, 19, 1979.
66. **Butler, P. A.,** Biological problems in estuarine monitoring, Paper EPA-600/4-74-004, 1974, 126, Proc. Seminar on Methodology for Monitoring the Marine Environment, U.S. Environmental Protection Agency, Washington, D.C., 1974.
67. **Bimbo, A.,** Personal communication, 1982.
68. **Schmitt, C. J., Ludke, J. L., and Walsh, D. F.,** Organochlorine residues in fish: National Pesticide Monitoring program, 1970—74, *Pest. Monit. J.*, 14, 136, 1981.
69. **Mellanen, R., Pyysalo, H., Wickstrom, K., and Linko, R.,** Time trends of chlordane, DDT, and PCB concentrations in pike *(Esox lucius)* and Baltic herring *(Clupea harengus)* in the Turku Archipelago, Northern Baltic Sea for the period 1971—1982, *Bull. Environ. Contam. Toxicol.*, 29, 334, 1982.
70. **Stout, V. F., Houde, C. R., and Beesheld, F. L.,** A survey of chlorinated hydrocarbon residues in menhaden fishery products, *Mar. Fish. Rev.*, 43(3), 1, 1981.
71. **Stout, V. F.,** Unpublished data.
72. **Koch, G., Poubel, P., and Monnerot, R. J.,** Organochlorine and mercury residues in peregrine falcon eggs in France, *Bull. Environ. Contam. Toxicol.*, 28, 705, 1982.
73. **Gordon, M., Knauer, G. A., and Martin, J. H.,** *Mytilus californianus* as a bioindicator of trace metal pollution: variability and statistical considerations, *Mar. Pollut. Bull.*, 11, 195, 1980.
74. **Jensen, A. and Lassen, H.,** Trend monitoring of contaminants. Sampling design considerations, *Int. Council Expl. Sea Mar. Environ. Qual. Comm.*, C.M., E 63, 1981.

MONS 005928

75 **Kaiser, K. L. E.**, Early trend determination of organochlorine contamination from residue ratios in the sea lamprey (*Petromyzon marinus*) and its lake whitefish (*Coregonus clupeaformis*) host. *Can. J. Fish Aquat. Sci.*, 39, 571, 1982.

76 **Lassen, H.** Trend monitoring II. Statistical theory. *Int. Council Expl. Sea Mar. Environ. Qual. Comm.* C.M., E 26, 1982.

77 **Cain, B. W.**, Nationwide residues of organochlorine compounds in wings of adult mallards and black ducks, 1979—80. *Pest. Monit. J.*, 15, 128, 1981.

78 **Gossett, R. W., Puffer, H. W., Arthur, R. H., Jr., and Young, D. R.**, DDT, PCB, and benzo(a)pyrene levels in white croaker (*Genyonemus lineatus*) from southern California. *Mar. Pollut. Bull.*, 14, 60, 1983.

79 **Haseltine, S. D., Heinz, G. H., Reichel, W. L., and Moore, J. F.**, Organochlorine and metal residues in eggs of waterfowl nesting on islands in Lake Michigan off Door County, Wisconsin, 1977—78. *Pest. Monit. J.*, 15, 90, 1981.

80 **Young, D. R., McDermott-Ehrlich, D., and Heesen, T. C.**, Sediments as sources of DDT and PCB. *Mar. Pollut. Bull.*, 8, 254, 1977.

81 **McDermott, D. J., Young, D. R., and Heesen, T. C.**, Polychlorinated Biphenyls in Marine Organisms off Southern California, TM 223, NTIS # PB274464/AS, Southern California Coastal Water Research Project, El Segundo, 1975.

82 **Sarkka, J., Hattula, M.-L., Janatuinen, J., Paasivirta, J., and Palokangas, R.**, Chlorinated hydrocarbons and mercury in birds of Lake Paijanne, Finland — 1972-74. *Pest. Monit. J.*, 12, 26, 1978.

83 **Blus, L. J.**, Further interpretation of the relation of organochlorine residues in brown pelican eggs to reproductive success. *Environ. Pollut.*, 28(A), 15, 1982.

84 **Heesen, M. M.**, Trend monitoring. III. Statistical analysis of factors affecting the concentrations of cadmium, copper, and zinc in three species of fish. *Int. Council Expl. Sea Mar. Environ. Qual. Comm.*, C.M., E 27, 1982.

85 **Jensen, A.**, Trend monitoring. IV. Statistical analysis of factors affecting the concentrations of mercury in flounder. *Int. Council Expl. Sea Mar. Environ. Qual. Comm.*, C.M., E 28, 1982.

86 **Scott, D. P., Uthe, J. F., and Chou, C. L.**, Further considerations of time trend determinations of contaminant levels in Canadian cod. *Int. Council Expl. Sea Mar. Environ. Qual. Comm.*, C.M., E 47, 1981.

87 **Klaas, E. E. and Bellis, A. A.**, Organochlorine pesticide and polychlorinated biphenyl residues in selected fauna from a New Jersey salt marsh — 1967 vs. 1973. *Pest. Monit. J.*, 10, 149, 1977.

88 **Pearce, P. A., Peakall, D. B., and Reynolds, L. M.**, Shell thinning and residues of organochlorines and mercury in seabird eggs, Eastern Canada, 1970—76. *Pest. Monit. J.*, 13, 61, 1979.

89 **Dreher, K. H., Rule, P., and Corte-Real, L.**, PCB residues in *Mercenaria mercenaria* from New Bedford harbor, 1978. *Bull. Environ. Contam. Toxicol.*, 27, 683, 1981.

90 **Frank, R., Holdrinet, M. V. H., Dusjardine, R. L., and Dodge, D. P.**, Organochlorine and mercury residues in fish from Lake Simcoe, Ontario, 1970—76. *Environ. Biol. Fish.*, 3, 275, 1978.

91 **Holden, A. V.**, Pollutants and seals — a review. *Mammal Rev.*, 8, 53, 1978.

92 **Jones, D., Ronald, K., Lavigne, D. M., Frank, R., Holdrinet, M., and Uthe, J. F.**, Organochlorine and mercury residues in the harp seal (*Pagophilus groenlandicus*). *Sci. Total Environ.*, 5, 181, 1976.

93 **Frank, R., Ronald, K., and Braun, H. E.**, Organochlorine residues in harp seals (*Pagophilus groenlandicus*) caught in eastern Canadian waters. *J. Fish. Res. Bd. Can.*, 30, 1053, 1973.

94 **Schneider, R.**, Polychlorinated biphenyls (PCBs) in cod tissues from the Western Baltic: significance of equilibrium partitioning and lipid composition in the bioaccumulation of lipophilic pollutants in gill-breathing animals. *Meeresforschung*, 29, 69, 1982.

95 **Lachas, B. and Lorenzen, W.**, Zum Vorkommen von chlororganischen Pestiziden und polychlorierten Biphenylen in Muttermilch der Kühe Schleswig-Holsteins. *Dtsch. Lebensm. Rundsch.*, 77, 437, 1981.

96 **Paasivirta, J. and Linko, R.**, Environmental toxins in Finnish wildlife. A study on time trends of residue contents in fish during 1973—1978. *Chemosphere*, 9, 643, 1980.

97 **Koppenaal, R. F.**, Personal Communication, 1982.

98 **Paasivirta, J., Sarkka, J., Abe, M., Sorma-Abe, K., Tarhanen, J., and Rose, A.**, Recent trends of biocides in pikes of the Lake Paijanne. *Chemosphere*, 10, 405, 1981.

99 **Frank, R., Braun, H. E., and Fleming, G.**, Organochlorine and organophosphorus residues in fat of bovine and porcine carcasses marketed in Ontario 1969—81. *J. Food Prot.*, 46, 893, 1983.

100 **Frank, R., Braun, H. E., Holdrinet, M., Sirons, G. J., Smith, E. H., and Dixon, D. W.**, Organochlorine insecticides and industrial pollutants in the milk supply of southern Ontario, Canada — 1977. *J. Food Prot.*, 42, 31, 1979.

101 **Great Lakes Water Quality Board.** 1981 Report on Great Lakes Water Quality. Report to the International Joint Commission, November 1981.

102 **Frank, R., Holdrinet, M., Braun, H. E., Dodge, D. P., and Sprangler, G. E.**, Residues of organochlorine insecticides and polychlorinated biphenyls in fish from Lakes Huron and Superior, Canada — 1968—76. *Pest. Monit. J.*, 12, 60, 1978.

MONS 005929

103. **Frank, R., Braun, H. E., Holdrinet, M., Dodge, D. P., and Nepszy, S. J.,** Residues of organochlorine insecticides and polychlorinated biphenyls in fish from Lakes Saint Clair and Erie, Canada — 1968—76. *Pest. Monit. J.*, 12, 69, 1978.
104. **Willford, W.,** Results of fish-contaminant monitoring, personal communication, 1982.
105. **Scott, W. B. and Crossman, E. J.,** *Freshwater Fishes of Canada*, Bulletin 184, Fisheries Research Board of Canada, Ottawa, 1973, 220.
106. **Jensen, A. L., Spigarelli, S. A., and Thommes, M. M.,** PCB uptake by five species of fish in Lake Michigan, Green Bay of Lake Michigan, and Cayuga Lake, New York, *Can. J. Fish. Aquat. Sci.*, 39, 700, 1982.
107. **Willford, W. A., Hesselberg, R. J., and Nicholson, L. W.,** Trends of polychlorinated biphenyls in three Lake Michigan fishes, in Proc. Natl. Conf. on Polychlorinated Biphenyls, Buckley, J. L., Ed., U.S. Environmental Protection Agency, Washington, D.C., 1976, 177.
108. **Mineau, P., Fox, G. A., Norstrom, R. J., Weseloh, D. V., Hallett, D. J., and Ellenton, J. A.,** Using the herring gull to monitor levels and effects of organochlorine contamination in the Canadian Great Lakes, in *Toxic Contaminants in the Great Lakes*, Nriagu, J. O. and Simmons, M. S., Eds., John Wiley & Sons, New York, 1984, 425.
109. **Bascom, W.,** Director's statement, in *Coastal Water Research Project Biennial Report for the Years 1979—1980*, NTIS # PB81-158271, Bascom, W., Ed., Southern California Coastal Water Research Project, Long Beach, 1980, 1.
110. **Young, D. R., McDermott, D. J., Heesen, T. C., and Jan, T. K.,** Pollutant inputs and distributions off southern California, in *Marine Chemistry in the Coastal Environment*, ACS Symp. Ser. 18, Church, T. M., Ed., American Chemical Society, Washington, D.C., 1975, 424.
111. **Schafer, H. A.,** Characteristics of municipal wastewater, in *Coastal Water Research Project Biennial Report for the Years 1979—1980*, NTIS #PB81-158271, Bascom, W., Ed., Southern California Coastal Water Research Project, Long Beach, 1980, 235.
112. **Young, D. R., Jan, T.-K., Gossett, R. W., and Hershelman, G. P.,** Trace pollutants in surface runoff, in *Coastal Water Research Project Biennial Report for the Years 1979—1980*, NTIS # PB81-158271, Bascom, W., Ed., Southern California Coastal Water Research Project, Long Beach, 1980, 163.
113. **Hom, W., Risebrough, R. W., Soutar, A., and Young, D. R.,** Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara Basin, *Science*, 184, 1197, 1974.
114. **MacGregor, J. S.,** Changes in the amount and proportions of DDT and its metabolites, DDE and DDD, in the marine environment off southern California, 1949—1972, *Fish. Bull.*, 72, 275, 1974.
115. **Neidermyer, W. J. and Hickey, J. J.,** Chronology of organochlorine compounds in Lake Michigan fish, 1929—66, *Pest. Monit. J.*, 10, 92, 1976.
116. **Gossett, R. W.,** Personal communication, 1982.
117. **Young, D. R. and Heesen, T. C.,** DDT, PCB and chlorinated benzenes in the marine ecosystem off southern California, in *Water Chlorination — Environmental Impact and Health Effects*, Vol. 2, Jolley, R. L., Gorchev, H., and Hamilton, D. H., Jr., Eds., Ann Arbor Science, Ann Arbor, Mich., 1978, 267.
118. **Skogsberg, T.,** *The Fishes of the Family Scianeidae (Croakers) of California*, Fish Bull. No. 54, California Division of Fish and Game, Bureau of Marine Fisheries, Sacramento, 1939, 48.
119. **Puffer, H. W. and Gossett, R. W.,** PCB, DDT and benzo(a)pyrene in raw and pan fried white croaker (*Genyonemus lineatus*), *Bull. Environ. Contam. Toxicol.*, 30, 65, 1983.
120. **Young, D., Changes** in chlorinated hydrocarbons and metals, in March 1978 report to LA/OMA on task order No. 3 — forecast effects (under the conditions of the baseline alternative), Bascom, W., Ed., p. 39, in *Modification of Secondary Treatment Requirements for Dischargers into Marine Waters*, Hearings before the Subcommittee of Water Resources of the Committee on Public Works and Transportation, HR 95-54, U.S. House of Representatives, 95th Congress, 2nd Session, May 24 and 25, 1978, 133.
121. **Hendricks, T.,** Changes in the bottom near Whites Point and Orange County as determined by a mathematical model using data on organic carbon, DDT, and copper, in March 1978 report to LA/MOA on task order No. 3 — forecast effects (under the conditions of the baseline alternative), Bascom, W., Ed., p. 9, in *Modification of Secondary Treatment Requirements for Dischargers into Marine Waters*, Hearings before the Subcommittee on Water Resources of the Committee on Public Works and Transportation, HR 95-54, U.S. House of Representatives, 95th Congress, 2nd Session, May 24 and 25, 1978, 133.
122. **Hendricks, T.,** Areal distribution of sewage particulate flux to Palos Verdes shelf; fate of particulates subsequent to deposition; resultant sediment chemical characteristics, in *Joint Water Pollution Control Plans Application for Modification of Secondary Treatment Requirements for Publicly Owned Treatment Works Which Discharge into Marine Waters, Vol. I, Appendix IX*, Garrison, W. E., Ed., Los Angeles County Sanitation Districts, Whittier, 1979.
123. **Horn, E. G., Hettling, L. J., and Teffeteller, T. J.,** The problem of PCBs in the Hudson River system, in *Health Effects of Halogenated Aromatic Hydrocarbons*, Nicholson, W. J. and Moore, J. A., Eds., *Ann. N.Y. Acad. Sci.*, 320, 591, 1979.

MONS 005930

124. **Martin, M., Crane, D., Lew, T., and Seto, W.**, Synthetic organic compounds in mussels, *Mytilus californianus*, and *M. edulis*, along the California coast and selected harbors and bays, in *California Mussel Watch, 1979—1980*, reprinted 1982, part II, State Water Resources Control Board, Sacramento, 1980.
125. **De Yonge, J.**, Poisonous chemical spills into Duwamish, *Seattle Post-Intelligencer*, September 21, 1974.
126. **MacGregor, J. S.**, DDT and its metabolites in the sediments off southern California, *Fish. Bull.*, 74, 27, 1976.
127. **Young, D. R., McDermott, D. J., and Heesen, T. C.**, Marine inputs of polychlorinated biphenyls off Southern California, in Proc. Natl. Conf. on Polychlorinated Biphenyls, Buckley, J. L., Ed., U.S. Environmental Protection Agency, Washington, D.C., 1976, 199.
128. **Southern California Coastal Water Research Project**, Chlorinated hydrocarbons in intertidal organisms of the bight, in *The Ecology of the Southern California Bight: Implications for Water Quality Management*, Section II 5.2, Southern California Coastal Water Research Project, El Segundo, 1973, 307.
129. **Flegal, A. R., Stephenson, M., Martin, M., and Martin, J. H.**, Elevated concentrations of mercury in mussels (*Mytilus californianus*) associated with pinniped colonies, *Mar. Biol.*, 65, 45, 1981.
130. **Berthiaux, E.**, Decrease of DDT in mussels, in *Coastal Water Research Project, NTIS # PB27446/AS, Annual Report for the Year Ending June 30, 1974*, Bascom, W., Ed., Southern California Coastal Water Research Project, El Segundo, 1974, 101.
131. National Marine Fisheries Service, Strategic Plan, U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Washington, D.C., 1983, 5.
132. **Blus, L. J. and Bunck, C. M.**, Personal communication, 1982.
133. **Blus, L., Cromartie, E., McNease, L., and Jaenen, T.**, Brown pelican: population status, reproductive success, and organochlorine residues in Louisiana, 1971—1976, *Bull. Environ. Contam. Toxicol.*, 22, 128, 1979.
134. **Peakall, D. B. and Gilman, A. P.**, Limitations of expressing organochlorine levels in eggs on a lipid-weight basis, *Environ. Contam. Toxicol.*, 23, 287, 1979.
135. **Gress, F.**, Personal communication, 1983.
136. **Butler, P. A., Kennedy, C. D., and Schutzmann, R. L.**, Pesticide residues in estuarine mollusks, 1977 versus 1972 — National Pesticide Monitoring Program, *Pest. Monit. J.*, 12, 99, 1978.
137. **White, D. H.**, Nationwide residues of organochlorines in starlings, 1974, *Pest. Monit. J.*, 10, 10, 1976.
138. **White, D. H.**, Nationwide residues of organochlorine compounds in starlings (*Sturnus vulgaris*), 1976, *Pest. Monit. J.*, 12, 193, 1979.
139. **Cain, B. W. and Bunck, C. M.**, Residues of organochlorine compounds in starlings (*Sturnus vulgaris*), 1979, *Environ. Monit. Assess.*, 3, 161, 1983.
140. **Heath, R. G. and Prouty, R. M.**, Trial monitoring of pesticides in wings of mallards and black ducks, *Bull. Environ. Contam. Toxicol.*, 2, 101, 1967.
141. **Heath, R. G. and Hill, S. A.**, Nationwide organochlorine and mercury residues in wings of adult mallards and black ducks during the 1969—70 hunting season, *Pest. Monit. J.*, 7, 153, 1974.
142. **Dindal, D. L. and Peterle, T. J.**, Wing and body tissue relationships of DDT and metabolite residues in mallard and lesser scaup ducks, *Bull. Environ. Contam. Toxicol.*, 3, 37, 1968.
143. **White, D. H. and Heath, R. G.**, Nationwide residues of organochlorines in wings of adult mallards and black ducks, 1972—73, *Pest. Monit. J.*, 9, 176, 1976.
144. **O'Shea, T. J., Fleming, W. J., III, and Cromartie, E.**, DDT contamination at Wheeler National Wildlife Refuge, *Science*, 209, 509, 1980.
145. **White, D. H.**, Nationwide residues of organochlorine compounds in wings of adult mallards and black ducks, 1976—77, *Pest. Monit. J.*, 13, 12, 1979.
146. **Anon.**, PCB widespread poisoning incident in Taiwan reported, *Food Chem. News*, 21(43), 23, 1980.
147. **King, W.**, Federal Agencies didn't move fast enought in PCB case, say critics, *Seattle Times*, November 11, 1979, B13.
148. **Elder D. L., Fowler, S. W., and Polikarpov, G. G.**, Remobilization of sediment-associated PCBs by the worm *Nereis diversicolor*, *Bull. Environ. Contam. Toxicol.*, 21, 448, 1979.
149. **Marinussel, A. C. and Berthe, R.**, Accumulation of the polychlorinated biphenyl Arochor 1242 from contaminated dentrus and water by the salmarsh dentivore, *Uca pugnax*, *Bull. Environ. Contam. Toxicol.*, 29, 326, 1982.
150. **Elder, D. L. and Fowler, S. W.**, Polychlorinated biphenyls: penetration into the deep ocean by zooplankton fecal pellet transport, *Science*, 197, 459, 1977.
151. Southern California Coastal Water Research Project, as quoted in Reference 35.
152. **Mendenhall, V. M. and Prouty, R. M.**, Recovery of breeding success in a population of brown pelicans, *Proc. Colon. Waterbird Group*, 1978, 65.
153. American Chemical Society Subcommittee on Environmental Analytical Chemistry, Crummett, W. B., Chairman, Guidelines for data acquisition and data quality evaluation in environmental chemistry, *Anal. Chem.*, 52, 2242, 1980.

MONS 005931

154 **Methot, R. and MacCall, A.,** U.S Department of Commerce NOAA, NMFS, Southwest Fisheries Center, Lapolla, Calif., 1983, unpublished data.

MONS 005932

Chapter 10

NONMETABOLIC ALTERATION OF PCBs

John A. G. Roach

TABLE OF CONTENTS

I. Introduction 208
II. Hydrolysis and Alcoholysis 208
III. Photolysis 208
IV. Oxidation and Thermal Alteration 209
References 211

MONS 005933

I. INTRODUCTION

Predictions about the nonmetabolic alteration of PCBs in the environment must address the fact the PCBs do not behave as a homogenous substance. The physical and chemical properties of PCBs vary greatly, depending on the degree and position of chlorine substitution on the biphenyl ring system. Differences in volatility and water solubility of the individual chlorinated biphenyls tend to fractionate the residue so that the actual composition of a thin film, a vapor, or a solution may differ markedly from the original material. It has even been argued that monochlorobiphenyls should be regulated differently from more highly chlorinated biphenyls because of the differences in their chemical and physical properties.

PCBs are stable to chemical alteration as evidenced by their use in a wide variety of applications that require inert behavior. However, nonmetabolic alteration of these compounds does occur in the environment. Processes which may be involved include aqueous hydrolysis, photo alteration, air oxidation, and thermal alterations. The study of the effects of any one of these processes on PCBs in the environment is a complex task. Thus, most of the information for this discussion has been obtained under the more controlled conditions of the laboratory.

II. HYDROLYSIS AND ALCOHOLYSIS

A chlorine on a chlorobiphenyl molecule is not easily displaced in a nucleophilic substitution reaction. Most PCBs are stable to hydrolysis under moderate conditions. The 4- and 4,4'- positions of decachlorobiphenyl are the positions most susceptible to chlorine displacement by hydroxide and alkoxide ions. Decachlorobiphenyl can be hydrolyzed to octachloro-4,4'-biphenylol by heating with aqueous alkali in an autoclave.[2,3] Refluxing with 2% potassium hydroxide in ethanol has been used to remove pesticides that interfere with PCB analysis[4] and to extract PCBs from paper products.[5] Under these conditions, decachlorobiphenyl is readily converted to diethoxyoctachlorobiphenyl. In contrast to decachlorobiphenyl, 2,5-dichlorobiphenyl must be heated with sodium methoxide to produce 2-chloro-5-biphenylol.[6] The nonmetabolic hydrolysis or alcoholysis of PCBs in the environment is unlikely because of the vigorous conditions required.

III. PHOTOLYSIS

PCBs are easily photodegraded. UV light can provide ring activation for both nucleophilic and radical reactions.[7] The photoreactivity of PCBs has been used to confirm PCB residues[8] and to remove PCB interferences in the analysis of chlorinated paraffin residues.[9] A pilot plant has even been constructed to test the feasibility of disposing of PCBs in industrial waste effluent with a combination of irradiation and ozone.[10]

The photoreactivity of a chlorinated biphenyl depends on the number and positions of chlorine atoms in the molecule. When chlorinated biphenyls are photolyzed in organic solvents, those molecules containing more chlorine dechlorinate more readily than the less chlorinated congeners.[6,11] Examination of the photoproducts of isomeric chlorinated biphenyls demonstrates that the ease of dechlorination is *ortho* > *meta* > *para*.[12]

Safe and Hutzinger[13] reported stepwise loss of chlorine, rearrangement, condensation, and polar products when 2,2',4,4',6,6-hexachlorobiphenyl was irradiated at 310 nm in organic solvents. These processes have since been observed with a number of pure chlorobiphenyls and PCB preparations using laboratory UV sources and sunlight. Reductive dechlorination is the predominant photochemical reaction of PCBs in hydrocarbon solvents.[11] Dechlorination proceeds at a faster rate in alcoholic solvents than in hydrocarbon solvents. Photolysis in fluorocarbon solvents and thin films results in chlorination and rearrangements

MONS 005934

in addition to dechlorination.[14] Hydroxylic organic solvents result in polar oxygenated PCB photoproducts as well as dechlorination of PCBs.[13,14]

Water reacts with PCBs during photolysis. Irradiation of a thin film without water results in dechlorination of the PCBs and the formation of PCB condensation products such as terphenyls and quaterphenyls.[13] Irradiation of a thin film in the presence of water yields hydroxylated products.[11] Irradiation of aqueous suspensions of PCBs with *ortho* chlorines has resulted in the formation of chlorinated dibenzofurans in very low yields.[16]

There are differences in the chemistry that occur in a thin film, a vapor, or a solution. Therefore, the location of a PCB residue determines which photoreactions will take place. Interactions between chlorinated biphenyls such as condensation and chlorination can be photoinduced in a thin film. In a solution, the effect of the solvent predominates. In the vapor state, PCBs photolyze rapidly or slowly depending on the presence of other substances. The location of a residue determines the amount of incident light that it receives. However, the result of this insolation is affected by sensitizers, quenchers, and reactants present with the residue. Thus, the diversity of the microenvironments in which PCB residues may be found limits the certainty with which laboratory data may be used to assess photo alteration of PCBs in the environment.

If incidents of accidental contamination are disregarded, PCBs enter our diet primarily from aquatic sources.[7] Thus, the aquatic chemistry of PCBs is highly relevant to our dietary intake of PCBs. Bunce et al.[16] estimated several environmental factors affecting the photo degradation of PCBs in the shallow waters of Lake Erie. They concluded that up to 5% of the lightly chlorinated PCBs might lose a chlorine each year, but that at least one chlorine should be lost from every highly chlorinated molecule annually. The less-chlorinated PCBs are more reactive metabolically than the highly chlorinated PCBs. This suggests that the most important effect of solar radiation on PCBs in the environment is replenishment of metabolically active PCBs from more highly chlorinated congeners.

IV. OXIDATION AND THERMAL ALTERATION

Good thermal stability and excellent dielectric properties led to the use of PCBs in applications where they would be subject to oxidation and considerable thermal and electrical stress. Analyses of PCBs have identified contaminants and products of use that are potentially more hazardous than the PCBs.[19,20]

Chlorinated dibenzofurans are contaminants at the parts per million level in PCB mixtures and other industrial chemicals.[21,22] Vos et al.[23] separated PCBs into fractions by column chromatography and found that PCB fractions containing chlorinated dibenzofurans were more toxic in a chick-embryo bioassay than the other PCB fractions. The possible presence of highly toxic contaminants in PCBs led to the examination of commercial PCB mixtures by several laboratories.[24-26] The results demonstrated the presence of chlorinated dibenzofurans containing two or more chlorines in all PCB mixtures examined except Aroclor® 1221.[27-29] Methodology to detect alteration products of PCBs must distinguish between these trace impurities and any products of use.

The alteration of PCBs in electrical components has not been satisfactorily demonstrated because of the difficulty in obtaining used and unused portions of the same production batch of PCBs. Phillipson et al.[30] carefully devised a procedure to quantitate chlorinated dibenzofurans in Aroclor® 1260-based insulating fluids (askarels) which had been used in high-voltage electrical network transformers for periods ranging from 13 to 20 years. After separation from PCBs and other askarel components by alumina and Florisil column chromatography, chlorinated dibenzofurans were identified by combined gas chromatography-mass spectrometry (GC/MS) and quantitated by electron capture gas-liquid chromatography. Recoveries of 9 di- to octachlorodibenzofurans from spiked askarel matrices ranged from

MONS 005935

72 to 103%. The behavior of 17 additional chlorinated dibenzofuran isomers in the procedure indicated that the method detected a large majority of the 131 possible di- to octachlorodibenzofurans. The total amount of chlorinated dibenzofuran in each of the used askarel samples was found to be not more than three times the chlorinated dibenzofuran content of an unused Aroclor® reference material. When asked about the significance of these findings, Phillipson concluded that the levels of chlorinated dibenzofurans in the used askarels were not sufficiently greater than the reference material and might simply reflect reduced levels of contaminants in Aroclors® of later manufacture.

Anodic oxidation of chlorinated biphenyls provides an insight into the events that occur when the electrified matrix is conducting rather than insulating. Fenn et al.[31] report 3-hydroxy-2,2',5,5'-tetrachlorobiphenyl is the major hydroxychlorobiphenyl product in the electrochemical oxidation of 2,2',5,5'-tetrachlorobiphenyl in an aqueous system. Any hydroxychlorobiphenyl formed in the large-scale electrolysis of PCBs is further oxidized at the potentials required for the oxidation of the PCBs. The principal electrolysis products of PCBs at controlled potentials are chlorophenylbenzoquinones. Chlorinated dibenzofurans are not formed during anodic oxidation of PCBs in this aqueous systems. Operation of electrical equipment containing PCB insulating fluids does not provide these aqueous reaction conditions. However, these products do suggest the fate of PCBs subjected to oxidative electrochemical disposal.[32]

The tragic Yusho incident provided the impetus to study the alteration of PCBs in heat exchange fluids. This accidental contamination of rice oil with PCB heat transfer fluid in February 1968, affected some 1696 people.[33] The manufacturer had used a PCB, Kanechlor® 400, to heat rice oil at reduced pressure in order to remove odorous matter from the oil. Small holes in the heating pipes permitted the PCB to leak into the oil.[34] Comparison of the contaminated oil with Kanechlor® 400 showed that the oil contained an inordinately high level of chlorinated dibenzofurans based on the level of PCBs in the oil.[35,36] Kanechlor® 400 was put into a sealed glass ampoule and heated at 300°C for 15 days, but no increase in chlorinated dibenzofurans was detected.[36] The chlorinated dibenzofuran level in the oil was about 250 times higher than the level found in Kanechlor® 400.[37] This large difference in levels made it difficult to attribute the chlorinated dibenzofuran content of the oil only to a simple concentration of these impurities during processing. Morita et al.[38] examined in detail several PCB preparations and contaminated rice oil samples. A PCB heat transfer fluid that had been used for 2 years appeared to contain about four times the amount of chlorinated dibenzofurans found in comparable unused fluids. They reported that the Yusho oil contained levels of chlorinated dibenzofurans about 500 times that of Kanechlor® 400. It was suggested that oxygen catalyzed by the metal heat transfer tubing would react with *ortho* substituents in the PCBs during processing to form chlorinated dibenzofurans in the heat transfer fluid. This led to a series of heating experiments with Aroclor® 1248. Samples were sealed in glass tubes with air, oxygen, or nitrogen and heated in an oven. Chlorinated dibenzofurans were formed with a maximum yield of about 0.2%. Temperatures over 270°C were necessary for the transformation but above 330°C the chlorinated dibenzofurans decomposed. The best yields were obtained with oxygen in about 1 week at 300°C. Prolonged heating at 300°C decreased the chlorinated dibenzofuran levels indicating that once formed, the chlorinated dibenzofurans were decomposed at this temperature.[39]

The U.S Food and Drug Administration, in evaluating the data from the Yusho incident to assess the health hazard associated with the ingestion of PCBs, noted an inconsistency in the Yusho data. The 1969 report of Tsukamoto et al.[40] said that the oil contained approximately 2000 to 3000 ppm PCBs. The 1976 report of Kuratsune et al.[36] indicated that oil contained 1000 ppm PCBs. In order to examine the oil more closely, the FDA requested a sample of the oil from Dr. Kuratsune of Kyushu University, Fukuoka, Japan. GC analysis showed that the sample contained 1000 ppm PCB. Neutron activation analyses showed that

MONS 005936

the oil contained twice the amount of chlorine that could be expected in 1000 ppm PCB. It was surmised that the sample contained more chlorinated compounds, but their nature was not evident until the samples were examined with a shorter GC column and higher operating temperatures than are normally used for PCB analysis. The resultant GC/MS analyses identified chlorinated quaterphenyls as the other major chlorinated contaminants in the oil.[41] Miyata et al.[42] published similar results concurrently. This group then simulated the oil deodorization step of rice oil processing in the laboratory to note the effect on the oil contaminants. Over 90% of the PCBs were removed from the oil during deodorization. The remaining PCBs were congeners of high chlorine content. The chlorinated quaterphenyls were unaffected by deodorization. The evaporation rate of the chlorinated dibenzofurans was lower than that of the PCBs so that the relative abundance of the chlorinated dibenzofurans was increased in the oil and the composition of this contaminant shifted to the more highly chlorinated dibenzofuran congeners. The relative amounts of these contaminants still did not coincide with those in the Yusho oil.[43] This suggested that the differences might be attributed to the composition of the heat transfer fluid involved in the Yusho incident. This brought the investigators back to the examination of alterations that occurred with use. Analyses of three used heat transfer fluids revealed chlorinated quaterphenyls at levels as high as 0.03%.[44] But these results did not demonstrate the formation of quaterphenyls with use. Experiments such as those of Morita et al.[36] were required. Accordingly, Kanechlor® 400 was heated in glass ampoules under varying conditions including the presence of stainless steel and water. The levels of chlorinated quaterphenyls and dibenzofurans in the Kanechlor® 400 rose markedly. Both water and steel accelerated the formation of these substances at 360°C.[44]

The number of variables involved in the alteration of Kanechlor® 400 in the Yusho incident was relatively small compared to that available in the general environment. However, it took 10 years to build a reasonably complete picture of the Yusho incident. The search for analogous substances[45] and processes in the environment has turned up one other significant source of toxic thermal alteration products. Chlorinated dibenzofurans have been found in the combustion products of waste incinerators.[46-49] These chlorinated dibenzofurans have been attributed to the incomplete incineration of PCBs.[50-51] Buser et al.[52] reported that the yield of chlorinated dibenzofurans at a combustion temperature of 550°C ranged from 3 to 25%. Thus, use and disposal are the two most important factors in the thermal formation of more toxic substances from PCBs. Fortunately, these are factors we should be able to control.

REFERENCES

1. Neely, W. B., Complex problems — simple solutions, *Chemtech*, 249, 1981.
2. Smith, F., Octachlorobiphenylquinone, U.S. Patent 2, 449, 088, 1984.
3. Societe d'Electrochimie, d'Electrometallurgie et des Aciéries Electriques d'Ugine, purification of Octachlorodihydroxybiphenyl, Belgian Patent 613, 066, 1962.
4. Trottier, W., Removing the interference of DDT and it analogs in the analysis for residues of polychlorinated biphenyls, *J. Assoc. Off. Anal. Chem.*, 58, 461, 1975.
5. Young, S. J. V., Flanderwalker, C., and Burke, J. A., Extraction and cleanup for determination of polychlorinated biphenyls in paper and paperboard, *J. Assoc. Off. Anal. Chem.*, 56, 957, 1973.
6. deCrouw, R., The principle of induced alternating polarity in connection with the reactions of derivatives of *p*-dichlorobenzene and other compounds with sodium methylate, *Rec. Trav. Chim.*, 50, 753, 1931.
7. Crosby, D. G., Mollahan, K. W., and Wong, A. S., Environmental generation and degradation of dibenzodioxins and dibenzofurans, *Environ. Health Perspect.*, 5, 259, 1973.
8. Hannan, E. J., Bills, D. D., and Herring, J. L., Analysis of polychlorinated biphenyls by gas chromatography and ultraviolet irradiation, *J. Agric. Food Chem.*, 21, 87, 1973.

MONS 005937

9 **Friedman, D. and Lombardo, P.**, Photochemical technique for the elimination of chlorinated aromatic interferences in the gas-liquid chromatographic analysis for chlorinated paraffins, *J Assoc. Off Anal Chem.*, 58, 703, 1975.

10 **Ariaman, R. K., Munich, R. C., Zeff, J. D., and Crane, T. C.**, Experience in operation of a ultraviolet-ozone (Ultrox®) pilot plant for destroying polychlorinated biphenyls in industrial waste influent, *Proc 35th Ind. Waste Conf.*, Ann Arbor Science, Ann Arbor, Mich., 1981, 802.

11 **Hutzinger, O., Safe, S., and Zitko, R.**, Photochemical degradation of chlorobiphenyls (PCBs), *Environ Health Perspect.*, 1, 15, 1972.

12 **Rune, L. O., Zabik, M. J., and Schoetz, R. D.**, Photochemistry of bioactive compounds photoproducts and kinetics of polychlorinated biphenyls, *J. Agric. Food. Chem.*, 22, 199, 1974.

13 **Safe, S. and Hutzinger, O.**, Polychlorinated biphenyls: photolysis of 2,4,6,2',4',6'-hexachlorobiphenyl, *Nature (London)*, 232, 641, 1971.

14 **Hustert, K. and Korte, F.**, Ecological chemistry, XXXVIII. Synthesis of polychlorinated biphenyls and their reactions under UV irradiation, *Chemosphere*, 1, 7, 1972.

15 **Hutzinger, O., Safe, S., and Zitko, V.**, Photodegradation of chlorobiphenyls, *The Chemistry of PCBs*, CRC Press, Boca Raton, Fla., 1974, 126.

16 **Crosby, D. G. and Moilanen, K. W.**, Photodecomposition of chlorinated biphenyls and dibenzofurans, *Bull. Environ. Contam. Toxicol.*, 10, 372, 1973.

17 **Corrie, F., Cornelissen, P., Jelinek, C., Nackley, B., Lehman, R., McLaughlin, J., Rhoden, R., and Shapiro, R.**, Human exposure to polychlorinated biphenyls and polybrominated biphenyls, *Environ. Health Perspect.*, 24, 157, 1978.

18 **Bunce, N. J., Kumar, Y., and Brownlee, B. G.**, An assessment of the impact of solar degradation of polychlorinated biphenyls in the aquatic environment, *Chemosphere*, 2, 155, 1978.

19 **Pomerantz, I., Burke, J., Firestone, D., McKinney, J., Roach, J., and Trotter, W.**, Chemistry of PCBs and PBBs, *Environ. Health Perspect.*, 24, 133, 1978.

20 **Kashimoto, T., Miyata, H., and Kunita, N.**, The presence of polychlorinated quaterphenyls in the tissues of Yusho victims, *Food Cosmet. Toxicol.*, 19, 395, 1981.

21 **Huff, J. E., Moore, J. A., Saracci, R., and Tomatis, L.**, Long-term hazards of polychlorinated dibenzodioxins and polychlorinated dibenzofurans, *Environ. Health Perspect.*, 36, 221, 1980.

22 **Buser, H. R.**, Identification of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in environmental and industrial samples using high-resolution gas chromatography and mass spectrometry, in *Recent Developments in Mass Spectrometry in Biochemistry and Medicine*, Vol. 6, Frigerio, A. and McCamish, M., Eds. Elsevier, Amsterdam, 1980, 515.

23 **Vos, J. G., Koeman, J. H., van der Maas, H. L., ten Noever de Brauw, and de Vos, R. H.**, Identification and toxicological evaluation of chlorinated dibenzofuran and chlorinated naphthalene in two commercial polychlorinated biphenyls, *Food Cosmet. Toxicol.*, 8, 625, 1970.

24 **Roach, J. A. G. and Pomerantz, I. H.**, The finding of chlorinated dibenzofurans in a Japanese polychlorinated biphenyl sample, *Bull. Environ Contam. Toxicol.*, 12, 338, 1974.

25 **Bowes, G. W., Simonett, B. R. T., Burlingame, A. L., and Rosebrough, R. W.**, Identification of chlorinated dibenzofurans in American polychlorinated biphenyls, *Nature (London)*, 256, 305, 1975.

26 **Nagayama, J., Masuda, T., and Kuratsune, M.**, Chlorinated dibenzofurans in Kanechlors and rice oils used by patients with Yusho, *Fukuoka Acta Med.*, 66, 593, 1975.

27 **Roach, J. A. G. and Pomerantz, I. H.**, The Finding of Chlorinated Dibenzofurans in Aroclor PCBs of Recent Manufacture, paper 58, 88th Annu. Meet. Assoc. Off. Anal. Chem., Washington, D.C., October 14, 1974.

28 **Bowes, G. W., Mulvihill, M. J., DeCamp, M. R., and Kende, A. S.**, Gas chromatographic characteristics of authentic chlorinated dibenzofurans: identification of two isomers in American and Japanese polychlorinated biphenyls, *J. Agric. Food Chem.*, 23, 1222, 1975.

29 **Roach, J. A. G., Sphon, J. A., and Donald, L. R.**, Application of selected ion recording techniques to the qualitative and quantitative analysis of impurities and metabolites of chlorinated biphenyl, 10th Middle Atlantic Regional Meet. American Chem. Soc., Philadelphia, February 23, 1976.

30 **Phillipson, D. W., Farrell, T. J., and Penn, B. J.**, Chlorinated dibenzofurans in Aroclor 1260 and Aroclor 1260-based transformer fluids, paper 76, 92nd Annu. Meet. Assoc. Off. Anal. Chem., Washington, D.C., October 16, 1978.

31 **Penn, R. J., Krantz, K. W., and Stuart, J. D.**, Anodic oxidation of two polychlorinated biphenyls, *J. Electrochem. Soc.*, 123, 1643, 1976.

32 **Miller, R. A., Johnson, J. D., Heinsl, R. W., and Pitts, D. M.**, Destruction of toxic chemicals by catalyzed wet oxidation, in *Proc. 35th Ind. Waste Conf.*, Ann Arbor Science, Ann Arbor, Mich., 1981, 425.

33 **Taki, I.**, Foreword, The eighth reports of the study on Yusho and PCB, *Fukuoka Acta Med.*, 72, 131, 1981.

MONS 005938

34. **Higuchi, K.**, *PCB Poisoning and Pollution*. Academic Press. New York. 1976, 17.
35. **Miyata, H., Kashimoto, T., and Kunita, N.**, Detection and determination of polychlorodibenzofurans in normal human tissues and Kanemi rice oils caused "Kanemi Yusho." *J. Food Hyg. Soc.*, 18, 260, 1977.
36. **Miyata, H., Nakamura, A., and Kashimoto, T.**, Separation and detection of polychlorodibenzofurans (PCDFs) on Japanese commercial PCBs (Kanechlors) and their heated preparation. *J. Food Hyg. Soc.*, 17, 227, 1976.
37. **Rappe, C. and Gara, A.**, Analysis of polychlorinated dibenzofurans in Yusho oil using high resolution gas chromatography-mass spectrometry. *Chemosphere*, 5, 231, 1977.
38. **Morita, M., Nakagawa, J., Akiyama, K., Mimura, S., and Isono, N.**, Detailed examination of polychlorinated dibenzofurans in PCB preparations and Kanemi Yusho oil. *Bull. Environ. Contam. Toxicol.*, 18, 67, 1977.
39. **Morita, M., Nakagawa, J., and Rappe, C.**, Polychlorinated dibenzofuran (PCDF) formation from PCB mixture by heat and oxygen. *Bull. Environ. Contam. Toxicol.*, 19, 665, 1978.
40. **Tsukamoto, H., Makimomi, S., Hirose, H., et al.**, Detection of toxic compounds in rice bran oils. *Fukuoka-Igaku-Zasshi*, 60, 496, 1969.
41. **Kamps, L. R., Trotter, W. J., Young, S. J., Carson, L. J., Reoch, J. A. G., Sphon, J. A., Tanner, J. T., and McMahon, B.**, Polychlorinated quaterphenyls identified in rice oil associated with Japanese "Yusho" poisoning. *Bull. Environ. Contam. Toxicol.*, 20, 589, 1978.
42. **Miyata, H., Kashimoto, T., and Kunita, N.**, Studies on the compounds related to PCB (V) detection and determination of unknown organochlorinated compounds in Kanemi rice oil caused the "Yusho". *J. Food Hyg. Soc.*, 19, 364, 1978.
43. **Miyata, H. and Kashimoto, T.**, Investigation on organochlorinated compound formed in Kanemi rice oil that caused the "Yusho". *J. Food Hyg. Soc.*, 20, 1, 1979.
44. **Miyata, H., Murakami, Y., and Kashimoto, T.**, Studies on the compounds related to PCB (VI) determination of polychlorinated quaterphenyl (PCQ) in Kanemi rice oil caused the "Yusho" and investigation on the PCQ formation. *J. Food Hyg. Soc.*, 19, 417, 1978.
45. **Bowes, G. W., Simonelt, B. R., Burlingame, A. L., deLappe, B. W., and Risebrough, R. W.**, The search for chlorinated dibenzofurans and chlorinated dibenzodioxins in wildlife populations showing elevated levels of embryonic death. *Environ. Health Perspect.*, 5, 191, 1973.
46. **Olie, K., Vermeulen, P. L., and Hutzinger, O.**, Chlorodibenzo *p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. *Chemosphere*, 8, 455, 1977.
47. **Buser, H. R. and Bosshardt, H. P.**, Identification of polychlorinated dibenzofuran isomers in fly ash and PCB pyrolysis. *Chemosphere*, 5, 419, 1978.
48. **Cavallaro, A., Bandi, G., Invernizzi, G., Luciani, L., Mangini, E., and Gorni, A.**, Sampling, occurrence and evaluation of PCDDs and PCDFs from incinerated solid urban waste. *Chemosphere*, 9, 611, 1980.
49. **Liberti, A., Brocco, D., Cecinato, A., and Possanzini, M.**, Determination of polychlorinated dibenzo-*p*- dioxins and dibenzofurans in the emission from urban incinerators. *Mikrochim. Acta*, 1, 271, 1981.
50. **Buser, H. R. and Rappe, C.**, *Formation of polychlorinated dibenzofurans* (PCDFs) from the pyrolysis of individual PCB isomers. *Chemosphere*, 3, 157, 1979.
51. **Duvall, D. S., Rubey, W. A., and Manaher, J. A.**, Applications of the thermal decomposition analytical system (TDAS), *Proc. Annu. Meet. Air Pollut. Control Assoc.*, 73, 80, 1980.
52. **Buser, H. R., Bosshardt, H. P., and Rappe, C.**, Formation of polychlorinated dibenzoferans (PCDFs) from the pyrolysis of PCBs. *Chemosphere*, 1, 109, 1978.

MONS 005939

INDEX

A

Absorption, 186
  gills, 122
Accumulation, see also Bioaccumulation of PCBs, 122, 169
  driving force for, 128
  equilibrium process, 186
  physicochemical process, 123
  rate, 168
  size, 168
Adsorbent/filter (A/F) ratios, 85—86
Adsorbents, 80—81
Adsorption, 87, 92, 126—127
Adsorption chromatography, 69
Adsorption gains, 85
Adsorption liquid solid chromatography (LSC), 17
Adverse symptoms, 2
Aerial concentrations, 85
Aerial fallout, 182
Aerial transport of PCBs, 80, 170, 176
African continent, 85
Age
  PCB level, effect on, 178
  specimens for biological sampling, 169—170
  specimens for trend assessment, 165
Agricultural drainage, 182
Air oxidation, 208
Air-to-sea transfer, 80
Air/water boundary, 91
Air/water concentration ratios, 93
Air/water exchange, 92
Air/water flux, 89
Air/water interface, 91, 168
Air/water partition coefficient, 91
Alabama, 193
Alcoholysis, 208
Alewives, 179
Alosa
  pseudoharengus, 179
  sapidissima, 186
Amazon River, 93
Ambient air, 80
Ambient atmosphere, 83—84
American eel, 187
American Samoa, 84
American shad, 186
Anacapa Island, 189, 191
Anacapa local spill, 189
Anaheim Bay, 189
Analysis of PCBs, 65—78
  analytical intercomparison studies, 73—75
  analytical procedures for environmental samples, 68—73
  chemical, for measuring trends, 165—167
  choice of standard, 165—166, 180
  composition of PCB residues, 66—68
  consistent pattern, 172
  indicator organisms, 181
  interference by TDE, 180
Analytical chemistry of PCBs, 1—45
  analytical sensitivity, 5
  chemical characterization, see also Chemical characterization, 7—39
  cleanup procedures, 5—7
  composition, 5
  contamination, 2—5
  extraction, 5—7
  global uses, 2—5
  incurred residues, 5, 13—14, 34
  industrial applications, 2
  metabolism, 6—7
  quantitation, approaches to, 34—35, 37, 40—43
  regulatory controls, need for, 2—5
  separation, 5—7
  trace analysis, implications in, 5
  weathering, 6—7
Analytical intercomparison, 73—75
Analytical sensitivity, 5
Analytical techniques, artifact of change in, 189
Analytical variability, 176
Analytical variance, 168
Anas
  platyrhynchos, 193
  rubripes, 193
Anchovy, 191
Anguilla rostrata, 187
Animal feed, 2, 4
Animals, bioaccumulation and biodegradation by, 59
Annual rainfall rate, 91
Anodic oxidation of chlorinated biphenyls, 210
Ano Nuevo Island, 189
Antarctic, 144, 146—147, 150—153
Antarctic Ocean, 144
Antarctic/Southern Ocean, 84
Antarctica, 80, 88, 93, 144—145, 164
Anthropogenic gases, 93
Aplodinotus grunniens, 180
Aquatic birds, 122
Aquatic chemistry of PCBs, 209
Aquatic ecosystems, 139—140
Aquatic food chains, 139
Aquatic organisms, 122, 124, 129, 168
Aqueous hydrolysis, 208
Aqueous phase, 140
Aqueous solubility, 102—105
Arctic, 145, 151, 153
Arctic Ocean, 84
Aroclor 1016, 10, 26, 34
  atmospheric removal rates, 90
  blank values, 81
  breakthrough, 82, 83
  deposition parameters, 90
  elution profile, 16
Aroclor 1221, 8, 23

MONS 005940

elution profile, 16
physical properties, 3
thermal alteration, 209
toxicological properties, 3
vaporization rate, 54—55
Aroclor 1232, 3, 9, 16, 24, 55
Aroclor 1242, 2, 9, 25, 49
atmospheric removal rates, 90
blank values, 81—82
deposition parameters, 90
elution profile, 16
flux to ocean surface, 94
LC/MS, 36
physical properties, 3, 53
semiquantitative analysis by NMR, 40
toxicological properties, 3
vaporization rate, 55
Aroclor 1248, 11, 27, 37—38, 40—42
elution profile, 16
heating experiments with, 210
LC/MS, 36
physical properties, 3, 53
semiquantitative analysis by NMR, 40
toxicological properties, 3
vaporization rate, 55
Aroclor 1254, 5, 12, 28, 49
atmospheric removal rates, 90
blank values, 81—82
breakthrough volumes, 83
deposition parameters, 90
elution profile, 16
flux to ocean surface, 94
physical properties, 3, 53
semiquantitative analysis by NMR, 40
toxicological properties, 3
vaporization rate, 55
Aroclor 1260, 12, 29, 49
chlorinated dibenzofurans in, 209—210
elution profile, 16
physical properties, 3, 53
semiquantitative analysis by NMR, 40
toxicological properties, 3
vaporization rate, 55
Aroclor 1262, 3, 14, 16, 30
Aroclor 1268, 3, 12, 14, 16, 31
Aroclor 4465, 14, 16
Aroclor 5432, 13, 16
Aroclor 5442, 15, 16
Aroclors, see also specific types, 2, 17, 20, 32, 35, 37
airwater concentration ratios, 93
chlorobiphenyls in, 49, 54
isomer composition, 105
K_{ow}, 103—104
K_{oc}, 103—104
mobility in soils, 113—115
molecular composition, 105
physical properties, 2—3, 49, 53
preparation, 49, 67
semiquantitative analysis by NMR, 40
soil sorption constant, 107—110
solubilities, 54, 102—104, 106
toxicological properties, 3
vaporization rates, 54—55
Arylation, 48, 52
Asian continent, 85
Askareis, 209
Atlantic Coast, 191
Atlantic Flyway, 193—194
Atlantic Ocean, 145, 147, 151—153, 155—156
Atmosphere
bioaccumulation of PCBs, 122
PCBs in, 144—146
Atmospheric contamination, decreases in, 182
Atmospheric deposition, 80
Atmospheric fallout, 166, 194
Atmospheric flux, 95
Atmospheric input, 87
Atmospheric inputs to ocean, 89—95
Atmospheric lifetime of PCBs, 146
Atmospheric removal processes for PCBs, 86—89
Atmospheric removal rates, 90
Atmospheric reservoirs of PCBs, 80, 83, 85
Atmospheric transport of PCBs, 79—100, 178
atmospheric inputs on PCBs to the ocean, 89—95
atmospheric removal processes, 86—89
collection methods, 80—83
concentrations in air, 83—84
vapor-particle partitioning of PCBs, 85—86
Automated collector, 87
Availability, 172

B

"Background" concentrations, 85
Ballona Creek, 183
Baltic Sea, 140, 178, 197
Barbados, 84
Baseline data, 171
Beaver Island, Lake Michigan, 88, 90
Beef, 178
Benthic organisms, 123
Bering Sea, 151—154
Bermuda, 84
Bimodal loss process, 190
Bioaccumulation by animals, 59
Bioaccumulation factor (BCF), 123—133, 136, 138
Bioaccumulation of PCBs, 121—133, 136—137, 181
along food chains, 136
atmosphere, 122
biological sampling issues, 168
chlorine substitution, 126
compartmental model for, 129
degree of chlorination, 123
enthalpy, 128
entropy, 128—129
environmental distribution, 122
factors controlling, 121—133
food, 122
mechanisms of, 122—123

MONS 005941

models for, 129—130
open ocean organisms, 151
partition coefficients, 123—125
physicochemical properties, 123—127, 130
potential for, 123
retention, 122
routes of, 122—123
stereochemistry, 125—127
thermodynamic aspects of, 127—129
uptake, 122
water, 122
water solubility, 123—125
Bioaccumulation potential, 140
Bioamplification, 136
Bioavailability, 168—169, 182
Biochemical activities, 169
Biochemical circulation, 157
Biochemical factors, 156
Bioconcentration, 122, 127
Bioconcentration factors, 123, 124, 153
Biodegradation, 58—60
Biological activities, 169
Biological half-lives, see Half-lives
Biological samples, PCB residues in, 6—7
Biological sampling issues, 164—173
age of specimens, 169—170
collection site, 170—171
natural biological fluctuations, 171
new approaches, 172—173
number of specimens, 170—172
pooling of specimens, 171—172
sex of specimens, 170
size of specimens, 169—170, 172
species choice, 167—169
timing of collection, 169—170
tissues sampled, 171
Biological variability, see Variability
Biological variation, 197
Biomagnification, 136—140
Biomass vs. water mass, 155
Biomembrane, 129
Biphenyl ring system, numbering in, 48, 52
Biphenyls, 103
Birds, 154, 165, 168
droppings, 87
Black duck, 193—194
Blank values, 80—81
Blossom, 179, 181
Blow-off, 85
Bottom dwellers, 168
Bottom feeding, 194
Bottom sediments, 123
Breakthrough, 81
Breakthrough volumes (V_B), 82
Breeding, 169
Breeding season, 191
Breeding status, 169
Brevoortia
patronus, 177
tyrannus, 177
British East Coast, 88
Brown bullhead, 186
Brown pelicans, 169—170, 190—191, 197
Building materials, 116
Bulk collection, 86
Bulk collectors, 87
Bulk rain, 88
Bulk snow, 88
Burial, 187
Buried PCB deposits, 184
Buzzards Bay, 176

C

California Mussel Watch, 188—189
California sea lions, 189
Capacitor manufacturers, 81, 83
Cape Cod, 176
Capillary chromatography, 70—73
Capillary column chromatography, 68
Capillary-column GC, 165, 167
Capillary columns, 70, 75—76
Capitella capitata, 125
Carassius auratus, 186
Carbonaceous materials, 117
Carnivores, 191
Carnivorous birds, 140
Casmerodius conversum, 194
Cellulose adsorption, 154
Central Flyway, 194
Central Pacific, 95
Central tendency, 173
Cetaceans, 153
Channel catfish, 194
Charcoal, 126—128
Chemical absorption efficiency, 139
Chemical breakdown, 87
Chemical characterization, see also Chemistry and properties, 7—39, 47—64
gas chromatography, 7—15
gas chromatography/mass spectrometry, 14—31
liquid chromatography, 17, 32—35
nuclear magnetic resonance, 21—22, 24—26, 28—29, 31, 34, 37—39
Chemical derivatization, 6
Chemical ionization mass spectra, 18—19
Chemical ionization (CI) spectra of PCBs, 15
Chemistry and properties, 47—64
commercial PCBs, 49
degradation, 56—61
general physical properties, 49, 53, 54
nomenclature, 48, 50—52
solubility, 49, 54
sorption reactions, 55—56
synthesis, 48—49, 52—53
vapor pressure and vaporization, 54—55
Chicago, 11, 84, 86, 88, 90
Chlordane, 7, 60, 83, 87, 88, 166
Chlorinated biphenyls, 210
Chlorinated dibenzofurans, 208—211
Chlorinated hydrocarbons, 168, 170—173, 177, 178

MONS 005942

Chlorinated naphthalenes, 69
Chlorinated quaterphenyls, 211
Chlorination, 48—49, 55, 59, 66
Chlorine substitution, 126
Chlorobenzenes, 116
2-Chloro-5-biphenylol, 208
Chlorobiphenyls, 48—51, 54, 123
Chlorophenylbenzoquinones, 210
Chromasorb 102, 81
Chromatogram, 67
Chromatography on charcoal, 126—128
Cisco, 179
Clapper rails, 175
Cleanup procedures, 5—7, 69, 81
Clearance rate constants, 130
Clophen, 2, 33, 49, 67, 70, 73
Clophen A-30, 10, 16
Clophen A-40, 11, 16
Clophen A-50, 12, 16, 90
Clophen A-60, 13, 16
Clupea harengus, 178
Coastal China, 93
Coastal environment, 144
Coastal population centers, 85
Coastal waters, 116
Cod, 178
Coefficient of variation (C.V.), 74, 76, 166, 177
Coho salmon, 179—181
Collection efficiency, 80—82
Collection methods, 80—83
  aerial deposition, 86—88
  PCBs in air, 80—83
Collection plates, 87
Collection site, 170—171
Collection studies, 81—82
College Station, Tex., 84
Colloid material, 92—93
Columbia, S.C., 84, 86, 90
Column chromatography, 6
Co-metabolism, 59
Commercial PCBs, 49
Common carp, 194
Common terns, 170, 174, 176
Compartmental model for bioaccumulation, 129
Complexities of PCB analysis, 164
Composting specimens, 172, 174
Composition, 5
  atmospheric PCBs, 83
  PCB residues, 66—68
Concentrations of PCBs in ambient atmosphere, 83—84
Concentrations of PCBs in environment, 68
Concurrent trends for PCB and DDT, 189
Condensation, 53
Condensation reactions, 48
Congeners, see PCB congeners
Congo River, 95
Contaminant burden from mothers, 169
Contaminant data, 180
Contaminant distributions, 181
Contaminant quotient, 168, 172
Contaminant ratios, 173
Contaminated food, 122, 129, 130, 137
Contaminated sediments, 184
Contamination, 2—5, 87
  incidence, 194, 196
  level, 194
  trend, 197
Continental areas, 89
Coregonus
  artedii, 179
  clupeaformis, 166
  hoxi, 179
Cormorant, 166
Corona del Mar, 189
Correlation between length or weight and PCB concentration, 185—186
Correlation between lipid content and PCB concentration, 186
Cost of monitoring, 172
County sanitation districts, 182
Cow's milk, 179
Crassostrea
  gigas, 170
  sp., 190
  virginica, 176
Cycling, 96
Cyprinus carpio, 194
Czechoslovakia, 90

D

Dall's porpoise, 153—154
Data
  adequacy of, 179
  baseline, 171
  contaminant, 180
  dropping, 174
  eggs, 175, 182
  evaluating, 171
  extrapolating contaminant, 175
  limitations in, 178
  polluted sites, 171
3,3'-DCB, 82
DDT, 87, 136, 144, 146, 148—150, 164, 189
Dead specimens, 170
Decachlorobiphenyl, 40
Dechlorination, 208, 209
Decrease in environmental PCB concentrations, 83, 193
Deep sea fish, 147
Deep sea sediments, 147
Deep water, 95, 148, 157
Degradation of PCBs, 56—61, 67, 136, 167, 198
Degradation rates, 137
Degree of chlorination, 123
Denver, Colorado, 84, 86
Deposition, 89, 90, 92
Deposition velocities (V_d), 87, 90
Depth tolerance, 168
Depuration, 130, 136, 169

MONS 005943

Detection limit, 80
Detritivores, 197
Dibenzodioxins, 7
Dibenzofurans, 7, 61
Dichlorobiphenyls, 103
Diet, 182
Diethoxyoctachlorobiphenyl, 208
Diffuse contamination, 175
Diffusion, 91
Digestive tracts, 154
Dilution through growth, 169
Direct absorption, 129
Direct intervention, 179
Direct sources of PCBs, 171
Disappearance, 167
Discharge from sewer outfalls, 184
Dispersal of contaminated sediments, 194
Dispersion, 189
Disproportionality of response, 7
Dissipation, 167, 197—198
Dissolved PCBs, 92—93
Dogfish, 181
Dover sole, 183—184
Dredge spoil sites, 117
Dredging, 186, 189
Dropping data, 174
Dry deposition, 86—94
Dry flux, 89—90
Dry pans, 87
Dry surface pans, 87
Ducks, 164, 169, 191, 193—194
Dumping, 171, 183, 185
  regulations, 189
Dumps, 116—117, 164
Dust flux, 95
Duwamish River, 189

E

Earth materials
  correlation of K values with, 111—113
  sorption of PCBs by, 105—111
East Coast mussels, 190
Eastern brown pelican, 170
Eastern Canada, 175
East Indian Ocean, 84
Ecological magnification, 136
Efficiency factor, 137
Efficiency transfer coefficients, 122
Egg laying, order of, 170
Eggs, 169—170, 173—176, 181—182, 191
Electrical components, alteration of PCBs in, 209
Electrical equipment, 155
Electrochemical oxidation, 210
Electron capture (EC), 7—8, 15, 37, 66
Electron capture detector (ECD), 5, 68
Electron impact (EI) spectra of PCBs, 14
Elution profiles, 5, 7, 9—10, 12, 16
Elution time, 127—128
Endangered species, 170, 172
Enewetak Atoll, 80, 84, 88, 90
Engraulis mordax, 191
Enthalpy, 111, 128
Entropy, 110—111, 128—129
Environmental distribution, 122
Environmental fluctuation, 197
Environmental photodegradation, 58
Environmental samples, analytical procedures for, 68—73
Enzymatic capability, 168
Epidermis, 122
Epithelial tissues, 122
Equilibrium partition, 123, 130, 140
Escambia Bay, 176
Esox lucius, 178
Estuaries, 168, 171
Estuarine contaminant data, 168
Estuarine disposal sites, 164
Estuarine fish, 191
Estuarine organisms, 191—192
Estuary-by-estuary analysis, 173
Ethanol, 111
Ethylene glycol-water-filled pans, 87
Europe, 95
Eutrophic ocean environment, 157
E values, 122
Event rain and snow, 88
"Event" sampling, 86
Excretion, 138
Extraction, 5—7, 69

F

Face velocities, 85
Fallout fluxes, 87—88
Fat content, see Lipid content
Fathead minnows, 128
Fat lake trout, 166
Fat-rich milk, 168
Fatty foods, 6
FDA tolerances, 4
Fecal concentrations, 189
Fecal contamination, 189
Field comparisons, 88
Filtering water, 186
Filtration, 87
Final sink, 157
Finland, 178
First order kinetics, 129—130, 137
Fish, see also specific types, 2, 5—6, 127, 129, 136, 154, 165, 168—169, 197
  main uptake route in, 139
  model for bioaccumulation of PCBs by, 129
  open ocean, 150, 152
  twenty-year old, 168
  uptake of PCBs, 128
Fish-eating birds, 139
Flame ionization detection (FID), 7—8, 12
Flatfish, 184
Fledging, 165

MONS 005944

Floods, 187
Florida, 191
Florida Bay, 191
Florisil, 80—82
Florisil columns, 69
Fluctuations, 169—171, 176, 180
Flushing, 182
Flux estimates, 94
Food abundance, 181
Food chain, see also Biomagnification, 4, 135—141, 182
Food packagings, 4
Foods, 3
  bioaccumulation of PCBs, 122
  FDA tolerances for PCBs, 4
Food supplies, 169
Food web, 140
Free energy, 127
Freons, 93
Fresh eggs, 170
Fresh water, 94, 116
Fresh water areas, 93
Freshwater drum, 180
Freshwater ecosystems, 165
Freshwater fish, 164, 174, 191, 194—197
Frontal chromatography system, 82
Fugacity, 55

G

Gainesville, Fla., 84
Gas chromatography, 7—15
Gas chromatography/mass spectrometry (GC/MS), 5, 14—31
Gas constant, 91
Gases
  dry deposition, 91—93
  wet deposition, 93—94
Gas exchange, 91, 96
Gas exchange processes, 94
Gas exchange rate, 93
Gas films, 91
Gas liquid chromatography (GLC), 66, 69—73
Gas phase, 94
Gas-phase controlled gas exchange, 92
Gas-phase dissolution, 94
Gas-phase PCBs, 94
Gas transfer, 91
Gas transfer flux, 94
Gate compartments, 130
Gel permeation chromatography, 69
General physical properties of PCBs, 49
Gerromerus lineatus, 184
Geochemical circulation, 157
Gill membrane permeability, 122
Gills, 122, 127, 129, 136, 138, 154, 186
  absorption by, 122
Glass-fiber filter, 80, 92
Global atmosphere, 85
Global average of PCB concentration, 85
Global uses, 2—3
Glycerol, 87
Glycerol-sprayed pans, 87
Goatfish, 164
Goldfish, 186
Grain silos, 4
Gravitational settling, 87
Gray seals, 177, 197
Great Lakes, 84, 89, 172—173, 179—182
Great Lakes Eastern Canada, 88
Green Bay, 182
Green sunfish, 123, 128
Growth rates, 169
Gulf Coast, 191
Gulf of Mexico, 84, 86, 93
Gulf of St. Lawrence, 178, 197
Gulls, 164, 170
Gut, 186

H

Half-lives, 123, 139, 179, 181—182, 190
Halichoerus grypus, 177
Hall electrolytic conductivity detector (HECD), 5, 7—8, 10, 13, 37
Halocarbons, 85
Hamilton, Ont., 88
Hamuren function, 127
Harp seals, 178, 197
Hawaii, 164
Hazards in estributing change, 180
HCHs, 145—146, 148—150
Heavily polluted areas, 185
Henry's Law calculations, 92
Henry's Law constants, 91
Herring, 178, 197
Herring gulls, 169, 173, 181—182
Hexachlorobenzene (HCB), 82—83
Hexachlorobiphenyls, 103, 125
Hexachloro isomers, 123
High performance liquid chromatography, 124
High volume (hi-vol) sampling system, 80, 82
Home ar, 81
Homologs, 66
Houston, Tex., 84
Hudson River, 139, 164, 185—188, 195
Hydrocarbon solvents, 208
Hydrolysis, 208
Hydrophobic fragmental constant, 124, 127
Hydrophobic sorption, 110—111
3-Hydroxy-2,2',5,5'-tetrachlorobiphenyl, 210

I

i° character, 124
Ice cores, 87—88
Iceland, 90
Ictalurus
  nebulosus, 186

MONS 005945

punctatus, 194
Identification of chlorobiphenyls, 49
Immobilization of sediment, 187
Impaction, 87
Incidence of quantifiable PCB levels, 173—174
Incinerators, 81, 83
Incomplete incineration of PCBs, 211
Increase in PCB levels, 188—189
Incurred residues, 5, 13—14, 34
Indian Ocean, 144, 147, 152, 156
Indicator organisms, 168—169, 181
Indirect sources of PCBs, 171
Individual animals, 171—172
Individual PCBs, 167
Individual transfer coefficient, 91
Industrial applications, 2
Industrialized areas, 85
Industrial wastes, 116
Initial restrictions on usage, 190
Inputs of PCBs to water bodies, 89
Insectivorous birds, 139
Insects, 87
Intake from food, 137
Intercalibration, 76
Intercomparison studies, 73—76
Interfacial films, 93
Interference, 167
  chlordane, 166
  TDE, 180
  toxaphene, 166, 179, 181
Interlaboratory calibration, 166—167
International Atomic Energy Agency (IAEA), 75
International Council for the Exploration of the Sea (ICES), 74—75
International monitoring program, 165—166
Interspecies ratios, 173
Intertidal animals, 168
Invertebrates, 129
Ion clusters, 14
Irradiation, 209
Irreversible sedimentation, 182
Isle Royale, 88, 166
Isomers, 3, 66, 102, 117, 146, 150—151

J

Jacksonville, Fla., 84
Juvenile dogfish, 169
Juvenile estuarine fish, 169
Juvenile salmon, 168

K

Kanechlor, 2
Kanechlor 400, 11, 16, 34, 110—111
Kenya, 90
Kiel Bay, West Germany, 178
Kingston, R.I., 90
K_{ow}, 102—104, 111, 113
K_{oc}, 102—104, 106, 111—113

L

Lactation, 170
La Jolla, Calif., 90
Lake Erie, 180—182
Lake Huron, 88—90, 179, 181—182
Lake Michigan, 84, 86, 88—89, 93, 180—182
Lake Michigan air, 81
Lake Ontario, 181—182
Lake Päijänne, 178
Lake St. Clair, 180
Lake Simcoe, Canada, 177, 197
Lake Superior, 84, 88—89, 93, 166—167, 179, 181—182
Lake Superior air, 81
Lake surface, 87
Lake trout, 166, 173, 179—181
Lake whitefish, 166, 172—173, 179
Lampreys, 172—173
Landfills, 83, 102, 117—118, 197
Langmuir adsorption theory, 86
Largemouth bass, 194
Larger game fish, 139
Larus argentatus, 169
Lepomis
  cyanellus, 123, 128
  gibbosus, 186
Leuciscus rutilus, 170
Life span, 137, 154
Lipid-based PCB concentration, 186
Lipid compartment, 130
Lipid content, 123, 176—179, 185
Lipid/water partitioning, 154
Lipoid phase, 140
Lipophilic compounds, 125
Lipophilic contaminants, 122
Lipophilicity, 124—125, 127
Liquid chromatography, 5, 17, 32—35
Liquid chromatography/mass spectrometry (LC/MS), 17
Liquid films, 91
Liquid-phase controlled gas exchange, 92
Liver, 171—172
Long-term pollution, 181
Los Angeles, 182
Los Angeles County, 185
Los Angeles County Sanitation District, 183, 188
Los Angeles River, 183
Loss of water, 170
Louisiana, 190—191
Lower trophic levels, pelagic biota at, 140
Lung walls, 122

M

Madison, Wisc., 84, 86

MONS 005946

Mallards, 193—194, 197
Mammals, 122
Marine del Mar, 189
Marine areas, 93
Marine atmosphere, 84, 85, 91
Marine boundary layer, 91
Marine ecosystems, 139, 165, 183
Marine environment, 95
Marine fish, 164
Marine food chains, 154
Marine mammals, 150—151, 153, 170, 197
  pups, 168
Marine pollution, focus of, 188
Marine/remote areas, 85
Mass balance, 96
Maximum gas exchange, 94
Mechanism of PCB deposition, 140
Membrane passage, 125
Membranes, 127
Menhaden, 177
Mergus serrator, 182
Metabolic processes, 170
Metabolism, 6—7, 154, 168
Metabolization by bacteria, 58
Meteorological factors, 87, 96
Meteorological variables, 83
Microbial breakdown, 87
Microlayer, 93
Micrometeorological parameters, 87
Microparticulates, 92
Micropterus
  dolomieu, 180
  salmoides, 194
Microstomus pacificus, 183—184
Migratory/anadromous species, 185, 187
Migratory/marine species, 186
Milk, 4
Milwaukee, Wisc., 84, 86
Mineral oil-coated glass plates, 87
Minneapolis, Minn., 84, 90
Mirounga angustirostris, 189
Mississippi Flyway, 194
Mississippi River Delta, 95
Mississippi River Flyway, 193
Mixed adsorbent cartridges, 81
Mobile environmental reservoir, 85
Mobility, 193
Mobility in soils of PCBs and Aroclors, 113—115
Mobilization, 189
Mobilization of sediments, 187
Models, 89, 96, 129—130
Modern monitoring programs, 165
Molecular size, 125, 154
Molecular stereochemistry, 124
Mollusks, 168, 183, 191—192
Monitoring networks, 87
Monitoring organisms, 168
Monitoring parameters, 165
Monitoring programs, 164, 165, 174, 179—197
  brown pelicans, 190—191
  California Mussel Watch, 188—189
  Great Lakes, overall, 179—182
  Hudson River, 185—187
  National Mussel Watch, 189—190
  NPMP: ducks, 193—194
  NPMP: estuarine organisms, 191—192
  NPMP: fresh water fishes, 194—197
  NPMP: starlings, 192—193
  Southern California Bight, 182—185
Monitoring whole flyway, 193
Monochlorobiphenyls, 103
Monomoy Island, 176
Morone saxatilis, 187
Mt. Olympus, Wash., 88
Mugil cephalus, 125
Mulloidichthys auriflamma, 164
Mussels, 164, 168—169, 172, 184, 188, 190
Mycteophid, 153
Mytilus
  californianus, 184, 188
  edulis, 188
  sp., 190

N

National Academy of Sciences, 85
National Mussell Watch, 189—190
Nationwide evaluation, 193
Natural biological fluctuations, 171
Natural water surface, 87, 89
Nesting birds, 169
Nets for collection, 87
New Bedford, Mass., 86
New Bedford Harbor, 176
Newfoundland, 84
New Jersey, 175
NIOSH criterion, 83
Nomenclature of PCBs, 48
Nonmetabolic alteration of PCBs, 207—213
Nonpolar PCB molecule, 128
Nonurban continental areas, 83
Normalization, 172—173
North Atlantic, 86, 93
North Atlantic Ocean, 144
North Atlantic waters, 144
Northern elephant seals, 189
Northern Hemisphere, 85, 144, 147, 150, 155, 181
North Inlet Estuary, S.C., 84, 90
North Pacific, 144
North Sea, 89, 155, 178
Norway, 84, 88
Notropis hudsonius, 180
Nuclear magnetic resonance (NMR), 5, 21—22, 24—26, 28—29, 31, 34, 37—40
Number of specimens, see Samplings
Numbering in biphenyl ring system, 48, 52
Numbering of chlorobiphenyls, 48, 50—51
Nylon mesh screen, 87

MONS 005947

O

n* character, 124
Ocean, 80
Ocean air, 81
Ocean area, 94
Ocean environment, 143—161
  atmosphere, 144—146
  distribution of PCBs in, 144—155
  estimated load of PCBs in, 155—157
  general concentration levels, 155—157
  organisms, 150—155
  PCB composition, 149, 151, 153—154
  prospects of PCBs in ocean reservoir, 157—158
  surface waters, 147
  ultimate fate of PCBs in ocean reservoir, 157—158
  water, 146—150
Oceanic TSP, 86
Ocean reservoir, 95
Ocean surface, 86—87, 90, 94
Octachloro-4,4'-biphenylol, 208
n-Octanol/water partition coefficient, see K_{ow}, P_{ow}
Oil-coated surfaces, 87
Oklahoma stream, 140
Old transformer, fall of, 189
Oligotrophic ocean environment, 157
Oncorhynchus kisutch, 179
Ontario, 84, 88, 179
Ontario, Southern, 88
Open-coast mussel, 184
Open ocean ecosystems, 153
Open ocean environment, see Ocean environment
Open ocean fish, 150, 152
Open ocean mixing layer, 157
Open ocean plankton, 150—153
Open ocean regions, 85
Orange County, 182
Organic dry deposition, 87
Organic vapor sampling, 80
Organisms, PCBs in, 150—155
Organization for Economic Cooperation and Development (OECD), 73—74
Organochlorine dry deposition, 87
Organochlorine insecticides, 145, 147—148
Organochlorine pesticides, 66, 69, 73
Organochlorines, 80, 149
Organochlorine uptake ratios, 173
Osmerus mordax, 179
Ostrea sp., 190
Ostsee (Kiel Bight), 178
Overall flux, 89
Overall transfer coefficient, 91
Oxidation, 208—211
Oxygen mass transfer rates, 92
Oysters, 168, 170, 176, 190—191
Oyster surveillance, 189

P

Pacific Flyway, 194
Pacific Ocean, 95, 144—145, 147, 152—153, 155—156
Packed column chromatography, 68
Packed glass columns, 69
Pagophilus groenlandicus, 178
Palos Verdes, 184
Palos Verdes Peninsula, 182
Particle-borne PCBs, 91
Particle chemistry, 85
Particle deposition, see Dry deposition, Wet deposition
Particle deposition velocity (V_D), 89—90
Particle feeders, 191
Particles, 87, 89—91, 94
Particle washout factor, 94
Particulate matter, 80, 149, 184—185
Particulate organics, 91
Particulates, 86, 92—94
Partition coefficient, 56, 94, 136
Partitioning, 55
Partition process, 138
Pb, 91
PCB 1221, 186
PCBs, see also specific topics
  analytical chemistry, 1—45
  atmospheric transport to oceans, 79—100
  bioaccumulation, 121—133
  chemistry and properties, 47—64
  concentration, 196
  congeners, 82, 146, 150—151
  distribution, behavior and load in oceans, see also Ocean environment, 143—161
  flux, 94, 179
  food chain, 135—141
  isomers, see Isomers
  mixture, 93
  nonmetabolic alteration, 207—213
  reliability of analysis, 65—78
  reservoir, see Reservoir of PCBs
  soil mobility, 101—120
  solubility, 101—120
  spill, 83, 116, 164, 167, 171
  trend assessment, 163—205
Pelagic biota, 140
Pelecanus
  occidentalis californicus, 164, 170, 190
  occidentalis carolinensis, 164, 170, 190
Pelicans, 164, 170, 190
Pentachlorobiphenyls, 48, 52, 84, 103
Pentachloro isomers, 123
Pentachlorophenyl, 123
Perca
  flavescens, 177
  fluviatilis, 178
Perch, 177, 178
Perchlorination of PCBs, 40
Persistence of PCBs in environment, 49, 187

MONS 005948

Persistent lipophilic chemicals, 122
Persistent organochlorines, 144
Peruvian Coast, 84
Pesticide analysis, 69
Pesticides, 80
Petromyzon marinus, 172
Phalacrocorax carbo, 166
Phenocior, 2
Photo alteration, 208
Photochemical degradation, 56—57
Photochemical reaction of PCBs, hydrocarbon solvents, 208
Photolysis, 57—58, 208—209
Photoreactivity of PCBs, 208
Phthalate esters, 80
Physical data, 91
Physical properties of Aroclors, 2—3
Physicochemical data, 91
Physicochemical factors, 154
Physicochemical properties, 140
  bioaccumulation, 123—127, 130
  lipophilic contaminants, 122
Phytoplankton, 138, 140
π constants, 124
Pigeon Key, Fla., 84, 88, 90
Pike, 178
Pimephales promelas, 128
Pinnipeds, 153
Planar molecules, 126
Plankton, 150—154, 184
Plant foliage, 87
Plant uptake, 117
Point Conception, 183
Point-source discharge, 174
Point sources, 185
Polar fluid, 87
Pollutant sources, 170—171
Polluted sites, 170, 171
Polychaetes, 125
Polychlorinated biphenyls, see PCBs
Polychlorinated terphenyls (PCTs), 2, 7—8, 22
Polycyclic aromatic hydrocarbons (PAH), 80
Polymeric adsorbents, 80
Polytetrafluoroethylene, 87
Polyurethane foam, see PUF
Pooling, 193
Population half-life, 181—182
Pork, 178
Port Hueneme, 189
Port Phillip Bay, Australia, 190
Potential error, 76
P_{ow}, 123—125, 127, 128
Precipitation, 87—89, 91, 94, 169, 182
Precipitation-derived residues, 90
Precipitation monitoring, 86
Precipitation sampling methods, 86
Precipitation scavenging, 94
Precipitation-weighted mean, 88
Predators, 168
Predator species, 194
Predatory raptors, 139
Preening birds, 168
Preparation of individual chlorobiphenyls, 48
Preparation of PCBs, 48—49
Presumed "clean" sites, 170
Primary production, 149, 157
Pristine coastal area, 95
Pristine sites, 170—171
Production of PCBs, 153
Properties of PCBs, 49, 53—54
Protocols, 165
PUF, 81—83
Puget Sound, Wash., 122
Pumpkinseed, 186
P values, 125
Pyralene, 2
Pyralene 6000, 13, 16, 34
Pyrolysis, 59, 61

Q

Quantitation, approaches to, 34—35, 37, 40—43
Quantitation techniques, 165, 167, 193
Quantitative estimation of chlorobiphenyls, 49
Quartz-fiber filter, 80

R

Rain, 86, 88
  rate, 94
Rainbow smelt, 179—180, 186
Rainbow trout, 128
Rainfall, 116
  rate, 96
Rain-tripped sensor, 87
Rainwater, 93
Rallus longirostris, 175
Random samples, 172
Rapid thawing, 169
Rat abdominal fat, 125
Rate of absorption, 168—169
Rate of accumulation, 168
Rate of disappearance, 186—187, 189
Rate of elimination, 168—169
Rate of excretion, 137, 140
Rate of metabolism, 137
Rate of uptake, 137
Real surfaces, 88
Recirculation of pollutants, 189
Red-breasted merganser, 182
Reductive dechlorination, 57
Regulatory controls, need for, 2—5
Relative bioaccumulation factor, 127—128
Relative free energy change, 127
Reliability of PCB analyses, see Analysis of PCBs
Remobilization, 184, 197
Remote marine areas, 83
Remote sites, 87
Removal parameters, 88
Removal processes, 86—89

MONS 005949

Replicate pools, 172
Representative samples, 180
Reproduction, 170
Reservoir of DDT, 189
Reservoir of PCBs, 164
Reservoirs, 102
Reservoir sizes, 95
Residence time, 93, 157
Resident/fresh water species, 185—187
Residues, see also Incurred residues, 164, 167
  composition of, 66—68
  interfering, 69
  precipitation-derived, 90
  shifting of characteristics of, 194
Resuspension of sediments, 182, 186
Retention efficiencies, 80
Retention indexes, 70
Retention of a chemical, 122
Retention of PCBs, 125
Retention volume (V_R), 82
Reversed phase liquid chromatography (RPLC), 17
Revolatilization losses, 87
Rice bran oil incident, 145
Rice oil, 2, 210
Riverine flux, 95
Roach, 170
Royal Palms, 189
Royal Palms State Beach, 188
Runoff, 171, 182
Rural areas, 85
Rural/suburban/coastal atmosphere, 84

S

Saginaw Bay, Lake Huron, 89
Salinity, 168—169
Salmo gairdneri, 128
Salmon, 170, 181
Salvelinus
  fontinalis, 179
  namaycush, 166, 179
  namaycush siscowet, 166
Sample cleanup, 5—7
Sampling programs, 167
Samplings, see also Biological sampling issues, 80, 165
  age, 181
  consistent pattern, 172
  design, 190
  extent of, 169, 192
  grand total means, 192
  ideal specimens, 169
  migratory age, 181
  number of specimens, 179, 182, 185, 193
  regularity, 169
  requirements, 165
  size, 180—181, 192
  size of specimen for biological issues, 172
  specific location, 180
  specific size, 179
  statewide, 192
Sampling sites, 171
Sampling systems, 82
Sampling temperature, 86
Sampling variance, 168
Sampling volumes (V_s), 82
San Diego, 182
San Gabriel River, 183
Sanitary treatment, 184
San Miguel Island, 189
Santa Barbara, 183
Santa Barbara Basin, 183
Santa Monica Bay, 182, 184
Sargasso Sea, 155
Sault St. Marie, Ont., 88
Scotland, 197
Seabirds, 175
Seal, 154
Sea lamprey, 172
Sea mullet, 125
Seas, 80
Seasonal variability, 169
Seasonal variations in Antarctic atmosphere, 145—146
Seattle, Wash., 189
Sea water, 94
Second order kinetics, 130
Sediments, 116—117, 168, 197
  contaminated, 184
  disturbance of, 189
  immobilization, 187
  ingestion of, 186
  mobilization, 187
  resuspension, 182, 186
Semiquantitative analysis of Aroclors by NMR, 40
Sensitization of photoreaction in PCBs, 58
Separation, 5—7
Separation efficiency, 70
Separation from interfering residues, 69
Seto-Inland Area, Japan, 155
Sewage effluent, 184—185
Sewer lines, 189
Sewer outfalls, 164, 168, 183—185, 188—189
Sewer system, 183
Sex
  specimens for biological sampling, 170
  specimens for trend assessment, 165
Sharks, 197
Shell lengths, 169
Silica columns, 69
Silicone oil, 87
Sink, 91—92, 144
Sinking particles, 148—150
Size, 139, 165, 169—170
Size of accumulation, 168
Skin, 186
Small projects, 175—179
Smallmouth bass, 180
Snails, 139
Snow, 86—88
Snow cores, 88

MONS 005950

Soil mobility of PCBs, 102, 113—115, 118
Soil sorption, 112
Soil sorption constant, see K_{oc}
Soil thin-layer chromatography, 111, 113—114, 116
Solar radiation, 209
Sole, 168
Solid adsorbent, see also Adsorbent, 80—81
Solubility of PCBs, 49, 53—54, 91, 101—120
  aqueous, 102—106
  correlation of K values with earth material and compound properties, 111—113
  mechanism of sorption, 110—111
  mobility in soils, 113—115
  plant uptake, 117
  sorption by earth materials, 105—110
  surface runoff, 115—117
Solute-solvent interaction, 111
Solvent partition, 69
Solvents, 69
Sorption constant, 107—110
Sorption of PCBs by earth materials, 105—110
Sorption reactions, 55—56
Source emission strengths, 83
Sources, 91—92, 116, 170—171, 187, 190, 194
  accidents, 175
South American continent, 85
South Carolina, 88, 190, 197
Southern California, 87, 139, 184
Southern California Bight, 89, 182—185
Southern California Coastal Water Research Project, 182—183
Southern Hemisphere, 83, 85, 144, 147, 150
Southern Ocean, 144, 147—148
Sovol, 2
Sparrow hawk, 139
Spawning, 165, 170
Spawning season, 176
Specimens, see Samplings
Spills, see PCB spills
Splake, 179
Spotfail shiners, 180
Squalus acanthias, 169
Squid, 153
Stable water flow, 187
Stack gases, 81
Stagnant films of air, 91
Standard reference materials, 7, 9
Starlings, 164, 169, 191—193
Stationary phases, 70, 73
Statistical analysis, 190
Statistical aspects of trend assessment, 173—176, 178, 192—193, 195
Statistical studies, 177
Statistics, 172
Stereochemistry, 125—127
Steric configuration, 125
Steric effect coefficient (SEC), 125—127
Steric factors, 125
Sterna hirundo, 170, 176
Stizostedion vitreum vitreum, 177
Stockholm, Sweden, 84, 86
Stomach lining, 127
Stomach walls, 122
Storm frequency, 96
Storms, 95, 184
Storm-water runoff, 116
Stratification by length or weight, 172
Stress, 181
Striped bass, 187
Striped dolphin, 153
Stripping, 85
Strobane, 7
Structure activity relationships, 127
Structure of PCBs, 48—49
Structure of pentachlorobiphenyl, 52
Sturnus vulgaris, 169
Sulfuric acid treatment, 69
Supersaturation, 91—92
Surface adsorption properties, 130
Surface area, 107—110
Surface microlayers, 140
Surface ocean waters, 92
Surface properties, 87, 129
Surface runoff, 115—117
Surface sea water, 93
Surrogate surfaces, 87—88
Sweden, 84, 90
Swimming aquatic organisms, 123
Synthesis of individual chlorobiphenyls, 48—49
Synthesis of PCBs, 2
Syowa Station, Antarctica, 145

T

Taiwan, 197
2,4',5-TCB, 82
TDE, 180
Temperate climates, 91
Temperatures, 85, 95
Temporary tolerances, 4
Tenax-GC, 81—83
Tern, see also Commonern, 170, 173
Terrestrial ecosystems, 139, 140, 165
Terrestrial environment, 144
Terrestrial organisms, 122, 138, 169
Tetrachlorobiphenyl, 123
2,2',5,5'-Tetrachlorobiphenyl, 210
Texas, 191
Texas Gulf Coast, 84
Theoretical plates (N), 82
Thermal alteration, 208—211
Thermal degradation, 59, 61
Thermal formation of more toxic substances from PCBs, 211
Thermodynamic activities, 129
Thermodynamic aspects of bioaccumulation, 127—129
Thin layer chromatographic procedures, 6
Timing of collection, 169—170
Tissue, 171, 193
Top carnivore, 139—140

MONS 005951

Top predators, 140
Toronto, Ont., 86
Total body burden, 169
Total organic carbon (TOC) content, 107—110
Total PCB, 81
Total suspended particle, see TSP
Toxaphene, 7, 69, 83, 166, 179, 181
Toxicity, 73
Toxicological effects of PCBs, 4
Toxicological properties of Aroclors, 3
Toxic Substances Control Act (TSCA), 102
Trace analysis, implications in, 5
Trace metal scavenging, 91
Trace organics, 87
Trade names, see specific names
Transfer coefficient, 91—92, 129
Transformer manufacturers, 83
Transport compartment, 130
Transport of PCBs, see also Atmospheric transport of PCBs, 49, 55
Transport rates, 96
Trend assessment of PCBs, 163—205
  accuracy, 172
  biological sampling issues, see also Biological sampling issues, 167—173
  changes in methodology, 193
  chemical analyses for, see also Analysis of PCB, 165—167
  complexities of PCB analysis in, 164
  experimental design for, 165
  extensive monitoring programs, see also Monitoring programs, 179—195
  findings, 175—196
  initial level of PCBs, 178
  interferences, 166—167
  interpretation
    inadequate sample size, 178
    massive data sets, 193, 195
    small data sets, 178, 191
  location, 179
  new approaches, 172—173
  sampling requirements, 165
  small projects, 175—179
  specimens, 165
  statistical aspects of, 173—175
  type of sample, 179
Trend-monitoring programs, 165
Trichlorobiphenyls, 103, 123
Trophic contamination, 136
Trophic levels, 136—139, 153, 175
Trophic magnification, 136
Trophic pyramid, 136
Tropical climates, 91
Tropical Pacific, 93
Trout, 181
TSP, 86
Turbulent impaction, 87
Turku Archipelago, 178
Two-film resistance model of Whitman, 91

U

Undersaturation, 93
Undeveloped lands, 95
Unstructured food webs, 140
Upper Hudson Basin, 117
Uptake of chemicals and PCBs, 122
  aquatic organisms, 122
  benthic organisms, 123
  direct from water, 140
  fish, 128
  lipophilic compounds, 129
  routes of, 130
  swimming aquatic organisms, 123
  terrestrial organisms, 122
Uptake mechanisms, see Uptake of chemicals and PCBs
Urban air, 80—81
Urban atmosphere, 84
Urban centers, 83

V

Values below detection limit, 173
Vapor front, 81
Vaporization, 54—55
Vapor loss, 117
Vapor-particle partitioning of PCBs, 85—86
Vapor/particle (V/P) ratio, 85
Vapor pressure, 54—55, 86, 91
Vapors, 80
Vapor sampling, 81
Vapor trapping, 81
Variability, 73, 167, 169—172, 180
Ventilation and exhaust system, 116
Ventilation rate, 130
Ventura County, 182
Vertical deposition, 148
Vertical distribution, 83
Vertical profiles, 148
Vertical transport, 148
Volatility, 82
Volatilization, 91—92, 155

W

Walleye, 177, 179—180
Washout, 87, 96
Washout ratios, 88, 90, 94
Waste treatment, 189
Waste treatment systems, 116
Waste water, 184
Waste water discharges, 164, 182
Waste water treatment, 184
Water
  bioaccumulation of PCBs, 122
  PCBs in, 146—150
Water bodies, see also specific bodies, 89
Water column, 95, 148

MONS 005952

Water-filled pans, 87
Water flow, 169
Water mass, 155
Water/sediment interface, 168
Water solubility, 112, 123—125
Water vapor mass transfer rates, 92
Waukegan, Ill., 90
Weather, effect of, 169
Weathering of PCBs, 6—7, 167, 180, 183—184, 186—187, 195
Weather variations, 169
Weddell seal, 151
West Pacific, 84
Wet deposition, 86, 88, 91, 93—94
Wet surface pans, 87
Wheeler National Wildlife Refuge, 193
White croaker, 184
White Sands, N.M., 84
White sucker, 194
Whole fish, 194
Wind and wave action, 189
Wind speed, 95
Workplace air, 81
Worms, 197

X

XAD-2, 81—83
XAD resin column, 87

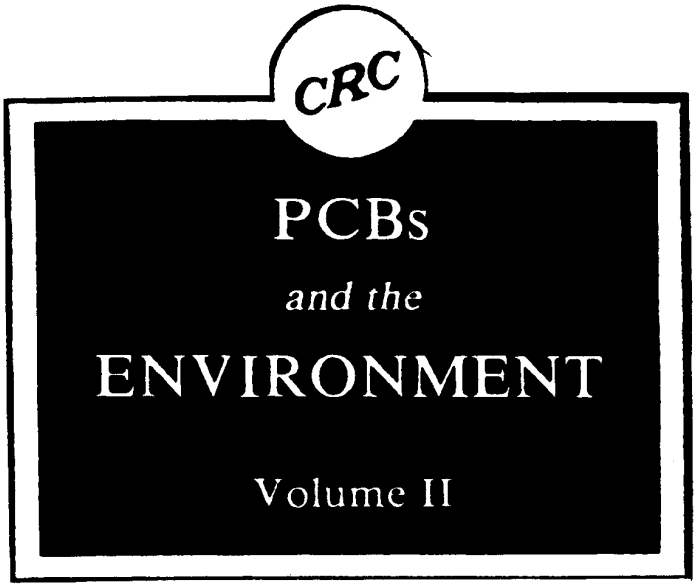
Y

Yangtze River, 95
Year-round residents, 181
Year-to-year variations, 180
Yellow perch, 177, 179, 194
Yellow pickerel, 180
"Yusho" incident, 3, 210

Z

Zalophus californianus, 189
Zero values, 173, 193
Zooplankton, 140

MONS 005953



John S. Waid



MONS 005954

PCBs and the Environment

Volume II

Editor

John S. Waid, D. Phil.(Oxford), F.I.Biol., M.A.S.M.
Chairman and Head
Department of Microbiology
La Trobe University
Bundoora, Victoria, Australia



CRC Press, Inc.
Boca Raton, Florida

MONS 005955

Library of Congress Cataloging-in-Publication Data

PCBs and the environment.

Includes bibliographies and indexes.
1. Polychlorinated biphenyls--Environmental aspects.
I. Weld, John S.
QH545.P6P236 1986 363.1'79 86-17549
ISBN 0-8493-5923-6 (v. 1)
0-8493-5924-4 (v. 2)
0-8493-5925-2 (v. 3)

This book represents information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Every reasonable effort has been made to give reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

© 1986 by CRC Press, Inc.

International Standard Book Number 0-8493-5923-6 (v. 1)
International Standard Book Number 0-8493-5924-4 (v. 2)
International Standard Book Number 0-8493-5925-2 (v. 3)
International Standard Book Number 0-8493-5929-5 (set)

Library of Congress Card Number 86-17549
Printed in the United States

MONS 005956

THE EDITOR

John S. Waid, D.Phil.(Oxford), F.I.Biol., M.A.S.M., is Chairman and Head, Department of Microbiology, La Trobe University, Bundoora, Victoria, Australia, a position he has held since 1974. He also served as Dean of the School of Biological Sciences from 1977-1979.

Prior to his offices at La Trobe University, Professor Waid served in various capacities at the Grassland Research Institute; the Nature Conservancy; Levington Research Station, Fissons, Ltd.; University of New England, New South Wales; Cornell University; Reading University; and the Univesity of Canterbury, New Zealand.

His experimental experience includes the post as joint editor of the proceedings and a convenor of an international symposium on the ecology of soil fungi held in Liverpool in 1968; initiator and Executive Editor of *Soil Biology and Biochemistry* from 1969 to the present; New Zealand delegate to the Committee on Microbial Ecology, International Association of Microbiology Societies (1972-1974); leader of the advisory team from New Zealand under the auspices of the Colombo Plan to review and report on science teaching at Khon Kaen University in northeast Thailand (1974); Victorian representative on the Standing Committee for Environmental Community Problems (SCENCOP) of the Australian Society for Microbiology (1975-1977); and the national representative for the Australian Society for Microbiology on the International Committee of Microbial Ecology (1979-present).

Professor Waid's research interests at present are root biology (in particular the decomposition of grass and legume roots and release of legume-nitrogen to the soil, a study which has been supported by ARGC grants since 1977) and polychlorinated biphenyls in the environment and their degradation. The PCB work has been supported by grants from the Rural Credits Development Fund (1976-1978), the Victoria Ministry for Conservation (1979-1989), and the Australian Marine Sciences and Technologies Advisory Committee (1980-1981). He has also had contracts with the Victoria Ministry for Conservation, and the Federal Department of Science and the Environment to review problems associated with PCBs and the monitoring of hazardous chemicals in the environment. He has made surveys of PCBs in soils and waterways on behalf of a government department, an urban authority, and a large industrial organization (all unnamed), and is consulted regularly on matters pertaining to PCBs by the Victoria Environment Protection Authority.

MONS 005957

CONTRIBUTORS

Richard F. Addison, Ph.D.
Head, Environmental Quality Division
Marine Ecology Laboratory
Bedford Institute of Oceanography
Dartmouth, Nova Scotia, Canada

Gene B. Fuller, Ph.D.
Assistant Director for Research
Primate Research Institute
New Mexico State University
Holloman AFB, New Mexico

Kensuke Furukawa, Ph.D.
Head
Genetics and Breeding Division
Fermentation Research Institute
Agency of Industrial Science
and Technology
Tsukuba Science City, Japan

Wilbert Gamble, Ph.D.
Professor
Department of Biochemistry and
Biophysics
Oregon State University
Corvallis, Oregon

Janet A. Gooch
National Marine Fisheries Service
Charleston, South Carolina

M. K. Hamdy, Ph.D.
Department of Food Science
University of Georgia
Athens, Georgia

Gareth C. Harding, Ph.D.
Research Scientist
Marine Ecology Laboratory
Bedford Institute of Oceanography
Dartmouth, Nova Scotia, Canada

William C. Hobson, Ph.D.
Director
Primate Research Institute
New Mexico State University
Holloman AFB, New Mexico

H. K. Mahanty
Senior Lecturer
Plant and Micropbial Sciences
University of Canterbury
Christchurch, New Zealand

David B. Peakall, Ph.D.
Chief, Wildlife Toxicology Division
National Wildlife Research Center
Canadian Wildlife Service
Ottawa, Ontario, Canada

David J. H. Phillips, Ph.D.
Senior Environmental Protection Officer
Environmental Protection Department
Kowloon, Hong Kong

MONS 005958

TABLE OF CONTENTS

Volume I

Chapter 1
Analytical Chemistry of PCBs 1
Thomas Cairns, Gregory M. Doose, Jerry E. Froberg, Robert A. Jacobson, and Emil G. Siegmund

Chapter 2
Chemistry and Properties of PCBs in Relation to Environmental Effects 47
B.L. Sawhney

Chapter 3
The Reliability of PCB Analysis 65
A.V. Holden

Chapter 4
Atmospheric Transport of PCB to the Oceans 79
E. Atlas, T. Bidleman, and C.S. Giam

Chapter 5
Solubility and Soil Mobility of Polychlorinated Biphenyls 101
S.F.J. Chou and R.A. Griffin

Chapter 6
Factors Controlling Bioaccumulation of PCBs 121
Glen R. Shaw and D.W. Connell

Chapter 7
Factors Controlling Bioaccumulation in Food Chains 135
G.R. Shaw and D.W. Connell

Chapter 8
Distribution, Behavior, and Load of PCBs in the Oceans 143
Shinsuke Tanabe and Ryo Tatsukawa

Chapter 9
What is Happening to PCBs? Elements of Environmental Monitoring as Illustrated by an Analysis of PCB Trends in Terrestrial and Aquatic Organisms 163
Virginia F. Stout

Chapter 10
Nonmetabolic Alteration of PCBs 207
John A.G. Roach

Index 215

MONS 005959

Volume II

Chapter 1
Polychlorinated Biphenyls: Accumulation and Effects Upon Plants 1
H.K. Mahanty

Chapter 2
Accumulation and Effects of PCBs in Marine Invertebrates and Vertebrates 9
G.C. Harding and R.F. Addison

Chapter 3
Accumulation and Effects on Birds 31
D.B. Peakall

Chapter 4
PCBs and the Environment: Perturbations of Biochemical Systems 49
Wilbert Gamble

Chapter 5
Uptake, Retention, Biodegradation, and Depuration of PCBs by Organisms 63
M.K. Handy and J.A. Gooch

Chapter 6
Modification of PCBs by Bacteria and Other Microorganisms 89
Kensuke Furukawa

Chapter 7
Effect of PCBs on Reproduction in Mammals 101
Gene B. Fuller and William C. Hobson

Chapter 8
Use of Organisms to Quantify PCBs in Marine and Estuarine Environments 127
David J.H. Phillips

Index 183

Volume III

Chapter 1
Differences Between Yusho and Other Kinds of Poisoning Involving Only PCBs .....
Takashi Kashimoto and Hideaki Miyata

Chapter 2
PCB Poisoning from Toxic Rice-Bran Oil in Taiwan .....
Paul H. Chen and Shu-Tao Hsu

Chapter 3
PCBs in Human Populations .....
Jon Mes

MONS 005960

Chapter 4
Polychlorinated Biphenyls in the Workplace .....
Alexander B. Smith and David P. Brown

Chapter 5
Disposal and Destruction of Waste PCBs .....
Jack D. Lauber

Chapter 6
The Great Lakes Ecosystem — Modeling of the Fate of PCBs .....
Robert V. Thomann, John P. Connelly, and Nelson A. Thomas

Chapter 7
PCBs in the Baltic Environment .....
Mats Olsson

Chapter 8
PCBs and the Environment: The Mediterranean Marine Ecosystem .....
Scott W. Fowler

Chapter 9
Case Study: The Australian Ecosystem .....
Bruce J. Richardson, Robert H. Smillie, and John S. Wald

Index .....

MONS 005961

Chapter 1

POLYCHLORINATED BIPHENYLS: ACCUMULATION AND EFFECTS UPON PLANTS

H. K. Mahanty

TABLE OF CONTENTS

I. Introduction 2

II. Toxicity of PCBs to Higher Plants 2
- A. Absorption of PCBs from the Atmosphere 2
- B. Translocation of PCBs from Soil into Plants 2
  - 1. Absorption 2
  - 2. Toxicity 2

III. Effects of PCBs on Phytoplankton 4
- A. Laboratory Studies of Effects of PCBs on Algae Including Diatoms 4
  - 1. Environmental Factors Affecting the Sensitivity of Algae and Diatoms to PCBs 4
    - a. Effects on Growth 5
    - b. Effects on Photosynthesis 5
    - c. Changes in Ultrastructure 6

IV. Conclusion 6

References 7

MONS 005962

I. INTRODUCTION

Polychlorinated biphenyls (PCBs) are an important group of chemicals which have become dispersed in our environment mainly as a result of industrial uses.[1] Following detection of their presence by Jensen[2] in 1966, in water and soil, it has been considered that PCBs represent a major environmental pollutant. Thereafter, extensive studies followed to determine their widespread persistence[3] in the environment and to evaluate their toxicological and physiological effects on the biota.[4] This chapter summarizes the information available on the accumulation and effects of PCBs on higher plants and algae including diatoms.

II. TOXICITY OF PCBs TO HIGHER PLANTS

A. Absorption of PCBs from the Atmosphere

The first comprehensive report on the presence of PCBs in a diverse flora was made by Klein and Weisberger.[5] The samples were taken from two selected areas — one from an area of densely growing vegetation near a highway which was presumably an industrial area containing higher levels of PCBs and another from a remote area in the European Alps. The levels of PCBs in various samples are shown in Table 1.

The plants sampled from the motorway contained 0.09 to 0.95 ppm of PCBs, whereas from the remote alpine region a minimal value of 0.05 to 0.15 ppm was recorded and the authors concluded that PCBs were transported by air to the remote area. It is also interesting to note that the different plants sampled showed variable amounts of PCBs. For example, raspberry leaves from both areas contained approximately the same level of PCBs, whereas larch leaves near the highways contained a much higher level than those from the alpine region. Further study would be needed to determine the rate of absorption and retention of PCBs by terrestrial plants in high and low polluted areas. However, this study does establish the fact that PCBs are absorbed preferentially by different species.

B. Translocation of PCBs from Soil into Plants

Because of their numerous applications, including possible usage in pesticide formulation, it is possible that these compounds could be present in soils of agricultural or forest areas. Furthermore, the application of municipal and industrial sewage sludge is becoming an inexpensive method of fertilizing agricultural lands. Factors controlling the transport of PCBs and estimates of the amounts present in various ecological reservoirs are detailed in other chapters of these volumes. At this point, I would like to summarize the evidence for translocation of PCBs from soil to plants and the effects on plants when grown in environments contaminated with PCBs.

1. Absorption

Several studies have shown that these compounds can be translocated from the soil to various parts of the plants. Furthermore, the PCBs can accumulate selectively in particular tissues in higher quantity than in others. For example,[9,10] it was shown that of the residue applied over 97% was present in the peel of a carrot, thereby indicating little translocation to other tissues. Similar preferential absorption was also recorded in soybean sprouts.[8] Using a ^{14}C-2,2'-dichlorobiphenyl, Moza et al.[11] showed, in two aquatic plants, concentration factors of 814 and 289 when compared to the amount of radioactivity present in water. Thus, it can be concluded PCB can be translocated into plants not only from soil but also from aquatic environments.

2. Toxicity

The effects of PCBs on the growth and development of plants, especially higher plants,

MONS 005963

Table 1
DISTRIBUTIONS OF PCBs IN TWO DIFFERENT LOCATIONS[a]

Near motorway		Remote alpine areas (Tegelberg or Hütensee)	
Plant	Dry weight (ppm)	Plant	Dry weight (ppm)
Moss	0.13	Moss	0.06
Heather	0.28	Heather	0.08
Raspberry leaves	0.15—0.27	Raspberry leaves	0.11
Larch leaves	0.95	Larch leaves	0.17
Rushes	0.12	Rushes	0.07
Hay	0.13	Fern	0.08—0.15
Grass	0.20—0.46	Juniper	0.07
Grass silage	0.40—0.42	Dwarf fir	0.09—0.10
Clover	0.33	Alder leaves	0.09
Mint	0.20		
Strawberry leaves	0.16—0.46		
Blackberry leaves	0.49		
Fir apex	0.31		
Oak foliage	0.50		
Pine leaves	0.11		
Water hemlock	0.23—0.57		

are not as well documented as for animals (see other chapters). It is feasible that since PCBs are lipophilic and less mobile chemicals their effects are difficult to monitor in the whole plant situation. However, a few studies have shown that these chemicals can interfere with the overall growth of the plant albeit, when applied at a much higher concentration than the available concentration in natural environments.[12,13]

These results which have been reviewed in a recent publication[47] are important in connection with the agricultural practice where soil is fertilized with industrial sludge which may contain very high levels of PCBs.[14] As mentioned earlier, root crops such as carrots and beets do tend to accumulate PCBs or their derivatives in the tissue without any visible damage and are thus more likely be used for animal consumption. It would be desirable to have information on other crops grown in fields fertilized with raw sewage in many countries of the Third World.

In a comprehensive study, Strek et al.[12] showed significant reductions in height, fresh top weight, and inhibition of cumulative water use in soybean and beet root at 1000 ppm Aroclor® 1254, but not in corn and sorghum. They concluded that less phytotoxic damage is likely to result from application of sludge containing moderate levels of PCBs (1 to 50 ppm), but the above contention is subject to a major criticism. Industrial sludge is usually a mixture of PCB compounds, with a variable chlorine content and perhaps, derivatives of PCB isomers resulting from microbial action. The effects of these chemicals on plants could be totally different from those of laboratory-simulated studies in which a pure isomer (Aroclor® 1254) has been used.

For example, Mahanty[13] showed in a free floating aquatic angiosperm, the duckweed *Spirodela oligorrhiza*, that a significant reduction in growth as measured by an estimation of fresh weight, occurred in the presence of less than 20 ppm of Aroclor® 1242. The treated plants had smaller fronds and a characteristic chlorotic pattern.[13] This observation was later confirmed as interference by PCBs in photosynthesis.[16-18] However, the effects of PCBs on photosynthesis and cell division will be discussed later. This particular plant has added advantages in monitoring the effects of environmental pollutants in laboratory or simulated

MONS 005964

conditions. These duckweeds can be easily maintained on a simple medium contained in vessels which are resistant to PCB adsorption and growth can be determined visually by an increased number of colonies and simply counting the number of fronds in each colony.

The above discussion on PCBs in relation to higher plants suggests that PCBs when distributed by air could be transported to remote areas and can be absorbed and accumulated preferentially in different plants. They may be absorbed from the soil by roots and become accumulated either in the metabolized or original form. This ability to move within or outside the plant depends on the structure and degree of chlorination.

Higher chlorinated compounds are metabolized to lesser chlorinated biphenyls and other derivatives after absorption. These products are more easily translocated within the internal tissue of plants than in the form originally applied. So far, no toxicity studies have been made using these metabolites. This particular information could be a contributory factor in deciding whether PCBs, as available commercially, present a potential hazard to plants or not. It is well known from animal studies that chemicals which are apparently harmless externally may be converted to potential carcinogens by enzymes present in the liver. Similar mechanisms may exist in plants. It is also important to note that these intermediary compounds are also fairly stable and therefore are likely to be dissipated through the food chain to other ecosystems[6] where decomposer microbes could further modify these compounds for easy absorption and bioconcentration in higher trophic levels.[19] Production of crops will be reduced if PCBs are present in the field at a high concentration and this effect might be reduced by the use of activated carbon to adsorb excessive pollutant from the soil. In laboratory studies PCBs inhibited photosynthesis in higher plants at lower concentrations. This is a serious interference when photosynthesis is considered as a primary process for the fixation of the energy of the sun.

III. EFFECTS OF PCBs ON PHYTOPLANKTON

PCBs are known to accumulate in aquatic environments as a result of dumping sewage and industrial effluents, runoff from terrestrial ecosystems, as well as atmospheric fallout and rainfall.[19] Separate chapters in this publication are devoted to reviewing our knowledge of the distribution of PCBs. Phytoplankton form the basis of many aquatic food chains and consequently numerous studies have been made, both in laboratory and in natural ecosystems, to evaluate the likely influence of these chemicals on phytoplankton. In a separate chapter the accumulation and effects of PCBs on phytoplankton communities will be considered. Here, I wish to discuss the work done mainly on algae including diatoms as representatives of lower plants. The majority of these are laboratory studies, the results of which seem to reflect the effects of PCBs on plants in general.

A. Laboratory Studies of Effects of PCBs on Algae Including Diatoms

As mentioned earlier there are advantages in using algae and diatoms as test organisms since they are present in almost every aquatic environment and act as primary producers as well as a direct food source to animals inhabiting these ecological niches. Experiments can be designed to test all aspects of plant growth, and to test plant-environment interactions which are not possible on a large scale using higher plants. More importantly, sensitivity to PCBs can be studied at the very low concentrations which are present in our ecosystem. These results should reflect the likelihood of damage, if any, by the continuous presence of these chemicals. All our knowledge of the sensitivity of higher plants to PCBs comes from very high levels of the compound — ranging from 20 to 200 ppm of PCBs, whereas phytoplankton have been shown to be sensitive at 10 ppb or less.

1. Environmental Factors Affecting the Sensitivity of Algae and Diatoms to PCBs

The sensitivity of phytoplankton has been shown to vary with temperature,[20] geographic

MONS 005965

location,[21] interspecific competition,[22,23] cell density,[24] osmotic pressure,[25] and the presence of other toxicants.[26] Consequently, the health, abundance, and distribution of selective phytoplankton feeders on other animals in the food chain could be indirectly affected by the presence of PCBs. Laboratory experiments have shown that PCBs can be taken up from the growth medium and accumulated to higher concentrations by the marine diatoms, *Cylindrotheca closterium*[27] and *Thalassiosira pseudonema*[28] and the unicellular green algae *Chlamydomonas reinhardii*,[29] *Chlorella pyrenoidosa*,[30] and *Dunaliella* sp.[31] A similar preferential absorption has also been noted in higher plants. Thus, environmental factors coupled with the preferential absorption, retention, and tolerance of high levels of PCBs by individual species,[32] could confer a selective advantage over sensitive species. These laboratory studies also provide information useful for assessing the ultimate consequences of PCBs present in the environment, however low these concentrations may be. They still could have an impact on species composition in natural environments.

a. Effects on Growth

Studies on the growth strategies of algae and diatoms indicate the following patterns.

Most marine diatoms tested so far are found to be sensitive to PCBs at a concentration ranging from as low as 0.1 part per thousand million (10^9 or ptm)[20] and higher.[27,33,34] The highest concentration used to show the inhibition of cell division was at 100 $\mu g/\ell$, which is still far below the concentration tested in any higher plants. These levels of PCBs are certainly present in some waters near estuaries or in agricultural fields fertilized with industrial sewage sludge. It is possible that the extreme toxicity of PCBs to diatoms is due to their intricate cell wall development during which silica particles are absorbed from the media and secreted in a biologically active form to build the cell wall. It is also known that glass surfaces which contain silica can absorb considerable amounts of PCBs from the media.[35] Therefore, in contaminated water, silica particles are likely to be modified by PCBs and thus available to the diatomous communities in an altered form which could affect normal developmental processes of the cell wall.

The effects of PCBs on the growth of algae are somewhat different from those of diatoms. Unlike diatoms, certain algae can absorb and accumulate PCBs to a greater concentration than available in the growth media[29,30,36] and like marine diatoms certain algae show extreme sensitivity to PCBs. For example, Larsson and Tillberg[37] showed that the growth of the unicellular green alga *Scenedesmus obtusiusculus* was inhibited at 300 ppb PCBs and above but its viability was only affected at a concentration of 1000 ppb. By contrast, *S. quadricauda* was inhibited at 5 ppb and above,[34] and *S. obliquus* at 0.25 ppm.[38] Similarly, Mahanty and Greeshoff[21] showed the toxicity of PCBs as variable in two closely related species of *Chlorella*. One species was found to be extremely resistant while the other was sensitive. Sensitivity or resistance to PCBs was also dependent on the chlorine content of the PCB compound used. Thus, Craigie et al.[39] showed different responses by the same alga *Dunaliella tertiolecta* to different PCB mixtures. Lower chlorinated forms were more toxic than higher chlorinated forms.

b. Effects on Photosynthesis

There has been much speculation on the exact nature of the inhibition of growth of phytoplankton caused by PCBs in sensitive species. Nevertheless, there is general agreement that the observed inhibition of growth is symptomatic expression of some interference in phytoplankton physiology. One of these physiological processes is photosynthesis which appears to be disturbed by PCBs in almost all the studies made so far. Once again, it should be emphasized that the disruption of the photosynthetic process or the overall inhibition of growth was only recorded for sensitive species. Thus, the nature of sensitivity or resistance is not known clearly or is as yet a matter of speculation. Resistance could be inherited as

MONS 005966

a genetic factor as has been shown in *Scenedesmus obliquus*.[18] In any case, for the disruption of physiological processes such as photosynthesis or respiration, PCBs have first to enter through the phospholipid membranes of cellular systems.[40] Therefore the nature of the phospholipid membrane could determine species specificity to PCBs but more detailed knowledge is needed to prove this speculation. However, in sensitive species, if the molecules are capable of penetrating the outer membrane then it is likely that they also penetrate organelle membranes and interfere with major processes in photosynthesis and respiration. Thus, the most frequently reported physiological effect of PCBs on phytoplankton is a reduction of ^{14}C-bicarbonate uptake which suggests inhibition of the photosynthetic process.[24,29,34,41-43] However, some authors have reported a slight stimulation of ^{14}C-bicarbonate uptake and stimulation of respiration in certain species of algae.[18,34] One of these was *Chlorella vulgaris*[18] which appeared to be highly resistant to PCBs even at 200 ppm concentration.[22] Inhibition of photosynthesis, as measured by oxygen evolution, was recorded with isolated spinach chloroplasts (*Spinacia oleracea*). Decreased amounts of chlorophyll in PCB-treated phytoplankton[18,28,44] and characteristic chlorosis in *Spirodela oligorrhiza*[18] also suggested disruption or interference with the photosynthetic process in both sensitive phytoplankton and higher plants. Detailed knowledge of the effects of PCBs on photosynthesis of higher plants is still very limited and further information is needed.

e. Changes in Ultrastructure

Inhibition of photosynthesis by disruption of chloroplast membranes has been substantiated by a number of electron microscope studies.[17,34,45] In one of these reports, Mahanty et al.[45] showed that when sensitive species were treated with PCBs they showed disruption of the internal membranes of chloroplasts but not for *Chlorella vulgaris*, a freshwater alga which was treated with a high concentration of PCBs. Apart from inhibition of photosynthesis, another interesting abnormality was recorded in a sensitive species of *Chlorella*;[45] this was the loss of cleavage of the cytoplasm following nuclear division. This failure of daughter colonies to separate from parent colonies in the duckweed, *S. oligorrhiza*[13] could also be an interference in the cytokinetic process. Thus, the overall inhibition of growth, as discussed earlier, by the measurement of cell density in phytoplankton might possibly be attributed to interference in the process of cell division.[46]

IV. CONCLUSION

Terrestrial plants including certain crops show no general phytotoxicity symptoms caused by PCBs, either in natural habitats or in field studies. Uptake of PCBs from soil and water and accumulation to a higher concentration are possible, especially with lower molecular weight chlorinated hydrocarbons. Thus, higher plants could act as a temporary reservoir for PCBs or their derivatives for future dissipation.

Algae and diatoms are comparatively more sensitive than higher plants; however, the phenomenon of sensitivity or resistance appears to be species specific. Most marine diatoms are extremely sensitive to very low levels of PCBs, whereas algae may be sensitive and resistant. The resistant species are able to accumulate PCBs to a higher concentration than present in their environment. For sensitive phytoplankton, a lack of cell division, lower chlorophyll index, disruption of chloroplast membranes, and inhibition of photosynthetic processes are the recorded features of PCB interference.

Thus, preferential absorption and accumulation in certain phytoplankton and the deleterious effects on others could lead to an alternation on species composition even in a very low-level contaminated environment.

MONS 005967

REFERENCES

1. **Fishbein, L.**, Chromatographic and biological aspects of polychlorinated biphenyls, *J. Chromatogr.*, 68, 345, 1972.
2. **Jensen, S.**, Report of a new chemical hazard, *New Sci.*, 32, 612, 1966.
3. **Risebrough, R. W., Rieche, P., Peakall, D. B., Herman, S. G., and Kirven, M. N.**, Polychlorinated biphenyls in the global ecosystem, *Nature (London)*, 220, 1098, 1968.
4. **Peakall, D. B.**, Polychlorinated biphenyls: occurrence and biological effects, *Residue Rev.*, 44, 1972.
5. **Klein, W. and Weisberger, I.**, PCBs and environmental contamination, in *Environmental Quality and Safety*, Vol. 5, Coulston, F. and Korte, F., Eds., George Thieme, Stuttgart, 1976, 237.
6. **Walsh, G. E., Hollister, T. A., and Forester, J.**, Translocation of four organochlorine compounds by red mangrove (*Rhizophora mangle* L.) seedlings, *Bull. Environ. Contam. Toxicol.*, 12(2), 129, 1974.
7. **Moza, P. N., Schonnert, I., Klein, W., and Korte, F.**, Long term uptake of lower chlorinated biphenyls and their conversion products by spruce trees (*Picea abies*) from soil treated with sewage sludge, *Chemosphere*, 6, 373, 1979.
8. **Suzuki, M., Azuwa, N., Okuno, G., and Takahashi, T.**, Translocation of polychlorobiphenyls in soil into plants: a study by a method of culture of soybean sprouts, *Arch. Environ. Contam. Toxicol.*, 5, 343, 1977.
9. **Iwata, Y., Gunther, F. A., and Westlake, W. E.**, Uptake of PCB (Aroclor 1254) from soil by carrots under field conditions, *Bull. Environ. Contam. Toxicol.*, 11, 523, 1974.
10. **Wallnöfer, P., Königer, M., and Engelhardt, G.**, Fate of xenobiotic chlorinated hydrocarbons (HCB and (PCBs) in plants and soils, *Z. Pflanzenkr. Pflanzenschutz.* 82, 91, 1975.
11. **Moza, P., Weisberger, I., Klein, W., and Korte, F.**, Metabolism of 2,2'-dichlorobiphenyl-^{14}C in two plant-water-soil-systems, *Bull. Environ. Contam. Toxicol.*, 12(5), 541, 1974.
12. **Sterk, H. J., Weber, J. B., Shea, P. J., Mrozek, E., Jr., and Overcash, M. R.**, Reduction of polychlorinated biphenyl toxicity and uptake of carbon-14 activity by plants through the use of activated carbon, *J. Agric. Food Chem.*, 29(2), 288, 1981.
13. **Mahanty, H. K.**, A study on the effects of polychlorinated biphenyl (Aroclor 1242) on an aquatic plant — *Spirodela oligorrhiza* (Kurz) Hein., *Bull. Environ. Contam. Toxicol.*, 14, 558, 1975.
14. **Bergh, A. K. and Peoples, R. S.**, Treatment and disposal of industrial wastewaters residues, *Proc. Natl. Conf.*, 1977, 4, 1977.
15. **Marvanicol, C. A. and Bartha, R.**, Biomagnification of Aroclor 1242 in decomposing *Spartina* litter, *Appl. Environ. Microbiol.*, 44, 669, 1982.
16. **Mahanty, K. D. and McWha, J. A.**, Sensitivity of *Spirodela oligorrhiza* (Kurz) Hegelm to a polychlorinated biphenyl (Aroclor 1242), *N.Z. J. Bot.*, 14, 9, 1976.
17. **Mahanty, H. K. and Floreon, B. A.**, Effects of a polychlorinated biphenyl (Aroclor 1242) on the ultrastructure of frond cells in the aquatic plant *Spirodela oligorrhiza* (Kurz) Hegelm, *N.Z. J. Bot.*, 14, 13, 1976.
18. **Sinclair, J., et al.**, Polychlorinated biphenyls and their effects on photosynthesis and respiration, *Can. J. Bot.*, 55, 2679, 1977.
19. **Hammond, A. L. J.**, Chemical pollution, polychlorinated biphenyls, *Science*, 175, 155, 1972.
20. **Fisher, N. S. and Wurster, C. F.**, Individual and combined effects of temperature and PCB's on the growth of three species of phytoplankton, *Environ. Pollut.*, 5, 205, 1973.
21. **Fisher, N. S., Graham, L. B., Carpenter, E. J., and Wurster, C. F.**, Geographic differences in phytoplankton sensitivity to PCB's, *Nature (London)*, 24, 548, 1973.
22. **Maurer, J. L., Fisher, N. S., and Wurster, C. F.**, Polychlorinated biphenyls and DDT alter species composition in mixed cultures of algae, *Science*, 176, 533, 1972.
23. **Fisher, N. S. and Wurster, C. F.**, Impact of pollutants on plankton communities, *Environ. Conserv.*, 1, 189, 1974.
24. **Cain, B. R. and Fleipp, F. W., Jr.**, Inhibition of growth and photosynthesis in *Chlorella pyrenoidosa* by a polychlorinated biphenyl and several insecticides, *Environ. Entomol.*, 3, 217, 1974.
25. **Fisher, N. S.**, On the differential sensitivity of estuarine and open-ocean diatoms to exotic chemical stress, *Am. Nat.*, 111, 871, 1977.
26. **Maurer, J. L., Teng, T. C., Walther, W. G., and Wurster, C. F.**, Interactions of PCB's, DDT and ODE in a marine diatom, *Bull. Environ. Contam. Toxicol.*, 12, 665, 1974.
27. **Keil, J. E., Preisler, L. E., and Sandifer, S. H.**, Polychlorinated biphenyl (Aroclor 1242): effects of uptake on growth, nucleic acids, and chlorophyll of a marine diatom, *Bull. Environ. Contam. Toxicol.*, 6(2), 156, 1971.
28. **Fisher, N. S., Guillard, R. R. L., and Wurster, C. F.**, Effects of chlorinated hydrocarbon pollutants on the growth kinetics of a marine diatom, in *Modelling Biochemical Processes in Aquatic Ecosystems*, Canale, R. P., Ed., Ann Arbor Science, Ann Arbor, Mich., 1976, 305.

MONS 005968

29. **Morgan, J. R.**, Effects of Aroclor 1242 (a polychlorinated biphenyl) and DDT on cultures of an alga, protozoan, daphnid, ostracod and guppy, *Bull. Environ. Contam. Toxicol.*, 8(3), 129, 1972.
30. **Södergren, A.**, Accumulation and distribution of chlorinated hydrocarbons in cultures of *Chlorella pyrenoidosa* (Chlorophyceae), *Oikos*, 22, 215, 1971.
31. **Scura, E. D. and Theilacker, G. H.**, Transfer of the chlorinated hydrocarbon, PCB, in a laboratory marine food chain, *Mar. Biol.*, 40, 317, 1977.
32. **Mahanty, H. K. and Greenhoff, P. M.**, Influence of polychlorinated biphenyls (PCB's) on growth of freshwater algae, *Bot. Gaz.*, 139(2), 202, 1976.
33. **Messer, J. L., Fisher, N. S., Teng, T. C., and Wurster, C. F.**, Polychlorinated biphenyls: toxicity to certain phytoplankters, *Science*, 175, 191, 1972.
34. **Glooschenko, V. and Glooschenko, W.**, Effect of PCB compounds on growth of Great Lakes phytoplankton, *Can. J. Bot.*, 53, 653, 1974.
35. **Greenhoff, P. M., Mahanty, H. K., and Gertner, E.**, Fate of polychlorinated biphenyl (Aroclor 1242) in an experimental study and its significance to the natural environment, *Bull. Environ. Contam. Toxicol.*, 17, 688, 1977.
36. **Urey, J. C., Kricher, J. C., and Boylan, J. M.**, Bioconcentration of four pure PCB isomers by *Chlorella pyrenoidosa*, *Bull. Environ. Contam. Toxicol.*, 16(1), 81, 1976.
37. **Larsson, C. M. and Tillberg, J. G.**, Effects of the commercial polychlorinated biphenyl mixture Aroclor 1242 on growth, viability, phosphate uptake, respiration and oxygen evolution in *Scenedesmus*, *Physiol. Plant.*, 33, 256, 1975.
38. **Mahanty, H. K.**, Kanamycin-resistant *Scenedesmus obliquus* showing simultaneous resistance to other antibiotics and polychlorinated biphenyls, *Nature (London)*, 277, 562, 1979.
39. **Craigie, J. S. and Hutzinger, O.**, Effects of commercial chlorinated hydrocarbon and specific chlorobiphenyls on the growth of seven species of marine phytoplankton, *Chemosphere*, 4, 139, 1975.
40. **Harding, L. W. and Phillips, J. H.**, Polychlorinated biphenyl (PCB) uptake by marine phytoplankton, *Marine Biol.*, 49, 103, 1978.
41. **Moore, S. A. and Harris, R. C.**, Differential sensitivity to polychlorinated biphenyls by phytoplankton, *Mar. Pollut. Bull.*, 5, 174, 1974.
42. **Laurd, E. J.**, Sensitivity of *Dunaliella* and *Scenedesmus* (Chlorophyceae) to chlorinated hydrocarbons, *Phycologia*, 12, 29, 1973.
43. **Biggs, D. C., Rowland, R. G., O'Connors, H. B., Powers, C. D., and Wurster, C. F.**, A comparison of the effects of chlordane and PCB on the growth, photosynthesis and cell size of estuarine phytoplankton, *Environ. Pollut.*, 15, 253, 1978.
44. **Ewald, W. G., French, J. E., and Champ, M. A.**, Toxicity of PCB's to *Euglena gracilis*: cell population growth, carbon fixation, chlorophyll level, oxygen consumption, and protein and nucleic acid synthesis, *Bull. Environ. Contam. Toxicol.*, 16(1), 71, 1976.
45. **Mahanty, H. K., Fiscaro, B. A., and Greenhoff, P. M.**, Effects of polychlorinated biphenyls (Aroclor 1242) on the ultrastructure of certain planktonic algae, *Bot. Gaz.*, 144, 56, 1983.
46. **Fisher, N. S.**, Chlorinated hydrocarbon pollutants and photosynthesis of marine phytoplankton: a reassessment, *Science*, 189, 463, 1975.
47. **Pal, D., Weber, J. B., and Overcash, M. R.**, Fate of polychlorinated biphenyls (PCBs) in soil-plant systems, *Residue Rev.*, 74, 45, 1980.

MONS 005969

Chapter 2

ACCUMULATION AND EFFECTS OF PCBs IN MARINE INVERTEBRATES AND VERTEBRATES

G.C. Harding and R. F. Addison

TABLE OF CONTENTS

I. Dynamics and Pathways 10

II. Effects of PCBs on Marine Biota 18
- A. Biochemical Effects: Mixed Function Oxidase Induction 18
- B. Biochemical Effects: ATPase Inhibition 20
- C. Miscellaneous Biochemical Effects 21
- D. Whole Organism Responses to PCBs 22

References 23

MONS 005970

I. DYNAMICS AND PATHWAYS

The accumulation of any anthropogenic substance by an organism from its environment involves two opposing processes, those of uptake and loss. Uptake occurs either by direct contact between the contaminant and the body of the organism or respiratory surfaces or through ingestion of contaminated food. Loss may occur with or without metabolism of the contaminant through the general body surface, through excretion of metabolic waste, through defecation of undigested material, through production of young, or voiding of other body tissues. The extent of contamination of an organism or a population at any time depends on the dynamic equilibrium between the processes of uptake and loss; these processes are illustrated thus:



The rate of adsorption of PCBs by marine organisms depends mainly on the amount and availability of PCBs present in sea water. Open ocean values for subsurface waters during the 1970s ranged up to 10 ng/ℓ with values as high as 40 ng/ℓ reported for the surface film.[1-8] Some continental seas were more contaminated, with levels up to 20 ng/ℓ in subsurface water and up to 2 μg/ℓ in surface films.[9-11] The worst cases of pollution have been reported near shore, as is to be expected, near point sources of industrial or domestic discharges; such values may approach 275 μg/ℓ.[12-14] These levels exceed the experimentally determined solubilities of commercial PCB formulations in sea water.[15-17] Marine biota from various habitats are therefore exposed to a wide range of PCB concentrations, depending on whether they are open ocean, neustonic, neritic, or benthic dwellers.

A brief digression is required to discuss the availability of PCBs to marine organisms at concentrations reported in sea water. First, more highly chlorinated PCB components are less soluble in sea water[15,16] yet the quantification of concentrations in sea water, sediments, and biota is usually carried out by reference to the best matching commercial formulation.[17,18] Our present estimates of PCB contamination in nature are therefore less precise than are analyses of discrete compounds, and intercomparisons between regions or laboratories are more difficult. Second, PCB availability to organisms depends not only on their size and activity but on the quality, quantity, and size of competing inert particles because organochlorine compounds are very hydrophobic and adsorb readily to other surfaces.[19,20] The extensive surface area associated with marine particles of less than 1-μm diameter implies that most organochlorines should occur in particulate form.[21] Organochlorines are also incorporated into colloidal micelles believed to be formed by the humic substances which comprise more than 90% of the dissolved organic matter in sea water.[22-24] "Solution" is defined operationally in oceanography as passage through a 0.5-μm pore-size filter,[25] and this definition would not include the micellar structures; the point is illustrated by the fact that filtration does not remove experimentally added organochlorines from humic solutions.[26]

All the reported concentrations of PCBs in sea water have been determined either by the direct solvent extraction approach, or by concentration of the samples on resins such as Amberlite® XAD-2, polyurethane foam, activated carbon, or other absorbent.[2,7,9,26] Obviously, the direct extraction approach combines PCBs in solution with those bound to particulates, both living and inert, whereas the sorbent methods allow an unknown fraction of particulates and associated organochlorines to escape sampling.[27] As our estimates of PCBs in sea water include a fraction adsorbed onto particles, it is important to know

MONS 005971

something about the dynamics of PCBs between particles and larger organisms. Several authors have attempted recently to evaluate the uptake of PCBs by organisms directly from particulate fractions. Fowler et al.[28] have examined the accumulation of Phenoclor DP-5 by the sandworm *Nereis* separately from contaminated sediments and from sea water. They assessed the relative importance of both these contaminant sources in the Mediterranean by applying their experimentally determined concentration factors to ambient PCB levels measured in both sediments (110 ng/g) and the overlying water (1.5 ng/ℓ). They concluded that 99% of the total uptake by sandworms in nature would be derived from sediments. However, it is not clear from this study whether PCBs were taken up directly from the sediment through contact with the cuticle, indirectly via the pore water, or through ingestion of sediment and subsequent absorption through the gut. It is likely that the sediment pore waters contain higher PCB levels than the overlying waters through the chemical partitioning process, because sediments have in general PCB concentrations at least three orders of magnitude higher than those in overlying water.[19] Goerke[29] has experimentally determined that the sandworm retains on average 79% of ingested PCBs so this avenue can be important especially if growth and metabolic activity are high. Halter and Johnson[21] exposed fathead minnows to PCB-contaminated sediment, with and without direct access to the sediment. Although the rate of PCB uptake was greater in fish allowed to contact the sediment, the chromatogram patterns in both groups of fish were similar, despite the presence of more highly chlorinated components in the sediments. These results implied that PCB uptake was essentially a two-step process, from sediment to water and then to fish. Lynch and Johnson[22] exposed freshwater amphipods directly and indirectly to PCB-contaminated sediment with very similar results; however, they found that *Gammarus* accumulated the least amount of PCB when exposed to the finest organic sediments; thus, organic content was more important in limiting desorption of PCBs from sediments than was particle size. Harding and Phillips[23] found that PCBs associated with natural particulates were rapidly transferred to several species of phytoplankton, with equilibria being reached in a matter of hours. They concluded that either a two-step process occurred, or that PCBs were transferred to diatoms during a transient association with the particulate matter. The important point is that a dynamic equilibrium was established rapidly between particulate material, phytoplankton, and sea water.

In conclusion, the reported values of PCBs in sea water overestimate what is truly dissolved, but these values may be realistic estimates of the contaminant pool available for uptake by larger planktonic and pelagic organisms. Organisms living in sediments are exposed to much higher PCB concentrations in their surroundings than are pelagic biota, but we cannot distinguish whether PCB uptake by benthic infauna is through direct contact with sediment, or through pore water. Organisms living close to the bottom are probably exposed to some level of contamination intermediate between that of the water column and of sediments.

The literature contains many descriptions of the accumulation of waterborne PCBs by aquatic organisms, but unfortunately the results are rarely intercomparable. The mathematical basis of first-order kinetic models was formulated many years ago for radionuclide research.[24,25] Only recently have investigators begun to use single compartment models to describe and predict the accumulation of organochlorines by aquatic organisms from their environment.[26-29] These models assume that the rates of uptake and clearance are proportional to the organochlorine concentration in sea water [W] and in or on the organism [Ø], thus:

$$\frac{d[Ø]}{dt} = k_u[W] - k_l[Ø]$$

where k_u and k_l are the rate constants onto and/or into, and out of, the organism, respectively.

MONS 005972

Both coefficients, as experimentally measured, incorporate a contaminant dilution factor which reflects growth of the organisms during the experimental exposure. We have already noted that the reported open ocean concentrations of PCBs have been consistently in the low nanogram per liter range during the past decade; thus, the assumption that sea water concentrations [W] are constant is justified. Many experimenters have shown independently that an exponential function best describes the clearance of organochlorines from aquatic organisms.[28,39,40,41] Both the basic assumptions in this model therefore appear to be reasonable.

In Table 1, we have compiled rate constants for organochlorine uptake and loss from various sources in the literature. We have included data pertaining to the DDT group of insecticides because of the limited data available for PCB dynamics in aquatic organisms. This is entirely justifiable, because of the close similarity of partition coefficients and bioconcentration factors among these organochlorines.[32-35] The most striking feature in this tabulation is the near constancy of the clearance rate coefficient, in spite of the range of compounds used and the other variables such as organism type and size and experimental conditions of temperature, salinity, and so forth. Even the route of uptake, either through ingestion of contaminated prey or direct uptake from water, appears not to be an important factor in governing the clearance rate constant. Laboratory studies show that clearance occurs mainly through excretion into the digestive tract, followed by elimination with fecal material in fish,[36] crustaceans,[37] and polychaetes.[38]

The values of the uptake rate constant range over three orders of magnitude (Table 1). In Ruzic's[28] formulation of the model, a surface-area term was used which is a prerequisite for describing the uptake of known hydrophobic substances. Harding and Vass[40] could not justify its use when modeling planktonic crustacea differing in surface area by an order of magnitude; however, the organisms listed in Table 1 represent a weight range of seven orders of magnitude. It is therefore worthwhile considering the extent of surfaces available for contaminant adsorption in the marine environment. Sheldon and his colleagues[39,60] have hypothesized that biomass is distributed equally between logarithmic size intervals in aquatic food webs:

$$[B] = a D^{-1},$$

where [B] is the concentration of particles in sea water (vol/vol), D is the equivalent spherical diameter of these particles, and a is a fitted constant. This hypothesis is applicable to organisms ranging in size from phytoplankton to commercial fish stocks.[61,62] The surface area present per unit volume of sea water [S] can also be expressed as a function of size:

$$[S] = bD^{-2},$$

where b is a proportionality constant. Organisms in motion are exposed to a continuously renewed supply of organochlorines. This point is important as organochlorines are believed to be adsorbed on contact. However, organisms ranging in size from zooplankton (where D is about 0.5 mm) to pelagic fish (where D = 100 mm) have been found to swim at speeds between 0.5 to 3.0 body lengths per second; the greater speeds occur during active foraging.[63,64] Thus, [S] per unit time is also proportional to D^{-2}, which means that the surface areas exposed per unit time of all pelagic fish weighing about 100 g would be about nine orders of magnitude less than that of all nannoplankters. Now, this difference is obviously overestimated because larger organisms have a greater surface area exposed than that assumed from a spherical shape primarily because of the convoluted respiratory surfaces. Respiratory surface is thought to be proportional to metabolic rate.[65,66] Metabolic rate is not directly proportional to weight,[54] and is described by the 3/4 allometric law

$$M \propto W^{0.75}$$

MONS 005973

Table 1

RATE CONSTANTS TAKEN OR DERIVED FROM LITERATURE FOR UPTAKE AND CLEARANCE OF PCBs AND DDT BETWEEN ORGANISMS AND THEIR ENVIRONMENT

Compound	k_1/day	k_2/day	Sources of OC	Temp (°C)	Species	Ref.
2,5-di CB	920	0.066[a]	Freshwater	23	Goldfish, *Carassius auratus*	42
2,2',5-tri CB	950	0.048				
2,4',5-tri CB	890	0.021				
2,3',5,5'-tetra CB	740	0.015				
2,3',4',5'-tetra CB	420	0.010				
Clophen® A30	—	0.018	Freshwater	21—23	Goldfish	43
Aroclor® 1254	510	0.017	Sea water	23—32	Spot, *Leiostomus xanthurus*	44
p,p'-DDT	1,147—1,206	0.024—0.026	Freshwater	19—23	Bluegill, *Lepomis macrochirus*	45
p,p'-DDT	—	0.015	Freshwater	18.5	Goldfish, *Carassius auratus*	46
		0.013			Bluegill, *Lepomis macrochirus*	
p,p'-DDT	—	0.004	Food	16	Rainbow trout, *Salmo gairdneri*	47
2,5,2',5'-tetra CB	—	0.008	Freshwater	11	Rainbow trout	48
2,5,2',5'-tetra CB	—	0.003	Freshwater	10—11	Rainbow trout eggs and sac fry	49
		0.047			Rainbow trout swimmeng fry	
2,2',4,4'-tetra CB	286	0.030	Freshwater	10—12	Rainbow trout muscle	38
p,p'-DDT	—	0.025	Pond	20	Mosquitofish, *Brevoortia tyrannus*	50
Phenoclor® DP-5	25	0.032	Sea water	17—19	Sandworm, *Nereis diversicolor*	28
2,2'-di CB	—	0.027	Pond	10	Sandworm, *Nereis virens*	41
2,4,6,2',4'-penta CB	—	0.010				
Aroclor® 1254	—	0.025	Sea water	24	Oyster, *Crassostrea virginica*	51
p,p'-DDT	7,600—12,100	0.043	Sea water	5—6	Euphausiid, *Thysanoessa raschi*	40
	10,400—25,100	0.048			Copepod, *Calanus finmarchicus*	

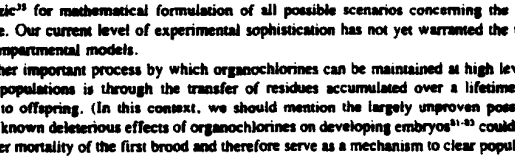
[a] Per fish.

MONS 005974

Thus, a 1-kg lobster, for example, has only about 5% of the weight-specific respiratory surface of a euphausiid weighing 10 mg. These considerations taken together, strongly suggest that direct adsorption from sea water must be a progressively less important route for the accumulation of organochlorines with increasing organism size. Marine mammals are a notable exception because their respiratory (adsorptive) surfaces do not come in direct contact with ambient sea water. The spherical model is the best approximation we have to predict organochlorine sorption through adsorptive surfaces until consistent techniques are developed to measure surface area directly.[65]

The importance of considering surface area available for adsorption on a unit-time basis is further illustrated by experimental studies which show that dead invertebrates and fish accumulate very low levels of organochlorines compared to their healthy counterparts.[67,68] Trout fry accumulated four times the concentration of tetrachlorobiphenyl than did sac fry, which in turn, accumulated seven times more than eggs;[69] these observations can be explained in terms of the greater surface area exposed by a swimming organism. Several studies have shown[33,66,70,71] that fish accumulate organochlorines at a faster rate at higher temperatures, within the normal thermal range of the species. In most cases, a doubling of contaminant levels in tissues is found with a 10°C rise in temperature. This corresponds to the "Q_{10}" law whereby a rise of 10°C doubles metabolic rates[72] and presumably, respiratory surface area exposed per unit time. Edgren et al.[71] found no measurable effect of temperature on organochlorine elimination, which corroborates the lack of variation found in the measured k_1 values (Table 1). Several authors[73,74] have shown that reduced salinity increases the uptake of organochlorines by fish from water. This too is probably related to the amount of water that comes in contact with body surfaces due to increased osmoregulatory activity. In general, then, the experimentally determined, organochlorine uptake rate-constants are a complex function of the exposed surface area; this explains why the measured k_1's are so variable between species and environmental conditions.

If we know little about the initial processes by which PCBs are taken up by marine biota, we know even less about how they are transported within the organism. It seems likely that organochlorines adsorbed to the external surfaces of marine organisms will partition into the hemolymph or blood plasma lipoproteins[75] and then would be transported to lipid-rich tissues, analogous to the experimental results following intravenous administration to invertebrates[76] and fish.[75,77-79] Several of these authors have reported blood plasma clearance curves of more than one phase, indicating the presence of more than one "compartment" in the organisms, clearing at different rates. Grzenda et al.[80] have shown in a thorough analysis that different tissues and organs in the goldfish have a different rate of DDT loss, but they could not prove this statistically.



See Ruzic[35] for mathematical formulation of all possible scenarios concerning the above structure. Our current level of experimental sophistication has not yet warranted the use of multicompartmental models.

Another important process by which organochlorines can be maintained at high levels in animal populations is through the transfer of residues accumulated over a lifetime from mother to offspring. (In this context, we should mention the largely unproven possibility that the known deleterious effects of organochlorines on developing embryos[81-83] could result in greater mortality of the first brood and therefore serve as a mechanism to clear populations

MONS 005975

of residues.) The documented high concentrations of PCBs and ΣDDT in the egg and developing embryos of starfish,[84] shrimp,[85] fish,[86-88] and marine mammals[89] are not surprising considering the affinity of these compounds for lipids. Butler and Schutzmann[90] present data which imply strongly that the female dogfish accumulates both ΣDDT and PCBs over an 18- to 20-year generation span, and then transfers these compounds to the ovarian egg and and mature fetus. Another illustration of this point is that whole body elimination of a PCB from experimentally exposed trout was more rapid in both sexes during the spawning season, and this appeared to be primarily due to the voiding of PCB-containing eggs and sperm. The great barracuda loses most of its abdominal fat during the development of gonads and is reported to lose most of its ΣDDT residues during the spawning period.[91] This internal redistribution of organochlorines has been observed experimentally in elevated organochlorine levels in eggs of both water-[92] and food-exposed[89] fish.

In a preliminary model the long-term importance of generation transfer of organochlorines was explored using the extensively studied marine copepod *Calanus*.[93] This work emphasizes the effect that increased generation length may have on the accumulation of organochlorines in animal populations. Slow developing populations in cooler climates are predicted to equilibrate at low bioconcentration levels over a longer period than tropical populations, which indirectly reflect differences in metabolic rate. Temperate populations with warm and cold water generations are also expected to equilibrate at different bioconcentration levels.

Organochlorines are also incorporated into organisms through feeding on contaminated food. A feeding term can be added to the kinetic model:

$$\frac{d[\emptyset]}{dt} = k_1[W] - k_2[\emptyset] + \alpha I_w[F]$$

where α is the organochlorine assimilation ratio from food, I_w is the weight-specific ingestion rate, and [F] is the concentration of organochlorine in the food.[42,93] This equation can be rewritten to span the maturation period from birth to adulthood, using the size dependency of ingestion rate as a function of time:

$$\frac{d[\emptyset]}{dt} = k_1[W] - k_2[\emptyset] + \alpha\beta t^{-\gamma}[F],$$

where t is time and β and γ are proportionality constants which depend on environmental temperature.[93] Several models have recently been described in the literature which use variations of this approach to simulate organochlorine residue dynamics in aquatic food webs.[94,95] In Table 2, we have collated all the best estimates of assimilation efficiencies of ingested PCBs and DDT by invertebrates and fish. These values are generally high and variable throughout the range of organisms and compounds studied. There appears to be no relationship between the amount of DDT or PCB retained and size of organism or trophic level. However, one study found that the assimilation of organochlorine decreases as food consumption increases.[93] When more than one level of contaminated food was offered to separate batches of experimental organisms, the results of different studies are conflicting with no clear overall relationship apparent between assimilation and the degree of contamination of food.[41,47,50,97,102,103] This result is to be expected unless the contaminant has a toxic effect on the organism at higher concentrations. In conclusion, it is not surprising that most of the modeling studies listed above have shown that food is the most important source of organochlorines to invertebrates and fish.

A lively controversy has persisted over the past decade about the relative importance of diet and direct uptake from water in the accumulation of organochlorines by aquatic organisms. Early field studies showed that organochlorine concentrations were greater at higher

MONS 005976

Table 2
THE ASSIMILATION (α) OF INGESTED ORGANOCHLORINES BY INVERTEBRATES AND FISH

Compound(s)	Species	Av. size	Experimental: Temp (°C)	Experimental: Duration	Food conc (ppm) wet wt	Ingestion rate	α %	Ref.
3,4,3',4'-tetra CB	Coho salmon	2.9 g	11—14	108 days	10	1 % bd. wt /day	56	96
2,4,5,2',4',5'-hexa CB	(*Oncorhynchus kisutch*)						55	
2,4,6,2',4',6'-hexa CB							55	
p,p'-DDT	Chinook salmon	3.2 g	10	65 days	6.2	—	56	97
	(*O. tshawytscha*)	2.5 g			25		19	
Tech. DDT	Coho salmon (*O. kisutch*)	6.5 g	10	39 days	6.2	—	48	
		5.5 g			25		46	
Aroclor® 1254	Rainbow trout	0.8 g	11—12	224 days	15	—	68	98
	(*Salmo gairdneri*)							
p,p'-DDT	Brook trout	15 cm	14	120 days	3	1.5% bd. wt/day	35	99
	(*Salvelinus fontinalis*)							
p,p'-DDT	Rainbow trout	15 g	16	168 days	0.2	2% bd. wt/day	20	47
	(*Salmo gairdneri*)				1.0		24	
p,p'-DDT	Lake trout	30 g	10	152 days	2.3	6% bd. wt/day	20	100
	(*Salvelinus namaycush*)							
Phenoclor® DP6	Grey mullets	56 g	—	30 days	50	—	71	101
	(*Chelon labrosus*)							
2,3-di CB	Goldfish	5 cm	23	150 days	10	1% bd. wt/day	56	42
2,2',3-tri CB	(*Crassius auratus*)						49	
2,4',3-tri CB							60	
2,2',3,3'-tetra CB							53	
2,3',4',5-tetra CB							48	
p,p'-DDT	Atlantic menhaden	64 mg	20	48 days	0.00058*	2—3% bd. wt/day	8—41	50
	(*Brevoorta tyrannus*)				0.009*		4—24	
					0.093*		8—26	
Clophen® A50,	Perch	12 g,	27	4 days	1.7	8% bd. wt/day	75	102
p,p'-DDT	(*Perca fluviatilis*)	17 g			0.1	3.5% bd. wt/day	80	
Aroclor® 1242	Crab	1—5 g	20	36 days	0.017	—	26	103
	(*Uca pugnax*)							

MONS 005977

2,5,4'-tri CB	Sandworm	5 g	10	21 days	~1.5	3% bd wt/day	58	41
2,2'-di CB	(*Nereis virens*)				~3		70	
2,4,6,2',4'-penta CB					~4		93	
p,p'-DDT	Krill	2—10 mg	10	24 hr	—	21—49 *Artemia*/day	62	HM
	(*Euphausia pacifica*)						76	
p,p'-DDT	Copepods	0.6 mg	1—6	24 hr	100—200	<200 cells/hr	66	93
	(*Calanus finmarchicus*)					>200 <600 cells/hr	32—94	
						1000 to 2000 cells/hr	7—33	

* Dry weight basis.

MONS 005978

trophic levels and these observations were used as evidence for "food chain magnification".[106,107] Population turnover times, however, are closely related to organism size,[29] thus, this apparent biological magnification at higher levels in the food chain could also be explained by increased exposure times to aqueous organochlorines. Experimental field studies in which organochlorines were added to a pond or marsh have shown either that fish continue to accumulate residues, presumably through ingestion, long after aqueous concentrations have declined below detection limits,[36,108] or conversely, that an equilibrium is reached before residue levels disappear from the water column.[109] Laboratory studies have shown that fish and crustaceans accumulate proportionally more organochlorines from water than from feeding when their prey was previously equilibrated to the same water concentrations.[110-112] However, when laboratory fish were exposed to water and to prey contaminated at levels similar to ambient levels in Lake Michigan, direct uptake from water was found to be of minor importance.[99,100] Similarly, analyses of laboratory feeding and water sorption studies with pelagic copepods,[93] euphausiids,[104] and benthic polychaetes[28] have all indicated that the "food" source of contamination is the more important.

These contradictory results can be explained if uptake from water is unrealistically high in laboratory studies. This is entirely possible, because organochlorines are either added with a surface-active carrier[113] or maintained at near-saturation levels by desorption from sands.[42,114] In either case, organochlorines are more biologically available for uptake by adsorptive surfaces than is the case in adventitiously contaminated systems, where organochlorines are present in low "solution" concentrations and are strongly associated with particles or micellar structures. Scura and Thielacker[115] tried to evaluate the relative importance of these routes by exposing a three-level food chain to organochlorines which had been prepared in a physical state similar to that in natural sea water by bubbling air through cleansed sea water. They interpreted their results as indicating direct partitioning of PCBs from sea water to all three levels of the food chain, but their measured values were so close to detection limits, particularly in sea water, that the problem remains unsolved.

It appears that we have gone from one extreme to the other in ascribing organochlorine contamination of marine organisms first to food chain transfer, and more recently to direct partitioning between sea water and the lipid pool of the biota. A growing number of papers demonstrate the usefulness of the octanol-water partition coefficient in predicting equilibrium concentrations of organochlorines in natural populations.[32,35,110,117] However, we feel that it is an oversight to ignore the laboratory studies which clearly show the importance of the "food" route in favor of the attractive simplicity of a partition model. The equilibrium concentrations observed in nature can be reached in a much shorter time through feeding[110] and may explain why some fish[119] and marine mammal[120] populations have higher organochlorine concentrations on a lipid weight basis than have lower links in the food web.

II. EFFECTS OF PCBs ON MARINE BIOTA

In this section, we consider the effects of PCBs on invertebrates, fish, and mammals. In many cases, marine organisms have not been studied specifically, and to draw an integrated picture of the effects of PCBs we have had to infer effects on marine biota from studies of terrestrial or freshwater biota. We have considered effects under the general topics of biochemical responses and whole organism effects, i.e., in terms of different levels of biological organization.

A. Biochemical Effects: Mixed Function Oxidase Induction

One of the most intensively studied effects of the PCBs is their induction of mixed function oxidase (MFO) enzymes. Since MFO induction in marine biota has been studied mainly from a comparative biochemical viewpoint, we introduce the subject with a description

MONS 005979

(probably oversimplified) of MFO systems in general; this information is derived mainly from studies on the laboratory rat.

The MFOs are a group of membrane-bound enzymes located in the endoplasmic reticulum. They are usually studied in, but are not exclusive to, liver and they sediment at about 100,000 × *g*. They require a characteristic electron transfer cytochrome P-450, oxygen and NADPH and they are inhibited by carbon monoxide. They catalyze various reactions which usually convert a lipophilic substrate to a more polar product; the substrates may be endogenous (such as steroid hormones) or exogenous (such as certain pollutants). The MFOs are inducible especially by some organic pollutants such as polynuclear aromatic hydrocarbons (PAHs), certain organochlorine compounds including PCBs, and barbiturate drugs; this has led to the conclusion that one of their roles may be to act as a kind of latent defense mechanism which remains at a low level under normal conditions but which springs into action when the organism is stressed by (among other chemicals) certain pollutants, including the PCBs. Until recently, MFO inducers and MFO systems could be classified into two groups: (1) those systems which were inducible by compounds such as phenobarbitone, which required cytochrome P-450 and which catalyzed a specific suite of reactions including aniline hydroxylation and aminopyrine demethylation, and (2) those systems which were inducible by PAHs, which required a modified cytochrome P-448 and which catalyzed a different series of reactions typified by benzpyrene hydroxylation. It now seems that this classification was an oversimplification, as some compounds, including some PCB components, function as "*mixed*" inducers and induce both types of MFO system. In any case, this description applies to the rat, and MFO systems in marine biota may differ.

The phyletic distribution of MFO systems in marine biota has attracted some interest. MFO systems appear to be present in phytoplankton[121] but is not clear that they are inducible by, e.g., biphenyl, which is a component of the simpler PCB mixtures.[122] (Biphenyl hydroxylase activity is present in tissues from various marine invertebrates,[123] but we do not know whether or not this is a MFO-catalyzed process.) Some invertebrates such as crustacea and polychaete worms[124] have MFO systems which share many of the characteristics of mammalian systems; these features include similar cytochrome P-450-carbon monoxide difference spectra, a requirement for oxygen, and localization of the system in the microsomal fraction. The only report of MFO induction by PCBs in invertebrates refers to the worm *Nereis*, and induction is indicated only by increases in cytochrome P-450 concentrations and not changes in enzyme activity.[124] In bivalves, whose MFO systems have been studied as possible monitors of the effects of organic pollutants (a biochemical "mussel watch") it now seems probable that MFOs are present only in certain tissues;[125] whether they are inducible or not remains to be seen.

The induction of MFO systems in fish by PCBs has been more intensively studied. Most information has come from studies on the trout because it is a convenient experimental animal, but the limited data from marine fish generally support those from trout studies. The characteristics of MFO systems in fish differ from those in the rat: cytochrome P-450 has different spectral binding features[126] and neither phenobarbitone[127] nor the insecticide *p,p'*-DDT[128] (which is a "phenobarbitone-type" inducer in the rat[129]) induce MFO systems in trout. Furthermore, some PCB components can be identified as either specifically P-450- or P-448-inducing compounds in the rat[130,131] but this classification does not hold for trout.[132] PCBs, however, induce MFO systems in several species of fish including trout,[133-135] carp,[136,137] catfish,[138,139] and marine species such as sheepshead.[140] MFO systems in other marine fish are induced by PAH[141-144] and since in trout both PAHs and PCBs induce MFOs rather similarly[132,145] it seems probable that PCBs would induce MFOs in the additional marine species. However, the details of MFO induction vary considerably from species to species: Aroclor® 1254 will induce a dramatic increase in ethoxycoumarin-*O*-de-ethylase in cod[146] but only a moderate increase in trout,[147] whereas it will not change ethoxyresorufin-*O*-de-

MONS 005980

ethylase activity in cod, but induces it dramatically in trout. In general, however, one consistent sublethal effect of the PCBs seems to be to induce various components of the MFO systems in fish.

There is no evidence that MFO systems are present or are inducible in marine mammals. However, since MFO systems are ubiquitous in the terrestrial mammals so far studied, it seems probable that they are also present in marine mammals. MFO systems have been reported in sea birds.[148]

Finally, although PCBs induce MFO systems in at least the higher aquatic organisms, the adaptive significance of this is not clear. For example, it has not yet been shown — even in the relatively intensively studied field of MFO induction by PAH components of petroleum oils — that MFO induction enhances the ability of the organism to degrade or excrete a foreign compound. We do not know whether MFO induction leads to disruption of the steroid hormone system (as we might expect from considerations of the natural role of MFO systems) although low levels of PCBs are reported[149] to disrupt the normal steroid hormone biochemistry of cod.

B. Biochemical Effects: ATPase Inhibition

The ATPases are a group of membrane-bound enzymes which contribute to ion transport across membranes.[150] They may therefore assist in osmoregulation and excretion. Following the observation[151] that rabbit brain ATPases were inhibited in vitro by organochlorine insecticides there have been several studies of the effects of related materials, including the PCBs, on these enzyme systems.

The addition of various PCB mixtures to ATPase preparations from sunfish (*Lepomis*) tissues in vitro resulted in an appreciable ATPase inhibition, especially by Aroclor® 1254 and generally in brain, liver, and kidney tissue.[152] Similar effects occur in ATPase preparations from rainbow trout.[153] In both studies, PCB concentrations in the tens of parts per million were required to produce an effect. However, attempts to reproduce these effects in the minnow (*Pimephales*) exposed for 4 months to aqueous concentrations in the parts per billion range of Aroclor® 1242 and 1254 yielded results not as clear as those from in vitro studies.[154] Although some inhibition of ATPase was described, especially in kidney tissue of fish exposed to Aroclor® 1242, no statistical analyses of the data were presented nor were any analyses of the putative target tissue for PCB residues reported. More recent studies have shown that feeding of PCBs to rats can cause inhibition of ATPases in brain, liver, and kidney.[155]

ATPases are inhibited by a wide variety of lipophilic products which may include pyrethroid insecticides,[156] chlorinated diphenyl ether derivatives,[157] phthalate esters,[158] toxaphene,[159] and mirex and kepone derivatives.[160,161] This implies that the inhibition of ATPases may be rather nonspecific, and Sharom and Mellors[162] have proposed that PCB inhibition of ATPases arises from a physical interaction between the toxicant and the phospholipid component which is required by the enzyme.[163] Most reports describing the effects of PCBs on ATPases have dealt with concentrations in the enzyme preparation of around 10^{-5} *M*; i.e., in the parts per million (w/w) range. It is at these concentrations that PCBs could act as a physical toxicant by interference with membrane lipid components.[162] Such concentrations are reported in some lipid storage tissues (e.g., depot fat) of adventitiously contaminated marine biota, though whether they are reached in the enzymatically active tissues remains to be established.

One possible result of inhibition of ATPase activity is interference with ion transport and a change (at the tissue or whole organism level) in osmolality or osmoregulatory capacity. In practice, this may be difficult to detect, because osmoregulation may not depend exclusively on ATPase activity. Many of the studies of this subject deal with the insecticide *p,p'*-DDT rather than with the PCBs, but since both materials probably act similarly, we shall discuss them together.

MONS 005981

Exposure of grass shrimp (*Palaemonetes pugio*) to PCBs at the parts per billion level in sea water did not affect chloride ion levels in hemolymph or chloride exchange kinetics, at least in adults, but juveniles showed some disruption of these features which might have been associated with acutely toxic effects.[164] Exposure to PCBs did not affect hemolymph free amino acid levels[165] which in this organism contribute to intracellular osmoregulation. *p,p'*-DDT at sub-parts per billion levels in water-reduced sodium and potassium levels in ashed hepatopancreas from a related penaeid shrimp.[166] Another genus of penaeid shrimp exposed to 3 ppb Aroclor® 1254 for 7 days and then exposed to salinity stress showed some response in hemolymph ions: at low salinity, total hemolymph cations were lower in treated shrimp than in controls but total hemolymph serum osmolality was not affected.[167] Taken together, the data suggest some interference of organochlorines, including PCBs, in ion transport, but this need not be reflected in tissue osmolality. It should be noted that although aqueous organochlorine concentrations in these studies were higher than those reported in "natural" circumstances, exposures were short and the tissue residue concentrations (where these have been reported) seem similar to those found in adventitiously contaminated samples.

ATPases of the rock crab (*Cancer irroratus*) were inhibited in vitro, and in vivo, following an injection of *p,p'*-DDT to yield hepatopancreas concentrations of about 1 ppm.[168] However, this crab is not an osmoregulator; even so, rather surprisingly, the possible effect of *p,p'*-DDT on serum osmolality was not described in this paper. In the blue crab *Callinectes sapidus*, which is a more effective osmoregulator, similar *p,p'*-DDT treatment produced a transient effect on serum osmolality after salinity stress, but 28 hr after transfer to low salinity water both ATPase and osmolality values had returned to levels similar to those in controls.[169] In other crabs, a similar general effect of organochlorines on ATPase activity, though not necessarily on hemolymph osmolality, has been observed.[170] The crab *Uca pugilator* exposed to Aroclor® 1254 and 1016 appeared not to be any more susceptible to salinity stress (in terms of acute lethality) than did unexposed animals; whether or not this crab osmoregulates is not specified.[171]

In fish, the impact of *p,p'*-DDT on ATPase inhibition is more clearly related to osmoregulatory effects. Marine teleosts drink continuously to replace water; intestinal mucosa and gill are both active in controlling ion transport. *p,p'*-DDT inhibits intestinal mucosal ATPase in *Fundulus heteroclitus* adapted to sea water and this is reflected in the increased (though variable) levels of plasma Na^+ and K^+; however, these increases resulted from a short and sharp exposure to *p,p'*-DDT.[172] Rainbow trout which had been fed *p,p'*-DDT showed reduced gill ATPase activity at three salinities, but in fresh water neither serum osmolality nor Na^+ was affected; at 33 and 100% sea water, both variables were significantly increased.[173]

Salmon injected with Aroclor® 1254 before smoltification showed no change in gill ATPase activity, even though appreciable concentrations (approximately 1 ppm) of PCB were deposited in the liver.[174] Since these analyses were carried out over a 6-week period, any transient effect due to sudden high concentrations of PCBs may not have been detected; alternatively, PCB concentrations in target tissues may have declined to the point where they were ineffective.

In summary, organochlorines in general, and PCBs in particular, affect ATPase activity, probably by acting as a physical toxicant. Although these effects may occur at environmentally realistic concentrations, ATPase inhibition may not be reflected in whole organism responses in lower biota, such as hemolymph osmolality changes; however, such transient changes may sometimes be detected in fish.

C. Miscellaneous Biochemical Effects

As well as inducing MFOs and inhibiting ATPases, PCBs have other biochemical effects which have been studied in less detail and which are more difficult to interpret.

MONS 005982

Relatively large doses of Aroclor® 1242 (8 ppm aqueous suspensions) reduced the dispersal of tissue melanophores[175] in the crab, *Uca pugilator*, through interference with eyestalk neurohormone release.[176] The net result was that the crabs became paler in appearance. PCBs may affect hormones in fish. Trout exposed to high dietary levels of Aroclor® 1254 showed no changes in serum thyroid hormone levels, although the organochlorine insecticide mirex induced such changes.[177] Cod (*Gadus morhua*) fed environmentally realistic doses of Aroclor® 1254 showed some disruption of steroid hormone biochemistry; the site of action of these effects was not identified, but it could presumably have been associated with MFO activity.[149]

The potential interaction of PCBs with lipid biochemistry has been reviewed;[178] in general, changes in lipid metabolism or in the fatty acid composition of lipids can be produced experimentally[179,180] though usually only with PCB doses far above those expected to be found in nature.

D. Whole Organism Responses to PCBs

The most commonly studied whole organism response has been death, in the form of measurements of acute toxicity (lethality). Acute toxicity data have been collated and reviewed elsewhere;[181,182] the main conclusions can be summarized as follows:

1. Acute toxicity varies considerably with the PCB preparation, with the species of organism tested, and with its age, sex, and condition
2. For what the generalizations are worth, acutely toxic concentrations (96 hr LC_{50}s) are usually in the microgram per liter range (parts per billion)
3. LC_{50}s in longer tests are usually lower than in short-term tests, which implies that PCBs are cumulative toxicants
4. For some species, especially marine invertebrates, the long term LC_{50}s may approach environmentally realistic concentrations (e.g., 0.01 μg/ℓ); however, adventitious PCBs may not be as available biologically as those deliberately introduced in toxicity tests

Despite the potential lethality of some environmentally realistic PCB concentrations to some species, there is no unequivocal evidence that biota from adventitiously contaminated environments have been killed by PCBs.

There is more convincing evidence that adventitious levels of PCBs in some biota may cause sublethal reproductive effects. In freshwater fish, high PCB concentrations are often associated with abnormal fry development[183] and there is a high correlation between PCB concentrations in salmon eggs and fry mortality. However, the structure of many marine ecosystems is so variable (for natural causes) that it is not clear whether similar effects induced by adventitious PCB levels could be reliably detected.

Minnows fed PCB-contaminated food showed an enhanced growth rate, possibly as a result of hormonal disturbances.[184]

Probably the best documented evidence for an effect of adventitious PCB concentrations comes from studies of marine mammal reproduction. Very high levels of both the DDT group of insecticides and of PCBs have been found in Californian sea lions[185,186] and premature births are associated with the higher levels; it is not possible to assign these effects to any specific organochlorine. The affected animals had blubber organochlorine concentrations in the 1000 ppm (wet weight) range. In ringed seals from the Baltic (Bothnian Bay), uterine occlusions which lead to resorption of the fetus are correlated with high DDT group and PCB levels;[187] pregnant females had lower residue levels than had females with uterine occlusions; normal nonpregnant females had levels similar to those with uterine occlusions. The residue concentration differences between animals with successful and unsuccessful pregnancies were relatively small (around 100 ppm) but were statistically significant. A

MONS 005983

more recent report[148] suggests that reproductive failure is becoming more frequent, but this report does not cite any organochlorine analyses to which these effects could be attributed. In related studies, Reijnders[149,150] has suggested that the higher juvenile mortality and lower pup production in Dutch than in Danish or North German harbor seals could be attributed to the higher PCB (but not higher DDT-group) levels in the former group. (High levels of PCBs occur in the Dutch seal population as a result of riverine input from the Rhine.) As in the Californian sea lions, PCB concentrations in the apparently affected group were around 700 ppm, whereas DDT group concentrations were about one tenth of that.

In short, there are suggestions that the adventitious levels of PCBs (possibly aggravated by those of the DDT group) may interfere with marine mammal reproduction. However, symptoms vary from place to place and this may indicate different modes of action.

REFERENCES

1. **Bidleman, T. F. and Olney, C. E.,** Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water, *Science*, 183, 516, 1974.
2. **Dawson, R. and Riley, J. P.,** Chlorine-containing pesticides and polychlorinated biphenyls in British coastal waters, *Estuarine Coast. Mar. Sci.*, 4, 55, 1977.
3. **Harvey, G. R., Steinhauer, W. G., and Miklas, H. P.,** Decline of PCB concentrations in North Atlantic surface water, *Nature (London)*, 252, 387, 1974.
4. **Osterroht, C.,** Dissolved PCB's and chlorinated hydrocarbon insecticides in the Baltic, determined by two different sampling procedures, *Mar. Chem.*, 5, 113, 1977.
5. **Sears, E. D. and McClure, V. E.,** Chlorinated hydrocarbons in sea water: analytical method and levels in the north eastern Pacific, *Mar. Chem.*, 3, 337, 1975.
6. **Stadler, D.,** Chlorinated hydrocarbons in the seawater of the German Bight and the western Baltic in 1975, *Dtsch. Hydrogr. Z.*, 30, 189, 1977.
7. **Tanabe, S. and Tatsukawa, R.,** Chlorinated hydrocarbons in the North Pacific and Indian Oceans, *J. Oceanogr. Soc. Jpn.*, 36, 217, 1980.
8. **Williams, P. M. and Robertson, K. J.,** Chlorinated hydrocarbons in sea-surface films and subsurface waters at nearshore stations and in the north central Pacific gyre, *Fish. Bull. (U.S.)*, 73, 445, 1975.
9. **Elder, D.,** PCBs in N.W. Mediterranean coastal waters, *Mar. Poll. Bull.*, 7, 63, 1976.
10. **Olsted, E. B., Lunde, G., and Drangsholt, H.,** Chlorinated organic compounds in the fatty surface film on water, *Int. J. Environ. Anal. Chem.*, 6, 119, 1979.
11. **Stadler, D. and Zielberth, U., *p,p'*-DDT, dieldrin und polychlorierte biphenyle (PCB) im oberflachenwasser der westlichen Ostsee 1974, *Dtsch. Hydrogr. Z.*, 29, 27, 1976.**
12. **Duce, R. A., Quinn, J. G., Olney, C. E., Piotrowicz, S. R., Ray, B. J., and Wade, T. L.,** Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island, *Science*, 176, 161, 1972.
13. **Duke, T. W., Lowe, J. I., and Wilson, A. J., Jr.,** A polychlorinated biphenyl (Aroclor 1254®) in the water, sediment, and biota of Escambia Bay, Florida, *Bull. Environ. Contam. Toxicol.*, 5, 171, 1970.
14. **Hirakimoni, Y., Maeshe, T., Takahashi, M., Nishida, K., Job, H., and Nishimura, H.,** Analysis of PCB contamination of sediment in coastal waters of the Seto inland sea, *La mer*, 13, 163, 1975.
15. **Dexter, R. N. and Pavlou, S. P.,** Mass solubility and aqueous activity coefficients of stable organic chemicals in the marine environment: polychlorinated biphenyls, *Mar. Chem.*, 6, 41, 1978.
16. **Mackay, D., Mascarenhas, R., Shiu, W. Y., Valvani, S. C., and Yalkowsky, S. H.,** Aqueous solubility of polychlorinated biphenyls, *Chemosphere*, 9, 257, 1980.
17. **Wiese, C. S. and Griffin, D. A.,** The solubility of Aroclor 1254 in sea-water, *Bull. Environ. Contam Toxicol.*, 19, 403, 1978.
18. **Murray, H. E., Ray, L. E., and Glam, C. S.,** Analysis of marine sediment, water and biota for selected organic pollutants, *Chemosphere*, 10, 1327, 1981.
19. **Haque, R. and Schmedding, D.,** Studies on the adsorption of selected PCB isomers on several surfaces, *J. Environ. Sci. Health*, B11, 129, 1976.
20. **Hirakimoni, Y., Takahashi, M., and Nishimura, H.,** Adsorption of PCB onto sea bed sediment, marine plankton, and other adsorbing agents, *Environ. Sci. Technol.*, 13, 580, 1979.
21. **Cox, J. L.,** DDT residues in seawater and particulate matter in the California current system, *Fish. Bull. (U.S.)*, 69, 445, 1971.

MONS 005984

22. **Boehm, P. D. and Quinn, J. G.**, Solubilization of hydrocarbons by the dissolved organic matter in sea water. *Geochim. Cosmochim. Acta*, 37, 2459, 1973.
23. **Poirrer, M. A., Bordeton, B. R., and Laseter, J. L.**, Adsorption and concentration of dissolved carbon-14 DDT by coloring colloids in surface waters. *Environ. Sci. Technol.*, 6, 1033, 1972.
24. **Worshaw, R. L., Bureau, P. J., and Goldberg, M. C.**, Interactions of pesticides with organic material. *Environ. Sci. Technol.*, 3, 271, 1969.
25. **Strickland, J. D. and Parsons, T. R.**, *A Practical Handbook of Sea Water Analysis*, Bull. No. 167, Fisheries Research Board of Canada, Ottawa, 1972.
26. **Shea, P. J., Strek, H. J., and Weber, J. B.**, Polychlorinated biphenyls: absorption and bioaccumulation by goldfish (*Carassius auratus*) and inactivation by activated carbon. *Chemosphere*, 9, 157, 1980.
27. **Bedford, J. W.**, The use of polyurethane foam plugs for extraction of PCB's from natural waters. *Bull Environ. Contam. Toxicol.*, 12, 622, 1974.
28. **Fowler, S. W., Polikarpov, G. G., Elder, D. L., Parsi, P., and Villeneuve, J.-P.**, Polychlorinated biphenyls: accumulation from contaminated sediments and water by the polychaete *Nereis diversicolor*. *Mar. Biol.*, 48, 303, 1978.
29. **Addison, R. F.**, *A Review of Organochlorines with Respect to the Ocean Dumping Control Act*, Ocean Dumping Report 3, Department of Fisheries and Oceans, Ottawa, 1980, 13.
30. **Goerke, H.**, *Nereis virens* (Polychaeta) in marine pollution research: culture methods and oral administration of a polychlorinated biphenyl, *Veroff. Inst. Meeresforsch. Bremerhaven*, 17, 151, 1979
31. **Halter, M. T. and Johnson, H. E.**, A model system to study the desorption and biological availability of PCB in hydrosols, in *Aquatic Toxicology and Hazard Evaluation*, Mayer, F. L. and Hamelink, J. L., Eds., American Society for Testing and Materials, Philadelphia, 1977, 178.
32. **Lynch, T. R. and Johnson, H. E.**, Availability of hexachlorobiphenyl isomer to benthic amphipods from experimentally contaminated natural sediments. *Aquatic Toxicology and Hazard Assessment*, Pearson, J. G., Foster, R. B., and Bishop, W. E., Eds., American Society for Testing and Materials, Philadelphia, 1982, 273.
33. **Harding, L. W., Jr. and Phillips, J. H., Jr.**, Polychlorinated biphenyls: transfer from microparticulates to marine phytoplankton and the effects on photosynthesis, *Science*, 202, 1189, 1978.
34. **Sheppard, C. W.**, *Basic Principles of the Tracer Method*, John Wiley & Sons, New York, 1962, 282.
35. **Ruele, I.**, Two-compartment model of radionuclide accumulation into marine organisms. I. Accumulation from a medium of constant activity, *Mar. Biol.*, 15, 105, 1972.
36. **Eberhardt, L. L., Meeks, R. L., and Peterle, T. J.**, Food chain model of DDT kinetics in a freshwater marsh, *Nature (London)*, 230, 60, 1971.
37. **Sodergren, A. and Svensson, B. J.**, Uptake and accumulation of DDT and PCB by *Ephemera danica* (Ephemeroptera) in continuous-flow systems, *Bull. Environ. Contam. Toxicol.*, 9, 345, 1973.
38. **Branson, D. R., Blau, G. E., Alexander, H. C., and Neely, W. B.**, Bioconcentration of 2,2',4,4'-tetrachlorobiphenyl in rainbow trout as measured by an accelerated test, *Trans. Am. Fish. Soc.*, 104, 785, 1975.
39. **Harding, G. C. H. and Vass, W. P.**, Uptake from seawater and clearance of ^{14}C-*p,p'*-DDT by the marine copepod *Calanus finmarchicus*, *J. Fish. Res. Board Can.*, 34, 177, 1977.
40. **Harding, G. C. H. and Vass, W. P.**, Uptake from seawater and clearance of *p,p'*-DDT by marine planktonic crustacea, *J. Fish. Res. Board Can.*, 36, 247, 1979.
41. **Goerke, H. and Ernst, W.**, Fate of ^{14}C-labelled di-, tri-, and pentachlorobiphenyl in the marine annelid *Nereis virens*. I. Accumulation and elimination after oral administration, *Chemosphere*, 9, 551, 1977.
42. **Bruggeman, W. A., Martron, L. B. J. M., Kaslander, D., and Hutzinger, O.**, Accumulation and elimination kinetics of di-, tri-, and tetrachlorobiphenyls by goldfish after dietary and aqueous exposure, *Chemosphere*, 10, 811, 1981.
43. **Hattula, M. L. and Karlog, O.**, Absorption and elimination of polychlorinated biphenyls (PCB) in goldfish, *Acta Pharmacol. Toxicol.*, 32, 237, 1973.
44. **Hansen, D. J., Parrish, P. R., Lowe, J. I., Wilson, A. J., Jr., and Wilson, P. D.**, Chronic toxicity, uptake, and retention of Aroclor 1254 in two estuarine fishes, *Bull. Environ. Contam. Toxicol.*, 6, 113, 1971.
45. **Bishop, W. E. and Maki, A. W.**, A critical comparison of two bioconcentration test methods, in *Aquatic Toxicology*, Eaton, J. G., Parrish, P. R., and Hendricks, A. C., Eds., American Society for Testing and Materials, Philadelphia, 1980, 61.
46. **Gakstatter, J. H. and Weiss, C. M.**, The elimination of DDT-C^{14}, dieldrin-C^{14}, and lindane-C^{14} from fish following a single sublethal exposure in aquaria, *Trans. Am. Fish. Soc.*, 96, 301, 1967.
47. **Macek, K. J., Rodgers, C. R., Stalling, D. L., and Korn, S.**, The uptake, distribution and elimination of dietary ^{14}C-DDT and ^{14}C-dieldrin in rainbow trout, *Trans. Am. Fish. Soc.*, 99, 689, 1970.
48. **Guiney, P. D., Petersen, R. E., Melancon, M. J., Jr., and Lech, J. J.**, The distribution and elimination of 2,5,2',5'-[^{14}C] tetrachlorobiphenyl in rainbow trout (*Salmo gairdneri*), *Toxicol. Appl. Pharmacol.*, 39, 329, 1977.

MONS 005985

49 **Guiney, P. D., Lech, J. J., and Peterson, R. E.,** Distribution and elimination of a polychlorinated biphenyl during early life stages of rainbow trout (*Salmo gairdneri*), *Toxicol. Appl. Pharmacol.*, 53, 521, 1980.

50 **Warlen, S. M., Wolfe, D. A., Lewis, C. W., and Colby, D. R.,** Accumulation and retention of dietary ^{14}C-DDT by Atlantic menhaden, *Trans. Am. Fish. Soc.*, 106, 95, 1977.

51 **Lowe, J. I., Parrish, P. R., Patrick, J. M., Jr., and Forester, J.,** Effects of the polychlorinated biphenyl Aroclor 1254 on the American oyster *Crassostrea virginica*, *Mar. Biol.*, 17, 209, 1972.

52 **Chiou, C. T., Freed, V. H., Schmedding, D. W., and Kohnert, R. L.,** Partition coefficient and bioaccumulation of selected organic chemicals, *Environ. Sci. Technol.*, 11, 475, 1977.

53 **Veith, G. D., Defoe, D. L., and Bergstedt, B. V.,** Measuring and estimating the bioconcentration factor of chemicals in fish, *J. Fish. Res. Bd. Can.*, 36, 1040, 1979.

54 **Konaga, E. E. and Goring, C. A. I.,** Relationship between water solubility, soil sorption, octanol-water partitioning, and concentration of chemicals in biota, in *Aquatic Toxicology*, Eaton, J. G., Parrish, P. R., and Hendricks, A. C., Eds., American Society for Testing and Materials, Philadelphia, 1980, 78.

55 **Mackay, D.,** Correlation of bioconcentration factors, *Environ. Sci. Technol.*, 16, 274, 1982.

56 **Melancon, M. J., Jr. and Lech, J. J.,** Isolation and identification of a polar metabolite of tetrachlorobiphenyl from bile of rainbow trout exposed to ^{14}C-tetrachlorobiphenyl, *Bull. Environ. Contam. Toxicol.*, 15, 181, 1976.

57 **Bend, J. R., Hart, L. G., Guarino, A. M., Ball, D. F., and Fouts, J. R.,** Distribution and excretion of [^{14}C]-2,4,5,2',5'-pentachlorobiphenyl in the lobster (*Homarus americanus*) and the dogfish shark (*Squalus acanthias*), in *Proc. Natl. Conf. on Polychlorinated Biphenyls*, U.S. Environmental Protection Agency, Washington, D.C., 1976, 292.

58 **Ernst, W., Geerke, H., and Weber, K.,** Fate of ^{14}C-labelled di-, tri-, and pentachlorobiphenyl in the marine annelid *Nereis virens*. II. Degradation and faecal elimination, *Chemosphere*, 9, 559, 1977.

59 **Sheldon, R. W., Prakash, A., and Sutcliffe, W. H., Jr.,** The size distribution of particles in the ocean, *Limnol. Oceanogr.*, 17, 327, 1972.

60 **Sheldon, R. W., Sutcliffe, W. H., Jr., and Prakash, A.,** The production of particles in the surface waters of the ocean with particular reference to the Sargasso Sea, *Limnol. Oceanogr.*, 18, 719, 1973.

61 **Sheldon, R. W., Sutcliffe, W. H., Jr., and Paranjape, M. A.,** Structure of pelagic food chain and relationship between plankton and fish production, *J. Fish. Res. Bd. Can.*, 34, 2344, 1977.

62 **Sheldon, R. W., Sutcliffe, W. H., Jr., and Drinkwater, K.,** Fish production in multispecies fisheries, *Can. Spec. Publ. Fish. Aquat. Sci.*, 59, 28, 1982.

63 **Hardy, A. C. and Bainbridge, R.,** Experimental observations on the vertical migrations of plankton animals, *J. Mar. Biol. Assoc. U.K.*, 33, 409, 1954.

64 **Ware, D. M.,** Bioenergetics of pelagic fish: theoretical change in swimming speed and ration with body size, *J. Fish. Res. Bd. Can.*, 35, 220, 1978.

65 **Harding, G. C. H.,** Surface area of the euphausiid *Thysanoessa raschii* and its relation to body length, weight, and respiration, *J. Fish. Res. Bd. Can.*, 34, 225, 1977.

66 **Hemmingsen, A. M.,** Energy metabolism as related to body size and respiratory surfaces, and its evolution, *Rep. Steno. Mem. Hosp. Nord. Insulin Lab.*, 9, 1, 1960.

67 **Whitish, D. J. and Zitko, V.,** Uptake of polychlorinated biphenyls from sea water by *Gammarus oceanicus*, *Mar. Biol.*, 9, 213, 1971.

68 **Murphy, P. G. and Murphy, J. V.,** Correlations between respiration and direct uptake of DDT in the mosquito fish, *Gambusia affinis*, *Bull. Environ. Contam. Toxicol.*, 6, 381, 1971.

69 **Broyles, R. H. and Noveck, M. I.,** Uptake and distribution of 2,5,2',5'-tetrachlorobiphenyl in developing lake trout, *Toxicol. Appl. Pharmacol.*, 50, 291, 1979.

70 **Reinert, R. E., Stone, L. J., and Willford, W. A.,** Effect of temperature on accumulation of methylmercuric chloride and *p,p'*-DDT by rainbow trout (*Salmo gairdneri*), *J. Fish. Res. Bd. Can.*, 31, 1649, 1974.

71 **Edgren, M., Olsson, M., and Romberg, L.,** Preliminary results on uptake and elimination at different temperatures of *p,p'*-DDT and two chlorobiphenyls in perch from brackish water, *Ambio*, 8, 270, 1979.

72 **Prosser, C. L.,** *Comparative Animal Physiology* 3rd ed., W.B. Saunders, Philadelphia, 1973.

73 **Murphy, P. G.,** Effects of salinity on uptake of DDT, DDE and DDD by fish, *Bull. Environ. Contam. Toxicol.*, 5, 404, 1970.

74 **Tulp, M. T. M., Hoya, K., Carson, W. G., Zitko, V., and Hutzinger, O.,** Effect of salinity on uptake of ^{14}C-2,2',4,5,5'-pentachlorobiphenyl by juvenile Atlantic salmon, *Chemosphere*, 4, 243, 1979.

75 **Dvorchik, B. H. and Maren, T. H.,** Distribution, metabolism, elimination and toxicity of ^{14}C-DDT in the dogfish, *Squalus acanthias*, *Comp. Gen. Pharmacol.*, 5, 37, 1974.

76 **Guarino, A. M., Pritchard, J. B., Anderson, J. B., and Ball, D. F.,** Tissue distribution of [^{14}C] DDT in the lobster after administration via intravascular or oral routes or after exposure from ambient sea water, *Toxicol. Appl. Pharmacol.*, 29, 277, 1974.

MONS 005986

77. **Pritchard, J. B., Guarino, A. M., and Kinter, W. B.,** Distribution, metabolism and excretion of DDT and mirex by a marine teleost, the winter flounder, *Environ. Health Perspect.*, 2, 45, 1973.
78. **Zinck, M. E. and Addison, R. F.,** The fate of 2-, 3-, and 4-chlorobiphenyl following intravenous administration to the thorny skate (*Raja radiata*) and the winter skate, (*Raja ocellata*), *Arch. Environ. Contam. Toxicol.*, 2, 52, 1974.
79. **Derrow, D. C. and Addison, R. F.,** The metabolic clearance of ^{14}C-*p,p'*-DDT from plasma and its distribution in the thorny skate, *Raja radiata*, *Environ. Physiol. Biochem.*, 3, 196, 1973.
80. **Grasenda, A. R., Paris, D. F., and Taylor, W. J.,** The uptake, metabolism and elimination of chlorinated residues by goldfish (*Crassius auratus*) fed a ^{14}C-DDT contaminated diet, *Trans. Am. Fish. Soc.*, 99, 385, 1970.
81. **Halter, M. T. and Johnson, H. E.,** Acute toxicities of polychlorinated biphenyl (PCB) and DDT alone and in combination to early life stages of coho salmon (*Oncorhynchus kisutch*), *J. Fish. Res. Bd. Can.*, 31, 1543, 1974.
82. **Dethlefsen, V.,** The influence of DDT and DDE on the embryogenesis and the mortality of larvae of cod (*Gadus morhua* L.), *Meeresforschung*, 25, 115, 1976/1977.
83. **Mauck, W. L., Mehrle, P. M., and Mayer, F. L.,** Effects of PCB Aroclor 1254 on growth, survival and bone development in brook trout *Salvelinus fontinalis*, *J. Fish. Res. Bd. Can.*, 35, 1084, 1978.
84. **McCloskey, L. R. and Doubert, K. H.,** Polychlorinated biphenyls in the seastar *Acanthaster planci*, *Bull. Environ. Contam. Toxicol.*, 10, 261, 1973.
85. **Edor, G., Schaefer, R. G., Ernst, W., and Goerke, H.,** Chlorinated hydrocarbons in animals of the Skagerrak, *Veroff. Inst. Meeresforschung Bremerhaven*, 16, 1, 1976.
86. **Van den Broek, W. L. F.,** Seasonal levels of chlorinated hydrocarbons and heavy metals in fish and brown shrimps from the Medway estuary, *Kent. Environ. Pollut.*, 19, 21, 1979.
87. **Cubit, D. A., Deichmann, W. B., and MacDonald, W. E.,** Determination of organochlorine pesticides in the tissues of the black mullet (*Mugil cephalus*) and the silver mullet (*Mugil curema*), *Am. Ind. Hyg. Assoc. J.*, 37, 8, 1976.
88. **Jessop, B. M. and Vikhayasai, C.,** Creel surveys and biological studies of the striped-bass fisheries of the Shubenacadie, Gaspereau and Annapolis Rivers, 1976, *Fish. Mar. Serv. Manuscript. Rep.*, No 1532, Department of Fisheries and Oceans, Ottawa, Canada, 1979.
89. **Tanabe, S., Tatsukawa, R., Maruyama, K., and Mitanakai, N.,** Transplacental transfer of PCBs and CH pesticides from the pregnant striped dolphin (*Stenella coeruleoalba*) to her fetus, *Agric. Biol. Chem.*, 46, 1249, 1982.
90. **Butler, P. A. and Schutzmann, R. L.,** Bioaccumulation of DDT and PCB in tissues of marine fishes, in *Aquatic Toxicology*, Marking, L. L. and Kimerle, R. A., Eds., American Society for Testing and Materials, Philadelphia, 1979, 212.
91. **Guiney, P. D, Melancon, M. J., Jr., Lech, J. J., and Peterson, R. E.,** Effects of egg and sperm maturation and spawning on the distribution and elimination of a polychlorinated biphenyl in rainbow trout (*Salmo gairdneri*), *Toxicol. Appl. Pharmacol.*, 47, 261, 1979.
92. **Smith, R. M. and Cole, C. F.,** Effects of egg concentrations of DDT and dieldrin on development in winter flounder (*Pseudopleuronectes americanus*), *J. Fish. Res. Bd. Can.*, 30, 1894, 1973.
93. **Harding, G. C., Vass, W. P., and Drinkwater, K. F.,** Importance of feeding, direct uptake from sea water and transfer from generation to generation in the accumulation of an organochlorine (*p,p'*-DDT) by the marine planktonic copepod *Calanus finmarchicus*, *Can. J. Fish. Aquat. Sci.*, 38, 101, 1981.
94. **Norstrom, R. J., McKinnon, A. E., and de Freitas, A. S. W.,** A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa River yellow perch (*Perca flavescens*), *J. Fish. Res. Bd. Can.*, 33, 248, 1976.
95. **Thomann, R. V.,** Equilibrium model of fate of microcontaminants in diverse aquatic food chains, *Can. J. Fish. Aquat. Sci.*, 38, 280, 1981.
96. **Gruger, E. H., Jr., Kerrick, N. L., Davidson, A. I., and Hruby, T.,** Accumulation of 3,4,3',4'-tetrachlorobiphenyl and 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl in juvenile coho salmon, *Environ. Sci. Technol.*, 9, 121, 1975.
97. **Bohlen, D. R., Rasmussen, M. E., and Shanks, W. E.,** Chronic oral DDT toxicity in juvenile coho and chinook salmon, *Toxicol. Appl. Pharmacol.*, 14, 535, 1969.
98. **Lieb, A. J., Bills, D. D., and Stanbacher, R. O.,** Accumulation of dietary polychlorinated biphenyls (Aroclor 1254) by rainbow trout (*Salmo gairdneri*), *Agric. Food Chem.*, 22, 638, 1974.
99. **Mauck, K. J. and Kaya, S.,** Significance of the food chain in DDT accumulation by fish, *J. Fish. Res. Bd. Can.*, 27, 1496, 1970.
100. **Reinert, R. E., Stone, L. J., and Bergman, H. L.,** Dieldrin and DDT: accumulation from water and food by lake trout (*Salvelinus namaycush*) in the laboratory, *Proc. 17th Conf. Great Lakes Res.*, International Association Great Lakes Research, Ann Arbor, Mich., 1974.
101. **Narbonne, J. F.,** Accumulation of polychlorinated biphenyl (Phenoclor DP6) by estuarine fish, *Bull. Environ. Contam. Toxicol.*, 22, 60, 1979.

MONS 005987

102. **Sodergren, A.**, Transport, distribution and degradation of chlorinated hydrocarbon residues in aquatic model ecosystems. *Oikos*, 24, 30, 1973.
103. **Marinucci, A. C. and Bartha, R.**, Accumulation of the PCB Aroclor 1242 from contaminated detritus and water by the salt marsh detritivore, *Uca pugnax*. *Bull. Environ. Contam. Toxicol.*, 29, 326, 1982.
104. **Cox, J. L.**, Uptake, assimilation and loss of DDT residues by *Euphausia pacifica*, a euphausiid shrimp. *Fish. Bull. (U.S.)*, 69, 627, 1971.
105. **McLeese, D. W., Metcalfe, C. D., and Pezzack, D. S.**, Bioaccumulation of chlorobiphenyls and endrin from food by lobsters (*Homarus americanus*). *Bull. Environ. Contam. Toxicol.*, 25, 161, 1980.
106. **Hunt, E. G. and Bischoff, A. I.**, Inimical effects on wild life of periodic DDD applications to Clear Lake. *Calif. Fish Game*, 46, 91, 1960.
107. **Woodwell, G. M., Wurster, C. F., Jr., and Isaacson, P. A.**, DDT residues in an east coast estuary: a case of biological concentration of a persistent pesticide. *Science*, 156, 821, 1967.
108. **Bridges, W. R., Kallman, B. J., and Andrews, A. K.**, Persistence of DDT and its metabolites in a farm pond. *Trans. Am. Fish. Soc.*, 92, 421, 1963.
109. **Hamelink, J. L. and Waybrant, R. C.**, DDE and lindane in a large-scale model lentic ecosystem. *Trans Am. Fish. Soc.*, 105, 124, 1976.
110. **Chadwick, G. G. and Brocksen, R. W.**, Accumulation of dieldrin by fish and selected fish food organisms. *J. Wild. Manage.*, 33, 693, 1969.
111. **Reinert, R. E.**, Accumulation of dieldrin in an alga (*Scenedesmus obliquus*), *Daphnia magna*, and the guppy, (*Poecilia reticulata*). *J. Fish. Res. Bd. Can.*, 29, 1413, 1972.
112. **Jarvinen, A. W., Hoffman, M. J., and Thorslund, T. W.**, Long term toxic effects of DDT food and water exposure on fathead minnows (*Pimephales promelas*). *J. Fish. Res. Bd. Can.*, 34, 2089, 1977.
113. **Mac, M. J. and Seelye, J. G.**, Potential influence of acetone in aquatic bioassays testing the dynamics and effects of PCBs. *Bull. Environ. Contam. Toxicol.*, 27, 359, 1981.
114. **Veith, G. D. and Comstock, V. M.**, Apparatus for continuously saturating water with hydrophobic organic chemicals. *J. Fish. Res. Bd. Can.*, 32, 1849, 1975.
115. **Sears, E. D. and Thielecker, G. H.**, Transfer of the chlorinated hydrocarbon PCB in a laboratory marine food chain. *Mar. Biol.*, 40, 317, 1977.
116. **Kanazawa, J.**, Bioconcentration potential of pesticides by aquatic organisms. *Jpn. Pest. Inform.*, 39, 12, 1981.
117. **Neely, W. B., Branson, D. R., and Blau, G. E.**, Partition coefficient to measure bioconcentration potential of organic chemicals in fish. *Environ. Sci. Technol.*, 8, 1113, 1974.
118. **Wyman, K. D. and O'Connors, H. B., Jr.**, Implications of short-term PCB uptake by small estuarine copepods (Genus *Acartia*) from PCB-contaminated water, inorganic sediments and phytoplankton. *Estuarine Coast. Mar. Sci.*, 11, 121, 1980.
119. **Goerke, H., Eder, G., Weber, K., and Ernst, W.**, Patterns of organochlorine residues in animals of different trophic levels from the Weser estuary. *Mar. Pollut. Bull.*, 10, 127, 1979.
120. **Risebrough, R. W., Walker, W., II, Schmidt, T. T., de Lappe, B. W., and Connors, C. W.**, Transfer of chlorinated biphenyls to Antarctica. *Nature (London)*, 264, 738, 1976.
121. **Dubay, D. J. and Menzies, R. A.**, Evidence for a cytochrome-P-450 mixed function oxidase system in algae. *Fed. Proc.*, 41, 1298, 1982.
122. **Willis, D. E. and Addison, R. F.**, Identification and estimation of the major components of a commercial polychlorinated biphenyl mixture, Aroclor 1221. *J. Fish Res. Bd. Can.*, 29, 592, 1972.
123. **Willis, D. E. and Addison, R. F.**, Hydroxylation of biphenyl *in vitro* by tissue preparations of some marine organisms. *Comp. Gen. Pharmacol.*, 5, 77, 1974.
124. **Lee, R. F.**, Mixed function oxygenases (MFO) in marine invertebrates. *Mar. Biol. Lett.*, 2, 87, 1981.
125. **Moore, M. N., Livingstone, D. R., Donkin, P., Bayne, B. L., Widdows, J., and Lowe, D. M.**, Mixed function oxygenases and xenobiotic detoxication/toxication systems in bivalve molluscs. *Helgoland. Meeresunters.*, 33, 278, 1980.
126. **Ahokas, J. T., Pulkonen, O., and Kaarki, N. J.**, Cytochrome P-450 and drug-induced spectral interactions in the hepatic microsomes of trout. *Salmo trutta lacustris*. *Acta Pharmacol. Toxicol.*, 38, 440, 1976.
127. **Solbwen, R. J. and Mannering, G. J.**, Hepatic cytochrome P-450-dependent monooxygenase systems of the trout, frog and snake. III. Induction. *Comp. Biochem. Physiol.*, 71B, 645, 1982.
128. **Addison, R. F., Zinck, M. E., and Willis, D. E.**, Mixed function oxidases in trout (*Salvelinus fontinalis*) liver: absence of induction following feeding of *p,p'*-DDT or *p,p'*-DDE. *Comp. Biochem. Physiol.*, 57C, 39, 1977.
129. **Bichara, D. R., Kappas, A., and Alvarez, A. P.**, Differences in inducibility of cutaneous and hepatic drug metabolizing enzymes and cytochrome P-450 by polychlorinated biphenyls and 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethane (DDT). *J. Pharmacol. Exp. Ther.*, 188, 300, 1974.
130. **Poland, A. and Glover, E.**, Chlorinated biphenyl induction of aryl hydrocarbon hydroxylase activity: a study of the structure-activity relationship. *Mol. Pharmacol.*, 13, 924, 1977.

MONS 005988

131 **Goldstein, J. A.**, The structure-activity relationships of halogenated biphenyls as enzyme inducers. *Ann N.Y. Acad. Sci.*, 320, 164, 1979.

132. **Franklin, R. B., Elcombe, C. R., Vodicnik, M. J., and Lech, J. J.**, Comparative aspects of hepatic monooxygenase induction in rat and rainbow trout by several PCB isomers, in *Microsomes, Drug Oxidations and Chemical Carcinogenesis*, Vol. 2, Coon, M. J., Ed., Academic Press, New York, 1980, 833.

133. **Addison, R. F., Zinck, M. E., and Willis, D. E.**, Induction of hepatic mixed function oxidase (MFO) enzymes in trout (*Salvelinus fontinalis*) by feeding Aroclor® 1254 or 3-methylcholanthrene, *Comp. Biochem. Physiol.*, 61C, 323, 1978.

134. **Fortin, L. and Lidman, U.**, Effects of Clophen A50 and 3-methylcholanthrene on the hepatic mixed function oxidase system in female rainbow trout, *Salmo gairdneri*, *Comp. Biochem. Physiol.*, 70C, 297, 1981.

135. **Elcombe, C. R. and Lech, J. J.**, Induction of monooxygenation in rainbow trout by polybrominated biphenyls: a comparative study, *Environ. Health Perspect.*, 23, 309, 1978.

136. **Ito, Y. and Murata, M.**, Studies on the influence of polychlorinated biphenyls (PCB) on aquatic organisms VIII. Influence of PCB on drug metabolising enzyme system in carp, *Eisei Kagaku*, 26, 21, 1980.

137. **Melancon, M., Elcombe, C. J., Vodicnik, M. J., and Lech, J. J.**, Induction of cytochromes P-450 and mixed function oxidase activity by polychlorinated biphenyls and β-naphthoflavone in carp, (*Cyprinus carpio*), *Comp. Biochem. Physiol.*, 69C, 219, 1981.

138. **Hill, D. W., Hejtmancik, E., and Camp, B. J.**, Induction of hepatic microsomal enzymes by Aroclor® 1254 in *Ictalurus punctatus* (channel catfish), *Bull. Environ. Contam. Toxicol.*, 16, 495, 1976.

139. **Lipsky, M. M., Kleonig, J. E., and Hinton, D. E.**, Comparison of acute response to polychlorinated biphenyl in liver of rat and channel catfish: a biochemical and morphological study, *J. Toxicol. Environ. Health*, 4, 107, 1978.

140. **James, M. O. and Little, P. J.**, Polyhalogenated biphenyls and phenobarbital: evaluation as inducers of drug metabolising enzymes in the sheepshead, *Archosargus probatocephalus*, *Chem. Biol. Interact.*, 36, 229, 1981.

141. **Spies, R. B., Felton, J. S., and Dillard, L.**, Hepatic mixed function oxidases in California flatfishes are increased in contaminated environments and by oil and PCB ingestion, *Mar. Biol.*, 70, 117, 1982.

142. **Bend, J. R., James, M. O., and Dansette, P. M.**, *In vitro* metabolism of xenobiotics in some marine animals, *Ann. N.Y. Acad. Sci.*, 298, 505, 1977.

143. **Stegeman, J. J., Klotz, A. V., Woodin, B. R., and Pajor, A. M.**, Induction of hepatic cytochrome P-450 in fish and the indication of environmental induction in scup (*Stenotomus chrysops*), *Aquat. Toxicol.*, 1, 197, 1981.

144. **Yarbrough, J. D. and Chambers, J. E.**, Crude oil effects on microsomal mixed-function oxidase system components in the striped mullet (*Mugil cephalus*), *Life Sci.*, 21, 1095, 1977.

145. **Fortin, L.**, Effects of Clophen A50, 3-methylcholanthrene, pregnenolone-16α-carbonitrile and phenobarbital on the hepatic microsomal cytochrome P-450-dependent monooxygenase system in trout, *Salmo gairdneri* of different age and sex, *Toxicol. Appl. Pharmacol.*, 54, 420, 1980.

146. **Hansen, P.-D., Addison, R. F., and Willis, D. E.**, Hepatic microsomal *O*-de-ethylases in cod (*Gadus morhua*): their induction by Aroclor 1254 but not by Aroclor 1016, *Comp. Biochem. Physiol.*, 74C, 173, 1983.

147. **Addison, R. F., Zinck, M. E., Willis, D. E., and Wrench, J. J.**, Induction of hepatic mixed function oxidase activity in trout (*Salvelinus fontinalis*) by Aroclor 1254 and some aromatic hydrocarbon PCB replacements, *Toxicol. Appl. Pharmacol.*, 63, 166, 1982.

148. **Knight, G. C., Walker, C. H., Cabot, D. C., and Harris, M. P.**, The activity of two hepatic microsomal enzymes in sea birds, *Comp. Biochem. Physiol.*, 68C, 127, 1981.

149. **Freeman, H. C., Sangalang, G., and Flemming, B.**, The sub-lethal effects of a polychlorinated biphenyl (Aroclor 1254) diet on the Atlantic cod (*Gadus morhua*), *Sci. Total Environ.*, 24, 1, 1982.

150. **Shaw, J. C.**, Enzymatic basis for active transport of Na^+ and K^+ across cell membranes, *Physiol. Rev.*, 45, 596, 1965.

151. **Koch, R. B.**, Chlorinated hydrocarbon insecticides: inhibition of rabbit brain ATPase activities, *J. Neurochem.*, 16, 289, 1969.

152. **Yap, H. H., Dominh, D., Cuthcomp, L. K., and Koch, R. B.**, Sensitivity of fish ATPases to polychlorinated biphenyls, *Nature (London)*, 233, 61, 1971.

153. **Davis, P. W., Freidhoff, J. M., and Wedemeyer, G. A.**, Organochlorine insecticide, herbicide, and polychlorinated biphenyl (PCB) inhibition of Na,K-ATPase in rainbow trout, *Bull. Environ. Contam. Toxicol.*, 8, 69, 1972.

154. **Koch, R. B., Dominh, D., Yap, H. H., and Cuthcomp, L. K.**, Polychlorinated biphenyls: effects of long-term exposure on ATPase activity in fish, *Pimephales promelas*, *Bull. Environ. Contam. Toxicol.*, 7, 87, 1972.

155. **La Roche, P. T. and Carlson, G. P.**, The effect of polychlorinated biphenyls on adenosine triphosphatase activity, *Toxicol. Appl. Pharmacol.*, 48, 185, 1979.

MONS 005989

156. **Desaiah, D., Cutkomp, L. K., Vea, E. V., and Koch, R. B.**, The effect of three pyrethroids on ATPases of insects and fish. *Gen. Pharmacol.*, 6, 31, 1975.

157. **Lorusso, D. J., Miller, T. C., and Deinzer, M. L.**, Effect of hydroxychlorodiphenyl ethers (chlorinated pre- and isoprediosins) on erythrocyte membrane adenosine triphosphatase activity. *J. Toxicol. Environ Health*, 8, 215, 1981.

158. **Srivastava, S. P., Agarwal, D. K., and Seth, P. K.**, Effect of di-2-ethyl-hexylphthalate on the activity of succinic dehydrogenase and adenosine triphosphatase of some vital organs of rats, *Toxicology*, 7, 163, 1977.

159. **Desaiah, D. and Koch, R. B.**, Toxaphene inhibition of ATPase activity in catfish, *Ictalurus punctatus* tissues. *Bull. Environ. Contam. Toxicol.*, 13, 238, 1975.

160. **Desaiah, D. and Koch, R. B.**, Preliminary investigation in the effects of mirex and its derivatives on adenosine triphosphatase activities from fire ants, *J. Agric. Food Chem.*, 23, 1216, 1975.

161. **Desaiah, D. and Koch, R. B.**, Inhibition of ATPases activity in channel catfish brain by Kepone® and its reduction product, *Bull. Environ. Contam. Toxicol.*, 13, 153, 1975.

162. **Sharom, F. J. and Mellors, A.**, Effects of polychlorinated biphenyls on biological membranes, physical toxicity and molar volume relationships, *Biochem. Pharmacol.*, 29, 3311, 1980.

163. **Tanaka, R. and Abgood, L. G.**, Phospholipid requirement of Na^+, K^+-activated adenosine triphosphatase from rat brain, *Arch. Biochem. Biophys.*, 108, 47, 1964.

164. **Roesjadi, G., Anderson, J. W., Petrocelli, S. R., and Glam, C. S.**, Osmoregulation of the grass shrimp *Palaemonetes pugio* exposed to polychlorinated biphenyls (PCBs). I. Effect on chloride and osmotic concentrations and chloride and water exchange kinetics, *Mar. Biol.*, 38, 343, 1976.

165. **Roejadi, G., Anderson, J. W., and Glam, C. S.**, Osmoregulation of grass shrimp *Palaemonetes pugio* exposed to polychlorinated biphenyl (PCBs). II. Effect on free amino acids of muscle tissue, *Mar. Biol.*, 38, 357, 1976.

166. **Nimmo, D. R. and Blackman, R. R.**, Effects of DDT on cations in the hepatopancreas of penaeid shrimp, *Trans. Am. Fish. Soc.*, 101, 547, 1972.

167. **Nimmo, D. R. and Bahner, L. H.**, Some physiological consequences of polychlorinated biphenyl- and salinity-stress in penaeid shrimp, in *Pollution and Physiology of Marine Organisms*, Vernberg, F. J. and Vernberg, W. B., Eds., Academic Press, New York, 1974, 427.

168. **Neufeld, G. J. and Pritchard, J. B.**, Osmoregulation and gill Na,K-ATPase in the rock crab, *Cancer irroratus*: response to DDT, *Comp. Biochem. Physiol.*, 62C 165, 1979.

169. **Neufeld, G. J. and Pritchard, J. B.**, An assessment of DDT toxicity on osmoregulation and gill Na,K-ATPase activity in the blue crab, in *Aquatic Toxicology*, Marking, L. L. and Kimerle, R. A., Eds., American Society for Testing and Materials, Philadelphia, 1979, 23.

170. **Caldwell, R. S.**, Osmotic and ionic regulation in decapod crustacea exposed to methoxychlor, in *Pollution and Physiology of Marine Organisms*, Vernberg, F. J. and Vernberg, W. B., Eds., Academic Press, New York, 1974, 197.

171. **Vernberg, F. J., Guram, M. S., and Savory, A.**, Survival of larval and adult fiddler crabs exposed to Aroclor® 1016 and 1254 and different temperature-salinity combinations, in *Physiological Responses of Marine Biota to Pollutants*, Vernberg, F. J., Calabrese, A., Thurberg, F. P., and Vernberg, W. B., Eds., Academic Press, New York, 1977, 37.

172. **Miller, D. S. and Kinter, W. B.**, DDT inhibits nutrient absorption and osmoregulatory function in *Fundulus heteroclitus*, in *Physiological Responses of Marine Biota to Pollutants*, Vernberg, F. J., Calabrese, A., Thurberg, F. P., and Vernberg, W. B., Eds., Academic Press, New York, 1977, 63.

173. **Lasdon, T. P., Campbell, R. D., and Johnson, D. W.**, Osmoregulatory responses to DDT and varying salinities in *Salmo gairdneri*. I. Gill Na-K-ATPase, *Comp. Biochem. Physiol.*, 49A, 197, 1974.

174. **Fehser, L. C., Dickhoff, W. W., Zaugg, W. S., and Hodgins, H. O.**, The effects of Aroclor 1254 and No. 2 fuel oil on smoltification and sea-water adaptation of coho salmon (*Oncorhynchus kisutch*), *Aquat. Toxicol.*, 2, 291, 1982.

175. **Fingerman, S. W. and Fingerman, M.**, Influence of the polychlorinated biphenyl preparation Aroclor 1242 on color changes of the fiddler crab, *Uca pugilator*, *Mar. Biol.*, 50, 37, 1978.

176. **Nagabhushanam, R., Fingerman, S. W., and Fingerman, M.**, Effects of the polychlorinated biphenyl preparation Aroclor 1242 on the quantity of neurosecretory material in the medulla terminalis x-organ of the fiddler crab, *Uca pugilator*, *Experienta*, 35, 1083, 1979.

177. **Leatherland, J. F. and Sonstergard, R. A.**, Effect of dietary mirex and PCB (Aroclor 1254) on thyroid activity and lipid reserves in rainbow trout *Salmo gairdneri* Richardson, *J. Fish Dis.*, 2, 43, 1979.

178. **Addison, R. F.**, Organochlorine compounds and marine lipids, *Progr. Lipid Res.*, 21, 47, 1982.

179. **Ito, Y. and Murata, T.**, Studies on the influence of PCB on aquatic organisms. IV. Changes in serum lipid contents and formation of lipid peroxide in the tissues of carp administered with PCB orally, *Bull. Jpn. Soc. Sci. Fish.*, 40, 261, 1974.

MONS 005990

180. **Caldwell, R. S., Calderone, E. M., and Rosene, B. A.,** Fatty acid composition of phospholipids in thermally acclimating sculpins (*Leptocottus armatus*) treated with PCBs (Aroclor 1254), in *Marine Pollution. Functional Responses*, Vernberg, W. B., Thurberg, F. P., Calabrese, A., and Vernberg, F. J., Eds., Academic Press, New York, 1979, 271.
181. **Anon.,** *Environmental Health Criteria 2: Polychlorinated Biphenyls and Terphenyls*, World Health Organization, Geneva, 1976.
182. **Roberts, J. R., Rodgers, D. W., Bailey, J. R., and Rorke, M. A.,** *Polychlorinated Biphenyls: Biological Criteria for an Assessment of their Effects on Environmental Quality*, NRCC #16077, National Research Council of Canada, Ottawa, 1978.
183. **Hogan, J. W. and Brusha, J. L.,** Abnormal rainbow trout fry from eggs containing high residues of a PCB (Aroclor 1242), *Progr. Fish. Cult.*, 37, 229, 1975.
184. **Bengtsson, B.-E.,** Increased growth in minnows exposed to PCBs, *Ambio*, 8, 169, 1979.
185. **LeBoeuf, B. J. and Bonnell, M. L.,** DDT in California sea lions, *Nature (London)*, 234, 108, 1971.
186. **DeLong, R. L., Gilmartin, W. G., and Simpson, J. G.,** Premature births in California sea lions: association with high organochlorine pollutant residue levels, *Science*, 181, 1168, 1973.
187. **Helle, E., Olsson, M., and Jensen, S.,** PCB levels correlated with pathological changes in seal uteri, *Ambio*, 5, 261, 1976.
188. **Helle, E.,** Lowered reproductive capacity in female ringed seals (*Pusa hispida*) in the Bothnian Bay, northern Baltic sea, with special references to uterine occlusions, *Ann. Zool. Fennici*, 17, 147, 1980.
189. **Reijnders, P. J. H.,** Organochlorine and heavy metal residues in harbour seals from the Wadden sea and their possible effects on reproduction, *Netherlands J. Sea Res.*, 14, 30, 1980.
190. **Reijnders, P. J. H.,** On the ecology of the harbour seal *Phoca vitulina* in the Wadden sea: population dynamics, residue levels and management, *Vet. Q.*, 4, 36, 1982.

MONS 005991

Chapter 3

ACCUMULATION AND EFFECTS ON BIRDS

D. B. Peakall

TABLE OF CONTENTS

I. Accumulation of PCBs in Birds 32

II. Pharmacodynamics of PCBs 32

III. Acute and Subacute Toxicity 32

IV. Reproduction 36
- A. Eggshell Thickness 36
- B. Effects on Males 36
- C. Teratogenic Effects 37
- D. Behavioral Effects 39

V. Other Physiological Effects 39
- A. Hepatic Enzyme Induction 39
- B. Thyroid Function/Vitamin A Levels 39
- C. Hydropericardium, Generalized Edema, and Porphyria 41
- D. Immunosuppressive Activity of PCBs 42
- E. Other Physiological Effects 42

VI. PCB Levels in Birds 43

VII. Conclusion 43

References 44

MONS 005992

I. ACCUMULATION OF PCBs IN BIRDS

The accumulation of PCBs in birds can be studied both under field and laboratory conditions. The former studies have the advantage of applying to the real world but the relationship between prey and predator is usually assumed rather than known. Most species of fish-eating birds will shift to other food sources if available. This is particularly true of gulls. In any case, the sampling of the prey may well not be typical of the total food intake. In laboratory studies the input of PCBs can be carefully controlled. Few studies on birds are available on accumulation of specific isomers, although there is growing evidence that this is of importance.

Laboratory data for the accumulation of PCBs from known diets are given in Table 1. It is clear that there are wide differences between species. The commonly used laboratory species — chicken, quail, dove, and mallard show little bioaccumulation. In contrast, high coefficients of bioaccumulation were found for the two fish-eating birds studied (herring gull, white pelican); the one raptorial bird studied (American kestrel) shows intermediate values.

Isomer specific studies appear to be limited to those of Bunyan and Page.[1] The residue levels given by these workers are for the heart, an organ rarely studied by others so that comparisons are difficult. What is clear is the wide difference between isomers. The dichloro isomers show low residue levels as would be expected; however, there are marked differences between the four tetrachloros and two hexachloros studied. A further point of interest is the residue levels of those isomers that do accumulate, viz., 3, 4, 5, 3', 4', 5' hexachloro and decachlorobiphenyl are some tenfold higher than the overall figure for Aroclor® 1254.

II. PHARMACODYNAMICS OF PCBs

The uptake of Aroclor® 1254 at a high dose (500 ppm) into four organs (muscle, liver, kidney, and brain) has been studied in the chicken.[20] An essentially linear uptake over a period of 10 to 60 days was found. The ratios of the tissue are given in Table 2. Lincer and Peakall[5] studied the levels in eggs of ring doves exposed to 10 ppm Aroclor® 1254 and found a linear rise for approximately 100 days, after which the values began to approach an asymptote value.

The distribution of PCB on an organ basis is largely governed by the lipid content of the tissue, although the values obtained both in the laboratory[5,21] and field[22] (Table 3) indicate the levels in the brain are lower than other organs and that fat serves as the main depot.

The mobilization of organochlorines in birds exposed to food stress has been considered to be a factor in deaths of wild birds.[23] The "wreck" of guillemots in the Irish Sea in 1969 was linked to high PCB levels.[16] Subsequently, Parslow and Jefferies[24] studied the relationship between liver levels and total body burden in this species. They found a marked increase in the percentage of PCBs found in the liver of guillemots involved in the wreck (and having no body fat) compared to those shot. The increase in the load in the liver was from 0.9 to 22.5%. In both groups there was a strong correlation between liver levels and total body burden. In ring doves, Lincer and Peakall[5] noted a 70-fold increase in liver residue values when the birds were food stressed to the point that they had no body fat. No differential mortality due to PCB mobilization was observed in this experiment.

Anderson and Hickey[10] studied the seasonal variation of PCB levels in herring gulls and observed a diphasic response in juveniles and a triphasic response in adults.

III. ACUTE AND SUBACUTE TOXICITY

PCBs have a low acute toxicity to birds. The 5-day LC_{50} for four species is given in

MONS 005993

Table 1
ACCUMULATION OF PCBs IN BIRDS FROM LABORATORY EXPERIMENTS

Species	Aroclor[a]	Dose	Duration (days)	Residue level (ppm, wet weight)						Ref.
				Whole body	Fat	Muscle	Liver	Brain	Eggs	
Chicken	1260	400	60				210—340			2
(*Gallus gallus*)	1242	100	28		283					3
		200			427					
		400			1686					
	1254	100			515					
		200			783					
		400			1557					
	1260	100			482					
		200			1427					
		400			2151					
	1248	0.5	56		3.1				0.22	4
		1.0			6.6				0.41	
		10			37				3.1	
		20			83				7.0	
Japanese quail	1254	5	84	5			1.9			29
(*Coturnix coturnix*)		25		20			12.5			
		100		88			72			
Ring dove	1254	10	200		736	8.1	15.3	5.5	15.5	5
(*Streptopelia risoria*)										
Mallard	1242	25	28	55 (9)					23	6
(*Anas platyrhynchos*)				64 (♂)						
Screech owl	1248	3	56	12.8					1.1	7
(*Otus asio*)			approx. 250						7.1	
American kestrel	1254	5	approx. 100						40	8
(*Falco sparverius*)										
White pelican	1254	144	70		2130		290	110		9
(*Pelecanus erythrorhynchos*)										
Herring gull	*	1	322	200						10
(*Larus argentatus*)										

* Fish diet averaging 2 ppm PCB.

MONS 005994

Table 2
TISSUE DISTRIBUTION OF PCBs

Species	Dosage	Levels in organs (ppm)						Ref.
		Muscle	Liver	Kidney	Brain	Heart	Fat	
Chicken	500 ppm Aroclor® 1254 Measurements at 50 days	108	285	470	145	—	—	20
Ring dove	10 ppm Aroclor® 1254	8	15	—	5.5	—	736	5
	Measurements at 200 days	172	1120	—	293	—	—	
Japanese quail	Aroclor® 1242	—	17	—	7.8	3.2	123	21
	Aroclor® 1254	—	28	—	7.7	7.0	304	
California gull (*Larus californicus*)	Field	—	0.79	—	0.29	—	18.87	22

Table 3
ACCUMULATION OF PCBs IN BIRDS FROM FIELD EXPERIMENTS

Avian species	Residue level in prey	Residue level (ppm, wet weight)					Ref.
		Whole body	Muscle	Liver	Brain	Eggs	
Great-crested grebe (*Podiceps cristatus*)	0.17 (0.16—0.18)	—	—	11—	—	—	11
	0.12 (0.04—0.35)	32	—	—	—	—	
	0.8—1.3	—	—	—	—	13	12
Brown pelican (*Pelecanus occidentalis*)	0.19 (0.17—0.23)	—	—	—	—	2.2	13
White pelican	0.05—0.11	2.3	3.1	4.5	—	1.7	14
Double-crested cormorant (*Phalacrocorax auritus*)		3.6	2.3	2.0	—	5.7	
White-crested cormorant (*Phalacrocorax carbo*)	1.6	6.2	—	—	4.4	2.9	15
White-tailed sea eagle (*Haliaetus albicilla*)	0.03—0.18	—	150—240	130	29—70	—	16
Common guillemot (*Uria aalge*)	0.27 (0.01—1.0)	—	—	—	—	7.9—21	17
	0.01—2.0	3.4	—	0.4	—	—	18
Herring gull	2.2	—	—	—	—	124—157	19

Table 4.[25] There is steady increase in toxicity as the degree of chlorination increases, although the percentage of chlorine alone does not determine the toxicity at least for the Japanese quail.[26] There are substantial differences between the LC_{50} values for the bobwhite and Japanese quail, with the former species being some three- to fourfold more sensitive. But even the lowest LC_{50} given (604 ppm for Aroclor® 1260 in bobwhite quail) is high compared to organochlorine pesticides.

Subacute experiments also show that PCBs have low toxicity (Table 5). The data on the chicken indicate that the middle chlorinated Aroclor® 1242 is more toxic than either the lightly or heavily chlorinated mixtures. Nevertheless, levels of 200 ppm are required to cause appreciable mortality.

Hurst et al.[27] showed the cold stress potentiated mortality and that, under cold stress, there was a sex-related difference (males being more susceptible than females). Nevertheless, the dosage level was high (500 ppm causing mortality starting at day 20 under cold conditions). Lincer and Peakall[5] found no differential mortality when food stress was applied to ring doves.

The report on the seabird wreck in the Irish Sea in 1969[16] concluded that one of the most striking findings was the presence of unusually high levels of PCBs in the livers of dead

MONS 005995

Table 4
5-DAY LC_{50} FOR FOUR AVIAN SPECIES (ppm)[15]

Aroclor[a]	Bobwhite	Japanese quail	Ring-necked pheasant	Mallard
1221	6,000	12,000	5,000	5,000
1232	3,002	5,000	3,106	6,000
1242	2,098	6,000	2,078	3,172
1254	1,175	4,844	1,312	2,798
1260	604	2,898	1,091	2,699
1262	747	2,186	1,260	1,975

Table 5
MORTALITY ASSOCIATED WITH FEEDING EXPERIMENTS

Species	Aroclor[a]	Dosage (ppm)	Duration (days)	Mortality	Ref.
Chicken	1221	500	38	None	27
	1242	38	28	None	38
		75		Increased from 4 to 21% in chicks; no effect poults	
		150		Increased to 75% in chicks; no poults	
		500	38	40% mortality	27
		100	28	No mortality	29
		200		40% mortality	
		400		100% mortality	
	1254	100		No mortality	
		200		20% mortality	
		400		60% mortality	
		500	30	No mortality	27
	1260	100	28	No mortality	29
		200		No mortality	
		400		No mortality	
	1268	500	30	No mortality	27
Japanese quail	1242	250	20	No mortality	21
		5000	21	No mortality mentioned	30
	1254	250	20	No mortality	21
		1250	21	No mortality mentioned	30
	1260	1000	21	No mortality mentioned	
Bobwhite quail (*Colinus virginianus*)	1260	500	—	Mortality started at 20 days, complete by 40 days in cold; in heated building, mortality of males complete in 60 days, females in 120 days	31
Pigeon (*Columbia livia*)	1242	500	28	No mortality	21
Ring dove	1254	100	56	No mortality	32
Mallard	1242	150	84	No mortality	33
White pelican	1254	144	70	No mortality	9
American kestrel	1254	5	100	No mortality	

guillemots. High levels would be expected due to the mobilization of body fat and the levels reported (mean 56 ppm, range 10 to 200 ppm), while high, are not outside the levels measured in apparently healthy herring gulls on the Great Lakes (50 to 200 ppm).[34] Levels in the early to mid 1970s were, presumably, even higher. While the data on the effects on target species under environmental realistic conditions are poor, there is little evidence that toxicity of PCBs has been the primary cause of mortality in the field.

MONS 005996

Table 6
EFFECT OF PCBs ON REPRODUCTION IN THE CHICKEN

PCB	Dosage (ppm)	Duration (weeks)	Egg production	Hatchability	Ref.
1221	20	9	No effect	No effect	35
1232			765 69	94 57	
1242	2	9	No effect	No effect	
	5	6	No effect	No effect	36
	10		No effect	No effect	
	20		No effect	91 75	
	20	1	—	55 44 (Leghorns)	37
				59 43 (Broilers)	
		6	—	69 7 (Leghorns)	
				65 6 (Broilers)	
		9	76 66	94 18	33
	40	6	No effect	91 50	36
	50	1	—	55 15 (Leghorns)	37
			—	59 40 (Broilers)	
		6		69 0 (Leghorns)	
				65 5 (Broilers)	
	80	6	No effect	91 0	36
1248	1	8	No effect	No effect	4
	2	9	No effect	No effect	35
	10	8	74 69	91 50	4
	20	8	74 65	91 2	
	20	9	76 66	94 12	
1254	2	9	No effect	No effect	
	5	14	83 72	No effect	38
	20	9	76 66	94 81	35
	50	14	83 62	Reduced to near zero	38
	50	6	No effect	Reduced to zero	39
1268	20		76 71	No effect	25

IV. REPRODUCTION

The effects of PCBs on the overall reproduction of birds are summarized in Tables 6 to 8. By far the most detailed information is available for the chicken (Table 6). It will be seen that hatchability is affected to a much greater extent than egg production. There is appreciable variation in the effects of the different Aroclors®. Taking the 20 ppm data, one sees that 1221, 1254, and 1268 have only minor effects, whereas this dosage level causes complete hatching failure when 1242 or 1248 is used. Other members of the Galliformes (Table 7) are less sensitive; hatchability of the Japanese quail was not affected by 20 ppm Aroclor® 1248, nor was bobwhite quail affected by 50 ppm Aroclor® 1254. Both these dosage regimes reduced the chicken to near zero hatchability.

A. Eggshell Thickness

The bulk of the evidence shows that PCBs do not affect the thickness of eggshells. The following studies found no significant eggshell thinning: mallard,[6,41,42] American kestrel,[8] screech owl,[7] ring doves,[46] bobwhite quail,[41] Japanese quail,[40] ring-necked pheasant,[42] and chicken.[6,35,36] The only study reporting eggshell thinnings appears to be that of Call and Harnell[35] on Japanese quail using high dosages of three Aroclors®.

B. Effects on Males

Platonow and Funnell[7] fed cockerels Aroclor® 1254 at a dietary level of 250 ppm. A

MONS 005997

Table 7
EFFECT OF PCBs ON REPRODUCTION OF OTHER GALLIFORMES

Species	PCB	Dosage	Duration	Egg production		Hatchability	Ref.
Japanese quail	1242	100 ppm	9 weeks	0.89	0.75	Not studied	40
		312 ppm	3 weeks	0.55	0.45	Not studied	30
		5000 ppm			0.24		
	1248	20 ppm	8 weeks	Not reported		No effect	4
	1254	78 ppm	3 weeks	0.55	0.29	Not studied	30
		1250 ppm			0.18		
	1260	62.5 ppm			0.48		
		1000 ppm			0.12		
Bobwhite quail	1254	50 ppm	2 seasons	No effect		No effect	41
	1260	500 ppm	14 weeks	Significant decrease for first 8 weeks; significant increase thereafter			31
Pheasant (*Phasianus colchicus*)	1254	12.5 mg/kg/day, 50 mg/kg/day	17 weeks	0.62	0.46 0.29	No effect	42

marked reduction in comb size was noted within 6 weeks, and the weight of the testes was reduced after 9 weeks. No direct studies of the reproductive performance of these birds were made. Lillie et al.[39] fed cockerels Aroclor® 1248 at 10 and 20 ppm for an 8-week period without finding any effect on semen or fertility.

In contrast, Ahmed et al.[40] found that 10 to 40 ppm of Aroclor® 1254 in the diet caused decreased semen volume, sperm concentration, and testes weight. Biessman[29] found that Clophen® 60 decreased testicular weight in Japanese quail. Bird et al.[30] found that 33 ppm Aroclor® 1254 fed to American kestrels caused a significant decrease in sperm concentration but did not affect semen volume.

C. Teratogenic Effects

Cariaon and Duby[31] found that 5 ppm of Aroclor® 1242 injected at day zero caused several malformations including development of only one eye, hydrocephalus, incomplete abdominal closure, and nervous tremors. Tumasonis et al.[39] noted leg, toe, and neck deformities in many chicks that hatched from eggs with a yolk level of 10 to 15 ppm Aroclor® 1254 or more. Cecil et al.[32] examined the effect of a diet of 20 ppm of a range of Aroclors® on the production of abnormal embryos. These workers found a marked increase of abnormal embryos as a percentage of fertile eggs for Aroclors® 1242 and 1248, a slight effect with Aroclor® 1232 and 1254, and no effect for Aroclors® 1221 and 1268. In all the treated groups, there were 843 dead embryos of which 286 were abnormal. The most common abnormality was edema, including edematous cysts and subcutaneous edema. Other abnormalities, in decreasing order of occurrence, were unabsorbed yolk, small body, external hemorrhage, skinny legs, rotated ankle, and deformed beaks.

Dahlgren and Linder[42] noted decreased chick weight in their studies on the pheasant, but no mention is made of abnormalities. Peakall et al.[33] found an increase in chromosomal abnormalities in embryos of ring doves exposed to 10 ppm Aroclor® 1254. Blazak and Marcum[34] injected Aroclor® 1242 into chicken eggs so that the final concentration was 10 or 20 ppm. They found increased mortality (64 and 67%, respectively, compared to 30% for controls), and a few abnormalities (2/64 at 10 ppm and 3/57 at 20 ppm). However, in contrast to the study on ring doves, no chromosomal breakage was observed.[34] In the dove

MONS 005998

Table 8
EFFECT OF PCBs ON REPRODUCTION OF NONGALLIFORM BIRDS

Species	Aroclor®	Dose	Time	Incubation	Clutch size	Survival to			Ref.
						Fertility (%)	Hatch (%)	3 weeks	
Mallard	1242	150 ppm	12 weeks	Artificial and natural	No effect	No effect	No effect	No effect	11
	1254	25 ppm	2 seasons	Artificial	No effect	No effect	No effect	No effect	41
		25 ppm	4 weeks	Natural	No effect	No effect	No effect	No effect	6
		40 ppm	16 weeks	Natural	No effect	No effect	Not studied	Not studied	43
Puffin (*Fratercula arctica*)	1254	30—35 mg/bird	1 season	Natural	No effect		No effect	No effect	45
Screech owl	1248	3 ppm	2 seasons	Natural	No effect	No effect	No effect	No effect	47
Ring dove	1254	10 ppm	12 weeks	Natural	No effect		Reduced	Reduced	
				Artificial	No effect		86 66	—	

MONS 005999

study the birds were fed PCBs over a prolonged period and alterations may have occurred in the body of the parent. Whether experimental design or species difference is responsible, it is clear that increased embryonic mortality was associated with chromosomal breakage in one case and not in the other.

D. Behavioral Effects

Delayed reproduction has been noted with DDE[11,16] but the effect of PCBs is either slight[11] or nonexistent.[16] Behavioral abnormalities leading to marked reduction of reproductive success were found in ring doves fed 10 ppm Aroclor® 1254.[44] Monitoring of egg temperature suggested that increased mortality was due to decreased parental attentiveness, which was confirmed by comparison of natural and artificial incubation. McArthur et al.[16] feeding ring doves a mixture of Aroclor® 1254, DDE, and mirex found effects on breeding synchrony, nest construction, incubation attentiveness, and parental care and were able to relate them to hormonal changes. Decreased reproductive success was marked in the higher dose (28 ppm PCB; 4.6 ppm DDE; 0.9 ppm mirex) groups. In contrast, the Custer and Heinz[9] study feeding 25 ppm Aroclor® 1254 to mallard did not reveal any behavioral abnormalities nor any reduction of breeding success.

V. OTHER PHYSIOLOGICAL EFFECTS

In this section, physiological changes not directly associated with reproduction are discussed (although indirect effects are possible).

A. Hepatic Enzyme Induction

There are considerable data on the induction of hepatic enzymes in birds by PCBs starting as far back as 1968.[37] It is clear from the data in Table 9 that the phenomenon is found in many species and that a number of different enzyme systems are involved. The studies of Bunyan and Page[1] show that the response is markedly different for different specific isomers and they relate these differences to degree of retention in the body. Elevated activity of hepatic enzymes has been found in the livers of herring gulls collected on the Great Lakes[62a] and the possibility of using this system for monitoring purposes has been put forward.

These hepatic enzymes (often called mixed function oxidases or MFO) have the role of converting liposoluble foreign compounds into water-soluble metabolites that may be more readily excreted. Thus, these systems are a defense against xenobiotics and a knowledge of the activity of MFO systems can be used to determine the half-lives of some xenobiotics. In general, the activity of MFO is mammal > bird > amphibian > fish.[63] Within the order Aves, considerable variation has been found, for example, the puffin shows much higher MFO activity than the cormorant.[64]

In addition to metabolizing xenobiotics, the MFO system also metabolizes endogenous compounds, especially steroids. The possible interrelationship of these changes with altered reproductive behavior has been discussed earlier.

B. Thyroid Function/Vitamin A Levels

Thyroid hormones play a major role in regulating oxidative metabolism, growth, and development and are interrelated with vitamin A metabolism.

Jefferies and Parslow[65] dosed lesser black-backed gulls with Aroclor® 1254, at 50, 100, 200, and 400 mg/kg/day for 8 weeks. An increase in thyroid weights (30 to 40 mg) was noted between the controls and dosed birds, but no dose-dependent increase was observed. Analysis of the colloid area showed a small increase. The major histological change was larger follicles well filled with colloid. In a subsequent experiment[66] on guillemots, dosages of 12 and 25 mg/kg/day caused increased thyroid weight, follicle size, and colloid area. Increasing doses (up to 400 mg/kg/day) caused dose-related decreases in these parameters.

MONS 006000

Table 9
EFFECT OF PCBs ON HEPATIC ENZYME INDUCTION

Species	PCB	Dosage	Duration (days)		Ref.
Chicken	1254 1260	1 mg/day, chicks	7	3—4-fold increase in rate of metabolism of testosterone, androsterone, & estradiol	58
	1254	10, 100 ppm	14	Marked increase of benzopyrene hydroxylase at both levels, no dosage dependence	59
	1254	0.1, 1 ppm 10 ppm 100 ppm	7	No effect Doubling of cytochrome P450 4-fold increase of cytochrome P450	60
	1221	5, 500 ppm 50 ppm	30	No effect Decrease of AHA and APD activity	27
	1242	5, 50, 500 ppm		No effect	
	1254	5, 50, 500 ppm		No effect on AHA, nondose related effect on APD activity	
	1268	5 ppm 50 ppm 500 ppm		No effect ADP increased AHA and APD increased	
Japanese quail	1242	250 ppm	20	4-fold increase of cytochrome P-450	21
	1254	250 ppm	20	8-fold increase of cytochrome P-450	
	1016	50 ppm	20	No effect	1
	1242			3-fold increase of cytochrome P-450	
	1254			5-fold increase of cytochrome P-450	
	3,3'- and 4,4'-dichloro			No effect Small increase of EMD activity	
	3,4'-dichloro			No effect	
	2,4,6,2'-tetrachloro				
	2,4,6,4'-tetrachloro			Doubling of EMD; 3.5-fold increase of cytochrome P-450	
	2,5,3',4'-tetrachloro			Doubling of EMD and cytochrome P-450	
	3,5,3',5'-tetrachloro			4-fold increase of cytochrome doubling of EMD and AHA activity	
	2,4,6,2',4',6'-hexachloro			No effect	
	3,4,5,3',4',5'-hexachloro			5-fold increase of cytochrome P-450, 2—3-fold increase of EMD & AHA	
	Decachloro			No effect	
Pigeon	1262	20 mg/kg, single i.p. injection	7	5-fold increase in metabolism of estradiol	57
	1242	500 ppm	28	6-fold increase of cytochrome P-450	21
American kestrel	1254	0.5, 5.0 ppm	14	Increased metabolism of estradiol	61
	1260	0.5, 5.0 ppm	14	Increased metabolism of estradiol	
Barn owl (*Tyto alba*)	1254	30 mg/kg injected into liver	3	Results difficult to interpret due to toxic effects on liver	62

Jefferies and Parslow considered that in the pituitary, the decrease of weight of which was significantly correlated with increasing dose, is one of the target sites for Aroclor® 1254.

Hurst et al.[31] studied the effect of Aroclor® 1260 at 5, 50, and 500 ppm for 1 to 4 months on bobwhite quail. Significantly different thyroid weights were found for all dose levels after 4 months, but this effect appears to be due to the abnormally low control value for

MONS 006001

this period. There was no actual rise in thyroid weights when compared to measurements made at 1, 2, or 3 months. There was a tendency for ^{131}I uptake for the total thyroid to be higher in quail exposed to the highest dose (500 ppm), but this increase was significant for only one time period and did not show up when expressed on a per 6 milligram of thyroid basis.

Cecil et al.[40] studied the effect of 100 ppm Aroclor® 1242 on liver vitamin A levels in quail. After 2 months on the diet, Aroclor® 1242 caused a marked reduction (approximately halved) in vitamin A in male quail, but the females were unaffected.

Speer[47] found that leghorn chicks receiving a low vitamin A diet developed hypothyroidism following two 10 mg/kg injections of 3,4,3',4'-tetrachlorobiphenyl (TCB). Plasma vitamin A concentration and growth rate were not affected by the toxicant. On a low iodine-low vitamin A diet, chicks exposed to TCB were subject to an alteration of thyroid hormone metabolism distinct from that occurring at the higher dietary level of iodine. Total T_4 decreased commensurate with a decrease in the binding of thyroid hormones in plasma such that the free thyroid hormone index remained constant. The result was interpreted to mean that the toxicant did not alter the concentration of unbound thyroid hormones at the lower level of dietary iodine.

Tori and Mayer[48] feed mourning doves (*Zenaidura macroura*) 40 ppm Aroclor® 1254 and found a significant effect on body temperature. The metabolic rates of PCB-fed doves increased more slowly with decreasing ambient temperatures than did the controls.

C. Hydropericardium, Generalized Edema, and Porphyria

McCune et al.[49] discovered hydropericardium when chickens were placed in a battery treated with unhardened paint. Additional studies revealed that Aroclor® 1242 caused hydropericardium at dosages, and in the abdominal and subcutaneous areas Aroclor® 1242 was pronounced in the chicks exposed to 400 ppm for 3 weeks, but was much less marked at 200 ppm. Rehfeld et al.[71] observed general edema in chicks when the diet contained over 20 ppm Aroclor® 1254. Chicks exposed to diets containing 50 to 150 ppm Aroclor® 1254 had extensive generalized edema. This included serious effusion into the pericardial sacs, muscles, subcutaneous tissues, and abdominal cavity.

Bayer and Bird[72] studied structural changes in the epicardium of chickens exposed for 11 weeks to a diet containing 20 ppm Aroclor® 1254. They found that all the birds exposed to PCB showed morphological changes in the pericardium and three out of four birds showed large quantities of ascites fluid. Vos and Koeman[2] studied the effects of 400 ppm of three different preparations of PCBs containing 60% chlorine. These were Phenoclor® DP6, Clophen® A60, and Aroclor® 1260. The chickens were exposed to this diet for 60 days. Hydropericardium was common in the Phenoclor® and Clophen® group. Similarly, abdominal and subcutaneous edema was observed only in the first two groups. These differences were considered to be due to the presence of chlorinated dibenzofurans in the first two preparations.[72] Nevertheless, there are considerable differences between Vos and Koeman's results on Arochlors® and those of other workers. These differences may be due to the fact that other workers have used lower chlorinated Arochlors® (1242 and 1254) which may themselves act differently or may contain more chlorinated dibenzofurans than Aroclor® 1260. Firestone[74] reviewed the etiology of chick edema disease and concluded that the chlorinated dioxins and furans were the chemical agents responsible. In view of the studies of Rehfeld et al.[71] and those of Bayer and Bird[72] which show effects at moderate levels, (about 20 ppm) it would be useful to examine the effect of pure PCBs to clear up the question of the agent causing chick edema.

In contrast to their findings on edema, Vos and Koeman[2] found that porphyria was induced by all preparations of PCBs studied. They found that the chicks increased fecal excretion of coproporphyrin, protoporphyrin, and fluorescence (indicating the presence of porphyrins)

MONS 006002

in the liver, bile, small intestine, and bone. Subsequently, Vos et al.[74] made a more detailed study using Japanese quail. Using Aroclor® 1260 at 50, 100, 250, and 500 ppm in the diet for 7 days on male quail they demonstrated a tenfold increase of mitochondrial δ-aminolevulinic acid synthetase in the liver of birds receiving 50 ppm, and a further increase at higher levels. Increased fluorescence of the liver only became marked at higher dosages. Lower levels were studied on female quail. A slight but statistically nonsignificant increase of δ-aminolevulinic acid synthetase was noted at a dosage of 0.1 mg/kg/day for 7 days, but the increase was significant at a dosage of 1 mg/kg. δ-Aminolevulinic acid synthetase catalyzed (ALA synthetase) the first step in porphyrin synthesis, for example, the reaction of succinyl CoA with glycine to form α-amino-β-keptoadipic acid. Metabolic control of porphyrin formation is excreted through a feedback mechanism operating at the first two steps of the pathway (ALA synthetase and δ-aminolevulinic acid dehydrase). ALA is also the precursor of the porphyrin moiety of chlorophyll and of the corrin ring of vitamin B_{12}.

Chick edema disease and hepatic porphyria have been described in herring gull embryos collected from Lake Ontario colonies in the early 1970s.[76] Substantial levels of PCBs were known to have been present, but also a wide variety of other compounds including 2,3,7,8-tetrachlorodibenzo-*p*-dioxins.[77]

D. Immunosuppressive Activity of PCBs

Friend and Trainer[78] examined the effect of Aroclor® 1254 on mortality of young mallards exposed to duck hepatitis virus. Three dose levels were used, 25, 50, and 100 ppm, in the diet. At all dosages, the mortality was increased markedly over control values, but the greatest increase was at 50 ppm. The actual values were control 14.3%, 25 ppm 35.05%, 50 ppm 65%, and 100 ppm 44.4%.

The importance of the effects of PCBs on the immunosuppressive mechanisms is hard to evaluate. The lack of clear dose dependence is one problem, and interrelation with other stresses is another. The possibility of the burden of PCBs and other organochlorines[79] increasing susceptibility to disease should be borne in mind.

E. Other Physiological Effects

Combs et al.[80] found that dietary PCBs (Aroclor® 1254) added to the diet of breeding hens increased the susceptibility of progeny to vitamin E-selenium deficiency when the ducks were deficient in vitamin E and contained only marginal concentrations of selenium. No effects were seen when the birds were maintained on normal diets. Subsequently, studies[80] indicated that PCBs did not affect the physiologic function of vitamin E in protecting biological membranes, but may interfere with the absorption-retention of the vitamin.

Srebocan et al.[81] studied the effect of Aroclor® 1254 on the levels of gluconeogenic enzymes in embryonic and growing chicks. In one experiment, Aroclor® 1254 was injected into chicken eggs so that the final concentrations were 0.05, 0.1, 0.5, or 5 ppm. At 14 days of incubation, modest decreases (values reduced to 80% of controls by highest dosage) were seen for phosphoenolpyruvate carboxykinase, phosphoenolpyruvate carboxykinase and fructose-1,6-diphosphatase but not glucose-6-phosphatase. In growing chicks, the levels of all of these enzymes, except phosphoenolpyruvate carboxykinase were severely reduced over dietary range of 0.1 to 200 ppm. The authors consider that effects on the energy utilization mechanism could be responsible for embryonic mortality and death at time of pipping. The pattern of enzymatic change, i.e., moderate in the embryo, marked in chicks, is the inverse of the pattern of mortality. However, it could be that energy demand is critical at the earlier life stages and much less so later.

Dieter[29] demonstrated significant increases of the levels of several plasma enzymes (creatine kinase, cholinesterase, fructose diphosphate aldolase, and lactate dehydrogenase) in quail fed 5 ppm Aroclor® 1254 for 12 weeks. These responses were dose dependent and the plot of enzyme activity against the log of the dose was linear.

MONS 006003

Table 10
PCB LEVELS IN GULLS AND THEIR EGGS

Species	Location	Tissue	Year of collection	Residue level (ppm wet weight)	Ref.
Herring	Norway (west coast)	Egg	1972	3.1—12.6	83
	Baltic (Gdansk Bay)	Muscle	1975—76	23—150	84
	Finland	Muscle	1972—74	0.68—18	85
	East Scotland	Muscle	1971—75	0.2—1.2	86
	Camargue, France	Egg	1972	16—160	87
	New Brunswick, Canada	Egg	1969—72	3.1—8.2	88
	Lake Ontario	Egg	1974—75	74—261	89
	Maine	Egg	1977	(0—32.0) 7.76 (30)	22
	Virginia	Egg	1977	(0.13—16.70) 9.06 (28)	90
	East Frisian Is., Germany	Egg	1975	26.5	90
			1971	5.5	
	Denmark (North Sea)	Egg	1971	2.1 (1.3—2.6)	91
	Baltic		1972	92 (21—190)	
California	Alberta	Egg	1969	0.87 (11)	92

Heinz et al.[93] examined the effects of 1, 10, and 100 ppm of Aroclor® 1254 on the levels of dopamine and norepinephrine in the brains of ring doves.[93] Significant decreases of both of these compounds were found at both 10 and 100 ppm dosages. It is considered that these changes (40% reduction at 10 ppm) could result in behavioral abnormalities.

VI. PCB LEVELS IN BIRDS

There has been a vast amount of literature on this subject since the initial finding that PCB contamination of birds is essentially global.[77] In this review only the most highly contaminated systems — Great Lakes of North America and the Baltic Sea — are considered. Temporal trends are considered in the chapter by Stout (Volume I, Chapter 9).

One of the avian species considered to be a good monitor of environmental pollution is the herring gull.[92] Some residue levels for that species are given in Table 10. Only in the case of the Lake Ontario birds were effects seen (poor reproduction). Other pollutants were also identified (DDE 23 ppm, mirex 5 ppm, tetrachlorodioxin 1 ppb, all on a wet weight basis) and it is not possible to separate the effects caused by different pollutants. Helander et al.[94] have recently summarized the levels of pollutants in White-tailed Sea Eagles and related them to productivity. They estimate the critical range as 500 to 600 ppm DDE and/or 800 to 900 ppm PCB on a lipid weight basis in the eggs of this species. The mean levels in the poorly reproducing Herring Gulls on Lake Ontario were 1700 ppm (lipid weight) compared to 700 ppm in the eggs from colonies reproducing normally in Lake Huron.[89]

VII. CONCLUSION

Based on laboratory experiments, it is clear that PCBs are not sufficiently toxic in either acute and chronic feeding studies to pose a hazard to birds. Studies on reproduction show marked interspecies variations with chickens highly sensitive. In the wild, galliformes are not at the end of food chains that are likely to accumulate PCBs. Other species tested are less sensitive than chickens, but most target species have not been tested. Behavioral abnormalities also show interspecies variations, with the ring dove affected at modest levels whereas the mallard is not. It is likely, but not proven, that PCBs were involved in the behavioral abnormalities found in gulls on the Great Lakes that led to reproductive failure in the early 1970s. Hepatic enzyme induction occurs at realistic environmental levels, but

MONS 006004

there is no evidence that these changes cause harm to the organism. Little is known about the toxicology of metabolites of PCBs, although phenolic metabolites have been identified in guillemots and seals[95] and sulfone metabolites in seals.[96]

REFERENCES

1. **Bunyan, P. J. and Page, J. M. J.**, Polychlorinated biphenyls. the effect of structure on the induction of quail hepatic microsomal enzymes, *Toxicol. Appl. Pharmacol.*, 43, 507, 1978.
2. **Vos, J. G. and Koeman, J. H.**, Comparative toxicological study with polychlorinated biphenyls in chickens with special reference to porphyrin, edema formation, liver necrosis and tissue residues, *Toxicol. Appl. Pharmacol.*, 17, 656, 1970.
3. **Harris, J. R. and Rose, L.**, Toxicity of polychlorinated biphenyls in poultry, *J. Am. Vet. Med. Assoc.*, 161, 1584, 1972.
4. **Scott, M. L., Effects of polychlorinated biphenyls, DDT and mercury compounds in chickens and Japanese Quail, *Fed. Proc.*, 36, 188, 1977.**
5. **Linzer, J. L. and Peakall, D. B.**, PCB pharmacodynamics in the Ring Dove and early gas chromatographic peak diminution, *Environ. Pollut.*, 4, 59, 1973.
6. **Custer, T. W. and Heinz, G. H.**, Reproductive success and nest attentiveness of Mallard Ducks fed Aroclor 1254, *Environ. Pollut. (Ser. A)*, 21, 313, 1980.
7. **McLane, M. A. R. and Hughes, D. L.**, Reproductive success of Screech Owls fed Aroclor 1248, *Arch. Environ. Contam. Toxicol.*, 9, 661, 1980.
8. **Linzer, J. L.**, The Effects of Organochlorine on the American Kestrel (*Falco sparverius* Linn.), Ph.D. thesis, Cornell University, Ithaca, N.Y., 1972.
9. **Gretchen, Y. A., Call, D. J., and Ammann, B. M.**, Physiological effects of polychlorinated biphenyls or a combination of DDT, DDD and DDE in penned White Pelicans, *Arch. Environ. Contam. Toxicol.*, 3, 330, 1975.
10. **Anderson, D. W. and Hickey, J. J.**, Dynamics of storage of organochlorine pollutants in Herring Gulls, *Environ. Pollut.*, 10, 183, 1976.
11. **Koeman, J. H., Hadderingh, R. H., and Bijleveld, M. F. I. J.**, Persistent pollutants in the White-tailed Eagle in the Federal Republic of Germany, *Biol. Conserv.*, 4, 373, 1972.
12. **Monroe, J., Aswald, K., Burgermeister, G., Machado, L., and Tarvadelhas, J.**, PCB in a Lake Geneva ecosystem, *Ambio*, 11, 355, 1982.
13. **Thompson, W. P., Rankin, P. W., Dorsey, P. E., Williams, L. E., Jr., and Nesbitt, S. A.**, Chlorinated hydrocarbon residues in the diet and eggs of the Florida Brown Pelican, *Bull. Environ. Contam. Toxicol.*, 18, 331, 1977.
14. **Gretchen, Y. A., Gretchen, A., and Emerich, R. J.**, Insecticides, polychlorinated biphenyls and mercury in wild cormorants, pelicans, their eggs, food and environment, *Bull. Environ. Contam. Toxicol.*, 9, 321, 1973.
15. **Gretchen, Y. A., Gretchen, A., Ammann, B. C., Call, D. J., Hansman, D. C. D., and Pott, R. M.**, Insecticides, polychlorinated biphenyls and metals in African lake ecosystems, *Arch. Environ. Contam. Toxicol.*, 6, 371, 1977.
16. **Bagge, P.**, Pesticide residues in some Baltic animals. A review of selected literature, *Pure Appl. Chem.*, 42, 129, 1975.
17. **Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G.**, DDT and PCB in marine animals from Swedish waters, *Nature (London)*, 224, 247, 1969.
18. **Holdgate, M. W., Ed.**, *The Seabird Wreck of 1969 in the Irish Sea*, Natural Environmental Research Council, London, 1971.
19. **Norstrom, R. J., Hallett, D. J., and Sonstegard, R. A.**, Coho Salmon (*Oncorhynchus kisutch*) and Herring Gulls (*Larus argentatus*) as indicator of organochlorine contamination in Lake Ontario, *J. Fish. Res. Bd. Can.*, 35, 1401, 1978.
20. **Platonow, N. S., Karstad, L. H., and Stenhaupthesher, P. W.**, Tissue distribution of polychlorinated biphenyls (Aroclor 1254) in cockerels. Relation to the duration of exposure and observations on pathology, *Can. J. Comp. Med.*, 37, 90, 1973.
21. **Bolby, S. and Bunyan, P. J.**, Interpretation of persistence and effects of polychlorinated biphenyls in birds, *Nature (London)*, 236, 24, 1972.
22. **Vermeer, K. and Reynolds, L. M.**, Organochlorine residues in aquatic birds in the Canadian prairie provinces, *Can. Field Nat.*, 84, 117, 1970.

MONS 006005

23 **Peakall, D. B.**, Deaths in cold weather. *Bird Study*. 12, 146, 1965.

24 **Parslow, J. L. F. and Jefferies, D. J.**, Relationship between organochlorine residues in livers and whole bodies of guillemots. *Environ. Pollut.*. 5, 87, 1973.

25 **Heath, R. G., Spann, J. W., Hill, E. F., and Kreitzer, J. F.**, Comparative dietary toxicities of pesticides to birds. *Special Scientific Report — Wildlife*. No. 152. U.S. Department of the Interior. 1972.

26 **Hill, E. F., Heath, R. G., Spann, J. W., and Williams, J. D.**, Polychlorinated biphenyl toxicity to Japanese Quail as related to degree of chlorination. *Poult. Sci.*. 53, 597, 1974.

27 **Cecil, H. C., Harris, S. J., and Bitman, J.**, Liver mixed function oxidases in chickens: induction by polychlorinated biphenyls and lack of induction by DDT. *Arch. Environ. Contam. Toxicol.*. 7, 283, 1978.

28 **Holleman, K. A., Barnett, B. C., and Wicker, G. W.**, Response of chicks and turkey poults to Aroclor 1242. *Poult. Sci.*, 55, 2354, 1976.

29 **Dieter, M. P.**, Plasma enzyme activities in Coturnix Quail fed graded doses of DDE, polychlorinated biphenyl, malathion and mercuric chloride. *Toxicol. Appl. Pharmacol.*, 27, 86, 1974.

30 **Cain, D. J. and Harrell, B. E.**, Effects of dieldrin and PCBs upon the production and morphology of Japanese Quail eggs. *Bull. Environ. Contam. Toxicol.*, 11, 70, 1974.

31 **Hurst, J. G., Newcomer, W. S., and Morrison, J. A.**, The effects of polychlorinated biphenyl on longevity of Bobwhite Quail (*Colinus virginianus*) — a sex differential. *Proc. Soc. Exp. Biol. Med.*, 144, 431, 1973.

32 **Heinz, G. H., Hill, E. F., and Contrera, J. F.**, Dopamine and norepinephrine depletion in Ring Doves fed DDE, dieldrin and Aroclor 1254. *Toxicol. Appl. Pharmacol.*, 53, 75, 1980.

33 **Haseltine, D. and Prouty, R. M.**, Aroclor 1242 and reproductive success of adult mallards (*Anas platyrhynchos*). *Environ. Res.*, 23, 29, 1980.

34 **Mineau, P., Fox, G. A., Norstrom, R. J., Weseloh, D. V., Hallett, D. J., and Ellenton, J. A.**, Using the herring gull to monitor levels and effects of organochlorine contamination in the Canadian Great Lakes. *Adv. Environ. Sci. Technol.*, 14, 425, 1984.

35 **Lillie, R. J., Cecil, H. C., Bitman, J., and Fries, G. F.**, Differences in response of caged white leghorn layers to various polychlorinated biphenyls (PCBs) in the diet. *Poult. Sci.*, 53, 726, 1974.

36 **Britton, W. M. and Huston, T. M.**, Influence of polychlorinated biphenyls in the laying hen. *Poult. Sci.*, 52, 1620, 1973.

37 **Briggs, D. M. and Harris, J. R.**, Polychlorinated biphenyls influence on hatchability. *Poult. Sci.*, 52, 1291, 1973.

38 **Platonow, N. W. and Reinhart, B. S.**, The effects of polychlorinated biphenyls (Aroclor 1254) on chicken egg production, fertility and hatchability. *Can. J. Comp. Med.*, 37, 341, 1973.

39 **Tumasonis, C. F., Bush, B., and Baker, F. D.**, PCB levels in egg yolks associated with embryonic mortality and deformity of hatched chicks. *Arch. Environ. Contam. Toxicol.*, 1, 312, 1973.

40 **Cecil, H. C., Harris, S. J., Bitman, J., and Fries, G. F.**, Polychlorinated biphenyl-induced in liver vitamin A in Japanese Quail and rats. *Bull. Environ. Contam. Toxicol.*, 9, 179, 1973.

41 **Heath, F. G., Spann, J. W., Kreitzer, J. F., and Vance, C.**, Effects of polychlorinated biphenyls on birds. *13th Int. Ornithol. Congr.*, 1972, 475.

42 **Dahlgren, R. B. and Linder, R. L.**, Effects of polychlorinated biphenyls on pheasant reproduction, behavior and survival. *J. Wildl. Manage.*, 35, 315, 1971.

43 **Blankenship, R. W. and Anderson, D. W.**, Some effects of DDE and PCB on Mallards and their eggs. *J. Wildl. Manage.*, 39, 308, 1975.

44 **Peakall, D. B. and Peakall, M. L.**, Effect of a polychlorinated biphenyl on the reproduction of artificially and naturally incubated dove eggs. *J. Appl. Ecol.*, 10, 863, 1973.

45 **Harris, M. P. and Osborn, D.**, Effect of a polychlorinated biphenyl on the survival and breeding of Puffins. *J. Appl. Ecol.*, 10, 471, 1981.

46 **Peakall, D. B.**, Effects of polychlorinated biphenyls (PCBs) on the eggshells of Ring Doves. *Bull. Environ. Contam. Toxicol.*, 6, 100, 1971.

47 **Platonow, N. S. and Funnell, H. S.**, Anti-androgenic-like effect of polychlorinated biphenyls in Cockerels. *Vet. Rec.*, 88, 109, 1971.

48 **Ahmed, T., Arnason, G. B., and Tinsley, I. J.**, Effect of chlorinated hydrocarbons on reproductive performance of white leghorn male chickens. *Poult. Sci.*, 56, 1692, 1977.

49 **Shimmura, A.**, Effects of PCBs on gonads, sex hormone balance and reproductive processes of Japanese Quail, *Coturnix coturnix japonica*, after ingestion during sexual maturation. *Environ. Pollut. (A)*, 27, 15, 1982.

50 **Bird, D. M., Tauber, P. H., Fox, G. A., and Lagacé, P. C.**, Synergistic effects of Aroclor® 1254 and mirex on the semen characteristics of American Kestrels. *Arch. Environ. Contam. Toxicol.*, 12, 633, 1983.

51 **Carlson, R. W. and Duby, R. T.**, Embryotoxic effects of three PCBs in the chicken. *Bull. Environ. Contam. Toxicol.*, 9, 264, 1973.

MONS 006006

52. **Cecil, H. C., Bitman, J., Lillie, R. J., Fries, G. F., and Verrett, J.**, Embryotoxic and teratogenic effects in unhatched fertile eggs from hens fed polychlorinated biphenyls (PCBs). *Bull. Environ. Contam Toxicol.*, 11, 489, 1974.
53. **Peakall, D. B., Linder, J. L., and Bloom, S. E.**, Embryonic mortality and chromosomal alterations caused by Aroclor 1254 in Ring Doves. *Environ. Health Perspect.*, 1, 103, 1972.
54. **Blazak, W. F. and Marcum, J. B.**, Attempts to induce chromosomal breakage in chicken embryos with Aroclor 1242. *Poult. Sci.*, 54, 310, 1975.
55. **Jefferies, D. J.**, The delay in ovulation produced by *p,p'*-DDT and its possible significance in the field. *Ibis*, 109, 266, 1967
56. **Peakall, D. B.**, *p,p'*-DDT effect on calcium metabolism and concentration of estradiol in the blood. *Science*, 168, 592, 1970.
57. **Risebrough, R. W., Reiche, P., Peakall, D. B., Herman, S. G., and Kirven, M. N.**, Polychlorinated biphenyls in the global ecosystem. *Nature (London)*, 220, 1098, 1968.
58. **Nowicki, H. G. and Norman, A. W.**, Enhanced hepatic metabolism of testosterone, 4-androstene-3,17-dione, and estradiol 17β in chickens pretreated with DDT or PCB. *Steroids*, 19, 85, 1972.
59. **Combs, G. F., Jr., Conner, A. H., and Scott, M. L.**, Effects of dietary PCB on vitamin E and selenium nutrition in the chick. *Poult. Sci.*, 54, 1143, 1975.
60. **Turner, J. C. and Green, R. S.**, Effect of PCB on poultry. II. Induction of liver microsomal enzymes. *N.Z. J. Agric. Res.*, 19, 231, 1976
61. **Linder, J. L. and Peakall, D. B.**, Metabolic effects of polychlorinated biphenyls in the American Kestrel. *Nature (London)*, 228, 783, 1970.
62. **Risby, A. and Perry, A. S.**, Induction of the mixed-function oxidase system in the liver of the Barn Owl, *Tyto alba*, by PCBs. *Pest. Biochem. Physiol.*, 16, 72, 1981.
62a. **Ellenton, J. A., Brownlee, L. J., and Hollebone, B. R.**, Aryl hydrocarbon hydroxylase levels in herring gull embryos from different locations on the Great Lakes. *Environ. Toxicol. Chem.*, 4, 615, 1985.
63. **Walker, C. H.**, Species variations in some hepatic microsomal enzymes that metabolize xenobiotics. *Progr Drug. Metab.*, 5, 113, 1980.
64. **Walker, C. H. and Knight, G. C.**, The hepatic microsomal enzymes of seabirds and their interaction with lipoluble pollutants. *Aquat. Toxicol.*, 1, 343, 1981.
65. **Jefferies, D. J. and Parslow, J. L. F.**, Effect of one polychlorinated biphenyl on size and activity of the gull thyroid. *Bull. Environ. Contam. Toxicol.*, 8, 308, 1972.
66. **Jefferies, D. J. and Parslow, J. L. F.**, Thyroid changes in polychlorinated biphenyl-dosed guillemots and their indication of one of the mechanisms of action of these materials. *Environ. Pollut.*, 10, 293, 1976.
67. **Spear, P. A., Mearn, T. W., and Peakall, D. B.**, Liver retinoid concentrations in natural populations of herring gulls (*Larus argentatus*) contaminated with 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and in ring doves (*Streptopelia risoria*) injected with a dioxin analogue. *Can. J. Zool.*, 64, 204, 1986.
68. **Tori, G.M. and Mayer, L. F.**, Effects of polychlorinated biphenyls on the metabolic rates of Mourning Doves exposed to low ambient temperatures. *Bull. Environ. Contam. Toxicol.*, 27, 678, 1981.
69. **McCune, E. L., Savage, J. E., and O'Dell, B. L.**, Hydropericardium and ascites in chicks fed a chlorinated hydrocarbon. *Poult. Sci.*, 41, 295, 1962.
70. **Flick, D. F., O'Dell, B. G., and Childs, V. A.**, Studies of the chick edema disease. III. Similarity of symptoms produced by feeding chlorinated biphenyls. *Poult. Sci.*, 44, 1460, 1965.
71. **Rehfeld, B. M., Bradley, R. L., Sonda, J., and Sonda, M. L.**, Toxicity studies on polychlorinated biphenyls in the chick. *Poult. Sci.*, 50, 1090, 1971.
72. **Boyer, R. C. and Bird, F. H.**, Surface changes in the epicardium of chickens fed polychlorinated biphenyls. *Poult. Sci.*, 53, 737, 1974.
73. **Vos, J. G., Van Der Maas, H. L., Ten Noever De Brow, M. C., and De Vos, R. H.**, Identification and toxicological evaluation of chlorinated dibenzofurans and chlorinated naphthalene in two commercial polychlorinated biphenyls. *Food Cosmet. Toxicol.*, 8, 625, 1970.
74. **Firestone, D.**, Etiology of chick edema disease. *Environ. Health Perspect.*, 5, 59, 1973.
75. **Vos, J. G., Strik, J. J. T. W. A., Van Holsteyn, C. W. M., and Penninga, J. H.**, Polychlorinated biphenyls as inducers of hepatic porphyria in Japanese Quail, with special reference to δ-aminolevulinic acid synthetase activity, fluorescence, and residues in the liver. *Toxicol. Appl. Pharmacol.*, 20, 232, 1971.
76. **Gilbertson, M. and Fox, G. A., Chick**, edema disease and hepatic porphyria in Lake Ontario Herring Gull embryos in the early 1970. Int. Symp. Chlorinated Dioxins, Washington, 1981.
77. **Norstrom, R. J., Hallett, D. J., Simon, M., and Moloffill, M. J.**, Analysis of Great Lakes Herring Gull eggs for tetrachlorodibenzo-p-dioxins. in *Chlorinated Dioxins and Related Compounds*, Hutzinger, O., Ed., Pergamon Press, New York, 1982, 173.
78. **Friend, M. and Trainer, D. O.**, Polychlorinated biphenyl: interaction with duck hepatitis virus. *Science*, 170, 1314, 1970.
79. **Friend, M. and Trainer, D. O.**, Duck hepatitis virus interactions with DDT and dieldrin in adult mallards, *Bull. Environ. Contam. Toxicol.*, 7, 202, 1972.

MONS 006007

80. **Combe, G. F., Jr. and Scott, M. L.**, PCB stimulated selenium deficiency in the chick. *Poult. Sci.*, 54, 1352, 1975.

81. **Srebocan, V., Pompe-Gotal, J., Brmalj, V., and Plazonic, M.**, Effect of polychlorinated biphenyls Aroclor 1254 on liver gluconeogenic enzyme activities in embryonic and growing chickens. *Poult. Sci.*, 56, 732, 1977.

82. **Gilman, A. P., Peakall, D. B., Hallett, D. J., Fox, G. A., and Norstrom, R. J.**, Herring Gulls (*Larus argentatus*) as monitors of contaminants in the Great Lakes, in *Animals as Monitors of Environmental Pollutants*, National Academy of Sciences, Washington, D.C., 1979, 280.

83. **Fimreite, N., Bjert, J. E., Kveseth, N., and Brun, E.**, DDE and PCBs in eggs of Norwegian seabirds. *Astarte J. Arctic Biol.*, 10, 15, 1977.

84. **Falandysz, J.**, Chlorinated hydrocarbons in gulls from the Baltic south coast. *Mar. Pollut. Bull.*, 11, 75, 1980.

85. **Särkkä, J., Hattula, M.-L., Paasivirta, J., and Janatuinen, J.**, Mercury and chlorinated hydrocarbons in the food chain of Lake Päijänne, Finland. *Holarctic Ecol.*, 1, 328, 1978.

86. **Bourne, W. R. P. and Bogan, J. A.**, Polychlorinated biphenyls in North Atlantic seabirds. *Mar. Pollut. Bull.*, 3, 171, 1972.

87. **Mendelsohn, J. T., Risebrough, R. W., and Blondel, J.**, Contamination of the bird fauna of the Camargue by organochlorine residue. *Environ. Pollut.*, 13, 21, 1977.

88. **Gilbertson, M. and Reynolds, L.**, DDE and PCB in Canadian birds, 1969—1972, Can. Wildl. Serv. Occasional Papers, Ottawa, No. 19, 1974.

89. **Gilman, A. P., Fox, G. A., Peakall, D. B., Teeple, S. M., Carroll, T. R., and Hayman, G. T.**, Reproductive parameters and egg contaminant levels of Great Lakes Herring Gulls. *J. Wildl. Manage.*, 41, 458, 1977.

90. **Sanro, R. C., Coon, N. C., and Kolbe, E.**, Pesticide and PCB of Common Eider, Herring Gull and Great Black-backed Gull eggs. *Bull. Environ. Contam. Toxicol.*, 22, 396, 1979.

91. **Becker, P. H., Conrad, B., and Sperveslage, H.**, Vergleich der gehalte an chlorierten kohlenwasserstoffen und PCBs in Silbermowen (*Larus argentatus*) eiern von mellum 1975 und 1979, *Die Vogelwarte*, 30, 294, 1980.

92. **Jorgensen, O. H. and Kraul, I.**, Eggshell parameters and residues of PCB and DDE in eggs from Danish Herring Gulls *Larus argentatus*, *Ornis Scand.*, 5, 1973, 1974.

93. **Heinz, G. H., Hill, E. F., and Contreras, J. F.**, Dopamine and norephinephrine depletion in Ring Doves fed DDE, dieldrin and Aroclor 1254, *Toxicol. Appl. Pharmacol.*, 53, 75, 1980.

94. **Helander B., Olsson, M., and Reutergårdh, L.**, Residue levels of organochlorine and mercury compounds in unhatched eggs and the relationships to breeding success in White-tailed Sea Eagles *Haliaeetus albicilla* in Sweden, *Holarctic Ecol.*, 5, 349, 1982.

95. **Jansson, B., Jonsson, S., Olsson, M., Romberg, L., Sundström, G., and Vaz, E.**, Identification by GC-MS of phenolic metabolites of PCB and *p,p'*-DDE isolated from Baltic guillemot and seal, *Ambio*, 93, 1975.

96. **Jansson, S. and Jansson, B.**, Anthropogenic substances in seal from the Baltic: methyl sulfone metabolites of PCB and DDE, *Ambio*, 5, 257, 1976.

MONS 006008

Chapter 4

PCBs AND THE ENVIRONMENT: PERTURBATIONS OF BIOCHEMICAL SYSTEMS

Wilbert Gamble

TABLE OF CONTENTS

I. Introduction 50

II. Chemical Properties of PCBs 50

III. Glycolysis and Gluconeogenesis 50

IV. Oxidative Phosphorylation 51

V. Glycerides and Fatty Acids 52

VI. Phospholipids 53

VII. Sterols and Lipoproteins 55

VIII. Microsomal Oxidation 56

IX. Proposed Mechanisms and Conclusions 56

References 59

MONS 006009

I. INTRODUCTION

Polychlorinated biphenyls (PCBs), as a result of their employment in a number of industrial processes and products, are ubiquitous in the environment.[1,2] Reports of their apparent toxicity to humans appeared as early as 1936[3] and in more recent years.[4] Some of the untoward effects observed after PCBs exposure include chloracne, swollen eyelids, and skin pigmentation. Several enzymes and metabolic systems are altered after PCB exposure. Enzymes of (1) glycolysis and gluconeogenesis,[5-8] (2) microsomal drug metabolism,[9-11] (3) oxidative phosphorylation,[12] (4) phospholipid metabolism,[13,14] (5) triglyceride metabolism,[15] and (6) sterol metabolism[16,17] are significantly perturbed by PCBs. It is evident from the list of enzymes altered that PCBs exhibit a variety of activities. The mechanism of transport and distribution of PCBs has not been described. There is a need to find the underlying mechanism(s) of action(s) of PCBs which permits them to elicit such a diverse number of responses. In this report, a review of some selected enzymes and reactions of metabolic systems altered by PCBs is presented. The results of the action of PCBs on the various enzymes are correlated to physical and chemical properties of the PCBs and affected enzymes in order to delineate a common mechanism of action. A mechanism which is compatible with the reported experimental results is presented.

II. CHEMICAL PROPERTIES OF PCBs

PCBs are chlorinated derivatives of biphenyl. They are sparingly soluble in water[18] and soluble in nonpolar solvents.[19] Thus, by definition they are hydrophobic. The hydrophobic effect of PCBs in water is predominantly due to water per se. Strong attractive forces between water molecules are disrupted or distorted when PCBs are placed in water in contrast to ionic or polar molecules which form strong bonds to water molecules. Consequently, the solution of PCBs is resisted. In physicochemical terms, it is a loss of entropy rather than bond energy that leads to the unfavorable free energy change for the solution of PCBs in water. These properties dictate that PCBs react with hydrophobic compounds and moieties in living systems such as lipids and hydrophobic polypeptide sequences.

PCBs as manufactured for commercial use are a mixture of isomers containing primarily 21, 42, 48, 54, and 60% chlorine by weight. They are sold under a number of trade names including Aroclor® (Monsanto Company, St. Louis) and Kanaclor® (Kanegafuchi Chemical Company Ltd., Osaka, Japan). There are 210 theoretically possible isomers. PCBs are stable compounds and are known to persist in the environment. It will be shown in the following discussions that these properties of PCBs are primarily responsible for the observed responses to PCB exposure.

III. GLYCOLYSIS AND GLUCONEOGENESIS

The metabolism of carbohydrates is a carefully regulated process. Central in the process is the control of the synthesis and degradation of glycogen, as well as the maintenance of glucose concentrations in plasma. Any interference with the control of the process constitutes a metabolic insult and, left uncompensated, leads to metabolic trauma. Several studies have shown that PCBs alter the activities of key enzymes of glycolysis and gluconeogenesis. It has been shown that PCBs decrease blood glucose concentrations in rats.[5-7] The activities of the gluconeogenic enzymes phosphoenol pyruvate carboxykinase, pyruvate carboxylase, and glucose phosphatase were decreased after rats were administered PCBs. Messner et al.[8] observed that a diet containing 0.05% PCB (Clophen® T64, 60% Cl) diminished the activity of phosphoenol pyruvate carboxykinase to about 50% with a feeding period of 7 days. Fructose diphosphatase activity was lowered to a lesser extent. Higher concentrations of

MONS 006010

PCB (Clophen® T64, 0.1 and 0.2%) decreased fructose diphosphatase activity significantly. PCBs decreased the ability of the rats to adapt phosphoenol pyruvate carboxykinase activity to gluconeogenic conditions.

Another important enzyme in the dynamic regulation of glucose metabolism is phosphorylase, the enzyme which catalyzes the breakdown of glycogen to glucose-1-phosphate. Its activities have been shown to be controlled by both covalent and allosteric modifications.[20-22] The enzyme exists in two metabolically significant forms, phosphorylase a and b. Phosphorylase b is converted to phosphorylase a by the action of phosphorylase kinase via phosphorylation of a single amino acid (serine 14) per monomer. Phosphorylase b requires AMP for activity and is inhibited allosterically by ATP, ADP, and glucose-6-phosphate. Phosphorylase a has no significant nucleotide requirement for activity. The amino acid sequence[23] and crystal structure of phosphorylase have been determined.[24,25] This information has been employed to describe the folding of the whole molecule and the loci of several binding sites for substrates and effectors. The AMP binding site of phosphorylase b is hydrophobic in nature.[26] Adenine derivatives substituted with hydrophobic groups with increasing substituent constant π value[27] were the most effective inhibitors. Soman and Philip[28,29] reported that soluble aromatic compounds, such as dinitrophenol, are allosteric inhibitors of phosphorylase b. The binding sites of the compounds were hydrophobic and the relative effectiveness of the inhibitors increased with the degree of hydrophobicity as indicated by the π values. It is widely accepted that the active site of phosphorylase is located in a crevice between two main domains in a hydrophobic pocket. Mead et al.[30] observed and investigated the differential inhibition of phosphorylase a and b by halogenated biphenyls and biphenylols. Polychlorinated biphenyls, polychlorinated biphenylols, and polybrominated biphenyls inhibited both phosphorylase a and phosphorylase b. The degree of inhibition was dependent upon the relative hydrophobicity of the compounds and steric hindrance. 2,4,5,2',4',5'-Hexachlorobiphenyl and 2,4,5,2',4',5'-hexabromobiphenyl did not significantly inhibit phosphorylase a. 2,4,5,2',4',5'-Hexabromobiphenyl and Firemaster BP-6 (a mixture of polybrominated biphenyls) were the most effective inhibitors (K_i, 15×10^{-6} *M*). Kinetic analysis showed the inhibition to be noncompetitive and mixed. It was concluded that the compounds bind to hydrophobic site(s) on phosphorylase, access to which is limited by phosphorylation of serine 14.

One can discern from the results of the studies presented that PCBs inhibit both enzymes involved in the synthesis and degradation of glycogen. The results indicate that the ability of PCBs to bind to hydrophobic domains of peptides is involved in the inhibition of glycogenolysis and suggest that similar interaction might occur with gluconeogenic enzymes.

IV. OXIDATIVE PHOSPHORYLATION

An in vitro study of the action of Aroclors® (1221, 1232, 1242, 1248, 1254, 1260, and 1262) on mitochondrial enzymes has been reported by Pardini.[12] Beef heart mitochondrial NADH-oxidase activity and succinic oxidase activity were inhibited by Aroclors® at 33 μM concentration. The inhibition range was 80 to 100%. There was no apparent inhibition of cytochrome oxidase as evidenced by the lack of inhibition by PCBs in the presence of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD). At the level tested, each Aroclor® elicited similar inhibition. The results suggest the inhibition occurs at NADH-cytochrome *c* reductase and succinate-cytochrome *c* reductase. Chesney and Allen[31] reported that Aroclors® 1248 and 1254 fed at 1000 ppm for 3 weeks to rats caused alterations in respiration and oxidative phosphorylation by liver mitochondria. When ADP was limited (state 4, no added exogenous ADP), there was a slight decrease in respiration with glutamate as substrate, but a greater than 75% increase over control mitochondria when succinate was the substrate. In state 3 (exogenous ADP added), there was a 50% increase of the Aroclor® experimental

MONS 006011

mitochondria over the controls with both substrates. The ADP/O ratios increased 11 to 16.6% in liver mitochondria from Aroclor®-treated rats. No significant differences in respiration and oxidative phosphorylation by hepatic mitochondria from rats fed 100 ppm PCBs for 20 weeks were observed. Mitochondria from rats fed low levels (100 ppm) of PCBs had 0.3 μg PCBs per milligram mitochondrial protein, whereas mitochondria from rats fed 1000 ppm had 2 to 3 μg PCBs per milligram mitochondrial protein. In vitro studies with mitochondria showed that concentrations of 50 μg/mg protein and above caused decreased respiration and oxidative phosphorylation in states 3 and 4 with both substrates. It was concluded that the amounts found in the mitochondria after in vivo treatment were insufficient to cause inhibition, since in vitro levels of 1 and 10 μg/mg mitochondrial protein had no significant effect. Aroclor® 1254 administered to rats for 2 weeks in the diet at 500 ppm increased the oxidation of succinate by liver mitochondria and caused a small but significant decrease in the ATP/O ratio (mol ADP used per atom mol O used) according to Gartholf and co-workers.[33] After 3 weeks of treatment, the liver contents of ATP and ADP were increased when expressed as micromoles per gram liver divided by gram DNA per gram liver, but not significantly altered when expressed as micromoles per gram wet liver. The mitochondrial matrix [NAD^+]/[NADH] ratio (glutamate substrate) was increased. The cristae [NAD^+]/[NADH] ratio β-hydroxybutyrate substrate) was slightly decreased. The cytoplasmic [NAD^+]/[NADH] ratio was decreased (32%) and the [$NADP^+$]/[NADPH] ratio was decreased (50%). PCBs of low chlorine content inhibited electron transfer in rat liver mitochondria at all concentrations in vitro in states 3 and 4, whereas PCBs of high chlorine content inhibited electron transfer at low concentration and uncoupled oxidative phosphorylation at higher concentration.[33] Similarly, PCBs were shown to uncouple respiration in cockroach muscle mitochondria.[34]

Yap et al.[35] and Koch and co-workers[36] have shown that PCBs in vitro inhibit Mg^{2+} ATPase and Na^+-K^+ ATPase activity and oligomycin-insensitive Mg^{2+} ATPase activity in fish. Inhibition was observed in brain, kidney, and liver. They observed in vivo inhibition and stimulation of ATPase activity. Stimulation occurred at the lower concentrations. PCBs were shown to inhibit (10 and 100 ppm) and stimulate (500 ppm) kidney and brain Na^+-K^+-ATPase and Mg^{2+} ATPase activities, and to inhibit (10, 100, 500 ppm) liver Na^+-K^+ ATPase and Mg^{2+} ATPase activities in vivo in rats.[37]

The effect of PCBs on oxidative phosphorylation, it is clear, is a function of the mitochondrial concentration. In vivo exposure yields relatively low organelle concentrations even at a 1000 ppm dose. The low levels give rise to increased respiration and increased adenine nucleotide liver content. In vitro studies indicate that high concentrations of PCBs inhibit respiration and uncouple oxidative phosphorylation.

It has been suggested by Chesney and Allen[21] that induction of hepatic mitochondrial activity may have occurred in rats treated with PCBs or the increase in respiration and oxidative phosphorylation may reflect a need for an increase in the amount of cellular ATP. The latter seems to be the more reasonable explanation of the observed results. ATPase activities are altered by PCBs, which no doubt alter cellular ATP balance and contribute to the observed gross responses to PCBs.

V. GLYCERIDES AND FATTY ACIDS

PCBs have been shown to alter the concentration, metabolism, and mobilization of lipids. Oral administration of Kanaclor® 400 induced hyperglyceridemia in rabbits.[15] After 4 weeks of treatment, free fatty acids and triglycerides in skin lipids of the rat were reduced.[15] One percent chlorobiphenyls in olive oil administered orally to rabbits for 3 days increased the content of total lipids and glycerides of liver, but did not alter serum glyceride concentrations.[38] After 11 days of administration of PCBs, the content of total lipids and glycerides

MONS 006012

of liver and the concentration of serum glycerides were increased. Similarly increased triglycerides content after 4 weeks of administration of Aroclor® at 0.5 to 500 ppm was reported by Litterst et al.[79] An investigation of the effect of the administration of PCB (0.1% w/w) in the diet fed to rats for 30 days on glyceride biosynthesis has been reported by Dzogbefia et al.[13] In mitochondria, the incorporation of [^{14}C]sn-glycerol-3-phosphate into monoglycerides (89%), diglycerides (16-fold), and triglycerides (6.8-fold) was increased. Incorporation of [^{14}C]palmitate into monoglycerides (1.6-fold) and diglycerides (35%) was increased by the PCB treatment, whereas incorporation into triglycerides was decreased (70%). Rat liver microsomal incorporation of [^{14}C]sn-glycerol-3-phosphate into mono-, di-, and triglycerides was not significantly altered. Similarly, incorporation of [^{14}C]palmityl CoA by microsomes into mono-, di-, and triglycerides was not significantly changed. There was increased incorporation of [^{14}C]sn-glycerol-3-phosphate by liver homogenates into monoglycerides (2.4-fold), diglycerides (13.8-fold), and triglycerides (10-fold). The incorporation of [^{14}C]palmitate by liver homogenates into triglycerides increased (70-fold), and into monoglycerides and diglycerides decreased 44% and 18-fold, respectively. Dzogbefia et al.[13] found that PCB in vitro increased (50%) the incorporation of [^{14}C]sn-glycerol-3-phosphate into total glycerides by rat liver microsomes. On the other hand, PCB inhibited the incorporation of [^{14}C]sn-glycerol-3-phosphate into triglycerides (76%), diglycerides (28%), and monoglycerides (26%) in homogenates in vitro. 2,4,5,2',4',5'-Hexachlorobiphenyl similarly decreased the incorporation of [^{14}C]sn-glycerol-3-phosphate by liver homogenates into glycerides (28%). Some time (72 hr) after administration of a single oral dose (50 mg/kg body weight) each of three PCB isomers, 3,4,5,3',4',5'-hexachlorobiphenyl, 2,4,5,2',4',5'-hexachlorobiphenyl, and 2,3,5,2',3',5'-hexachlorobiphenyl, it was found[14] that only 3,4,5,3',4',5'-hexachlorobiphenyl altered rat liver triglyceride content (sevenfold increase).

Kling and co-workers[40] investigated the in vivo and in vitro effect of Aroclor® 1254 on fatty acid synthesis. Aroclor® (0.1% w/w — 30 days in the diet) inhibited the incorporation of tritiated water (83%) and acetate (43%) into fatty acids. However, after 60 min incubation in vivo, there was an apparent increase in acetate incorporation into fatty acids while incorporation of tritiated water remained depressed. Aroclor® (50 ppm) inhibited (73%) the in vitro incorporation of acetate into fatty acids. Citrate cleavage enzyme which provides precursor for fatty acid synthesis was inhibited in vitro[40] and in vivo[41] by PCBs. However, no significant effect of PCBs on fatty acid synthase and acetyl CoA carboxylase, the rate limiting enzyme in fatty acid synthesis, was observed.[40] Yeast cells incubated with Aroclors®[42] exhibited decreased synthesis of fatty acids after 15 hr, whereas prolonged treatment up to 42 hr resulted in no significant change.[42] The biosynthesis of unsaturated fatty acids (C16:1 and C18:1) was decreased the most. Aroclors® of lower chlorine[43] content were more effective than those of higher chlorine content.[42] It is interesting to note that PCBs decrease synthesis of fatty acids during initial periods and either have no effect or increase synthesis upon prolonged incubation. These results were observed both in yeast[42] and in rat liver.[40]

Although, as can be seen from the literature cited, there are variations in response, PCBs primarily increase the synthesis of triglycerides. The increase appears to be due to a shift of common precursors from phospholipid synthesis to glyceride synthesis. The suggestion that liver lipase activity may be inhibited has not been experimentally substantiated, although serum lipoprotein lipase is apparently inhibited.

VI. PHOSPHOLIPIDS

Several authors[13,16,44-46] have observed both inhibition and stimulation and synthesis of phospholipids by PCBs. Elevated phospholipid levels in livers of laboratory animals following PCB administration have been reported.[13,43] Ishidate and Nakazawa[43] reported that

MONS 006013

rat liver microsomal phospholipid synthesis was decreased, whereas phospholipid content was increased after oral administration of suspensions of PCBs in 2% (w/v) sodium carboxycellulose daily for 3 days at 100 mg/kg/day, followed by intraperitoneal injection of [^{32}P] orthophosphate, [Me-^{14}C]choline, or [^{3}H]glycerol. Decreases in incorporation of the first two substrates into choline-containing phospholipids were observed, but not into other phospholipids. [^{3}H]Glycerol incorporation into total phospholipids was decreased after 15 min, but not significantly altered after 60 min. They suggested that the observed increased content of microsomal phospholipid was due to inhibition of catabolism of phospholipids.

When rats were administered Aroclor® 1254 by intraperitoneal injection (20 or 50 mg/kg) for 3 or 6 days, decreased synthesis and turnover of phospholipids occurred.[44] [^{14}C]Glycerol incorporation into phospholipids of homogenates and microsomes declined over a 10-min period when reported as disintegrations per minute per milligram phospholipid. The half-life of the radioactivity in the total phospholipid pool after a single injection of [^{14}C]glycerol was prolonged from 10 (control) to 20 hr (PCB) in homogenates and from 8 (control) to 13 hr (PCB) in microsomes.

Inhibition of [^{14}C]ethanolamine incorporation into phosphatidyl ethanolamine and stimulation of [^{14}C]choline into phosphatidyl choline by mouse L5178Y lymphoma cells in vitro was caused by exposure of the cells to 4-chlorobiphenyl.[45] There was no apparent increase in total phospholipid content after 60 min incubation. It was concluded that the enhanced incorporation of [^{14}C]choline into phosphatidyl choline was due to increased turnover of phosphatidyl choline.

After intraperitoneal injection of 2,4,2',4'-tetrachlorobiphenyl at 50 mg/kg body weight in peanut oil successively for 3 days, Holub et al.[46] found no significant change in the activities of acyl CoA:sn-glycerol-3-phosphate acyl transferase, CDP-choline:1,2 diacyl-sn-glycerol choline-phosphotransferase, acyl CoA:1,2-diacyl-sn-glycerol acyltransferase, and acyl CoA:1,acyl-sn-glycerol-3-phosphorylcholine acyltransferase. However, in vitro addition of 2,4,2',4'-tetrachlorobiphenyl (40 ppm) to rat liver microsomes caused inhibition (44%) of acyl CoA:sn-glycerol-3-phosphate acyltransferase and acyl CoA:1,acyl-sn-glycerol-3-phosphorycholine acyltransferase, whereas CDP-choline:1,2-diacyl-sn-glycerol choline phosphotransferase was stimulated 44%.

The effects of a single oral dose (50 mg/kg body weight) each of 3,4,5,3',4',5'-hexachlorobiphenyl, 2,4,5,2',4',5'-hexachlorobiphenyl, and 2,3,5,2',3',5'-hexachlorobiphenyl for 72 hr on liver phospholipids have been compared by Kohli et al.[18] Significant decreases in total phospholipids of liver were observed when the data were expressed as milligram per gram fresh liver for control and 2,4,5,2',4',5'-hexachlorobiphenyl-treated and 2,3,5,2',3',5'-hexachlorobiphenyl (approximately 12 to 13%), whereas 3,4,5,3',4',5'-hexachlorobiphenyl had no significant effect.

It should be noted that all of the above-mentioned studies employed short periods of treatment with PCBs, 3 to 6 days at the most. An assessment of the chronic effects of PCBs on phospholipid biosynthesis has been made by Dzogbefia et al.[13] The authors treated rats with Aroclor® 1254 (0.1% w/v) in the diet for 30 days. They observed an increase in the incorporation of [^{14}C]glycerol-3-phosphate into total phospholipids by rat liver mitochondria (14-fold), microsomes (1.7-fold), and homogenates (13.8-fold). Incorporation of [^{14}C]palmitate into total phospholipids by mitochondria and homogenates was increased 76 and 56%, respectively. However, microsomal incorporation of [^{14}C]palmityl CoA into phospholipids was not significantly altered. Dzogbefia and co-workers[13] in parallel in vitro experiments showed that PCBs inhibit (34%) the incorporation of [^{14}C]sn-glycerol-3-phosphate into total phospholipids of homogenates. PCBs inhibited microsomal incorporation of [^{14}C]sn-glycerol-3-phosphate into lysophosphatidate (77%), lysophosphatidyl choline, and phosphatidyl ethanolamine (36%). Similarly, 2,4,5,2',4',5'-hexachlorobiphenyl was shown to inhibit phospholipid biosynthesis in vitro.

MONS 006014

Administration of PCBs, it is clear from the literature cited, alters phospholipid metabolism. Inhibition of synthesis and catabolism occurs after acute in vivo and in vitro treatment. Relatively long-term administration of PCBs elicits increased synthesis of phospholipids. The apparent differences are most likely a reflection of the amounts of PCBs present at the locus of synthesis and catabolism at a given time. Chronic accumulation of PCBs appears to elicit several cellular responses which result in increased production of endoplasmic reticulum and lamellar membranes. Increased membrane production requires more phospholipid synthesis. Direct interaction of PCBs with certain enzymes in the process results in inhibition as seen in the in vitro studies. The observed response at a given time period is a result of the several interactions of PCBs with hydrophobic domains of proteins and lipids per se.

VII. STEROLS AND LIPOPROTEINS

After administering PCBs to rabbits, Koller and Zinkl[17] observed increased serum cholesterol levels. Elevated serum cholesterol levels were found in clinical cases of human PCB poisoning[13] and in rats treated orally with 500 ppm Aroclor® 1254.[12] Oral administration of Aroclor® 1254 at a dose of 1 mg/100 g body weight/day to rats for 12 days caused an increase in liver sterols and sterol esters.[11] A single oral dose of 3,4,5,3',4',5'-hexachlorobiphenyl after 72 hr caused an increase in total liver cholesterol (milligram per gram liver), according to Kohli and co-workers.[16] Livers from rats administered 2,3,5,2',3',5'-hexachlorobiphenyl showed a small decrease in total cholesterol compared to controls when results were expressed as milligram per gram liver, whereas those from rats administered 2,4,5,2',4',5'-hexachlorobiphenyl caused an increase in cholesterol ester (milligram per gram liver), but no significant change in free cholesterol (milligram per gram liver). In contrast, expression of the results as milligrams/100 g body weight yielded increases in ester and total cholesterol biosynthesis in rat livers. Kling and Gamble[47] have investigated the in vivo and in vitro effects of Aroclor® 1254 on cholesterol biosynthesis in rat livers. PCB at a dose of 0.1% w/w of the diet for 30 days decreased the conversion of [^{14}C]mevalonate (26%) and [^{14}C]acetate (29%) to cholesterol. After 30 days of PCB treatment followed by intraperitoneal injection of H_2^3O, [^{14}C]mevalonate, and [^{14}C]acetate, cholesterol biosynthesis was decreased with each substrate. In vitro, PCB (500 ppm) inhibited the incorporation of [^{14}C]mevalonate into cholesterol (86%) and [^{14}C]acetate into cholesterol (90%). It was found that cholesterol biosynthesis was inhibited between squalene and cholesterol, primarily at the demethylation and rearrangement reactions.[47] Aroclor® 1232 inhibited sterol biosynthesis in yeast (*Saccharomyces cerevisiae*) with a concomitant accumulation of squalene.[43] There were relatively large decreases in ergosterol and episterol synthesis, accompanied by smaller decreases in lanosterol and zymosterol synthesis. It was suggested that the results may be due to inhibition of squalene epoxidase and 2,3-oxidosqualene cyclase, because squalene accumulates and PCBs inhibit electron transport.

The effect of Aroclor® 1254 administered intraperitoneally (5 mg/100 g body weight) to rats for 6 to 8 days on the lipid composition of very low-density lipoproteins (VLDL) of rat liver microsomes, liver Golgi, and serum has been reported.[48] Although PCB treatment increased the amounts microgram per gram liver) of phospholipids, cholesterol, triglycerides, and total lipids, the percent composition of the lipids of microsomal VLDL did not significantly change. The rate of [^{14}C]glycerol incorporation into the triglycerides and total lipids of microsomes was enhanced by PCB. In contrast, a decreased labeling rate of lipoprotein triglycerides and total lipids of the Golgi apparatus was observed. The authors suggested that there was impairment of transport of VLDL particles from the endoplasmic reticulum to the Golgi apparatus. Since there was cytoplasmic accumulation, it was suggested that the lipids could not be exported from the cells, but were degraded intracellularly. Otshi[49] reported

MONS 006015

that PCBs increase rat serum β-globulin and decrease α_1-globulins. These results suggest that the changes in serum lipid composition observed after PCB administration may be related to alterations in plasma transport protein concentrations.

PCBs, it appears, primarily inhibit cholesterol metabolism. There may be species differences and differences in results due to acute or chronic exposure to PCBs as well as different doses. Increased serum levels of cholesterol observed after PCB exposure may be due to actions of PCBs on lipoprotein metabolism and transport.

VIII. MICROSOMAL OXIDATION

The interaction of PCBs with drug metabolizing enzymes is one of the most widely studied aspects of PCB toxicity. A detailed discussion of the subject is beyond the scope of this report. Briefly, it can be stated that, in general, administration of PCBs to animals induces drug metabolizing enzymes in the liver. Aniline hydroxylase, aminopyrine *N*-demethylase, cytochrome P-450, benzpyrene hydroxylase,[9] nitroreductase,[10] and *p*-nitroanisole-*o*-demethylase activities have been shown to be induced by PCBs.[11] It has been reported that enzymes induced by PCBs have different kinetic properties from the noninduced enzymes and are inhibited in vitro by PCBs.[10] Only aminopyrine demethylation was inhibited in microsomes from normal (control) rats. PCBs in vitro inhibited *p*-nitroanisole demethylation and aminopryine demethylation in microsomes of PCB-treated rats.

IX. PROPOSED MECHANISMS AND CONCLUSIONS

One can readily conclude from the above review of the literature that PCBs elicit a variety of profound effects on biochemical systems. One organ often affected is the liver. The morphological changes in the liver after PCB treatment of mice, rabbits, and rats serve to illustrate the characteristic alterations. In hepatocytes, the number of lipid bodies and mitochondria per cell is increased in livers from PCB-treated animals.[21] The mean cell volume, mean nuclear volume, and mean cytoplasmic volume are increased. The volumes of cytoplasmic components, liposomes, and rough and smooth endoplasmic reticulum are increased. It appears that the cellular response to PCBs is an enhancement or augmentation of the normal cellular processes which determine the morphological characteristics of cells. Some changes are relatively nonspecific such as the increased lipids and lipid bodies, which occur(s) with other lipophilic drugs and toxicants. Similarly, the proliferation of smooth endoplasmic reticulum is stimulated by drugs and toxicants to permit the cell to metabolize lipophilic compounds. The rough endoplasmic reticulum correspondingly is increased since it is thought to be a precursor of smooth endoplasmic reticulum.[22] It has been suggested[3] that the enlarged cells would have increased energy demands and demands for digestion, resulting in greater numbers of mitochrondria and liposomes per cell.

Some of the observed responses to PCB may be due to indirect actions. Consequently, it may not be possible to describe a mechanism which explains all of the effects of PCBs on living systems. However, a mechanism which explains the fundamental alterations in biochemical systems elicited by PCBs is desirable and perhaps more attainable. Perhaps the most outstanding chemical property of PCBs is their hydrophobicity. They have limited solubility and adhere readily to surfaces, including glass and plastics. They vary in their degree of chlorination and positional location of the chlorines. The molecules lacking substitution of chlorine in the 2,2',6, and 6' positions are planar or nearly so, whereas those possessing chlorine in those positions are nonplanar. They are soluble in lipids having larger partition coefficients for triolein/water than for phospholipid/water[23] due to the formation of bilayers by phospholipids and concomitant presence of surface charges. They are aromatic and this property has been shown to contribute to their interaction with enzymes.[10] PCBs

MONS 006016

were shown to inhibit phosphorylase, presumably by binding to the hydrophobic site on that enzyme, normally occupied by AMP. PCBs bind to albumin and low density lipoproteins,[14] proteins especially constituted to bind lipophilic molecules. Their capacity to bind to other molecules and alter their activities is a function of their conformations in addition to their hydrophobic properties. This point was illustrated by Poland and Glover,[15] who established the structure-activity relationship for the induction of aryl hydrocarbon hydroxylase activity in chick embryo liver. There are two apparent structural requirements for induction, the presence of at least two adjacent halogen atoms in the lateral positions of each benzene ring (positions 3,4,3',4' or 3,4,5,3',4',5') and the absence of halogen atoms adjacent to the biphenyl bridge (positions 2,6,2',6'). Mead and co-workers[10] observed that the positional location of the chlorine atom determined whether or not polychlorinated biphenylols inhibited phosphylase a. The active site of the enzyme is in a hydrophobic pocket of sufficient dimensions (6 × 8 × 20 Å) to allow entry of the halogenated biphenyls. It was suggested that steric hindrance prevented certain PCBs from entry into the hydrophobic pocket. That there is specificity of binding of PCBs to proteins was shown in the experiments of Poland and Glover[15] in which congeners having chlorine atoms in the 2,2',6,' position did not induce arylhydroxylase and did not bind to the hepatic cytosol binding protein, whereas those having the prerequisite of at least two adjacent halogen atoms in lateral positions of each benzene rings did bind the cytosol binding protein and induce aryl hydroxylase activity.

PCBs, it can be concluded, are lipophilic aromatic compounds which bind to hydrophobic domains of proteins and associate freely, with the nonpolar moieties of lipids. They are distributed in several tissues when administered to animals.[26-28] The rates of excretion are a function of the degree and positional location of the chlorine atoms, both of which dictate the rates of metabolism.[29-61] PCBs and their metabolites are excreted in the urine and feces, the latter being the major route.[26-28] The major storage sites for the nonexcreted PCBs are adipose tissue, liver, skin, and muscle.[28] The mechanism(s) by which they reach tissues and intracellular loci is not known. Environmental exposure to PCBs occurs usually via the diet or topically. Experimentally, PCBs have been administered orally, intraperitoneally, and topically. They have been shown to bind to lipoproteins[54] and albumin.[54] The lipoproteins are the most probable carrier molecules for PCBs. They will bind to any hydrophobic molecule, which suggests that other hydrophobic protein, carbohydrates, or lipid domains can act as carriers.

All of the presented factors considered, it is proposed that PCBs elicit the responses observed with biochemical systems by the following mechanism. A diagramatic description is shown in Figure 1. PCBs bind to the hydrophobic moieties of the carrier molecules lipoproteins, albumin, and other hydrophobic proteins. They form water-soluble "inclusion" complexes. These complexes are transported via the blood to the constituent tissues. PCBs "inclusion" complexes are passed from the blood capillary lumen by interaction of the lipoprotein — PCB inclusion complex (or other hydrophobic protein — PCB inclusion complexes) with the plasma membrane of the endothelial cell. They then pass through the transcellular channels in endothelium to the plasma membrane of the cells. The complex is taken up by the cells via endocytosis through the plasma membrane. The path taken at this juncture is primarily a function of the normal fate of the carrier molecule. For the sake of simplicity, let us assume the carrier molecule is a lipoprotein, either a chylomicron or a low density lipoprotein (LDL). The LDL-PCB inclusion complex enters the lysosome. The LDL is metabolized and the PCB is released. It associates immediately with the hydrophobic molecules of any LDL residual product or other proteins. When the PCB associates with endoplasmic reticulum, a conformational ordering occurs which results in lamellar structures (in some instances). These changes result from an interaction of the complex with water, a phenomenon described by Tanford[59] in his description of the hydrophobic effect. When the released PCBs bind to hydrophobic domains on an enzyme, the activity of the enzyme will

MONS 006017

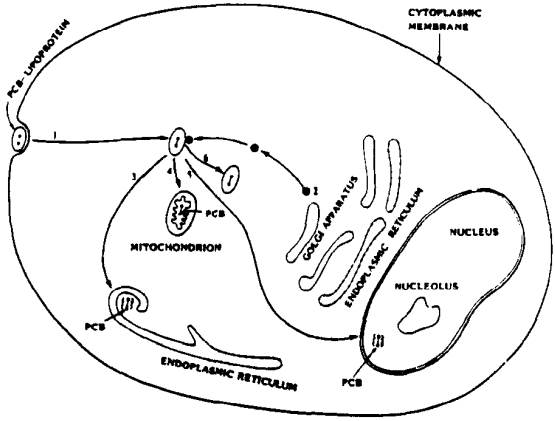


FIGURE 1. A diagrammatic representation of PCB-lipoprotein cellular interaction. (1) Endocytosis of the PCB-lipoprotein complex. (2) A primary lysosome fuses with the PCB-lipoprotein complex. (3) The lipoprotein moiety is metabolized and the PCB-protein remnant associates with the endoplasmic reticulum. (4) Uptake of the PCB-protein complex by the mitochondrion. (5) Uptake of the PCB-protein complex by the nucleus. (6) Formation of a PCB-protein-lipid cytoplasmic vesicle.

be altered in a manner which is a function of the locus of binding and the amount bound. If the hydrophobic site is at, or near, the active site, inhibition occurs. On the other hand, if the hydrophobic site is in some other locus than the active site, a conformational change will occur which may result in either stimulation or inhibition or both, depending upon the amount bound.

When the carrier PCB complex is a chylomicron-PCB inclusion complex, the complex will enter the adipocyte of adipose tissue as described above for cells in general. Metabolism of the chylomicron releases PCBs along with fatty acids. The large quantities of triglycerides present solubilize the PCBs and they remain there until fat is mobilized.

In some instances, PCBs form complexes with proteins and lipids which are not readily metabolized. These cause accumulation of PCB-protein-lipid complexes in vesicular and lamellar structural arrays. As pointed out earlier in this section, PCBs bind to some proteins which participate in gene expression and result in the induction of new enzyme protein. In all of these processes, it is the physicochemical property of PCBs to bind to hydrophobic moieties and form complexes which assemble in ordered arrays such that the PCB-water interaction is minimized that is the driving force.

The gross response observed with PCBs is the vector sums of the interaction with and exchange between the given hydrophobic domains in the biochemical systems. In some cases, the PCBs are covalently modified. The properties of these modified PCBs may be quite different; the observed responses in turn may be different. These are secondary to the initial interaction of the parent compound with the system. Hydroxypolychlorinated biphenyls are the major products of covalent modification.

MONS 006018

REFERENCES

1. Jensen, S., Report of a new chemical hazard, *New Sci.*, 32, 612, 1966.
2. Fishbein, L., Toxicity of chlorinated biphenyls, *Ann. Rev. Pharmacol.*, 14, 139, 1974.
3. Jones, F. N. and Alden, H. I., Acneform dermatogosis, *Arch. Dermatol. Syphol.* 33, 1022, 1936.
4. Kuratsune, M., An epidemiologic study on "Yusho" or chlorophenyls poisoning, *Fukuoka Acta Med.* 60, 403, 1969.
5. Mehlman, M. A., Friend, B., and Tobin, R. B., The effect of polychlorinated biphenyls on liver gluconeogenic enzyme activities in rats during exposure to cold, *Toxicology*, 2, 301, 1974.
6. Mehlman, M. A., Tobin, R. B., Friend, B., and Mackerer, C. R., The effects of polychlorinated biphenyl mixture (Aroclor 1254) on liver gluconeogenic enzymes of normal and alloxan-diabetic rats, *Toxicology*, 5, 89, 1975.
7. Friend, B., Tobin, R. B., Mehlman, M. A., and Mackerer, C., Effect of Aroclor 1254 (AR) on liver gluconeogenic enzyme activities and on blood glucose levels of normal and alloxan-diabetic rats, *Pharmacologist*, 15, 188, 1973.
8. Messner, B., Berndt, J., and Stift, J., Inhibition of PEP-carboxykinase in rat liver by polychlorinated biphenyls, *Nature (London)*, 263, 599, 1976.
9. Shimada, T. and Ugawa, M., Induction of liver drug metabolism by polychlorinated biphenyls whose gas chromatographic profile having much in common with that in human milk, *Bull. Environ. Contam. Toxicol.*, 19, 198, 1978.
10. Goldstein, J. A., Hickman, P., Burse, V. W., and Bergman, H., A comparative study of two polychlorinated biphenyl mixtures (Aroclors 1242 and 1016) containing 42% chlorine on induction of hepatic porphyria and drug metabolizing enzymes, *Toxicol. Appl. Pharmacol.*, 32, 461, 1975.
11. Hansell, M. M., Echebichon, D. J., Comeau, A. M., and Cameron, P. H., The relationship between retention of pure chlorobiphenyl congeners and hepatic function in the rat, *Exp. Mol. Pathol.*, 26, 75, 1975.
12. Pardini, R. S., Polychlorinated biphenyls (PCB): effect on mitochondrial enzyme systems, *Bull. Environ. Contam. Toxicol.*, 6, 539, 1971.
13. Dragoeffo, V. P., Kling, D., and Gamble, W., Polychlorinated biphenyls *in vivo* and *in vitro* modifications of phospholipids and glyceride biosynthesis, *J. Environ. Pathol. Toxicol.*, 1, 841, 1978.
14. Kohli, K. K., Gupta, B. N., Albro, P. W., Mushtaq, H., and McKinney, J. D., Biochemical effects of pure isomers of hexachlorobiphenyl: fatty livers and cell structure, *Chem. Biol. Interact.*, 25, 139, 1979.
15. Usuwa, H., Ito, Y., Natsui, A., Hori, S., Tiburu, Y., and Katsuki, S., Clinical and experimental studies on the hyperglyceridemia induced by oral ingestion of chlorinated biphenyls, *Fukuoka-Igaku-Zasshi*, 62, 66, 1971.
16. Linzer, J. L. and Peakall, D. B., Metabolic effects of polychlorinated biphenyls in the American kestrel, *Nature (London)*, 228, 783, 1970.
17. Keller, L. D. and Zinkl, J. G., Pathology of polychlorinated biphenyls in rabbits, *Am. J. Pathol.*, 70, 363, 1973.
18. Wallnofer, P. R., Kreiger, M., and Hutzinger, O., The solubilities of twenty-one chlorobiphenyls in water, *Anal. Chem. Inc. Res. Notes*, 13, 14, 1973.
19. Hutzinger, O., Safe, S., and Zitko, V., *The Chemistry of PCB's*, CRC Press, Cleveland, 1974, 7.
20. Fischer, E. H., Pocker, A., and Saari, J. C., The structure, function and control of glycogen degradation, *Essays Biochem.*, 6, 23, 1970.
21. Fischer, E. H., Heilmeyer, L. M. C., Jr., and Haschke, R. H., Phosphorylase and the control of glycogen degradation, *Curr. Top. Cell. Regul.*, 4, 211, 1971.
22. Graves, D. J. and Wang, J. H., *The Enzymes*, 3rd ed., 7, 435, 1972.
23. Titani, K., Koide, A., Hermann, J., Ericsson, L. H., Kumar, S., Wade, R. D., Walsh, K. A., Neurath, H., and Fischer, E. H., Complete amino acid sequence of rabbit muscle glycogen phosphorylase, *Natl. Acad. Sci. U.S.A.*, 74, 4762, 1977.
24. Fletterick, R. J., Sygusch, J., Semple, H., and Madsen, N. H., Structure of glucagon phosphorylase a at 3.0 Å resolution and its ligand binding sites at 6 Å, *J. Biol. Chem.*, 251, 6142, 1976.
25. Weber, I. T., Johnson, L. N., Wilson, K. S., Yeates, D. G. R., Wild, D. L., and Jenkins, J. A., Crystallographic studies on the activity of glycogen phosphorylase b, *Nature (London)*, 274, 433, 1978.
26. Anderson, R. A. and Graves, D. J., Chemistry of the adenosine monophosphate site of rabbit muscle glycogen phosphorylase. I. Hydrophobic nature and affinity of labeling of the allosteric site, *Biochemistry*, 12, 1895, 1973.
27. Fujita, T., Iwasa, J., and Hansch, C., A new substituent constant π, derived from partition coefficients, *J. Am. Chem. Soc.*, 86, 5175, 1964.
28. Soman, G. and Philip, G., The nature of the binding site for aromatic compounds in glycogen phosphorylase b, *Biochem. J.*, 147, 309, 1975.
29. Soman, G. and Philip, G., The binding sites for substrate and effectors on glycogen phosphorylase b, *Biochim. Biophys. Acta*, 358, 359, 1974.

MONS 006019

30 **Mead, R. C., Hart, M. H., and Gamble, W.,** Inhibition of purified rabbit muscle phosphorylase a and phosphorylase b by polychlorinated biphenyls, polychlorinated biphenylols and polybrominated biphenyls, *Biochim. Biophys. Acta*, 701, 173, 1982.

31 **Chesney, C. F. and Allen, J. R.,** Oxidative phosphorylation and respiration by liver mitochondria from polychlorinated biphenyl-intoxicated rats, *Biochem. Pharmacol.*, 23, 1577, 1974.

32 **Garthoff, L. H., Friedman, L., Farber, T. M., Locke, K. K., Sobitka, T. J., Green, S., Hurley, W. E., Peters, E. L., Story, G. E., Moreland, F. M., Graham, C. H., Kemp, T. E., Taylor, M. J., Scalera, J. V., Rothlein, J. E., Marks, E. M., Cerra, F. E., Rodi, S. B., and Spern, E. M.,** Biochemical and cytogenic effects in rats caused by short-term ingestion of Aroclor 1254 or Firemaster BP6, *J. Toxicol. Environ. Health*, 3, 769, 1977.

33 **Sivalingam, P. M., Yoshida, T., and Inada, Y.,** The modes of inhibitory effects of PCBs on oxidative phosphorylation, *Bull. Environ. Contam. Toxicol.*, 10, 242, 1973.

34 **Khan, H. M. and Cuthcomp, L. K.,** Effects of DDT, DDE, and PCBs on mitochondrial respiration, *Bull. Environ. Contam. Toxicol.*, 29, 577, 1982.

35 **Yap, H. H., Desaiah, D., Cuthcomp, L. K., and Koch, R. B.,** Sensitivity of fish ATPases to polychlorinated biphenyls, *Nature (London)*, 233, 61, 1971.

36 **Koch, R. B., Desaiah, D., Yap, H. H., and Cuthcomp, L. K.,** Polychlorinated biphenyls: effect of long-term exposure on ATPase activity in fish, *Pimephales promelas*, *Bull. Environ. Contam. Toxicol.*, 7, 87, 1972.

37 **Narbonne, J. F., Bourdichon, M., and Galle, J. L.,** Polychlorinated biphenyls: effect of diet level on ATPase activity in rats, *Bull. Environ. Contam. Toxicol.*, 20, 184, 1978.

38 **Ito, Y., Unawa, H., and Nesemi, A.,** Lipid composition of the rabbit liver poisoned with chlorobiphenyls, *Fukuoka-Igaku-Zasshi*, 62, 48, 1971.

39 **Litterst, C. L., Farber, T. M., Baker, A. M., and Van Loon, E. J.,** Effect of polychlorinated biphenyls on hepatic microsomal enzymes in the rat, *Toxicol. Appl. Pharmacol.*, 23, 112, 1972.

40 **Kling, D., Kunkle, J., Keller, A. S., and Gamble, W.,** Polychlorinated biphenyls: in vivo and in vitro modifications of cholesterol and fatty acid biosynthesis, *J. Environ. Pathol. Toxicol.*, 1, 813, 1978.

41 **Kling, D. and Gamble, W.,** *In vivo* inhibition of esterase cleavage enzyme by polychlorinated biphenyls, *Experientia*, 37, 1258, 1981.

42 **Bolaye, G., Hernandez, L. M., and Gonzalez, M. J.,** Accumulation of polychlorinated biphenyls by *Saccharomyces cerevisiae* and their effects on lipid biosynthesis, *Bull. Environ. Contam. Toxicol.*, 28, 105, 1982.

43 **Ishidate, K. and Nakazawa, Y.,** Effect of polychlorinated biphenyls (PCBs) administration of phospholipid biosynthesis in rat liver, *Biochem. Pharmacol.*, 25, 1255, 1976.

44 **Hinton, D. E., Gloemann, H., and Trump, B. F.,** Studies on the cellular toxicity of polychlorinated biphenyls, *Arch. Cell. Pathol.*, 27, 279, 1978.

45 **Spalding, J. W., Ford, E., and Lane, D.,** Effects of 4-chlorobiphenyl on subcellular transport and phospholipid metabolism in mouse L5178Y lymphoma cells, *Biochem. Pharmacol.*, 25, 2051, 1976.

46 **Hahn, B. J., Pierkarski, J., and Nilsen, K.,** Effect of a PCB (2,4,2',4'-tetrachlorobiphenyl) on lipid synthesizing enzymes in rat liver microsome, *Bull. Environ. Contam. Toxicol.*, 11, 415, 1975.

47 **Kling, D. and Gamble, W.,** Cholesterol biosynthesis in polychlorinated biphenyl-treated rats, *Environ. Res.*, 27, 10, 1982.

48 **Sandberg, F. and Glaumann, H.,** Studies on the cellular toxicity of polychlorinated biphenyls (PCBs): partial block and alteration of intracellular migration of lipoprotein particles in rat liver, *Exp. Mol. Pathol.*, 32, 1, 1980.

49 **Ohbi, S.,** Influence of polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) to serum protein components in rats, *Bull. Environ. Contam. Toxicol.*, 18, 773, 1977.

50 **Schmeidt, A., Herzberg, W., and Bonthe, R. P.,** On the inhibition of microsomal drug metabolism by polychlorinated biphenyls (PCB) and related phenolic compounds, *Chem. Biol. Interact.*, 16, 191, 1977.

51 **Carter, J. W. and Cameron, L. L.,** Subtlethal effects of a pure polychlorobiphenyl on mice, *Exp. Mol. Pathol.*, 28, 228, 1977.

52 **Orrenius, S. and Ernster, J. L. E.,** Enzyme-membrane relationship in phenobarbital induction of synthesis of drug-metabolizing enzyme system and proliferation of endoplasmic membranes, *J. Cell Biol.*, 28, 181, 1966.

53 **Chiou, C. T. and Schmedding, D. W.,** Partitioning of organic compounds in octanol water systems, *Environ. Sci. Technol.*, 16, 4, 1982; personal communication from Dr. C. T. Chiou.

54 **Bonthe, W. M. and Gamble, W.,** Determination of the binding of 2,4,5,2',4',5'-hexachlorobiphenyl by low density lipoproteins and bovine serum albumin, *J. Toxicol. Environ. Health*, 9, 225, 1982.

55 **Poland, A. and Glover, E.,** Chlorinated biphenyl induction of aryl hydrocarbon hydroxylase activity: a study of the structure-activity relationship, *Mol. Pharmacol.*, 13, 924, 1977.

56 **Sipes, I. G., Slocumb, M. L., Perry, D. F., and Carter, D. E.,** 4,4'-Dichlorobiphenyl: distribution, metabolism, and excretion in the dog and the monkey, *Toxicol. Appl. Pharmacol.*, 65, 554, 1980.

MONS 006020

57. **Sipes, I. G., Slocumb, M. L., Chen, H.-S. G., and Carter, D. E.,** 2,3,6,2',3',6'-hexachlorobiphenyl: distribution, metabolism, and excretion in the dog and monkey, *Toxicol. Appl. Pharmacol.*, 62, 317, 1982.
58. **Sipes, I. G., Slocumb, M. L., Perry, D. F., and Carter, D. E.,** 2,4,5,2',4',5'-hexachlorobiphenyl: distribution, metabolism, and excretion in the dog and the monkey, *Toxicol. Appl. Pharmacol.*, 65, 264, 1982.
59. **Tanford, C.,** The hydrophobic effect and the organization of living matter, *Science*, 200, 1012, 1978.

MONS 006021

Chapter 5

UPTAKE, RETENTION, BIODEGRADATION, AND DEPURATION OF PCBs BY ORGANISMS

M. K. Hawdy and J. A. Gooch

TABLE OF CONTENTS

I. Introduction 64

II. Bioaccumulation and Degradation of PCBs by Bacteria 64

III. Uptake of PCBs by Yeast and Fungi 69

IV. Uptake of PCBs by Phytoplankton 69

V. Uptake and Bioconcentration of PCBs by Other Aquatic Invertebrates 70

VI. Fish: Uptake and Degradation of PCBs 74

VII. Metabolism of PCBs by Birds and Mammals 76

VII. Biological Half-Life and Depuration of PCBs by Various Organisms 77

References 84

MONS 006022

I. INTRODUCTION

Since 1900, the large-scale use of synthetic compounds (e.g., solvents, propellants, dielectric fluids, plasticizers, flame retardants, pesticides, herbicides) has added greatly to our comfort as well as to increased industrial and agricultural productivity. However, the environmental persistence of some of these compounds, notably DDT, chlorinated dibenzodioxins, chlorophenols, and polychlorinated biphenyls (PCBs) has required curtailment of their use due to possible public health hazards.[1,2] The environmental persistence of such compounds results primarily from the inability of natural aquatic and soil biota to metabolize these compounds at a reasonable rate.[1]

Because aqueous environment (rivers, lakes, estuaries, and oceans) is the ultimate repository for all synthetic chemicals,[3] these contaminants may undergo bioconcentration through organisms in food chain systems or by direct uptake from water[4] and exhibit delayed symptoms of biological activity and toxicity, carcinogenicity, mutagenicity, or teratogenicity.[3]

PCBs are remarkable among organic industrial chemicals for their low solubility in water, their high octanol/water partition coefficients, accumulation coefficients, and their resistance to in vivo degradation.[4] As a result, they exhibit extraordinarily high values for bioaccumulation in animal tissues, especially fish and other aquatic organisms.[4]

There are several factors that affect PCB bioaccumulation. These include concentration in the surrounding environment; duration of exposure; temperature, solubility of the pollutant; species age, weight, feeding habits and lipid content; trophic level variations; and adsorption.[4-6,7]

II. BIOACCUMULATION AND DEGRADATION OF PCBs BY BACTERIA

The large quantities of chlorinated hydrocarbons released into the environment have evidently exerted a strong selective effect on microorganisms to detoxify or utilize these compounds rapidly and effectively.[1] Genetic rearrangements have probably occurred to form a conjugative plasmid with degradative capabilities.[1] One group of researchers found that mono- and dichlorobiphenyls were rapidly degraded by a *Nocardia* spp. and a *Pseudomonas* spp. but that trichlorobiphenyls and tetrachlorobiphenyls were degraded at a much slower rate.[8] It was postulated by these same authors that the mono- and dichlorobiphenyls were degraded with little or no further adaptation of the biphenyl degrading organisms, whereas adaptation would be necessary if the more highly chlorinated components were to be degraded and organisms which were adapted to simple PCBs might also be capable of metabolizing the more complex structures.[8] Maximum uptake of 39.7% was noted for a *Pseudomonas aeruginosa* culture growing in basal salt media after 72 hr with most of the PCB being located in the lipid fraction of the bacterial cells (walls and membranes) as shown in Table 1.[9] Evaluation of PCB destruction using a large volume of waste contaminated with Aroclor® 1248 PCB (150 and 800 mg PCB per liter) showed that the *P. aeruginosa* was able to degrade most of the PCB during 90 to 130 days incubation (Figure 1).[9]

Bacteria capable of degrading PCBs can occur in response to PCB contamination.[10] Seven genera of PCB-degrading bacteria (*Aeromonas* spp., *Pseudomonas* spp., *Micrococcus* spp., *Acinetobacter* spp., *Vibrio/Aeromonas* spp., *Bacillus* spp., and a *Streptomyces* spp.) have been isolated from estuarine samples, whereas sea water and ocean sediment contained only two predominant PCB-degrading genera (*Pseudomonas* and *Vibrio*).[10]

Several studies have been conducted to ascertain the effects of PCB on growth of bacteria. One of these reported that the growth of 26 isolates out of 85 estuarine bacteria was inhibited (in various amounts) by 0.5 mg of either Aroclor® 1016 or 1242 per milliliter solvent on saturated paper disks.[11] The identified genera sensitive to PCBs, as reported by these authors, included *Flavobacterium*, *Bacillus*, *Corynebacterium*, *Pseudomonas*, *Achromobacter*, *Micrococcus*, and *Serratia*, but a slightly greater percent of the sensitive strains were Gram

MONS 006023

Table 1
CHEMICAL DISTRIBUTION OF ^{14}C-PCB AMONG CELLULAR FRACTIONS OF TEST ORGANISMS AFTER GROWTH IN GBSB FOR 72 HR

Cellular fractions	*Serratia liquefaciens*[a] (%)	*Pseudomonas aeruginosa*[a] (%)	*Bacillus #2*[b] (%)	*Bacillus #9*[b] (%)
Cold TCA soluble (transient intermediates)	0.7	1.1	3.60	9.87
Alcohol soluble (lipids and proteins)	42	50	67.36	59.93
Alcohol-ether soluble (lipids and proteins)	57	48.5	19.59	17.07
Hot TCA soluble (nucleic acid)	0.1	0.3	5.28	3.95
Residual precipitate (protein)	0.2	0.1	5.05	7.19

[a] Results are average of 4 experiments and computed as percent total activities recovered in all fractions.
[b] Results are average of 2 experiments and computed as percent total activities recovered in all fractions.

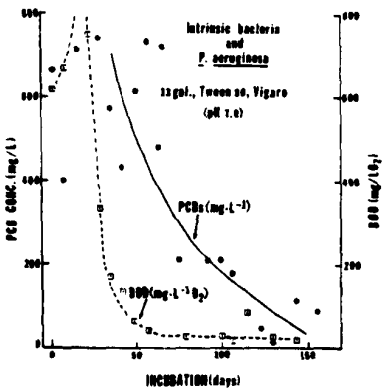


FIGURE 1. Biodegradation of PCB 1248 in reactor system as a function of incubation (37°C) time.

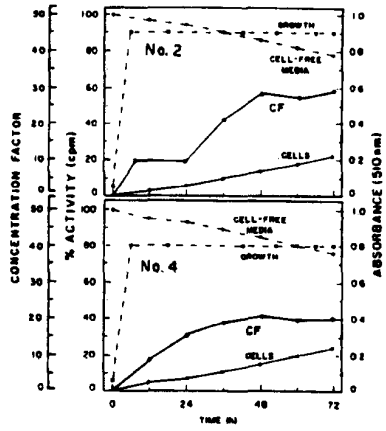


FIGURE 2. Uptake and concentration factor of ^{14}C-PCB by *Bacillus* spp., no. 2 and 4 during growth (at 510 nm). Initial activity of cell-free media = 100%.

positive.[11] The important correlation brought out by this study was that the inhibition by PCBs of specific heterotrophic bacteria could limit the normal turnover of carbon in estuarine sediments.[11] The data for growth, uptake, and CF of ^{14}C-PCB by PCB-resistant *Bacillus* culture nos.-2 and 4, following incubation in glucose basal salt broth (GBSB) containing 200 μg nonradioactive Aroclor® 1254 are presented in Figure 2.[12] Very little effect was noted on the growth of these organisms.[12] Maximal uptake of 22% for culture no. 2 and 24% for culture no. 4 was reached after 72-hr incubation with a CF of 28 and 21 for these bacteria, respectively (CF = specific activity of bacterial cells [cpm/g]/specific activity of medium [cpm/g]).[12] The increase in uptake of ^{14}C-PCB as a function of time during growth was accompanied by a decrease of ^{14}C-PCB in the cell-free media.[12] However, two genera of lake water bacteria (*Achromobacter* and *Pseudomonas*) were not inhibited by concentrations up to 0.1% of Aroclors® 1221, 1242, and 1254.[13] Stimulated bacterial growth has been noted in the presence of Aroclors® 1242 and 1254.[14-16] Growth was inhibited by Aroclor® 1254 in two open-ocean isolates, one a pseudomonad and the other a tetrad-forming coccus.[17] Growth of the pseudomonad culture in the 10 μg Aroclor® 1254 per liter media had an altered filamentous morphology.[17] Two species of bacteria (*Serratia liquefaciens* and *Pseudomonas aeruginosa*) grew well in the presence of 200 μg PCB per milliliter media (Figure 3).[9] These cultures were also able to resist high levels of PCB in phosphate buffer (Figure 4).[9]

Ten different colony types of aerobic, Gram-negative motile rods were grown in parachlorobiphenyl (pCB) or biphenyl (BP) as the sole carbon source and analyzed for an increase in the number of colony-forming units (CFU) as well as for a concomitant disappearance

MONS 006025

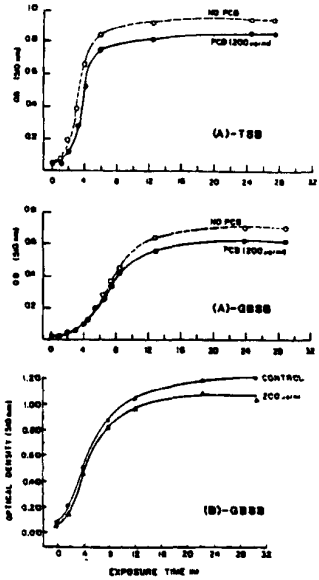


FIGURE 3. Comparative effects of Aroclor® 1254 on growth of (A) *S. liquifaciens* and (B) *P. aeruginosa* as measured spectrophotometrically during incubation (37°C).

of the substrate (pCB or BP).[18] The strains showed an increase of about 2 log counts with an accompanying decrease in extractable pCB or BP from the medium.[18] In a few cultures, the disappearance of pCB was associated with the appearance of possible transient intermediates which were either yellow or gray in color.[18] These observations indicated that the strains isolated were not merely producing a cellular exudate that solubilized pCB, but were able to partially degrade the molecule.[18]

A similar but earlier study yielded more conclusive results on the degradation of pCB and BP by bacteria. Two species of *Achromobacter* were isolated from sewage effluent that used BP and pCB, respectively, as sole carbon sources.[19] The *Achromobacter* spp. were named in accordance to their respective utilizable carbon sources. The *Achromobacter* BP, grown on biphenyl, accumulated a product with a UV absorption maximum at 257 nm which was not identified.[19] Both bacterial isolates produced *meta* cleavage products by fission of the benzene ring and benzoic and *p*-chlorobenzoic acids were produced from the degradation of BP and pCB, respectively, by *Achromobacter pCB*.[19] One of the intermediates in the

MONS 006026

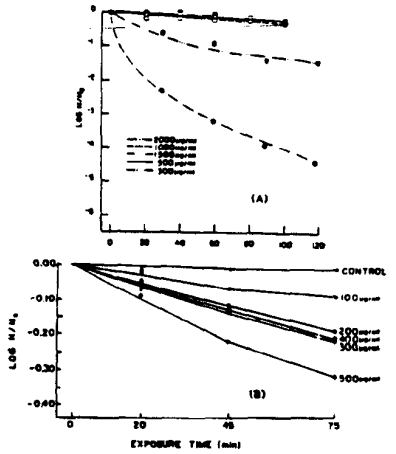


FIGURE 4. Comparative survival of (A) *S. liquefaciens* and (B) *P. aeruginosa* in phosphate buffer and Aroclor® 1254 incubated at 37°C for various intervals (min).

degradation process leading to benzoic acid is possibly a diol, which means that oxygenation of the parent molecule had occurred.[20] Mixed bacterial cultures isolated from activated sludge when grown with 4,4'-dichlorobiphenyl as the only carbon source present produced 4-chlorobenzoic acid and 4,4'-dichloro-2,3-biphenyldiol as degradation products.[21] However, no hydroxylated or carboxylic acid metabolites could be isolated when 2,4',5-tri-, 2,2',5,5'-tetra-, 2,2',3,4,5'-penta-, 2,2',3,4,5,5'-hexa-, and decachlorobiphenyl were used as the sole carbon sources with the same cultures.[21] Another group of researchers found that a bacterial culture isolated from lake water in Ontario degraded Aroclor® 1242 with the major metabolites being aliphatic and aromatic hydrocarbons.[22] Here, no evidence was found to indicate that any metabolite contained chlorine.[22]

An *Alcaligenes* spp. was isolated that could metabolize various PCB components including a pentachlorobiphenyl through an oxidative route that included the production of colored metabolic intermediates.[23] Tetrachlorobiphenyls were also degraded by three mixed microbial cultures that included *Alcaligenes odorans*, *Alcaligenes denitrificans*, and an unidentified Gram positive bacterium.[24]

When microorganisms are utilizing one compound as an energy source, co-metabolism of another compound may occur.[25] Co-metabolism is described as the process in which a microorganism oxidizes a substance without being able to utilize the energy derived from this oxidation to support growth.[15] Co-metabolism of PCBs in the presence of sodium acetate showed enhanced degradation of higher chlorinated isomers.[26] These authors found that when the microorganisms were allowed to grow on PCBs alone, little additional biomass

MONS 006027

was produced because of the limited amount of carbon present in the medium.[24] However, when acetate or carbohydrates were present, the microorganisms were utilizing acetate for growth and oxidizing the PCBs slightly.[24] This author established that if the number of microorganisms increased greatly, even a slight oxidation of PCBs by each microorganism would lead to a more complete degradation of PCB molecules.[24] Thus, more rapid degradation could be attributed also to the other species of microorganisms (in a mixed culture) removing potentially harmful intermediates.[24]

Mammals oxidize aromatic hydrocarbons to arene oxides which yield *trans*-arenediols by enzymatic hydration.[26] Many researchers assumed that bacteria also oxidized aromatic hydrocarbons through *trans*-arenediols.[26] However, research has shown that *cis*-hydroxylation is a common reaction in bacterial degradation of aromatic hydrocarbons.[27] Unsubstituted biphenyl can be hydroxylated in the 2,3-positions and then a *meta*-type cleavage of the aromatic ring can occur.[28] An acid lactone metabolite was isolated from mixed cultures of near-shore marine bacteria, but no evidence of complete mineralization of ^{14}C-labeled tetrachlorobiphenyl to CO_2 was observed by one group of authors.[29]

III. UPTAKE OF PCBs BY YEAST AND FUNGI

In 1979, Tejedor et al.[30] ascertained the response of *Saccharomyces cerevisiae* grown in fermentable (1% glucose) and nonfermentable (3% ethyl alcohol) substrates in the presence of 25 μg Aroclors® 1232, 1242, 1248, 1254, and 1260 per milliliter media. In fermentable media, all Aroclors® showed an inhibitory effect on yeast growth.[30] The intensity of this inhibition followed an order inversely related to chlorine content of the Aroclor®.[30] In nonfermentable media, the two lesser chlorinated Aroclors® inhibited growth much more than the same in fermentable substrates.[30] The higher chlorinated PCBs stimulated yeast growth.[30] The main conclusion these authors drew was that since PCBs disturb the electron transport system at the cytochrome level of the respiratory chain, if both types of substrates were equally available to a fermentative *Saccharomyces* strain, the presence of PCBs would force the microorganism to use the fermentative pathway for obtaining energy instead of the Krebs cycle.[30] The yeast, *Rhodotorula rubra*, showed bioconcentration factors of 307 ± 63 for biphenyl and 1547 for 4-chlorobiphenyl.[31]

The presence of PCBs can alter the growth patterns of fungi. The dry mycelium weight of *Aspergillus flavus* in liquid cultures decreased as the dose rate rose from 5 to 50 μg Aroclor® 1254 per milliliter medium.[32] The magnitude of this effect was greatest for Aroclor® 1232 and lowest for Aroclor® 1260.[32] In 1980, Schwartz et al.[33] examined 15 species of fungi for their ability to hydroxylate biphenyl. Ten of these fungi produced 4-hydroxybiphenyl and seven of the ten also produced 4,4'-dihydroxybiphenyl.[33] The most efficient strains were *Absidia pseudocylindrospora* NRRL 2770 and *Absidia* spp. NRRI 1341.[33]

IV. UPTAKE OF PCBs BY PHYTOPLANKTON

In 1980, Biggs et al.[34] studied the uptake of ^{14}C-PCB (approximately 54% chlorine by weight) by mixed species of estuarine phytoplankton and naturally occurring particulate matter.[34] The natural particulate assemblages, dominated by the centric diatom *Skeletonema costatum*, had a calculated index of sorption (the ratio of ^{14}C-PCB sorbed onto particles of phytoplankton to that in an equal volume of water) averaged $2 \pm 1 \times 10^6$.[34] Another marine diatom, *Cylindrotheca closterium*, absorbed and concentrated Aroclor® 1242 900 to 1000 times the level in sea water.[35] At 0.1 μg PCB per milliliter sea water, the Aroclor® 1242 inhibited growth and diminished levels of RNA and chlorophyll of this diatom.[35] Other authors found that both Aroclor® 1242 and 1254 were toxic to phytoplankton populations at levels as low as 1 to 2 μg PCB per liter of water.[36] The two Aroclors® showed LC_{50}

MONS 006028

values of 6.5 μg PCB per liter and 15 μg PCB per liter, respectively, for phytoplankton.[36] Another group of researchers investigated the effects of PCB on the growth, photosynthesis, and cell size of estuarine phytoplankton and reported that 5 or 10 μg Aroclor® 1254 added daily to 1 ℓ dialysis cultures consisting of mixed species of phytoplankton reduced algal growth rate and ^{14}C-uptake per unit of chlorophyll a.[37] These authors stated that PCB inhibited growth of large centric diatoms and microflagellates (greater than 8 μm in size) by a reduction in cell division and chlorophyll a synthesis, thus causing community composition to shift in favor of small-size algae.[37]

Lab measurements were obtained concerning the relationship between ambient concentrations of PCBs and the amounts adsorbed and absorbed by phytoplankton.[38] Time-course studies conducted by these authors revealed concentration factors greater than 10^5 on a volume per volume basis.[38] Rapid uptake and the short time required for equilibrium suggested that the uptake process involved adsorption rather than absorption. These researchers also stated that phytoplankton are capable of accumulating substantial amounts of PCBs, and therefore constitute an important means for the introduction of these compounds into marine food webs.[38]

In 1982, a mathematical model of PCB (Aroclor® 1254) bioaccumulation in plankton was devised.[39] In batch experiments exposing individual plankton constituents to Aroclor® 1254, the rate at which the organism approaches partitioning equilibrium appears to be partly size-dependent while the extent of PCB accumulation is species-specific.[39] When ingestion rates exceed desorption and excretion rates, a consuming organism will accumulate PCB above the levels predicted by equilibrium partitioning relationships.[39]

One author found that tetrachloro- and hexachlorobiphenyl isomers were concentrated by dead *Chlorella pyrenoidosa* cells by factors of 6000 to 15,000.[40] These researchers reported that these amounts were greater than that noted in living cells, and pointed out that since concentration of PCBs did occur in dead cells, it was due to a possible chemical partitioning between the water of the medium and the hydrophobic lipids of the cell.[40]

The presence of PCBs reduces phytoplankton biomass and size.[41] These changes could increase the number of trophic levels and divert the flow of biomass from harvestable fish to gelatinous predators.[41] The presence of PCBs can cause other alterations in community composition.[42] Distortion of chloroplast lamellae and increased cytoplasmic vacuole formation plus gross cell morphology changes in algal cultures treated with 50 μg PCB per liter media have been noted.[43]

Aroclor® 1254 can reduce growth rates and population densities in a ciliate, *Tetrahymena pyriformis*.[44] Thus, the availability of these protozoa as food organisms and nutrient regenerators would be reduced and that would permit the toxicant to enter and be translocated through aquatic food chains.[44]

V. UPTAKE AND BIOCONCENTRATION OF PCBs BY OTHER AQUATIC INVERTEBRATES

Young oysters (*Crassostrea virginica*) were continuously exposed to Aroclor® 1254 for 24 weeks by Lowe et al.[45] in 1972. These authors observed that the growth rate was significantly reduced in the presence of 5 μg PCB per liter water with the greatest PCB residue being 425 mg PCB per kilogram (whole body) or 85,000 times the concentration in the water.[45] In oysters exposed to 1 μg PCB per liter water, the greatest residue was 101 mg PCB per kilogram (101,000 times the concentration in the water).[45]

Clams which were fed Aroclor® 1254 adsorbed onto the surface of alumina particles at 1.25 and 12.5 parts/10^9 sea water for 21 days showed a maximal concentration factor of 1.8×10^3 with visceral mass:muscular foot residues less than 5:1 in general.[46]

One study in 1982 compared PCB (Aroclor® 1242) uptake by fiddler crabs (*Uca pugnax*)

MONS 006029

from ingested detritus and from contaminated water.[47] These authors reported that PCB accumulation from detritus was more rapid than from water alone.[47] The rate of accumulation from detritus was approximately linear (1 μg PCB per day per animal).[47] The rate from water was 0.1 μg per PCB per day per animal.[47] Looking at the data from a weight standpoint, the PCB concentration by the animals was independent of the weight of the animal, and PCB concentration of the animals was inversely related to the animals' weight.[47] This second relationship was the result of PCB dilution in larger crabs as compared to smaller ones.[47] Relative differences in gestation rates plus the water concentration of a pollutant control the PCB accumulation and concentration by the fiddler crabs.[48]

The uptake from sediments by a PCB mixture (Phenoclor® DP-5) by the benthic worm *Nereis diversicolor* is dose dependent, attaining equilibrium concentration factors of approximately 3 to 4 after 2 months.[49] In a comparison study, the accumulation of PCBs from water by this worm was much more rapid; concentration factors reached approximately 80 after only 2 weeks.[49] Calculations based on experimentally derived PCB concentration factors and ambient PCB levels in sediments and water suggested that sediments contributed the bulk of these compounds to the worms.[49] After 5 days in sediments containing 1 μg PCB (Aroclor® 1254) per gram, *Arenicola marina* and *Nereis diversicolor* contained 0.24 ± 0.08 and 0.36 ± 0.12 μg PCB per gram worm (wet weight), respectively, and there was significant, although smaller, increase in residues to 0.39 ± 0.2 and 0.49 ± 0.25 μg PCB per gram worm after a further exposure of 5 days.[50]

Nymphs of the mayfly (*Ephemera danica*) were used to study kinetics of uptake and degradation of Clophen® A50.[51] Accumulation of PCB in the insects followed a first order kinetic equation with equilibrium being reached after 4 to 5 days, and no degradation of PCB was observed.[51]

Crayfish, *Oronectes nais*, were observed to be more susceptible to Aroclor® 1242 (7 day LC_{50} = 30 μg PCB per liter water) than they were to Aroclor® 1254 (7 day LC_{50} = 80 μg PCB per liter water).[52] The uptake of PCB was linear, and PCB residues in the crayfish did not reach equilibrium after a 28-day exposure to Aroclor® 1254.[52]

In 1974, Nebeker and Puglisi[53] studied the effect of PCBs on survival and reproduction of *Daphnia*, *Gammarus*, and *Tanytarsus*.[53] Continuous-flow and static bioassays were conducted with survival and reproduction as measures of relative toxicity of the following eight PCBs: Aroclor® 1221, 1232, 1242, 1248, 1254, 1260, 1262, and 1268.[53] These authors reported that Aroclor® 1248 was the most toxic to *Daphnia magna* of the eight forms tested in static tests and that after 3 weeks, the LC_{50} was 25 μg Aroclor® 1248 per liter water.[53] Aroclor® 1254 was the most toxic to *Daphnia* in continuous-flow tests with a 3-week LC_{50} of 1.3 μg PCB per liter water.[53] After 96 hr the LC_{50} values for 1242 and 1248 on *Gammarus pseudolimnaeus* in continuous-flow tests were 73 and 20 μg PCB per liter, respectively.[53] Tissue residues in *Gammarus* ranged from 4 μg PCB (1254) per gram tissue in controls to 552 μg PCB (1248) per gram tissue in scuds held for 60 days in water containing 5.1 μg 1248 per liter water.[53] *Gammarus pulex* was used as an indicator organism in a study on the presence of DDT and PCB in south Swedish streams.[54] These authors stated that there are two ways of attaining a particular level of a persistent substance in an organism: the first by progressive accumulation, the rates of excretion and metabolism being more or less negligible, the second by reaching equilibrium between uptake and excretion (with or without preceding metabolic breakdown) at a certain level.[54] In the first case, the concentration of the residue will rise continuously with age, while, in the second case, no further rise will occur after equilibrium has been reached.[54] The level at which equilibrium is attained is a function of the rates of uptake and elimination of the substance.[54]

When 3- and 5-day-old mosquito larvae, kept at 27°C were exposed to ^{14}C-PCB in water, the percent uptake by 3-day-old larvae gradually increased during incubation to 5.1% after 94 hr.[12] However, 5-day-old larvae showed a maximum uptake of 6.2% at 48 hr followed

MONS 006030

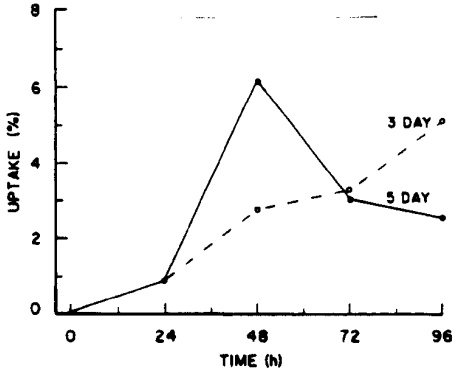


FIGURE 5. Uptake of ^{14}C-PCB by 3- and 5-day-old mosquito larvae.

by a decline thereafter to 2.6% at 96 hr (Figure 5).[12] Similarly, the CF by 3-day-old larvae increased gradually to 553 after 96 hr, whereas that of 5-day-old larvae reached its maximum at 48 hr of 638, followed by a decline at 96 hr (Figure 6).[12] These results indicate that both time of incubation and age of the larvae affected the uptake and CF by the larvae.[12] The decline in rates of uptake and CF by the 5-day-old larvae may be due to accelerated depuration.[12]

In 1976, Khan et al.[39] studied adsorption of Aroclor® 1254 onto unpeeled and peeled shrimp and found that unpeeled shrimp had more PCB adsorption potential than peeled shrimp.[39] These authors stated that PCB are likely to be adsorbed on the outer shell of chitinous material.[39] The toxicity of Aroclor® 1254 to adult, juvenile, and larval stages of the shrimp, *Palaemonetes pugio* was examined and it was observed that larval and juvenile shrimp were more sensitive to 1254 than adults.[36] The authors also reported that at a concentration of 15.6% μg PCB 1254 per liter water, 75% of the larvae died on the 5th and 6th days of exposure and all died within 11 days.[36] Juvenile shrimp showed 96 hr LC_{50} values ranging from 6.1 to 7.8 μg PCB 1254 per liter water.[36]

Fish, shrimp, and oysters were exposed to Aroclor® 1254 in acute (96 hr or less) laboratory experiments.[37] In another test conducted by these authors, juvenile pink shrimp and blue crabs were exposed to concentrations of Aroclor® 1254 for 20 days.[37] No effect was noted on juvenile pinfish exposed to 100 μg PCB per liter water for 48 hr.[37] However, there was 100% mortality of juvenile pink shrimp at the end of 48 hr exposure to 100 μg PCB per liter water.[37] Shell growth of oysters exposed to 100 μg PCB per liter water for 96 hr was completely inhibited.[37] The oysters did live, and after 3 weeks in PCB-free water, their shell growth equaled that of the controls.[37] The chronic toxicity of Aroclor® 1254 to grass shrimp was ascertained and concentration factors were reported ranging from 3000 to 11,000.[36] These investigators also stated that whole body concentrations produced after 5 weeks exposure to 0.04, 0.09, and 0.62 g PCB 1254 per liter water ranged from 200 to 26,000 times the concentration in test water and that the concentrations did not reach equilibrium.[36]

PCB (Aroclor® 1254) concentrations in Atlantic zooplankton on the continental shelf and

MONS 006031

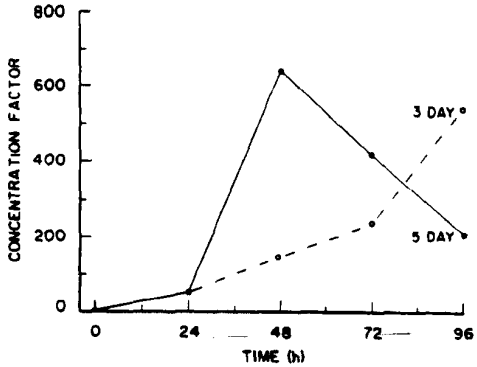


FIGURE 6. Concentration factor of ^{14}C-PCB by 3- and 5-day-old mosquito larvae.

slope ranged from 2.4 to 260 μg PCB per milliliter water.[39] The author assumed that the PCB present in the zooplankton was in physical-chemical equilibria with that in the ambient aqueous environment.[39] These results were confirmed in 1977 when Clayton et al.[40] stated that bioaccumulation of PCBs in zooplankton was controlled by equilibrium partitioning of the chemical between the internal lipid pools of the biota and ambient water.[40] Amplification factors of 10^6 were determined in terms of lipid-water concentration ratios.[40] These researchers seemed to think that for pelagic biota at the lower trophic levels, food chain biomagnification was not a controlling factor in the zooplankton residue levels.[40]

The rate of accumulation and biomagnification of ^{36}Cl-Aroclor® 1254 from water by eight species of aquatic invertebrates was examined.[41] The organisms tested were four species of crustacea: scud, grass shrimp, crayfish, and a daphnid, along with four species of immature aquatic insects; dobsonfly larvae, mosquito larvae, stonefly naiads, and phantom midges.[41] The daphnid, *Daphnia magna*, accumulated total body concentrations 48,000 times greater than those in water.[41] Mosquito larvae exhibited a 12,600-fold magnification within 24 hr.[41] This accumulation continued until the 7th day of exposure when the larvae metamorphosed into pupae.[41] At 7 days, the magnification factor was 20,000 in the mosquito larvae.[41] Grass shrimp had a magnification factor of 16,600 after 21 days exposure.[41] Scud showed a magnification factor of 27,000 after 21 days of exposure.[41] PCB residues taken up by scud were characterized by progressively greater uptake of lower chlorinated isomers over time.[41]

There is more evidence to substantiate the theory that the rate of uptake decreases with PCB isomers of increasing chlorine content.[42] However, other data indicate that organisms tend to accumulate the more highly chlorinated PCB isomers since these are much more difficult to metabolize and excrete.[43]

It has been reported that PCBs are carried to ocean waters adsorbed onto suspended organic particles in river water.[4] Sewage sludge as well as polluted dredged spoils being dumped near coastal areas also contribute to the concentration of PCBs in the ocean.[4] Again, it was pointed out that most of the PCBs carried to the ocean either remain in solution or

MONS 006032

are adsorbed onto suspended solids, so it is probable that most of the PCBs delivered to coastal regions are deposited in the sediment.[4] Several studies have been conducted on the flux of PCBs between water and sediment. Particle size distribution and total organic carbon seem to be important factors in determining the extent of partitioning of two tetrachlorobiphenyls to natural sediments.[64,65] The dissolved concentrations of Aroclors® 1016 and 1242 are low, so when highly sorbed to sediments, these PCBs would be transported in association with particulate matter.[66] If the PCBs are not highly sorbed, volatilization does occur.[66] Atmospheric transport and deposition can dominate PCB input to lake sediments.[67] Uptake of PCBs in sediments is governed by equilibrium partitioning between suspended phases and ambient water and the adsorption of Aroclor® 1254 from sea water by sediments is influenced by the sediment type; this also affects desorption from sediment to sea water.[68] The difference between adsorption and desorption isotherms indicates that adsorption of PCBs is relatively irreversible; PCB is firmly bound to the sediment.[69]

VI. FISH: UPTAKE AND DEGRADATION OF PCBs

Spot fish, *Leiostomus xanthurus*, were exposed to 1 μg Aroclor® 1254 per liter water for 56 days.[70] The maximum concentration in the whole fish was 3.7×10^4 times that in the water with the liver concentrating the greatest amount.[70] The accumulation of Aroclor® 1248 and 1254 by bluegills exposed to 2 to 10 μg PCB per liter water was 26,300 to 71,400 times the exposure levels for both PCBs.[72] Ninety-six-hr LC_{50} values for newly hatched and 3-month-old fathead minnows have been established.[73] The LC_{50} for Aroclor® 1242 in newborns was 15.0 μg PCB per liter water whereas, for 3-month-olds it was 300 μg PCB per liter water.[53] Growth of young fish was affected above 2.2 μg PCB 1249 per liter water, and none survived above 5.1 μg PCB 1248 per liter water after a 1-month exposure.[53] In a contrasting experiment, stimulated growth in adult minnows, *Phoxinus phoxinus*, fed food containing different concentrations of Clophen® A50 has been observed.[71] It was postulated that the PCB might have affected some hormone system in the fish, such as an increase in thyroid or pituitary activity.[71]

Biological accumulation of Aroclor® 1248 and 1254 by channel catfish was 56,370 to 61,190 times the levels in water after 77 days.[72] Coho salmon exposed to concentrations of 1254 up to 14,500 μg/kg body weight per day showed no effects of growth.[72] After 260 days, however, signs of toxicosis appeared and all fish exposed to the highest concentration were dead within 5 days thereafter.[72]

In 1974, Hansen et al.[73] determined chronic toxicity to and uptake of Aroclor® 1016 by pinfish (*Lagodon rhomboides*).[73] The PCB was not toxic to the fish at 100 μg PCB per liter water for 96 hr, but significant mortality occurred when pinfish were exposed to 32 μg PCB 1016 per liter water for 42 days.[73] Guppies exposed to Aroclor® 1254 died after 7 days incubation in the presence of 20 μg PCB per milliliter water.[12] Guppies incubated in beakers containing either 5, 10, or 15 μg Aroclor® 1254 per milliliter water lived longer but all of these died within 3 weeks.[12] Direct uptake of ^{14}C-PCB by these guppies during incubation at 27°C increased gradually to reach 3.6% after 96 hr with a CF of 198 (Figure 7) at that time.[12]

Figure 8 depicts data for the direct uptake and CF of ^{14}C-PCB by cichlid organs.[12] The head and fins accumulated the greatest percentage of ^{14}C-PCB in water.[12] After 72-hr exposure, uptake by the head decreased to 28% probably due to washing and/or depuration, while the uptake by fins remained fairly constant at 15.5%.[12] On the other hand, the liver showed an increasing uptake reaching 18.6% after 72 hr.[12] The CF by various cichlid organs tended to also increase over time.[12] The spleen, fins, liver, and muscle exhibited the highest CF values after 72-hr exposure to ^{14}C-PCB in water with values ranging from 1862 in spleen, 268 in fins, 173 in liver, and 164 in muscle tissue.[12]

MONS 006033

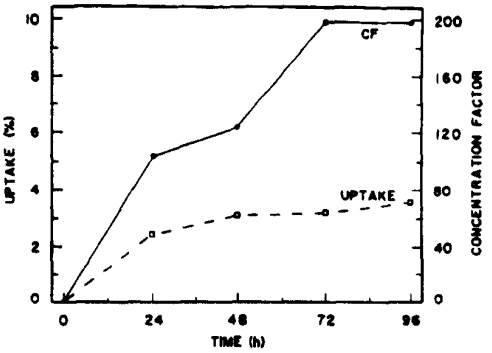


FIGURE 7. Uptake and concentration factor of ^{14}C-PCB by guppies.

Pinfish were exposed to 1 μg PCB per liter water for 56 days. The accumulation factor (maximum whole-body residue) was 17,000 times the nominal concentration in test water.[74] These authors also determined the bioconcentration factor of a tetrachlorobiphenyl isomer in rainbow trout muscle after 5 days exposure was 9550 ± 1610.[74] The average bioaccumulation factor for hexachlorobiphenyl in killifish, *Fundulus similis*, after 11 days exposure was 375.[75]

There are certain factors within the different fish species themselves that determine PCB accumulation factors. Among these are age, weight, percent lipids, and feeding habits.[64] One investigator reported that the concentration of PCBs progressively increased with maturity in a series of lake trout.[76] The effect of age on accumulation of Phenoclor® DP6 in gray mullets showed that DP6 concentrations in 3.5-year-old fish were always higher than those in 2.5-year-old fish when both groups were fed a dry fish diet contaminated with 50 μg DP6 per gram food.[77] PCB concentration in fish can be dependent on the amount of food ingested.[77] Two other studies also indicated that fish accumulate PCBs on a weight-ratio basis.[78,79]

The accumulation of Aroclor® 1016 by fish (Hudson River) in 14 days was 15,000 times the water concentration, and the amount of PCBs accumulated by the different species of fish was closely related to the fat content and weight of the fish.[80] Female fathead minnows accumulated about twice as much PCBs as the males due to a greater amount of lipid in the females.[81] Fish species that contain a greater percent lipid body weight tend to accumulate more PCB.[82] Concentrations of PCB (Clophen® A50) in the fat tissue of goldfish were calculated to be more than 10,000 times greater than the PCB concentrations in the test water.[83]

The concentration coefficient of Phenoclor® DP6 from water and from food in juvenile gray mullets was measured.[77] There was higher accumulation of PCB from water than from food.[64] Other studies supported this premise[52,59,80] although one author stated that in the environment the kinetics of residue uptake from dietary sources could be more important because PCBs have a high affinity for sediments and particulate matter.[52]

MONS 006034

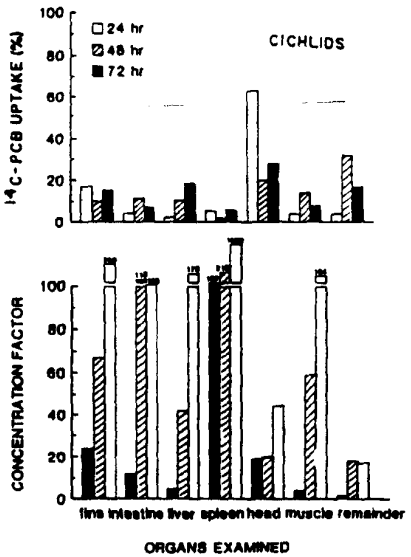


FIGURE 8. Uptake and organ distribution and concentration factor of ^{14}C-PCB by cichlids.

Not many researchers have concrete evidence that fish can metabolize PCBs, but there are a few.[87-89] These different authors were able to isolate hydroxy metabolites from fish (the green sunfish, rainbow trout, and goldfish) exposed to certain tri- and tetrachlorobiphenyls.[87-89]

VII. METABOLISM OF PCBs BY BIRDS AND MAMMALS

Bobwhite quail were fed Aroclor® 1254 for 14 days and significant alteration of certain PCB isomers appeared to have taken place.[90] These authors showed that dechlorination of the molecules was apparent and isomeric transformation was suggested.[90] Pigeons fed wheat contaminated with 500 μg Aroclor® 1242 per gram wheat metabolized the lower chlorinated isomers at a faster rate.[91] A mono-, di-, and tetrachlorobiphenyl was transformed into monohydroxylated derivatives by the pigeon and rat, but no hydroxylated products of a hexachlorobiphenyl were detected from either.[92]

In rats, mono-, di-, and pentachlorobiphenyls can be metabolized to more polar compounds and then excreted in the bile.[93] Two adjacent unsubstituted carbon atoms are important to

MONS 006035

the metabolism of PCBs because their presence facilitates the formation of arene oxides.[91] Other studies also showed that rats were capable of metabolizing di-, tri-, and pentachlorobiphenyls to more polar components via hydroxylation.[89,94,95]

The biological half-lives of tetrachlorobiphenyls have been studied. It seems that the half-lives of some isomers were determined by the rate of releasing PCB from body fat rather than by the rate of its metabolism.[96] Rabbits were fed food pellets contaminated with 1% hexachlorobiphenyl for 7 days to give a total concentration of 1 mg PCB per kilogram feed.[97] The urine showed the presence of two major metabolites formed from the HCB by hydroxylation and hydroxylation with concomitant dechlorination, respectively.[97] When male and female rhesus monkeys were given either 1.5 or 3.0 mg Aroclor® 1248 per kilogram body weight in a single oral dose, hydroxylated metabolites were formed in the liver and excreted in bile and urine.[98] Again, these authors showed that the lower chlorinated isomers were rapidly metabolized and excreted, while the highly chlorinated isomers remained in the fat tissue for more than 2.5 years.[98] A urinary metabolite (*trans*-3,4,-dihydro-3,4-dihydroxy-tetrachlorobiphenyl) was isolated that suggested metabolism occurs through an arene oxide intermediate.[98]

VIII. BIOLOGICAL HALF-LIFE AND DEPURATION OF PCBs BY VARIOUS ORGANISMS

The depuration of ^{14}C-PCB (Aroclor® 1254) by selected organisms representing a simple aquatic ecosystem (bacteria, mosquito larvae, guppies, and cichlids) was examined.[99] Each system was labeled by growing for 48-hr in ^{14}C-PCB medium at a specified temperature. They were then incubated in an isotope-free environment.[99] Two or three phases of depuration were noted in all systems (Figure 9).[99] Most phases followed first order kinetics but with different magnitudes. In bacteria, rapid depuration was noted on the 7th day followed by a slow rate (Table 2). No evidence of biological half-life (BHL) was observed during the entire experiment.[99] Larvae showed three depuration phases: -0.023/day (0 to 1 day), -0.086/day (1 to 2 days), and -0.0899/day (2 to 6 days) with a BHL of 5.5 days.[99] Guppies had depuration rates (k, slope of line) of -0.131/day for the first phase and -0.137/day for the 2nd with a BHL of 4.7 days.[99] Cichlids had a rapid rate during the 1st day ($k = -0.102$/day), followed by a slower one thereafter ($k = -0.057$/day) and a BHL of 6.1 days (Table 2).[99]

Experiments were also conducted to ascertain if depuration was due to excretion of PCB or by merely washing of PCB absorbed onto the cell wall. Data obtained (Figure 10) revealed that after 5 washes in pesticide-grade hexane, a total of 90.6 and 79.5% of the ^{14}C-PCB (based on initial activites as 100%) radioactivities were lost from the fresh and frozen cells, respectively. When the labeled cells were first washed (five times) with 0.05 *M* sodium phosphate buffer, a total of 44.3 and 25.4% of the ^{14}C-PCB radioactivities was lost from the fresh and frozen cells, respectively.[99] After the remaining five washes with pesticide-grade hexane, an additional 39.5% was lost from the fresh cells and 51.9% from the frozen.[99] This indicated that the percent of the ^{14}C-PCB lost by washing is dependent upon the condition of the cells, the solvent, and the number of washes.[99]

The benthic worm *Nereis diversicolor* eliminated Phenoclor® DP-5 at a rate which closely approximated a single exponential phase during the first 2 months following the exposure.[99] Thereafter, the loss rate appeared to decrease. These elimination rates were concentration dependent, with higher initial loss rates in worms containing higher levels of PCBs.[99] However, no significant loss in body load of Aroclor® 1254 by *Arenicola marina* and *Nereis diversicolor* during a postexposure period of 3 weeks was noted.[99]

In 1974, Nimmo et al.[99] studied the concentration and loss of Aroclor® 1254 in grass shrimp (*Palaemonetes pugio*). After several 1-week exposures to a range of concentrations

MONS 006036

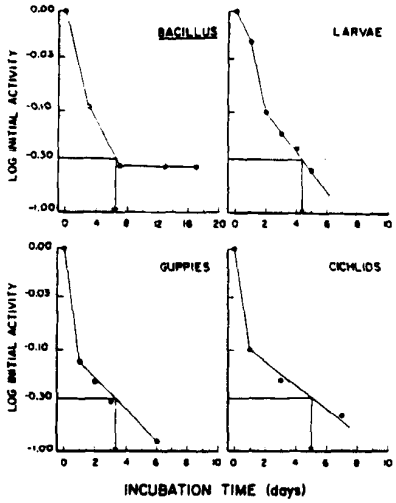


FIGURE 9. Depuration and biological half-life of ^{14}C-PCB in four trophic systems. Initial activity = 1.0.

of this PCB (0.17 to 9.1 μg PCB per liter), the concentration factors ranged from 3000 to 11,000.[99] Whole body levels after 5 weeks exposure to 0.04, 0.09, and 0.62 μg PCB per liter ranged from 200 to 26,000 times the PCB concentration in test water.[99] The concentrations did not reach equilibrium and from 60 to 90% of PCB 1254 was lost from shrimp within 4 weeks after exposure was stopped.[99]

The retention properties of PCBs were examined in the mussel (*Mytilus edulis*) over an 89-day period.[100] These authors reported that when the mussels were transferred from a site of relatively high PCB contamination to a site of relatively low PCB concentration in Puget Sound, Washington, the retention of PCB components increased with increasing chlorine content.[100] It is of interest to point out that the concentrations of PCB decayed logarithmically with calculated half-lives ranging from 3 days for a PCB component with 2 and 3 chlorines to 50 days for a PCB containing 6 and 7 chlorines.[100] Components chosen to best represent the commercial mixtures Aroclor® 1242, 1254, and 1260 were estimated to exhibit half-lives of 8, 23, and 39 days, respectively. The selective retention of the higher chlorinated biphenyls appears to be the result of lower water solubility of these components.[100]

Young oysters (*Crassostrea virginica*) were exposed to Aroclor® 1254.[43] Growth rate was significantly reduced in oysters exposed to 5 μg PCB per liter for 24 weeks.[43] Growth rate was not affected when oysters were exposed to 1 ppb for 30 weeks. When oysters were exposed to 5 ppb, the greatest PCB residue (whole body) was 425 mg/kg (ppm), 85,000

MONS 006037

Table 2
DEPURATION RATE (K, SLOPE OF LINE) IN VARIOUS TROPHIC LEVELS LABELED WITH ^{14}C-PCB

	Incubation time days	k Value[a] (day)	Correlation coefficient	Biological half-life (day)	
				Graph[b]	Calculated[c]
Bacteria	0—3	−0.0305	−1.0	6.4	10.46
(PCB-resistant	3—7	−0.0863	−1.0		(0—17)
Bacillus spp.)	7—17	−0.0009	−0.8030		55.94
Mosquito larvae	0—1	−0.0229	−1.0	4.4	4.47
(*Aedes aegypti*)	1—2	−0.0859	−1.0		(0—5)
	2—5	−0.0899	−0.9707		4.35
Guppies	0—1	−0.1308	−1.0	3.3	2.47
(*Lebistes reticulatus*)	1—6	−0.1373	−0.9927		(0—6)
					2.54
Cichlids	0—1	−0.1024	−1.0	5.1	4.62
(*Cichlasoma facetum*)	1—7	−0.0574	−0.9988		(0—7)
					4.57

[a] Slopes were calculated from graphs of initial activities vs. incubation time.
[b] From graph of log values.
[c] Regression analyses.

times the concentrations in the water, and less than 0.3 ppm was retained after 28 weeks depuration in PCB-free water.[45] When oysters were exposed to 1 ppb, the greatest residue was 101 ppm, 101,000 times the concentration in the water, and less than 0.2 ppm was retained after 12 weeks depuration.[39] Shell growth of oysters exposed to 100 ppb Aroclor® 1254 for 96 hr was completely inhibited.[37] However, the oysters did survive and their shell growth equaled that of controls after 3 weeks in PCB-free water.[37] When oysters were exposed to 10 ppb PCB for 96 hr and then placed in uncontaminated water for 4 days, their PCB residues had dropped to 33 ppm.[37] Oysters exposed to 1 ppb for 96 hr and then transferred to PCB-free water for 4 days showed PCB residues of 8.1 ppm.[37]

Aroclor® 1254 adsorbed onto the surface of alumina particles at 1.25 and 12.5 ppb sea water was fed to hard-shell clams, *Mercenaria mercenaria* for 21 days.[46] The clams showed a maximum concentration factor of 1.8×10^3 with visceral mass:muscular foot residues of less than 5:1 in general.[46] Only the muscular foot of clams on a high dosage showed a diminution in PCB content after 6 months in clean seawater.[46] There was no change in tissue residues of clams held in clean seawater after exposure to 1.25 ppb PCB 1254.[46] However, in clams exposed to 12.5 ppb PCB 1254 there was a persistent significant decrease in the residues of the foot so that, after 6 months, the ratio of PCB in the visceral mass to the muscular foot was 10.6:1.[46] Feces collected from clams kept in clean water indicated that PCBs were being lost from the animals at a slow but consistent rate.[46]

Blue crabs (*Callinectes sapidus*) were exposed to Aroclor® 1254 for 20 days.[37] At this time, the crabs contained an average whole body residue of 23 ppm.[37] Residues in five crabs held in PCB-free water for 1 week averaged 22 ppm.[37] Six crabs held in clean water for 4 weeks, following the 20 day exposure, contained an average of 11 ppm — an example of the persistence of Aroclor® 1254 in animal tissue.[37]

Lobsters were fed 2,2',4,5'-tetrachlorobiphenyl (TCB) and 2,2,'4,4', 5,5'-hexachlorobiphenyl (HCB) in a 1:1 ratio applied to shucked mussel tissue at concentrations of 1.7 and 17 mg/kg (ppm) for each chlorobiphenyl.[101] Each lobster was fed every other day for 6 weeks followed by 6 weeks of feeding uncontaminated mussel tissue.[101] The lobsters were sacrificed at 2 week intervals and tissues (hepatopancreas, tail and claw muscle) were

MONS 006038

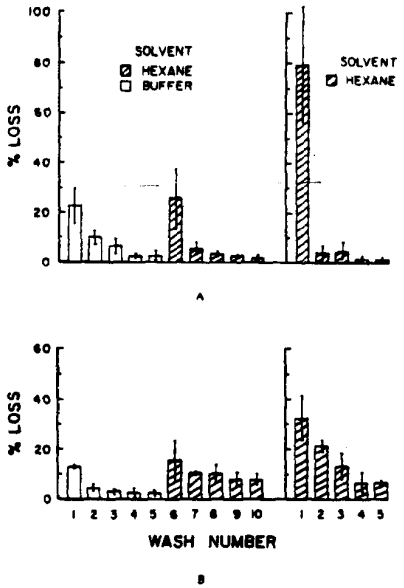


FIGURE 10. Loss of ^{14}C-PCB from bacterial cells by washing. (A) Data for fresh cells and (B) frozen (thawed) cells.

analyzed.[101] The concentrations of TCB and HCB in food were 0.60 and 0.55 mg/kg at low dosage feeds and 4.0 and 4.9 mg/kg at high dosage levels.[101] Data on the uptake and excretion of TCB and HCB in the hepatopancreas indicated that concentrations of these compounds approached an equilibrium within 4 weeks, except that HCB concentrations in high dosage feeds increased throughout the uptake phase.[101] Maximum CFs were 5.1 and 7.3 for TCB and HCB, respectively, at the high dietary level.[101] In all cases there was a decrease in the concentration of chlorobiphenyls in the hepatopancreas during the 6-week clearance period.[101] In low dosage tests, the concentration approached control values after 6-weeks clearance, and in high dosage tests, concentrations of TCB and HCB declined by approximately 60 and 40%, respectively.[101] Maximum concentrations for TCB and HCB in tail and claw muscle were lower than those in the hepatopancreas, and by the end of the excretion phase, concentrations in muscle tissues were approaching control values indicating that most of the residue had been eliminated.[101] In 1975, Bend et al.[108] studied the distribution and excretion of (^{14}C)-2,4,5,2',5'-pentachlorobiphenyl administered parenterally to lobsters.[109] The he-

MONS 006039

pstopancreas contained much higher amounts of radioactivity (per milligram tissue) than any other organ and accounted for between 91 and 96% of the total radioactivity recovered at all times.[102] The half-life for radioactivity in tissues was estimated from semilogarithmic plots of the specific activity (dpm/mg) vs. time (day).[102] The tissues which had a $t_{1/2}$ of 3 weeks or longer were the hepatopancreas (45 days), egg masses (39 days), stomach (28 days), gills (24 days), and intestines (23 days).[102] Those tissues in which the $t_{1/2}$ was 1 week or less were the green gland, heart, tail muscle, claw muscle, male gonads, and plasma.[102] Over 95% of hepatopancreas extract showed that the PCB level was unchanged.[102] The very slow metabolism and excretion of PCB in the lobster are probably related to the very low microsomal mixed-function oxidase activities of lobster hepatopancreas.[103]

Adult minnows, *Phoxinus phoxinus*, were fed food containing Clophen® A50 in the following concentrations: control 0.09, low 25, medium 270, and high 2500 μg PCB per gram dry weight for 40 days.[71] The next 5 days were the "accumulation period", and the remaining 255 days of the experiment served as a "clearance period".[71] On day 45, the efficiency in uptake of PCB from the food varied between 22 and 36%.[71] Levels of total PCB corresponded to 1-, 5-, 100-, and 500-fold, respectively, that of the background levels of PCB in minnows from the catching area.[71] At day 300, the low, medium, and high levels showed decreases to 74, 38, and 35% of the level at day 45.[71] Stimulated growth in the minnows was noted; PCB might have had an effect on some hormone system, such as an increase in thyroid or pituitary activity.[71]

Fathead minnows (*Pimephales promelas*) were exposed to Aroclor® 1248 and 1260 to determine acute and chronic toxicity as well as bioconcentration of the PCB mixtures in the fish.[51] The bioconcentration factor for PCBs was independent of the PCB level in the water; in adult females at 25°C, it was approximately 1.2×10^5 for PCB 1248 and 2.7×10^5 for PCB 1260.[51] Females accumulated about twice as much PCBs as the males because of the greater amount of lipid in the female tissues. Exposed fish placed in untreated water eliminated less than 18% of the body burden after 60 days.[51] Fish exposed to PCB 1248 had eliminated only 18% of the original PCB burden after 28 days.[51] Fish exposed to PCB 1260 lost only 1% after 42 days.[51]

The adsorption, accumulation, and elimination of PCB (Clophen® A50) in goldfish have also been studied. When fish remained for 13 days in water containing 0.1 ppm Clophen® A50, a PCB concentration of about 70 ppm accumulated in the fish.[63] The fish were then transferred to freshwater to determine elimination.[63] The PCB content in the fish was halved during the first 3 weeks of the experiment, but the half-life for PCB increased during the experimental period.[63] Concentrations of PCB in fat tissue of the fish were calculated to be more than 10,000 times greater than PCB content in water.[63] Research conducted in 1982 showed guppies exhibiting half-life of ^{14}C-PCB (Aroclor® 1254) to be 3.3 days.[99] This same study also showed cichlids (*Cichlasoma facetum*) to have a half-life of ^{14}C-PCB of 5.1 days (Table 2).[99]

The rate and extent of bioaccumulation of HCB in killifish (*Fundulus similis*) continuously exposed to low concentrations of HCB have been determined along with the rate and extent of depuration in these animals.[75] After an 11-day exposure, HCB-exposed fish were removed from the dosing tank and placed into the depuration tank.[75] The HCB concentration decreased exponentially for 2 days; during this time, tissue concentration fell from about 70 to 1.8 mg/g; after 1 week tissue concentration in the depurated fish had leveled off at 0.8 mg/g.[75] The half-life for loss of HCB from the whole body was calculated to be 9.3 hr.[75]

The average bioaccumulation factor for HCB in *F. similis* was calculated to be 375.[75] The concentration in tissue fell exponentially with a half-life of 9 to 12 hr to within control levels.[75]

Data collected on the uptake, retention, and elimination of Aroclor® 1254 by larval striped bass (*Morone saxatilis*) showed that maximal transfer of ^{14}C-Aroclor® 1254 from water to

MONS 006040

fish was noted after 48 hr, at which time, the fish had accumulated 60% of the PCB available in the system.[79] PCB uptake between 24 and 48 hr was slow and became nearly asymptotic between 34 and 48 hr, suggesting that an equilibrium had developed.[79] No further uptake was noted between 48 and 120 hr.[79] After 48 hr of release, whole body concentrations of PCB were about 18% less than the concentration accumulated during uptake.[79] The 48-hr release concentrations were significantly less than the concentration levels after 24 hr of uptake, and significantly less after 24 hr of release.[79]

Spot fish (*Leiostomus xanthurus*) were exposed to Aroclor® 1254 (1 ppb) for 56 days and then placed in flowing water free of PCB for 84 days.[76] Residue analyses of pooled samples of brain, gills, liver, muscle, and remaining tissues were conducted.[76] Residues in all tissues were summed to compute levels in the whole fish.[76] The maximum concentration in the whole fish was 3.7×10^4 times that in the water. Liver concentrated the greatest amount.[76] After 84 days of flushing, the relative amount (parts per million) in the whole fish dropped 73% and the absolute amount in micrograms decreased 61%.[76]

Acute and chronic toxicity uptake and retention of Aroclor® 1016 to pinfish (*Lagodon rhomboides*) has been determined.[73] The PCB was not toxic to pinfish at 100 μg PCB per liter for 96 hr, but significant mortality occurred when pinfish were exposed to 32 μg PCB (Aroclor® 1016) per liter for 42 days.[73] Pinfish exposed to 1 μg PCB per liter for 56 days accumulated the PCB with maximum concentrations attained in whole fish by 21 to 28 days.[73] Maximum whole-body residue (wet weight) was 17,000 times the nominal concentration in test water.[73] After 56 days exposure to 1 μg PCB per liter, the pinfish were placed into PCB-free water for 56-day depuration. At this time, concentrations in the fish had decreased by 51%.[73]

Rainbow trout (*Salmo gairdneri*) were exposed to 1.6 and 9.0 μg 2,2',4,4'-tetrachlorobiphenyl per liter for 5 days, and then transferred to fresh water.[74] The bioconcentration factor at steady state was 9550 ± 1610 in trout muscle with a clearance half-life of 28 days.[74]

Residues of PCBs in lake trout ranging from 1 to 12 years old have been analyzed.[103] The residues were found to increase progressively with age reaching an average of 15.7 ppm PCBs (measured as Aroclor® 1254) in 12-year-old fish.[103] In 1978, lake trout of increasing age (6 to 12 years) were again sampled to study the persistence of these compounds in the fish.[103] Fresh weight concentrations in flesh of 12-year-old fish were about 13 ppm of PCBs, which showed that the concentrations had remained the same.[103]

The distribution and persistence of 2,5,2',5'-(¹⁴C) tetrachlorobiphenyl in rainbow trout (*Salmo gairdneri*) for 140 days have been studied.[104] The trout were exposed to ¹⁴C-TCB for 26 hr and then transferred to PCB-free water.[104] The distribution of ¹⁴C was determined immediately following the exposure and at 1, 2, 7, 15, 28, and 56 days later.[104] Carcass muscle, skin, lower gastrointestinal tract, and fat contained most of the ¹⁴C and a total of 88% of the radioactivity was detected in these tissues.[104] During the first 14 days, ¹⁴C in adipose tissues, carcass, and eyes increased, possibly at the expense of other tissues.[104] The disappearance of ¹⁴C from most tissues studied appeared to be a biphasic process.[104] Approximately 30% of the compound was eliminated after 2 weeks, but only a 6% loss was observed in the following 126 days.[104] The initial rapid loss of the ¹⁴C-TCB had a half-life of 2.66 years.[104] The bile and blood initially contained relatively high concentrations of ¹⁴C, but disappearance from these sites was rapid and nearly complete.[104]

In 1976, Hansen et al.[105] observed a slight net decrease (218 to 182 μg) in body burden of PCB in 56 days when channel catfish (*Ictalurus punctatus*) were no longer given Aroclor® 1242-contaminated feed after 84 days of exposure.[105] However, when fish were fed PCB for 140 days, there was no change in body burden after 56 days of PCB-free feed.[105]

The distribution and excretion of a (¹⁴C)-pentachlorobiphenyl in the lobster and the dogfish shark have also been determined.[102] These authors reported that the specific radioactivity (dpm/mg tissue) was higher in dogfish shark liver than in any other tissue following the

MONS 006041

parenteral administration of PCB.[102] The delayed biliary excretion of radioactivity and the excretion of only very small quantities of biliary metabolites suggested that dogfish sharks biotransformed the dosed compound very slowly.[102] Unaltered PCB was not excreted in the bile and the biliary radioactivity was not converted to organic soluble material by β-glucuronidase hydrolysis indicating that glucuronide conjugates of phenols were not major biliary metabolites.[102]

The disappearance of radioactivity from blood followed a multiple exponential decay relationship with time.[102] The $T_{1/2}$ of ^{14}C-PCB was estimated for the three components of the curve. The α, β, and γ components of the radioactivity disappearance curve had $t_{1/2}$ values of 4, 27, and 730 min, respectively.[102]

Many marine species have some hepatic microsomal mixed-function oxidase activity, but this activity is generally considerably lower than that found in mammalian liver.[102] Reduced rates of oxidative xenobiotic metabolism in marine vertebrates and invertebrates would partially account for the persistence of lipophilic compounds, such as PCBs, in these species.[102]

In 1977, Mizutani et al.[98] studied all possible isomers of symmetrically substituted tetrachlorobiphenyls (TCBs) in connection with their structures. Twenty female mice were fed (*ad libitum*) a diet containing 10 ppm of each isomer for 20 days at which time treated diets were replaced with a control diet.[98] Biological half-lives were calculated from slopes and intercepts of regression lines. The liver was removed and analyzed separately from the remainder of carcass and showed the following:

2,3,2',3'-TCB	Carcass 0.9 days	
2,4,2',4'-TCB	Carcass 9.2 days	Liver 7.8 days
2,5,2',5'-TCB	Carcass 3.4 days	Liver 2.6 days
2,6,2',6'-TCB	No residues detected at end of 20 days' exposure	
3,4,3',4'-TCB	Carcass 0.9 days	
3,5,3',5'-TCB	Carcass 2.1 days	Liver 2.2 days

There were clear differences in the BHL of the isomers, but no apparent relationship between substitution pattern and BHL could be observed.[98] Lower storage ratio values for 2,3,2',3'-, 3,4,3',4'-, and 2,6,2',6'-TCB imply that these orientations of chlorine substituents are favored for ready metabolic degradation.[98] The actual magnitude of accumulation during the course of a prolonged daily exposure depends upon both the BHL and storage ratio of each compound.[98] For example, the BHL of 3,5,3',5'-TCB was at most two times that of 2,3,2',3'-TCB, whereas the former exhibited more than a 40-fold accumulation at the end of exposure.[98] This discrepancy can be accounted for by the large difference in storage ratio between these two isomers.[105] No apparent relationship between substitution patterns and BHC was observed.[98]

Later in 1980, Muzutani et al.[106] examined the biological half-lives of all symmetrically substituted HCB and decachlorobiphenyl isomers in mice and reported that the half-lives for HCB isomers were much greater than those for tetrachlorobiphenyl isomers previously studied.[98] However, 2,3,6,2',3',6'-HCB was rapidly metabolized and showed a very short half-life.[100] Mizutanis' 1977 study[98] did point out that the biological half-lives of some tetrachlorobiphenyls seem to be determined by the rate of releasing from body fat mass rather than by the rate of metabolism. Therefore, another likely explanation for the rapid decline of 2,3,6,2',3',6'-HCB may be offered by a certain physicochemical nature which permits easy releasing of this isomer from the fatty compartment.[106]

^{14}C-labeled 2,2',4,4',6-pentachlorobiphenyl was fed to rats for 8 days in their chow and organ and tissue samples taken at necropsy. The authors reported that the highest concentrations were in (1) abdominal fat, (2) subcutaneous fat, (3) lymph nodes, (4) ovaries, (5) adrenal, (6) sciatic nerve, and (7) liver.[98] The elimination of 2,2',4,4',6-PCB followed a

biexponential rate expression with an α-phase half-life of 0.90 ± 0.1 and 0.95 ± 0.1 days for females and males, respectively.[79] The β-phase half-lives were 4.2 ± 0.1 and 3.8 ± 0.1 days for females and males, respectively. In 7 days, the males excreted 46.6% and the females 38.3% of the administered dose.[79] The majority of the excreted radioactivity was found in the feces: 83% in males and 81% in females.[79] Hydroxylated metabolic products were also found.[79]

Pigeons which were fed for 28 days with wheat dressed with 500 ppm Aroclor® 1242 showed muscle and fat with a steady logarithmic decay with half-lives of 50 and 125 days, respectively.[81] The brain exhibited a logarithmic decay with a half-life of 50 days.[81] After an initial drop in levels, the liver residues also follow a logarithmic decay with a half-life of 140 days.[81] More highly chlorinated biphenyls are the most potent inducers of hepatic microsomal systems.[81] Pigeons and quail metabolize PCBs at a rate generally dependent on the amount of chlorine in the molecule.[81] These authors also reported that hepatic microsomal enzymes are sensitive to inducing by chlorinated hydrocarbons.[81]

Male and female rhesus monkeys receiving various levels (1.5 or 3.0 g Aroclor® 1248 per kilogram in a single oral dose) of PCBs demonstrated 90% absorption of PCBs from the gastrointestinal tract and distribution in organs of high lipid content.[98] Hydroxylated metabolites were formed in the liver and excreted through the biliary and urinary routes.[98] Lower chlorinated components were more rapidly metabolized and excreted, while concentrations of the highly chlorinated biphenyls persisted in the adipose tissue in excess of 2½ years.[98] The detection of the urinary metabolite (trans-3,4-dihydro-3,4-dihydroxytetrachlorobiphenyl suggests that the mechanism of metabolism is through an arene oxide intermediate.[98] In vivo and in vitro studies demonstrated binding of PCBs with macromolecules.[98]

REFERENCES

1. Chakraborty, A. M., Molecular mechanisms in the biodegradation of environmental pollutants. *ASM News*, 44, 687, 1978.
2. Hartings, J., Major American toxics disasters, *EPA J.*, 4, 8, 1978.
3. Metcalf, R. L., *Fate of Pollutants in the Air and Water Environments*, Part 2, Suffett, I. H., Ed., John Wiley & Sons, New York, 1977, 196.
4. National Research Council, *Polychlorinated Biphenyls*, National Academy of Sciences, Washington, D.C., 1979.
5. Warner, R. E., Bioassay for macrochemical environmental contaminants with special reference to water supplies, *Bull. WHO*, 36, 181, 1967.
6. Richardson, B. J. and Weld, J. S., *PCBs in the Port Phillip Region, The Environmental Significance of Polychlorinated Biphenyls (PCBs)*, Ministry for Conservation, Victoria, Australia, 1979.
7. Kalmus, E. V. and Kalmus, G. D., Transport distributions and toxic effects of PCB's in ecosystems, *Ecol. Modol.*, 6, 223, 1979.
8. Bunce, R. A., Gilbert, P. E., Lidgett, R. A., Mahaprtra, J. N., and Vedden, H. A., The degradation of polychlorinated biphenyls by marine organisms, *Sci. Total Environ.*, 4, 53, 1975.
9. Hamdy, M. K. and Lin, Y. C., Biodegradation of Chlorinated Hydrocarbons, presented at 83rd Annual Meeting American Society Microbiology, New Orleans, March 6, 1983.
10. Seyler, G. S., Thomas, R., and Colwell, R. R., Polychlorinated biphenyl (PCB) degrading bacteria and PCB in estuarine and marine environments, *Estuarine Coastal Mar. Sci.*, 6, 553, 1978.
11. Bourquin, A. W. and Cassidy, S., Effect of polychlorinated biphenyl formulations on the growth of estuarine bacteria, *Appl. Microbiol.*, 29, 125, 1975.
12. Gooch, J. A., Uptake and Bioaccumulation of Polychlorinated Biphenyls within a Food Chain System, M.S. thesis, University of Georgia Press, Athens, 1982.
13. Wong, P. T. S. and Kaiser, K. L. E., bacterial degradation of polychlorinated biphenyls. II. Rate studies, *Bull. Environ. Contam. Toxicol.*, 13, 249, 1975.
14. Seyler, G. S., Shaw, M., and Colwell, R. R., Growth of an estuarine *Pseudomonas* sp. on polychlorinated biphenyl, *Microbiol. Ecol.*, 3, 241, 1977.

MONS 006043

15. **Kolt, J. E., Grabar, C. D., Priester, L. E., and Sandifer, S. H.**, Polychlorinated biphenyls (Aroclor 1242): effects of uptake on *E. coli* growth, *Environ. Health Perspect.*, 1, 175, 1972.
16. **Greer, D. E., Kolt, J. E., Stillway, L. W., and Sandifer, S. H.**, The effect of DDT and PCB on lipid metabolism in *E. coli* and *B. fragilis*, *Bull. Environ. Contam. Toxicol.*, 12, 293, 1974
17. **Bishomore, R. P. and Carey, A. E.**, Effects of polychlorinated biphenyls on growth and respiration and heterotrophic marine bacteria, *Appl. Environ. Microbiol.*, 35, 323, 1978.
18. **Sylvestre, M.**, Isolation method for bacterial isolates capable of growth on p-chlorobiphenyl, *Appl. Environ. Microbiol.*, 39, 1223, 1980.
19. **Ahmed, M. and Focht, D. D.**, Degradation of polychlorinated biphenyls by two species of *Achromobacter*, *Can. J. Microbiol.*, 19, 47, 1983.
20. **Catelani, D., Sorlini, C., and Treccani, V.**, The metabolism of biphenyl by *Pseudomonas putida*, *Experientia*, 27, 1173, 1971
21. **Tulp, M. T. M., Schmitz, R., and Hutzinger, O.**, The bacterial metabolism of 4,4'-dichlorobiphenyl and its suppression by alternative carbon sources, *Chemosphere*, 7, 103, 1978
22. **Kaiser, K. L. E. and Wong, P. T. S.**, Bacterial degradation of polychlorinated biphenyls. I. Identification of some metabolic products from Aroclor 1242, *Bull. Environ. Contam. Toxicol.*, 11, 291, 1974
23. **Furukawa, K. and Matsumura, F.**, Microbial metabolism of polychlorinated biphenyls. Studies on the relative degradability of polychlorinated biphenyl components by *Alkaligenes* sp., *J. Agric. Food Chem.*, 24, 251, 1976.
24. **Clark, B. R., Chian, E. S. K., and Griffin, B. A.**, Degradation of polychlorinated biphenyls by mixed microbial cultures, *Appl. Environ. Microbiol.*, 37, 680, 1979.
25. **Horvath, R. S.**, Microbial co-metabolism and the degradation of organic compounds in nature, *Bacteriol. Rev.*, 36, 146, 1972.
26. **Gibson, D. T., Roberts, R. L., Wells, M. C., and Kobal, V. M.**, Oxidation of biphenyl by a *Beyerinckia* species, *Biochem. Biophys. Res. Commun.*, 50, 211, 1973.
27. **Gibson, D. T., Cardini, G. E., Maseles, F. C., and Kallis, R. E.**, Incorporation of oxygen-18 into benzene by *Pseudomonas putida*, *Biochemistry*, 9, 1631, 1970.
28. **Lunt, D. and Evans, W. C.**, The microbial metabolism of biphenyl, *Biochem. J.*, 18, 54, 1970
29. **Carey, A. E. and Harvey, G. R.**, Metabolism of polychlorinated biphenyls by marine bacteria, *Bull. Environ. Contam. Toxicol.*, 20, 527, 1978.
30. **Tejedor, M. C., Murado, M. A., and Baluja, G.**, Oxidative metabolism in *Saccharomyces cerevisiae* as affected by polychlorinated biphenyls, *Bull. Environ. Contam. Toxicol.*, 22, 439, 1979
31. **Cole, M. A., Reichert, P. B., and Button, D. K.**, Reversible bioconcentration of monochlorobiphenyls by *Rhodococcus rubra*: correlations with aqueous solubility of substrate, *Bull. Environ. Contam. Toxicol.*, 23, 44, 1979
32. **Murado, M. A., Tejedor, M. C., and Baluja, G.**, Interactions between polychlorinated biphenyls (PCBs) and soil microfungi. Effects of Aroclor 1254 and other PCBs on *Aspergillus flavus* cultures, *Bull. Environ. Contam. Toxicol.*, 15, 768, 1976.
33. **Schwartz, R. D., Williams, A. L., and Hutchinson, D. B.**, Microbial production of 4,4'-dihydroxybiphenyl: biphenyl hydroxylation by fungi, *Appl. Environ. Microbiol.*, 39, 702, 1980.
34. **Biggs, D. C., Powers, C. D., Rowland, R. G., O'Connors, H. B., Jr., and Wurster, C. F.**, Uptake of polychlorinated biphenyls by natural phytoplankton assemblages: field and laboratory determination of ^{14}C-PCB particle-water index of partition, *Environ. Pollut.*, 22, 101, 1980.
35. **Kolt, J. E., Priester, L. E., and Sandifer, S. H.**, Polychlorinated biphenyl (Aroclor 1242): effects of uptake on growth, nucleic acids, and chlorophyll of a marine diatom, *Bull. Environ. Contam. Toxicol.*, 6, 156, 1971.
36. **Moore, S. A., Jr. and Harriss, R. C.**, Effects of polychlorinated biphenyl on marine phytoplankton communities, *Nature (London)*, 240, 356, 1972.
37. **Biggs, D. C., Rowland, R. G., O'Connors, H. B., Jr., Powers, C. D., and Wurster, C. F.**, Comparison of the effects of Chlordane and PCB on the growth, photosynthesis, and cell size of estuarine phytoplankton, *Environ. Pollut.*, 15, 253, 1978.
38. **Harding, L. W., Jr. and Phillips, J. H., Jr.**, Polychlorinated biphenyl (PCB) uptake by marine phytoplankton, *Mar. Biol.*, 49, 103, 1978.
39. **Brown, M. P., McLaughlin, J. J. A., O'Connor, J. M., and Wyman, K.**, A mathematical model of PCB bioaccumulation in plankton, *Ecol. Model.*, 15, 29, 1982.
40. **Urey, J. C., Krieber, J. C., and Boylan, J. M.**, Bioconcentration of four pure PCB isomers by *Chlorella pyrenoidosa*, *Bull. Environ. Contam. Toxicol.*, 16, 81, 1976.
41. **O'Connors, H. B., Jr., Wurster, C. F., Powers, C. D., Biggs, D. C., and Rowland, R. G.**, Polychlorinated biphenyls may alter marine trophic pathways by reducing phytoplankton size and production, *Science*, 201, 737, 1978.
42. **Hansen, D. J.**, Aroclor 1254: effect on composition of developing estuarine animal communities in the laboratory, *Contrib. Mar. Sci.*, 18, 19, 1974.

MONS 006044

43. Gluschenko, V. and Gluschenko, W., Effect of polychlorinated biphenyl compounds on growth of Great Lakes phytoplankton, *Can. J. Bot.*, 53, 653, 1975.
44. Cooley, N. R., Keltner, J. M., Jr., and Forester, J., Mirex and Aroclor 1254: effect on and accumulation by *Tetrahymena pyriformis* strain W, *J. Protozool.*, 19, 636, 1972.
45. Lowe, J. I., Parrish, P. R., Patrick, J. M., Jr., and Forrester, J., Effects of the polychlorinated biphenyl Aroclor 1254 on the American oyster, *Crassostrea virginica*, *Mar. Biol.*, 17, 209, 1972.
46. Courtney, W. A. M. and Denton, R. W., Persistence of polychlorinated biphenyls in the hard-clam (*Mercenaria mercenaria*) and the effect upon the distribution of these pollutants in the estuarine environment, *Environ. Pollut.*, 10, 55, 1976.
47. Marinucci, A. C. and Bartha, R., Accumulation of the polychlorinated biphenyl Aroclor 1242 from contaminated detritus and water by the saltmarsh detritivore, *Uca pugnax*, *Bull. Environ. Contam. Toxicol.*, 29, 326, 1982.
48. Neratram, R. J., McKinnon, A. E., and DeFreitas, A. S. W., A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa River yellow perch (*Perca flavescens*), *J. Fish. Res. Bd. Can.*, 33, 248, 1976.
49. Fowler, S. W., Pellkarpov, G. G., Elder, D. L., Parul, P., and Villeneuve, J. P., Polychlorinated biphenyls: accumulation from contaminated sediments and water by the polychaete *Nereis diversicolor*, *Mar. Biol.*, 48, 303, 1978.
50. Courtney, W. A. M. and Langston, W. J., Uptake of polychlorinated biphenyl (Aroclor 1254) from sediment and from seawater in two intertidal polychaetes, *Environ. Pollut.*, 15, 303, 1978.
51. Sodergren, A. and Svensson, B. J., Uptake and accumulation of DDT and PCB by *Ephemera danica* (Ephemeroptera) in continuous-flow systems, *Bull. Environ. Contam. Toxicol.*, 9, 345, 1973.
52. Stalling, D. L. and Mayer, F. L., Jr., Toxicities of PCBs to fish and environmental residues, *Environ. Health Perspect.*, 1, 159, 1972.
53. Nebeker, A. V. and Puglisi, F. A., Effect of polychlorinated biphenyls (PCBs) on survival and reproduction of *Daphnia*, *Gammarus*, and *Tanytarsus*, *Trans. Am. Fish. Soc.*, 103, 722, 1974.
54. Sodergren, A., Svensson, B. J., and Ullstrand, S., DDT and PCB in south Swedish streams, *Environ. Pollut.*, 3, 25, 1972.
55. Khan, M. A., Rao, R. M., and Novak, A. F., Adsorption of polychlorinated biphenyl (Aroclor 1254) on shrimp, *Bull. Environ. Contam. Toxicol.*, 16, 503, 1976.
56. Rosenfeld, G., Petrocelli, S. R., Anderson, J. W., Glass, C. S., and Neff, G. E., Toxicity of polychlorinated biphenyls (Aroclor 1254) to adult, juvenile, and larval stages of the shrimp, *Bull. Environ. Contam. Toxicol.*, 15, 297, 1976.
57. Duke, T. W., Lowe, J. I., and Wilson, A. J., Jr., A polychlorinated biphenyl (Aroclor 1254) in the water, sediment, and biota of Escambia Bay, Florida, *Bull. Environ. Contam. Toxicol.*, 5, 171, 1970.
58. Nimmo, D. R., Forrester, J., Heitmuller, P. T., and Cook, G. H., Accumulation of Aroclor 1254 in grass shrimp (*Palaemonetes pugio*) in laboratory and field exposures, *Bull. Environ. Contam. Toxicol.*, 11, 303, 1974.
59. Rhodebaugh, R. W., Residues in Atlantic zooplankton, *Bull. Environ. Contam. Toxicol.*, 8, 345, 1972.
60. Clayton, J. R., Jr., Pavlou, S. P., and Breitner, N. F., Polychlorinated biphenyls in coastal marine zooplankton: bioaccumulation by equilibrium partitioning, *Environ. Sci. Technol.*, 11, 676, 1977.
61. Sanders, H. O. and Chandler, J. H., Biological magnification of a polychlorinated biphenyl (Aroclor 1254) from water by aquatic invertebrates, *Bull. Environ. Contam. Toxicol.*, 7, 257, 1972.
62. Langston, W. J., Accumulation of polychlorinated biphenyls in the cockle *Cerastoderma edule* and the tellin *Macoma balthica*, *Mar. Biol.*, 45, 265, 1978.
63. Metcalf, R. L., Sanborn, J. R., Lu, P. Y., and Nye, D., Laboratory model ecosystem studies of the degradation and fate of radiolabeled tri-, tetra-, and pentachlorobiphenyl compared with DDE, *Arch. Environ. Contam. Toxicol.*, 3, 151, 1975.
64. Stenn, W. C., Parks, D. F., and Baughman, G. L., Partitioning of selected polychlorinated biphenyls to natural sediments, *Water Res.*, 12, 655, 1978.
65. Hirakawa, Y., Takahashi, M., and Nishimura, H., Adsorption of polychlorinated biphenyl onto sea bed sediment, marine plankton, and other adsorbing agents, *Environ. Sci. Technol.*, 13, 580, 1979.
66. Parks, D. F., Stenn, W. C., and Baughman, G. L., Role of physico-chemical properties of Aroclor 1016 and 1242 in determining their fate and transport in aqueous environments, *Chemosphere*, 7, 319, 1978.
67. Ellenrieth, S. J., Rolfed, G. J., and Johnson, T. C., Accumulation of polychlorinated biphenyls (PCBs) in surficial Lake Superior sediments: Atmospheric deposition, *Environ. Sci. Technol.*, 13, 569, 1979.
68. Pavlou, S. P. and Dexter, R. N., Distribution of polychlorinated biphenyls (PCB) in estuarine ecosystems. Testing the concept of equilibrium partitioning in the marine environment, *Environ. Sci. Technol.*, 13, 65, 1979.
69. Willish, D. J., Metcalfe, C. D., Akagi, H. M., and McLeese, D. W., Flux of Aroclor 1254 between estuarine sediments and water, *Bull. Environ. Contam. Toxicol.*, 24, 20, 1980.

MONS 006045

70. Hansen, D. J., Parrish, P. R., Lowe, J. I., Wilson, A. J., Jr., and Wilson, P. D., Chronic toxicity, uptake, and retention of Aroclor 1254 in two estuarine fishes. *Bull. Environ. Contam. Toxicol.*, 6, 113, 1971.

71. Seegaseen, B. E., Long-term effects of PCB (Clophen A50) on growth, reproduction and swimming performance in the minnow *Phoxinus phoxinus*, *Water Res.*, 14, 681, 1980.

72. Mayer, F. L., Mehrle, P. M., and Sanders, H. O., Residue dynamics and biological effects of polychlorinated biphenyls in aquatic organisms, *Arch. Environ. Contam. Toxicol.*, 5, 501, 1977

73. Hansen, D. J., Parrish, P. R., and Forrester, J., Aroclor 1016: toxicity to and uptake by estuarine animals, *Environ. Res.*, 7, 363, 1974.

74. Branson, D. R., Blau, G. E., Alexander, H. C., and Neely, W. B., Bioconcentration of 2,2',4,4'-tetrachlorobiphenyl in rainbow trout as measured by an accelerated test, *Trans. Am. Fish. Soc.*, 104, 785, 1975.

75. Glass, C. S., Murvoy, H. E., Ray, L. E., and Kiro, S., Bioaccumulation of hexachlorobenzene in killifish, (*Fundulus similis*), *Bull. Environ. Contam. Toxicol.*, 25, 891, 1980.

76. Backe, C. A., Servos, J. W., Youngs, W. D., and Link, D. J., Polychlorinated biphenyl residues accumulation in cayuga trout with age, *Science*, 177, 1191, 1972.

77. Narbonne, J. F., Polychlorinated biphenyl accumulation in grey mullets (*Chelon labrosus*): effect of age, *Bull. Environ. Contam. Toxicol.*, 22, 65, 1979b.

78. Zitko, V., Polychlorinated biphenyls and organochlorine pesticides in some freshwater and marine fishes, *Bull. Environ. Contam. Toxicol.*, 6, 464, 1971.

79. Cailhaus, R. J., O'Connor, J. M., and Petrov, L. S., Uptake, retention, and elimination of PCB (Aroclor 1254) by larval striped bass (*Morone Saxatilis*), *Bull. Environ. Contam. Toxicol.*, 24, 467, 1980.

80. Shen, J. C., Shumate, H. A., Dunn, H. J., Colquhoun, J. R., Spagnoli, J. J., and Veith, G. D., Bioaccumulation of Aroclor 1016 in Hudson River fish, *Bull. Environ. Contam. Toxicol.*, 22, 332, 1979.

81. DeFoe, D. L., Veith, G. D., and Carlson, R. W., Effects of Aroclor 1248 and 1260 on the fathead minnow (*Pimephales promelas*), *J. Fish. Res. Bd. Can.*, 35, 997, 1978.

82. Kjeldsen, A. E., Polychlorinated biphenyls (PCBs) in the rivers Avon and Frome, *Bull. Environ. Contam. Toxicol.*, 14, 687, 1975.

83. Hattula, M. L. and Kerling, O., Adsorption and elimination of polychlorinated biphenyls (PCB) in goldfish, *Acta Pharmacol. Toxicol.*, 32, 237, 1973.

84. Narbonne, J. F., Accumulation of polychlorinated biphenyl (Phenoclor DP6) by estuarine fish, *Bull. Environ. Contam. Toxicol.*, 22, 60, 1979a.

85. Zitko, V. and Hutzinger, O., Uptake of chloro- and bromobiphenyls, hexachloro- and hexabromobenzene by fish, *Bull. Environ. Contam. Toxicol.*, 16, 665, 1976.

86. Camp, B. J., Hajtmanneik, E., Armour, C., and Lewis, D. H., Acute effects of Aroclor 1254 (PCB) on *Ictalurus punctatus* (catfish), *Bull. Environ. Contam. Toxicol.*, 12, 204, 1974.

87. Seaborn, J. R., Childers, W. F., and Metcalf, R. L., Uptake of three polychlorinated biphenyls, DDT, and DDE by the green sunfish, *Lepomis cyanellus* Raf., *Bull. Environ. Contam. Toxicol.*, 13, 209, 1975.

88. Matsumura, M. J., Jr. and Lamb, J. J., Isolation and identification of a polar metabolite of tetrachlorobiphenyl from bile of rainbow trout exposed to ^{14}C-tetrachlorobiphenyl, *Bull. Environ. Contam. Toxicol.*, 15, 101, 1976.

89. Hinz, R. and Matsumura, F., Comparative metabolism of PCB isomers by three species of fish and the rat, *Bull. Environ. Contam. Toxicol.*, 18, 631, 1977.

90. Bagley, G. E. and Crummett, E., Elimination pattern of Aroclor 1254 components in the bobwhite, *J. Chromatogr.*, 75, 219, 1973.

91. Bailey, S. and Bunyan, P. J., Interpretation of persistence and effects of polychlorinated biphenyls in birds, *Nature (London)*, 236, 34, 1972.

92. Hutzinger, O., Nash, D. M., Safe, S., DeFreitas, A. S. W., Norstrom, R. J., Wildish, D. J., and Zitko, V., Polychlorinated biphenyls: metabolic behavior of pure isomers in pigeons, rats, and brook trout, *Science*, 178, 312, 1972.

93. Matthews, H. B. and Anderson, M., PCB chlorination versus PCB distribution and excretion, in Proc. National Conference on Polychlorinated Biphenyls, Ayer, F. A., Compiler, U.S. Environmental Protection Agency, Office of Toxic Substances, U.S. Department of Commerce, Washington, D.C., 1975, 50.

94. Grob, W., Klein, W., Coulston, F., Golberg, L., and Korte, F., Beitrage zur Oekologischen Chemie. LXXXIII. In vitro metabolism of polychlorinated biphenyls-^{14}C, *Bull. Environ. Toxicol.*, 13, 424, 1975.

95. Falk, C. R., Mueller, W. F., Coulston, F., and Korte, F., Distribution and excretion of 2,2',4,4',6-pentachlorobiphenyl in the rat, *Bull. Environ. Contam. Toxicol.*, 22, 582, 1979.

96. Matsumura, T., Hidaka, K., Ohe, T., and Matsumura, M., A comparative study on accumulation and elimination of tetrachlorobiphenyl isomers in mice, *Bull. Environ. Contam. Toxicol.*, 18, 452, 1977

97. Hutzinger, O., Jamieson, W. D., Safe, S., Poulsumm, L., and Ammon, R., Identification of metabolic dechlorination of highly chlorinated biphenyl in rabbit, *Nature (London)*, 252, 698, 1974.

MONS 006046

98. Allen, J. R. and Norback, D. H., Pathobiological responses of primates to polychlorinated biphenyl exposure. in Proc. National Conference on Polychlorinated Biphenyls. Ayer, F. A., Compiler. U.S. Environmental Protection Agency, Office of Toxic Substances, U.S. Department of Commerce, Washington, D.C., 1975, 43.
99. Geerts, J. A. and Handy, M. K., Depuration and biological half-life of ^{14}C-PCB in aquatic organisms. *Bull. Environ. Contam. Toxicol.*, 28, 305, 1982.
100. Calambokidis, J., Mowrer, J., Boag, M. W., and Harmon, S. G., Selective retention of polychlorinated biphenyl components in the mussel, *Mytilus edulis*, *Arch. Environ. Contam. Toxicol.*, 8, 299, 1979.
101. McLeese, D. W., Metcalfe, C. D., and Peamch, D. S., Bioaccumulation of chlorobiphenyls and Endrin from food by lobsters (*Homarus americanus*), *Bull. Environ. Contam. Toxicol.*, 25, 161, 1980.
102. Bend, J. R., Hart, L. G., Guarino, A. M., Ball, D. P., and Fouts, J. R., Distribution and excretion of [^{14}C]-2,4,5,2',5'-pentachlorobiphenyl in the lobster (*Homarus americanus*) and the dogfish shark (*Squalus acanthias*), in Proc. National Conference on Polychlorinated Biphenyls, Ayer, F. A., Compiler, U.S. Environmental Protection Agency, Office of Toxic Substances, U.S. Department of Commerce, Washington, D.C., 1975, 292.
103. Wszolek, P. C., Lisk, D. J., Wacha, T., and Youngs, W. D., Persistence of polychlorinated biphenyls and 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene (p,p'-DDE) with age in lake trout after 8 years, *Environ. Sci. Technol.*, 12, 1289, 1979.
104. Guiney, P. D., Petersen, R. E., Melancon, M. J., and Lech, J. J., The distribution and elimination of 2,5,2',5'-[^{14}C] tetrachlorobiphenyl in rainbow trout (*Salmo gairdneri*), *Toxicol. Appl. Pharmacol.*, 39, 329, 1977.
105. Hansen, L. G., Wichhorst, W. B., and Simon, J., Effects of dietary Aroclor 1242 on channel catfish (*Ictalurus punctatus*) and the selective accumulation of PCB components, *J. Fish. Res. Bd. Can.*, 33, 1343, 1976.
106. Mizutani, T., Hidaka, K., Obe, T., Matsumoto, M., Yamamoto, K., and Tajima, K., Comparative study on accumulation and elimination of hexachlorobiphenyls and decachlorobiphenyl in mice, *Bull Environ. Contam. Toxicol.*, 25, 181, 1980.

MONS 006047

Chapter 6

MODIFICATION OF PCBs BY BACTERIA AND OTHER MICROORGANISMS

Kensuke Furukawa

TABLE OF CONTENTS

I. Introduction 90

II. PCBs and Microorganisms 90

III. Biodegradability of PCBs 91

IV. Microbial Metabolism of PCBs 93

V. Biodegradation of Commercial PCBs and Their Metabolic Products 94

VI. Total Degradation of PCBs and Plasmids 96

Acknowledgments 96

References 98

MONS 006048

I. INTRODUCTION

Metabolic breakdown of PCBs by microorganisms is considered to be one of the major routes of environmental degradation for these widespread pollutants.[1] Environmental monitoring has demonstrated that the PCBs found in environmental samples are the more highly chlorinated biphenyls, i.e., those containing five or more chlorines per biphenyl molecule.[2,3] This is circumstantial evidence that the less-chlorinated biphenyls degrade more rapidly than the more highly chlorinated ones. The occurrence and distribution of PCB-degrading microorganisms and their capability of biodegrading PCBs have been investigated in the last decade. Since the report by Ahmed and Focht[4] in 1973 that two species of *Achromobacter* are capable of growing on biphenyl and 4-chlorobiphenyl, a number of studies have indicated that pure cultures of microorganisms and naturally occurring microbial populations are capable of degrading PCBs.[5-14] There is evidence that a variety of factors affect the microbial degradation of PCBs in the environment. The degree of chlorination in the various components of PCBs might be the most significant factor. Water solubility and volatility of PCBs, pH, temperature, oxygen, nutrient supplies in the environment, emulsification of PCBs and adsorption by various materials such as soil, sediment, sludge, and biological materials all combine to varying extents, to affect microbial degradation of PCBs in ecosystems. The present review describes interactions between PCBs and microorganisms (mainly bacteria), biodegradability, and metabolic transformations of various PCBs.

II. PCBs AND MICROORGANISMS

The ubiquitous occurrence of bacteria which can utilize biphenyl as a sole carbon and energy has been reported. Ohmori et al.[15] isolated 39 bacterial strains capable of utilizing biphenyl from soil. Lunt and Evans[16] described a Gram negative soil bacterium that oxidized biphenyl to phenylpyruvic acid. A strain of *Pseudomonas putida* metabolized biphenyl to benzoic acid via 2,3-dihydro-2,3-dihydroxybiphenyl, 2,3-dihydroxybiphenyl, and 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoic acid.[17,18] Gibson et al.[19] position further evidence for initial oxidative attack at the 2,3-position on the biphenyl molecule. In 1973 degradation of mono- and dichlorobiphenyl to chlorobenzoic acids was shown by two species of *Achromobacter*.[4] Later, conversion of PCBs to chlorobenzoic acids was shown for certain pure strains and by naturally occurring microorganisms.[9,10]

Furukawa et al.[20] described the interaction of PCBs and bacteria, demonstrating that an *Alcaligenes* sp. and an *Acinetobacter* sp. rapidly adsorbed a large amount of ^{14}C-labeled 2,5,2'-trichlorobiphenyl onto the cell surface and then the compound was gradually metabolized. The metabolic products containing radioactive carbon, such as a ring-cleaved compound and 2,5-dichlorobenzoic acid were gradually released from the cells and moved into the aqueous layer.

PCB-degrading or PCB-resistant bacteria recovered from estuarine and marine samples represent seven bacterial genera: *Pseudomonas*, *Vibrio*, *Aeromonas*, *Micrococcus*, *Acinetobacter*, *Bacillus*, and *Streptomyces*.[21] Twenty isolates of PCB-degrading bacteria from the Hudson River represented five genera: *Acetobacter*, *Acinetobacter*, *Alcaligenes*, *Klebsiella*, and *Pseudomonas*.[22] Sylvestre[23] described a method for the isolation of 4-chlorobiphenyl-degrading bacteria from soil samples and activated sludge samples. The method is based on the observation that when a PCB solution is spread over an agar plate previously inoculated with an environmental sample, the film of PCB deposited on the surface of the plate becomes clarified around some of the colonies. Fourteen strains obtained by this method were all strictly aerobic, motile, Gram negative rods, and able to grow on 4-chlorobiphenyl as the sole carbon source.

PCB-sensitive bacteria are also known. The lipophilic nature of these chlorinated hydro-

MONS 006049

carbons enhances their toxic properties by promoting the efficient binding of such substances to cells. Of 85 different estuarine bacteria, growth of 26 strains was inhibited to a varying extent by PCBs.[24] In contrast to resistant bacteria, sensitive strains were mainly amylolytic and proteolytic. Of 17 bacterial cultures tested, growth of two open-ocean isolates, including one *Pseudomonas*, was consistently inhibited by Aroclor® 1254 at a concentration as low as 10 μg/ℓ.[25] The *Pseudomonas* also had reduced carotenoid levels and an altered filamentous morphology. The effect of Aroclor® 1254 was immediate and reversible for at least 18 hr after initial exposure. The PCBs had no effect on respiration rates and protein synthesis at the growth-inhibiting concentration of the Aroclor®. On the other hand, rates per cell of adenine uptake and adenine incorporation into DNA and total nucleic acids by the cells treated with PCBs were significantly lower than in control cells. Lower chlorinated PCBs were highly mutagenic to *Salmonella typhimurium*, whereas higher chlorinated ones were only weakly mutagenic.[26]

In contrast to bacteria, there is relatively little information about interaction between PCBs and fungi or yeasts. The following effects were observed between *Aspergillus flavus* and PCBs:[27] no metabolic change of PCBs, accumulation of various Aroclors in the mycelium, no significant effect on nucleic acid content, an obvious delay of sporulation, and a decrease of colony diameter. The magnitude of these effects was highest for Aroclor® 1232 and lowest for Aroclor® 1260. Tejedor et al.[28] observed that growth and oxygen uptake of *Saccharomyces cerevisiae* were suppressed by PCBs and that these effects increased as the chlorine content of the PCBs decreased. There is evidence that fungi, yeast, and a cyanobacterium oxidized biphenyl primarily at the 4-position to form 4-hydroxybiphenyl and 4,4'-dihydroxybiphenyl.[5,29-32] These results are similar to those reported for the mammalian metabolism of biphenyl and chlorinated biphenyls.[33-39]

III. BIODEGRADABILITY OF PCBs

Chlorine is known to alter the resonant properties of aromatic substrates and alter the electron density of specific sites. These alterations may result in a deactivation of the primary oxidation of chlorinated biphenyls by microorganisms. Furthermore, the positions occupied by substituted chlorines have stereochemical effects on the affinity between enzymes and their substrate molecules. Many workers have reported that both pure chlorobiphenyls and commercial PCBs are degraded by certain pure strains or by mixed cultures. Mixed cultures, dominated by *Alcaligenes odrans*, *A. denitryficans*, and an unidentified bacterium, degraded Aroclor® 1242.[13] The gas chromatography profile of Aroclor® was greatly altered after 5 days incubation. Tucker et al.[7] demonstrated that commercial PCB mixtures which contain predominantly mono- and dichlorobiphenyls readily undergo primary biodegradation by activated sludge microorganisms, and that as the levels of tri-, tetra-, and pentachlorobiphenyls increase, the degradation rates decrease accordingly. Similar results were obtained for the degradation of Kanaclor® (KC) 200, 300, 400, and 500, which are primarily di-, tri-, tetra-, and pentachlorobiphenyls, respectively.[40] Baxter et al.[8] showed that addition of biphenyl to the substrate enhanced the biodegradation of certain PCBs, indicating that co-metabolism could be involved in the degradation process of highly chlorinated biphenyls. Liu[14] also observed the enhanced biodegradation of Aroclor® 1254 by the addition of Aroclor® 1221 to the growth medium. Further investigation demonstrated that the rate of PCB biodegradation is greatly enhanced by growing *Pseudomonas* cells in a PCB-lignin-sulfonate emulsion. The use of lignin-sulfonate in the growth medium allow the cells to overcome the substrate-limiting factor of surface area. A kinetic study, using resting cells, indicated that Aroclor® 1221 was degraded much faster (980 μg/mg cell dry weight/hr) than Aroclor® 1254 (43 μg/mg cell dry weight/hr).

Furukawa et al.[41] studied the effect of chlorine substitution on biodegradability of PCBs.

MONS 006050

Table 1
EFFECT OF CHLORINE SUBSTITUTION ON BIODEGRADABILITY OF VARIOUS ISOMERIC PCBs BY BACTERIA

Isomer group	PCB chlorine position	Degradation rate[a] (nmol/ml/hr) *Alcaligenes sp.* Y42[b]	*Acinetobacter sp.* P6[b]
A	2-	>50	>50
	3-	>50	>50
	4-	>50	>50
B	2,3-	>50	46.4
	2,4-	>50	>50
	2,5-	>50	>50
	2,6-	0	4.1
	3,4-	>50	>50
	3,5-	>50	>50
C	2,2'-	6.3	14.0
	2,4'-	48.2	49.1
	3,3'-	—	18.5
	4,4'-	16.2	25.2
D	2,3,4-	35.1	32.0
	2,3,6-	0	0
	2,4,5-	46.0	32.4
	2,4,6-	3.1	46.0
E	2,5,2'-	1.6	5.1
	2,5,3'-	42.1	41.3
	2,5,4'-	21.8	30.6
	2,4,4'-	41.3	40.2
	3,4,2'-	15.6	38.6
F	2,3,4,5-	25.8	19.1
	2,3,5,6-	0	0
G	2,3,2',3'-	8.7	7.3
	2,4,2',4'-	0	0
	2,4,3',4'-	0	0
	2,5,2',5'-	0	3.5
	2,6,2',6'-	0	0
	3,4,3',4'-	0	0
H	2,4,5,2',5'-	0.6	0

[a] A 500 nmol amount of each compound dissolved in ethanol (10 ml/l each) was suspended in 10 ml of phosphate buffer (pH 7.5). Degradation rate was calculated after 1 hr of incubation for mono-, di-, and trichlorobiphenyls and after 2 hr of incubation for tetra- and pentachlorobiphenyls.

[b] The cell number was 2×10^9 cells/ml in *Alcaligenes* Y42 and 4.4×10^9 cells/ml in *Acinetobacter* P6.

From Furukawa, K., Tonomura, K., and Kamibayashi, A., *Appl. Environ. Microbiol.*, 35, 223, 1978. With permission.

Chlorinated biphenyls can theoretically consist of as many as 210 different components. Of the possible isomers, 103 are considered most probable. For this study 33 pure isomers of PCBs and single strains of the bacteria, *Alcaligenes* sp. and *Acinetobacter* sp. were employed. The former was grown on biphenyl, and the latter was grown on 4-chlorobiphenyl as a sole carbon source. Both strains could co-metabolize a variety of PCB components to varying extents. The results presented in Table 1 indicate the following general information on the

MONS 006051

Table 2
METABOLIC PRODUCTS OF VARIOUS PCB ISOMERS TRANSFORMED BY *ACINETOBACTER* sp.

Group	Major product	PCB isomers
i	Chlorobenzoic acids (Cl no. 1 to 4)	2-, 3-, 4-, 2,3-, 2,4-, 2,5-, 3,4-, 3,5-, 2,2'-, 3,3'-, 4,4'-, 2,3,4-, 2,4,5-, 2,5,2'-, 3,4,2'-, 2,3,4,5-, 2,4,2',4'-, 3,4,3',4'-
ii	*Meta*-cleavage compounds	2,4'-, 2,4,4'-, 2,5,4'-
iii	Dihydroxy compounds	2,6-, 2,3,6-, 2,4,2',5'-, 2,4,5,2',5'-
iv	Trihydroxy compounds	2,4,6-
v	Unknown compounds	2,3,2',3'-, 2,3,2',5'-, 2,4,5,2',3'-
vi	No metabolite	2,3,5,6-, 2,6,2',6'-

relationship between chemical structure and microbial breakdown of PCBs. (1) Degradation rate markedly decreases as chlorine substitution increases. (2) PCBs containing two chlorines in the *ortho*-position of a single ring (i.e., 2,6-) and each ring (i.e., 2,2'-) show a striking resistance to degradation, as illustrated in the studies with 2,6-, 2,2'-, 2,3,6-, 2,5,2'-, 2,3,5,6-, and 2,6,2',6'-chlorobiphenyls. 2,4,6-Trichlorobiphenyl is the exception in this series of PCBs. This compound is rapidly metabolized through an alternative pathway by *Acinetobacter* sp., while the same compound is slowly metabolized by *Alcaligenes* sp. through the major pathway to 2,4,6-trichlorobenzoic acid. (3) PCBs containing all chlorines on a single ring are generally degraded faster than those containing the same number on both rings. (4) PCBs having two chlorine atoms at the 2,3-position of one ring such as 2,3,2',3'-, 2,3,2',5'-, and 2,4,5,2',3'-chlorobiphenyls are much more susceptible to microbial attack, compared with other tetra- and pentachlorobiphenyls. Members of this series of PCBs are metabolized through an alternative pathway with accumulation of unknown compounds. (5) Preferential ring cleavage of the biphenyl molecules occurs with a nonchlorinated or lesser chlorinated ring.

It is also known that chlorine substitution greatly affects metabolism and excretion of PCBs by mammalian and avian species. A number of less-chlorinated PCBs (i.e., mono-, di, tri-, and tetrachlorobiphenyls) are readily metabolized and excreted by mammals and birds.[43-46] However, the rate of metabolism drops sharply as the number of chlorines per biphenyl molecule increases.[46,47]

IV. MICROBIAL METABOLISM OF PCBs

In bacterial metabolism studies with 36 pure PCB isomers (chlorine numbers 1 to 5), Furukawa et al.[48,49] demonstrated that 33 compounds were oxidized by an *Acinetobacter* sp. (Table 2). From the analysis of metabolic intermediates, it was found that a number of the PCB components listed in Table 2 are converted to the corresponding chlorobenzoic acids by an oxidative route as illustrated in Figure 1. Like other aromatic hydrocarbons,[50,51] PCBs are considered to be metabolized via a deoxygenase catalyzed reaction such as Gibson et al.[19] had demonstrated with biphenyl. A species of *Beijerinckia* metabolized biphenyl to *cis*-2,3-dihydroxy-1-phenylhexa-4,6-diene (*cis*-2,3-dihydro-2,3-dihydroxybiphenyl). This suggests that a cyclic peroxide is an initial oxidation product in the metabolism of biphenyl. Two atoms of molecular oxygen might be incorporated at the 2,3-position of a nonchlorinated

MONS 006052

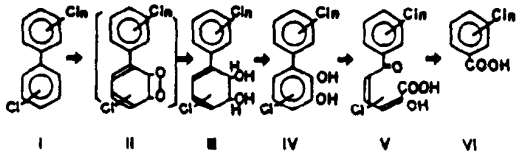


FIGURE 1. Major metabolic pathway of PCBs by bacteria.

or lesser chlorinated ring of PCBs to form *cis*-dihydrodiol compounds (III in Figure 1). The dihydrodiols are then dehydrogenated to yield 2,3-dihydroxy compounds (IV). The *meta*-cleavage occurs between C1 and C2 of the 2,3-dihydroxy compounds to yield chlorinated derivative of 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoate (V). For many PCB isomers the *meta*-cleavage compounds thus formed are usually hydrolyzed readily to chlorobenzoic acids (VI). Of 36 PCBs, 18 isomers were converted to the corresponding chlorobenzoic acids by this major pathway in *Acinetobacter* sp. This major pathway to chlorobenzoates is also common in other pure cultures such as *Alcaligenes* sp.,[9,48] *Achromobacter* sp.,[4] and *Pseudomonas putida*[17,18] and naturally occurring microbial cultures[10] with both isomeric chlorobiphenyls and commercial PCB mixtures.[49] However, alternative pathways to the chlorobenzoate pathway are demonstrated with other PCB isomers as shown in Table 2. For example, 2,4'-, 2,4,4'-, and 2,5,4'-chlorobiphenyls which all have chlorine substituents at the 2,4'-position are readily converted to the *meta*-cleavage compounds through the major pathway illustrated in Figure 1. These *meta*-cleavage compounds are rather stable and accumulate in the reaction mixture during prolonged incubation. Dihydroxy compounds accumulate in the reaction mixture from the 2,6-, 2,3,6-, 2,4,2',5'-, 2,5,2',5'-, and 2,4,5,2'-chlorobiphenyls. 2,4,6-Trichlorobiphenyl is quickly metabolized to a trihydroxy compound via a dihydroxy compound. Thus, the trihydroxy compound predominantly accumulates during the late stages of incubation. PCBs which possess chlorine atoms at the 2,3-position such as 2,3,2',3'-, 2,3,2',5', and 2,4,5,2',3'-chlorobiphenyls seem to be metabolized by an alternative route. Large amounts of unidentified product always accumulate along with the appropriate chlorobenzoic acid from this series of PCBs. These unidentified compounds are also produced from the commercial PCB mixtures, Kaneclor® 400.[49] Thus, the metabolic alterations of PCBs by bacteria are greatly dependent on chlorine substitution.

There is evidence that fungi, yeast, and a cyanobacterium (*Oscillatoria* sp.) metabolize biphenyl and low chlorinated biphenyls to monohydroxy and dihydroxy compounds as is also demonstrated by mammalian systems.[33-39] Fungal species of several genera are able to grow on biphenyl and form 2- and 4-hydroxybiphenyls and 4,4'-dihydroxybipheynyl.[39] Dodge et al.[39] demonstrated that *Cunninghamella elegans* grown in dextrose broth transformed biphenyl to produce 2-, 3-, and 4-hydroxybiphenyls as well as 4,4'-, 2,4'-, and 2,5-dihydroxybiphenyls. Walnöffer et al.[3] observed that *Rhizopus japonicus* converted 4-chlorobiphenyl to 4-chloro-4-hydroxybiphenyl. There is a report that *Candida tropicallis* oxidizes biphenyl to 4-hydroxybiphenyl.[35] A cyanobacterium, *Oscillatoria* sp. also oxidizes biphenyl to 4-hydroxybiphenyl.[32] However, ring cleavage which is common in bacteria has not been reported in fungi and yeasts.

V. BIODEGRADATION OF COMMERCIAL PCBs AND THEIR METABOLIC PRODUCTS

Based upon observation with pure isomers of PCBs, Furukawa et al.[40] using *Acinetobacter*

MONS 006053

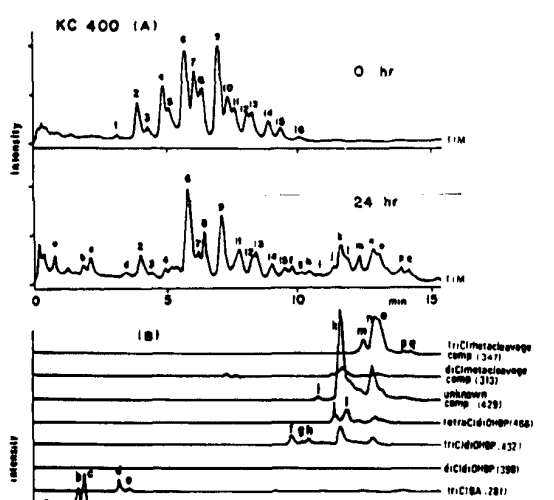


FIGURE 2. Biodegradation of Kaneclor® 400 by *Acinetobacter* sp. and metabolic products. (A) Total ion manner on GC/MS of KC 400 at 0 hr and after 24 hr incubation with organisms. PCB components are numbered and the metabolites are expressed by letters. (B) Mass chromatogram of metabolite was monnored by mass chromatography. Abbreviations: BA, benzoic acid; BP, biphenyl.

sp. examined the biodegradability and metabolic products of commercial PCB mixtures (Kaneclors®). KC 200 (primarily dichlorobiphenyls) and KC 300 (primarily trichlorobiphenyls) were readily degraded by *Acinetobacter* sp. so that total ion monitor (TIM) readings on gas chromatography/mass spectrometry (GC/MS) were greatly changed after 4 hr incubation. The peaks of PCB components disappeared rapidly or decreased in size and were replaced by the peaks of metabolic products. Monochlorobenzoic acids accumulated predominantly in the reaction mixture from KC 200. Several metabolic products such as mono- and dichlorobenzoic acids, dichloro- and trichlorodihydroxy compounds, the *meta*-cleavage products with two and three chlorines were observed from KC 300. KC 400 (primarily tetrachlorobiphenyls) is also susceptible to biodegradation. The TIM profile was greatly changed after 24 hr incubation by the decrease of various PCB components (di-, tri-, and tetrachloro isomers) and by the concomitant formation of metabolites as presented in Figure 2. A variety of metabolites of mono-, di-, and trichlorobenzoic acids, trichloro- and tetrach-

MONS 006054

loro dihydroxybiphenyls, the *meta*-cleavage products (chlorine no. 2 to 4), and in addition certain unknown compounds with two chlorines in the molecules were detected. The unknown compounds can be derived from 2,3,2',3'- or 2,3,2',5'-tetrachlorobiphenyls or both (see Table 2). On the other hand, KC 500 components (primarily pentachlorobiphenyls) were refractory and hardly metabolized. Only dihydroxy compounds of pentachlorobiphenyls were detected. Thus, a variety of metabolic products can be formed and accumulate from commercial PCB mixtures by bacteria.

VI. TOTAL DEGRADATION OF PCBs AND PLASMIDS

A number of bacterial strains are known to convert various PCB components into the corresponding chlorobenzoates, so that this oxidative route appears to be a common pathway for PCB degradation by bacteria. In the natural environment a mixed culture acting on the many components of PCBs might be expected to give a more complete degradation than would a single organism. Chlorobenzoates formed from many PCB components by bacteria can be decomposed by other bacteria. Horvath and Alexander[33] demonstrated that 20 isolates representing 9 bacterial genera co-metabolized one or more of 22 substituted benzoates. Some of the chlorinated benzoates can be acted upon by pure cultures of such genera as *Arthrobacter*,[34] *Brevibacterium*,[35] *Alcaligines*,[36] and *Pseudomonas*[37,38] and the metabolic processes have been studied in detail. The transformation and fate of chlorobenzoates under natural conditions has been studied by some workers. Dewey et al.[39] observed biological degradation of 2,3,6-trichlorobenzoic acid in soil. GiGeronimo et al.[40] reported that microorganisms in sewage decomposed *o*-, *m*-, and *p*-chlorobenzoic acids and also 3,4-dichlorobenzoic acid.

It is well known that plasmids can endow bacterial species with the ability to catabolize various hydrocarbons and other organic compounds.[41-43] A plasmid encoding conversion of 4-chlorobiphenyl to 4-chlorobenzoic acid has been demonstrated in *Klebsiella* sp.[44] Furukawa and Chakrabarty[45] also suggested that the plasmid pKF1 specified the catabolism of biphenyl and chlorinated biphenyls into benzoate and chlorobenzoates in *Acinetobacter* sp. and *Arthrobacter* sp. On the other hand, Hartman et al.[46] and Chaterjee and Chakrabarty[47] have demonstrated that introduction of TOL and other plasmids (pAC25) specifying chlorobenzoate degradation and subsequent selection in a chemostat with 4-chloro- or 3,5-dichlorobenzoic acid leads to the development of strains that can rapidly utilize 4-chloro- and 3,5-dichlorobenzoic acids. The 4-chlorobenzoate-degrading *Pseudomonas putida* harbors a plasmid pAC27, while the 3,5-dichlorobenzoate-degrading strain harbors a plasmid pAC31.[46] Both of the strains carry a portion of the TOL on the chromosome, and the plasmids pAC27 and pAC31 specify the corresponding chlorocatechol-degradative pathway i.e., 4-chlorocatechol and 3,5-dichlorocatechol. A combined culture of the PCB-dissimilating *Acinetobacter* sp. or *Arthrobacter* sp. (harboring the putative 53 Mdal plasmid specifying conversion of chlorobiphenyls to chlorobenzoic acids) and genetically constructed mono- or dichlorobenzoate-utilizing pseudomonads (harboring plasmids encoding complete utilization of mono- or dichlorobenzoates) allowed more than 98% utilization of mono- or dichlorobiphenyls with the liberation of equivalent amounts of chloride ions (Figure 3).[48] A combination of PCB-degrading strains and chlorobenzoate-degrading strains leading to total degradation of mono- and dichlorobiphenyls is an example of the role of various degradative plasmids in the total mineralization of some chlorinated synthetic compounds.

ACKNOWLEDGMENTS

I express my thanks to Dr. Fumio Matsumura of Michigan State University, Dr. Kenzo Tonomura of the University of Osaka Prefecture, Dr. A. M. Chakrabarty of the University

MONS 006055

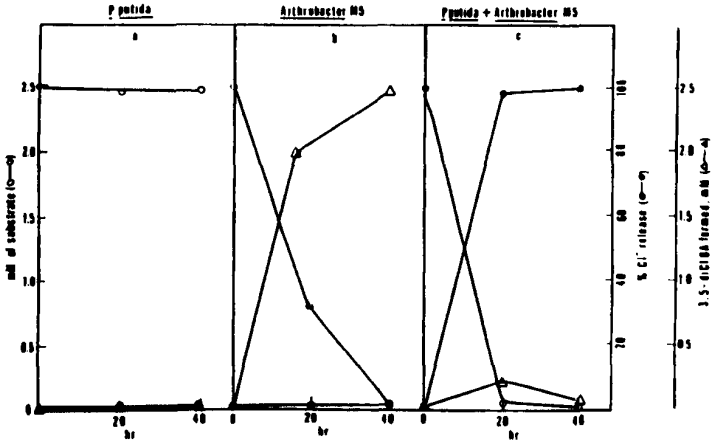


FIGURE 3. Total degradation of 3,5-dichlorobiphenyl by a mixed culture of *Arthrobacter* sp. M5 (harboring plasmid pKF1 specifying degradation of chlorobiphenyls to chlorobenzoic acids) and *Pseudomonas putida* (harboring plasmid pAC31 specifying utilization of 3,5-dichlorobenzoic acid). Substrate (3,5-dichlorobiphenyl) consumption (○), product (3,5-dichlorobenzoic acid) formation (△), and chloride release (●) by resting cells of 3,5-dichlorobenzoate-degrading *P. putida* (a), PCB-degrading *Arthrobacter* M5 (b), and a mixed culture of *P. putida* and *Arthrobacter* M5 (c). An extensive chloride release and little 3,5-dichlorobenzoate accumulation were observed in the mixed culture. However, a large amount of 3,5-dichlorobenzoate accumulation, and no chloride release was observed in pure culture of *Arthrobacter* M5. *P. putida* strain had no effect on the degradation of the 3,5-dichlorobiphenyl. (From Furukawa, K. and Chakrabarty, A. M., *Appl. Environ. Microbiol.*, 44, 619, 1982. With permission.)

MONS 006056

of Illinois at Chicago, and Dr. Noboru Tomizuka and Dr. Akira Kamibayashi of the Fermentation Research Institute for their kind suggestions and helpful discussion.

REFERENCES

1. **Furukawa, K.**, Microbial degradation of polychlorinated biphenyls (PCBs), in *Biodegradation and Detoxification of Environmental Pollutants*, Chakraborty, A. M., Ed., CRC Press, Boca Raton, Fla., 1982, 33.
2. **Holmes, D. C., Simmons, J. H., and Tatton, J. O'G.**, Chlorinated hydrocarbons in British wildlife, *Nature (London)*, 216, 227, 1967.
3. **Koeman, J. H., Ten Noever De Brauw, M. C., and De Vos, R. H.**, Chlorinated biphenyls in fish, mussels and birds from the River Rhine and the Netherland coastal area, *Nature (London)*, 221, 1126, 1969.
4. **Ahmed, M. and Focht, D. D.**, Degradation of polychlorinated biphenyls by two species of *Achromobacter*, *Can. J. Microbiol.*, 19, 47, 1973.
5. **Wellinöffer, P. R., Engelhardt, G., Safe, S., and Hutzinger, O.**, Microbial hydroxylation of 4-chlorobiphenyl and 4,4'-dichlorobiphenyl, *Chemosphere*, 2, 69, 1973.
6. **Wong, P. T. S. and Kaiser, K. L. E.**, Bacterial degradation of polychlorinated biphenyls. II. Rate studies, *Bull. Environ. Contam. Toxicol.*, 13, 249, 1975.
7. **Tucker, E. S., Saeger, V. W., and Hicks, O.**, Activated sludge primary biodegradation of polychlorinated biphenyls, *Bull. Environ. Contam. Toxicol.*, 14, 705, 1975.
8. **Baxter, R. A., Gilbert, P. E., Lidgett, R. A., Mainprize, J. H., and Veddon, H. A.**, The degradation of polychlorinated biphenyls by microorganisms, *Sci. Total Environ.*, 4, 53, 1975.
9. **Furukawa, K. and Matsumura, F.**, Microbial metabolism of polychlorinated biphenyls: studies on relative degradability of polychlorinated biphenyl components by *Alcaligenes sp.*, *J. Agric. Food Chem.*, 24, 251, 1976.
10. **Ballschmiter, K., Ungiert, K. C., and Neu, H. T.**, Abbau von chlorierten Aromaten: Mikrobiologischer Abbau der polychlorierte Biphenyle (PCB). III. Chlorierte Benzoesauren als Metabolite der PCB, *Chemosphere*, 1, 51, 1977.
11. **Seyler, G. S., Shou, M., and Colwell, R. R.**, Growth of an estuarine *Pseudomonas* sp. on polychlorinated biphenyls, *Microb. Ecol.*, 3, 241, 1977.
12. **Carey, A. E. and Harvey, G. R.**, Metabolism of polychlorinated biphenyls by marine bacteria, *Bull. Environ. Contam. Toxicol.*, 20, 527, 1978.
13. **Clark, R. R., Chinn, E. S. K., and Griffin, R. A.**, Degradation of polychlorinated biphenyls by mixed microbial cultures, *Appl. Environ. Microbiol.*, 37, 680, 1979.
14. **Liu, D.**, Enhancement of PCBs biodegradability by sodium lignosulfonate, *Water Res.*, 14, 1467, 1980.
15. **Ohmori, T., Iiuk, T., Minoda, Y., and Yamada, K.**, Utilization of polyphenol and polyphenyl-related compounds by microorganisms, *Agric. Biol. Chem.*, 37, 1599, 1973.
16. **Lunt, D. and Evans, C.**, The microbial metabolism of biphenyl, *Biochem. J.*, 118, 54, 1970.
17. **Catelani, D., Sorlini, C., and Treccani, V.**, The metabolism of biphenyl by *Pseudomonas punda*, *Experientia*, 27, 1173, 1971.
18. **Catelani, D., Colombi, A., Sorlini, C., and Treccani, V.**, Metabolism of biphenyl: 2-Hydroxy-6-oxo-6-phenylhexa-2,4-dienoate: the meta-cleavage product from 2,3-dihydroxybiphenyl by *Pseudomonas punda*, *Biochem. J.*, 134, 1063, 1973.
19. **Gibson, D. T., Roberts, R. L., Wells, M. C., and Kobal, U. M.**, Oxidation of biphenyl by *Beijerinckia* species, *Biochem. Biophys. Res. Commun.*, 50, 211, 1973.
20. **Furukawa, K., Matsumura, F., and Tonomura, K.**, *Alcaligenes* and *Acinetobacter* strains capable of degrading polychlorinated biphenyls, *Agric. Biol. Chem.*, 42, 543, 1978.
21. **Seyler, G. S., Thomas, R., and Colwell, R. R.**, Polychlorinated biphenyl (PCB) degrading bacteria and PCB in estuarine and marine environment, *Estuarine Coastal Mar. Sci.*, 6, 553, 1978.
22. **Fritz, A. K. and So, T. M.**, The isolation and characterization of bacteria that degrade polychlorinated biphenyls (PCB), *Abstracts of the ASM Annu. Meet.*, 1978, 203.
23. **Sylvestre, M.**, Isolation method for bacterial isolates capable of growth on *p*-chlorobiphenyl, *Appl. Environ. Microbiol.*, 39, 1223, 1980.
24. **Bourquin, A. W. and Cassidy, S.**, Effect of polychlorinated biphenyl formulations on the growth of estuarine bacteria, *Appl. Microbiol.*, 29, 125, 1975.

MONS 006057

25. **Blakemore, R. P. and Carey, A. E.,** Effect of polychlorinated biphenyls on growth and respiration of heterotrophic marine bacteria. *Appl. Environ. Microbiol.*, 35, 323, 1978.
26. **Wyndham, C., Devenish, J., and Safe, S.,** The *in vitro* metabolism, macromolecular binding and bacterial mutagenicity of 4-chlorobiphenyl, a model PCB substrate. *Res. Commun. Chem. Pathol. Pharmacol.*, 15, 563, 1976.
27. **Murado, M. A., Tejedor, M. C., and Baluja, G.,** Interactions between polychlorinated biphenyls (PCBs) and soil microfungi. Effect of Aroclor 1254 and other PCBs on *Aspergillus flavus* cultures. *Bull. Environ. Contam. Toxicol.*, 15, 768, 1976.
28. **Tejedor, M. C., Murado, M. A., and Baluja, G.,** Oxidative metabolism in *Saccharomyces cerevisiae* as affected by polychlorinated biphenyls. *Bull. Environ. Contam. Toxicol.*, 22, 439, 1979.
29. **Smith, R. V. and Rosazza, J. P.,** Microbial models of mammalian metabolism. Aromatic hydroxylation. *Arch. Biochem. Biophys.*, 161, 551, 1974.
30. **Dodge, R. H., Cerniglia, C. E., and Gibson, D. T.,** Fungal metabolism of biphenyl. *Biochem. J.*, 178, 223, 1979.
31. **Wiseman, A., Gondal, J. A., and Sims, P.,** 4-Hydroxylation of biphenyl by yeast containing cytochrome P-450: radiation and thermal stability, comparisons with liver enzymes (oxidized and reduced forms). *Biochem. Soc. Trans.*, 3, 278, 1975.
32. **Cerniglia, C. E., Van Baalen, C., and Gibson, D. T.,** Oxidation of biphenyl by cyanobacterium, *Oscillatoria* sp. strain JCM. *Arch. Microbiol.*, 125, 203, 1980.
33. **Bloch, W. D. and Cornish, H. H.,** Metabolism of biphenyl and 4-chlorobiphenyl in the rabbit. *J. Biol. Chem.*, 234, 3301, 1959.
34. **Raig, P. and Ammon, R.,** Gaschromatographische Analyse der phenolischen Stoffwechselprodukte des Biphenyls. *Drug Res.*, 20, 1266, 1970.
35. **Meyer, T. and Schallen, R. R.,** The metabolism of biphenyl. II. Phenolic metabolites in the rat. *Acta Pharmacol. Toxicol.*, 39, 419, 1976.
36. **Hutzinger, O., Nash, D. M., Safe, S., DeFreitas, A. S. W., Norstrom, R. J., Wildish, D. J., and Zitko, V.,** Polychlorinated biphenyls: metabolic behavior of pure isomers in pigeons, rats and brook trout. *Science*, 178, 313, 1972.
37. **Gardner, A. M., Chen, J. T., Roach, J. A. G., and Ragelis, E. P.,** Polychlorinated biphenyls: hydroxylated urinary metabolites of 2,5,2',5'-tetrachlorobiphenyl identified in rabbits. *Biochem. Biophys. Res. Commun.*, 55, 1377, 1973.
38. **Safe, S., Hutzinger, O., and Esobichon, D.,** Identification of 4-chloro-4'-hydroxybiphenyl and 4,4'-dichloro-3-hydroxybiphenyl as metabolites of 4-chloro- and 4,4'-dichlorobiphenyl fed to rats. *Experientia*, 30, 720, 1974.
39. **Hass, J. R., Jao, L. T., Wilson, N. K., and Matthew, H. B.,** Metabolism of 4-chlorobiphenyl and 4,4'-dichlorobiphenyl in the rat: qualitative and quantitative aspects. *J. Agric. Food Chem.*, 25, 1330, 1977.
40. **Furukawa, K., Tomizuka, N., and Kamibayashi, A.,** Bacterial degradation of commercial PCB mixtures (Kanechlors) and their metabolites. *J. Pharm. Dyn.*, 3, S-4, 1980.
41. **Furukawa, K., Tonomura, K., and Kamibayashi, A.,** Effect of chlorine substitution on the biodegradability of polychlorinated biphenyls. *Appl. Environ. Microbiol.*, 35, 223, 1978.
42. **DeFreitas, A. S. and Norstrom, R. J.,** Turnover and metabolism of PCBs in relation to their chemical structure and movement of lipids in the pigeon. *Can. J. Physiol.*, 52, 1080, 1974.
43. **Berlin, M., Gage, J., and Holm, S.,** The distribution and metabolism of 2,4,5,2',5'-pentachlorobiphenyl. *Arch. Environ. Health*, 30, 141, 1975.
44. **Matthews, H. B., Fries, G., Gardner, A., Garthoff, L., Goldstein, J., Ku, Y., and Moore, J.,** Metabolism and biological toxicity of PCBs and PBBs. *Environ. Health Perspect.*, 24, 147, 1978.
45. **Melves, B. and Brandt, I.,** The distribution and metabolism of labeled polychlorinated biphenyls in mice and quails, presented at PCB Conference, III., *National Swedish Environment Board Publication*, 4E, 1973, 87.
46. **Matthew, H. B. and Anderson, M. W.,** Effect of chlorination on the distribution and excretion of polychlorinated biphenyls. *Drug Metab. Dispos.*, 3, 371, 1975.
47. **Lester, G. W., McDaniel, O. S., Schiller, C. M., and Matthews, H. B.,** Structural requirements for the accumulation of chlorinated biphenyl metabolites in the fetal rat intestine. *Drug Metab. Dispos.*, 6, 584, 1978.
48. **Furukawa, K., Tomizuka, N., and Kamibayashi, A.,** Effect of chlorine substitution on the bacterial metabolism of various polychlorinated biphenyls. *Appl. Environ. Microbiol.*, 38, 301, 1979.
49. **Furukawa, K., Tonomura, K., and Kamibayashi, A.,** Metabolism of 2,4,4'-trichlorobiphenyl by *Acinetobacter* sp. P6. *Agric. Biol. Chem.*, 43, 1577, 1979.
50. **Gibson, D. T., Cardini, G. E., Maseles, F. C., and Kallo, R. E.,** Incorporation of oxygen-18 into benzene by *Pseudomonas putida*. *Biochemistry*, 9, 1631, 1970.

MONS 006058

51. **Reiner, A. M. and Hegeman, G. D.**, Metabolism of benzoic acid by bacteria. Accumulation of (−)3,5-cyclohexadiene-1,2-diol-1-carboxylic acid by a mutant strain of *Alcaligenes eutrophus*. *Biochemistry*, 10, 2530, 1971.
52. **Jerina, D. M., Daly, D. W., Jeffery, A. M., and Gibson, D. T.**, *cis*-1,2-Dihydroxy-1,2-dihydronaphthalene: a bacterial metabolite from naphthalene. *Arch. Biochem. Biophys.*, 142, 394, 1971.
53. **Horvath, R. S. and Alexander, M.**, Co-metabolism of *m*-chlorobenzoate by an *Arthrobacter*. *Appl. Microbiol.*, 20, 254, 1970.
54. **Reinleger, S., Klages, U., and Lingens, F.**, Abbau der 4-Chlorobenzoesaure durch eine *Arthrobacter* Species. *Arch. Microbiol.*, 110, 253, 1976.
55. **Horvath, R. S.**, Co-metabolism of the herbicide 2,3,6-trichlorobenzoate. *J. Agric. Food Chem.*, 19, 291, 1971.
56. **Knackmuss, H. J. and Reinecke, W.**, Der Einfluss von Chlorsubstituenten auf die Oxygenierung von Benzoat durch *Alcaligenes eutrophus* B9. *Chemosphere*, 2, 225, 1973.
57. **Dorn, E., Hellwigm, M., and Knackmuss, H. J.**, Isolation and characterization of a 3-chlorobenzoate degrading *Pseudomonas*. *Arch. Microbiol.*, 99, 61, 1974.
58. **Hartmann, J., Reinecke, W., and Knackmuss, H. J.**, Metabolism of 3-chloro-, 4-chloro-, and 3,5-dichlorobenzoate by a pseudomonad. *Appl. Environ. Microbiol.*, 37, 421, 1979.
59. **Dewey, O. R., Lyndsey, R. V., and Hartley, G. S.**, Biological destruction of 2,3,6-trichlorobenzoic acid in soil, *Nature* (*London*), 195, 1232, 1962.
60. **GiGerenimo, M. J., Nikaido, M., and Alexander, M.**, Utilization of chlorobenzoates by microbial populations in sewage. *Appl. Environ. Microbiol.*, 37, 619, 1979.
61. **Chakrabarty, A. M.**, Plasmids in *Pseudomonas*. *Ann. Rev. Genet.*, 10, 7, 1976.
62. **Chakrabarty, A. M.**, Plasmids and dissimilation of synthetic environmental pollutants, in *Plasmids and Transposons: Environmental Effects and Maintenance Mechanisms*. Stuttard, C. and Rozee, K. R., Eds., Academic Press, New York, 1980, 21.
63. **Farrell, R. and Chakrabarty, A. M.**, Degradative plasmids: molecular nature and mode of evolution, in *Plasmid of Medical, Environmental and Commercial Importance*. Timmis, K. N. and Puhler, A., Eds., Elsevier/North-Holland, Amsterdam, 1979, 97.
64. **Kamp, R. F. and Chakrabarty, A. M.**, Plasmids specifying *p*-chlorobiphenyl degradation in enteric bacteria, in *Plasmids of Medical, Environmental and Commercial Importance*, Timmis, K. N. and Puhler, A., Eds., Elsevier/North-Holland, Amsterdam, 1979, 97.
65. **Furukawa, K. and Chakrabarty, A. M.**, Involvement of plasmids in total degradation of chlorinated biphenyls, *Appl. Environ. Microbiol.*, 44, 619, 1982.
66. **Chatterjee, D. K. and Chakrabarty, A. M.**, Genetic rearrangements in plasmids specifying total degradation of chlorinated benzoic acids. *Mol. Gen. Genet.*, 188, 279, 1982.

MONS 006059

Chapter 7

EFFECT OF PCBs ON REPRODUCTION IN MAMMALS

Gene B. Fuller and William C. Hobson

TABLE OF CONTENTS

I. Introduction 102

II. Differentiation and Development 102
- A. Morphology 102
- B. Reproductive Function 103
- C. Summary 103

III. Male Reproduction 103
- A. Sex Organs 104
- B. Spermatogenesis 104
- C. Fertility 105
- D. Summary 105

IV. Female Reproduction 105
- A. Sex Organs 106
- B. Puberty 106
- C. Estrous or Menstrual Cycles 106
- D. Fertility 107
- E. Summary 107

V. Pregnancy, Parturition, and Lactation 107
- A. Fecundity 108
- B. Lactation 110
- C. Summary 111

VI. Mechanism of Action 111
- A. Liver 111
- B. Gonads 112
- C. Estrogenic Activity 113
- D. Central Nervous System 114
- E. Thyroid 114
- F. Adrenal 115
- G. Summary 115

VII. Conclusions 116

References 121

MONS 006060

I. INTRODUCTION

Chemically induced reproductive abnormalities have been documented among mammalian wildlife species throughout the industrialized world. Some of these effects have been attributed to the polychlorinated biphenyls (PCBs) which have accumulated in the environment due to their widespread industrial use and chemical stability. Most mammals are exposed to these chlorinated hydrocarbons via an aquatic or terrestrial food chain. The lipophilic nature of the PCBs result in their accumulation in adipose tissue. Although a constant exchange between fatty deposits and plasma probably occurs, increased mobilization of PCBs takes place during pregnancy, lactation, stress, and in a time of starvation. This persistence has stimulated many acute and chronic toxicity studies over the past decade to delineate the potentially harmful effects of exposure on reproductive function.

Reproduction can be modified at several developmental stages, the consequences of which may be expressed immediately or at a later time in life. Subacute or chronic exposure to PCBs pre- or postnatally, pre- or postpubertally, or as adults has been found to be detrimental to reproductive function. In experimental studies, the demonstrable consequences of exposure are dependent upon the type and level of PCB utilized, route of administration, the test animal used, and the physiologic endpoint. The definitive characterization of the toxicologic properties of PCBs is difficult due to the fact that the commercial products are mixtures of isomers; the problem is further complicated by the frequent presence of other toxic contaminants.

It is the purpose of this chapter to provide a current assessment of the effects of PCBs on reproduction in mammals. The chapter will be organized by reference to maturational reproductive stages. The possible site(s) and/or mechanism(s) of action will be discussed although these aspects remain largely speculative due to the tenuous nature of present evidence.

II. DIFFERENTIATION AND DEVELOPMENT

In recent years there has been a growing concern about the exposure of pregnant women to chemicals and possible teratogenic effects on the developing fetus. Prenatal exposure to PCBs may place reproductive development at risk, the effects of which may not be immediately apparent but could be expressed later as functional or behavioral abnormalities. Unfortunately, few studies have been conducted concerning the effects of prenatal exposure to the chlorinated biphenyls on subsequent postnatal reproductive function. That PCBs cross the placenta, albeit slowly, has been demonstrated in mice,[1] rats,[2] rabbits,[3] and monkeys.[4]

A. Morphology

No teratogenic effects of PCBs have been demonstrated on reproductive structures. There are reports, however, of cleft palate, cleft lip, brachydactyly, and syndactyly induced in mouse pups[5] and pigs[6] by prenatal exposure to PCBs. Chow et al.[7] reported histological changes in the central nervous system of mice exposed in utero to pure tetra-CB from days 6 to 10 of gestation. These authors found cylindrical CNS peninsulas in the spinal and cranial nerve roots, suggesting that the PCB may have affected the early organization of interneuronal junctions or development of synapses. This change in nervous tissue organization is associated with a malady known as "spinning syndrome" which developed in mice prenatally exposed to PCB.[7,8] Although not an established detriment to reproduction, these results illustrate the potential for untoward effects on intrauterine differentiation.

Adult reproductive abnormalities may be attributed to subtle developmental alterations caused by exposure to PCB in utero. While not teratisms by strict definition there are morphological and functional differences which, either directly or indirectly, resulted from

MONS 006061

exposure to PCBs during development. Gellart and Wilson[9] administered 30 mg/kg/day Aroclors® 1221, 1242, or 1260 to pregnant Sprague-Dawley rats from days 14 to 20 of gestation. Sacrifice at 6 months of age revealed a significant increase in the absolute weight of the testes of males exposed to Aroclor® 1260. Fertility was not affected.

B. Reproductive Function

The reproductive neurotoxicity of PCBs was corroborated by Gellart[10] when he injected neonatal rats with Aroclor® 1221 during the postnatal "critical period" of CNS development. In rats during the first 5 days following birth the hypothalamo-pituitary axis is "programmed" for cyclic or acyclic release of gonadotropins. It has been experimentally demonstrated that this period of development is sensitive to hormonal perturbations which alter sex-specific hormone patterns.[11] Specifically, neonatal injection of estrogens or androgens into certain rodents causes functional and behavioral sterility. Thus, female rat pups injected with Aroclor® 1221 (10 mg/day) on the second and third days following birth presented an acyclic gonadotropin pattern resulting in the anovulatory-persistent vaginal estrus syndrome. The reported estrogenic activity of the lower chlorinated biphenyls (<48% chlorination)[12] probably accounts for the altered neuroendocrine differentiation in rats, especially as the administered dose was very high (2000 mg/kg/day). A direct toxic effect on the CNS could not account for these results as Aroclors® 1242, 1254, and 1260 were ineffective.

Because reproduction is a highly integrated function with behavioral and metabolic as well as hormonal components, exposure to an environmental compound could alter behavior or extragenital systems producing infertility even in the absence of toxic effects on the reproductive endocrine system or genital tract morphology. As an example, liver function can be reprogrammed or "imprimed" by exogenous gonadal steroids.[13-15] Female rat pups so treated demonstrate, at puberty, enzymatic rates for reductive and oxidative steroid reactions characteristic of the male liver. Consequently, changes in hepatic metabolism of steroids induced by any compound during development could modify reproductive function and/or behavior. An hepatic "imprinting" effect has, in fact, been reported for some pure PCB congeners. Lucier and McDaniel[16] administered PCBs orally on days 8 to 18 of gestation to pregnant rats at the following doses: 4-chlorobiphenyl, 30 mg/kg/day; 3,4,3',4'-tetrachlorobiphenyl, 3 mg/kg/day; 2,4,5,2',4',5'-hexachlorobiphenyl, 30 mg/kg/day. Generally speaking, the congeners were specific enzyme inducers although there was some overlap in activities. Tetrachlorbiphenyl was the most potent transplacentally as it "feminized" the postpubertal male liver by repressing the normally high activity of UDP glucuronyltransferase. Because of the reported estrogenic activity of the lower chlorinated biphenyls, one might speculate that the PCB interacts with the cytosol receptor. It could be translocated to the nucleus where it acts on genetic material resulting in either immediate modulation of enzyme levels or latent gene expression at puberty.

C. Summary

Although the labile nature of the developing conceptus is well known, relatively few studies concerning prenatal exposure to the ubiquitous PCBs on the subsequent postnatal fertility of the offspring have been conducted. The limited evidence indicates that the PCBs do not affect organogenesis of the genital tract. Of concern are those studies which reveal morphological and functional neurotoxic effects and the latent effect on hepatic steroid metabolizing enzymes. Both consequences of PCB exposure could compromise the capacity of an organism to reproduce itself. However, the relationship of these observations in laboratory rodents to human fetal development has yet to be established.

III. MALE REPRODUCTION

The primary role of the reproductive system lies in the continuation of the species. The

male reproductive system is organized to develop and transmit the male germ cells to the female ultimately resulting in the formation of a third animal of the same species. However, from fertilization through sexual maturity, the male reproductive system is susceptible to chemically induced modifications which could prevent a successful mating.

A. Sex Organs

As previously discussed, PCBs have no known teratogenic effects on the development of the male reproductive tract in mammals. Likewise, a direct effect of postnatal administration of PCBs on adult male reproductive organs has not been clearly demonstrated. Oral administration of Aroclor® 1254 at levels ranging from 62.5 to 4000 ppm/day for 2 weeks to adult male albino mice was reported to have no effect on sex organ weights.[17] Similarly, Orberg and Lundberg[18] reported that 0.25 g/day of Clophen® A-60 for 28 days had no significant effect on sex organ weights of intact adult male albino mice. Castrated males were administered the same dosage of Clophen® A-60 for 28 days but in addition were given 70 μg testosterone propionate for 10 days beginning on the 19th day of PCB administration. When compared with castrated male controls receiving testosterone propionate only, the seminal vesicle weights were significantly lower in the PCB plus androgen treated males. The authors suggested that the lack of an effect of PCB in intact males contrasted with an effect in castrates was due to two factors: enhanced androgen metabolism and the absence of the testes-hypophysis feedback mechanism to compensate for altered hormone removal. Merson and Kirkpatrick[19] on the other hand, reported a significant decrease in seminal vesicle weights of mature male white-footed mice *(Peromyscus)* fed 200 ppm/day Aroclor® 1254 for 4 weeks. There was no weight change at 100 ppm for the 4-week period. In a related study it required 400 ppm/day of Aroclor® 1254 to cause a reduction in seminal vesicle weight when a 2-week feeding period was utilized.[20] There was no change in organ weights of the *Peromyscus* males when 100 and 200 ppm/day was fed for 2 weeks.

Kanechlor® 500 was included in the diet of adult male Sprague-Dawley rats for 4 weeks at a dose level of 100 ppm/day.[21] No effect on reproductive organs were observed. Likewise, testes, prostate, and seminal vesicle weights were not changed in cottontail rabbits fed 25 ppm Aroclor® 1254 for 20 days.[22] In contrast, when male rats were given Aroclor® 1254 at 500 mg/kg by oral gavage as a single treatment and sacrificed 12 days later[23] or 500 ppm of Aroclors® 1254 and 1260 in the feed for 8 months,[24] there was a significant increase in testes weight. In spite of the inconsistency of the existing reports, organ weight analysis could be a useful parameter for assessing the effects of PCBs. This would require more uniform and rigid experimental conditions. Perhaps such studies could be combined with histological examination of the affected tissue to determine whether the effect of the PCB was direct or indirect.

B. Spermatogenesis

Testicular toxicity should be reflected by some impairment of spermatogenesis. Sanders et al.[25] reported that Aroclor® 1254 in the diet of adult albino male mice at a level of 200 ppm/day significantly reduced the number of sperm per milligram of testis but did not affect gonadal weights. They found no effect at 50 ppm after the 15-day treatment period. A similar effect of Aroclor® 1254 was observed in adult white-footed male mice by Sanders and Kirkpatrick.[20] A treatment regimen of 400 ppm/day for 2 weeks reduced the number of sperm per testis. There was no effect at 100 or 200 ppm.

The frequency of mitotic figures in adult rat spermatogonia decreased following oral gavage of an acute dose of 5000 mg/kg Aroclor® 1242.[26] Acutely administered levels of 2500 or 1250 mg/kg had no effect on spermatogonia. Interestingly, when 500 mg/kg were administered per os for 4 days there was a significant decrease in spermatogonia. This suggests duration of exposure is an important parameter to consider when assessing toxicity of PCBs.

MONS 006063

Mink are reportedly very susceptible to the toxic effects of PCBs. When adult males were fed 20 ppm daily of Aroclor® 1016 or 5, 10, 20, or 40 ppm Aroclor® 1242, mortality was 100% within 6 months at treatment levels of 20 ppm or greater.[27] Spermatogenesis, however, was not affected during the exposure period. Platonow and Karstad[28] earlier described the lack of an effect of Aroclor® 1254 on male mink, noting that they continue to produce normal numbers of viable spermatozoa throughout exposure.

Male beagles fed Aroclor® 1254 (100 ppm) for 2 years showed aspermatogenesis and diffuse hyperplasia of the interstitial cells of the testes.[29] One of four rhesus monkeys developed a low sperm count between 12 and 18 months while on a diet containing 5 ppm Aroclor® 1248.[30] The sperm count returned to normal 1 year after PCB was removed from the diet.

C. Fertility

Fertility evaluation in males following prenatal, postnatal, or adult exposure could be a more sensitive assessment of a functional impairment than changes in organ weights or altered spermatogenesis. Subtle changes in testicular weights, sperm numbers, and libido may not be apparent when examined as a single endpoint, but when indirectly assessed as an estimate of fertility might result in a measurable effect on fecundity. Orberg[31] administered daily oral doses of 50 μg of pure trichlorobiphenyl or hexochlorobiphenyl to mice from days 5 to 19 of gestation or from birth through day 12 of lactation. Male pups subjected to each treatment were subsequently mated with nonexposed females which resulted in no differences in numbers of pups sired when compared with controls. Kihlstrom et al.[32] injected postpartum NMRI strain mice with 50 mg/kg Clophen® A-60. Treatment began on the day of delivery and then weekly for three successive weeks during lactation. After reaching sexual maturity, the male mice which received the PCBs via their mother's milk were mated with control females. The frequency of implantations and the resorption rate was not different from control matings. Interestingly, when both treated males and females were mated, the number of implantations decreased significantly; whereas similar to males, when treated females were mated to control males, there was no effect on implantation.

Pregnant Sprague-Dawley rats were gavaged daily from days 14 to 20 with 30 mg/kg of either Aroclor® 1221, 1242, or 1260.[9] At sexual maturity the prenatally exposed male offspring were placed with nontreated breeder females for 2 weeks. Based on the number of young produced, there was no apparent detrimental effect of the Aroclors®. Daily exposure of mature rats to 70 ppm Aroclor® 1254 for 9 weeks in the drinking water did not affect fertility.[33]

Four mature male rhesus monkeys were fed a diet containing 5 ppm Aroclor® 1248 for approximately 1 year with no loss of breeding capacity.[30] However, as previously mentioned, one of these males had a decreased sperm count following 12 to 18 months exposure.

D. Summary

Definitive conclusions regarding the hazard of PCB exposure to male reproductive function cannot be reached because of the different experimental conditions utilized by various authors. In general, however, chronic exposure to levels of PCB at or near concentrations humans may encounter in the environment has minimal or no effect in animal models. While certain aspects of male reproductive function were altered by high levels of PCBs, no changes in male fertility have been reported.

IV. FEMALE REPRODUCTION

The cyclic nature of female reproductive function presents a series of physiological events subject to the influence of drugs and chemicals. Complex interactions within the hypoth-

alamo-hypophyseal-gonadal axis increase the vulnerability of the pre- and postpubertal female to direct chemical influences upon fertility.

A. Sex Organs

Morphological consequences of PCB exposure on the female reproductive tract have been infrequently examined. Sanders and Kirkpatrick[34] fed 25 or 100 ppm of Aroclor® 1254 to adult female white-footed mice for 3 weeks. No notable effects of PCB ingestion were seen on ovarian or uterine weights. Female rat pups were injected (s.c.) with 1 or 10 mg of Aroclor® 1221 or 1 mg of Aroclors® 1242, 1254, or 1260 on the second and third days following birth.[10] Sacrifice at 7 to 8 months of age revealed no changes in ovarian or uterine weights but an increase in the absolute weight of the pituitary gland was found in rats receiving 10 mg of Aroclor® 1221 as a neonate. This difference, however, might not have been significant if relative rather than absolute gland weights had been calculated.

Gellart[10] investigated the uterotrophic activity of Aroclors® 1221, 1242, 1254, and 1260 in immature female (22 day) Sprague-Dawley rats. A single s.c. injection was administered followed by sacrifice at 24 hr. A significant increase in uterine weight was observed only in those animals treated with Aroclor® 1221 at a dose level of 1 g/kg. In a similar study Ecobichon and MacKenzie[35] injected 8-mg doses of several pure PCBs and commercial Aroclors® i.p. into immature female rats. The animals were sacrificed 18 hr after treatment and uterine weights, fluid, and glycogen contents were determined. In general, the lower-chlorinated PCBs increased uterine weights while the higher-chlorinated biphenyls increased uterine fluid and glycogen. The increase in uterine weight as well as increased fluid retention and glycogen content are indicators of estrogen action and support Bitman and Cecil's[12] report of estrogenic activity of the lower chlorinated Aroclors® (< 48% chlorination). In contrast, uteri from New Zealand white rabbits were significantly smaller following exposure to 300 mg Aroclor® 1254 administered weekly by oral intubation for 14 weeks.[36] Aroclors® 1221 and 1242 failed to affect the size of the uterus.

B. Puberty

The factors controlling the onset of puberty remain largely unresolved. Nevertheless, the normal maturation of the hypothalamo-hypophyseal-gonadal axis is requisite for cyclic reproductive function in female mammals. Thus, any chemically induced lesion during this critical developmental phase might modify the onset of puberty and subsequent reproductive success.

Unfortunately, there is a paucity of information on PCB exposure during this labile developmental period. Gellart[10] injected neonatal rats with 10 mg of Aroclor® 1221 on days 2 and 3 following birth. He reported the average age of vaginal opening in treated rats as less than 28 days compared to 42 days for untreated controls. This "precocious" puberty indicates an altered neuroendocrine function possibly induced by the reported estrogenic activity of high levels of Aroclor® 1221.[12] No other studies were identified which examined the effects of PCBs on pubertal development.

C. Estrous or Menstrual Cycles

The discrete neurological, neuroendocrine, and endocrine components that are manifest at puberty persist as the integrated control of estrous and menstrual cycles. These components exert some measure of control over each other and are additionally influenced by elements in the internal and external environments. Concern for harmful external factors such as the ubiquitous PCBs has stimulated many studies to evaluate their effects on estrous cycles.

Albino mice (NMRI strain) were given a single intraperitoneal (i.p.) injection of Clophen® A-60 at 20 mg/kg/24 hr after exhibiting a cornified vaginal smear.[37] The length of the estrous cycle was significantly increased for three cycles after which cycle length returned to normal. Orberg and Kihlstrom[38] administered 0.025 mg/kg Clophen® A-60 orally for 75 days to

MONS 006065

adult NMRI strain mice. The average length of the estrous cycle was 8.7 days as compared to 6.6 days for controls. Conversely, cycle lengths were not altered in mature white-footed mice fed 100 ppm Aroclor® 1254 for 3 weeks[34] or in adult rats fed 75 or 150 ppm Aroclor® 1242 daily for 36 weeks.[39]

Microscopic examination of ovaries from rats exposed to 150 ppm Aroclor® 1242 for 36 weeks revealed a reduction in the number of follicles.[39] Whether this was a direct or indirect effect on the follicles was not established but the reduction correlated well with the total inhibition of mating also reported.

The sequence of endocrine events occurring during the estrous and menstrual cycles is essentially the same. Consequently, it is not surprising that chronic exposure to low levels of PCBs has profound effects upon cyclic phenomenon in rhesus monkeys. Menstrual cycles were affected by 2.5 and 5.0 ppm Aroclor® 1248 fed in the diet daily for 7 months.[40] There were increases in the duration of menses and in menstrual bleeding, especially in the 5.0 ppm treatment group. Menses were 5 to 7 days longer in animals on the PCB diet than in the controls. Occasional amenorrhea was also noted in the treated animals.

Mueller et al.[41] administered 4 mg/kg daily of Clophen® A-30 via gastric intubation to mature cycling female rhesus monkeys. Treatment was initiated after confirmation of ovulation by laparoscopy and continued through the following cycle. The PCB treatment blocked ovulation in two of four monkeys in the ensuing cycle while inducing a double ovulation in one of four females. The site of action of Clophen® A-30 could not be established but in both anovulatory animals there was an indication of inadequate estrogen secretion. This suggests an ovarian site of action which is supported by the histopathological findings of Jonsson et al.[39] of decreased ovarian follicles in PCB treated rats.

D. Fertility

The failure to produce young is an excellent toxicity marker for chronic exposure to PCBs although single or multiple sites of action cannot be distinguished. Overall reproductive performance was completely blocked in rats receiving Aroclor® 1242 at 150 ppm/day for 36 weeks.[39] Treated females were exposed to normal males but no matings occurred, even though vaginal cytology indicated normal estrous cycles. It is difficult to reconcile apparent normal conditions during the cycle with the reported decrease in numbers of follicles and an absence of mating behavior.

Bleavins et al.[27] fed mature female mink from 5 to 40 ppm Aroclor® 1242 daily for 9 months. Complete reproductive failure occurred in animals fed diets containing 5 to 20 ppm. Subsequent mortality was 100% in mink on 20 or 40 ppm and 67% with the diet containing 10 ppm. Aroclor® 1016 reduced reproductive success 50% at 20 ppm but caused no deaths. These authors reported ferrets to be less sensitive than mink to the effects of PCBs as 20 ppm Aroclor® 1016 had no reproductive effects and 20 ppm Aroclor® 1242 was the minimal level required to block reproductive function. No mortality occurred in ferrets.

E. Summary

It is apparent that PCBs cause perturbations in female reproductive function. Depending upon the animal model utilized, PCBs variously affect the reproductive tract, neuroendocrine function (puberty, estrous, and menstrual cycles, ovulation) and general reproductive performance. The relationship of these observations in experimental animals to the human female is not yet established. The data must, however, be considered to provide an ominous warning of the potential danger in chronic low-level exposure.

V. PREGNANCY, PARTURITION, AND LACTATION

The complexity of pregnancy and maternal behavior from fertilization through weaning offers many physiological and behavioral intricacies vulnerable to alteration by extrinsic

factors. Consequently, the pregnancy, the fetus, and the young are potentially at risk; the increasing concern about exposure of pregnant women to drugs or chemicals and the possible overt effects on the offspring is thus understandable. New life begins at fertilization with the union of the two germ cells. Under normal conditions, the zygote passes into the uterus where implantation and the formation of the placenta occur. The developing embryo is there nurtured until term and parturition. Studies of PCB-induced lesions in this process have not identified a site of action in the preimplantation events of pregnancy. The endpoint most accessible during early pregnancy for toxicity studies is the number of implantation sites. Otherwise, the number of live young born is utilized to assess toxic intervention during pregnancy.

A. Fecundity

Orberg and Kihlstrom[38] fed Clophen® A-60 daily for 10 weeks at a treatment level of 0.025 mg which reduced the number of implantations in mated NMRI mice. Orberg[42] subsequently administered 0.05 or 0.5 mg/kg pure tri(2,5,4') or hexachlorobiphenyl (2,4,5,2',4',5') via oral intubation to NMRI mice from days 1 to 6 of pregnancy. Females given 0.5 mg of either chlorinated compound had a significantly lower frequency of implanted ova than control females. In an earlier study, Torok[43] dosed pregnant NMRI strain mice per os from days 1 to 3 of gestation with 375 or 750 mg/kg daily of dichlorobiphenyl (2,2'). Both treatment levels resulted in decreased litter size due to high embryo mortality and decreased implantations in the high dose group. Conversely, Kanechlor® 500 in the diet of pregnant mice had no effect on the number of fetuses or offspring at 10 or 100 ppm/day throughout pregnancy.[44]

Linder et al.[34] conducted two-generation studies in Sherman rats with Aroclors® 1254 and 1260. Aroclor® 1254 was fed at dietary levels of 1, 5, 20, and 100 ppm daily while Aroclor® 1260 was fed at levels of 5, 20, and 100 ppm. Chronic exposure was initiated at 3 to 4 weeks of age in the F_0 generation and at weaning in the F_1 animals. Treatment was continuous through mating, gestation, and lactation. The F_0 rats fed 100 ppm of Aroclor® 1254 for either 62 or 188 days before each mating produced smaller litters than controls in both pregnancies (F_{1A} and F_{1B}). Small litters (F_{1B}) also resulted from 20-ppm in the 188-day parental treatment group. F_{1B} rats bred after exposure for 129 or 274 days (conception to mating) to 20 or 100 ppm had smaller litters than age-matched controls. No effect on reproduction resulted from treatment with Aroclor® 1260 except at 500 ppm for 67 days which reduced litter size. Baker et al.[35] reported fetal resorptions in rats treated with 70 ppm Aroclor® 1254 in their drinking water for 9 weeks. The females were placed with the males 1 week after the initiation of treatment.

In rats, chronic low-level exposure to PCBs is potentially more hazardous to a successful pregnancy than is subacute exposure except at extremely high levels. It required 500 ppm Aroclor® 1254 throughout gestation to reduce litter size in Osborn-Mendle rats.[45] In studies in which Aroclor® 1254 was fed to pregnant Sherman[2,36] or Wistar[46] rats between days 6 and 15 of gestation, there were no effects on litter size or number of live births. Dose levels ranged from 6.25 to 100 mg/kg daily. Survival to weaning was reduced by the 100 mg/kg treatment level.

Rabbits and guinea pigs are apparently more susceptible to the effects of PCBs than are rats and mice. Treatment of pregnant rabbits with PCB 1254 at levels of 12.5 mg/kg or greater from days 7 to 28 caused abortions, resorptions, stillbirths, and maternal deaths.[40] Less than 12.5 mg/kg for the duration of pregnancy had no effect on live litter size.[5] Guinea pigs were given a technical grade PCB (Clophen® A-50) or a pure hexachlorobiphenyl (2,4,5-2'4'5') via oral intubation.[47] The treatment level of Clophen® A-50 was 2.2 mg/day (total of 100 mg) from days 16 to 60 of gestation. The hexachlorobiphenyl was similarly administered to two groups, one receiving a total of 25 mg and the other 100 mg from days

MONS 006067

16 to 60 of pregnancy. The Clophen® A-50 caused a significantly higher incidence of fetal death whereas 6-CB had no effect at either dose level.

Reports by mink ranchers of severe reproductive failures and high kit mortality in their colonies which were given diets containing fish and animal byproducts focused suspicion on the possibility of PCB contamination. This prompted several investigative studies to substantiate the magnitude of this problem. Aulerich et al.[48] fed adult mink diets containing 30% Lake Michigan coho salmon or the control diet of ocean perch plus PCBs for 6 months or greater. Tissue levels of PCBs in most Great Lakes fish are known to be relatively high (approximately 10 to 15 ppm). The PCBs were combined and added to the control diet at 30 ppm, 10 ppm each of Aroclors® 1242, 1248, and 1254. Total reproductive failure occurred in females fed 30% coho salmon as their source of PCBs. Of 65 females, 59 failed to whelp and from the six term pregnancies only ten kits were born; two were alive but died with 24 hr. No term pregnancies were observed in those females which received control diet supplemented with the PCB mixture. All mink receiving the PCB supplemented diet died between the beginning of the breeding season and the end of the whelping period. In a later study, Aulerich and Ringer[49] mixed different amounts of Aroclor® 1254 ranging from 1 to 15 ppm with the diet for 5 or 11 months of exposure. The degree of 1254 toxicity was directly proportional to the total intake of the compound. Females fed Aroclor® 1254 at 5 ppm for 2 months before breeding averaged 0.8 kit per litter which compares with 0.3 kits per litter from females fed 1254 at 2 ppm for 7 months prior to breeding. They also compared the chronic reproductive toxicity of 2 ppm daily of Aroclors® 1016, 1221, 1242, or 1254 fed for approximately 11 months. Only 1254 had any detrimental effect on reproductive function at the low chronic exposure level.

Jensen et al.[50] fed 3.3 or 11 ppm PCB to adult female mink for 66 days. The number of implantation sites were not different between treated and control females but the number of kits delivered was significantly reduced in the low dose treatment group while no kits were born in the high dose group. Platonow and Karstad[20] fed 1 and 10 mg/kg of Aroclor® 1254 to cows 10 days before slaughter. Following slaughter, the muscles and organs were ground and combined into rations for adult mink containing 0.64 and 3.57 ppm of total PCB. No live kits were produced by females receiving the greatest level of PCB and only 1 of 12 females whelped in the low level diet group.

Forty-six bred bitches were given Aroclor® 1254 in the diet at concentrations of 0.25, 1.0, or 5.0 mg/kg daily from the day of breeding.[6] Significant decreases in the number of term pregnancies, the number of live pups per litter at birth, and the number of pups alive after 2 weeks resulted from dietary exposure to the 5.0 mg/kg dose. There was no effect of the lower dose levels on reproductive performance.

Domestic livestock have been exposed to PCBs from such sources as paints and sealants on silo walls being accidentally incorporated into rations. In addition to the potential danger of human exposure by consumption of animal products, the economic impact of impaired reproductive performance on livestock breeding programs would be damaging. Hansen et al.[51] fed 20 ppm Aroclor® 1242 to sows of proven fertility. Treated sows were exposed from one cycle prior to mating until the young were weaned. Control sows farrowed significantly more pigs per litter than treated sows (11.4 ± 1.1 vs. 6.4 ± 4.4). In addition, treated sows weaned fewer pigs per litter and at much lighter weaning weights. Similarly, Earl et al.[6] reported dose-related decreases in the number of pregnancies and the number of pigs farrowed per litter in miniature sows receiving 1.0, 10.0, or 30.0 mg/kg Aroclor® 1254. Exposure was from 21 days prior to breeding through weaning. Studies of PCB effects on reproductive performance in cattle, sheep, or goats have not been conducted, at least to this author's knowledge, which leaves a rather large void regarding PCB influences on livestock production.

Nonhuman primates have been found to be susceptible to PCBs when treated with levels

MONS 006068

at or near that to which humans may be environmentally exposed. Adult female rhesus monkeys were fed a diet containing 2.5 or 5.0 ppm of Aroclor® 1248.[4,30,40] After 7 months of exposure to the PCB, attempts were made to breed the females to nontreated males. All females on the 2.5 ppm diet and six of eight animals on the 5.0 ppm diet conceived. Only one live term infant was born in the high dose group due to resorptions, abortions, and one stillbirth. Five of eight females delivered live infants at the low exposure level. At birth, the surviving infants were smaller than controls but otherwise appeared normal. During the nursing interval, the surviving infant from the mother receiving 5.0 ppm and two infants from mothers receiving 2.5 ppm died of PCB intoxication. At weaning all surviving infants showed rapid improvement in toxic PCB symptoms.

Following removal from the experimental diet for 1 year, the female rhesus monkeys were rebred.[30,32] Although conception rate, pregnancies, and live births were normal, the infants were smaller and unthrifty. Two infants born to mothers which had received 5.0 ppm Aroclor® 1248 in the diet subsequently died.

Allen et al.[30] examined the effect of lower exposure levels of Aroclor® 1248 in rhesus monkeys. Dietary levels of 0.5 and 1.0 ppm were administered three times per week for 7 months. The females were bred to control males with normal term pregnancies resulting. The infants, however, were smaller and gained weight less rapidly than controls.

The insidiousness of chlorinated biphenyl contamination was illustrated in a report by Altman et al.[53] Harems of breeding age rhesus monkeys at the Perrine Primate Center in Miami showed similar reproductive problems as reported in experimental studies. There was a high incidence of abortions and stillbirths. The offspring were small and unthrifty with a poor survival rate. The cause was determined to be PCBs in the concrete sealant on cage floors. The floors were resurfaced and the problem disappeared with time. Interestingly, a breeding colony of squirrel monkeys was housed on these concrete floors but showed no PCB intoxication symptoms.

A pilot study conducted with three pregnant cynomolgus monkeys (*Macaca fascicularis*) also illustrated the detrimental effect of PCB 1254 on pregnancy.[54] Two females receiving 100 μg/kg daily beginning on day 60 of pregnancy delivered stillborn infants. One female similarly dosed with 400 μg/kg delivered a term infant which died at 139 days postpartum of acute confluent bronchopneumonia. Although numbers were small, these results support the findings in rhesus monkeys.

It is difficult to speculate at which stage of pregnancy PCBs exert their effect. Limited numbers of studies in which chronic administration of PCBs were initiated before mating and continued until the young were weaned indicated that ovulation and fertilization were essentially unaffected. The adverse effects of the chlorinated hydrocarbons appear to be blocked or delayed implantation or fetal loss through resorption, abortion, or stillbirth. Whether these consequences result from transplacental effects on the fetus or to nonspecific physiological changes in the maternal organism is difficult to differentiate. Several studies have demonstrated that PCBs are minimally transferred across the placenta in many mammalian species.[40,44,50,59] Transplacental passage ranges from less than 1% of the maternal dose[35,60,61] to as high as 6%[57] being dependent upon the stage of pregnancy when the fetal PCB level was determined. Although the placenta is an effective barrier to PCB transfer, the PCB used, percentage of chlorination, and duration of dosing are variables in determining fetal uptake.

B. Lactation

Although PCBs do not directly affect lactation, the most significant source of PCB exposure for offspring is mother's milk.[25,30,61,66] The lipophilic nature of PCBs is exemplified by the magnitude of their accumulation in animal fat depots. Thus, milk, rich in fats provides a vehicle by which the fat soluble PCBs can be transferred from mother to infant. Vodicnik

MONS 006069

and Lech[57] injected virgin mice with pure 6-CB (2,4,5,2',4',5') 2 weeks before mating. Sacrificing pre- and postpartum animals, they confirmed that transfer of the chlorinated biphenyl to offspring through the milk is much greater than transplacentally, at least for the hexochlorobiphenyl. The lactating mice eliminated almost all of their body burden of 6-CB in one lactation period. Bailey et al.[66] treated lactating rhesus monkeys with Clophen® A-30 at 16 mg/kg daily for 30 days. Concentrations of PCBs were higher in the milk than in the serum of dosed mothers. Serum levels of PCBs in the infants were two to three times higher than in their mothers. Sacrifice of a mother-infant pair revealed a 2- to 93-fold greater tissue concentration in the majority of infant tissues. Whether this situation applies to humans awaits determination of PCB pharmacodynamic similarities between humans and laboratory animals. Measurable concentrations of PCBs have been reported in the milk of "non"-exposed women.[67,68]

C. Summary

It is now well established that PCBs can be found in wildlife in many areas of the environment. Definitive studies, however, on the relationship between PCBs and reproductive function in terrestrial mammals is nonexistent. There have been efforts to correlate high tissue residues of the chlorinated biphenyls with breeding deficiencies in marine mammals. High tissue levels of PCBs were associated with low reproduction in Baltic seals[69] and Harbour seals[70] and in premature births of California sea lions.[71] A later study of the premature parturient females and offspring suggested an interrelationship between PCBs and disease agents, i.e., the San Miguel Sea Lion Virus and *Leptospira pomona* were recovered from specimens obtained from prematurely delivering cows and pups.[72] Reproductive failure has also been reported to be associated with PCB-induced pathological changes in the uteri of Baltic gray, common, and ringed seals.[73]

The suspected correlation between high tissue levels of PCBs and poor reproductive performance in selected marine mammal populations is a foreboding signal for all mammals, both terrestrial and aquatic, especially endangered species. More definitive observations of the effect of PCBs on pregnancy and fetal or neonatal survival in experimental animals substantiate the vulnerability of this period of life. Perhaps more ominous is the possibility that in utero exposure may alter subsequent adult reproductive success, an effect not apparent at birth. Potentially, the survival of whole species or populations is at risk.

VI. MECHANISM OF ACTION

Despite numerous studies concerning the deleterious effects of PCBs on mammalian reproduction, the mechanism and/or site of action remains virtually unknown. The complex interrelationships of female cyclic reproductive function offer many sites for a PCB-induced lesion in contrast to the male; nevertheless, it takes only one alteration in either sex to produce infertility. Reproductive success can be modified directly via a toxic PCB action on the differentiated reproductive tract or indirectly via a lesion in the neuro-gonadal axis. Other possible sites of action which might induce reproductive dysfunction are the nonreproductive endocrine organs, hepatic function, and behavior. One or any combination of these organs/structures might be affected by exposure to PCBs thus altering some aspect of reproduction either directly or indirectly.

A. Liver

One of the more apparent toxic manifestations of PCBs is on the liver. That the liver is a primary target organ is supported by studies which revealed a relatively high accumulation of orally administered PCBs in the livers of mammals, fetal through adult.[1,4,23,66,74] Grossly observable changes include hepatomegaly, and depending on dosage, a fatty infiltration of the liver. Cellular changes reported include an increase in smooth endoplasmic reticulum,

MONS 006070

an increase in cytoplasm around the nucleus, cytoplasmic inclusion, and atypical mitochondria.[24,30,75,76]

Commercial preparations and purified PCBs are potent inducers of hepatic mixed function oxidases and cytochrome P-450. This has been adequately demonstrated in several mammalian species including mice,[42,77,78] rats,[80-82] rabbits,[1,36] mink,[83] and ferrets.[83] In addition Chen and Dubois[79] reported that in rats enzyme induction was greater in males than females and in young rather than adults fed Aroclors® 1221, 1254, and 1260. Enzyme induction has also been reported in fetal and neonatal mice and rats exposed to PCBs either transplacentally or through breast milk.[16,77,78,84,85]

Generally, discontinuation of exposure to PCBs results in a slow decay of enzyme activity. There are reports, however, that suggest that the PCB induction may be permanent. Lucier and McDaniel[16] and Dieringer et al.[84] reported that transplacental and lactational exposure of neonatal rats to 4-CB or 6-CB feminized the male liver. UDP glucuronyltransferase activity, a nonsteroid metabolizing enzyme was repressed in neonatally exposed adult males to levels similar to that found in females. Thus, in rats, the chlorinated biphenyls not only alter hepatic metabolism by transient enzyme induction but possibly by an irreversible "imprinting" of postpubertal hepatic enzymes.

Liver homogenate preparations have been the experimental approach utilized most often to demonstrate changes in enzyme activity following exposure to PCBs. Although these studies show increased activity in specific steroid hydroxylating enzymes and suggest a mechanism by which PCBs could alter reproductive function, the in vitro system cannot account for compensatory homeostatic mechanisms which operate to offset induced hepatic steroid metabolism.

Studies designed to assess in vivo steroid metabolism following PCB exposure are scarce. Derr[86] injected rats i.p. with either 10 or 40 mg Aroclor® 1254 every third day for 2 weeks followed by i.v. administration of progesterone 4-[^{14}C] on day 16. The ratio of parent progesterone to metabolites decreased at both PCB treatment levels resulting in a 2.6-fold increase in progesterone metabolism. Other studies not designed to directly examine steroid metabolism have reported changes in steroid patterns following PCB exposure. Whether these alterations resulted from PCB-induced liver enzymes or direct gonadal effects were not determined. Platonow et al.[87] reported a significant decrease in urinary estrogens and dehydroepiandrosterone (DHA) in boars administered 100 mg of Aroclor® 1254, either as a single dose of 10 mg/day for 10 days. Rhesus monkeys were dosed with 4 mg/kg daily of Clophen® A-30 via gastric intubation and serum hormone levels monitored from ovulation through the following ovulation.[41] Three of four PCB-treated monkeys had subnormal serum estrogen levels.

Jonsson et al.[39] fed rats 150 ppm of Aroclor® 1242 for 36 weeks which completely eliminated mating and significantly decreased plasma progesterone. There were no significant changes in 17-α-hydroxyprogesterone although mean levels in PCB-treated animals were lower than controls. An antisteroid effect of Aroclor® 1254 was reported by Spencer.[88] He noted that administration of the PCB during decidualized pseudopregnancy reduced uterine glycogen. As glycogen is a sensitive indicator of estrogenic activity, he interpreted the results as evidence for the antisteroidal role of the PCB although no site of action was indicated.

B. Gonads

In spite of indisputable changes in mixed function oxidases, a direct effect of the chlorinated biphenyls on the gonads and/or steroidogenesis is a distinct possibility. A direct action on steroid production would preclude any homeostatic compensatory mechanism thus accounting for depressed circulating steroids. Several studies support a gonadal site of action. Jonsson et al.[39] in addition to reporting reduced progesterone levels, also noted histologically distinct ovarian stromal changes after prolonged exposure of rats to Aroclor® 1242. In

MONS 006071

harmony with these findings Brandt[1] injected (i.v.) either a mixture of two 6-CB-[^{14}C] isomers or 8-CB-[^{14}C] to pregnant female and adult male mice. The animals were sacrificed at various intervals from 4 min to 32 days after treatment for autoradiographic localization of the carbon label. In pregnant females there was a marked and selective uptake of 6-CB-[^{14}C] in the corpora lutea with a much lower concentration in the follicular walls and ovarian interstitium. Testicular uptake was low but persistent during the first few days following treatment. The radiocarbon-CB appeared to localize in the interstitial tissue and androgen-producing cells of the testes. The octachlorobiphenyl-[^{14}C] also accumulated in the corpora lutea but after a few hours was much higher in the ovarian stroma than the luteal tissues. This author found a similar pattern of accumulation of 6-CB in the hamster.[59] In contrast, the lower [^{14}C] chlorinated biphenyls as well as radiolabeled Aroclor® 1242 and 1254 did not accumulate in the gonads. Apparently, the degree of chlorination and the stereostructure determine the affinity of the molecule for different tissues. Nevertheless, the accumulation of some PCBs in gonadal tissues provides support for a direct effect on these steroid producing organs.

An intriguing effect of PCB on steroidogenesis was reported by Fuller et al.[60] Heavily lutinized ovaries were induced by PMS-HCG priming of immature albino rats. Following formation of corpora lutea 20 mg/kg of Clophen® A-30 was administered i.p. for 2 days, then the ovaries were removed, sliced, and incubated for 2 hr in the presence of luteinizing hormone (LH). Addition of LH to vials containing PCB-exposed luteal tissue resulted in approximately a 100% increase in progesterone synthesis above basal levels, whereas there was only a 31% increase with LH in nonexposed luteal tissue. This is suggestive of a synergistic relationship between PCB and LH or a priming effect due to estrogenic activity of the Clophen® A-30. These results appear contradictory to the PCB-induced decrease in steroid levels reported earlier; however, the closed in vitro system and the induced corpora lutea are different from the complex physiological interactions of an in vivo model.

C. Estrogenic Activity

The estrogenic activity of Clophen® A-30 suggested above is supported by reports of weak estrogenic activity of the lower chlorinated Aroclors®. Gellart[9] found 1 g/kg of Aroclor® 1221 to be uterotrophic in immature rats, whereas Bitman and Cecil[12] reported Aroclors® 1221, 1232, 1242, and 1248 to be minimally estrogenic based on the 18-hr glycogen response of the immature rat uterus to a single 8-mg injection. Ecobichon and MacKenzie[35] measured uterine weight, percent water, and percent glycogen in immature rats following an 8-mg injection (i.p.) of various PCBs. They tested a series of Aroclors® from 1016 to 1260 and isomerically pure chlorobiphenyls (mono-, di-, tetra-, and hexa-CB). In general, at least two of the uterine parameters were increased by each of the commercial preparations except Aroclor® 1016. Of the pure chlorobiphenyls, only those labeled in the 2 position affected the uterus, all parameters being increased with 2-chlorobiphenyl, but only tissue weight by the 2,2' isomer. Little estrogenic activity was noted with increased chlorination except for an increase in uterine weight with the 2,4,6,2',4',6'-hexa-chlorobiphenyl.

Estrogen-sensitive cells in target organs contain cytoplasmic receptors. Binding to a specific receptor is one of the initial events required for estrogen action. Thus, interaction of any of the PCBs with the receptor would be supportive evidence for the reported estrogenic activity. Nelson[61] correlated the inhibition of [^{3}H]-estradiol binding in vitro to the rat uterine receptor by Aroclors® 1221 and 1254 to the uterotropic effect of these PCBs in vivo. The Aroclors were injected i.p. at a level of 50 mg/kg to assess their uterotropic activity. A significant increase in uterine weight was induced by Aroclor® 1221 with a slight but nonsignificant increase following Aroclor® 1254. This correlated well with the in vitro results showing greater than 40% inhibition of binding for Aroclor® 1221 and less than 30% binding

MONS 006072

for Aroclor® 1254. The greater affinity of Aroclor® 1221 for the estrogen receptor does not establish its estrogenicity but does give credibility to reports of weak estrogenic activity of the lower chlorinated biphenyls. Whether this effect is environmentally consequential has not been determined.

D. Central Nervous System

During development the central nervous system (CNS) passes through a "critical steroid-sensitive period" in which organization of the neural mechanisms regulating hormonal and behavioral patterns in the adult are determined. This period occurs following birth in some rodents[91,92] and during fetal development in higher mammals.[91-93] Evidence indicates that behavioral disruption is not primarily attributed to demonstrated alterations in patterns of steroidogenesis in gonads of treated animals but rather to an alteration of the nervous tissues regulating sexual behavior.

As described earlier, Aroclor® 1221, similar to neonatally administered steroids, significantly advanced the age of vaginal opening and induced subsequent sterility in rats treated with 10 mg on days 2 and 3 following birth.[10] Sexual behavior was not studied in these animals but as the results parallel studies using estrogens a modification of reproductive behavior by the PCB is likely.

There are limited data which support a PCB-induced disorganization of nervous elements underlying the expression of normal behavior. Any effect of an animal's behavior patterns could potentially result in infertility. The mechanism by which the PCBs affect the nervous system is obscure. Chow et al.[7] reported that mice exposed to 3,4,3',4'-tetrachlorobiphenyl in utero developed morphological changes in the spinal and cranial nerve roots. These histopathologic alterations were associated with the motor dysfunction "spinning syndrome" in the 4-CB exposed mice. Earlier, Offner et al.[96] had shown Aroclor® 1254 to cause degeneration of neurons in rat brain cell cultures within 25 days of exposure.

Sexual behavior has not been studied following perinatal exposure to PCBs in any mammalian species to this author's knowledge. Nevertheless, other behavioral activities have been compared between perinatally PCB-exposed and control animals which illustrate neurotoxic lesions and potential adverse effects on reproduction. Pregnant rats fed 20 or 100 mg/kg Kaneclor® 500 produced offspring with retarded learning as measured by the number of errors in water-filled multiple T-maze testing at 13 weeks of age.[97] Open field behavior was not affected by this treatment. Bowman et al.[98] reported locomotor hyperactivity and deficiency in learning discrimination problems in three infant rhesus monkeys whose mothers had been fed 2.5 ppm Aroclor® 1248 throughout pregnancy and lactation. The PCB-exposed group showed fourfold the locomotor activity of controls at both 6 and 12 months of age. These same monkeys were retested at 44 months of age for locomotor activity.[99] Unexpectedly, there was a marked hypoactivity in previously hyperactive monkeys. The change in locomotor activity appeared 4 years after exposure and reportedly 3 years after fat biopsies revealed a clearance of PCB residues from the mesenteric fat. Although the number of animals was small, those results underscore the potential neurotoxic hazard to the developing organism.

E. Thyroid

Another extragenital effect of PCBs which could possibly alter reproductive function is the reported depression of circulating thyroxine. Thyroid hormones have been implicated in reproductive function for a long time, both clinically and experimentally. The reproductive system in the immature animals is more readily affected than the adult. Rats made hypothyroid by feeding thiouracil during pregnancy and lactation produced smaller litters at weaning with retarded sexual development of the young. In many species reproduction occurs despite hypothyroidism but fecundity is usually subnormal. In the human female one finds a tendency

MONS 006073

for abortion. Thyroidectomized rabbits become pregnant but exhibit a high incidence of abortions and stillbirths. Similar results have been reported for guinea pigs, sows, and ewes. Delayed puberty, infertility, and estrus and menstrual cycle irregularities are all symptoms of hypothyroidism. In males, hypothyroidism is associated with a reduction in libido and atrophy of seminiferous tubules and Leydig cells. The excess secretion of TSH induced by thyroid deficiency may reduce hypophyseal secretion of gonadotropin, thus reducing testis function. It should be noted that many of the signs of hypothyroidism are the same as those commonly seen after chronic exposure to PCB.

The literature concerning the relationship of the thyroid to reproduction is extensive[100] although a direct relationship has never been established. Nevertheless, ultrastructural lesions of thyroid follicle walls and decreased serum thyroxine were reported in offspring of rats fed 500 ppm Aroclor® 1254 from conception through lactation. This was associated with a reduction in litter size and body weights at weaning.[69,101] The concentration of PCBs in the thyroid of an infant-mother pair of rhesus monkeys was reported by Bailey et al.[99] as 93 to 1 at sacrifice. The mother was treated with 16 mg/kg of Clophen® A-30 for 30 days during lactation. Mink exposed to 5 ppm Aroclor® 1254 were hypothyroid during estrus and the breeding season.[102] They failed to bear young. Pigs farrowed by sows treated with 20 ppm of Aroclor® 1242 for the duration of pregnancy had atrophied thyroids when sacrificed at weaning (8 weeks).[31] The site of action of PCB has not been determined but could result from a direct effect of PCB on the secretion of thyroid hormone or possibly on hypothalamic control of TSH. Although information regarding the effect of PCBs on thyroid function is limited, the evidence justifies continued investigation.

F. Adrenal

Certain disorders of the adrenal gland, especially in females, may lead to oligo-ovulation, anovulation, amenorrhea, precocious or delayed puberty, and infertility. This effect on reproductive function may be directly or indirectly correlated with abnormal adrenal function. This is due to the fact that the gonads and adrenals have overlapping functions. Gonadal abnormalities may affect the normal pituitary-adrenal axis and adrenal malfunction may disturb the normal pituitary-gonadal relationship. Therefore, it is reasonable to assume that a PCB effect on the adrenal could disrupt reproductive development and/or function.

Brandt[1] described a rapid accumulation of [^{14}C]-6-CB and [^{14}C]-8-CB in the adrenal cortexes of male, pregnant female, and fetal mice. Prolonged retention (> 30 days) in the adrenal was observed with both labeled congeners after a single oral or i.v. dose. Sanders and Kirkpatrick[20,34] showed decreased plasma corticoid levels in white-footed mice treated with Aroclor® 1254. Inao[103] reported atrophy of the adrenals and a decreased corticosteroid production in rats after feeding Kanechlor® 400. A significant decrease in plasma corticosteroids was also noted by Bruckner et al.[104] in male rats following i.p. injections of Aroclor® 1242. Conversely, Sanders et al.[17,23] reported an increase in corticords in adult white mice treated with Aroclor® 1254. Wasserman et al.[105] also observed a hyperfunction of the zona fasciculata associated with elevated plasma levels of corticosterone in rats treated with "PCB's 1221".

An explanation for the conflicting reports of hypo- and hyperadrenal function is not apparent. The differences in experimental conditions and stress factors make comparisons futile.

G. Summary

When all potential mechanisms by which mammalian reproductive function can be modified by PCBs are considered, it becomes apparent that no single site of action predominates. First, it is difficult, if not impossible, to distinguish PCB-induced changes in hepatic steroid-metabolizing enzymes from a direct effect on endocrine function. While direct chemical

MONS 006074

damage to the secretory organ may result in decreased hormonal output, the weakly estrogenic PCBs could effect endocrine function by virtue of their competitive affinity for hormone receptors within the organ. Altered receptor availability and/or increased hormone metabolism change trophic hormone thresholds, thus disrupting feedback patterns between the endocrine organs and hypothalamus. This might directly or indirectly modify some phase of the reproductive process. Determination of the definitive site(s) of action remains an elusive goal.

VII. CONCLUSIONS

This chapter has attempted to summarize and integrate as many relevant studies as possible into hypotheses of how environmental PCBs affect mammalian reproductive function. The many studies of varying species, sex, dosages, route and duration of administration and PCB preparations, as well as conflicting findings between studies have made such a goal almost unattainable. Nevertheless, several generalizations relating to their potential deleterious actions on reproduction in wildlife, livestock, and human populations through chronic exposure were derived from the experimental literature.

A point which becomes immediately apparent is that sensitivity to chronic (sublethal) exposure to PCBs increases with higher mammalian orders. In addition, developing organisms are more sensitive than adults and females more sensitive than males to the chlorinated biphenyls. The liver is undoubtedly a major target organ but conclusive evidence that establishes a direct relationship between PCB-induced steroid metabolizing enzymes and reproductive dysfunction is lacking. A demonstration of the accumulation of PCBs in the gonads in conjunction with reports of altered steroid patterns in various mammalian models was suggestive of a direct action of PCBs on endocrine function. Evidence of estrogenic activity for the lower chlorinated biphenyls supports a direct effect on reproductive function. Nevertheless, whether the effect of the PCBs is directly on the reproductive system or acts indirectly through hepatic enzyme induction or on nonreproductive endocrine organs, the outcome is a diminished capacity of the organism to reproduce itself. Finally, the persistence of PCBs in our environment threatens the very existence of the most vulnerable species of wildlife.

MONS 006075

Table 1
SUMMARY OF PCB EFFECTS ON DIFFERENTIATION AND DEVELOPMENT

PCB	Dose	Treatment (days)	Major effect	Species	Ref.
Kanechlor® 500	100 mg/kg	15—21 P	Low weight female fetuses	Mouse	97
2,4',5-Trichlorobiphenyl, 2,4,5,2',4',5'-hexachlorobiphenyl	50 µg	5—22 P	Increased postnatal growth		42
2,2'-Dichlorobiphenyl	750 mg/kg	1—3 P	Reduced fetal weights		56
	500 mg/kg	1 - 6 P			
3,4,3',4'-Tetrachlorobiphenyl	32 mg/kg	10—16 P	Motor dysfunction in offspring		7, 8
Aroclor® 1221	1 g/kg	2	Persistent vaginal estrus syndrome	Rat (neonatal)	10
3,4,3',4'-Tetrachlorobiphenyl	3 mg/kg	5, 11, 13, 15, 18 P	Feminized postpubertal male liver	Rat	16, 84
Aroclor® 1248	2.5 ppm	1—165 P	Low birth weights	Rhesus monkey	52
	5.0 ppm				

Note: P = pregnancy.

MONS 006076

Table 2
SUMMARY OF PCB EFFECTS ON MALE REPRODUCTION

PCB	Dose	Treatment (days)	Major effect	Species	Ref.
Aroclor® 1254	62.5 ppm	14	No effect	Mouse	17
	4000 ppm	14	No effect		
Aroclor® 1254	40 ppm	15	Reduction in sperm per mil-ligram testis		25
	200 ppm				
3-CB	50 μg/day	5 P—W	Offspring showed no effects		31
6-CB			on reproduction as adults		
Aroclor® 1254	200 ppm	28	Decreased terminal vesicle weights	White-footed mouse	19
	400 ppm	14	Decrease in terminal vesicle weight; decrease in number of sperm per testis		20
Aroclor® 1242	5000 mg/kg	1	Decreased number of dividing spermatogonia	Rat	26
	500 mg/kg	4			
Aroclor® 1254	500 mg/kg	1	Increased testis weight		23
Aroclor® 1260	30 mg/kg	14—28 P	Increased testis weight		9
Kanechlor® 500	100 ppm	28	No effect		21
Aroclor® 1254	70 ppm	63	No effect		33
Aroclor® 1254	25 ppm	20	No effect	Cottontail rabbit	22
Aroclor® 1016	20 ppm	270	No effect	Mink/ferrets	27
Aroclor® 1242	5—40 ppm	270	No effect		
Aroclor® 1254	100 mg/kg	1	Decreased urine DNA and renal estrogens	Boar	87
	10 mg/kg	10			
Aroclor® 1248	5 ppm	365	Decreased sperm count in 1 of 4 exposed males	Rhesus monkey	30

Note: P = pregnancy; W = weaning.

Table 3
SUMMARY OF PCB EFFECTS ON FEMALE REPRODUCTION

PCB	Dose	Treatment (days)	Major effect	Species	Ref.
Clophen® A-60	20 mg/kg	1	Increased length of estrous cycles	Mouse	37
Clophen® A-60	0.025 mg/day	75	Increased length of estrous cycles		38
3-CB	50 μg/day	5 P-W	Offspring showed no effects		31
6-CB			on reproduction as adults		
Aroclor® 1254	25 ppm	21	No effect	White-footed mouse	34
	100 ppm				
Aroclor® 1221	1000 mg/kg	1	Uteroatrophic	Immature rat	10
	10 mg/day	2	PVE syndrome	Neonatal rat	
Aroclor® 1254	70 ppm	63	No effect	Rat	33
Aroclor® 1016	20 ppm	180	50% Reproductive failure	Mink/ferrets	27
Aroclor® 1242	5 ppm	180	Reproductive failure		
	10 ppm	180	Greater than 66% mortality		
Arochlor® 1242	20 ppm	180	Reproductive failure		
Aroclor® 1254	300 mg/week	100	Decreased uterine weight	Prepubertal rabbit	36
Aroclor® 1242	2.5 ppm	210	Altered menstrual cycles, amenorrhea, increased urinary heteroestrogens	Rhesus monkey	40
	5.0 ppm				
Clophen® A-30	4 mg/kg	36	Decreased estrogen levels, blocked ovulation in 50% of animals		41

Note: P = pregnancy; W = weaning.

MONS 006077

Table 4
SUMMARY OF PCB EFFECTS ON PREGNANCY AND PARTURITION

PCB	Dose	Treatment (days)	Major effect	Species	Ref.
3-CB	0.5 mg/day	1—6 P	Decreased frequency implantation	Mouse	42
2-CB	375 mg/kg 750 mg/kg	1—3 P	Increased duration of pregnancy, decreased litter size, decreased term pregnancies		43
Aroclor® 1254	25 ppm	6—15 P	Reduced uterine glycogen and ovarian protein during pseudopregnancy (decidualized) and pregnancy	Rat	88
Aroclor® 1254	300 ppm	6—15 P	Reduced fetal survival rate		—
Aroclor® 1254	100 ppm	W—67 or 186	Reduced survival to weaning		
	500 ppm	W—67 or 186	Fewer litters, smaller litter size, 100% pup mortality		
Aroclor®1254	20 ppm	W—62 or 188 2 Generations	Fewer pups per litter F_1 and F_2		24
	100 ppm	2 Generations	Increased mortality in F_1; decreased mating performance of F_1 adults		
Aroclor® 1260	500 ppm	M—67 and 186	Reduced live litter size and survival to weaning in F_1, and F_{1b}		
Aroclor® 1254	100 mg/kg	7—16 P	Decreased pup survival to weaning		
Aroclor® 1254	10—15 mg/kg	7—15 P	No effect		2
Aroclor® 1254	6.25—100 mg/kg	6—15 P	No effect		46
Aroclor® 1254	50 ppm	1—21 P	No effect reproduction; reduced serum T_3 and T_4		45
	500 ppm	1—21 P	Decreased litter size; reduced serum T_3 and T_4		
Aroclor® 1254	70 ppm	63	Fetal resorption		33
Aroclor® 1221	10 mg/kg	1—28 P	No effect reproduction	Rabbit	3
Aroclor® 1254	10 mg/kg	1—28 P	No effect		
Aroclor® 1254	12.5 mg/kg 25.0 mg/kg	1—28 P	Resorptions, abortions, fetal deaths, maternal deaths		46
Clophen® A-50	2.2 mg	16—60 P	Increased fetal deaths	Guinea pig	47
6-CB	2.2 mg	16—60 P	No effect reproduction		
Aroclor® 1221 Aroclor® 1248 Aroclor® 1254	30 ppm (combined)	180	Failed to reproduce	Mink	48
Aroclor® 1016	2 ppm	300 ±	No effect		49
Aroclor® 1221	2 ppm	300 ±	No effect		
Aroclor® 1242	2 ppm	300 ±	No effect		
Aroclor® 1254	2 ppm	300 ±	Reduced litter size		
Aroclor® 1254 (Contaminated beef)	0.64 ppm 3.57 ppm	160	Total reproductive failure		28
Aroclor® 1254	0.5 ppm	270	No effect reproduction		102
	2.0 ppm	270	Failed to bear young		
	5.0 ppm	270	Failed to bear young		

MONS 006078

Table 4 (continued)
SUMMARY OF PCB EFFECTS ON PREGNANCY AND PARTURITION

PCB	Dose	Treatment (days)	Major effect	Species	Ref.
Aroclor® 1254	1.0 mg/kg	0—60 P	No effect	Dog	6
	5.0 mg/kg	0—60 P	Reduced pregnancies, live pups; increased resorptions		
Aroclor® 1242	20 ppm	182 ±	Farrowed and weaned fewer pigs	Sow	51
Aroclor® 1254	1 mg/kg	182 ±	Farrowed and weaned fewer pigs		6
Aroclor® 1248	2.5 ppm	180	Conception normal but 3 of 8 resorbed	Rhesus monkey	40
	5.0 ppm	180	6 of 8 pregnant; 3 aborted, 1 resorbed, 1 stillbirth		

Note: P = pregnancy; W = weaning; M = mating.

Table 5
SUMMARY OF POSSIBLE PCB SITES OF ACTION

PCB	Dose	Treatment (days)	Major effect	Species	Ref.
Aroclor® 1254	500 mg	1 (day 19 P)	Induced hepatic enzymes in offspring	Mouse	77
Aroclor® 1254	62.5 ppm	14	Increased corticosteroids		17
	4000 ppm	14	Increased corticosteroids and adrenal weights		
6-CB	100 mg/kg	1	Induced hepatic enzymes		78
Aroclor® 1254	400 ppm	14	Decreased corticosterone	White-footed	20
Aroclor® 1254	400 ppm	21	Decreased plasma corticoids	Mouse	34
	100 ppm				
Aroclor® 1254	10 mg/day	5 (over 2 weeks)	Increased metabolism of progesterone	Rat	86
Aroclor® 1242	75 ppm	252	Decreased plasma progesterone		39
	150 ppm	252	Decreased plasma progesterone Decreased ovarian follicles		
Aroclor® 1254	50 ppm	7	Induced hepatic enzymes		81
	10 ppm	14	Induced hepatic enzymes		80
	100 μM	27	Degeneration of cultured brain cells		96
Clophen® A-30	20 mg/kg	1	Enhanced LH induced ovarian progesterone synthesis in vitro	——	90
Aroclor® 1221	250 ppm	70	Increased plasma corticosterone		105
Aroclor® 1254	70 ppm	63	Induced hepatic enzymes		33
1-CB	30 mg/kg	5, 11, 13, 15, 18 P	No effect on liver		16
6-CB	3 mg/kg	5, 11, 13, 15, 18 P	Induced hepatic enzymes; female and adult male liver		84
6-CB	30 mg/kg	5, 11, 13, 15, 18 P	Induced hepatic enzymes; female and adult male liver		82
Aroclor® 1254	25 mg/kg	6	Induced hepatic enzymes		
Aroclor® 1254	50 ppm	1—21	Reduced serum T_3 and T_4		45
	500 ppm		Reduced serum T_3 and T_4		
Aroclor® 1221	100 ppm	—	Greater than 40% inhibition of E_2 binding to uterine receptor in vitro	Rat (immature)	91
Aroclor® 1254	100 ppm	—	Less than 30% inhibition of E_2 binding to uterine receptor in vitro		

MONS 006079

Table 5 (continued)
SUMMARY OF POSSIBLE PCB SITES OF ACTION

PCB	Dose	Treatment (days)	Major effect	Species	Ref.
Aroclor® 1221	50 mg/kg	1	Uterotrophic		
Aroclor® 1254	50 mg/kg	1	No effect		
Aroclor® 1221	8 mg/kg	1	Increased uterine glycogen		12
Aroclor® 1232	8 mg/kg	1	Increased uterine glycogen		
Aroclor® 1242	8 mg/kg	1	Increased uterine glycogen		
Aroclor® 1248	8 mg/kg	1	Increased uterine glycogen		
Aroclor® 1254	8 mg/kg	1	No effect		
Aroclor® 1260	8 mg/kg	1	No effect		
Aroclor® 1262	8 mg/kg	1	No effect		
Aroclor® 1268	8 mg/kg	1	No effect		
Aroclor® 1016	20 ppm	28	Weak induction of liver enzymes	Mink/ferrets	83
Aroclor® 1242	20 ppm	28	Induced liver enzymes		
Aroclor® 1254	0.5 ppm	270	Increased T_3		102
	2 ppm	270	Hypothyroid		
	5 ppm	270	Hypothyroid		
Aroclor® 1254	10 mg/kg	1	No effect	Boar	87
	1 mg/kg	10	No effect		
	100 mg/kg	1	Decreased urine DMA and estrogens		
	10 mg/kg	10	Decreased urine DMA and estrogens		
Aroclor® 1248	2.5 ppm	1 P—W	Hyperactive at 6 and 12 months of age; learning deficiencies	Rhesus monkey	98
Aroclor® 1248	2.5 ppm	1 P—W	Hyperactive at 44 months of age		99
Clophen® A-30	4 mg/kg	36	Decreased serum estrogen		41

Note: P = pregnancy; W = weaning.

REFERENCES

1. **Brandt, I.**, Tissue localization of polychlorinated biphenyls. Chemical structures related to pattern of distribution, *Acta Pharmacol. Toxicol.*, 40(2), 1, 1977.
2. **Carley, A., Burse, V. W., and Grim, M. E.**, Polychlorinated biphenyls: evidence of transplacental passage in the Sherman rat, *Food Cosmet. Toxicol.*, 11, 471, 1973.
3. **Villeneuve, D. C., Grant, D. L., Phillips, W. E. J., Clark, M. L., and Clegg, D. J.**, Effects of PCB administration on microsomal enzyme activity in pregnant rabbits, *Bull. Environ. Contam. Toxicol.*, 6, 120, 1971.
4. **Allen, J. R. and Barsotti, D. A.**, The effects of transplacental and mammary movement of PCBs on infant rhesus monkeys, *Toxicology*, 6, 331, 1976.
5. **Watanabe, M. and Sugahara, T.**, Experimental formation of cleft palate in mice with polychlorinated biphenyls (PCB), *Toxicology*, 19(Abstr.), 49, 1981.
6. **Earl, F. L., Courtney, J. L., and Van Loon, E. J.**, The reproductive effects of PCB 1254 in Beagle dogs and miniature swine, *Toxicol. Appl. Pharmacol.*, 29, 104, 1974.
7. **Chow, S. M., Miike, T., Payne, W. M., and Davis, G. J.**, Neuropathology of "spinning syndrome" induced by prenatal intoxication with a PCB in mice, *Ann. N.Y. Acad. Sci.*, 31, 373, 1979.
8. **Tilson, H. A., Davis, G. J., McLachlan, J. A., and Lucier, G. W.**, The effects of polychlorinated biphenyls given prenatally on the neurobehavioral development of mice, *Environ. Res.*, 18, 466, 1979

MONS 006080

9. **Gellert, R. J. and Wilson, C.,** Reproductive function in rats exposed prenatally to pesticides and polychlorinated biphenyls (PCB). *Environ. Res.*, 18, 437, 1979.
10. **Gellert, R. J.,** Uterotropic activity of polychlorinated biphenyls (PCB) and induction of precocious reproductive aging in neonatally treated female rats, *Environ. Res.*, 16, 123, 1978.
11. **Harris, G. W. and Levine, S.,** Sexual differentiation of the brain and its experimental control, *J. Physiol. (London)*, 181, 379, 1965.
12. **Bitman, J. and Cecil, H. C.,** Estrogenic activity of DDT analogs and polychlorinated biphenyls, *J. Agric. Food Chem.* 18, 1108, 1970.
13. **Denef, C. and De Moor, P.,** The "puberty" of the rat liver. II. Permanent changes in steroid metabolizing enzymes after treatment with a single injection of testosterone propionate at birth, *Endocrinology*, 83, 791, 1968.
14. **Denef, C. and De Moor, P.,** "Puberty" of the rat liver. IV. Influence of estrogens upon the differentiation of cortisol metabolism induced by neonatal testosterone, *Endocrinology*, 85, 259, 1969.
15. **Gustafsson, J. A. and Stenberg, A.,** Masculinization of rat liver enzyme activities following hypophysectomy, *Endocrinology*, 95, 891, 1974.
16. **Lucier, G. W. and McDaniel, O. S.,** Developmental toxicology of the halogenated aromatics: effects on enzyme development, *Ann. N.Y. Acad. Sci.*, 31, 449, 1979.
17. **Sanders, O. T., Lepp, R. L., and Kirkpatrick, R. L.,** Effect of PCB ingestion on sleeping times, organ weights, food consumption, serum corticosterone and survival of Albino mice, *Bull. Environ. Contam. Toxicol.*, 12, 394, 1974.
18. **Orberg, J. and Lundberg, C.,** Some effects of DDT and PCB on the hormonal system in the male mouse, *Environ. Physiol. Biochem.*, 4, 116, 1974.
19. **Morson, M. H. and Kirkpatrick, R. L.,** Effects of dietary exposure to PCB on testicular characteristics, organ weights and plasma corticoids of male White-footed mice, *Va. J. Sci.*, 26(Abstr.), 58, 1975.
20. **Sanders, O. T. and Kirkpatrick, R. L.,** Effects of a polychlorinated biphenyl (PCB) on sleeping times, plasma corticosteroids, and testicular activity of White-footed mice, *Environ. Physiol. Biochem.*, 5, 308, 1975.
21. **Ohshi, S., Morita, M., and Fukuda, H.,** Comparative toxicology of polychlorinated biphenyls and dibenzofurans in rats, *Toxicol. Appl. Pharmacol.*, 43, 13, 1978.
22. **Warren, R. J., Kirkpatrick, R. L., and Vogelsang, R. W.,** Effects of Mirex and a PCB on pentobarbitol-induced sleeping times and organ weights of male Cottontail rabbits, *Va. J. Sci.*, 26(Abstr.), 60, 1974.
23. **Grant, D. L., Phillips, W. E. J., and Villeneuve, D. C.,** Metabolism of a polychlorinated biphenyl (Aroclor® 1254) mixture in the rat, *Bull. Environ. Contam. Toxicol.*, 6, 102, 1971.
24. **Linder, R. E., Gaines, T. B., and Kimbrough, R. D.,** The effect of polychlorinated biphenyls on rat reproduction, *Food Cosmet. Toxicol.*, 12, 63, 1974.
25. **Sanders, O. T., Kirkpatrick, R. L., and Scanlon, P. E.,** Polychlorinated biphenyls and nutritional restriction: their effects and interactions on endocrine and reproductive characteristics of male white mice, *Toxicol. Appl. Pharmacol.*, 40, 91, 1977.
26. **Gross, S., Palmer, R. A., and Oswald, E. J.,** Cytogenic effects of the polychlorinated biphenyls (Aroclor® 1242) on rat bone marrow and spermatogonial cells, *Toxicol. Appl. Pharmacol.*, 25(Abstr.), 482, 1973.
27. **Bleavins, M. R., Aulerich, R. J., and Ringer, R. K.,** Polychlorinated biphenyls (Aroclors® 1016 and 1242): effect on survival and reproduction in mink and ferrets, *Arch. Environ. Contam. Toxicol.*, 9, 627, 1980.
28. **Platonow, N. S. and Karstad, L. H.,** Dietary effects of polychlorinated biphenyls on mink, *Can. J. Comp. Med.*, 37, 391, 1973.
29. **Kimbrough, R., Buckley, J., Fishbein, L., Flamm, G., Kanno, L., Marcus, W., Shibko, S., and Tuthe, R.,** Animal toxicology, *Environ. Health Perspect.*, 24, 173, 1973.
30. **Allen, J. R., Barsotti, D. A., Lambrecht, L. K., and Van Miller, J. P.,** Reproductive effects of halogenated aromatic hydrocarbons in nonhuman primates, *Ann. N.Y. Acad. Sci.*, 230, 419, 1979.
31. **Orberg, J.,** Placental and mammary transfer of two PCBs (2,4',6-TCB and 2,2',4,4',5,5'-HCB) and their effect on reproductive capacity in mice, *Ambio*, 6, 278, 1977.
32. **Kihlstrom, J. E., Lundberg, C., Orberg, J., Danielson, P. O., and Bydtheff, J.,** Sexual functions of mice neonatally exposed to DDT or PCB, *Environ. Physiol. Biochem.*, 5, 54, 1975.
33. **Baker, F. O., Bush, B., Tomasunis, C. V., and Lo, F.,** Toxicity and persistence of low-level PCB in adult Wistar rats, fetuses, and young, *Arch. Environ. Contam. Toxicol.*, 5, 143, 1977.
34. **Sanders, O. T. and Kirkpatrick, R. L.,** Reproductive characteristics and corticoid levels of female White-footed mice fed *ad libitum* and restricted diets containing a polychlorinated biphenyl, *Environ. Res.*, 13, 358, 1977.
35. **Easterbrook, D. J. and MacKenzie, D. O.,** The uterotrophic activity of commercial and isomerically-pure chlorobiphenyls in the rat, *Res. Commun. Chem. Pathol. Pharmacol.*, 9, 85, 1974.
36. **Keller, L. D. and Zinkin, J. G.,** Pathology of polychlorinated biphenyls in rabbits, *Am. J. Pathol.*, 70, 363, 1973.

MONS 006081

37. Orberg, J., Johanneson, N., Kihlstrom, J. E., and Lundberg, C., Administration of DDT and polychlorinated biphenyls prolongs estrous cycle in mice. *Ambio*, 1, 148, 1972.
38. Orberg, J. and Kihlstrom, J. E., Effects of long-term feeding of polychlorinated biphenyls (PCB, Clophen A-60) on the length of the oestrous cycle and on the frequency of implanted ova in the mouse. *Environ. Res.*, 6, 176, 1973.
39. Jonsson, H. T., Keil, J. E., Gaddy, R. G., Landholt, G. B., Hennigan, G. R., and Walker, E. M., Prolonged ingestion of commercial DDT and PCB: effects on progesterone levels and reproduction in the mature female rat. *Arch. Environ. Contam. Toxicol.*, 3, 479, 1976.
40. Barsotti, D. A., Marlar, R. J., and Allen, J. R., Reproductive dysfunction in rhesus monkeys exposed to low levels of polychlorinated biphenyls (Aroclor® 1248). *Food Cosmet. Toxicol.*, 14, 99, 1976.
41. Mueller, W. F., Hobson, W., Fuller, G. B., Knauf, V., Coulston, F., and Korte, F., Endocrine effects of chlorinated hydrocarbons in rhesus monkeys. *Ecotoxicol. Environ. Safety*, 2, 161, 1978.
42. Orberg, J., Effects of pure chlorobiphenyls (2,4',5-trichlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl) on the reproductive capacity in female mice. *Acta Pharmacol. Toxicol.*, 42, 323, 1978.
43. Terao, F., Delayed pregnancy in NMRI mice treated with PCB: 2,2'-dichlorobiphenyl. *Bull. Environ. Contam. Toxicol.*, 16, 33, 1976.
44. Masuda, Y., Kagawa, R., Takudome, S., and Kuratsune, M., Transfer of polychlorinated biphenyls to the fetuses and offspring of mice. *Food Cosmet. Toxicol.*, 16, 33, 1978.
45. Collins, W. T. and Capen, C. C., Fine structural lesions and hormonal alterations in thyroid glands of perinatal rats exposed *in utero* and by the milk to polychlorinated biphenyls. *Am. J. Pathol.*, 99, 125, 1980.
46. Villeneuve, D. C., Grant, D. L., Khera, K., Clegg, D. J., Bass, H., and Phillips, W. E. J., The fetotoxicity of a polychlorinated biphenyl mixture (Aroclor® 1254) in the rabbit and rat. *Environ. Physiol.*, 1, 67, 1971.
47. Brunstrom, B., Kihlstrom, I., and Lundkvist, U., Studies of foetal death and foetal weight in guinea pigs fed polychlorinated biphenyls (PCB). *Acta Pharmacol. Toxicol.*, 50, 100, 1982.
48. Aulerich, R. J., Ringer, R. K., and Iwamoto, S., Reproductive failure and mortality in mink fed on Great Lakes fish. *J. Reprod. Fertil. Suppl.*, 19, 365, 1973.
49. Aulerich, R. J. and Ringer, R. K., Current status of PCB toxicity to mink and effect on their reproduction. *Arch. Environ. Contam. Toxicol.*, 6, 279, 1977.
50. Jensen, S., Kihlstrom, J. E., Olsson, M., Lundberg, C., and Orberg, J., Effects of PCB and DDT on mink (*Mustela vison*) during the reproductive season. *Ambio*, 6, 239, 1977.
51. Hansen, L. G., Byerly, C. S., Metcalf, R. L., and Bevill, R. F., Effect of a polychlorinated biphenyl mixture on swine reproduction and tissue residue. *Am. J. Vet. Res.*, 36, 23, 1975.
52. Allen, J. R., Barsotti, D. A., and Carstens, L. A., Residual effects of polychlorinated biphenyls in adult nonhuman primates and their offspring. *J. Toxicol. Environ. Health*, 6, 55, 1980.
53. Altman, N. H., New, A. E., McConnell, E. E., and Ferrell, T. L., A spontaneous outbreak of polychlorinated biphenyl (PCB) toxicity in rhesus monkeys. (*Macaca mulatta*): clinical observations. *Lab. Anim. Sci.*, 29, 661, 1979.
54. Truelove, J., Grant, D., Mes, J., Tryphonas, H., Tryphonas, L., and Zawidska, Z., Polychlorinated biphenyl toxicity in the pregnant cynomolgus monkey: a pilot study. *Arch. Environ. Contam. Toxicol.*, 11, 583, 1972.
55. Masuda, U., Kagawa, R., Kuroki, H., Takudome, S., and Kuratsune, M., Transfer of various polychlorinated biphenyls to the fetuses and offspring of mice. *Food. Cosmet. Toxicol.*, 17, 623, 1979.
56. Terao, F., Effect of 2,2'-dichlorobiphenyl (PCB) on the embryonic development of the NMRI mouse. in *Pesticides. Environmental Quality and Safety*, Vol. 3, Coulston, F. and Korte, F., Eds., George Thieme, Stuttgart, 1975, 788.
57. Vodicnik, M. J. and Lech, J. L., The transfer of 2,4,5,2',4',5'-hexachlorobiphenyl to fetuses and nursing offspring. *Toxicol. Appl. Pharmacol.*, 54, 293, 1980.
58. Ando, M., Transfer of 2,4,5,2',4'5'-hexachlorobiphenyl and 2,2-bis (p-chlorophenyl), 1,1,1-trichloroethane (p,p'-DDT) from maternal to newborn and suckling rats. *Arch. Toxicol.*, 41, 179, 1978.
59. Platonow, N. and Chen, N. Y., Transplacental transfer of polychlorinated biphenyls (Aroclor® 1254) in a cow. *Vet. Rec.*, 92, 69, 1973.
60. Brandt, I., Distribution of 2,2',4,4',5,5'-hexachlorobiphenyl in mice and Chinese hamsters. *Arch. Toxicol.* 34, 111, 1975.
61. Takagi, Y., Otake, T., Kataoka, M., Murata, Y., Aburada, S., Akaike, S., Hashimoto, K., Uda, H., and Kimura, T., Studies on the transfer and distribution of [^{14}C] polychlorinated biphenyls from maternal to fetal and suckling rats. *Toxicol. Appl. Pharmacol.*, 38, 549, 1976.
62. Zabik, M. E., Beebe, C., and Schoenmel, R., Effect of rat's diet on PCB accumulation in nursing Osborne Mendel pups. *Arch. Environ. Contam. Toxicol.*, 4, 246, 1976.

MONS 006082

63. **Perry, T. W., Everson, R. J., Hendrix, K. S., Peterson, R. C., Weinland, K. M., and Robinson, F. R.,** Dietary Aroclor® 1254 in the milk of lactating cattle. *Conf. Trace Substances Environ. Health*, 13, 271, 1979.
64. **Saschenbrecker, P. W., Funnell, H. S., and Platonow, N. S.,** Persistence of polychlorinated biphenyls in the milk of exposed cows. *Vet. Rec.*, 90, 100, 1972.
65. **Tuinstra, L. G. M. Th., Vreeman, K., Roos, A. H., and Keukens, J. J.,** Excretion of certain chlorobiphenyls into the milk fat after oral administration. *Neth. Milk Dairy J.*, 35, 147, 1981.
66. **Bailey, J., Kaouf, V., Mueller, W., and Hobson, W.,** Transfer of hexachlorobenzene and polychlorinated biphenyls to nursing infant rhesus monkeys: enhanced toxicity. *Environ. Res.*, 21, 190, 1980.
67. **Acker, L. and Schulte, E.,** Ueber das Vorkommen von chlorierten Biphenylen und Hexachlorbenzol neben chlorierten Insektiziden in Human milch und menschlichen Fettgeweben. *Naturwissenschaften*, 57, 497, 1970.
68. **Musial, C. J., Hutzinger, O., Zitko, V., and Crocker, J.,** Presence of PCB, DDE, and DDT in human milk in the provinces of New Brunswick and Nova Scotia, Canada. *Bull. Environ. Contam. Toxicol.*, 12, 258, 1974.
69. **Jonsson, S. and Jonsson, B.,** Number and identity of anthropogenic substances known to be present in Baltic Seals and their possible effects on reproduction. *Ann. N.Y. Acad. Sci.*, 320, 436, 1979.
70. **Reijnders, P. J. H.,** Organochlorine and heavy metal residues in Harbour Seals from the Wadden Sea and their possible effects on reproduction. *Neth. J. Sea Res.*, 14, 30, 1980.
71. **DeLong, R. L., Gilmartin, W. G., and Simpson, J. G.,** Premature births in California Sea Lions: association with high organochlorine pollutant residue levels. *Science*, 181, 1168, 1973.
72. **Gilmartin, W. G., DeLong, R. L., Smith, A. W., Sweeney, J. C., DeLappe, B. W., Risebrough, R. W., Grimer, L. A., Dailey, M. D., and Peakall, D. B.,** Premature parturition in the California Sea Lion. *J. Wildl. Dis.*, 12, 104, 1976.
73. **Dunkin, P., Mann, S. V., and Hamilton, E. I.,** Polychlorinated biphenyl, DDT and Dieldrin residues in Grey Seal (*Halichoerus grypus*) males, females and mother-foetus pairs sampled at the Farne Islands, England, during the breeding season. *Sci. Total Environ.*, 19, 121, 1981.
74. **McCormack, K. M., Melrose, P., Richert, D. E., Dent, J. G., Gibson, J. E., and Hook, J. B.,** Concomitant dietary exposure to polychlorinated biphenyls and polybrominated biphenyls: tissue distribution and arylhydrocarbon hydroxylase activity in lactating rats. *Toxicol. Appl. Pharmacol.*, 47, 95, 1979.
75. **Allen, J. R.,** Response of the non-human primate to polychlorinated biphenyl exposure. *Fed. Proc.*, 34, 1675, 1975.
76. **Vos, J. G. and Beems, R. B.,** Dermal toxicity studies of technical polychlorinated biphenyls and fractions thereof in rabbits. *Toxicol. Appl. Pharmacol.*, 19, 617, 1971.
77. **Jannotti, R. A. and Anderson, L. M.,** Dimethylnitrosamine demethylase activity in fetal, suckling and maternal mouse liver and its transplacental and transmammary induction by polychlorinated biphenyls. *J. Natl. Cancer Inst.*, 67, 461, 1981.
78. **Vodicnik, M. J., Elcombe, C. R., and Lech, J. J.,** The transfer of 2,4,5,2',4',5'-hexachlorobiphenyl to fetuses and nursing offspring. II. Induction of hepatic microsomal monooxygenase activity in pregnant and lactating mice and their young. *Toxicol. Appl. Pharmacol.*, 54, 301, 1980.
79. **Chen, T. S. and DuBois, K. P.,** Studies on the enzyme inducing effect of polychlorinated biphenyls. *Toxicol. Appl. Pharmacol.*, 26, 504, 1973.
80. **DenTonkelaar, E. M. and Van Esch, G. J.,** No-effect levels of organochlorine pesticides based on induction of microsomal liver enzymes in short-term toxicity experiments. *Toxicology*, 2, 371, 1974.
81. **Litterst, C. L. and van Loon, E. J.,** Time-course of induction of microsomal enzymes following treatment with polychlorinated biphenyl. *Bull. Environ. Contam. Toxicol.*, 11, 206, 1974.
82. **Ajwens, A. F. and Koppes, A.,** Induction of aryl-hydrocarbon hydroxylase by polychlorinated biphenyls in the feto-placental unit and neonatal livers during lactation. *FEBS Lett.*, 50, 172, 1975.
83. **Shull, L. R., Bleavins, M. R., Olson, B. A., and Aulerich, R. J.,** Polychlorinated biphenyls (Aroclors® 1016 and 1242): effect on hepatic microsomal mixed function oxidases in mink and ferrets. *Arch. Environ. Contam. Toxicol.*, 11, 313, 1982.
84. **Dieringer, C. S., Lamartiniere, C. A., Schiller, C. M., and Lucier, G. W.,** Altered ontogeny of hepatic steroid-metabolizing enzymes by pure polychlorinated biphenyl congeners. *Biochem. Pharmacol.*, 28, 2511, 1979.
85. **Inoue, K., Takeuchi, A., Mizukami, R., Fujimori, K., Sunouchi, M., Kamiya, Y., and Omori, Y.,** Effects of polychlorinated biphenyls on the monooxygenase systems in fetal livers of rats. *Toxicol. Appl. Pharmacol.*, 59, 540, 1981.
86. **Derr, S. K.,** *In vivo* metabolism of exogenous progesterone by PCB treated female rats. *Bull. Environ. Contam. Toxicol.*, 19, 729, 1978.
87. **Platonow, N. S., Lipsrapp, R. M., and Geisinger, H. D.,** The distribution and excretion of polychlorinated biphenyls (Aroclor® 1254) and their effect on urinary gonadal steroid levels in the boar. *Bull. Environ. Contam. Toxicol.*, 7, 358, 1972.

MONS 006083

88. **Spencer, F.**, An assessment of the reproductive toxic potential of Aroclor® 1254 in female Sprague-Dawley Rats. *Bull. Environ. Contam. Toxicol.*, 28, 290, 1982.
89. **Brandt, I.**, Distribution of 2,2',4,4',5,5'-hexachlorobiphenyl in mice and Chinese hamsters: dose dependent accumulation in the mouse bronchial mucosa, *Arch. Toxicol.*, 34, 111, 1975.
90. **Fuller, G. B., Knauf, V., Mueller, W., and Hobson, W. C.**, PCB augments LH-induced progesterone synthesis. *Bull. Environ. Contam. Toxicol.*, 25, 65, 1980.
91. **Nelson, J. A.**, Effects of dichlorodiphenyltrichloroethane (DDT) analogs and polychlorinated biphenyls (PCB) mixtures on 17-[^{3}H] estradiol binding to rat uterine receptor, *Biochem. Pharmacol.*, 23, 447, 1974.
92. **Brown-Grant, K. and Sherwood, M. R.**, The early androgen syndrome in the guinea pig, *J. Endocrinol.*, 49, 227, 1971.
93. **Korth, F. J., Dierschke, D. J., and Knobil, E.**, Sexual differentiation of pituitary function: apparent difference between primates and rodents, *Science*, 179, 484, 1973.
94. **Ehrenreich, F. and Parvizi, N.**, Estrogen feedback in the pig: sexual differentiation and the effect of prenatal testosterone treatment, *Biol. Reprod.*, 20, 1187, 1979.
95. **Fuller, G. B., Yoss, D. E., Hutton, E. D., and Hobson, W. C.**, Diethylstilbestrol reversal of gonadotropin patterns in infant rhesus monkeys, *J. Steroid Biochem.*, 15, 497, 1981.
96. **Offner, H., Kamat, G., and Clemens, J.**, The effect of DDT, Lindane and Aroclor® 1254 on brain cell culture, *Environ. Physiol. Biochem.*, 3, 204, 1973.
97. **Shiota, K.**, Postnatal behavioral effects of prenatal treatment with PCBs (polychlorinated biphenyls) in rats, *Okajimas Fol. Anat. Jpn.*, 53, 105, 1976.
98. **Bowman, R. E., Heironimus, M. P., and Allen, J. R.**, Correlation of PCB body burden with behavioral toxicology in monkeys, *Pharmacol. Biochem. Behav.*, 9, 69, 1978.
99. **Bowman, R. E. and Heironimus, M. P.**, Hyposctivity in adolescent monkeys perinatally exposed to PCBs and hyperactive as juveniles, *Neurobehav. Toxicol. Teratol.*, 3, 15, 1981.
100. **Leathem, J. H.**, Role of the thyroid, in *Reproductive Biology*, Balin, H. and Glasser, S., Eds., Excerpta Medica, Amsterdam, 1972, chap. 23.
101. **Greenberg, A. H., Naijar, S., and Blizzard, R. M.**, Effect of thyroid hormone on growth, differentiation, and development, in *Handbook of Physiology*, Vol. 3, Knobil, E. and Sawyer, W. H., Eds., Williams & Wilkins, Baltimore, 1974.
102. **Byrne, J. J., Reiosha, E. P., Ringer, R. K., and Aulerich, R.**, Influences of polychlorinated biphenyl mixture (Aroclor® 1254) administration on reproduction and thyroid function in mink (*Mustela vison*), *Fed. Proc.*, 34(Abstr.), 321, 1975.
103. **Inoe, S.**, Adrenocortical insufficiency induced in rats by prolonged feeding of Kanechlor® (chlorobiphenyl), *Kumamoto Med. J.*, 23, 27, 1970.
104. **Burchner, J. V., Khanna, K. L., and Cornish, H. H.**, Polychlorinated biphenyl-induced alteration of biologic parameters in the rat, *Toxicol. Appl. Pharmacol.*, 28, 189, 1974.
105. **Wasserman, D., Wasserman, M., Cucos, S., and Djavaherian, M.**, Function of adrenal gland-zona fasciculata in rats receiving polychlorinated biphenyls, *Environ. Res.*, 6, 334, 1973.

MONS 006084

Chapter 8

USE OF ORGANISMS TO QUANTIFY PCBs IN MARINE AND ESTUARINE ENVIRONMENTS

David J. H. Phillips

TABLE OF CONTENTS

I. Abstract 128

II. Introduction 128

III. PCB Quantification in the Aquatic Environment 129
- A. Analysis of Water 129
- B. Analysis of Sediments 132
- C. Analysis of Organisms 136

IV. Isomer Quantification, Behavior, and Kinetics in Organisms 137

V. The Influence of Lipid 151

IV. The Effects of Season/Organism Condition 156
- A. Temporal Fluctuations in Pollutant Delivery 157
- B. Biological Changes Influencing PCB Accumulation 157
  - 1. Spawning 158
  - 2. Growth 159
  - 3. Migration 160
- C. Seasonal Variations in Water Quality 161
- D. Conclusions on the Effects of Season/Organism Condition 161

VII. Size (Weight, Age) of Individuals Sampled 162

VIII. Sex of Individuals Sampled 166

IX. Vertical Position of Sampling 169

Acknowledgments 171

References 171

MONS 006085

I. ABSTRACT

PCBs have entered the environment from a variety of industrial sources. Their low water solubility, highly lipophilic character, and considerable resistance to degradation are the cause of their bioaccumulation and persistence in biota. The quantification of PCBs in the aquatic environment is possible through the analysis of water, sediments, or biota. Of these methods, the analysis of so-called bioindicator or sentinel organisms has certain practical and theoretical advantages, and is increasingly becoming the method of choice in surveys of PCBs.

Several problems must, however, be overcome if the results of such surveys are to give an accurate picture of the general contamination of aquatic ecosystems by PCBs. The first of these concerns is the accurate analytical quantification of PCB residues in aquatic biota. Difficulties arise because of a lack of standardized methods for the analysis and quantification of PCBs, coupled with the selective accumulation of some PCB compounds by organisms. Improvements in analytical techniques are required to permit separation of PCBs into individual components, each of which should be considered a unique contaminant in its own right.

The other problems inherent in the use of bioindicator organisms to monitor PCBs mainly concern biological variables. The lipid content of the organisms studied is of very considerable importance in determining the levels of PCBs accumulated within the tissues. The effects of this parameter on the results may be reduced or eliminated by basing analytical data on both wet and lipid weights. Season of collection or organism condition is also important; temporal variability may occur due to fluctuations in pollutant availability, biological changes (commonly involving the sexual cycle, but including in some instances factors such as growth and migration of organisms), and alterations in water quality (particularly salinity and temperature). Size, age, or weight of the individuals sampled may also influence the PCB concentrations present, particularly in finfish. Finally, both organism's sex and its vertical position in the water column may affect its content of PCBs.

Each of these variables must be taken into account by the researcher undertaking bioindicator surveys for PCBs. The influence of each variable can be reduced, or sometimes eliminated, by certain methods, many of which involve care at the stage of organism sampling. If such precautions are taken, the use of bioindicators to monitor PCBs in aquatic environments is a powerful tool, giving rise to accurate and rapid estimates of the time-integrated bioavailability of these compounds in the various study locations.

II. INTRODUCTION

Polychlorinated biphenyls (PCBs) were first produced commercially in 1929 in the U.S. Between 1929 and 1977, about 600,000 t of PCBs were manufactured in the U.S. alone; a similar additional amount was manufactured in Japan, the U.S.S.R., and parts of Europe.[1-5] These compounds were used for a variety of purposes, e.g., as dielectric fluids in transformers and capacitors, as heat transfer or hydraulic fluids, and as lubricating oils and plasticizers. Many of the uses can be classified as dissipative, i.e., recovery of the PCBs has not occurred, and the PCBs have therefore entered the general environment.

Estimates of the total amount of PCBs in the global environment vary, but it is probable that about 15% of the PCBs manufactured to date has already escaped to enter a "mobile environmental reservoir"; much of the remainder is not in closed systems and may reach the general environment at some future time.[2,4,6,7]

The possible persistence of effects of PCBs in the environment received remarkably little attention for more than 35 years after their introduction into commercial usage. However, in the mid-1960s, chemists began to take note of unidentified peaks on chromatograms of

MONS 006086

extracts of biota containing DDT and its metabolites.[8,9] These compounds were identified by Sören Jensen in 1966 as PCBs, and he showed that they were present in biological tissues prior to the introduction of DDT.[9,10]

PCBs enter the general environment by a variety of routes.[6] One of the most important routes is transportation in air, which permits the efficient and rapid dissipation of PCBs from point sources to distant areas.[11-14] In addition to the airborne route, marine environments receive PCBs from urban run-off,[15,16] from wastewater discharges,[17,18] from rivers,[20] and directly from dumped sewage sludge[21] and antifouling paints.[22,23]

Once in the aquatic environment, PCBs exhibit a bioaccumulative tendency similar to that of DDT and its metabolites. This similarity is based upon the very low water solubilities of the two groups of compounds, coupled with their extreme lipophilic nature and great resistance to degradation. As a result of the diffuse airborne and waterborne inputs and the great persistence and stability of PCBs, these compounds may be found in biota throughout the world, including both poles,[24-26] the deep sea,[27] the offshore oceans,[11,28-30] and inland lakes and coastal waters.

The recent realization of the ubiquity, persistence, and possible toxic effects of PCBs in aquatic environments has given rise to partial bans or restrictions on the use of these compounds.[3,5,30,31,32] However, such restrictions will not solve the current or even the future problems, as considerable amounts of PCBs have already been introduced to the general environment and will continue to leach to the final marine sediment sink from all sources. In addition, the restrictions to date apply in general only to the developed nations of the Northern Hemisphere, and PCB usage in the tropics and subtropics continues unabated; indeed, in some areas usage is increasing to keep pace with industrial development.

As a result, it is clear that PCBs will continue to be present in aquatic environments for many decades. Their effects in the ecosphere depend, of course, on dosage; if sufficient data on the amounts of PCBs present in an aquatic ecosystem can be accumulated, decisions can be made on how to deal with the problems engendered by their presence. It is therefore clear that one of the primary needs is the development of an accurate and efficient method of quantifying PCBs in aquatic environments. This chapter addresses the methods available for this purpose, with particular emphasis on the use of aquatic organisms (so-called "biological indicators").

III. PCB QUANTIFICATION IN THE AQUATIC ENVIRONMENT

As Phillips[33-35] has pointed out, conservative pollutants such as trace metals, organochlorine pesticides, or PCBs, may be quantified in the aquatic environment by the analysis of natural waters, sediments, or aquatic organisms. None of these methods is ideal, each possessing certain disadvantages. The three methods are discussed briefly below.

A. Analysis of Water

Considerable amounts of data have been amassed concerning PCB concentrations in marine and fresh waters. Table 1 shows typical concentrations reported for open oceans, coastal waters, and estuaries or rivers. It is evident that PCB levels vary over a considerable range in any one type of water. However, as might be expected, open ocean concentrations of PCBs[36-40] are generally less than those found in coastal waters[41-46] and rivers exposed to industrial sources of PCBs are commonly even more highly contaminated.[47,48]

The PCBs present in aquatic environments partition between the soluble phase and the particulate phase of the water mass. Pavlou and Dexter[41] considered this partitioning in detail, and concluded that at the normal suspended loads encountered in coastal waters (0.5 to 10 g/m^3), less than 20% of the PCB would be adsorbed to inorganic particulate matter. However, this situation will alter under conditions where either particularly large amounts

MONS 006087

Table 1
RANGES IN PCB CONCENTRATIONS (ng/ℓ) REPORTED FOR OPEN OCEANS, COASTAL WATERS, AND ESTUARIES OR RIVERS

Area	Location	Range in PCBs (ng/ℓ)	Ref.
Open oceans	North Atlantic	<1—150	36
		0.4—41	37
	Sargasso Sea	0.9—3.6	38
	North-South Atlantic	0.3—8.0	39
	Mediterranean Sea	0.2—8.6	40
Coastal waters	Southern California	2.3—36	41
	Northwest Mediterranean	1.5—38	42
	Atlantic coast, U.S.	10—700	43
	Baltic coasts	0.3—139	44
		0.1—28	45
	Dutch coast	0.7—8	46
Estuaries/rivers	Wisconsin rivers, U.S.	<10—380	47
	Rhine-Meuse system, Holland	10—200	48
	Tiber Estuary, Italy	9—1000[a]	48
	Brisbane River, Australia	ND—50	49
	Hudson River, U.S.	<100—2.8 × 10⁶	50

Note: ND, not detectable (no limits quoted).

[a] As decachlorinated biphenyl equivalents.

Table 2
CONCENTRATIONS OF PCBs (RANGES, ng/ℓ) IN THE DISSOLVED AND SUSPENDED FRACTIONS OF WATER SAMPLES FROM RIVERS DRAINING TO THE RHINE-MEUSE ESTUARY[46]

Rivers	Date	PCB conc. in water (ng/ℓ) Dissolved	Suspended
Lek	June 1974	14—80	40—300
Maas	August 1976	13—26	25—40
Waal/Oude Maas	June 1974	40—100	50—230
	August 1976	120—200	130—160
Nieuwe Maas	June 1974	80—200	50—100
	December 1974	10—75	20—400
	August 1976	60—180	80
Estuary mixing zone	June 1974	50—120	80—200
	December 1974	20—100	40—100
	August 1976	40—65	25—40

Note: Filtration was by Whatman GF/C filters.

of suspended material are present, or PCB concentrations are unusually high. Thus, in turbid rivers, concentrations of PCBs in the particulate fraction may exceed those in solution; an example of such a situation is shown in Table 2. In highly contaminated areas, PCBs may exceed their water solubilities by adsorbing to particulates.[30,52]

MONS 006088

Although these general comments may be made concerning the partitioning of PCBs between solution and particulates, it must be emphasized that present knowledge of such matters is far from adequate. Thus, it is uncertain as to precisely how PCBs partition between all the various components of natural waters, which may include inorganic particulates of various sizes and geochemical types, plankton (zooplankton, phytoplankton, and microplankton), and colloids, humates, and several other ill-defined classes of particulates. Indeed, the data gathered to date frequently suffer from a lack of attention to the methods of filtration employed[33] and results are in any event applicable only in terms of the filtration methods employed. While there is little doubt that PCBs exhibit high affinities for phytoplankton and zooplankton,[59-61] their affinities for inorganic particulates, microplankton, and colloids or humates are much less well understood, and the transfer of PCBs from one phase or compartment to another has received little attention.[63]

In addition to partitioning between the soluble and various particulate components of natural waters, PCBs also partition between surface films and subsurface waters. Thus, for example, Raybaud[64] found higher concentrations of DDT, DDE, lindane, and PCBs in surface films of sea water near the mouth of the River Huveaune, off Marseilles. The surface film exhibited PCB levels of 46 to 121 $\mu g/\ell$, whereas water from 40 cm below the surface contained only 0.1 to 0.21 $\mu g/\ell$ PCBs. Other authors have confirmed the disparity between PCB concentrations in the surface microlayer and subsurface waters,[12,31,65-67] and many other contaminants are also known to be present at higher concentrations in surface films. This factor is important not only in terms of the sampling of water for PCBs but also because of the possibility of volatilization or codistillation of PCBs from the surface microlayer to the atmosphere.[67]

The researcher wishing to quantify PCBs by analysis of water is thus faced with several practical problems. Decisions must be made not only on how and at what depth the sample should be taken, but also on what method of filtration will be used. There is no standard methodology, and it is obvious from the examples given above on the effects of particulate load and surface films that the results of any survey depend heavily on the particular methodology employed. As a result, as Bernhard[68] states, "... in the present state of knowledge, probably only data from the same author can be used for the detection of differences between samples taken at different sites and/or different dates."

Other problems also exist in attempting to quantify PCBs in aquatic ecosystems by the analysis of water. The concentrations of PCBs present are low compared to many other types of pollutants such as trace metals, commonly varying between nanograms per liter and micrograms per liter levels. The contamination of samples by extraneous sources of PCBs or by the collection equipment employed is therefore a real and ever-present problem.[22] In addition, large volumes of water must be collected and (usually) filtered before preconcentration, presenting practical problems.

Even if such problems of contamination and sample handling can be overcome, the temporal fluctuation of PCB concentrations in water may be extreme. This is particularly the case in estuarine sites close to PCB sources but occurs also in coastal waters more remote from inputs. In the Tiber Estuary, Puccetti and Leoni[46] found variations of greater than an order of magnitude between samples taken sequentially at the same site, and similar variations have been noted by others.[46] These fluctuations in ambient PCB levels in water may be caused by hydrological factors, the episodic nature of inputs from industrial sources, scavenging by plankton, or several other factors. The effects of such fluctuations are severe in terms of the efforts required to elucidate real mean levels of PCBs in a study area. Some method of time-averaging samples must be found, or several samples must be collected at each site, to confirm representative concentrations. If bulking of samples (which is difficult owing to the large volumes required and possibilities of contamination) is not possible, and time-integrating water samplers are not available, the investigator has no real choice but to

MONS 006089

Table 3
RANGES IN CONCENTRATION OF PCBs (ng/g DRY WEIGHT) REPORTED FOR SEDIMENTS IN AREAS RANGING FROM RELATIVELY UNCONTAMINATED TO HIGHLY CONTAMINATED

Area	PCB conc.	Ref.
Mediterranean Sea	0.8—9.0	42
Gulf of Mexico	0.2—35.0	50
Chesapeake Bay	4—400	43
Lake Superior	5—390	12
Tiber Estuary	28—770	48
Rhine-Meuse Estuary	50—1,000	46
New York Bight	0.5—2,200	69
Palos Verdes Peninsula	30—7,900	70
Hudson River	tr—6,700	50
Escambia Bay	190—61,000	50

Note: tr, trace.

collect and analyze several samples at each location studied. This effectively diminishes the number of locations which may be sampled.

In summary, the analysis of natural waters as a method for quantifying PCBs in the aquatic environment is fraught with problems. Practical problems involve the need for multiple sampling at each location studied to overcome temporal fluctuations in ambient PCB levels, and the requirement for large-volume samples. Researchers must ensure the sample is taken while avoiding extraneous sources of PCBs and contamination by the sampling equipment. Once the samples are collected, they must be filtered, and this introduces an arbitrary element into the results, as any method chosen will relegate PCBs in certain particulates to the "suspended" phase while retaining PCBs on finer material in the "soluble" phase. Finally, as there is no definite relationship of bioavailability of PCBs to the operationally defined soluble and particulate phases, uncertainty remains as to the possible effects of any PCB concentrations found in waters on the indigenous aquatic biota.

B. Analysis of Sediments

The use of sediment analysis as a method of quantifying PCBs in aquatic environments has definite advantages over the analysis of water considered above, although certain practical and theoretical problems remain.

The concentrations of PCBs found in sediments are generally much higher than those in water. Typical concentrations of PCBs in sediments are shown in Table 3, values being selected to represent a range from sediments in relatively uncontaminated ocean areas,[42,50] through moderately contaminated coastal or lake sediments,[12,43] to highly polluted estuarine sediments.[46,48,50,69,70]

Because PCB levels in sediments are greater than those in water, the practical problems at sampling are diminished somewhat. Samples of reasonably small volume are generally sufficient and analysis is simpler as organic extraction procedures replace the preconcentration techniques used for water analysis. The problem of contamination, while ever-present, is substantially reduced compared to water analysis, because of the greater amounts of PCBs in the sample.

In addition, PCB levels in sediments represent a time-averaged indication of contamination at the sampling site, rather than a space/time-defined sample as in the case of water analysis.

MONS 006090

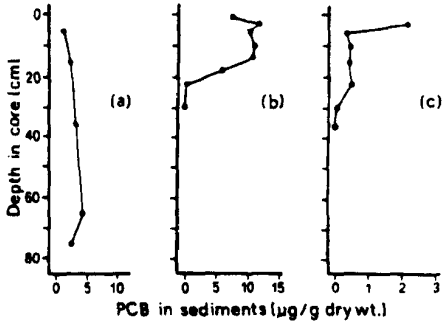


FIGURE 1. Variation in PCB concentrations in sediments with depth. (a) New York Harbor;[28] (b) Hudson River, 83 mi upstream of Manhattan Island;[28] (c) the Christiaensen Basin (note altered horizontal scale).[29]

This time integration facility is important, as it maximizes information output per sample, and permits detailed large-scale surveys to be completed with the minimum of effort, each study location being sampled (usually) only once.

Despite these advantages, the use of sediment analysis to quantify PCBs in aquatic environments is open to certain criticisms, both in terms of practical difficulties and interpretive uncertainties. The practical problems essentially involve the requirement for sediments to be representative of the bottom in the locations sampled, and to be undisturbed. Most sampling involves the use of remote coring or grab devices, deployed from a vessel some considerable distance above the sediments. Under these conditions it is generally impossible to satisfy the skeptic that undisturbed samples which are representative of the general bottom have been taken.

The requirement for sediment samples to be representative of the location studied is self-evident and need not be elaborated, except perhaps to point out that in coastal areas sediments are commonly very heterogeneous over short distances. The requirement for undisturbed samples merits further discussion, however. It will be clear that all sediments must exhibit vertical heterogeneity of PCBs, as these compounds have only been in use for about half a century. The depth to which PCBs penetrate will thus be equivalent (approximately, ignoring reworking of sediments) to about 50 years' worth of sedimentation, assuming that significant deposition of PCBs to sediments has occurred throughout their commercial usage. This depth will vary markedly from place to place, depending on the rate of sedimentation. In open oceans, sedimentation is very slow and only a thin layer of the surface sediments will be contaminated. Elder et al.[43] found PCBs only in the top 1 cm of open-sea Mediterranean sediments, and considered that most or all of the contaminants were present in the top 1 mm. By contrast, the sedimentation rate in turbid estuaries may be very rapid, approaching or even exceeding 1 cm/year. Thus, West and Hatcher[29] found significant quantities of PCBs at 36 to 39 cm depth of sediment in the Christiaensen Basin of the New York Bight. Similarly, Bopp et al.[28] noted PCBs at greater than 40 cm sediment depth in areas of known rapid sedimentation in the Hudson River system, which drains to the New York Bight. These data are shown in Figure 1. It is evident on scrutiny of the profiles shown that different results will be obtained from different types of sampling methods

MONS 006091

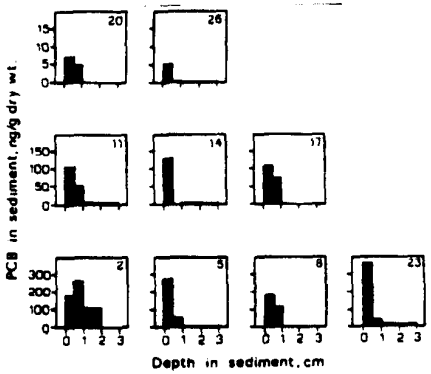


FIGURE 2. Vertical distributions of PCBs in sediments from various sites in Lake Superior. Numbers at upper right of each figure denote station sampled. Note different vertical scale of each horizontal row.[12]

if the methods vary in ability to retain the surface sediment. This view is echoed by Eisenreich et al.,[12] who noted that their values of PCB concentrations in Lake Superior sediments exceeded those of other authors by factors of 2 to 10. They ascribed this difference to their use of an oceanographic box corer, which they felt to be superior to grab samplers or gravity/piston corers because the recently deposited sediment was retained. The conclusion appears valid, as their data show that PCB concentrations in Lake Superior sediments are generally much higher in the surface 0.5 cm, although the vertical distribution of PCBs varied between stations (Figure 2). It is thus evident that researchers must be cautious in comparing data for PCBs in samples of sediments taken with different types of sampling equipment. Much benefit would accrue from the standardization of methods, and it would appear that the use of box corers would be preferable.

In addition to this practical problem, a major theoretically based problem exists in using sediment samples to quantify PCBs in aquatic environments. This involves the effect of the rate of sedimentation on the PCB levels present in sediments, and this problem has been almost completely ignored to date. In general, authors treat results of PCBs in sediments as a direct function of the degree of contamination of areas by these compounds, i.e., as a function of the magnitude of a PCB source in the various areas. Thus if one area contains sediments with PCB levels fivefold greater than those of a second area, the conclusion is generally that the area exhibiting higher PCB levels is exposed to a PCB source of greater magnitude. This interpretation may, however, be completely erroneous, as the PCB levels in sediments depend on at least two major factors; one of these is the magnitude of the PCB source, and the other is the rate of particle sedimentation. Thus, the concentrations of PCBs present in sediments depend not on the PCB loading from a source, but on the relationship of this loading to the amounts of suspended material upon which the PCBs sediment. In areas of rapid sedimentation (e.g., turbid estuaries draining urbanized deforested catchments), PCBs will be "diluted" by the large available particulate load, and concentrations of PCBs in the sediments downstream may be expected to be relatively low. By contrast, PCBs may be present at higher concentrations in sediments of estuaries with low turbidity, as the solids

MONS 006092

load available for PCB adsorption is much smaller. This argument is of course somewhat simplistic, as the particulate load in an estuary may influence partitioning of the PCBs between the soluble and particulate-adsorbed phases; however, it is clear that the PCB levels in sediments cannot be simply correlated to the magnitude of local PCB sources.

Certain other factors also influence the PCB concentrations found in aquatic sediments. The first and most important of these is sediment grain size. Several authors have reported that the finer fractions of sediments contain higher concentrations of PCBs, and this relationship (which is similar to that for trace metals) is considered to be due to the greater surface area available for PCB adsorption onto smaller particles.[71,72] In some instances, the effects of grain size can be extreme; for example, Duinker and Hillebrand[46] reported values for PCBs in Waal and Lek sediments of the Rhine-Meuse system as <40 ng/g dry weight for the coarse fraction and 2400 to 3400 ng/g dry weight for the fine fraction. If no account is taken of the effects of particle size on the results of surveys of PCBs in sediments, the survey results may be interpreted erroneously, with areas of fine sediments being considered to be closer to PCB sources. Few authors have addressed this problem to date, and no standard methodology exists to take account of the influence of particle size on results of PCBs in sediments. Authors studying trace metals in sediments (which also vary in concentration with particle size) often sieve whole sediments to collect a defined fraction which is then analyzed. Some authors go further than this and propose the need for measurement of surface areas of sediments.[73] By contrast, researchers studying PCBs in sediments generally extract whole sediments for analysis, thus leaving the results open to the interference of the effects of particle size.

In addition to particle size, the organic matter content of sediments may influence the PCB levels present. If a survey area varies in organic content of sediments, this effect may interfere with the distribution of PCBs and lead to erroneous conclusions concerning the magnitude and location of PCB sources.

Finally, it must be mentioned that sediments act as a long-term sink for PCBs. Thus, PCBs sedimented on organic or inorganic particulate material may become buried by further material and hence be lost to the general PCB cycle. In this event, the contamination is of little significance (except perhaps as an indicator of historical PCB inputs at that location), and may bear little relation to present-day levels of contamination of the biota in the water column. This argument was used by Phillips[23,38] to support the use of bioindicators rather than sediments for monitoring trace elements; in this case, metals deposited even to surface sediments are generally of relatively low bioavailability (except perhaps to benthic deposit feeders). In the case of PCBs, however, the argument is rather less valid, as it is known that PCBs in surface sediments are bioavailable both to benthic organisms and to those in the overlying water column.[62,76-81] Indeed, in areas where inputs of DDT or PCB have diminished following controls, sediments are thought to act as a major source of these compounds. This is the case for DDT off the California coast[82-84] and for PCBs in the Great Lakes.[66] PCBs desorbed from sediments re-enter the global cycle and may not only be accumulated by local biota, but may also be released to the atmosphere via the surface microlayer.[67]

In summary, there can be little doubt that the analysis of sediments can be a most useful tool in attempts to quantify PCBs in aquatic ecosystems. Several advantages exist in the use of sediments rather than water; these include greater ease of sample handling and existence of time-averaged PCB levels. However, certain problems remain concerning the use of sediments and this author cannot improve on the words of Pavlou and Dexter[31] who considered that " . . . sediments can provide a rapid assessment of the mean residue levels and dynamics of persistent organic chemicals such as PCBs . . . However, it should be emphasized that such data must be interpreted with care. Even though the levels in sediments represent temporal mean concentrations, they depend also on other factors, such as the sedimentation

MONS 006093

rate in the area, the depth of sediment taken for analysis, the particle size, and the natural organic matter content."

C. Analysis of Organisms

The use of aquatic biota as quantitative indicators of pollutant levels in aquatic environments is a relatively recent development. Early studies of this type were carried out in the 1960s and involved quantification of radionuclide abundance in marine ecosystems. In the last decade, the technique has been adapted to the study of stable trace elements, organochlorine pesticides and PCBs, and most recently, hydrocarbons.

The basic theory behind the use of so-called indicator (or sentinel) organisms is that these species accumulate pollutants in their tissues in amounts proportionate to those in their ambient environment. The analysis of pollutant levels within their tissues thus provides a time-averaged indication of pollutant bioavailability at each study location.[33-35]

The ideal indicator organism has the following attributes:[36-38]

1. It accumulates the pollutant studied in proportion to the average levels present in the ambient waters
2. It should be sedentary in order to be representative of the area in which it is collected
3. It should be abundant throughout the study area and should tolerate brackish water
4. It should tolerate the presence of high levels of the pollutant studied without being toxicologically affected
5. It should be of reasonable size, giving adequate tissue for analysis
6. It should be easy to sample and should preferably be hardy enough to survive in the laboratory
7. It should be relatively long-lived, to permit time-integration of pollutant levels over several months or years

The use of such an indicator organism to quantify pollutants in aquatic environments has several advantages over the analysis of water or sediments. Pollutant concentrations accumulated by the organism will generally be several orders of magnitude greater than those in the surrounding water; hence analysis is simpler. The time-integration of ambient levels of pollutants exhibited by the organism permits the elucidation of average levels of contamination, without the need for multiple sampling at each study location. In addition, the analysis of pollutant levels in the indicator organism eliminates the problems of estimating bioavailability of pollutants, such as is required with water or sediment analysis; pollutants present in the organism are by definition bioavailable, although it must be remembered that "bioavailability" may vary with species.

However, the use of biological indicators to quantify pollutants in aquatic environments is subject to various problems. Thus, certain extraneous variables exist, the effects of which will interefere with the simple correlation between pollutant levels in the organism and those in the ambient waters. In the case of PCB monitoring, the most important of these factors is the lipid content of the organism used. Other factors of possible importance include the kinetics of PCB isomers in the organism, the condition, age or sex of the organism, the mobility of the organism, and so on. Researchers wishing to employ indicator organisms to monitor PCBs in the aquatic environment should be cognizant of these problems, and should design surveys carefully so as to minimize the influence of extraneous variables on the results of the surveys. If used correctly, biological indicators will give rise to extremely accurate and detailed profiles of PCB abundance in various locations. This may act as a basis for the elucidation of PCB sources or for the monitoring of temporal trends in PCB abundance. However, if biological indicator surveys are not planned correctly, the conclusions therefrom may be completely erroneous.

MONS 006094

Table 4
THE MOLECULAR COMPOSITION OF AROCLORS® 1242 AND 1254[1]

Component	Abundance (% by weight) Aroclor® 1242	Aroclor® 1254
$C_{12}H_{10}$	<0.1	<0.1
$C_{12}H_9Cl$	1.0	<0.1
$Cl_2H_8Cl_2$	16.0	0.5
$Cl_3H_7Cl_3$	49.0	1.0
$C_{12}H_6Cl_4$	25.0	21.0
$C_{12}H_5Cl_5$	8.0	48.0
$C_{12}H_4Cl_6$	1.0	23.0
$C_{12}H_3Cl_7$	<0.1	6.0
$C_{12}H_2Cl_8$	ND	ND

Note: ND, not detected.

The remainder of this chapter addresses the major problems inherent in the use of indicator organisms to quantify PCBs in aquatic environments, and proposes solutions to these problems.

IV. ISOMER QUANTIFICATION, BEHAVIOR, AND KINETICS IN ORGANISMS

The theoretical number of PCB isomers which may exist is 210.[69] Commercial preparations of PCBs, manufactured by chlorinating biphenyl with anhydrous chlorine using iron filings or ferric chloride as a catalyst contain mixtures of compounds of different degrees of chlorination and different positions of chlorine substitution. Table 4 shows the composition of Aroclors® 1242 and 1254 as an example.[1] Other commercial PCB preparations, such as Phenochlors® and Clophens®, are also sold as several products, each a mixture of compounds differing in their overall degree of chlorination.

This heterogeneity of commercial PCBs gives rise to a number of problems in terms of quantification of these compounds. These problems should be clearly understood by researchers wishing to use biological indicators to quantify PCBs in the aquatic environment. The first of these problems is that the usual method of analysis employed for PCB studies (electron capture gas chromatography) may not sufficiently separate the individual compounds present in a sample. Thus, peaks commonly contain more than one isomer and the separation of individual components is taxing. This problem is now being at least partially overcome by the use of glass capillary columns, which are preferable to the earlier packed columns; however, the analytical techniques merit particular attention and future improvements are anticipated.[1,5]

The second (and equally important) problem concerning PCB analysis is that PCBs in environmental samples are generally quantified by comparing peak heights in the sample to those in commercial standards. No standardized method exists, however, which gives rise to inconsistencies. Authors generally choose a standard which is closest in relative peak heights to the sample chromatogram. Unfortunately, the two rarely match completely, and quantification therefore depends on which peaks are chosen. Some authors prefer to choose a peak corresponding to the major peak in the standard, others use four or more different peaks, and still others may use total peak area or publish two sets of results based on two different standards.

MONS 006095

It is clear from this that the analytical quantification of PCBs is no straightforward matter. However, a third problem exists where organisms are used as indicators of PCBs, and this involves the unusual capacity of aquatic biota to selectively accumulate PCB isomers. Thus, whereas in studies of PCBs in water or sediments, PCB profiles generally vary only marginally from commercially available standards,[90,99,91] the PCBs found in aquatic biota may vary dramatically from those in the standards.

The selective accumulation by organisms of different PCB isomers or PCB components varying in chlorination is a function of the physicochemical properties of PCB components in the environment in addition to the biological effects at accumulation. Both aspects merit attention here, as they both influence the PCB profiles found in studies of indicator organisms.

PCB components of different chlorination exhibit differences in their solubility in water.[6,92-96] As a general rule, the higher the chlorination of a biphenyl component, the lower its water solubility. Thus, for example, Haque and Schmedding[92] reported solubilities of 1 $\mu g/\ell$ for 2,4,5,2',5'-pentachlorobiphenyl, 27 $\mu g/\ell$ for 2,2',5,5'-tetrachlorobiphenyl, and 638 $\mu g/\ell$ for 2,4'-dichlorobiphenyl. This difference is also exhibited by the PCB mixtures, as these also vary in overall chlorination: for example, Mackay and Wolkoff[95] reported solubilities of 2.7 $\mu g/\ell$ for Aroclor® 1260, 12 $\mu g/\ell$ for Aroclor® 1254, 54 $\mu g/\ell$ for Aroclor® 1248, and 240 $\mu g/\ell$ for Aroclor® 1242. Although different authors report different absolute solubilities of PCBs due to the different methodologies employed to study this parameter, all results show this general inverse relationship between water solubility and degree of chlorination. It should be noted in addition that different isomers with the same degree of chlorination also vary in solubility; Table 5 shows extensive data from Lee et al.[96] which confirm these variations.

These differences in water solubility of the various PCB components are particularly important, as they influence the partition coefficients of the components. A molecule with high chlorination (and thus low water solubility) will favor the inorganic particulate phase rather than remaining in solution. By contrast, a biphenyl of low chlorination with high water solubility may remain in solution, and a much smaller proportion of the total load of the component will be adsorbed to inorganic particulates.[96,99] This is important when considering the dispersion of PCBs from a point source; components of lower chlorination may be expected to exhibit greater dispersion than those of higher chlorination, as they will remain in solution longer. This tendency was revealed particularly well in the studies of Richardson and Waid,[97] who found that the PCBs in sediments of Port Phillip Bay varied according to distance from the shore-based sources. Inshore sediments in Corio Bay, close to the major inputs of PCBs, exhibited a large proportion of highly chlorinated components, resembling Aroclors® 1254 and 1260. By contrast, offshore sediments contained mainly lower-chlorinated biphenyls, chromatograms resembling Aroclor® 1242. Essentially similar results, although on a larger geographical scale, were noted by Tanabe et al.,[100] in studies of PCBs in the Antarctic, Western Pacific, and Indian Oceans. Greater amounts of the higher-chlorinated biphenyls were found in coastal areas than in the open oceans. In this case, the higher vapor pressures of the lower-chlorinated PCBs, and hence a more efficient aerial transport, undoubtedly also played a part. A similar effect may be responsible for the unusually high proportion of PCBs represented by components of lower chlorination in the central part of the Southern Bight of the North Sea, offshore from the Rhine-Meuse Estuary, as mentioned by Duinker and co-workers.[98,99] It is notable here in addition, that individual isomers with the same degree of chlorination may also exhibit differences in partitioning between solution and particulate material,[71] although these differences are generally minor compared to those between components of different chlorination.

The differences between PCB components in terms of water solubility not only lead to variations in partitioning between solution and inorganic particulates as described above, but also give rise to differences in bioaccumulative tendencies. Several authors have shown

MONS 006096

Table 5
COMPARATIVE WATER SOLUBILITIES OF ISOMERS OF AROCLOR® 1242; NOTE THE DIFFERENCES BETWEEN THE RAPIDITY OF DISSOLUTION OF DIFFERENT ISOMERS[98]

Peak no.	No. of chlorines	Identification	Concentrations (μg/ℓ) attained in days shown					
			7	20	30	50	149	251
1	1	2					124.60	121.59
2	1	3						
3	1	4					7.50	15.07
4	2				1.00	1.69	5.83	9.06
5	2	2,2'			3.18	1.78	20.80	21.18
6	2					2.93	23.24	23.76
7	2	2,3'			9.10	14.07	19.63	30.60
8	2	2,4'	2.90	27.30	71.18	78.45	141.85	138.93
9	3	2,6,2'			1.40	1.72	8.13	8.33
10	3	2,5,2'	5.52	22.97	41.05	41.20	62.48	61.35
11	3							2.15
12	3	2,4,2'						0.48
13	3					1.71	10.00	4.50
14	2	3,4'						2.98
15	2 & 3	4,4';2,3,2'		8.83	16.25	17.19	26.15	35.30
16	3	2,4,3'					29.83	27.47
17	3	2,4,4'	2.55		4.08	4.63	9.83	9.87
18	3	2,5,4'	20.22	35.15	43.28	48.20	63.76	65.07
19	3	3,4,2'					2.59	2.59
20	4	2,5,2',5'	1.58	6.67	8.94	8.78	24.05	22.25
21	4					0.64	2.66	3.59
22	4				0.55	0.49	3.78	4.09
23	3 & 4	2,4,2',5'				2.11	17.95	19.51
24	4	2,4,2',4'	11.12	7.39	8.93	9.12	19.85	15.88
25	4						4.15	3.37
26	4						1.11	1.09
27	4	2,3,2',5'				0.69	12.75	12.83
28	4					0.74	4.10	3.13
29	4					1.42		2.50
30	4	2,5,3',4'					9.15	7.21
31	3					0.59	4.53	4.70
32	4						4.10	2.70
33	4						5.43	2.63
34	3						0.73	0.82
35	4	2,4,3',4'	1.96			2.18	13.83	11.62
36	5							
37	5						2.53	0.99
38	5							
39	5		0.71				4.79	2.47
40	5							2.84
Total			46.56	108.31	208.94	240.33	671.86	702.67

that the tendency of a pollutant to become concentrated in aquatic biota (the "bioconcentration potential") is correlated to the partition coefficient of that pollutant in the *n*-octanol/water system.[101-105] Thus, in general, contaminants of low water solubility, and high affinity for organic phases, will be of high bioconcentration potential. It should be realized that this rule is only generally true, and the precise tendency of a pollutant to bioaccumulate is governed not only by its lipophilicity but also by other factors, such as the biodegradability

MONS 006097

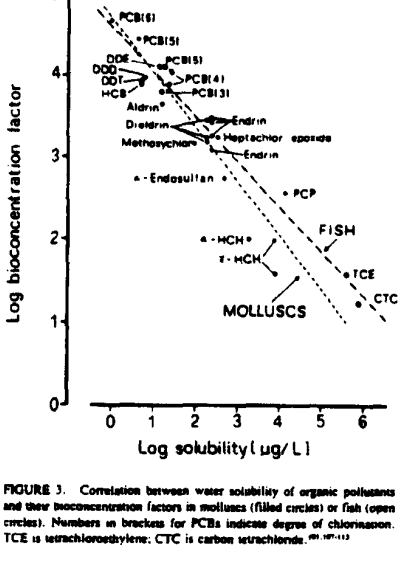


FIGURE 3. Correlation between water solubility of organic pollutants and their bioconcentration factors in molluscs (filled circles) or fish (open circles). Numbers in brackets for PCBs indicate degree of chlorination. TCE is tetrachloroethylene; CTC is carbon tetrachloride.[101,107-113]

or persistence of the contaminant in the organism. However, the use of *n*-octanol/water partition coefficients is certainly valid in a broad sense as an index of the bioconcentration potential of contaminants.

Data on the correlation between the bioconcentration of pollutants and either their water solubility or their partition coefficients in the *n*-octanol/water system have been recently summarized in the form of figures by Ernst;[107] Figures 3 and 4 show these summaries, which are a synthesis of results from several authors.[101,109-113] It should be noted that both figures are plotted on log-log scales; hence, while the correlations appear particularly good, they would be less impressive on linear plots. Nevertheless, the general relationships are sound, and the relatively minor variability imposed thereon is due to differences in biodegradability of contaminants and other factors, such as uncertainties in accurately assessing water solubilities of the various compounds. It is also notable that the PCB components shown are among the most highly bioconcentrated contaminants, correlating to their very low water solubilities and high *n*-octanol/water partition coefficients. The differences between the different PCB components follow the rules described above, biphenyls of greatest chlorination exhibiting lowest water solubilities and highest partition coefficients.

The discussion above deals with the physicochemical aspects of bioaccumulation only, and could be summarized by the statement that biphenyls of higher chlorination should accumulate to greater extents in biota than lower chlorinated types. However, the organisms themselves may also exhibit selective accumulation of isomers, and this need not be consistent with the above picture. This selective bioaccumulation of PCB components will be discussed

MONS 006098

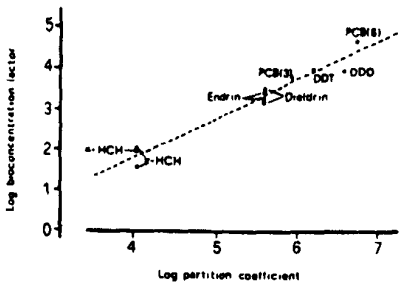


FIGURE 4. Correlation between partition coefficients (in n-octanol/water system) of organic pollutants and their bioconcentration factors in bivalve molluscs. Numbers in parentheses for PCBs indicate degree of chlorination.[97,110,116,117]

here in relation to the food web, citing data for primary producers first and progressing up trophic levels through other families to top predators.

Very little information is available on selective accumulation of PCB components by phytoplankton, despite considerable studies of the uptake of either commercial PCBs or individual PCB components by phytoplankton[97,30,91,116,119] and of the effects of PCBs on phytoplankters.[52,116-123] Most authors consider the uptake of PCBs by phytoplankton to be a passive adsorption process initially, followed by absorption into the cell. There is little evidence for selectivity in the accumulation of different PCB components over and above that which may be explained on the basis of the physicochemical properties of the isomers themselves. Thus, for example, Wang et al.[115] found that higher chlorinated PCB components were taken up to a greater extent by *Chlorella fusca* than were lower chlorinated components. This tendency correlated to the water solubility of each compound, i.e., to its lipophilicity, and no overt biological selectivity was noted.

Information on selective uptake of PCB components by macroalgae is also very sparse. Macroalgae have been used very little as bioindicators of PCBs[124] compared to their frequent use for studies of trace metals. However, Amico et al.[125] published comparative studies of PCBs in 12 species of seaweed and the mussel *Mytilus edulis* from the east coast of Sicily. They noted that the algae exhibited much larger proportions of lower chlorinated PCB components than the mussels, and speculated that this may be based on a lack of metabolic breakdown of the lower chlorinated components in the algae, or on differential uptake of components by the different organisms. Without information on the PCBs in the surrounding waters, these two alternative hypotheses cannot be tested. It might also be noted here that the salt marsh cordgrass *Spartina alterniflora* was shown to exhibit selective uptake of PCBs by Mrozek et al.[126] Analysis of both stems and roots of *S. alterniflora* revealed an enrichment of lower chlorinated biphenyls and a paucity of higher chlorinated components in the plant, compared to Aroclor® 1254 used for dosing.

The selective uptake of PCB components by zooplankton was studied by Clayton et al.[34] in Puget Sound. Table 6 shows data for concentration factors (PCBs in lipids/PCBs in water) for chlorobiphenyls of different chlorine content for various sites, and the corresponding dominant plankton group at each site. It is evident that at most sites, the PCB components of higher chlorination were accumulated in greater amounts; this tends to reflect the con-

MONS 006099

Table 6
PARTITIONING VALUES OR CONCENTRATION FACTORS (PCBs in lipids/PCBs in water) FOR ZOOPLANKTON IN DIFFERENT REGIONS OF PUGET SOUND[a]

Region	Conc. factor × 10^6 N = 4[b]	N = 5	N = 6	Dominant fauna
Elliott Bay	1.06 (±0.81)[c]	1.42 (±1.06)	2.17 (±1.64)	*Euphausiids*
Main Basin	1.07 (±0.61)	1.90 (±1.25)	3.18 (±2.32)	Copepods
Whidbey Basin (Port Gardner)	0.80 (±0.38)	1.09 (±0.51)	1.47 (±0.75)	Copepods/ euphausiids
Hood Canal	0.98 (±0.56)	0.74 (±0.52)	0.43 (±0.32)	Ctenophores
Sinclair Inlet	1.12 (±0.68)	3.61 (±2.02)	6.90 (±3.45)	Ctenophores
Admiralty Inlet and Straits of Juan de Fuca	0.34 (±0.21)	0.28 (±0.18)	0.29 (±0.18)	Copepods

[a] N = number of chlorines/biphenyl.
[b] Values in parentheses are standard deviations.

clusions from the physicochemical considerations above. However, at Hood Canal and Admiralty Inlet, the opposite pattern was found, tetrachlorobiphenyls being accumulated to greater extents than penta- or hexachlorobiphenyls. These patterns presumably rely on species differences in preferred components, and may possibly be correlated to the particular lipids present in the dominant species. It is relevant, in addition, that Wyman and O'Connors[77] reported that copepods of the genus *Acartia* accumulate much of their PCBs from phytoplankton food; the possibility that the selective accumulation of PCB components in secondary and higher levels of the food web depends on selectivity at the primary level must *not* be overlookad.

Selective accumulation of PCB components has also been reported in the scud *Gammarus pseudolimnaeus* by Sanders and Chandler,[127] who measured ^{36}Cl-labeled PCB uptake from water in continuous flow laboratory studies. Table 7 shows the results of this study, which revealed progressively greater uptake of lower chlorinated biphenyls. "Enrichment factors", representing the relative peak areas of the sample peak and the equivalent peak in Aroclor® 1254, decrease from 2.00 in the trichlorobiphenyl, to 1.71 to 1.90 for tetrachlorobiphenyls, 1.00 to 1.31 for pentachlorobiphenyls, 0.49 to 0.85 for hexachlorobiphenyls, and 0.25 to 0.50 for heptachlorobiphenyls. The ranges given for biphenyls containing four to seven chlorine atoms reflect differences between individual isomers. The authors noted that no lower-chlorinated components than those in the dosed Aroclor® 1254 were present in scud, confirming the absence of reductive dechlorination, and suggesting that this is truly selective uptake. However, it is possible that the observed results were brought about at least partially by the higher water solubilities of the components of lower chlorination leading to greater bioavailability, particularly as the exposure level was quite high at 1.6 μg/ℓ; as discussed previously, the biphenyls of higher clorination exhibit low water solubilities and their dissolution may not have occurred.

McLeese et al.[76] also reported interesting data on the selective accumulation of PCB components, in this case in a sea water/sand system using the polychaete *Nereis virens* and the shrimp *Crangon septemspinosa*. Unfortunately only five peaks of Aroclor® 1254 were quantified in samples, which tends to limit the usefulness of the data. However, as shown in Figure 5, spiked sand exhibited rather greater amounts of lower chlorinated components than the parent Aroclor® 1254 mixture, and *Nereis virens* tended to preferentially accumulate biphenyls of lower chlorination to accentuate this effect. However, the biphenyls present in

MONS 006100

Table 7
ENRICHMENT FACTORS FOR COMPONENTS OF AROCLOR® 1254 IN SCUD (*GAMMARUS PSEUDOLIMNAEUS*)[127]

Peak no.	Relative retention time	Number of chlorines	Enrichment factor, sample 1	Enrichment factor, sample 2	Average 1 + 2	Aroclor® 1254 RPA
1	0.27	3	2.00	2.00	2.00	0.03
2	0.37	4	1.69	1.72	1.71	0.29
3	0.45	4	1.81	1.81	1.81	0.11
4	0.50	4	1.80	2.00	1.90	0.05
5	0.63	5	1.31	1.31	1.31	0.51
6	0.77	5	1.00	1.00	1.00	1.00
7	0.98	5	1.13	1.16	1.15	0.38
8	1.07	5	1.07	1.16	1.12	0.57
9	1.19	6	0.33	0.66	0.49	0.03
10	1.31	6	0.84	0.85	0.85	0.65
11	1.59	6	0.55	0.55	0.55	0.33
12	1.67	6	0.80	0.80	0.80	0.30
13	1.79	7	0.43	0.57	0.50	0.07
14	2.04	6	0.56	0.60	0.58	0.45
15	2.61	6	0.50	0.62	0.56	0.08
16	3.22	7	0.25	0.50	0.37	0.04
17	3.68	7	0.25	0.25	0.25	0.04

Note: The enrichment factor in each case represents the relative peak area (RPA) of the sample peak and the equivalent peak in Aroclor® 1254.

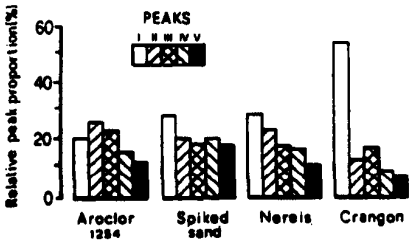


FIGURE 5. Proportion of quantified Aroclor® 1254 peaks as a percentage of total amount for Aroclor® 1254 standard, spiked sand, and *Nereis virens* or *Crangon septemspinosa* exposed to the spiked sand for 32 days.[76]

Crangon septemspinosa after an exposure of 32 days showed an even greater preferential accumulation of components of lower chlorination. In these cases, it is possible that uptake of components occurred after solubilization from the spiked sand. In the case of the polychaete, this may have occurred via interstitial water, with additional uptake occurring directly from the sand. The shrimp, however, would be dependent wholly on solubilized PCB components. This hypothesis explains the selective uptake found, as biphenyls of lower

MONS 006101

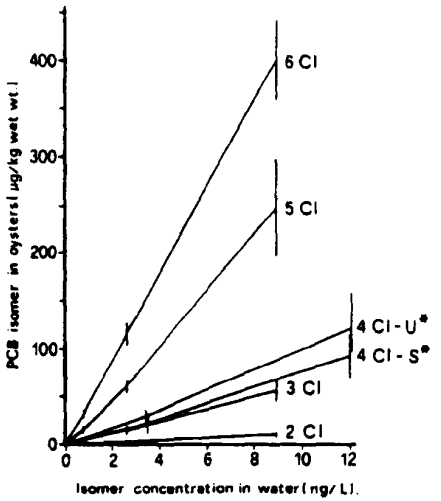


FIGURE 6. Relationship between PCB concentrations attained in oysters (*Crassostrea virginica*) and PCB exposure concentration in ambient sea water. Oyster values are means from days 28 and 65 of uptake; vertical lines are standard deviations. Isomers used were 2,3-dichlorobiphenyl (2 Cl); 3,4,2'-trichlorobiphenyl (3 Cl); 2,5,2',5'-tetrachlorobiphenyl (4 Cl-S*); 2,3,2',5',-tetrachlorobiphenyl (4 Cl-U*); 2,3,4,2',5'-pentachlorobiphenyl (5 Cl); and 2,4,5,2',4',5'-hexachlorobiphenyl (6 Cl).[109]

chlorination are known to be easier to solubilize from particulates (see above). It may be noted here also that, despite similar studies of PCB uptake by polychaetes from sediment and water, other authors[76,79] did not report selective uptake of PCB components: this probably reflects the fact that many authors do not attach particular significance to alterations in relative peak heights of chromatograms of PCBs.

The selective accumulation of PCB components by bivalve molluscs has been the subject of several studies, although it is notable that no consensus may be derived from these. Vreeland[108] investigated the uptake of six individual biphenyls by the oyster *Crassostrea virginica*. She found uptake to be proportional to PCB dose, and to vary dramatically with the degree of chlorination of the isomer (Figure 6). Equilibrium concentration factors based on wet weights were quoted as follows: dichlorobiphenyl, 1200; trichlorobiphenyl, 6200; symmetrical tetrachlorobiphenyl, 7400; unsymmetrical tetrachlorobiphenyl, 11,000; pentachlorobiphenyl, 27,000; and hexachlorobiphenyl, 48,000.

By complete contrast, Courtney and Denton[120] found that clams (*Mercenaria mercenaria*) fed Aroclor® 1254 adsorbed to the surface of alumina preferentially retained biphenyls of lower chlorination in the muscular foot and visceral mass (Table 8). This correlated to the excretion of disproportionately large amounts of higher chlorinated isomers in the feces. Clams from Southampton water also exhibited preferential enrichment of lower chlorinated

MONS 006102

Table 8
VARIATION IN PEAK HEIGHT OF TISSUE AND FECES RESIDUES OF PCBs COMPARED TO AROCLOR® 1254[a,m]

Aroclor® peaks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Chlorine atoms/mol	3	4	4	4	5	4 & 5	5	5	5	6	5	5 & 6	6	6	6	7	7
Standard	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Visceral mass																	
21-day exposure	318	190	227	337	135	184	113	122	117	74	97	69	59	49	55	37	30
1-month postexposure	322	181	210	414	133	185	115	122	117	77	96	70	55	50	54	38	32
3-month postexposure	274	152	162	257	120	173	114	121	120	74	100	75	60	52	54	30	34
6-month postexposure	361	151	162	312	123	177	113	118	120	77	101	74	53	47	56	44	41
Feces																	
2-week postexposure	48	26	27	61	44	35	65	60	68	129	97	141	132	177	182	217	229
3-month postexposure	227	56	74	151	83	84	86	99	105	108	95	105	87	126	129	192	252
6-month postexposure	224	60	81	200	67	79	66	82	91	123	84	110	108	170	161	290	275

Note: Clams (*Mercenaria mercenaria*) were exposed to 12.5 μg/ℓ Aroclor® 1254 (adsorbed to the surface of aluminal for 21 days; residues were determined immediately after exposure and at various postexposure intervals.

MONS 006103

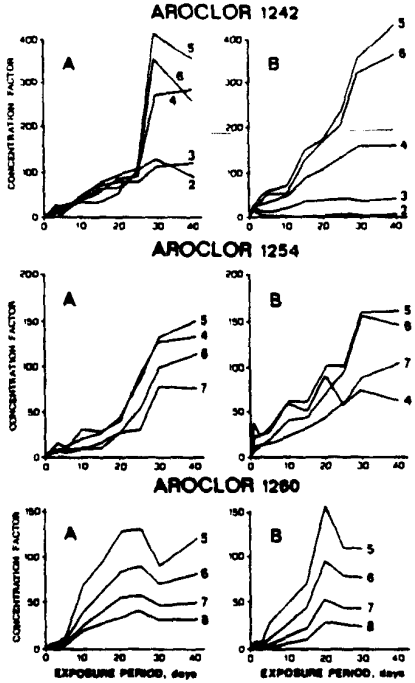


FIGURE 7. Concentration factors describing the uptake of PCBs varying in degree of chlorination from Aroclors® 1242, 1254, and 1260 by (A) *Macoma balthica* and (B) *Cerastoderma edule*. The numbers 2 to 8 represent the degree of PCB chlorination. Uptake was from aluminum oxide particles in water.[131]

biphenyls compared to Aroclor® 1254.[129] A more recent report from Deubert et al.[130] has confirmed the preferential uptake of lower chlorinated biphenyls by *M. mercenaria*.

These differences between species were compounded by the investigations of Langston,[131,132] who found yet another pattern of selective accumulation of PCB components in the bivalves *Cerastoderma edule* and *Macoma balthica*. Both these species were found to preferentially accumulate pentachlorobiphenyls; isomers with less chlorine atoms were accumulated in decreasing amounts from 4 to 2 atoms, and those with more chlorine atoms in decreasing amounts from 6 to 8 atoms (Figure 7). Such a pattern of accumulation has also been noted for PCB uptake in the oyster *Crassostrea virginica* by Nimmo et al.[133] Langston[132] also noted, however, that differences existed in the persistence of chlorobiphenyls

MONS 006104

containing the same number of chlorine atoms in different substitution positions. As a general rule, isomers with the most *ortho*-substituted chlorine atoms were the least persistent. Species differences were also found; *C. edule* excreted dichlorobiphenyls much faster than did *M. balthica*.

It is clear from the above discussion that at least with respect to bivalves, considerable interspecific differences exist with respect to PCB kinetics. Langston[132] has speculated that such differences may be based on interspecific differences in the chemical structure of lipid pools in bivalves. If this is the case, it is possible that preferential accumulation of PCB isomers may vary not only with species, but also in any single species with season, if lipid pools vary chemically with time. In any event, it must be acknowledged that the various components of commercial PCBs exhibit very heterogeneous kinetics in bivalves; there is a case for treating each component as a separate pollutant.

Selective accumulation of PCB components has also been noted in finfish, but again no general trend is obvious from the information reported to date. Sanborn et al.[134] found that the green sunfish (*Lepomis cyanellus*) exhibited higher concentration factors for the more highly chlorinated PCB isomers when exposed to three pure PCBs in water. Concentration factors calculated were 1510 for a pentachlorobiphenyl, 460 for a tetrachlorobiphenyl, and only 54 for a trichlorobiphenyl. The fish was apparently able to metabolize the trichlorobiphenyl to a hydroxy derivative, which at least partially explains its low persistence. Several other authors[135-141] have also reported data consistent with greater uptake or longer persistence of higher chlorinated biphenyls in fish, and this pattern is considered to be due to the greater lipophilicity of these compounds compared to the lower chlorinated isomers. However, not all reports concur with such a pattern. Thus, Stalling and Mayer[142] reported preferential accumulation of lower chlorinated PCB isomers in fish, and Hansen et al.[143] found a tetrachlorobiphenyl to be more persistent in channel catfish (*Ictalurus punctatus*) than more highly chlorinated components.

In addition to such differences in kinetics of PCB components varying in chlorination, a few authors have noted, in detailed studies, that compounds of the same degree of chlorination but differing in substitution positions also vary in kinetics. Bruggeman et al.[140] investigated the uptake of PCBs containing two to four chlorine atoms by goldfish (*Carassius auratus*), using both aqueous and dietary exposure routes. They noted that the major reason for variation in biomagnification of different compounds was the variation in clearance (excretion) rates; absorption efficiencies were similar for each compound. The overall pattern (Figure 8) showed excretion rates decreased with increasing degree of chlorination, half-lives varying from 10 days for 2,5-dichlorobiphenyl to 60 days for 2,3',4',5-tetrachlorobiphenyl. Within each group of biphenyls, chlorine substitution patterns also affected retention. Chlorine substitution *para* to the phenyl-phenyl bond influenced the clearance rates much more strongly than substitution in the *ortho* position. This pattern correlated to the aqueous solubilities of the various compounds.

Similar data have been reported by Tanabe et al.[141] for PCB kinetics in carp (*Cyprinus carpio*), after dietary exposure to individual chlorobiphenyls. These authors found that absorption efficiencies of the compounds varied, from 67 to 93%, decreasing as the number of chlorine atoms increased. This pattern appeared to be based on the molecular size differences of the various PCBs; hence, when the molecular weight was taken into account, the observed differences between the compounds disappeared (Figure 9). In terms of biological half-life, Tanabe et al.[141] found that there was essentially no loss of hexa-, hepta- or octochlorobiphenyls from carp over a 90-day excretion period, but PCBs containing two to five chlorine atoms were excreted. The overall pattern showed faster excretion of biphenyls with lower chlorination, but there were large differences in half-lives of individual compounds within each chlorobiphenyl series. Table 9 shows these differences for the trichlorobiphenyls. It is clear that compounds with more *ortho* substituted chlorine atoms tend to have shorter

MONS 006105

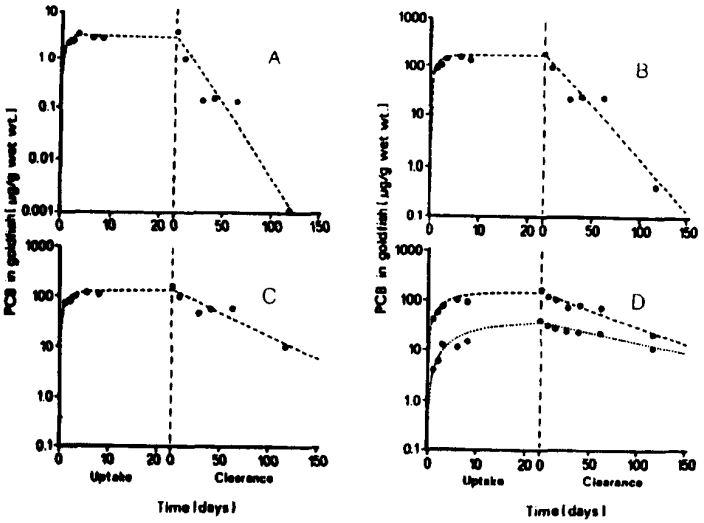


FIGURE 8. Kinetics of uptake and clearance of five individual PCBs by goldfish, *Carassius auratus*. In each case, an exposure period of 23 days was followed immediately by a depuration period of 116 days. (A) 2,5-Dichlorobiphenyl, $t_{1/2}$ of 10.5 days; (B) 2,2',5-trichlorobiphenyl, $t_{1/2}$ of 14.4 days; (C) 2,4',5-trichlorobiphenyl, $t_{1/2}$ 33 days; (D) 2,2',5,5'-tetrachlorobiphenyl with a $t_{1/2}$ of 46 days (dashed line) and 2,3',4',5-tetrachlorobiphenyl with a $t_{1/2}$ of 69 days (dotted line).[100]

MONS 006106

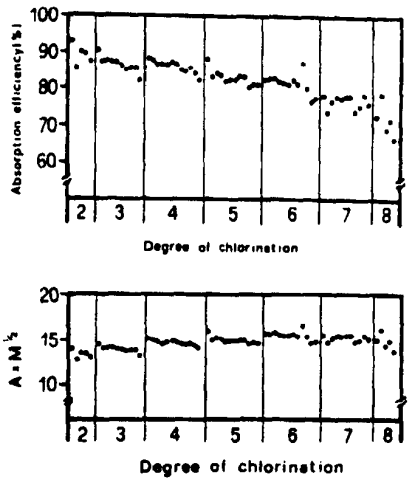


FIGURE 9. Absorption efficiencies of individual chlorobiphenyls in carp (*Cyprinus carpio*) and their variation with the degree of chlorination (top). Also shown is the absorption efficiency (A) multiplied by molecular weight to the ½ (M ½), showing that the variation in absorption efficiencies is a function of molecular weight differences.[191]

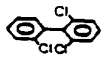
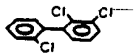
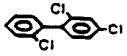
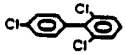
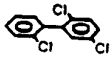
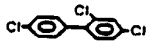
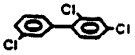
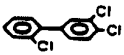
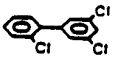
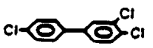
half-lives, i.e., are more easily metabolized. Interestingly, Sparling and Safe[144] failed to confirm this effect of *ortho* substitution on PCB kinetics in trout, although it is evident from their work that considerable differences between species exist with respect to the behavior of PCB isomers. It should be noted that the method of PCB administration (by gastric lavage) in this latter study is somewhat unusual and may influence the overall kinetics of the compounds studied.

Final mention may be made here of PCB kinetics in marine mammals, including seals and dolphins. Several authors have noted that the higher chlorinated PCB compounds predominate in seal tissues,[140-142] and this appears to be the case also for dolphins.[130,131] These mammals are considered by most authors to accumulate the majority of their body load of PCBs from their diet. It is likely, therefore, that the predominance of the higher chlorinated PCB isomers in seal and dolphin tissues reflects a similar profile in ingested food, coupled with a long persistence of highly chlorinated PCBs in the mammals themselves.

Several conclusions may be drawn with respect to this difficult aspect of PCB quantification in marine organisms. First, it is clear that the quantification of PCBs by methods involving a simple comparison of areas of only one or a few peaks in the sample chromatogram with a complex standard (which is essentially chosen arbitrarily) is a crude method at best. There is an urgent need for improvement in analytical techniques, and the commercial availability of pure individual PCB components would assist such improvements. Current methods commonly ignore all-important differences between organisms (or these and standards) in relative peak heights, and our understanding of PCB kinetics in organisms suffers as a result.

MONS 006107

Table 9
RELATIONSHIP BETWEEN THE BIOLOGICAL HALF-LIFE AND NUMBER OF CHLORINE ATOMS SUBSTITUTED IN *ORTHO* POSITIONS OF TRICHLOROBIPHENYLS FOR CARP, *CYPRINUS CARPIO*[141]

	Peak no.	Structure	No. of *ortho* chlorine atoms	Biological half-life (days)
Less ↑ Metabolism ↓ More	310		0	94.4
	36		1	62.4
	39		1	56.8
	37		1	56.3
	38		1	46.5
	32		2	18.2
	35		2	9.4
	33		2	8.7
	34		2	5.3
	31		3	1.8

MONS 006108

Second, there can be no doubt that in some cases — perhaps the majority of cases — the uptake and excretion of PCBs by organisms (and hence the net uptake or persistence of PCBs in organisms) is defined by simple physicochemical properties of the compounds themselves. Thus, it is common observation that the more highly chlorinated PCBs are of greater persistence in biota. This correlates to their lower water solubility and higher P_{ow} values (octanol-water partition coefficients). Within each chlorobiphenyl series, however, physicochemical differences also occur. The pattern of chlorine substitution in a chlorobiphenyl may influence the symmetry of the molecule, its molecular size, and its susceptibility to chemical (enzymic) attack. Certain authors are now beginning to probe this vital area, observing consistent differences between the kinetics of PCB isomers in biota. Shaw and Connell,[123,133] from their work on PCBs in mussels and mullet in Australian waters, have proposed the use of an empirically derived "steric effect coefficient" which permits predictions of uptake kinetics for PCBs. This is covered in greater detail in Volume I, Chapter 6.

It must also be noted that some observations of PCB kinetics in marine organisms cannot be simply explained on the basis of physicochemical properties of the compounds themselves, either in terms of lipophilicity, aqueous solubility, or steric effects. Thus, certain organisms appear to exhibit selective uptake of compounds which depend on the biological matrix rather than the physicochemical properties of the pollutant. There is a vital need for more information in this area.

Opinion thus appears to be crystallizing that the hitherto crude methods for quantifying PCBs are inadequate and must be replaced. Each PCB isomer present in an organism should essentially be considered as an individual pollutant in its own right, with its own kinetics and toxicology. While it may be some time before this is routinely possible, the current situation might be compared to the analysis of organisms for "total trace metals", and in such a situation there can be little doubt that interferences between the pollutants cloud the issues at present.

Notwithstanding the need for future improvements in analytical techniques, it is certain that the quantification of PCBs in marine organisms is required *now* as a management tool. The remainder of this chapter is therefore devoted to discussions concerning the optimal use of bioindicator organisms, as a method to quantify PCBs in marine and estuarine environments.

V. THE INFLUENCE OF LIPID

It has already been stated that both the affinity of PCBs for biota and their persistence in aquatic organisms are due to the hydrophobic, lipophilic nature of these compounds. It is therefore no surprise that the lipid content of an organism has a highly significant influence on the amounts of PCBs sequestered by that organism.

This covariance of lipid content and PCB levels within organisms has been cited by various authors as a root cause of, or partial contributor to, the following:

1. The apparent amplification of PCBs with trophic level
2. The variation between species in PCB concentrations
3. The differences in PCB concentrations present in different individuals of a given species
4. The variation in PCB levels in different tissues of a species
5. The differences found in PCB levels in various portions of a single organ or tissue in a species

The last three of the above items are highly relevant in terms of using bioindicators to monitor PCB contamination of the aquatic environment. The first two, by contrast, are of more peripheral interest and can be dealt with very briefly.

The question of whether PCBs (and other organochlorines) are amplified in concentration

MONS 006109

with trophic level has been discussed at length by Phillips,[35] but firm conclusions are difficult. Some authors[149,154,155] have reported that PCB concentrations in food web components show a stepwise increase at each trophic level when the contaminant concentrations are based on wet weights of the organisms, but that the differences disappear or are very much reduced if concentrations are based on lipid weights. However, other workers[156] claim more convincing profiles of trophic amplification when lipid weights are used for calculating PCB concentrations. Still other reports[27,157,158] include no evidence on either basis for an increase in PCB concentrations in ascending food chains. The argument has more recently shifted in emphasis slightly, in attempts to discover whether the food chain is in any event a significant source of PCBs to predators. The lipid-water partitioning theory of organochlorine uptake, first proposed by Hamelink et al.[159] with reference to DDT, has also received some support as a basis for PCB uptake by organisms.[160] However, this contention appears to be defensible for organisms only at lower trophic levels, as discussed by Phillips;[35] at higher trophic levels, food chain transfer predominates, at least according to an equilibrium model of trophic level transfer of PCBs constructed by Thomann.[161]

The effects of lipid on the concentrations of PCBs found in organisms are perhaps more convincingly displayed if species differences in PCB contents are considered. Many authors have noted, both for PCBs, and for other lipophilic organochlorines such as DDT and dieldrin,[162-166] that species which have high lipid contents also accumulate relatively large concentrations of organic pollutants. Thus, species differences in bioaccumulation capacities appear considerable when based on concentrations of pollutants calculated on wet weights; however, when based on lipid weights, species differences are reduced markedly. Jensen et al.[154,160] noted that data for herring (*Clupea harengus*) and cod (*Gadus morhua*) reflected this factor particularly well, PCB concentrations in the former being much higher because of the greater lipid content of herring than cod. Hattula et al.[166] confirmed this observation in extensive studies of fresh water fish from a Finnish lake. Similar conclusions have been made in other studies concerning PCBs in fish,[27,167] and other phyla also are believed to conform to this pattern.[120,168]

While the influence of lipid on trophic level amplification of PCBs or on species differences in PCB accumulation is of a certain interest with respect to bioindicator use to monitor PCBs, it is not of central importance, except perhaps as an aid to selection of species which accumulate large amounts of PCBs. Of much greater importance is the effect of lipid on PCB concentrations in different individuals of a monitoring species, or in the tissues of these individuals. Thus, bioindicator surveys involve the analysis of a number of individuals (either whole, or their tissues) from several locations to reach conclusions concerning the relative contamination of each area. The following potential effects of lipid must be recognized:

1. Individuals of the chosen species may exhibit heterogeneous levels of lipid, either within or between populations. This may give rise to a large intra-site variation in PCB concentrations, or may cause erroneous conclusions with respect to interlocation differences, or both.
2. Decisions concerning which tissue(s) of the chosen bioindicator species should be taken for analysis are influenced by the lipid levels found in the tissues (and hence the PCB distribution among the tissues), and the temporal changes in these.
3. If subsampling from a single tissue or organ is used, it is important to recognize the possibility of heterogeneity of PCB distribution within tissues, which may correlate to an uneven lipid distribution or to heterogeneous lipid chemistries in the organ.

With respect to the first of these, it is known that populations of some aquatic species may reveal highly variable lipid levels among the individuals. Thus, for example, Jensen et al.[154] reported variation of greater than an order of magnitude in lipid levels in herring

MONS 006110

(*Clupea harengus*) from Swedish waters, and similar variations have been recorded in other fish species.[169-176] Bivalves such as mussels are also known to exhibit considerable variability in lipid levels.[175-179] In some instances the sources of such variation are identifiable, e.g., lipid content or condition relates in most species to sexual condition and the spawning/resting/gametogenesis cycle, and may also correlate to size in some cases. However, the multiplicity of factors influencing lipid levels of a species may in some instances defy complete analysis.

This variation in lipid contents of individuals is important, as it is known that in many cases, the concentrations of PCBs (and other lipophilic pollutants) correlate to the lipid contents of the individual. Thus, where a population exhibits heterogeneity of lipid content, PCB concentrations (based on wet tissue weights) will also vary widely. This has two consequences: first, a greater number of individuals must be sampled at each location to fully characterize the PCB levels in the population, and second, interpopulation differences in PCB levels are more difficult to distinguish.[180] Both consequences are obviously undesirable in terms of bioindicator surveys, and the option of basing PCB concentrations on lipid weights of the sample must be considered.

Phillips[24,35] has argued that the use of lipid weights as a basis for organochlorine concentrations is defensible only in certain circumstances. If the kinetics of PCB accumulation by a species are such that ambient PCBs partition into body lipids until an equilibrium is attained, it is clear that basing PCB concentrations on lipid weights of an organism is perfectly valid, and will give rise to much more homogeneous intrapopulation levels and hence comparisons between PCB levels (in different populations) will be of greater validity. However, if the uptake kinetics are such that a given amount of PCB accumulated from the ambient environment is distributed about the available lipid pool in an organism, an inverse relationship between body lipid and PCB concentrations in that lipid would result. In this event, basing PCB concentrations on lipid weights would give rise to no improvements over the use of wet tissue weights as a basis, either with respect to intra- or interpopulation variability.

This argument is tantamount to that discussed above, on whether PCBs are accumulated by lipid-water partitioning or via the food chain. As previously stated, there is no consensus of opinion as yet on this subject. However, research results support both points of view in different phyla. Thus, for example, Roberts et al.[181] found that the net uptake of chlordane into the northern redhorse sucker (*Moxostoma macrolepidotum*) was directly proportional to the size of the lipid pool in the fish. Similar results were reported by Stegeman and coworkers[182,183] for petroleum hydrocarbon uptake by the oyster *Crassostrea virginica*, and also by DeFoe et al.[127] for PCB uptake by fathead minnows (*Pimephales promelas*) of different sexes and lipid pool sizes (see Section VIII). These reports support a lipid-water partitioning theory of uptake and would therefore also support the use of lipid weights as a basis for PCB concentrations. However, other data on seals reveal an inverse relationship between concentrations of DDT or PCB and blubber thickness,[184,185] and this supports the alternative concept of a defined PCB uptake being distributed about the available lipid pool. It may be that different major uptake mechanisms exist at different trophic levels, as suggested previously by Phillips;[24,35] however, no firm conclusion is possible. It is therefore advisable for researchers undertaking bioindicator work with PCBs to determine lipid levels in their samples, and to interpret analytical results using concentrations based on both wet and lipid weights. In this fashion, erroneous conclusions due to the interfering effects of sample lipids are most likely to be avoided.

The second major influence of lipid on the PCB concentrations found in organisms is on the tissue distribution of PCBs. This is important in terms of bioindicator surveys, as it helps the researcher select the most appropriate tissue for analysis. Data on the tissue distributions of PCBs in aquatic organisms are available for crustaceans, molluscs, fish, and marine

MONS 006111

Table 10
CONCENTRATIONS OF ΣDDT BY WET AND LIPID WEIGHTS (mg/kg) IN 6 TISSUES OF A SINGLE PORPOISE (*PHOCAENA PHOCAENA*) FROM SCOTLAND[197]

Parameter	Blubber	Kidney	Liver	Muscle	Spleen	Brain
ΣDDT by wet weight	3.80	0.04	0.58	0.56	0.12	0.02
Percent lipid	67.00	1.4	13.20	6.10	5.10	8.30
ΣDDT by lipid weight	5.60	2.90	4.80	9.20	2.40	0.27

mammals. Nimmo et al.[186,187] found that the distribution of both DDT and PCB in shrimp tissues was correlated to that of lipids, the majority of the residues being accumulated by the hepatopancreas and least by abdominal muscle and the exoskeleton. Ernst et al.[188] reached similar conclusions on the effects of lipid on PCB distributions in the scallop *Chlamys opercularis* and three finfish species, and many other authors have confirmed that PCBs and lipids in finfish correlate in terms of distribution among the tissues, at least as a general rule.[79,130,177,189,191]

The tissues of marine mammals also exhibit a covariance of lipids and PCBs. Lipid-rich tissues (principally the blubber) contain the great majority of the PCB load in these animals, concentrations in the other tissues (which have much less lipid) being considerably lower on a wet weight basis.[140-150,183,192-196]

In all of the cases cited above, the very marked differences between PCB concentrations (based on wet weights) of the various tissues are substantially reduced when PCB levels are recalculated on a lipid weight basis. This indicates that the lipid distribution in an organism is a major factor in determining the distribution of PCBs.

There is therefore an argument for researchers wishing to undertake bioindicator studies for PCBs to concentrate on organs which are relatively lipid-rich. In this fashion, the concentrations of PCBs in the sample will be increased and analytical accuracy improved. In addition, it would be an advantage to select a tissue which exhibits relatively constant levels of lipids and a slow net turnover of lipids, as this would give rise to more constant PCB levels in the chosen tissue.

The final aspect requiring discussion in this section concerns the possible influence of lipid chemistry on the distribution of PCBs both between and within tissues of aquatic organisms. This subject is particularly important, as researchers commonly wish to subsample material for analysis from a single individual, and in some cases this may be extremely difficult to do in a reproducible fashion.

An early indication of the possible influence of lipid chemistry on PCB accumulation by organisms arose from work concerning the PCB distribution in tissues of marine mammals, referred to briefly above. Holden and Marsden[197] were the first authors to note that organochlorine concentrations in marine mammals revealed some interesting anomalies. They discovered that ΣDDT concentrations (i.e., levels of DDT plus its metabolites) in the porpoise *Phocaena phocaena* differed considerably among the tissues on a wet weight basis (Table 10). Conversion of the data to a lipid weight basis gave rise to much smaller differences between the ΣDDT concentrations in different tissues, except for the brain, which exhibited pollutant levels an order of magnitude lower than those of other tissues. This inability of brain lipids to sequester ΣDDT to the same extent as other tissues has since been confirmed for PCBs in other mammals, including sea lions,[198,199] various seal species,[149,183,193,195,199] and the striped dolphin *Stenella coeruleoalba*.[150] Frank et al.[193] felt that a blood brain barrier might exist, but other authors have suggested that the unusual lipid chemistry of the brain tissues is the cause. Brain tissues are exceptionally rich in phospholipids, as opposed to triglycerides which are normal constituents of lipids in other tissues and in depot fat. It is

MONS 006112

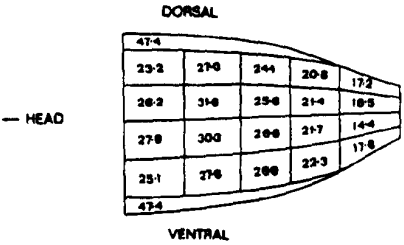


FIGURE 10. The variation in total lipids as a percentage of biochemical components in different regions of the axial muscle of herring, *Clupea harengus*. Differences between right and left muscle fillets were not observed.[269,270]

very likely that PCBs are sequestered much more efficiently by triglycerides than phospholipids, because of the lipophilic nature of PCBs (phospholipids are more polar). Tanabe et al.[130] give particular support to this hypothesis, noting that the isomers of HCH (hexachlorocyclohexane) vary in tissue distribution in the striped dolphin, the more hydrophilic α-HCH being more abundant in the brain than the β-HCH isomer. In a later paper,[131] the same authors suggested that transplacental transfer of PCBs in the dolphin to the fetus was reduced because of the existence of large amounts of phospholipids in the blood, the placenta, and the blubber of the fetus.

These reports are important, as they give substance to the supposition that the covariance of lipid and PCBs in organisms is a function not of a nonspecific affinity of PCBs for all lipids, but of specific affinities of PCBs for certain types of lipids. The paucity of PCBs in the brains of marine mammals is matched by similar profiles in finfish,[162,269-282] and this influence of lipid chemistry on PCB uptake by brain tissues may be expected to be universal. Cahn et al.[283] have noted that elasmobranchs, which exhibit unusual PCB tissue distributions compared to teleosts, also have an unusual lipid chemistry.[284] Langston[132] considered that species differences in PCB kinetics in bivalve molluscs might also be based on differences in the chemical structures and percentage compositions of their lipid pools. It is therefore important to realize that the correlations between PCB distribution and lipids in organisms, found by so many authors, are approximate only, because of the nonspecific methods employed to extract and determine lipid weights. There is considerable room for both theoretical and practical research on this aspect of PCB accumulation by biota.

Differences in lipid chemistries or lipid amounts within different portions of a tissue may be of considerable practical importance with respect to the use of bio-indicators to monitor PCBs. Figure 10 shows a profile describing the variation of total lipids in different parts of the musculature of the herring, *Clupea harengus*.[269,270] It is clear that considerable differences in lipid content occur both longitudinally and dorsoventrally in the axial muscle of this species. Other finfish species also exhibit such differences, although the sites of preferential lipid storage vary according to their ecological niche (swimming habits in particular). It is known that these variations in lipid composition of fish muscle give rise to heterogeneous distributions of ΣDDT in the tissues (see discussion of Reinert,[205] Stout et al.[206] and Reinert and Bergman,[269] in Phillips[35]), and the distribution of PCBs within the tissues will also almost certainly be affected. However, the only mention of PCB heterogeneity within finfish muscle published to date appears to be that of Shaw and Connell,[49] who mention briefly that mullet exhibit this phenomenon. More detailed information[270] reveals that the differences

MONS 006113

Table 11
CONCENTRATIONS (mg/g WET WEIGHTS) OF VARIOUS ORGANOCHLORINES IN BLUBBER AND MUSCLE OF A STRIPED DOLPHIN, *STENELLA COERULEOALBA*, AND THEIR VARIATION WITH AREA WITHIN EACH TISSUE[120]

Organs & tissues	PCBs	*p,p'*-DDE	*p,p'*-DDD	*p,p'*-DDT	ΣDDT[a]	α-HCH	β-HCH	γ-HCH	ΣHCH[b]	HCB
Blubber										
Front	23600	27800	1100	4800	33700	53	390	20	463	126
Center	23300	28200	1100	4600	33900	57	434	22	513	133
Rear	20800	26700	900	3500	31100	49	368	18	435	129
Mean	22600	27600	1000	4300	32900	53	397	20	470	129
Muscle										
Dorsal front	232	297	15	23	335	0.9	6.5	0.4	7.8	2.7
Ventral front	855	980	38	98	1116	2.5	18.6	1.2	22.3	9.0
Dorsal center	166	204	15	8	227	0.5	3.7	0.2	4.4	2.0
Ventral center	233	284	9	24	317	0.8	7.0	0.4	8.2	2.7
Dorsal rear	314	413	34	16	463	1.2	9.6	0.6	11.4	3.3
Ventral rear	209	287	27	12	326	0.9	7.5	0.5	8.9	2.5
Mean	335	411	23	30	464	1.1	8.8	0.6	10.5	3.7

[a] ΣDDT = *p,p'* DDE + *p,p'* DDD + *p,p'* DDT.
[b] ΣHCH = α-HCH + β-HCH + γ-HCH (δ-HCH was not detected).

in PCB concentrations between different areas of the musculature of mullet are considerable, concentrations covarying with lipid over almost an order of magnitude.

Similar within-tissue heterogeneity has also been reported for seals and dolphins. Anas and Worlund[207] found that ΣDDT and PCBs in the blubber of fur seals (*Callorhinus ursinus*) were distributed heterogeneously and that different methods of subsampling from the blubber gave rise to different results. Tanabe et al.[120] also reported differences in concentrations of PCBs and other organochlorines in blubber and (particularly) muscle of the striped dolphin (Table 11).

It is therefore clear that researchers wishing to subsample from a single tissue of a bioindicator species for the analysis of PCBs in a monitoring program must take particular care in terms of the reproducibility of subsampling. Thus, in all cases, tissues should be subsampled from the same site on a species, to the same depth. It is also important to note that, at least in salmonids, the PCB levels vary markedly between skinless and skin-on fillets of axial muscle;[207,209] skinless fillets are no doubt the better alternative for bioindicator work, but care must be taken upon dissection to avoid contamination from the skin.

The discussion above has been confined to the influence of lipid levels per se on PCB concentrations encountered in marine organisms. Data also exist which indicate that the amounts of lipid present in biota frequently underlie the influence of other extraneous parameters (e.g., season, size, and sex of organism) on PCB levels. Such examples will be covered in the following sections of the present review.

IV. THE EFFECTS OF SEASON/ORGANISM CONDITION

Season and organism condition are particularly important variables in bioindicator surveys. If sufficient attention is not given to correct sampling, spurious conclusions may result due to the influence of these parameters.

Several mechanisms exist by which the levels of PCBs or other pollutants in bioindicators may vary seasonally. Three major possibilities exist:

MONS 006114

1. Temporal fluctuations may occur in the delivery of the pollutant to coastal waters
2. Biological changes may occur within the selected bioindicator species, which may influence the accumulation of PCBs or other pollutants
3. Alterations in water quality may occur with season, and these may also influence the bioaccumulation of PCBs.

The effects of each of these three types of events will be considered here in turn.

A. Temporal Fluctuations in Pollutant Delivery

It is known that the concentrations of many organochlorines in rivers or receiving coastal waters fluctuate considerably with time. In cases where the major source of the pollutant is from its use in agriculture, this fluctuation in pollutant delivery is often regular and predictable. Hence, Butler et al.[209] showed that concentrations of ΣDDT in the oyster *Crassostrea virginica* varied seasonally in different fashions in three Texas estuaries. In two of the estuaries, a single peak in ΣDDT levels was observed in early summer; by contrast, oysters from the Laguna Madre area exhibited three peaks, in about February, July, and November. These profiles correlated precisely to DDT application in the catchments; the Laguna Madre region was multiply harvested and DDT was applied three times a year, whereas the other estuary catchments received only single annual applications of the pesticide. A similar regular variation in organochlorine abundance in aquatic ecosystems has been observed elsewhere, e.g., Yamato et al.[210,211] reported summertime peaks and winter minima in BHC and HCH levels in Japanese waters. These profiles of temporal variation are defined by the application period of the pesticide and by the timing of rainfall and subsequent run-off carrying the pollutant to rivers and then to estuaries.

The PCBs are, of course, not used as agricultural pesticides, hence their seasonal abundance is not defined by this factor. However, in certain instances, the delivery of PCBs to coastal waters may be extremely variable temporally. Studies in Sweden, notably by Olsson et al.,[173] and Södergren et al.,[150] have shown that peak abundance of PCBs occurs at the time of the spring thaw in ice cover. The data of the former authors, concerning PCBs in roach (*Leuciscus rutilus*) from Lake Roxen are shown in Figure 11. Temporal variability may also occur in instances where a continual, relatively stable PCB source is subject to dilution by run-off. In these cases, PCB levels in water vary inversely to the degree of run-off. Such an explanation was cited by Livingston et al.[212] to define seasonal variation in PCBs of biota from Apalachicola Bay in Florida.

Finally, it is evident that in many cases, the industrial sources of PCBs may fluctuate in magnitude with time. Duke et al.[213] followed the reduction in PCB concentrations in effluents receiving waters and oysters in Escambia Bay, Fla., where a single industrial source was suspected. Other authors have noted a lack of consistency in PCB levels in biota, and this is probably caused by variations in the magnitude of PCB sources, coupled with temporal changes in run-off.

B. Biological Changes Influencing PCB Accumulation

Superimposed on the temporal fluctuation of PCB concentrations in coastal waters referred to above is a range of changes which occurs in the bioindicator species themselves. These changes may be extremely important in determining the PCB concentrations present in the individuals sampled in a bioindicator survey and their effects should be taken into account during the design phase of any survey.

Biological events of importance with respect to PCB accumulation in bioindicators include the spawning cycle (and associated variation in lipid contents of bioindicators), growth, and migration. The effects of these will be discussed in turn.

MONS 006115

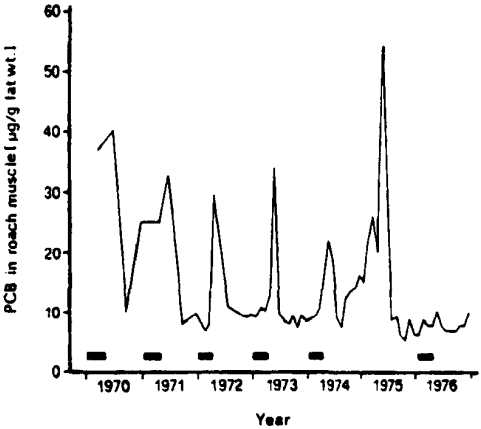


FIGURE 11. Mean concentrations of PCBs (by lipid weight) in muscle of roach, *Leuciscus rutilus*, taken from Lake Rotsen in Sweden between 1970 and 1977. The bars at the bottom of the figure represent the timing of ice cover in the lake; there was no ice cover in the winter of 1974—75.[179]

1. Spawning

The gametogenesis/spawning/resting cycle is of profound importance in a bioindicator to be used to monitor organochlorines, including PCBs. This is generally considered to be caused by the variation in lipoid levels of organisms with the sexual cycle. Most organisms exhibit regular and marked increases in lipid contents during gametogenesis, followed by a dramatic loss of lipid with the gametes at spawning. It has already been noted in Section V that the lipid content of organisms defines, to a large extent, their concentrations of PCBs; hence, it is evident that PCBs will vary in concentration with the sexual cycle.

Several authors have reported data showing that the mature sex organs or gametes of aquatic biota are rich in lipid and exhibit high levels of PCBs and other organochlorines. Among crustaceans, for example, it is known that DDT in particular is heavily concentrated in gametes and mature sexual organs,[216-218] and the same is almost certainly true of PCBs. Bivalves also store large amounts of organochlorines in gametes,[217-220] and whole-body levels of these compounds are reduced markedly at spawning. The loss of DDT and PCBs in finfish at spawning is also known to be considerable,[130,171,203,209,221-223] although in most cases it appears that females are much more affected than males, as the loss of organochlorines in milt is small compared to that in eggs.[130,220,223]

The importance of this dependence of PCBs in biota on their sexual condition becomes evident when one considers the simultaneous variation in condition of different populations. Figure 12 shows an example for the mussel *Mytilus edulis*, collected from different positions on the shore in two locations at close proximity to each other.[178] It is clear that even these closely sited subpopulations of mussels varied considerably in condition. If such individuals were selected for use as bioindicators, PCB concentrations would be expected to be greater

MONS 006116

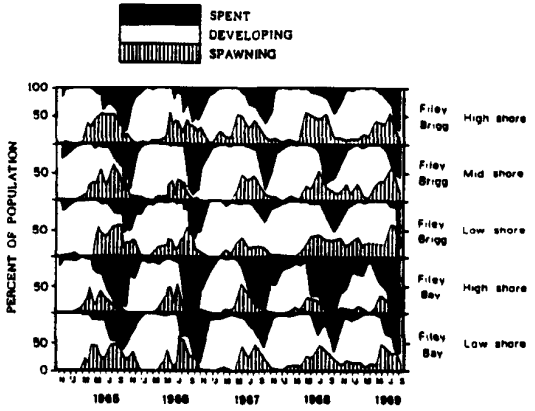


FIGURE 12. Seasonal variation in condition (expressed as percentage of population spent, developing, or spawning) for five subpopulations of the mussel *Mytilus edulis* between 1964 and 1969 in North Yorkshire waters, England.[170]

in the samples which were of greater sexual maturity, simply because of the interference of the covarying lipid parameter.

Such differences between individuals, subpopulations, or populations of organisms in sexual condition are by no means restricted to bivalve molluscs; most other species also exhibit variations in condition at any one time. The effects of this factor may be reduced by timing sampling to coincide with the period of least difference in condition between individuals, and by the use of lipid weights as a basis for PCB concentrations in the animals studied, rather than wet weights. It was mentioned in Section V that analytical results for PCBs in bioindicators should be quoted based on both lipid and wet weights of the samples to improve interpretation; this method would nicely highlight the reasons for unusual differences between samples, where these are based on concurrent variations in lipids. The best example of this concerns the seasonality of ΣDDT in coho salmon from the Great Lakes, reported by Reinert and co-workers.[163,209] These authors reported an increase in ΣDDT in salmon from Lake Michigan over the summer, but stated that the same species from Lake Erie exhibited no such seasonal variations. However, on recalculating the data based on lipid weights, Phillips[34,35] showed that the differences were a function of variation in lipid seasonality between the two locations (Table 12), and that salmon from both lakes exhibited increased ΣDDT concentrations (based on lipid weights) over the summer period.

2. Growth

The influence of the growth of an organism on its content of PCBs merits brief mention here. It is well known that in temperate waters, organism growth commonly occurs mainly during the spring and summer periods of warm water temperatures. This could produce seasonal fluctuations in contaminant levels, if the uptake of pollutants were constant throughout the year and the body load were distributed throughout the body tissues or body lipid

MONS 006117

Table 12
SEASONALITY OF ΣDDT RESIDUES IN WHOLE COHO SALMON (*ONCORHYNCHUS KISUTCH*) FROM LAKES MICHIGAN AND ERIE, AND THE INFLUENCE OF LIPIDS ON THE TEMPORAL CHANGES[34,38,200]

Lake	Year-class and date of collection	No. of fish	Weight (g)	ΣDDT (wet wt)	OR (%)	ΣDDT (lipid wt)
Michigan	1965 year-class					
	21—22 April 1968	5	1.054	3.3	7.4	44.6
	4—7 May 1968	3	1.180	3.5	5.3	66.0
	21 August 1968*	10	3.514	12.3	13.2	93.2
	18 October 1968*	10	3.486	12.6	7.1	177.5
Michigan	1966 year-class					
	1 May 1969	4	1.328	3.5	9.0	38.9
	3—11 September 1969	10	3.903	11.8	11.6	101.7
Michigan	1967 year-class					
	4 May 1970	5	967	2.9	6.9	42.0
	21—28 August 1970	13	3.663	14.0	13.8	101.4
Michigan	1968 year-class					
	17 April 1971	12	1.029	1.8	7.6	23.7
	28 August 1971	15	4.254	9.9	13.0	76.2
Erie	1966 year-class					
	4 April 1969	6	811	1.3	10.8	12.0
	5 May 1969	5	1.050	2.1	10.0	21.0
	7—8 October 1969	10	2.027	2.2	5.2	42.3

* Two 25-mm thick steaks and the brain had been removed from these fish.

pool. Niimi and Cho[226] have discussed the influence of growth on contaminant kinetics in finfish, and have in particular emphasized that biological half-life data for contaminants are often calculated without recognizing the influence of growth dilution of pollutants on the data. While organism growth is not considered a major variable in defining PCB seasonality in aquatic biota, it is nevertheless of potential significance. It is also of interest that various authors have found PCBs to influence growth rates of biota in laboratory studies, at least in the case of certain crustaceans,[227] bivalve molluscs,[210,228] and some finfish.[130,163,229-233] It is more than possible that this effect is linked to an influence of PCBs on steroid hormones,[234,235] but whether it exists at PCB concentrations likely to be encountered in natural waters is uncertain.

3. Migration

Migration is the final biological factor which may lead to seasonality of contaminants, including PCBs, in aquatic biota. Unfortunately, most authors ignore this factor almost completely in designing bioindicator surveys, despite its enormous importance, particularly in estuaries and in studies of finfish. However, several authors have recognized the possible influence of migration of finfish on organochlorine surveys.[101,160,190,230,237] Many coastal species of finfish display annual migration subsequent to sexual maturity, spawning in estuaries, and moving away from shore at other times. As noted by Phillips,[35] the concentrations of a pollutant in a migratory animal are a complex function of its uptake through both space and time. It is presently impossible to interpret data from surveys employing migratory bioindicators, at least where the species is not sampled more than once. The basic prerequisite that a bioindicator should be sedentary in order to represent its area of sampling (see Section III above) has been much abused by authors, to the detriment of their own research.

MONS 006118

C. Seasonal Variations in Water Quality

The final major factor which may give rise to seasonality of PCBs in aquatic biota concerns various aspects of water quality, the most important of which are salinity and temperature. Research on trace metal uptake by bioindicators has frequently shown an influence of these parameters on metal uptake by aquatic biota, although data for organochlorines are much harder to find.

However, it is known that salinity is an important factor in determining the uptake of DDT by finfish, at least in some cases.[238] While no data showing a direct influence of salinity on PCB uptake by organisms are known, several authors have suggested that the partitioning of PCBs between water and sediments (or suspended inorganic particulates) may be influenced by salinity.[56,67] Further research on this aspect, and its importance in terms of defining uptake of PCBs by biota, is required as an adjunct to aiding the interpretation of bioindicator surveys.

Water temperature is also known to affect the uptake of organochlorines by finfish. Murphy and Murphy[239] reported faster uptake of DDT by mosquitofish (*Gambusia affinis*) at 20°C than at 5°C, and a similar increase in DDT uptake at higher temperatures was noted by Reinert et al.[240] for rainbow trout (*Salmo gairdneri*). More recently, Powell and Fielder[241] have shown that the sea mullet *Mugil cephalus* also takes up DDT residues to a greater extent at higher temperatures. Edgren et al.[242] reported data on the influence of temperature on the uptake of DDT and two individual PCBs (2,3',4',5-tetrachlorobiphenyl and 2,2',4,4',5,5'-hexachlorobiphenyl) by perch, *Perca fluviatilis*. Once again, increased temperatures were accompanied by greater accumulation of each organochlorine. However, no consistent effects of temperature on the elimination of these pollutants could be confirmed. By contrast, Langston[133] noted faster rates of both accumulation and elimination of 4,4'-dichlorobiphenyl in the cockle *Cerastoderma edule* at higher temperatures (Figure 13). Half-lives for excretion of this isomer were 7 days at 8°C and 5 days at 15°C.

The influence of temperature on PCB and DDT uptake may also be based, at least partially, on an effect on the partitioning of these chemicals between solution and suspension;[56,67] it is known that organochlorines exhibit greater solubilities in water at higher temperatures.[243] Certain authors have also theorized that the increase in respiration rate of finfish at higher temperatures may also be significant.[239,242]

D. Conclusions on the Effects of Season/Organism Condition

Seasonal fluctuations in the concentrations of PCBs in aquatic biota can be severe in some instances. The causes of such fluctuations are multiple and may include temporal changes in PCB abundance (correlated to source emissions or run-off), biological effects from the bioindicator itself (particularly lipid changes correlating to the sexual cycle), and variations in water quality (particularly salinity and temperature).

A bioindicator survey for PCBs seeks, ideally, to take a "snap shot" of relative pollution conditions at various sites at any one time, in order to reach conclusions on the areas and relative magnitudes of pollutant sources or abundance. This is most efficiently and accurately achieved when:

1. Samples are taken over as short a period as possible
2. The period of sampling is selected such that no major changes in pollutant availability, water quality, or organism biology (particularly lipids), are occurring
3. The organism selected for study is not migratory

The period corresponding to that of least change, noted in item (2) above, will depend on the nature of both the area and the species studied. In temperate waters, it has been suggested that the best period for sampling bivalves for organochlorine analysis would be about 2

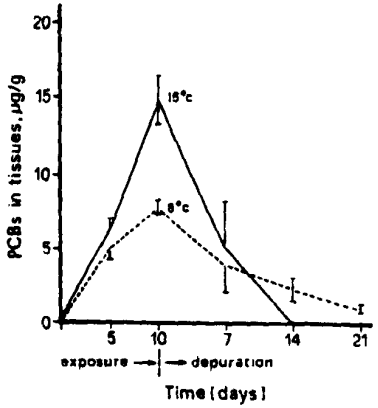


FIGURE 13. The uptake and clearance of 4,4'-dichlorobiphenyl by the cockle *Cerastoderma edule* at different temperatures. Bars represent standard errors, and tissue concentrations are in µg/g wet weights. Half-life calculations suggested a $t_{1/2}$ of 5 days at 15°C and 7 days at 8°C.

months prior to spawning.[66] However, while this has advantages in that the levels of lipid should be high and relatively similar between individuals and populations, other factors (e.g., gross variability in source emissions or water quality at this period) may outweigh these advantages. It is clear from the literature that some species exhibit only very minor seasonality of PCBs. Thus, for example, studies in the U.S. Musselwatch Program have consistently revealed only small changes in the concentrations of PCBs or other organochlorines with season.[199,266,349] However, other authors have found considerable seasonal fluctuations, sometimes over short periods, using similar or identical species.[175,212,266] While this is likely to depend on the stability or otherwise of inputs of PCBs, and the extent and rapidity of spawning of the species studied, no general rule may be drawn in advance of any detailed knowledge. It is therefore recommended that researchers take account of the potential influence of seasonal variation on the results of bioindicator surveys, by sampling as proposed above.

VII. SIZE (WEIGHT, AGE) OF INDIVIDUALS SAMPLED

The most important variable influencing PCB levels in aquatic biota, after lipid levels and season of collection or animal condition, is animal size. Bioindicator surveys must take account of the potential influence of organism size on the PCB contents of the samples studied; again, much can be done at sampling to reduce the influence of this variable on survey results.

There are various basic mechanisms whereby PCB levels might alter with organism size within a species:

MONS 006120

- Uptake of PCBs may be a size-related phenomenon, i.e., small individuals may attain higher PCB concentrations during episodic exposure to PCBs because of their higher surface area/volume ratio. (This assumes PCB uptake is dominated by uptake from solution across the body surface of an organism.)
- Individuals of different size of a species may exhibit differences in lipid contents, leading to variation in PCB levels with size.
- If PCB excretion is very slow in a species, these pollutants may be accumulated throughout the lifetime of a species, leading to size-dependent (or, more strictly, age-dependent) variations.[247]
- Various changes which occur with an increase in individual size or age of a species might incidentally influence PCB accumulation. Two major changes of potential importance in this respect concern diet and migration, but in some instances other factors may also be significant, particularly the attainment of sexual maturity.

With the possible exception of the third of these, evidence exists to suggest that each single mechanism, or a combination of more than one, may be effective in certain circumstances in defining size-related variation in PCB concentrations in a species.

The available data relating PCBs to size, weight, or age of individuals in any given species mostly concern finfish. However, a limited amount of information is available with respect to other phyla, and this will be considered first.

Several authors have reported that the concentrations of either DDT or PCBs accumulated by zooplankton (mainly planktonic crustaceans) are size related.[98,60,248-250] Smaller organisms accumulate greater concentrations of the pollutants, and the authors have theorized that this is due to their higher surface area/volume ratio compared to larger animals. Neff and Giam[237] cited a similar hypothesis to explain differential uptake of Aroclor® 1016 by two groups of horseshoe crabs (*Limulus polyphemus*) differing in size. The explanation assumes that these populations do not attain equilibrium conditions on exposure to PCBs, either because the exposure period is episodic in nature or for other reasons. McLeese et al.[70] have reported that accumulation of PCBs by the polychaete *Nereis virens* and the shrimp *Crangon septemspinosa* varied with size of individual: in both cases, smaller individuals took up greater concentrations of PCBs.

Some information is also available for molluscs. Ernst et al.[188] found that PCB concentrations in mantle musculature of the squid, *Loligo forbesi*, from the English Channel, tended to decrease with increased animal weight, using either a wet or lipid weight basis for concentrations. However, these trends were not statistically significant and the sample size was small. The same authors found no influence of size on PCB concentrations in digestive gland or adductor muscle of the scallop *Chlamys opercularis*. Other negative reports also exist with respect to size effects on PCBs in bivalves; no difference in PCB concentrations with size could be found for *Acanthocardia tuberculata* (foot or digestive gland),[251] or *Mercenaria mercenaria* (whole soft parts).[130] In addition, Vreeland[108] noted that PCB concentrations in oysters (*Crassostrea virginica*) used in long-term uptake experiments in the laboratory stayed constant after equilibration, even though the PCB body burdens increased to keep pace with oyster growth. This consistency of PCB levels in bivalves with variations in individual size is matched by other organochlorines. Cowan[177] for example, could find no influence of size on dieldrin concentrations in mussels, *Mytilus edulis*, from Scottish coastal waters, and no reports of variations in DDT levels of bivalves with size of individual are known. Phillips[35] has theorized that the major reason for this difference between the bivalve molluscs and finfish (see below) is that bivalve molluscs do not exhibit consistent increases in lipid levels with age or size.

By contrast to the above, there are numerous reports indicating that organochlorine concentrations vary with size of individuals for many finfish species. The majority of these

MONS 006121

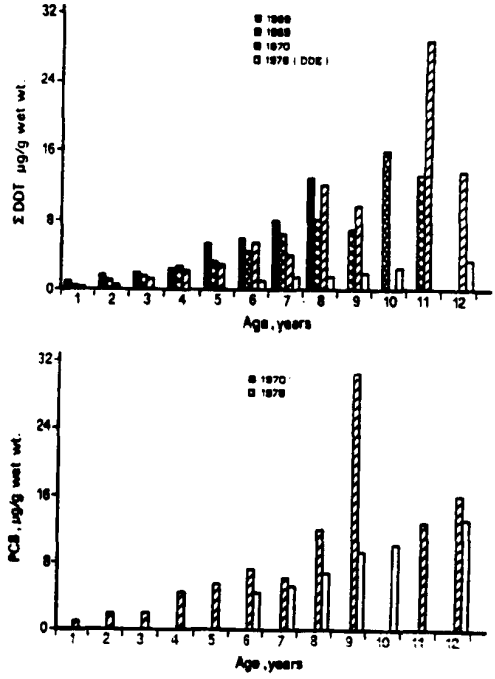


FIGURE 14. Concentrations of ΣDDT (1968, 1969, 1970) or DDE (1978) and PCBs in lake trout *Salvelinus namaycush* from Cayuga Lake, New York State, and their variation with age. Data from 1968, 1969, and 1970 are for whole eviscerated trout and are redrawn from Youngs et al.[205] for ΣDDT and Bache et al.[205] for PCBs. Data from 1978 are for the edible flesh only and are from Wanolek et al.[204]

reports concern DDT and its metabolites rather than PCBs, and these will not be discussed here, except in isolated instances where comparative profiles for DDT and PCBs are instructive.

Perhaps the most comprehensive information on the relationship of PCB concentrations in finfish with size or age, at least in terms of length of study, is that concerning lake trout (*Salvelinus namaycush*) from Cayuga Lake in New York State. Bache et al.[232] first reported that PCB concentrations (based on wet weights) in these trout varied with age. A different but concurrent report from the same group[233] showed that DDT residues followed a similar pattern. More recently, Wanolek et al.[204] produced data for DDE and PCBs in trout taken from the same lake 8 years later. These data are shown in Figure 14. It is notable that the PCB levels reported changed little over the study period; by contrast, the concentrations of

MONS 006122

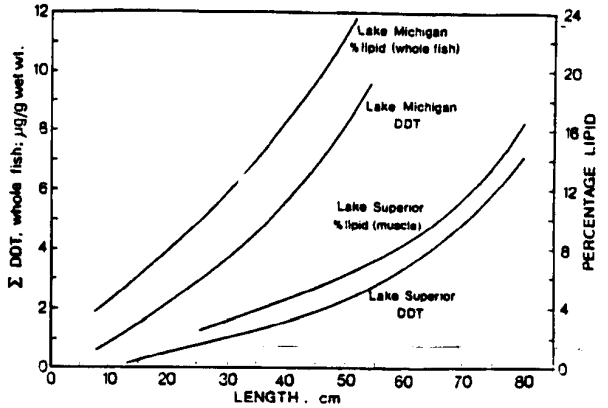


FIGURE 15. Concentrations of ΣDDT and percentage lipid in lake trout *Salvelinus namaycush* from Lakes Michigan and Superior, and their variation with fish length. Data for lipids in Lake Superior fish are from Eschmeyer and Phillips;[205] all other data are from Reinert.[163]

DDE in the later study (while still exhibiting significant increases with fish size), were considerably lower than ΣDDT levels in the previous investigations. Unfortunately, none of these reports included data on lipid levels of the fish analyzed; hence, it is impossible to know whether this effect of size on organochlorine levels is due to increases in lipid contents of the fish with age. A similar problem exists in other studies which have reported data for PCBs or hexachlorobenzene in lake trout.[226,235] However, Reinert and co-workers,[163,200] who worked on DDT accumulation in the same species from the Great Lakes, reported most convincing evidence showing that the increased DDT concentrations with length in lake trout are caused by a similar variation in lipid levels with fish length (Figure 15). It may therefore be quite safely assumed that this mechanism underlies the change in PCB levels in lake trout from Lake Cayuga.

Other fresh water finfish species are also known to exhibit size- or age-dependent variations in PCB concentrations in the field, including coho salmon (*Oncorhynchus kisutch*) from Lake Ontario,[232] carp (*Cyprinus carpio*) from Lake Huron,[227] yellow perch (*Perca flavescens*), white bass (*Morone chrysops*) and smallmouth bass (*Micropterus dolomieui*) from Lake Erie,[170] and yellow perch from the Ottawa River.[230] The data of Hattula et al.[166] are of particular note, as they involve more than 1700 individuals of 12 species from Lake Päijänne in Finland. Both pike (*Esox lucius*) and bream (*Abramis brama*) exhibited a direct dependence of lipid content on fish lengths; PCB concentrations were also length dependent as a result. In addition, studies of PCB uptake by sheepshead minnows, *Cyprinodon variegatus*, have revealed size-dependent uptake.[229] In many of these instances, the underlying basis for the increase in PCB levels with age is known to be a concomitant increase in lipid levels.

Some data are also available for marine and estuarine finfish species. Zitko[160] noted a possible influence of size on PCB concentrations in herring *Clupea harengus* from Canadian

MONS 006123

waters. Jensen et al.[165] confirmed this effect in extensive studies of herring and cod in Sweden. Herring revealed moderate increases of PCB levels in axial muscle with age even when data were based on lipid weights; by contrast, cod *(Gadus morhua)* exhibited no such age-dependence of pollutant concentrations, and a later report from the same group[201] showed no age dependence of PCBs (based on lipid weights) in pike, *Esox lucius*. Ernst et al.[166] reported data for PCBs in various tissues of the yellow gurnard, *Trigla lucerna*, from the English Channel. Significant correlations between PCB concentration and animal weight were found only for visceral adipose tissue when the concentration data were based on wet tissue weights; when concentrations were based on lipid weights, no significant size effect could be found. Stout[167] noted significant correlations between lipid and size, and between lipid and PCB concentrations for red snapper and king mackerel from the Atlantic Ocean and Gulf of Mexico, but size/PCB concentration relationships were apparently not significant. Young and Mearns[156] found a direct relationship between fish length and PCB concentrations for mullet (*Mugil cephalus*) from Californian waters; lipid levels were also greater in the larger individuals. Similar data correlating size, lipid levels, and PCBs have been reported for striped mullet, *Mullus barbatus*, from five areas in the Saronikis Gulf, off Greece.[202]

By contrast to the above reports which show that PCB concentrations increase with size in several finfish species, some authors have reported either no correlation of size to PCB concentration, or an inverse relationship. Thus, Van den Broek[169] found that PCBs did not vary significantly with size in muscle of whiting *Merlangus merlangus*, but tended to decrease with length in plaice, *Pleuronectes platessa*. Fowler and Elder[39] reported that size did not influence PCB levels of the vertically migrating fish *Myctophum glaciale* from the Mediterranean Sea, although ratios of PCBs to either ΣDDT or DDE altered with fish size. Hattula et al.[166] found that the lipid levels of perch, *Perca fluviatilis*, from Lake Päijänne in Finland decreased with increased fish length in some samples; this gave rise to an inverse relationship between PCB concentrations and length for this species. Similarly, Klauda et al.[203] noted a trend toward an inverse relationship between PCB levels and size in Atlantic tomcod (*Microgadus tomcod*) from the Hudson River Estuary, although the data were significant statistically only for residues in the liver.

We may conclude from the above review that there is no general rule governing the relationship between PCB concentrations and animal size in aquatic biota. While some species (particularly of finfish) exhibit direct relationships between size and PCB levels, others (notably most bivalve molluscs, but also some finfish) exhibit no such correlation. In a few cases, inverse relationships have been noted. It is clear that size-dependent variations in lipid levels are commonly a major factor in determining the size/PCB relationships found, but other variables such as dietary changes and migration may also play a part in certain instances. Researchers undertaking bioindicator surveys would do well to attempt in all cases to reduce the potential influence of this variable; this is most simply achieved by sampling individuals of a restricted size or age range and by determining the lipid contents of the individuals analyzed. A case can again be made for basing the PCB concentrations quoted on both wet and lipid weights of tissues, as this aids interpretation of data markedly.

It should be mentioned finally in this section that age-dependent variation in PCB levels has also been noted for marine mammals. However, this variability is intimately connected with the sex of the individuals studied; hence these data are discussed in the following section.

VIII. SEX OF INDIVIDUALS SAMPLED

In certain instances, it is known that the accumulation of PCBs by potential aquatic bioindicator species depends on the sex of the individual concerned. It is clear that such an effect may be based upon the differential ability of male and female gonads to accumulate

MONS 006124

Table 13
CONCENTRATIONS OF VARIOUS ORGANOCHLORINES (MEANS ± SE, µg/g DRY WEIGHTS) IN 6 MALE AND 6 FEMALE COMPOSITES OF MUSSELS (*MYTILUS CALIFORNIANUS*) FROM 2 SITES IN CALIFORNIAN WATERS[264]

Compound	Royal Palm (outfall region)		Point Sal (control region)	
	Male	Female	Male	Female
Total DDT	4.100 ± 0.700	6.40 ± 0.320	0.110 ± 0.0040	0.110 ± 0.0070
p,p'-DDT	0.040 ± 0.005	0.06 ± 0.005	0.008 ± 0.0005	0.007 ± 0.0006
o,p'-DDT	0.030 ± 0.003	0.04 ± 0.004	0.004 ± 0.0001	0.004 ± 0.0005
p,p'-DDE	3.500 ± 0.640	5.40 ± 0.280	0.077 ± 0.0030	0.067 ± 0.0030
o,p'-DDE	0.410 ± 0.060	0.73 ± 0.050	0.015 ± 0.0010	0.026 ± 0.0070
p,p'-DDD	0.110 ± 0.010	0.18 ± 0.007	0.009 ± 0.0006	0.008 ± 0.0004
Total PCBs	0.640 ± 0.060	0.94 ± 0.040	0.044 ± 0.0060	0.054 ± 0.0020
1242 PCB	0.120 ± 0.010	0.19 ± 0.010	0.016 ± 0.0030	0.019 ± 0.0010
1254 PCB	0.530 ± 0.060	0.76 ± 0.040	0.028 ± 0.0040	0.035 ± 0.0030

Note: Each composite was 5 individuals of shell length 40—50 mm; both samples were collected in late June 1974.

PCBs, or on differences between the amounts of body weight or lipids lost by the sexes at spawning, or on other such mechanisms. It is also evident that differences between the sexes may vary with season; the most marked divergence might be expected in ripe, prespawning individuals.

The majority of the data relating sex to organochlorine content of biota involve finfish and marine mammals, particularly seals. Very little information is available for molluscs or crustaceans. In the case of molluscs this may be because of their unusual sex lives in many cases; a large number of species are either functional or successive hermaphrodites. The reason for such a dearth of data on crustaceans is unclear, but is probably a function of the overall paucity of studies on organochlorines in this phylum.

The only report known concerning possible sex effects on PCBs in molluscs is that of Young et al.,[264] involving the mussel *Mytilus californianus*. These authors reported data for DDT and its metabolites, and PCBs, in male and female mussels from two locations on the coast of California. The results for mussels from the relatively uncontaminated area showed very little influence of sex on the organochlorine concentrations encountered, although both *o,p'* DDE and PCBs tended to be greater in females (Table 13). These trends were even more evident in the results for mussels from the polluted Palos Verdes area. However, the authors stated that additional (unpublished) data showed no statistically significant influence of sex on organochlorine uptake. It is possible that changes in sexual maturity of the samples occurred during the course of the uptake studies, thus masking a sex effect; further studies would be needed to clarify this.

With respect to crustaceans, no data could be found directly showing a difference between the sexes in PCB accumulation. Vernberg et al.[260] noted that there was no sex-based difference in the toxicity of Aroclors® 1016 and 1254 to fiddler crabs (*Uca pugilator*). By contrast, the accumulation and tissue distribution of kepone in blue crabs (*Callinectes sapidus*) is known to be heavily sex-dependent.[266,267]

Some finfish species are known to exhibit sex-dependence of PCB concentrations, although this is by no means the rule. Authors who have failed to find significant differences between the sexes for PCBs include Hattula et al.,[166] studying various species, Olsson and Jensen,[261] who noted significant differences in levels of DDT and its metabolites with sex of the pike

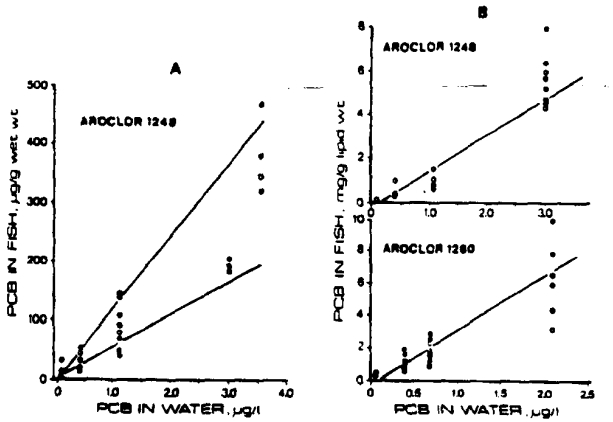


FIGURE 16. Uptake profiles for Aroclors® 1248 or 1260 in male (closed circles) and female (open circles) fathead minnows, *Pimephales promelas*, exposed to various PCB levels in water for 250 days. The profile in (A) is based on wet weights of the fish, whereas those in (B) are based on lipid weights.[127]

Esox lucius but no such variation for PCBs, and Kaiser,[180] for PCBs in the lake whitefish *Coregonus clupeaformis*. However, the levels of PCBs have sometimes been found to vary between testes and ovaries of fish in detailed tissue distribution studies.[171,202] It has been pointed out that differences generated thus are exacerbated because female finfish lose a greater percentage of total body weight at spawning than do males.[176] Such effects no doubt underlie the sex-based variation observed in certain species, e.g., by Zabik et al. for carp from Lake Huron.[227]

The most impressive example of sex-based variation in PCB accumulation by finfish, however, is based on an influence of total-body lipid differences. Thus, DeFoe et al.,[127] working with the fathead minnow *Pimephales promelas*, showed that females took up about twice as much PCBs as males because of the greater lipid contents of the former sex. Concentration factors (based on wet tissue weights) for the uptake of Aroclor® 1248 were 60,000 and 120,000 for males and females, respectively; for Aroclor® 1260 the respective concentration factors were 160,000 and 270,000. These differences between the PCB kinetics in the two sexes were almost completely eliminated by basing the tissue levels of PCBs on lipid weights (Figure 16), indicating that the effect is due almost totally to sex-based differences in lipid content. The residual differences may be caused by divergent lipid chemistries in the sexual organs of this species.

Very little information is available on PCB differences between the sexes in elasmobranchs, which is unfortunate, as the sex-based differences for mercury in these species are particularly interesting. Forrester et al.[205] and Walker[209] have shown that mercury accumulates slower with length in females than males of elasmobranchs, and this is thought to be due to the faster growth rate of females. Similar studies of PCBs in elasmobranchs would be of particular interest, as the results would indicate whether these compounds are taken up from food or from water at this trophic level. It is in any event likely that sex-based differences exist

MONS 006126

with respect to PCBs in viviparous species of elasmobranchs, as PCBs are known to be transferred from the mother to the ovarian egg and the mature fetus.[270]

The transfer of PCBs to the offspring, noted above for viviparous elasmobranchs, is matched by marine mammals, although transplacental transfer of PCBs in mammals is not particularly high due to the predominance of polar lipids (phospholipids) in the blood, placenta, and fetus.[131] After birth, marine mammals suckle their young and organochlorines are again lost from the mother to the young by this route,[271] although once again a partial barrier appears to exist, possibly for the same reason.

The loss of PCBs (and other organochlorines) by female marine mammals to the fetus during gestation and to the young by suckling gives rise not only to sex-based differences in these species after sexual maturity, but also to divergences in the age/concentration relationships for the sexes. Thus, data from various authors[146,149,184,192-195,271-273] show that young seals or other marine mammal species are born with relatively low levels of PCBs, derived transplacentally from the mother during gestation. After birth, PCB concentrations rise, initially because of their transfer in milk, and later because of high PCB levels in the solid diet (fish, etc.). Prior to the attainment of sexual maturity there is no evidence of any difference in PCB concentrations of the two sexes. However, once the breeding age is attained, females are able to lose more PCBs than males because of pollutant transfer to the fetus, and later suckling. Thus, the levels of PCBs in breeding females may level off at the attainment of sexual maturity, or may go on increasing, but at a slower rate than PCBs in the males. An exception to this pattern occurs if the females are not breeding successfully. Helle et al.[272,273] reported studies of ringed seals (*Pusa hispida*) from the Baltic Sea: PCBs are believed to have caused pathological changes in the uterus of ringed seal females, eliminating any chance of breeding in a large percentage of the population. Female seals exhibiting these changes had higher PCB levels than those without such pathology or those which were pregnant, showing clearly that parturition and lactation are major routes of PCB loss for female marine mammals. A similar problem may exist with California sea lions.[194]

In a sense, the dramatic sex differences in PCB accumulation seen in marine mammals are merely an extension of such effects in finfish, as both are a function of the greater involvement of the female in species propagation. The influence is, of course, greater for the mammals because of the entire mammalian habit of bearing live young and suckling the young. Viviparous elasmobranchs might be considered to be in an intermediate position in this respect.

Whatever the mechanisms behind sex-based divergence in PCB levels, it is clear that in some cases this factor should be taken into account when sampling animals for bioindicator surveys. In these instances, researchers should strive to stratify samples for sex, either by collecting animals of only one sex from all study locations, or by maintaining a given ratio of male to female animals in all samples. As noted above, such a requirement is likely to be particularly important if sampling takes place at a time when the individuals are ripe, i.e., just prior to spawning.

IX. VERTICAL POSITION OF SAMPLING

The final variable which merits attention here because of its potential influence on the results of bioindicator surveys is the depth of sampling of biota, or more strictly, the vertical position of sampling in relation to both the surface and the sea bed.

Three potential effects exist with respect to this variable:

The water column itself may be vertically stratified. In such instances, either the absolute amounts of PCBs present may vary vertically, or the factor causing the stratification may influence the bioaccumulation of the PCBs present.

MONS 006127

- Organisms living intertidally may be exposed to unusual concentrations of PCBs compared to those living subtidally.
- In some instances, bottom sediments may be a major source of PCBs and the levels of PCBs available to biota may depend on their vertical distance from the bottom sediments.

With respect to the first of these, it is well known that certain types of waters exhibit vertical stratification. Thus, estuaries draining large catchments will commonly exhibit salinity-based stratification, with a more-or-less well-developed halocline between an underlying salt wedge and an overlying brackish or freshwater layer. In enclosed embayments with little freshwater inflow, thermal stratifications may occur. Either of these may vary seasonally if large differences exist throughout the year in run-off or in ambient temperature and insolation.

This vertical stratification of the water column may give rise to vertical heterogeneity of PCBs. Thus, in the case of estuarine areas, the brackish water may contain greater amounts of PCBs (from terrestrial sources, delivered to the estuary in run-off) than the underlying salt wedge. Such a profile may also be produced in areas where the major source of PCBs is via wash-out of airborne contaminants, as these too will be introduced at the water surface.[274] In these and similar instances,[273] biota which are sessile may be expected to reflect the vertical variation in abundance of PCBs in the water column, i.e., concentrations of PCBs in a bioindicator will vary with depth.

A second possibility also exists in areas of vertical stratification based on water salinity or temperature. As noted in Section VI.C, both salinity and water temperature may influence the bioavailability of PCBs. Thus, even in areas where the absolute ambient levels of PCBs in the water column do not vary vertically, differences with depth may occur with respect to PCBs in a sessile bioindicator because of direct effects of salinity or temperature on its accumulation of PCBs.

The second mechanism whereby depth of biota may influence their PCB concentrations is in a sense a special case of vertical stratification. It has already been mentioned in Section III.A that surface films may be exceedingly rich in PCBs compared to subsurface waters.[12,59,65-67] A sessile bioindicator living in the intertidal zone may be exposed to PCBs in surface films, either if it irrigates the gills close to the water surface (e.g., as the tide recedes), or if the film is broken up and dispersed vertically by wave action on the shore. This mechanism could give rise to enhanced accumulation of PCBs by bioindicators in the intertidal zone compared to the same species living subtidally.

Finally, the influence of sediments must be considered. PCBs exhibit a high affinity for particulates, and sediments are considered to be a major environmental sink for these contaminants. In the absence of biodegradation, the burial of PCBs in marine sediments is essentially the sole mechanism of their loss from the ecosystem. However, evidence has been accumulating for some years that sediments might also be viewed as a source of PCBs for biota. Laboratory experiments by various authors have shown that particulate-associated or sediment-associated PCBs may be available for uptake by phytoplankton,[80] crustaceans such as fiddler crabs and shrimp,[78,81,270] polychaetes,[76-79,78] and fish.[277] Similar conclusions have been reached in field studies of a wide variety of organisms, notably in Californian waters.[52-56,153,204] Perhaps the most convincing data are those reported by Young et al.[204] concerning uptake of DDT and PCBs in mussels (*Mytilus californianus*) transplanted from a relatively noncontaminated area to various depths at Palos Verdes, Calif. These authors found that both pollutants were taken up to a far greater extent by mussels closer to the bottom sediments (Figure 17). It is known that the sediments at Palos Verdes are particularly contaminated by DDT and PCBs, and are probably now the major source of these contaminants in the region; hence, this is possibly an extreme example. However, it is clear that

MONS 006128

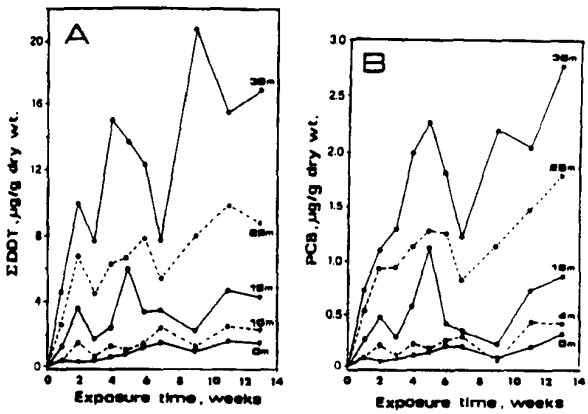


FIGURE 17. The net uptake of (A) ΣDDT and (B) PCBs by whole soft parts of mussels (*Mytilus californianus*) transplanted from Point Sal to various depths in the water column at Palos Verdes, Calif.[86]

bottom sediments may act as a particularly important source of PCBs, and this may also give rise to vertical variation of PCBs in bioindicators.

It may be concluded from the above that several mechanisms exist whereby bioindicators (particularly sessile or sedentary species) may exhibit depth-dependent variations in PCB accumulation. Researchers wishing to employ such species in monitoring surveys should take this into account and should sample at similar regions in all study locations with respect to tide marks and/or distance above the sediments. In instances where it is suspected that vertical heterogeneity may exist, it may be worthwhile to sample individuals at various depths in the water column.

ACKNOWLEDGMENTS

It is a pleasure for me to thank Mr. K. K. So, who contributed talent to the figures, and Dr. Bruce J. Richardson, who proofread the chapter superbly. I also wish to thank my wife for her patience, understanding, and encouragement.

REFERENCES

1. Hutzinger, O., Safe, S., and Zitko, V., *The Chemistry of Polychlorinated Biphenyls*, CRC Press, Cleveland, 1974.
2. National Academy of Sciences, *Polychlorinated Biphenyls*, NAS, Washington, D.C., 1979.
3. Richardson, B. J. and Webb, J. S., *PCBs in the Port Phillip Region: The Environmental Significance of Polychlorinated Biphenyl (PCBs): Final Report*, Publ. No. 248, Ministry for Conservation, Victoria, Australia, 1979.

MONS 006129

4. **Richardson, B. J. and Wold, J. S.**, Polychlorinated biphenyls (PBCs): an Australian viewpoint on a global problem, *Search*, 13, 17, 1982.
5. **Miller, S.**, The persistent PCB problem, *Environ. Sci. Technol.*, 16, 98A, 1982.
6. **Nisbet, I. C. T. and Sarofim, A. F.**, Rates and routes of transport of PCBs in the environment, *Environ. Health Perspect.*, 1, 21, 1972.
7. **Nicholson, W. J. and Moore, J. A., Eds.**, *Health Effects of Halogenated Aromatic Hydrocarbons*, New York Academy of Science, New York, 1979.
8. **Jensen, S.**, The PCB story, *Ambio*, 1, 123, 1972.
9. **Holden, A. V.**, Organochlorines — an overview, *Mar. Pollut. Bull.*, 12, 110, 1981.
10. **Jensen, S.**, Report of a new chemical hazard, *New Sci.*, 32, 612, 1966.
11. **Harvey, G. and Steinhauer, W. G.**, Transport pathways of polychlorinated biphenyls in Atlantic water, *J. Mar. Res.*, 34, 561, 1976.
12. **Eisenreich, S. J., Holled, G. J., and Johnson, T. C.**, Accumulation of polychlorinated biphenyls (PCBs) in surficial Lake Superior sediments. Atmospheric deposition, *Environ. Sci. Technol.*, 13, 569, 1979.
13. **Eisenreich, S. J., Looney, B. B., and Thornton, J. D.**, Airborne organic contaminants in the Great Lakes ecosystem, *Environ. Sci. Technol.*, 15, 30, 1981.
14. **Donkey, P. V. and Andren, A. W.**, Modelling the flux of atmospheric polychlorinated biphenyls across the air/water interface, *Environ. Sci. Technol.*, 15, 705, 1981.
15. **Murphy, C. B., Jr. and Carlea, D. J.**, The contribution of mercury and chlorinated organics from urban runoff, *Water Res.*, 12, 531, 1978.
16. **Young, D. R., Jan, T.-K., Gossett, R. W., and Hershelman, G. P.**, Trace pollutants in surface runoff, *Southern California Coastal Water Research Project, Annual Report 1979—80*, 1980, 163.
17. **Schafer, H. A.**, Characteristics of municipal wastewater discharges, 1977, *Southern California Coastal Water Research Project, Annual Report 1978*, 1978, 97.
18. **Schafer, H. A.**, Characteristics of municipal wastewater, *Southern California Coastal Water Research Project, Annual Report 1979—80*, 1980, 235.
19. **Bascom, W. and the staff of SCCWRP**, The effects of sludge disposal in Santa Monica Bay, *Southern California Coastal Water Research Project, Annual Report 1979—80*, 1980, 197.
20. **Bopp, R. F., Simpson, H. J., Olsen, C. R., and Kostyk, N.**, Polychlorinated biphenyls in sediments of the tidal Hudson River, New York, *Environ. Sci. Technol.*, 15, 210, 1981.
21. **West, R. H. and Hatcher, P. G.**, Polychlorinated biphenyls in sewage sludge and sediments of the New York Bight, *Mar. Pollut. Bull.*, 11, 126, 1980.
22. **Jensen, S., Renberg, L., and Olsson, M.**, PCB contamination from boat bottom paint and levels of PCB in plankton outside a polluted area, *Nature (London)*, 240, 358, 1972.
23. **Young, D. R. and Heesen, T. C.**, Inputs and distributions of chlorinated hydrocarbons in three southern California harbors, presented at the 4th Annu. Tech. Conf. on Estuaries of the Pacific Northwest, Corvallis, Ore., March 14, 1974.
24. **Peakall, D. B.**, Polychlorinated biphenyls: occurrence and biological effects, *Residue Rev.*, 44, 1, 1972.
25. **Peakall, D. B.**, PCBs and their environmental effects, *Crit. Rev. Environ. Control*, September, 469, 1975.
26. **World Health Organization**, *Polychlorinated Biphenyls and Terphenyls*, WHO, Geneva, 1976.
27. **Barber, R. T. and Warlen, S. M.**, Organochlorine insecticide residues in deep sea fish from 2500 m in the Atlantic Ocean, *Environ. Sci. Technol.*, 13, 1146, 1979.
28. **Harvey, G. R., Steinhauer, W. G., and Teal, J. M.**, Polychlorobiphenyls in north Atlantic Ocean water, *Science*, 180, 643, 1973.
29. **Harvey, G. R. and Steinhauer, W. G.**, Atmospheric transport of polychlorobiphenyls to the north Atlantic, *Atmos. Environ.*, 9, 777, 1974.
30. **Jernelöv, A.**, Heavy metals, metalloids and synthetic organics, in *The Sea*, Goldberg, E. D., Ed., John Wiley & Sons, New York, 1974, 799.
31. **Anon.**, Protection for Baltic seals, *Mar. Pollut. Bull.*, 13, 146, 1982.
32. **Anon.**, PCBs/wildlife, *Environ. Rep.*, 9/13/82, 1982.
33. **Phillips, D. J. H.**, The use of biological indicator organisms to monitor trace metal pollution in marine and estuarine environments — a review, *Environ. Pollut.*, 13, 281, 1977.
34. **Phillips, D. J. H.**, Use of biological indicator organisms to quantitate organochlorine pollutants in aquatic environments — a review, *Environ. Pollut.*, 16, 167, 1978.
35. **Phillips, D. J. H.**, *Quantitative Aquatic Biological Indicators: Their Use to Monitor Trace Metal and Organochlorine Pollution*, Applied Science, London, 1980.
36. **Harvey, G. R., Steinhauer, W. G., and Teal, J. M.**, Polychlorobiphenyls in north Atlantic Ocean water, *Science*, 180, 643, 1973.
37. **Harvey, G. R., Steinhauer, W. G., and Miklas, H. P.**, Decline of PCB concentrations in North Atlantic surface water, *Nature (London)*, 252, 387, 1974.
38. **Bidleman, T. F. and Olney, L. E.**, Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water, *Science*, 183, 156, 1974.

MONS 006130

39. **Harvey, G. R. and Steinhauer, W. G.**, Transport pathways of polychlorinated biphenyls in Atlantic water. *J. Mar. Res.*. 34, 561, 1976.
40. **Elder, D. L. and Villeneuve, J. P.**, Polychlorinated biphenyls in the Mediterranean Sea. *Mar. Pollut. Bull.*. 8, 19, 1977.
41. **Scura, E. D. and McClure, V. E.**, Chlorinated hydrocarbons in sea-water: analytical method and levels in the northeastern Pacific. *Mar. Chem.*. 3, 337, 1975.
42. **Elder, D. L., Villeneuve, J. P., Parsi, P., and Harvey, G. R.**, Polychlorinated biphenyls in sea-water, sediments and over-ocean air of the Mediterranean, in *Activities of the International Laboratory of Marine Radioactivity, Monaco. 1975*, Rep. Tech. Doc. IAEA-187, International Atomic Energy Agency, Vienna, 1976, 136.
43. **Sayler, G. S., Thomas, R., and Colwell, R. R.**, Polychlorinated biphenyl (PCB) degrading bacteria and PCB in estuarine and marine environments. *Estuarine Coast. Mar. Sci.*, 6, 553, 1978.
44. **Brügmann, L. and Luckas, B.**, Zum Vorkommen von polychlorierten Biphenylen und DDT — Metaboliten im Plankton und Wasser der Ostsee, Fischerei-Forschung, *Wiss. Schriftreihe*, 16, 31, 1978.
45. **Ehrhardt, M.**, Organic substances in the Baltic Sea, *Mar. Pollut. Bull.*, 12, 210, 1981.
46. **Duinker, J. and Hillebrand, M. T. J.**, Behaviour of PCB, pentachlorobenzene, hexachlorobenzene, α-HCH, γ-HCH, β-HCH, dieldrin, endrin and *p,p'* DDD in the Rhine-Meuse Estuary and the adjacent coastal area, *Neth. J. Sea Res.*, 13, 256, 1979.
47. **Dennis, D. S.**, Polychlorinated biphenyls in the surface waters and bottom sediments of the major drainage basins of the United States, in Proc. Natl. Conf. Polychlorinated Biphenyls, EPA-560/6-75-004, U.S. Environmental Protection Agency, Washington, D.C., 1976, 183.
48. **Pucconi, G. and Leoni, V.**, PCB and HCB in the sediments and waters of the Tiber Estuary, *Mar. Pollut. Bull.*, 11, 22, 1980.
49. **Shaw, G. R. and Connell, D. W.**, Polychlorinated biphenyls in the Brisbane River Estuary, Australia, *Mar. Pollut. Bull.*, 11, 356, 1980.
50. **Nisbet, I. C. T.**, Criteria Document for PCBs, Rep. No. 440/9-76-021, U.S. Environmental Protection Agency, Washington, D.C., 1976.
51. **Pavlou, S. P. and Dexter, R. N.**, Distribution of polychlorinated biphenyls (PCB) in estuarine ecosystems. Testing the concept of equilibrium partitioning in the marine environment, *Environ. Sci. Technol.*, 13, 65, 1979.
52. **Tulp, M. T. M. and Hutzinger, O.**, Some thoughts on aqueous solubilities and partition coefficients of PCB and the mathematical correlation between bioaccumulation and physico-chemical properties, *Chemosphere*, 7, 849, 1978.
53. **Danielsson, L. G.**, On the use of filters for distinguishing between dissolved and particulate fractions in natural waters, *Water Res.*, 16, 179, 1982.
54. **Clayton, J. R., Jr., Pavlou, S. P., and Breitner, N. F.**, Polychlorinated biphenyls in coastal marine zooplankton: bioaccumulation by equilibrium partitioning, *Environ. Sci. Technol.*, 11, 676, 1977.
55. **Harding, L. W., Jr. and Phillips, J. H., Jr.**, Polychlorinated biphenyl (PCB) uptake by marine phytoplankton, *Mar. Biol.*, 49, 103, 1978.
56. **Hiraizumi, Y., Takahashi, M., and Nishimura, H.**, Adsorption of polychlorinated biphenyl onto sea bed sediment, marine plankton, and other adsorbing agents, *Environ. Sci. Technol.*, 13, 580, 1979.
57. **Harvey, G. R., Miklas, H. P., Bowen, V. T., and Steinhauer, W. G.**, Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms, *J. Mar. Res.*, 32, 103, 1974.
58. **Ware, D. M. and Addison, R. F.**, PCB residues in plankton from the Gulf of St. Lawrence, *Nature (London)*, 246, 519, 1973.
59. **Fowler, S. W. and Elder, D. L.**, Chlorinated hydrocarbons in pelagic organisms from the open Mediterranean Sea, *Mar. Environ. Res.*, 4, 87, 1980.
60. **Wyman, K. D. and O'Connors, H. B., Jr.**, Implications of short-term PCB uptake by small estuarine copepods (Genus *Acartia*) from PCB-contaminated water, inorganic sediments and phytoplankton, *Estuarine Coast. Mar. Sci.*, 11, 121, 1980.
61. **Lederman, T. C. and Rhee, G. Y.**, Influence of a hexachlorobiphenyl in Great Lakes phytoplankton in continuous culture, *Can. J. Fish. Aquat. Sci.*, 39, 388, 1982.
62. **Mikhaels, R. A., Rowland, R. G., and Wurster, C. F.**, Polychlorinated biphenyls (PCB) inhibit photosynthesis per cell in the marine diatom *Thalassiosira pseudonana*, *Environ. Pollut. Ser. A*, 27, 9, 1982.
63. **Harding, L. W., Jr. and Phillips, J. H., Jr.**, Polychlorinated biphenyls: transfer from macroparticulates to marine phytoplankton and the effects on photosynthesis, *Science*, 202, 1189, 1978.
64. **Reyhaud, M.**, Les Biocides Organochlorés et les Détergents dans le Milieu Marin, thesis, University of Aix-Marseille II, Marseille, France, 1972.
65. **Duce, R. A., Quinn, J. G., Olney, C. E., and Piotrowicz, S. R.**, Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island, *Science*, 176, 161, 1972.
66. **Liss, P. S.**, Chemistry of the sea surface microlayer, in *Chemical Oceanography*, Vol. 2, Riley, J. P. and Skirrow, G., Eds., Academic Press, New York, 1975, 193.

MONS 006131

67. **Södergren A. and Larsson, P.**, Transport of PCBs in aquatic laboratory model ecosystems from sediment to the atmosphere *via* the surface microlayer. *Ambio*. 11, 41, 1982.
68. **Bernhard, M.**, Heavy metals and chlorinated hydrocarbons in the Mediterranean. *Ocean Manage*., 3, 253, 1978.
69. **West, R. H. and Hatcher, P. G.**, Polychlorinated biphenyls in sewage sludge and sediments of the New York Bight. *Mar. Pollut. Bull*., 11, 126, 1980.
70. **Pavlou, S. P., Dexter, R. N., Hom, W., and Kreagsland, K. A.**, Polychlorinated biphenyls in Puget Sound: baseline data and methodology. Spec. Rep. No. 74, Ref. no. M77-36. University of Washington, Seattle, 1977.
71. **Steen, W. C., Parks, D. F., and Baughman, G. L.**, Partitioning of selected polychlorinated biphenyls to natural sediments. *Water Res*., 12, 655, 1978.
72. **Hirakawa, Y., Takahashi, M., and Nishimura, H.**, Adsorption of polychlorinated biphenyl onto sea bed sediment, marine plankton, and other adsorbing agents. *Environ. Sci., Technol*., 13, 580, 1979.
73. **Mayer, L. M. and Fink, L. K., Jr.**, Granulometric dependence of chromium accumulation in estuarine sediments in Maine. *Estuarine Coast. Mar. Sci*., 11, 491, 1980.
74. **Fowler, S. W., Pellikorpov, G. G., Elder, D. L., Parsi, P., and Villeneuve, J.-P.**, Polychlorinated biphenyls: accumulation from contaminated sediments and water by the polychaete *Nereis diversicolor*. *Mar. Biol*., 48, 303, 1978.
75. **Courtney, W. A. M. and Langston, W. J.**, Uptake of polychlorinated biphenyl (Aroclor 1254) from sediment and from seawater in two intertidal polychaetes. *Environ. Pollut*., 15, 303, 1978.
76. **Elder, D. L., Fowler, S. W., and Pellikorpov, G. G.**, Remobilization of sediment-associated PCBs by the worm *Nereis diversicolor*. *Bull. Environ. Contam. Toxicol*., 21, 448, 1979.
77. **Wyman, K. D. and O'Connors, H. B., Jr.**, Implications of short-term PCB uptake by small estuarine copepods (Genus *Acartia*) from PCB-contaminated water, inorganic sediments and phytoplankton. *Estuarine Coast. Mar. Sci*., 11, 121, 1980.
78. **McLeese, D. W., Metcalfe, C. D., and Pezzack, D. S.**, Uptake of PCBs from sediment by *Nereis virens* and *Crangon septemspinosa*. *Arch. Environ. Contam. Toxicol*., 9, 507, 1980.
79. **Courtney, W. A. M. and Langston, W. J.**, Accumulation of polychlorinated biphenyls in turbot (*Scophthalmus maximus*) from seawater sediments and food. *Helgol. Wiss. Meeresunters*., 33, 333, 1980.
80. **Neu-Ritter, G. M., Wurster, C. F., and Rowland, R. G.**, Polychlorinated biphenyls (PCB) desorbed from clay particles inhibit photosynthesis by natural phytoplankton communities. *Environ. Pollut. Ser. A*, 28, 177, 1982.
81. **Nimmo, D. R., Wilson, P. D., Blackman, R. R., and Wilson, A. J.**, Polychlorinated biphenyls absorbed from sediments by fiddler crabs and pink shrimp. *Nature (London)*, 231, 50, 1971.
82. **Young, D. R. and Heesen, T. C.**, DDT, PCB and chlorinated benzenes in the marine ecosystem off Southern California, in *Water Chlorination, Environmental Impact and Health Effects*. Vol. 2. Ann Arbor Science, Ann Arbor, Mich., 1978, 257.
83. **Stanley, P. E., Young, D. R., and Gerd, K. L.**, DDTs in marine fishes following termination of dominant California input: 1970—77. *Mar. Pollut. Bull*., 10, 331, 1979.
84. **Young, D. R., McDermott-Ehrlich, D., and Heesen, T. C.**, Sediments as sources of DDT and PCB. *Mar. Pollut. Bull*., 8, 254, 1977.
85. **Willford, W. A., Hesselberg, R. J., and Nicholson, L. W.**, Trends in polychlorinated biphenyls in three Lake Michigan fish, in Proc. Natl. Conf. on Polychlorinated Biphenyls, EPA-560/6-75-004, U.S. Environmental Protection Agency, Washington, D.C., 1976, 177.
86. **Butler, P. A., Andren, L., Bendz, G. J., Jernelöv, A., and Reish, D. J.**, Monitoring organisms, in *FAO Technical Conference on Marine Pollution and its Effects on Living Resources and Fishing*, FAO Fish. Rep. No. 99, Suppl. 1, New York, 1971, 101.
87. **Skei, A., Melhum, S., and Omang, S.**, Estimation of heavy metal pollution in two Norwegian Fjord areas by analysis of the brown alga *Ascophyllum nodosum*. *Environ. Pollut*., 7, 179, 1974.
88. **National Academy of Sciences**, *The International Mussel Watch*, NAS, Washington, D.C., 1980.
89. **Roberts, J. R., Rodgers, D. W., Bailey, J. R., and Rorke, M. A.**, Polychlorinated biphenyls: biological Criteria for an Assessment of their Effects on Environmental Quality, Publ. No. NRCC 16077, National Research Council, Ottawa, Canada, 1978.
90. **Duinker, J. C., Hillebrand, M. T. J., Nolting, R. F., and Wellershaus, S.**, The River Vurde Å: processes affecting the behaviour of metals and organochlorines during estuarine mixing. *Neth. J. Sea Res*., 14, 237, 1980.
91. **Richardson, B. J. and Wold, J. S.**, Polychlorinated biphenyls in sediments and mussels from Port Phillip Bay, Victoria, Australia, in *Biogeochemistry of Ancient and Modern Environments*, Australian Academy of Science, Canberra, 1980, 423.
92. **Haque, R. and Schmedding, D.**, A method of measuring the water solubility of hydrophobic chemicals: solubility of five polychlorinated biphenyls. *Bull. Environ. Contam. Toxicol*., 14, 13, 1975.

MONS 006132

93. **Weß, K., Dure, G., and Quentin, K.-E.,** Wasserlöslichkeit von insektiziden chlorierten Kohlenwasserstoffen und polychlorierten Biphenylen im Hinblick auf eine Gewässerbelastung mit diesen Stoffen. *Z. Wasser Abwasser Forsch.*, 7, 169, 1974.
94. **Wellhöfer, P. R., Koniger, N., and Hutzinger, O.,** The solubility of polychlorinated biphenyls. *Analab Res. Notes*, 13, 14, 1973.
95. **Mackay, D. and Wolkoff, A. W.,** Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. *Environ. Sci. Technol.*, 7, 611, 1973.
96. **Haque, R., Schmedding, D. W., and Freed, V. H.,** Aqueous solubility, adsorption, and vapor behaviour of polychlorinated biphenyl Aroclor 1254. *Environ. Sci. Technol.*, 8, 139, 1974.
97. **Parris, D. F., Steen, W. C., and Baughman, G. L.,** Role of physicochemical properties of Aroclors 1016 and 1242 in determining their fate and transport in aquatic environments. *Chemosphere*, 4, 319, 1978.
98. **Lee, M. C., Chian, E. S. K., and Griffin, R. A.,** Solubility of polychlorinated biphenyls and capacitor fluid in water. *Water Res.*, 13, 1249, 1979.
99. **Haque, R. and Schmedding, D. W.,** Studies of adsorption of selected polychlorinated biphenyl isomers on several surfaces. *J. Environ. Sci. Health*, 2(B), 1976.
100. **Tanabe, S., Kawano, M., and Tatsukawa, R.,** Chlorinated hydrocarbons in the Antarctic, Western Pacific and Eastern Indian Oceans. *Trans. Tokyo Univ. Fish.*, No. 5, 97, 1982.
101. **Neely, W. B., Branson, D. R., and Blau, G. E.,** Partition coefficient to measure bioconcentration potential of organic chemicals in fish. *Environ. Sci. Technol.*, 8, 1113, 1974.
102. **Leo, A. J.,** Calculation of partition coefficients useful in the evaluation of the relative hazards of various chemicals in the environment, in *Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms*. Veith, G. D. and Konasewich, D. E., Eds., Great Lakes Research Advisory Board, Windsor, Ontario, Canada, 1975, 151.
103. **Chiou, C. T., Freed, V. H., Schmedding, D. W., and Kohnert, R. L.,** Partition coefficient and bioaccumulation of selected organic chemicals. *Environ. Sci. Technol.*, 11, 475, 1977.
104. **Neely, W. B.** Estimating rate constants for the uptake and clearance of chemicals by fish. *Environ. Sci. Technol.*, 13, 1506, 1979.
105. **Kenaga, E. E.,** Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical and chemical properties. *Environ. Sci. Technol.*, 14, 553, 1980.
106. **Mackay, D.,** Correlation of bioconcentration factors. *Environ. Sci. Technol.*, 16, 274, 1982.
107. **Ernst, W.,** Effects of pesticides and related organic compounds in the sea. *Helgol. Wiss. Meeresunters.*, 33, 301, 1980.
108. **Vreeland, V.,** Uptake of chlorobiphenyls by oysters. *Environ. Pollut.*, 6, 135, 1974.
109. **Metcalf, R. L., Sanborn, J. R., Lu, P.-Y., and Nye, D.,** Laboratory model ecosystem studies of the degradation and fate of radiolabelled tri-, tetra-, and pentachlorobiphenyl compared with DDE. *Arch. Environ. Contam. Toxicol.*, 3, 151, 1975.
110. **Ernst, W.,** Determination of the bioconcentration potential of marine organisms — a steady state approach. I. Bioconcentration data for seven chlorinated pesticides in mussels (*Mytilus edulis*) and their relation to solubility data. *Chemosphere*, 6, 731, 1977.
111. **Butler, P. A.,** Influence of pesticides on marine ecosystems. *Proc. R. Soc. London Ser. B*, 177, 321, 1971.
112. **Mason, J. W. and Rowe, D. R.,** The accumulation and loss of dieldrin and endrin in the eastern oyster. *Arch. Environ. Contam. Toxicol.*, 4, 349, 1976.
113. **Ernst, W.,** Factors affecting the evaluation of chemicals in laboratory experiments using marine organisms. *Ecotoxicol. Environ. Safety*, 3, 90, 1979.
114. **Biggs, D. C., Powers, C. D., Rowland, R. G., O'Connors, H. B., Jr., and Wurster, C. F.,** Uptake of polychlorinated biphenyls by natural phytoplankton assemblages: field and laboratory determination of ^{14}C-PCB partition-water index of sorption. *Environ. Pollut. Ser. A*, 22, 101, 1980.
115. **Wang, K., Roll, S., and Korte, F.,** Uptake and bioaccumulation of three PCBs by *Chlorella fusca*. *Chemosphere*, 11, 525, 1982.
116. **Harding, L. W., Jr. and Phillips, J. H., Jr.,** Polychlorinated biphenyl (PCB) effects on marine phytoplankton photosynthesis and cell division. *Mar. Biol.*, 49, 93, 1978.
117. **Mosser, J. L., Fisher, N. S., Teng, T.-C., and Wurster, C. F.,** Polychlorinated biphenyls: toxicity to certain phytoplankters. *Science*, 175, 191, 1972.
118. **Mosser, J. L., Fisher, N. S., and Wurster, C. F.,** Polychlorinated biphenyls and DDT alter species composition in mixed cultures of algae. *Science*, 176, 533, 1972.
119. **Fisher, N. S. and Wurster, C. F.,** Individual and combined effects of temperature and polychlorinated biphenyls on the growth of three species of phytoplankton. *Environ. Pollut.*, 5, 205, 1973.
120. **Fisher, N. S., Grahame, L. B., Carpenter, E. J., and Wurster, C. F.,** Geographic differences in phytoplankton sensitivity to PCBs. *Nature (London)*, 241, 548, 1973.
121. **Moore, S. A. and Harrison, R. C.,** Effects of polychlorinated biphenyl on marine phytoplankton communities. *Nature (London)*, 240, 356, 1972.

MONS 006133

122. **Moore, S. A. and Harriss, R. C.**, Differential sensitivity to PCB by phytoplankton. *Mar. Pollut. Bull.*, 5, 174, 1974.
123. **Menzel, D. W., Anderson, J., and Randtke, A.**, Marine phytoplankton vary in their response to chlorinated hydrocarbons. *Science*, 167, 1724, 1970.
124. **Parker, J. G. and Wilson, F.**, Incidence of polychlorinated biphenyls in Clyde seaweed. *Mar. Pollut. Bull.*, 6, 46, 1975.
125. **Amico, V., Oriente, G., Piattelli, M., and Tringali, C.**, Concentrations of PCBs, BHCs and DDTs residues in seaweeds of the east coast of Sicily. *Mar. Pollut. Bull.*, 10, 177, 1979.
126. **Mrenak, E., Jr., Seneca, E. D., and Hobbs, L.**, Polychlorinated biphenyl uptake and translation by *Spartina alterniflora* Loisel. *Water Air Soil Pollut.*, 17, 3, 1982.
127. **Sanders, H. O. and Chandler, J. H.**, Biological magnification of a polychlorinated biphenyl (Aroclor 1254) from water by aquatic invertebrates. *Bull. Environ. Contam. Toxicol.*, 7, 257, 1972.
128. **Courtney, W. A. M. and Denton, G. R. W.**, Persistence of polychlorinated biphenyls in the hard-clam (*Mercenaria mercenaria*) and the effect upon the distribution of these pollutants in the estuarine environment. *Environ. Pollut.*, 10, 55, 1976.
129. **Denton, G. R. W.**, The Uptake and Elimination of Polychlorinated Biphenyls (PCBs) in the Hard-Shell Clam *Mercenaria mercenaria*. Ph.D. thesis, University of London, 1974.
130. **Deubert, K. H., Rule, P., and Corte-Real, I.**, PCB residues in *Mercenaria mercenaria* from New Bedford Harbor, 1978. *Bull. Environ. Contam. Toxicol.*, 27, 683, 1981.
131. **Langston, W. J.**, Accumulation of polychlorinated biphenyls in the cockle *Cerastoderma edule* and the tellin *Macoma balthica*. *Mar. Biol.*, 45, 265, 1978.
132. **Langston, W. J.**, Persistence of polychlorinated biphenyls in marine bivalves. *Mar. Biol.*, 46, 35, 1978.
133. **Nimmo, D. R., Hansen, D. J., Couch, J. A., Cooley, N. R., Parrish, P. R., and Lowe, J. I.**, Toxicity of Aroclor 1254 and its physiological activity in several estuarine organisms. *Arch. Environ. Contam. Toxicol.*, 3, 22, 1975.
134. **Sanborn, J. R., Childers, W. F., and Metcalf, R. L.**, Uptake of three polychlorinated biphenyls, DDT, and DDE by the green sunfish, *Lepomis cyanellus* Raf., *Bull. Environ. Contam. Toxicol.*, 13, 209, 1975.
135. **Hattula, M. L. and Karlog, O.**, Absorption and elimination of polychlorinated biphenyls (PCB) in goldfish. *Acta Pharmacol. Toxicol.*, 32, 237, 1973.
136. **Lieb, A. J., Bills, D. D., and Sheshubor, E. O.**, Accumulation of dietary polychlorinated biphenyls (Aroclor 1254) by rainbow trout (*Salmo gairdneri*). *Agric. Food Chem.*, 22, 638, 1974.
137. **DeFoe, D. L., Veith, G. D., and Carlson, R. W.**, Effects of Aroclor 1248 and 1260 on the fathead minnow (*Pimephales promelas*). *J. Fish. Res. Bd. Can.*, 35, 997, 1978.
138. **Bengtsson, B.-E.**, Long-term effects of PCB (Clophen A50) on growth, reproduction and swimming performance in the minnow, *Phoxinus phoxinus*. *Water Res.*, 14, 681, 1980.
139. **Addison, R. F., Zinck, M. E., and Willis, D. E.**, Time- and dose-dependence of hepatic mixed function oxidase activity in brook trout *Salvelinus fontinalis* on polychlorinated biphenyl residues: implications for biological effects monitoring. *Environ. Pollut. Ser. A*, 25, 211, 1981.
140. **Bruggeman, W. A., Martron, L. B. J. M., Kooiman, D., and Hutzinger, O.**, Accumulation and elimination kinetics of di-, tri- and tetrachlorobiphenyls by goldfish after dietary and aqueous exposure. *Chemosphere*, 10, 811, 1981.
141. **Tanabe, S., Maruyama, K., and Tatsukawa, R.**, Absorption efficiency and biological half-life of individual chlorobiphenyls in carp (*Cyprinus carpio*) orally exposed to Kanechlor products. *Agric. Biol. Chem.*, 46, 891, 1982.
142. **Stalling, D. L. and Mayer, F. L., Jr.**, Toxicities of PCB to fish and environmental residues in fish. *Environ. Health Perspect.*, 1, 159, 1972.
143. **Hansen, L. G., Wichhorst, W. B., and Simon, J.**, Effects of dietary Aroclor 1242 on channel catfish (*Ictalurus punctatus*) and the selective accumulation of PCB components. *J. Fish. Res. Bd. Can.*, 33, 1343, 1976.
144. **Sparling, J. and Safe, S.**, The effects of *ortho* chloro substituents on the retention of PCB isomers in rat, rabbit, Japanese quail, guinea pig and trout. *Toxicol. Lett.*, 7, 23, 1980.
145. **Holden, A. V.**, Monitoring organochlorine contamination of the marine environment by the analysis of residues in seals, in *Marine Pollution and Sea Life*. Ruivo, M., Ed., Fishing News (Books) Ltd., London, 1972, 266.
146. **Addison, R. F., Kerr, S. R., Dale, J., and Sergeant, D. E.**, Variation of organochlorine residue levels with age in Gulf of St. Lawrence harp seals (*Pagophilus groenlandicus*). *J. Fish. Res. Bd. Can.*, 30, 595, 1973.
147. **Jansson, B., Jonsson, S., Olsson, M., Ramberg, L., Sundström, G., and Vas, E.**, Identification by GC-MS of phenolic metabolites of PCB and *p,p'* DDE isolated from Baltic guillemot and seal. *Ambio*, 4, 93, 1975.
148. **Duinker, J. C., Hillebrand, M. T. J., and Nolting, R. F.**, Organochlorines and metals in harbour seals (Dutch Wadden Sea). *Mar. Pollut. Bull.*, 10, 360, 1979.

MONS 006134

149. Reijnders, P. J. H., Organochlorine and heavy metal residues in harbour seals from the Wadden Sea and their possible effects on reproduction. *Neth. J. Sea Res.*. 14, 30. 1980.
150. Tanabe, S., Tatsukawa, R., Tanaka, H., Maruyama, K., Miyazaki, N., and Fujiyama, T., Distribution and total burdens of chlorinated hydrocarbons in bodies of striped dolphins (*Stenella coeruleoalba*). *Agric. Biol. Chem.*, 45, 2569, 1981.
151. Tanabe, S., Tatsukawa, R., Maruyama, K., and Miyazaki, N., Transplacental transfer of PCBs and chlorinated hydrocarbon pesticides from the pregnant striped dolphin (*Stenella coeruleoalba*) to her fetus, *Agric. Biol. Chem.*, 46, 1249, 1982.
152. Shaw, G. R. and Connell, D. W., Relationships between steric factors and bioconcentration of polychlorinated biphenyls (PCB's) by the sea mullet (*Mugil cephalus* Linnaeus), *Chemosphere*, 9, 731, 1980.
153. Shaw, G. R. and Connell, D. W., Factors influencing concentrations of polychlorinated biphenyls in organisms from an estuarine ecosystem, *Aust. J. Mar. Freshwater Res.*, 33, 1057, 1982.
154. Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G., DDT and PCB in marine animals from Swedish waters, *Nature (London)*, 224, 247, 1969.
155. Ten Berge, W. F. and Hillebrand, M., Organochlorine compounds in several marine organisms from the North Sea and the Dutch Wadden Sea, *Neth. J. Sea Res.*, 8, 361, 1974.
156. Young, D. R. and Mearns, A. J., Pollutant flow through food webs, *Southern California Coastal Water Research Project, Annual Report 1978*, 1978, 185.
157. Fowler, S. W. and Elder, D. L., PCB and DDT residues in a Mediterranean pelagic food chain, *Bull. Environ. Contam. Toxicol.*, 19, 244, 1978.
158. Södergren, A., Svensson, B., and Ulfstrand, S., DDT and PCB in south Swedish streams, *Environ. Pollut.*, 3, 25, 1972.
159. Hamelink, J. L., Waybrant, R. C., and Ball, R. C., A proposal: exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments, *Trans. Am. Fish. Soc.*, 100, 207, 1971.
160. Sears, E. D. and Theilacker, G. H., Transfer of the chlorinated hydrocarbon PCB in a laboratory marine food chain, *Mar. Biol.*, 40, 317, 1977.
161. Thomann, R. V., Equilibrium model of fate of microcontaminants in diverse aquatic food chains, *Can. J. Fish. Aquat. Sci.*, 38, 280, 1981.
162. Duffy, J. R. and O'Connell, D., DDT residues and metabolites in Canadian Atlantic coast fish, *J. Fish. Res. Bd. Can.*, 25, 189, 1968.
163. Reinert, R. E., Pesticide concentrations in Great Lakes fish, *Pest. Monit. J.*, 3, 233, 1970.
164. Hansen, M. E., Grotheer, Y. A., Applegate, R. L., and Fox, A. C., Ecological distribution of pesticides in Lake Poinsett, South Dakota, *Trans. Am. Fish. Soc.*, 99, 496, 1970.
165. Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G., DDT and PCB in herring and cod from the Baltic, the Kattegat and the Skagerrak, *Ambio Spec. Rep.*, No. 1, 71, 1972.
166. Hattula, M. L., Jaanukainen, J., Särkkä, J., and Paasivirta, J., A five-year monitoring study of the chlorinated hydrocarbons in the fish of a Finnish Lake ecosystem, *Environ. Pollut.*, 15, 121, 1978.
167. Stout, V. F., Organochlorine residues in fishes from the Northwest Atlantic Ocean and Gulf of Mexico, *Fish. Bull. U.S.*, 78, 51, 1980.
168. Amico, V., Impellitteri, G., Ortenzo, G., Piattelli, M., Scinto, S., and Tringali, C., Levels of chlorinated hydrocarbons in marine animals from the central Mediterranean, *Mar. Pollut. Bull.*, 10, 282, 1979.
169. Holden, A. V., Organochlorine insecticide residues in salmonid fish, *J. Appl. Ecol., Suppl.* 3, 45, 1966.
170. Kolbe, J. R. M. and Frank, R., Organochlorine residues, mercury, copper and cadmium in yellow perch, white bass and small-mouth bass, Long Point Bay, Lake Erie, *Trans. Am. Fish. Soc.*, 103, 577, 1974.
171. Linko, R. R., Kallaranta, J., Rantamäki, P., and Kronan, L., Occurrence of DDT and PCB compounds in Baltic herring and pike from the Turku archipelago, *Environ. Pollut.*, 7, 193, 1974.
172. Bulkley, R. V., Keling, R. L., and Shannon, L. R., Sex-related factors associated with dieldrin concentrations in muscle tissue of channel catfish *Ictalurus punctatus*, *Trans. Am. Fish. Soc.*, 105, 301, 1976.
173. Olsson, M., Jensen, S., and Reutergård, L., Seasonal variation of PCB levels in fish — an important factor in planning aquatic monitoring programmes, *Ambio*, 7, 66, 1978.
174. Armstrong, F. A. J. and Lutz, A., Lake Superior 1974: PCB, Chlorinated Insecticides, Heavy Metals and Radioactivity in Offshore Fish, Tech. Rep. no. 695, Fisheries and Marine Service, Fisheries Research Board of Canada, Ottawa, 1977.
175. Marchand, M., Van, D., and Deurzana, E. K., Levels of PCBs and DDTs in mussels from the N.W. Mediterranean, *Mar. Pollut. Bull.*, 7, 65, 1976.
176. Risebrough, R. W., De Lappe, B. W., and Schmidt, T. T., Bioaccumulation factors of chlorinated hydrocarbons between mussels and seawater, *Mar. Pollut. Bull.*, 7, 225, 1976.
177. Cowan, A. A., Organochlorine compounds in mussels from Scottish coastal waters, *Environ. Pollut. Ser. B*, 2, 129, 1981.
178. Seed, R., *Reproduction in Mytilus (Mollusca: Bivalvia) in European Waters*, Pubblicazioni della Stazione Zoologica di Napoli, Milan, Italy, 1975.

MONS 006135

179. **Seed, R.**, Ecology, in *Marine Mussels: Their Ecology and Physiology*. Bayne, B. L., Ed., Cambridge University Press, Cambridge, England, 1976, 13.
180. **Kaiser, K. L. E.**, Early trend determination of organochlorine contamination from residue ratios in the sea lamprey (*Petromyzon marinus*) and its lake whitefish (*Coregonus clupeaformis*) host. *Can. J. Fish. Aquat. Sci.*, 39, 571, 1982.
181. **Roberts, J. R., de Freitas, S. W., and Gidney, M. A. J.**, Influence of lipid pool size on bioaccumulation of the insecticide Chlordane by northern redhorse suckers (*Moxostoma macrolepidotum*). *J. Fish. Res. Bd. Can.*, 34, 89, 1977.
182. **Stegeman, J. J. and Teal, J. M.**, Accumulation, release and retention of petroleum hydrocarbons by the oyster *Crassostrea virginica*. *Mar. Biol.*, 22, 37, 1973.
183. **Stegeman, J. J.**, Hydrocarbons in shellfish chronically exposed to low levels of fuel oil, in *Pollution and Physiology of Marine Organisms*. Vernberg, F. J. and Vernberg, W. B., Eds., Academic Press, New York, 1974, 329.
184. **Addison, R. F. and Smith, T. G.**, Organochlorine residue levels in Arctic ringed seals: variation with age and sex. *Oikos*, 25, 335, 1974.
185. **Drescher, H. E., Harms, U., and Huschenbeth, E.**, Organochlorines and heavy metals in the harbour seal *Phoca vitulina* from the German North Sea coast. *Mar. Biol.*, 41, 99, 1977.
186. **Nimmo, D. R., Wilson, A. J., and Blackman, R. R.**, Localization of DDT in the body organs of pink and white shrimp, *Bull. Environ. Contam. Toxicol.*, 5, 333, 1970.
187. **Nimmo, D. R., Blackman, R. R., Wilson, A. J., and Forester, J.**, Toxicity and distribution of Aroclor 1254 in the pink shrimp *Penaeus duorarum*. *Mar. Biol.*, 11, 191, 1971.
188. **Ernst, W., Goerke, H., Ederer, G., and Schaefer, R. G.**, Residues of chlorinated hydrocarbons in marine organisms in relation to size and ecological parameters. I. PCB, DDT, DDE, and DDD in fishes and molluscs from the English Channel. *Bull. Environ. Contam. Toxicol.*, 15, 55, 1976.
189. **Yoshida, T., Takashima, F., and Watanabe, T.**, Distribution of (14C) PCBs in carp, *Ambio*, 2, 111, 1973.
190. **Van den Broek, W. L. F.**, Seasonal levels of chlorinated hydrocarbons and heavy metals in fish and brown shrimps from the Medway Estuary, Kent. *Environ. Pollut.*, 19, 21, 1979.
191. **Teal, P. T. P. and McCart, P. J.**, Chlorinated hydrocarbon residues and heavy metals in several fish species from the Cold Lake area in Alberta, Canada. *Int. J. Environ. Anal. Chem.*, 10, 277, 1981.
192. **Gaskin, D. E., Holdrinet, M., and Frank, R.**, Organochlorine pesticide residues in harbour porpoises from the Bay of Fundy region, *Nature (London)*, 233, 499, 1971.
193. **Frank, R., Ronald, K., and Braun, H. E.**, Organochlorine residues in harp seals (*Pagophilus groenlandicus*) caught in Eastern Canadian waters, *J. Fish. Res. Bd. Can.*, 30, 1053, 1973.
194. **DeLong, R. L., Gilmartin, W. G., and Simpson, J. G.**, Premature births in California sea lions: association with high organochlorine pollutant residue levels. *Science*, 181, 1168, 1973.
195. **Gaskin, D. E., Frank, R., Holdrinet, M., Ishida, K., Watson, C. J., and Smith, M.**, Mercury, DDT, and PCB in harbour seals (*Phoca vitulina*) from the Bay of Fundy and Gulf of Maine, *J. Fish. Res. Bd. Can.*, 30, 471, 1973.
196. **Buhler, D. R., Claeys, R. R., and Mate, B. R.**, Heavy metal and chlorinated hydrocarbon residues in California sea lions (*Zalophus californianus californianus*), *J. Fish. Res. Bd. Can.*, 32, 2391, 1975.
197. **Holden, A. V. and Marsden, K.**, Organochlorine pesticides in seals and porpoises, *Nature (London)*, 216, 1274, 1967.
198. **Le Boeuf, B. J. and Bonnell, M. L.**, DDT in California sea lions, *Nature (London)*, 234, 108, 1971.
199. **Holden, A. V.**, The accumulation of oceanic contaminants in marine mammals, *Rapp. P.-V. Reun. Cons. Int. Explor. Mer.*, 169, 353, 1975.
200. **Reinert, R. E. and Burgmann, H. L.**, Residues of DDT in lake trout (*Salvelinus namaycush*) and coho salmon (*Oncorhynchus kisutch*) from the Great Lakes, *J. Fish. Res. Bd. Can.*, 31, 191, 1974.
201. **Allison, D., Kallman, B. J., Cope, O. B., and Van Valin, C. C.**, Insecticides: effects on cutthroat trout of repeated exposure to DDT, *Science*, 142, 958, 1963.
202. **Anderson, R. B. and Pemberton, O. C.**, An analysis of variation of insecticide residues in landlocked Atlantic Salmon (*Salmo salar*), *J. Fish. Res. Bd. Can.*, 27, 1, 1970.
203. **Cahn, P. H., Pechenik, J., and Gaggino, W.**, PCB levels in certain organs of some feral fish from New York State, in *Physiological Responses of Marine Biota to Pollutants*, Vernberg, F. J., Calabrese, A., Thurberg, P., and Vernberg, W. B., Eds., Academic Press, New York, 1977, 51.
204. **Love, R. M.**, *The Chemical Biology of Fishes*, Academic Press, New York, 1970.
205. **Reinert, R. E.**, Insecticides and the Great Lakes, *Limnos*, 2, 4, 1969.
206. **Stout, V. F., Beinhold, F. L., and Hinds, C. R.**, DDT residue levels in some U.S. fishery products and some treatments in reducing them, in *Marine Pollution and Sea Life*, Ruivo, M., Ed., Fishing News (Books) Ltd., London, 1972, 550.
207. **McCrachan, W. E.**, Edible tissue sampling for fish contaminant analysis, paper presented at Int. Symp. PCBs in the Great Lakes, Michigan State University, Lansing, Mich., March 15, 1982.

MONS 006136

208. Rohrer, T. K., Hartig, J. H., and Forney, J. C., Organochlorine and Heavy Metal Residues in Coho and Chinook Salmon of the Great Lakes — 1980, Publ. No. 3730-0031, Michigan Dept. of Natural Resources, Detroit, 1981.

209. Butler, P. A., Childress, R., and Wilson, A. J., The association of DDT residues with losses in marine productivity, in *Marine Pollution and Sea Life*, Ruivo, M., Ed., Fishing News (Books) Ltd., London, 1972, 262.

210. Yamato, Y., Suzuki, M., and Akiyama, T., Persistence of BHC in river water in the Kitakyushu District, Japan, 1970—1974, *Bull. Environ. Contam. Toxicol.*, 14, 380, 1975.

211. Yamato, Y., Suzuki, M., Shimohara, K., and Akiyama, T., Behavior of HCH (1,2,3,4,5,6-hexachlorocyclohexane) residue in the aquatic environment, *Water Res.*, 14, 247, 1980.

212. Livingston, R. J., Thompson, N. P., and Meeter, D. A., Long-term variation of organochlorine residues and assemblages of epibenthic organisms in a shallow North Florida (USA) estuary, *Mar. Biol.*, 46, 355, 1978.

213. Duke, T. W., Lowe, J. I., and Wilson, A. J., Jr., A polychlorinated biphenyl (Aroclor 1254) in the water, sediment, and biota of Escambia Bay, Florida, *Bull. Environ. Contam. Toxicol.*, 5, 171, 1970.

214. Sprague, J. B. and Duffy, J. R., DDT residues in Canadian Atlantic fishes and shellfishes in 1967, *J. Fish. Res. Bd. Can.*, 28, 59, 1971.

215. Sheridan, P. F., Uptake, metabolism, and distribution of DDT in organs of the blue crab, *Callinectes sapidus*, *Chesapeake Sci.*, 16, 20, 1975.

216. Hueckenbeck, E. and Harms, U., On the accumulation of organochlorine pesticides, PCB and certain heavy metals in fish and shellfish from Thai coastal and inland waters, *Arch. Fischereiwiss.*, 26, 109, 1975.

217. Butler, P. A., The problem of pesticides in estuaries, in *A Symposium on Estuarine Fisheries*, *Trans. Am. Fish. Soc.*, Special Publ., 3, 110, 1966.

218. Lowe, J. I., Parrish, P. R., Patrick, J. M., Jr., and Forester, J., Effects of the polychlorinated biphenyl Aroclor 1254 on the American oyster *Crassostrea virginica*, *Mar. Biol.*, 17, 209, 1972.

219. Roberts, D., The assimilation and chronic effects of sublethal concentrations of endosulfan on condition and spawning in the common mussel *Mytilus edulis*, *Mar. Biol.*, 16, 119, 1972.

220. Lunsford, C. A. and Bloom, C. B., Annual cycle of Kepone residue and lipid content of the estuarine clam, *Rangia cuneata*, *Estuaries*, 5, 121, 1982.

221. Burdick, G. E., Harris, E. J., Dean, H. J., Walker, T. M., Skea, J., and Colby, D., The accumulation of DDT in lake trout and the effect on reproduction, *Trans. Am. Fish. Soc.*, 93, 127, 1964.

222. Grande, A. R., Taylor, W. J., and Park, D. F., The uptake and distribution of chlorinated residues by goldfish (*Carassius auratus*) fed a ^{14}C-dieldrin contaminated diet, *Trans. Am. Fish. Soc.*, 100, 215, 1971.

223. Ballschmiter, K., Buchert, H., Bihler, S., and Zell, M., Baseline studies of the global pollution. IV. The pattern of pollution by organo-chlorine compounds in the North Atlantic as accumulated by fish, *Fresenius' Z. Anal. Chem.*, 308, 323, 1981.

224. Anderson, R. B. and Everhart, W. H., Concentrations of DDT in landlocked salmon (*Salmo salar*) at Sebago Lake, Maine, *Trans. Am. Fish. Soc.*, 95, 160, 1966.

225. Anderson, R. B. and Fenderson, O. C., An analysis of variation of insecticide residues in landlocked Atlantic salmon (*Salmo salar*), *J. Fish. Res. Bd. Can.*, 27, 1, 1970.

226. Niimi, A. J. and Cho, C. Y., Elimination of hexachlorobenzene (HCB) by rainbow trout (*Salmo gairdneri*), and an examination of its kinetics in Lake Ontario salmonids, *Can. J. Fish. Aquat. Sci.*, 38, 1350, 1981.

227. Neff, J. M. and Giam, C. S., Effects of Aroclor 1016 and Halowax 1099 on juvenile horseshoe crabs *Limulus polyphemus*, in *Physiological Responses of Marine Biota to Pollutants*, Vernberg, F. J., Calabrese, A., Thurberg, P., and Vernberg, W. B., Eds., Academic Press, New York, 1977, 21.

228. Duke, T. W. and Dumas, D. P., Implications of pesticide residues in the coastal environment, in *Pollution and Physiology of Marine Organisms*, Vernberg, F. J. and Vernberg, W. B., Eds., Academic Press, New York, 1974, 137.

229. Bengtsson, B.-E., Increased growth in minnows exposed to PCBs, *Ambio*, 8, 169, 1979.

230. Mauck, W. L., Mehrle, P. M., and Mayer, F. L., Effects of the polychlorinated biphenyl Aroclor 1254 on growth, survival, and bone development in brook trout (*Salvelinus fontinalis*), *J. Fish. Res. Bd. Can.*, 35, 1084, 1978.

231. Mehrle, M. T. and Johnson, H. E., Acute toxicities of a polychlorinated biphenyl (PCB) and DDT alone and in combination to early life stages of coho salmon (*Oncorhynchus kisutch*), *J. Fish. Res. Bd. Can.*, 31, 1543, 1974.

232. Gregor, E. H., Jr., Hruby, T., and Kerrick, N. L., Sublethal effects of structurally related tetrachloro-, pentachloro-, and hexachlorobiphenyl on juvenile coho salmon, *Environ. Sci. Technol.*, 10, 1033, 1976.

233. Gregor, E. H., Jr., Kerrick, N. L., Davidson, A. I., and Hruby, T., Accumulation of 3,4,3',4'-tetrachlorobiphenyl and 2,4,5,2',4',5'- and 2,4,6,2',4',6'-hexachlorobiphenyl in juvenile coho salmon, *Environ. Sci. Technol.*, 9, 121, 1975.

MONS 006137

234. **Freeman, H. C. and Sangalang, G.**, Changes in steroid hormone metabolism as a sensitive method of monitoring pollutants and contaminants, in Proceedings of the 3rd Aquatic Toxicity Workshop, Halifax, Nova Scotia, November 1976, 123.

235. **Freeman, H. C., Uthe, J. F., and Sangalang, G.**, The use of steroid hormone metabolism studies in assessing the sublethal effects of marine pollution, *Rapp. P.-V. Reun. Cons. Int. Explor. Mer.*, 179, 16, 1980.

236. **Robinson, J., Richardson, A., Crabtree, A. N., Coulson, J. C., and Potts, G. R.**, Organochlorine residues in marine organisms, *Nature (London)*, 214, 1307, 1967.

237. **Smith, R. M. and Cole, C. F.**, Chlorinated hydrocarbon insecticide residues in winter flounder, *Pseudopleuronectes americanus*, from the Weweantic River estuary, Massachusetts, *J. Fish. Res. Bd. Can.*, 27, 2374, 1970.

238. **Murphy, P. G.**, Effects of salinity on uptake of DDT, DDE and DDD by fish, *Bull. Environ. Contam. Toxicol.*, 5, 404, 1970.

239. **Murphy, P. G. and Murphy, J. V.**, Correlations between respiration and direct uptake of DDT in the mosquitofish *Gambusia affinis*, *Bull. Environ. Contam. Toxicol.*, 6, 144, 1971.

240. **Reinert, R. E., Stone, L. J., and Willford, W. A.**, Effect of temperature on accumulation of methylmercuric chloride and *p,p'* DDT by rainbow trout (*Salmo gairdneri*), *J. Fish. Res. Bd. Can.*, 31, 1649, 1974.

241. **Powell, J. H. and Fielder, D. R.**, Temperature and accumulation of DDT by sea mullet (*Mugil cephalus* L.), *Mar. Pollut. Bull.*, 14, 17, 1983.

242. **Edgren, M., Olsson, M., and Ronberg, L.**, Preliminary results on uptake and elimination at different temperatures of *p,p'* DDT and two chlorobiphenyls in perch from brackish water, *Ambio*, 8, 270, 1979.

243. **Biggar, J. W., Dawson, L. D., and Riggs, R. L.**, Soil Interaction with Organically Polluted Water, Summary report, Dept. of Water Sciences and Engineering, University of California, Davis, 1966.

244. **Goldberg, E. D., Bowen, V. T., Farrington, J. W., Harvey, G., Martin, J. H., Parker, P. L., Risebrough, R. W., Robertson, W., Schneider, E., and Gamble, E.**, The mussel watch, *Environ. Conserv.*, 5, 101, 1978.

245. **Farrington, J. W., Risebrough, R. W., Parker, P. L., Davis, A. C., de Lappe, B., Winters, J. K., Boatwright, D., and Frew, N. M.**, Hydrocarbons, polychlorinated biphenyls, and DDE in mussels and oysters from the U.S. coast, 1976—1978, — the mussel watch, Tech. Rep. WHOI-82-42, Woods Hole Oceanographic Institution, Woods Hole, Mass., 1982.

246. **Brown, D. A., Perkins, E. M., Jenkins, K. D., Oshida, P. S., Bay, S. M., Allsbrn, J. F., and Raco, V.**, Seasonal changes in mussels, *Southern California Coastal Water Research Project, Biennial Report 1981—1982*, 1982, 179.

247. **Fowler, S. W.**, Biological transfer and transport processes, in *Pollutant Transfer and Transport in the Sea*, Vol. 2, Kullenberg, G., Ed., CRC Press, Boca Raton, Fla., 1982, 1.

248. **Cox, J. L., Uptake, assimilation and loss of DDT residues by *Euphausia pacifica*, a euphausiid shrimp**, *Fish. Bull. U.S.*, 69, 627, 1971.

249. **Harding, G. C. H. and Vass, W. P.**, Uptake from seawater and clearance of *p,p'* DDT by marine planktonic crustacea, *J. Fish. Res. Bd. Can.*, 36, 247, 1979.

250. **Widdish, D. J. and Zitko, V.**, Uptake of polychlorinated biphenyls from sea water by *Gammarus oceanicus*, *Mar. Biol.*, 9, 213, 1971.

251. **Schneider, R. G., Ernst, W., Goerke, H., and Eder, G.**, Residues of chlorinated hydrocarbons in North Sea animals in relation to biological parameters, *Ber. Dtsch. Wiss. Komm. Meeresforsch.*, 24, 225, 1976.

252. **Banks, C. A., Serum, J. W., Youngs, W. D., and Link, D. J.**, Polychlorinated biphenyl residues: accumulation in Cayuga Lake trout with age, *Science*, 177, 1191, 1972.

253. **Youngs, W. D., Gutenmann, W. H., and Link, D. J.**, Residues of DDT in lake trout as a function of age, *Environ. Sci. Technol.*, 6, 451, 1972.

254. **Wszolek, P. C., Link, D. J., Weeks, T., and Youngs, W. D.**, Persistence of polychlorinated biphenyls and 1,1-dichloro-2,2-bis (p-chlorophenyl) ethylene (*p,p'*DDE) with age in lake trout after 8 years, *Environ. Sci. Technol.*, 13, 1269, 1979.

255. **Nihai, A. J.**, Gross growth efficiency of fish (K$_1$) based on field observations of annual growth and kinetics of persistent environmental contaminants, *Can. J. Fish. Aquat. Sci.*, 38, 250, 1981.

256. **Loehmoyer, P. H. and Phillips, A. M.**, Fat content of the flesh of steelhead and lake trout from Lake Superior, *Trans. Am. Fish. Soc.*, 94, 62, 1965.

257. **Zabik, M. E., Merrill, C., and Zabik, M. J.**, Predictability of PCBs in carp harvested in Saginaw Bay, Lake Huron, *Bull. Environ. Contam. Toxicol.*, 28, 592, 1982.

258. **Norstrom, R. J., McKinnon, A. E., and deFreitas, A. S. W.**, A bioenergetics-based model for pollutant accumulation by fish. Simulation of PCB and methylmercury residue levels in Ottawa River yellow perch (*Perca flavescens*), *J. Fish. Res. Bd. Can.*, 33, 248, 1976.

259. **Hansen, D. J., Schimmel, S. C., and Forester, J.**, Effects of Aroclor 1016 on embryos, fry, juveniles and adults of threespined stickleback (*Cyprinodon variegatus*), *Trans. Am. Fish. Soc.*, 104, 584, 1975.

MONS 006138

260. Zitko, V., Polychlorinated biphenyls and organochlorine pesticides in some freshwater and marine fishes, *Bull. Environ. Contam. Toxicol.*, 6, 464, 1971.
261. Olsson, M. and Jensen, S., Pike as the Test Organism for Mercury, DDT and PCB Pollution. A Study of the Contamination in the Stockholm Archipelago, Rep. No. 54, Freshwater Instit. Drottningholm, Sweden, 1975, 83.
262. Voutsinou-Taliadouri, F. and Setsmadjis, J., Influence of metropolitan waste on the concentration of chlorinated hydrocarbons and metals in striped mullet, *Mar. Pollut. Bull.*, 13, 266, 1982.
263. Klauda, R. J., Peck, T. H., and Rice, G. K., Accumulation of polychlorinated biphenyls in Atlantic tomcod (*Microgadus tomcod*) collected from the Hudson River estuary, New York, *Bull. Environ. Contam. Toxicol.*, 27, 829, 1981.
264. Young, D. R., Heesen, T. C., and McDermott, D. J., An offshore biomonitoring system for chlorinated hydrocarbons, *Mar. Pollut. Bull.*, 7, 156, 1976.
265. Vernberg, F. J., Garson, M. S., and Savory, A., Survival of larval and adult fiddler crabs exposed to Aroclor 1016 and 1254 and different temperature — salinity combinations, in *Physiological Responses of Marine Biota to Pollutants*, Vernberg, F. J., Calabrese, A., Thurberg, P., and Vernberg, W. B., Eds., Academic Press, New York, 1977, 37.
266. Bender, M. E., Huggett, R. J., and Hargis, W. J., Jr., Kepone residues in Chesapeake Bay biota, in Proceedings of the Kepone Seminar II, U.S. Environmental Protection Agency, Washington, D.C., 1977, 14.
267. Roberts, M. H., Jr., Kepone distribution in selected tissues of blue crabs, *Callinectes sapidus*, collected from the James River and lower Chesapeake Bay, *Estuaries*, 4, 313, 1981.
268. Forrester, C. R., Ketchen, K. S., and Wong, C. C., Mercury content of spiny dogfish (*Squalus acanthias*) in the Strait of Georgia, British Columbia, *J. Fish. Res. Bd. Can.*, 29, 1487, 1972.
269. Walker, T. I., Effects of species, sex, length and locality on the mercury content of school shark *Galeorhinus australis* (Macleay) and gummy shark *Mustelus antarcticus* Guenther from south-eastern Australian waters, *Aust. J. Mar. Freshwater Res.*, 27, 603, 1976.
270. Butler, P. A. and Schutzmann, R. L., Bioaccumulation of DDT and PCB in tissues of marine fishes, in *Aquatic Toxicology*, Marking, L. L. and Kimerle, R. A., Eds., American Society for Testing and Materials, Philadelphia, 1979, 212.
271. Addison, R. F. and Brodie, P. F., Organochlorine residues in maternal blubber, milk, and pup blubber from grey seals (*Halichoerus grypus*) from Sable Island, Nova Scotia, *J. Fish. Res. Bd. Can.*, 34, 937, 1977.
272. Helle, E., Olsson, M., and Jensen, S., DDT and PCB levels and reproduction in ringed seal from the Bothnian Bay, *Ambio*, 5, 188, 1976.
273. Helle, E., Olsson, M., and Jensen, S., PCB levels correlated with pathological changes in seal uteri, *Ambio*, 5, 261, 1976.
274. Williams, P. M. and Robertson, K. Y., Chlorinated hydrocarbons in the sea surface and subsurface waters at nearshore stations and in the North Central Pacific gyre, *Fish. Bull. U.S.*, 73, 645, 1975.
275. Neu-Ritter, G., Wurster, C. F., and Rowland, R. G., Partitioning of (^{14}C) PCB between water and particulates with various organic contents, *Water Res.*, 16, 1615, 1982.
276. Nimmo, D. R., Forester, J., Heitmuller, P. T., and Cook, G. H., Accumulation of Aroclor 1254 in grass shrimp (*Palaemonetes pugio*) in laboratory and field exposures, *Bull. Environ. Contam. Toxicol.*, 11, 303, 1974.
277. Soulye, J. G., Hunsaiberg, R. J., and Mac, M. J., Accumulation by fish of contaminants released from dredged sediments, *Environ. Sci. Technol.*, 16, 459, 1982.
278. Shaw, G. W. and Connell, D. W., personal communication.
279. Brandes, C. H. and Dietrich, R., On the distribution of fat in the body of herrings, *Veroff. Inst. Meeresforsch. Bremerhaven*, 2, 109, 1953.

MONS 006139

INDEX

A

Abnormal embryos, 37
Abortions, 108, 110, 115
Abramis brama, 165
Absidia pseudocylindrospora, 69
Absorption of PCBs from atmosphere, 2
Acanthocardia tuberculata, 163
Acarina, 142
Accumulation of PCBs, see also specific topics
  biological changes influencing, 157—160
  processes involved in, 10
Acetobacter, 90
Acetyl CoA carboxylase, 53
Achromobacter, 64, 66—67, 90, 94
Acinetobacter spp., 64, 90, 92—96
Acute toxicity of PCBs, 22, 32, 34—35
Acyl CoA:1-acyl-sn-glycerol-3-phosphorylcholine acyltransferase, 54
Acyl CoA:1,2-diacyl-sn-glycerol acyltransferase, 54
Acyl CoA:sn-glycerol-3-phosphate acyltransferase, 54
Adipose tissue, 57
ADP, 51—52
Adrenal gland, 115
Adsorption potential, 72
Adult minnows, 81
Aedes aegypti, 79
Aerial transport of PCBs, 129, 131, 138
Aeromonas spp., 64, 90
Age of bioindicator organisms, 136, 162—166, 169
Albumin, 57
Alcaligenes
  denitrificans, 68, 91
  odorans, 68, 91
  spp., 68, 90, 92, 94, 96
Algae, 4—6
Amenorrhea, 115
American kestrel, 22, 23, 25—27, 40
δ-Aminolevulinic acid dehydrase, 42
δ-Aminolevulinic acid synthetase, 42
Aminopyrine *N*-demethylase, 56
AMP, 51
Analysis of PCBs, 128, 131, 137, 149
Anas platyrhynchos, 33
Aniline hydroxylase, 56
Anovulation, 115
Antifouling paints, 129
Aquatic invertebrates, 70—74
Arene oxide, 77
Arenicola marina, 71, 77
Aroclor, 50
Aroclor 1016, 75
Aroclor 1232, 55
Aroclor 1242, 137
Aroclor 1254, 55, 67—68, 70, 72, 74
  metabolism, 76
  molecular composition, 137
Arthrobacter, 96—97
Aspergillus flavus, 69, 91
Assimilation efficiencies of ingested organochlorines, 15—17
Atlantic menhaden, 16
Atlantic zooplankton, 72—73
Atmosphere, absorption of PCBs from, 2
ATP, 51—52
ATPase inhibition, 20—21

B

Bacillus spp., 64, 66, 79, 90
Bacteria, 64—69, 77, 79, 89—100
  biodegradability of PCBs, 91—93
  biodegradation of commercial PCBs, 94—96
  microbial metabolism of PCBs, 93—94
  total degradation of PCBs and plasmids, 96—97
Bans on PCBs, 129
Barn owl, 40
Beagles, 105
Beans, 3
Behavior of bioindicator organisms, 137—151
Behavioral abnormalities, 39, 43, 102
Beijerinckia, 93
Benzpyrene hydroxylase, 56
BHC, 157
Bioaccumulation, 64—69, 73, 128, 139, 152, 169
Bioaccumulation factor, 81
Bioavailability, 132, 135—136
Biochemical systems, 49—61
  chemical properties of PCBs, 50
  fatty acids, 52—53
  gluconeogenesis, 50—51
  glycerides, 52—53
  glycolysis, 50—51
  lipoproteins, 55—56
  microsomal oxidation, 50, 56
  oxidative phosphorylation, 50—52
  phospholipids, 50, 53—55
  proposed mechanisms, 56—58
  sterols, 50, 55—56
Bioconcentration, aquatic invertebrates, 70—74
Bioconcentration factor, 75, 81—82
Bioconcentration potential, 139
Biodegradability of PCBs, 91—96
Bioindicator organisms, 127—181
  advantages of use of, 136
  age, 136, 162—166, 169
  analysis of, 136
  attributes of, 136
  behavior, 137—151
  biological changes influencing PCB accumulation, 157—160
  growth, 128, 157, 159—160, 163, 168
  isomer quantification, 137—151
  kinetics in, 137—151

MONS 006140

lipid content, 128, 136, 147, 151—160, 162, 166, 168—169
migration, 128, 157, 160, 163, 166
organisms analysis, 136
problems inherent in use of, 128
salinity of water, 128
sampling, 128
season of collection, 128, 147, 156—162, 167
seasonal variations in water quality, 161
sediment analysis, 132—136
sediments, 170—171
sex, 128, 136, 158, 166—169
sexual cycle, 161
size, 15, 18, 128, 163—166
spawning, 157—160, 162, 167, 169
temperature of water, 128
temporal fluctuations in pollutant delivery, 157
vertical position of sampling, 128, 169—171
water analysis, 129—132
Biological accumulation, 74
Biological changes influencing PCB accumulation, 157—160
Biological half-life, see *Half-lives*
Biological indicators, see Bioindicator organisms
Biomagnification of PCBs, 151
Biphenyl, 90
Birds, 31—47
accumulation of PCBs in, 32—33
acute toxicity of PCBs, 32, 34—35
behavioral abnormalities, 43
edema, 41—42
hepatic enzyme induction, 39—40, 43
hydropericardium, 41—42
immunosuppressive activity of PCBs, 42
metabolism of PCBs by, 76—77
PCB levels, 43
pharmacodynamics of PCBs, 32, 34
physiological effects, 39—43
porphyria, 41—42
reproduction, see also Reproduction, 36—39
subacute toxicity of PCBs, 32, 34—35
thyroid function/vitamin A levels, 39—41
vitamin E deficiency, 42
Bivalves, 19, 141, 144, 146—147, 166
growth rate, 160
lipids, 147, 153, 155
season for sampling, 161
sexual condition, 159
sites, 163
spawning, 158
tissue distribution of PCBs, 154
water quality, 161
water temperature, 162
Blood brain barrier, 154
Blood glucose, 50
Blubber organochlorine concentrations, 22
Blue crab, 21, 79, 167
Bluegill, 13
Bobwhite, 34, 35
Bobwhite quail, 35—37, 40, 76
Bream, 165
Brevibacterium, 96
Brevoortia tyrannus, 13, 16
Brook trout, 16
Brown pelican, 34

C

Calanus, 15
finmarchicus, 13, 17
California, 135
California gulls, 34, 43
Californian sea lions, 22—23
Callinectes sapidus, 21, 79, 167
Callorhinus ursinus, 136
Cancer irroratus, 21
Candida tropicalis, 94
Carassius auratus, 13, 16, 147—148
Carp, 19, 147, 149—150, 165
Carrots, 2—3
Catfish, 19
CDP-choline:1,2 diacyl-sn-glycerol choline-phosphotransferase, 54
Central nervous system, 114
Cerastoderma edule, 146—147, 161—162
Channel catfish, 74, 82, 147
Chelon labrosus, 16
Chemical properties of PCBs, 50
Chicken, 32—37, 40—42
Chinook salmon, 16
Chlamydomonas reinhardii, 5
Chlamys opercularis, 154, 163
Chloracne, 50
Chlordane, 153
Chlorella
fusca, 141
pyrenoidosa, 5, 70
sp., 5
vulgaris, 6
Chlorinated azobenzenes, 41
Chlorinated dioxins, 41
Chlorinated diphenyl ether derivatives, 20
Chlorine content, 78
Chlorine substitution, 92, 94, 150
Cholesterol biosynthesis, 55
Cholinesterase, 42
Chromosomal abnormalities, 37
Chromosomal breakage, 37, 39
Chronic toxicity, 72, 74
Cichlasoma facetum, 79, 81
Cichlids, 74, 76, 77, 79, 81
Citrate cleavage enzyme, 53
Clams, 70, 79, 144
Clearance, 11—13
Clophen A50, 73, 81
Clophen T64, 50—51
Clupea harengus, 152—153, 155, 165
Cockle, 161—162
Cod, 19—20, 22, 152, 166
Coho salmon, 16, 159—160, 165
Cold stress potentiated mortality, 34

MONS 006141

Colinus virginianus, 35
Columba livia, 35
Co-metabolism, 68, 92
Commercial production of PCBs, 128
Commercial standards, 137
Common guillemot, 34
Concentration coefficient, 75
Contaminant dilution factor, 12
Contaminated food, 10, 15
Copepod, 13, 17—18
Coregonus clupeaformis, 168
Cormorant, 39
Corpora lutea, 113
Corticosteroid production, 115
Corynebacterium, 64
Coturnix coturnix, 33
Crab, 16, 21—22
Crangon septemspinosa, 142—143, 163
Crassostrea virginica, see also Oysters, 13, 70, 78, 144, 146, 153, 157, 163
Crayfish, 71
Creatine kinase, 42
Crustaceans, see also specific types
  growth rate, 160
  sex, 167
  size, 163
  spawning, 158
  tissue distribution of PCBs, 153
  uptake of PCBs, 170
Cunninghamella elegans, 94
Cylindrotheca closterium, 5, 69
Cyprinodon variegatus, 165
Cyprinus carpio, 147, 149—150, 165
Cytochrome oxidase, 51
Cytochrome P-450, 19, 40, 56, 112

D

Daphnia, 71
  magna, 71, 73
DDE, 164—167
DDT, 161, 164—167, 170
Decachlorobiphenyl, 32
Dechlorination, 76—77
Defecation of undigested material, 10
Degradation
  by bacteria, 64—69
  by fish, 74—76
Depuration, 77—84
Desorption isotherms, 74
Diatoms, 4—6
Dieldrin, 163
Diet, 15
Differential mortality, 34
Direct contact with contaminant, 10
Dogfish shark, 82—83
Dogs, 109
Dolphins, 149, 154—156
Double-crested cormorant, 34
Dove, 32
Duckweed, 2—4
Dunaliella
  sp., 5
  tertiolecta, 5
Dynamic equilibrium between uptake and loss, 10
Dynamics of PCBs, 10—18

E

Edema, 37, 41—42
Egg production, 36
Eggshell thinning, 36
Embryonic mortality, 39
Entropy, 50
Environmental persistence, 64
Enzymes, 50, 56—57, 112
Ephemera danica, 71
Epicardium, 41
Episterol, 55
Equilibrium partitioning, 74
Ergosterol, 55
Esox lucius, 165—166, 168
Estrogen receptor, 114
Estrogenic activity, 113—114
Estrous cycles, 106—107, 115
Euphausia pacifica, 17
Ephausiid, 13, 18
Excretion, 10, 20, 71, 151
Eyestalk neurohormone release, 22

F

Falco sparverius, 33
Fathead minnows, 81, 153, 168
Fat tissue, 75
Fatty acid composition of lipids, 22
Fatty acid synthase, 53
Fatty acids, 52—53
Feces residues, PCBs compared to Aroclor 1251, 145
Fecundity, 108—110, 114
Female dogfish, 15
Female reproduction, 105—107
Ferrets, 107
Fertility, 37, 105, 107
Fertilization, 110
Fiddler crabs, 70—71, 167, 170
Flatfish, 140, 148—149, 152, 158, 170
  age, 163—164
  growth rate, 160
  lipids, 165—166
  migration, 160
  seasonality, 159
  sex, 167—169
  size, 163, 166
  spawning, 158
  tissue distribution of PCBs, 154—155
  uptake of DDT, 161
  water temperature, 161

MONS 006142

Firemaster BP-6, 51
First-order kinetic models, 11
Fish, 19, 21, 70, 72, 147
  accumulation of Aroclor 1016, 75
  accumulation of organochlorines at faster rate at higher temperatures, 14
  degradation of PCBs, 74—76
  tissue distribution of PCBs, 153
  uptake of PCBs, 74—76, 170
Flavobacterium, 64
Food, 75
Food chains, 4, 70, 152—153
  biomagnification, 73
  magnification, 18
Food stress, 32, 34
Fratercula arctica, 38
Freshwater fish, 22
Fructose diphosphatase, 50—51
Fructose-1,6-diphosphatase, 42
Fructose diphosphate aldolase, 42
Fundulus
  heteroclitus, 21
  similis, 61
Fungi, 69
Furans, 41

G

Gadus morhua, 22, 152, 166
Galliformes, 36—37
Gallus gallus, 33
Gambusia affinis, 161
Gammarus, 11, 71
  pseudolimnaeus, 71, 142—143
  pulex, 71
Generation transfer of PCBs, 14—15
Gluconeogenesis, 50—51
Gluconeogenic enzymes, 42
Glucose preapnease, 50
Glucose-6-phosphatase, 42
Glycoside biosynthesis, 53
Glycosides, 52—53
sn-Glycerol-3-phosphate, 53
Glycolysis, 50—51
Goldfish, 13, 16, 81, 147—148
Gonads, 112—113
Grass shrimp, 21, 72, 77
Great-crested grebe, 34
Great Lakes, 135, 159—160, 165
Green sunfish, 147
Grey mullets, 76
Growth, 5, 128, 157, 159—160, 163, 168
Growth patterns of fungi, 69
Guillemots, 32, 39, 44
Guinea pigs, 108—109
Guppies, 74—75, 77, 79, 81

H

Half-lives, 77—84, 150, 160
Haliaetus albicilla, 34
Harbor seals, 23
Hatchability of eggs, 36
Hepatic enzyme induction, 39—40, 43
Hepatic mixed function oxidases, 112
Hepatocytes, 56
Hepatomegaly, 111
Hepatopancreas, 81
Herring, 152, 155, 165, 166
Herring gull, 32—35, 39, 42, 43
2,4,5,2',4',5'-Hexabromobiphenyl, 51
2,2',4,4',5,5'-Hexachlorobiphenyl (HCB), 79—81, 83
2,3,5,2',3',5'-Hexachlorobiphenyl, 53—55
2,4,5,2',4',5'-Hexachlorobiphenyl, 51, 53—55
Hexachlorocyclohexane (HCH), 155, 157
Higher plants, 2—3
Horseshoe crabs, 163
Hudson River, 75, 90
Hydrocephalus, 37
Hydropericardium, 41—42
Hydroxylation, 77
Hydroxypolychlorinated biphenyls, 58
Hypothyroidism, 114—115

I

Ictalurus punctatus, 82, 147
Immunosuppressive activity of PCBs, 42
Implantations, 108
Indicator organisms, see also Bioindicator organisms, 71
Infertility, 115
Ingestion of contaminated food, 10
Inhibition of growth, 69
Interference by PCBs, 3
Interstitial tissue, 113
Invertebrates, 19
Ion transport, 20—21
Isomer quantification, 137—151
Isomers, 50, 68, 70, 73, 94

J

Japanese quail, 33—37, 40, 42
Juvenile grey mullets, 75

K

Kanechlor, 50
Kanechlor 400, 52, 95
KC 200, 95
KC 300, 95
KC 400, 95
KC 500, 96
Kapona, 20, 167
Killifish, 81
Kinetics in bioindicator organisms, 137—151

MONS 006143

Klebsiella sp., 90, 96
Krill, 17

L

Lactate dehydrogenase, 42
Lactation, 110—111
Lagodon rhomboides, 74, 82
Lake Superior, 134
Lake trout, 16, 164—165
Lanosterol, 55
Larus
  argentatus, 33
  californicus, 34
Lebistes reticulatus, 79
Leiostomus xanthurus, 13, 74, 82
Lepomis, 20
  cyanellus, 147
  macrochirus, 13
Lesser black-backed gulls, 39
Leuciscus rutilus, 158
Limulus polyphemus, 163
Lipid bodies, 56
Lipid metabolism, 22
Lipids, see also Bioindicator organisms, 151—156
Lipid-water partitioning theory, 152—153
Lipoproteins, 55—57
Liver size, 108, 115
Liver, 57, 111—112
Liver Golgi, 55
Lobsters, 79, 82
Locomotor activity, 114
Lolige forbesi, 163
Loss, 10
Low density lipoproteins (LDL), 57
Luteinizing hormone (LH), 113
Lysophosphatidase, 54
Lysophosphatidyl choline, 54

M

Macoma fasciolaria, 110
Macoma balthica, 146—147
Macrolepis, 141
Magnification factor, 73
Male birds, 36—37
Male reproduction, 103—105
Malformations, 37
Mallard
  accumulation of PCBs, 32, 33
  behavioral abnormalities, 39, 43
  eggshell thinning, 36
  5-day LC_{50}, 35
  immunosuppressive activity of PCBs, 42
  mortality, 35
  reproduction, 38
Mammals, 149
  metabolism of PCBs by, 76—77
  reproduction in, see Reproduction in mammals
  sex, 167
  tissue distribution of PCBs, 154
Marine biota, 9—23
  ATPase inhibition, 20—21
  availability of PCBs, 10
  biochemical effects, 18—22
  effects of PCBs on, 18—23
  dynamics and pathways, 10—18
  fatty acid composition of lipids, 22
  lipid metabolism, 22
  mixed function oxidase induction, 18—20
  rate of adsorption of PCBs by, 10
  steroid hormone biochemistry, 22
  thyroid hormone levels, 22
  whole organism responses to PCBs, 22—23
Marine invertebrates and vertebrates, see Marine biota
Marine mammals, 15
  breeding deficiencies, 11
  reproduction, 22—23
Mayfly, 71
Menhaden, 13
Menstrual cycles, 106—107, 115
Mercenaria mercenaria, 79, 144, 146, 163
Merlangus merlangus, 166
Metabolic breakdown of PCBs, 90
Metabolic pathway of PCBs by bacteria, 94
Metabolic products, 93—96
Metabolic systems, 50
Metabolism, 57, 68, 71, 147, 149
  birds, 76—77
  contaminant, 10
  mammals, 76—77
Mg^{2+} ATPase, 52
Mice, 83, 104—108, 111
Microbial degradation of PCBs, 90
Microbial metabolism of PCBs, 93—94
Micrococcus spp., 64, 90
Microgadus tomcod, 166
Microlayer, 131
Microorganisms, see specific microorganisms
Microperus dolomieui, 165
Microsomal mixed-function oxidase activities, 81, 83
Microsomal oxidation, 50, 56
Migration, 157, 160, 163, 166
Mineralization, 69
Mink, 105, 107, 109
Minnow, 20, 22
Mirex, 20, 22
Mixed function oxidase (MFO) induction, 18—20, 39—40
Mobilization, 32, 35
Model of PCB, 70
Modification of PCBs by bacteria and other microorganisms, see also Bacteria, 89—100
Molluscs, 140, 144, 163, 166
  growth rate, 160
  sex, 167
  sexual condition, 159
  tissue distribution of PCBs, 153

MONS 006144

Monkeys, see Rhesus monkeys
Morone
  chrysops, 165
  saxatilis, 81
Mosquitofish, 161
Mosquito larvae, 71—73, 77, 79
Morning doves, 41
Mosostoma macrolepidotum, 153
Mugil cephalus, 166
Mullet, 166
Mullus barbatus, 166
Muscle, 57
Mussel, 78, 153
  sexual differences, 167
  size, 163
  spawning, 158—159
  uptake by, 170—171
Myctophum glaciale, 166
Mytilus
  californianus, 167, 170—171
  edulis, 78, 141, 158—159, 163

N

NADH-cytochrome *c* reductase, 51
NADH-oxidase activity, 51
Na^+-K^+ATPase, 52
Nereis, 11, 19
  diversicolor, 13, 71, 77
  virens, 13, 17, 142—143, 163
Neuroendocrine differentiation, 103
New York Bight, 133
p-Nitroanisole-*o*-demethylase, 56
Nitroreductase, 56
Nocardia spp., 64
Nongalliform birds, 38
Northern redhorse sucker, 153

O

Octanol-water partition coefficient, 18, 151
n-Octanol/water system, 139—141
Oligo-ovulation, 115
Oncorhynchus
  kisutch, 16, 160, 165
  tshawytscha, 16
Organochlorines, 10, 15, 18
Ornectes sexs, 71
Oscillatoria sp., 94
Osmolality, 20—21
Osmoregulation, 20
Osmoregulatory capacity, 20
Otus asio, 33
Ovarian stroma, 113
Ovulation, 107, 110
Oxidative phosphorylation, 50—52
Oxidative xenobiotic metabolism, 83
2,3-Oxidosqualene cyclase, 55
Oysters, 13, 70, 72, 78—79, 144, 146, 153
  size, 163
  temporal fluctuations in pollutant delivery, 157

P

Palaemonetes pugio, 21, 72, 77
Particulate matter, 75
Partition coefficients, 139—141
Partitioning of PCBs in water, 129, 131, 138
Partitioning values, 142
Parturition, 107—111
Pathways of PCBs, 10—18
PCB-degrading bacteria, 90
PCB-lipoprotein cellular interaction, 57—58
PCB-resistant bacteria, 90
PCB-sensitive bacteria, 90—91
Pelecanus
  erythrorhynchos, 33
  occidentalis, 34
Penaeid shrimp, 21
Perca
  flavescens, 165
  fluviatilis, 16, 166
Perch, 16, 166
Pericardium, 41
Peromyscus, 104
Persistence of PCBs, 128, 151
Persistent substance, 71
Persistent vaginal estrus syndrome, 103
Phalacrocorax
  auritus, 34
  carbo, 34
Pharmacodynamics of PCBs, 32
Phasianus colchicus, 37
Pheasant, 37
Phenacior DP6, 75
Phenolic metabolites, 44
Phocaena phocaena, 154
Phosphatidyl ethanolamine, 54
Phosphoenolpyruvate carboxykinase, 42, 50—51
Phospholipids, 50, 53—55
Phosphorylase, 51
Photosynthesis, 3, 5—6
Phoxinus phoxinus, 81
Phthalate esters, 20
Physiological effects, 39—43
Phytoplankton
  effect of PCBs on, 4—6
  uptake of PCBs by, 69—70, 141, 170
Phytotoxic damage, 4
Pigeons, 35, 40, 84
Pike, 165—168
Pimephales, 20
  promelas, 81, 153, 168
Pinfish, 74—75, 82
Pituitary weight, 40
Plaice, 166
Plants
  higher, 2—4
  phytoplankton, 4—6

MONS 006145

Plasmids, 96
Pleuronectes platessa, 166
Podiceps cristatus, 34
Point sources, 10
Polybrominated biphenyls, 51
Polychaetes, 18, 142—143, 163, 170
Polychlorinated biphenylols, 51
Polychlorinated biphenyls (PCBs), see specific topics
Polynuclear aromatic hydrocarbons (PAH), 19
Population turnover times, 18
Porphyria, 41—42
Porpoise, 154
Postnatal reproductive function, 102—103
Predators, 70
Pregnancy, 107—111
Prenatal exposure to PCBs, 102—103
Production of young, 10
Progesterone synthesis, 113
Pseudomonas
  aeruginosa, 65—68
  putida, 90, 94, 96—97
  spp., 64, 66, 90—91, 96
Puberty, 106, 115
Puffin, 38, 39
Puso hispida, 169
Pyrethroid insecticides, 20
Pyruvate carboxylase, 50

Q

Quail, 32, 41
Quantification
  in aquatic environment, see also Water, 129—136
  in sea water, 10

R

Rabbits, 104, 106, 108—109
Rainbow trout, 13, 16, 82, 161
Rate constants, 12—13
Rats, 83
  estrus or menstrual cycles, 107
  fecundity, 108
  fertility, 105, 107
  liver adenomatosis, 55
  metabolism of PCBs, 76—77
  puberty, 106
  reproduction, 103
  sex organs, 104, 106
  spermatogenesis, 104
Reproduction, see also specific animal or organism, 36—37, 39
  in mammals, see also other subtopics hereunder, 101—125
    adrenal gland, 115
    central nervous system, 114
    development, 102—103
    differentiation, 102—103
    estrogenic activity, 113—114
    estrous cycles, 106—107
    fecundity, 108—110
    female reproduction, 105—107
    fertility, 105, 107
    gonads, 112—113
    lactation, 110—111
    liver, 111—112
    male reproduction, 103—105
    mechanism of action, 111—116
    menstrual cycles, 106—107
    morphology, 102—103
    parturition, 107—111
    pregnancy, 107—111
    puberty, 106
    reproductive function, 103
    sex organs, 104, 106
    spermatogenesis, 104—105
    teratogenic effects, 102
    thyroid, 114—115
Retention properties of PCBs, 15, 78
Rhesus monkeys, 84, 105, 107, 110, 111
Rhizopus japonicus, 94
Rhodosorula rubra, 69
Ring dove, 32—39, 43
Ringed seals, 22
Ring-necked pheasant, 35, 36
Roach, 158
Rock crab, 21
Rough endoplasmic reticulum, 56

S

Saccharomyces cerevisiae, 69, 91
Salinity, 14, 161, 170
Salmo gairdneri, 13, 16, 82, 161
Salmon, 21—22
Salmonella typhimurium, 91
Salvelinus
  fontinalis, 16
  namaycush, 16, 164—165
Sandworm, 11, 13, 17
Scallop, 154, 163
Scenedesmus
  obliquus, 5—6
  obtusiusculus, 5
  quadricauda, 5
Screech owl, 33, 36, 38
Sea birds, 20
Seals, 44, 149, 153, 154, 156, 167, 169
Semen, effects in bioindicator surveys, see Bioindicator organisms
Sedimentation rate, 133
Sediments, 74—75, 138, 170—171
  analysis of, 132—136
Sediment sampling, 134
Selective accumulation, 140—142, 144, 147
Selective bioaccumulation, 140
Semen volume, 37
Seminal vesicle, 104

MONS 006146

Serrasa. 64
liquefaciens. 65—68
Serum cholesterol. 55
Serum glyceride. 52—53
Sewage sludge. 73. 129
Sex organs. 104. 106
Sexual behavior. 114
Sexual condition. 153
Sexual cycle. 161
Sexual maturity. 160. 163
Sheepshead. 19
Sheepshead minnows. 165
Shrimp. 15. 72. 142—143
size. 163
tissue distribution of PCBs. 154
uptake of PCBs. 170
Size of bioindicator organisms. see Bioindicator organisms
Skeletonema costatum. 69
Skin. 57
Skin pigmentation. 50
Sludge used for fertilization. 2—3
Smallmouth bass. 165
Smooth endoplasmic reticulum. 56. 111
Soil. translocation of PCBs into plants from. 2—4
Solubility. see also Water solubility. 50. 56
Sources of PCBs. 129
Sows. 109
Soybean sprouts. 2—3
Spartina alterniflora. 141
Spawning. 157—160. 162. 167. 169
Spermatogenesis. 104—105
Sperm concentration. 37
Spinacia oleracea. 6
Spinning syndrome. 102
Spirodela oligorrhiza. 3. 6
Spot fish. 13. 74. 82
Squasene. 55
Squalene epoxidase. 55
Squid. 163
Starfish. 15
Stenella coeruleoalba. 154. 156
Steric effect coefficient. 151
Steroid hormone biochemistry. 22
Steroid metabolism. 112
Steroidogenesis. 113
Stomach. 50. 55—56
Stillbirths. 108. 110. 115
Streptomyces spp.. 64. 90
Streptopelia risoria. 33
Striped bass. 81—82
Striped mullet. 166
Subacute toxicity of PCBs. 32. 34—35
Subsurface waters. 131
Succinate-cytochrome *c* reductase. 51
Succinic oxidase activity. 51
Sulfone metabolites. 44
Sunfish. 20
Surface area. 12. 14
Surface films. 131. 170
Swine. 109
Swollen eyelids. 50

T

Tanytarsus. 71
Teleosts. 21
Temperature. 161. 170
Teratogenic effects. 37. 39. 102
Terrestrial plants. 6
Testes weight. 37
2.2'.4.5'-Tetrachlorobiphenyl (TCB). 79—80. 82—83
2.4.2'.4'-Tetrachlorobiphenyl. 54
3.4.3'.4'-Tetrachlorobiphenyl (TCB). 41
2.3.7.8-Tetrachlorodibenzo-*p*-dioxins. 42
Tetrahymena pyriformis. 70
Thalassiosira pseudonana. 5
Thyroid. 114—115
Thyroid function/vitamin A levels. 39—41
Thyroid hormone. 22. 41
Thyroid weights. 39—41
Thyroxine. 114—115
Thysanoessa raschii. 13
Tissue distribution of PCBs. 34. 153—156
Tissue residues. 71. 145
Tomcod. 166
Total degradation of PCBs. 96—97
Toxaphene. 20
Toxicity of PCBs. 50. 71—72
higher plants. 2—4
Toxicosis. 74
Translocation of PCBs from soil into plants. 2—4
Trigla lucerna. 166
Trophic level. 15. 70. 79. 151—152
Trout. 19—20. 22
TSH. secretion of. 115
Tyto alba. 33

U

Uca
pugilator. 21—22. 167
pugnax. 16. 70
Ultrastructure. changes in. 6
Uptake. 10—11. 13. 151—153. 170—171
aquatic invertebrates. 70—74
DDT. 161
direct. 74
direct from water. 15. 18
fish. 74—76
from food. 15
fungi. 69
migration. 160
phytoplankton. 69—70
salinity and. 14
yeast. 69
Uptake rate constant. 12—13
Uria aalge. 34

MONS 006147

Uses of PCBs, 128
Uterine glycogen, 113
Uterine receptor, 113
Uterotrophic activity, 106, 113

V

Vaginal opening, 106
Vertical position of sampling, 128, 169—171
Very low-density lipoproteins (VLDL), 55
Vibrio, 90
Vibrio/Aeromonas spp., 64
Vitamin A metabolism, 39—41
Vitamin E, 42
Voiding of body tissues, 10

W

Water
  analysis of, 129—136, 157
  salinity, 161, 170
  seasonal variations in quality of, 161
  temperature, 161—162, 170
Water solubility, see also Solubility, 129, 138—140, 147, 151
White bass, 165
White-crested cormorant, 34
Whitefish, 168
White-footed mice, 104, 106
White pelican, 32—35
White-tailed sea eagle, 34, 43
Whitung, 166
Whole organism responses to PCBs, 22—23
Worm, 71, 77

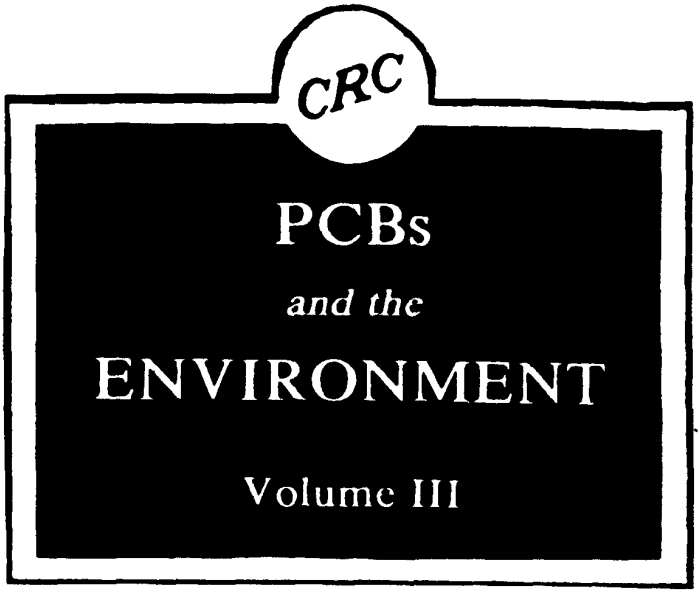
Y

Yeast, 69
Yellow gurnard, 166
Yellow perch, 165

Z

Zenaidura macroura, 41
Zooplankton, 141—142, 163
Zymosterol, 55

MONS 006148



John S. Waid



MONS 006149

PCBs and the Environment

Volume III

Editor

John S. Waid, D. Phil.(Oxford), F.I.Biol., M.A.S.M.
Chairman and Head
Department of Microbiology
La Trobe University
Bundoora, Victoria, Australia



CRC Press, Inc.
Boca Raton, Florida

MONS 006150

Library of Congress Cataloging-in-Publication Data

PCBs and the environment.

Includes bibliographies and indexes.
1. Polychlorinated biphenyls--Environmental aspects.
I. Wasd, John S.
QH545.P6P236 1986 363.1'79 86-17549
ISBN 0-8493-5923-6 (v. 1)
0-8493-5924-4 (v. 2)
0-8493-5925-2 (v. 3)

This book represents information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Every reasonable effort has been made to give reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

All rights reserved. This book, or any parts thereof, may not be reproduced in any form without written consent from the publisher.

Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

© 1987 by CRC Press, Inc.

International Standard Book Number 0-8493-5923-6 (v. 1)
International Standard Book Number 0-8493-5924-4 (v. 2)
International Standard Book Number 0-8493-5925-2 (v. 3)
International Standard Book Number 0-8493-5929-5 (set)

Library of Congress Card Number 86-17549
Printed in the United States

MONS 006151

THE EDITOR

John S. Waid, D.Phil.(Oxford), F.I.Biol., M.A.S.M., is Chairman and Head, Department of Microbiology, La Trobe University, Bundoora, Victoria, Australia, a position he has held since 1974. He also served as Dean of the School of Biological Sciences from 1977-1979.

Prior to his offices at La Trobe University, Professor Waid served in various capacities at the Grassland Research Institute; the Nature Conservancy; Levington Research Station, Fissons, Ltd.; University of New England, New South Wales; Cornell University; Reading University; and the University of Canterbury, New Zealand.

His experimental experience includes the post as joint editor of the proceedings and a convenor of an international symposium on the ecology of soil fungi held in Liverpool in 1968; initiator and Executive Editor of *Soil Biology and Biochemistry* from 1969 to the present; New Zealand delegate to the Committee on Microbial Ecology, International Association of Microbiology Societies (1972-1974); leader of the advisory team from New Zealand under the auspices of the Colombo Plan to review and report on science teaching at Khon Kaen University in northeast Thailand (1974); Victorian representative on the Standing Committee for Environmental Community Problems (SCENCOP) of the Australian Society for Microbiology (1975-1977); and the national representative for the Australian Society for Microbiology on the International Committee of Microbial Ecology (1979-present).

Professor Waid's research interests at present are root biology (in particular the decomposition of grass and legume roots and release of legume-nitrogen to the soil, a study which has been supported by ARGC grants since 1977) and polychlorinated biphenyls in the environment and their degradation. The PCB work has been supported by grants from the Rural Credits Development Fund (1976-1978), the Victoria Ministry for Conservation (1979-1989), and the Australian Marine Sciences and Technologies Advisory Committee (1980-1981). He has also had contracts with the Victoria Ministry for Conservation, and the Federal Department of Science and the Environment to review problems associated with PCBs and the monitoring of hazardous chemicals in the environment. He has made surveys of PCBs in soils and waterways on behalf of a government department, an urban authority, and a large industrial organization (all unnamed), and is consulted regularly on matters pertaining to PCBs by the Victoria Environment Protection Authority.

MONS 006152

CONTRIBUTORS

David P. Brown, M.P.H.
Assistant Chief
Industrywide Studies Branch
NIOSH
Cincinnati, Ohio

Paul H. Chen, Ph.D.
Professor
Department of Biochemistry
National Yang Ming Medical College
Taipei, Taiwan

John P. Connolly, Ph.D.
Associate Professor
Environmental Engineering and Science
Manhattan College
Bronx, New York

Scott W. Fowler
Head
Biology Section
International Laboratory of
Marine Radioactivity
International Atomic Energy Agency
Monaco

Shu-Tao Hsu
Director
Bureau of Communicable Diseases
Control
National Health Administration
Taipei, Taiwan

Takashi Kashimoto
Professor
Faculty of Pharmaceutical Sciences
Setsunan University
Osaka, Japan

Jack D. Lauber, P.E.
Associate Air Pollution Control
Engineer
New York State Department of
Environmental Conservation
Albany, New York

Jos Mes
Chemist
Food Research Division
Bureau of Chemical Safety
Health Protection Branch
Ottawa, Ontario, Canada

Hideaki Miyata
Assistant Professor
Faculty of Pharmaceutical Sciences
Setsunan University
Osaka, Japan

Mats Olsson
Associate Professor
Swedish Environmental Monitoring
Programme
Swedish Museum of Natural History
Stockholm, Sweden

Bruce J. Richardson, Ph.D.
Division of Biological and Health
Sciences
Deakin University
Geelong, Victoria, Australia

Robert H. Smillie, Ph.D.
Department of Microbiology
La Trobe University
Bundoora, Victoria, Australia

Alexander B. Smith, M.D.
Chief
Medical Section
Hazard Evaluation and Technical
Assistance Branch
NIOSH
Cincinnati, Ohio

Robert V. Thomann, Ph.D.
Professor
Environmental Engineering and Science
Manhattan College
Bronx, New York

MONS 006153

Nelson A. Thomas, Ph.D.
Chief
Water Quality Branch
U.S. Environmental Protection Agency
Environmental Research Laboratory
Duluth, Minnesota

John S. Waid, D.Phil.(Oxford)
Chairman and Head
Department of Microbiology
La Trobe University
Bundoora, Victoria, Australia

MONS 006154

TABLE OF CONTENTS

Volume I

Chapter 1
Analytical Chemistry of PCBs 1
Thomas Cairns, Gregory M. Doose, Jerry E. Froberg, Robert A. Jacobson, and Emil G. Siegmund

Chapter 2
Chemistry and Properties of PCBs in Relation to Environmental Effects 47
B.L. Sawhney

Chapter 3
The Reliability of PCB Analysis 65
A.V. Holden

Chapter 4
Atmospheric Transport of PCB to the Oceans 79
E. Atlas, T. Bidleman, and C.S. Giam

Chapter 5
Solubility and Soil Mobility of Polychlorinated Biphenyls 101
S.F.J. Chou and R.A. Griffin

Chapter 6
Factors Controlling Bioaccumulation of PCBs 121
Glen R. Shaw and D.W. Connell

Chapter 7
Factors Controlling Bioaccumulation in Food Chains 135
G.R. Shaw and D.W. Connell

Chapter 8
Distribution, Behavior, and Load of PCBs in the Oceans 143
Shinsuke Tanabe and Ryo Tatsukawa

Chapter 9
What is Happening to PCBs? Elements of Environmental Monitoring as Illustrated by an Analysis of PCB Trends in Terrestrial and Aquatic Organisms 163
Virginia F. Stout

Chapter 10
Nonmetabolic Alteration of PCBs 207
John A.G. Roach

Index 215

MONS 006155

Volume II

Chapter 1
Polychlorinated Biphenyls: Accumulation and Effects Upon Plants 1
H.K. Mahanty

Chapter 2
Accumulation and Effects of PCBs in Marine Invertebrates and Vertebrates 9
G.C. Harding and R.F. Addison

Chapter 3
Accumulation and Effects on Birds 31
D.B. Peakall

Chapter 4
PCBs and the Environment: Perturbations of Biochemical Systems 49
Wilbert Gamble

Chapter 5
Uptake, Retention, Biodegradation, and Depuration of PCBs by Organisms 63
M.K. Hamdy and J.A. Gooch

Chapter 6
Modification of PCBs by Bacteria and Other Microorganisms 89
Kensuke Furukawa

Chapter 7
Effect of PCBs on Reproduction in Mammals 101
Gene B. Fuller and William C. Hobson

Chapter 8
Use of Organisms to Quantify PCBs in Marine and Estuarine Environments 127
David J.H. Phillips

Index 183

Volume III

Chapter 1
Differences Between Yusho and Other Kinds of Poisoning Involving Only PCBs 1
Takashi Kashimoto and Hideaki Miyata

Chapter 2
PCB Poisoning from Toxic Rice-Bran Oil in Taiwan 27
Paul H. Chen and Shu-Tao Hsu

Chapter 3
PCBs in Human Populations 39
Jes Mes

MONS 006156

Chapter 4
Polychlorinated Biphenyls in the Workplace 63
Alexander B. Smith and David P. Brown

Chapter 5
Disposal and Destruction of Waste PCBs 83
Jack D. Lauber

Chapter 6
The Great Lakes Ecosystem — Modeling of the Fate of PCBs 153
Robert V. Thomann, John P. Connelly, and Nelson A. Thomas

Chapter 7
PCBs in the Baltic Environment 181
Mats Olsson

Chapter 8
PCBs and the Environment: The Mediterranean Marine Ecosystem 209
Scott W. Fowler

Chapter 9
Case Study: The Australian Ecosystem 241
Bruce J. Richardson, Robert H. Smillie, and John S. Waid

Index 265

MONS 006157

Chapter 1

DIFFERENCES BETWEEN YUSHO AND OTHER KINDS OF POISONING INVOLVING ONLY PCBs

Takashi Kashimoto and Hideaki Miyata

TABLE OF CONTENTS

I. Introduction 2

II. Chlorinated Compounds in the Rice-Bran Oil Causing Yusho 2
- A. Discovery of PCDFs and PCQs in PCB Products 2
- B. Cause of the Contamination 6

III. Amounts of Residual Chlorinated Compounds in Patients with Yusho, Workers Occupationally Exposed to PCBs, and Healthy Persons 7

IV. PCB Poisoning in Taiwan 11

V. Biological Study of Yusho 13
- A. Investigation of Characteristic PCB Components Retained in Patients with Yusho 13
- B. Distribution of PCBs and Their Related Compounds 15
- C. Transfer of PCBs and Related Compounds from Mother to Fetus or Offspring 16
- D. Biological Effects of PCBs and Their Related Compounds 18

VI. Causal Agents of the Yusho and Taiwan Incidents 20

References 22

MONS 006158

I. INTRODUCTION

Yusho refers to a case of mass food poisoning caused by consumption of a rice-bran oil contaminated with a commercial polychlorinated biphenyl (PCB) mixture (Kanechlor® 400 containing 48% chlorine, produced by Kanegafuchi Industrial Co. Ltd., Japan) which had been used as a heat exchanger fluid to deodorize the oil.[1,2]

In 1968, an outbreak occurred in the western parts of Japan and more than 1600 people were affected. The characteristic clinical symptoms of Yusho are as follows:[2,3]

1. Dermal signs: eruptions of acne on the face, back, and external genitalia, dark pigmentation on the face, nails and gingivae, edema on the face and especially on the eyelids, hyperkeratosis of the trunk and external genitalia, and hyperidrosis.
2. Ocular signs: dark pigmentation of the conjunctiva, swelling of the Meibomian glands, and hypersecretion of a cheese-like discharge from the eyes.
3. Respiratory signs: chronic bronchitis with a persistent cough and sputum.
4. Neurological signs: headache, numbness of the limbs, and a decline in vision.
5. Other signs: irregular menstrual cycles, general fatigue, and anorexia.

The levels of PCBs in the blood of the Yusho patients declined rapidly once oil ingestion was terminated and 5 years later were only two to three times larger than those of unexposed persons.[6,7] However, the above symptoms were reported to persist for more than 10 years.[8,9] On the other hand, in the case of workers occupationally exposed to PCBs whose daily intake of PCBs was similar in quantity to that taken by the patients, despite high PCB levels in blood, only a minority had mild dermal lesions, such as acne eruptions and hyperpigmentation.[10-13] The discontinuation of handling PCBs resulted in the rapid disappearance of dermal symptoms.[10,13]

Thus, Yusho is clearly symptomatically different from occupational PCB poisoning. In Japan, however, there has been a tendency to treat cases of the latter or the effects of PCBs as a general environmental pollutant on living things as being identical to the former.

II. CHLORINATED COMPOUNDS IN THE RICE-BRAN OIL CAUSING YUSHO

A. Discovery of PCDFs and PCQs in PCB Products

In 1970, Vos et al.[14] reported that polychlorinated dibenzofurans (PCDFs) (Figure 1) were present as a by-product at a parts per million (ppm) level in both West German and French PCB products containing 60% chlorine. The toxic effect of these products was proportional to the level of PCDFs present, suggesting they were extremely more toxic than PCBs. In view of the high toxicity of PCDFs to the rabbit shown in an experiment by Bauser et al.,[15] the above findings were thought to be important to the understanding of Yusho because the oil that was implicated in Yusho was reported to be contaminated with a Japanese manufactured PCB mixture, Kanechlor® 400 (KC-400), which had been used as a heat exchanger liquid at over 200°C at a reduced pressure of 3 to 4 mmHg during the deodorization processing of the oil product. Therefore, we analyzed six samples of bottled suspect rice oil manufactured on various dates for PCDFs.[16,17]

As shown in Table 1, an oil sample produced on February 5, 1968, the first product following the leakage of KC-400 from a heat exchanger pipe into the processed oil in a deodorization tank, was the most heavily contaminated with PCBs and PCDFs. The concentrations of both chemicals decreased rapidly during the period following the start of the PCB leakage. This suggests that the oil produced from February 5, 1968 to the middle of that month was most likely to have been responsible for Yusho. PCBs in all samples examined contained relatively larger amounts of higher-chlorinated biphenyl congeners with more than

MONS 006159

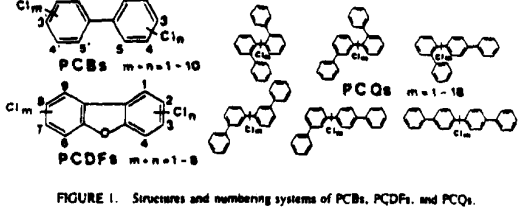


FIGURE 1. Structures and numbering systems of PCBs, PCDFs, and PCQs.

Table 1
CONCENTRATIONS (ppm) OF PCBs, PCDFs, AND PCQs AND THEIR RATIOS IN VARIOUS MATERIALS

Sample	PCBs	PCDFs	PCQs	PCDFs/PCBs (g/g)	PCQs/PCBs (g/g)
Yusho causal oil					
Feb. 5, 1968[a]	968	7.4	866	7.6×10^{-3}	8.9×10^{-1}
Feb. 9, 1968[a]	151	1.9	490	1.3×10^{-2}	3.2
Feb. 10, 1968[a]	155	2.3	536	1.4×10^{-2}	3.5
Feb. 11, 1968[a]	43.7	0.48	—	1.1×10^{-2}	—
Feb. 15, 1968[a]	12.3	0.085	—	6.9×10^{-3}	—
Feb. 18, 1968[a]	1.8	0.012	—	6.7×10^{-3}	—
Unused KC-400	999,800	33	209	3.3×10^{-5}	2.1×10^{-4}
Used KC-400[b]	968,400	510	31,000	5.2×10^{-4}	3.2×10^{-2}
Used KC-400[c]	999,000	277	690	2.8×10^{-4}	6.9×10^{-4}
Used KC-400[d]	971,900	20	28,000	2.1×10^{-5}	2.9×10^{-2}

[a] Production date.
[b, c, d] KC-400 used as a heat exchanger for 14 years at 180 to 270°C (b), for 3 years at 200 to 220°C (c), and under unknown conditions (d), respectively.

four chlorine atoms in comparison with that in the unused KC-400 (Table 2). The composition of PCBs present varied depending on the production date of the oil and considerably larger contents of the higher-chlorinated compounds were found in oil produced on February 10 and 11, 1968. The concentration and composition of PCDFs in these oil samples were also affected.[16,17] PCDFs present were composed of more than 40 isomers including as major components 2,3,7,8-tetra-, 2,3,4,7,8-penta-, 1,2,3,7,8-penta-, 2,3,4,6,8-penta-, and 1,2,3,4,7,8-hexachlorinated isomers.[18] Both the 2,3,7,8-tetra- and the 2,3,4,7,8-penta-chlorinated isomers are highly toxic compounds.[19,20] It is noteworthy that the concentration ratios (6.7×10^{-3} to 1.4×10^{-2}) of PCDFs to PCBs in the oil specimens are 203 to 424 times that (3.3×10^{-5})[21] in unused KC-400. Another similar finding was also confirmed in three samples of the canned suspect oil shipped on February 5, 1968 by Nagayama et al.[22]

At the time of the Yusho outbreak, all of the chlorine in the Yusho oil was thought to be derived from the chlorine atoms substituted in the PCB molecules and the level of PCBs present was calculated from the total chlorine concentration, showing the oil samples manufactured on February 5, 9, and 10, 1968, to contain PCBs at levels of 2125 to 3125, 812 and 792 to 1458 ppm, respectively.[1,2] As shown in Table 1, the actual levels of PCBs present were only 968, 151, and 155 ppm, respectively, being equivalent to about a half to a third, a fifth and a fifth to a ninth, respectively, of the above-estimated values. A subsequent

MONS 006160

Table 2
COMPONENT RATIO (%) OF PCBs IN SAMPLES OF YUSHO CAUSAL OIL AND UNUSED KC-400

Sample	No. of chlorine						
	2	3	4	5	6	7	8
Yusho causal oil							
Feb. 5, 1968*	0.0	7.6	45.2	43.3	0.8	3.2	0.0
Feb. 9, 1968*	0.0	5.6	37.8	48.9	1.4	6.3	0.0
Feb. 10, 1968*	0.0	3.1	32.7	55.4	1.5	6.6	0.8
Feb. 11, 1968*	0.0	4.8	32.2	55.0	1.4	6.5	0.0
Feb. 15, 1968*	0.0	7.8	34.0	50.0	1.4	6.9	0.0
Feb. 18, 1968*	0.0	11.0	35.6	48.3	0.9	3.7	0.0
Unused KC-400	0.7	22.3	58.9	17.5	0.3	0.0	0.0

* Production date.

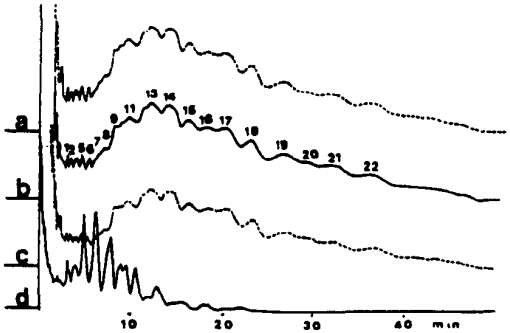


FIGURE 2. Gas chromatograms of new chlorinated compounds in Yusho oil and a PCT product (Aroclor® 5460) (245°C, 2 m × 2 mm glass column containing 2% OV-210 on Gaschrom® Q 100—120 mesh, carrier gas nitrogen, 30 ml/min). (a, b, and c) New chlorinated compounds from samples of Yusho oil manufactured on February 5, 9, and 10, 1968, respectively; (d) PCT (Aroclor® 5460).

reexamination of the oil samples by activation, fluorescene X-ray, and chemical analyses confirmed the total chlorine contents to be similar to those reported in the original data.[23,24] Accordingly, the difference between these two PCB levels suggested the oil specimens consisted largely of chlorinated compounds other than PCBs and PCDFs.

In 1978, some new chlorinated compounds were separated from oil samples causing Yusho by gel permeation chromatography[23,24] or Florisil® column chromatography.[25] As shown in Figure 2, the gas chromatograms in samples manufactured upon different dates resembled each other, showing an unresolved mass with a larger retention time than that of polychlorinated terphenyls (PCTs, Aroclor® 5460 containing 60% chlorine). As a result of GC/MS analysis, the compounds were deduced to be composed of polychlorinated quaterphenyls (PCQs) containing penta- to decachlorinated isomers as their major components and PCTs

MONS 006161

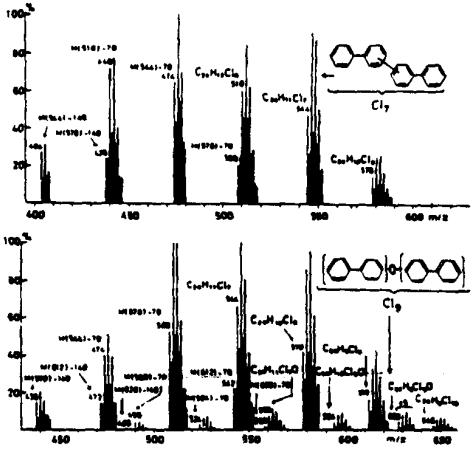


FIGURE 3. 70 eV Mass spectra of peak no. 7 (top) and 20 (bottom) shown in Figure 2.

and polychlorinated quaterphenyl ether (PCQEs) as minor ones (Figure 3). The components of peak No. 7 shown in Figure 3 (top) could be identified as a complex of hexa- to octadecachlorinated quaterphenyls. The tentative heptachlorinated quaterphenyl gives a molecular ion at *m/z* 544 and fragmental ions eliminated double chlorine atoms and further additional loss of double chlorine atoms from the parent ion, respectively, at *m/z* 474 and 404. Peak No. 16 was inferred to contain hepta- to decachlorinated isomers and hepta- to nonachlorinated quaterphenyl ether isomers (Figure 3, bottom).

There are six possible types of PCQ skeleton (Figure 1). When positional isomers are considered, the number of individual isomers that may exist is more than 100,000. As shown in Figure 2, these prevented the GC system from separating the PCQ isomers. Accordingly, the PCQs were perchlorinated[26] with antimony pentachloride according to a modification of Armour's method,[27] thus providing an easy method to identify PCQs because of the conversion of numerous PCQ isomers to only six perchlorinated PCQ isomers (octadecachlorinated quaterphenyls, $C_{24}Cl_{18}$). Perchlorinated compounds yielded three completely separated peaks on an OV-210 GC column.[26] All of these peaks were confirmed to be perchlorinated PCQs by the coincidences of the molecular ion (M^+), ion clustering due to the chlorine isotopics, and the major fragmentation (M^+-Cl, M^+-2Cl, M^+-4Cl, etc.) with those of authentic standards.[25,26]

The chlorine concentration derived from PCQs in oil samples that had been manufactured on February 5, 9, and 10, 1968, were 450, 207, and 248 ppm, respectively, being equivalent to 84, 70, and 72%, respectively, of the chlorine levels from chlorinated compounds other than PCBs and PCDFs.[25,29] It is surprising that the actual level of PCQs was 0.9 to 3.5 times higher than that of PCBs (Table 1). In addition, the oils contained additional unidentified chlorinated compounds with higher molecular weights than those of PCQs.[25,29]

MONS 006162

B. Cause of the Contamination

As already mentioned, the samples of Yusho oil manufactured on February 5, 9, and 10, 1968 were shown to have extremely high ratios of PCQ to PCB and PCDF to PCB concentrations, 0.9 to 3.5 and 7.6×10^{-3} to 1.4×10^{-2}, respectively,[27-29] equivalent to 4200 to 17,000 and 230 to 420 times, respectively, those (2.1×10^{-4} and 3.3×10^{-5}, respectively)[29,30] of the unused KC-400 (Table 1) and to have a fairly different composition of PCBs or PCDFs corresponding to that[16,22] found in KC-400 (Table 2). In order to investigate the above findings, three samples of KC-400 used as a heat exchanger liquid for from 3 to 14 years at 200 to 270°C were analyzed for PCBs, PCQs, and PCDFs, showing the levels of PCQs and PCDFs in them to be two digits and one digit higher, respectively, than those in the unused KC-400 (Table 1). This suggested a possible generation of both chemicals from PCBs through thermal reaction.

Therefore, the pyrochemical reaction of KC-400 was studied.[31-33] PCBs sealed in glass ampoules were shown to convert to PCDFs when heated at temperatures ranging from 300 to 360°C.[31-33] This reaction was catalyzed by copper,[32] iron,[32] stainless steel,[31] and their salts.[33] In addition, oxygen was essential for the formation of PCDFs.[32,33] According to Buser and Rappe,[26] the formation of PCDFs can follow competing reaction pathways, involving the loss of ortho-Cl_2, ortho-H_2, and ortho-HCl with and without a 2,3 chlorine shift in the biphenyl system.

On the other hand, the dimerization of PCBs was shown to occur by heating above 180°C. At temperatures above 300°C, the yield of the conversion of PCBs to PCQs markedly increased to a maximum level of 14,000 ppm.[29,30] This reaction was also catalyzed by iron,[29] tin,[29] nickel,[29] or stainless steel,[29] showing the PCQ level in heated KC-400 to reach a maximum of 47,000 ppm.[29]

The above results provided evidence that both PCDFs and PCQs can be pyrochemically generated from KC-400 during its use as a heat exchanger liquid at high temperatures. However, both ratios of PCQs to PCBs and PCDFs to PCBs in used KC-400 samples, $<3.3 \times 10^{-2}$, and $<5.2 \times 10^{-4}$, respectively, were still lower than those of the Yusho oil specimens (Table 1). Furthermore, the chemical composition of PCBs in the former was also quite different from those in the latter and was rather similar to that of the unused KC-400.

Subsequently, changes of components and concentrations of PCBs, PCQs, or PCDFs during the deodorization process of rice-bran oil were investigated using a laboratory deodorizer.[29] It was first demonstrated that the conversion of PCBs (KC-400) to PCDFs or PCQs is unlikely to occur during a deodorization period of 1 hr at 230 to 240°C at reduced pressure (30 mmHg). However, as shown in Figure 4, both relative concentrations of PCDFs and PCQs to PCBs retained in the processed oil rapidly increased with increase of deodorizing temperature, due to considerable differences in evaporation rates (PCBs > PCDFs >> PCQs). For example, in the range from 240 to 250°C, the ratios of PCQs to PCBs and PCDFs to PCBs in the oil were 10 and 34 times higher, respectively, than the corresponding ones in the undeodorized oil. In addition, it was observed that the relatively greater evaporation of less chlorinated biphenyls or dibenzofurans resulted in the relative elevation of the proportions of the respective high chlorinated congeners with more than four chlorine atoms in the oil. In the range from 220 to 270°C, the composition of residual PCBs became similar to that characteristic of Yusho oil samples. However, no changes in both components and concentrations of PCQs in the oil were noted in the deodorization process.

All of the results described above indicate that a PCB heat-exchanger liquid (KC-400), in which the amounts of PCQs and PCDFs are of the order 10,000 and 100 ppm, respectively, could have been thermochemically generated, leaked out into the suspect oil during the deodorizing stage of manufacture and that the observed high ratios of PCQs and PCDFs to PCBs or the special compositions of PCBs and PCDFs in the oil could have been produced

MONS 006163

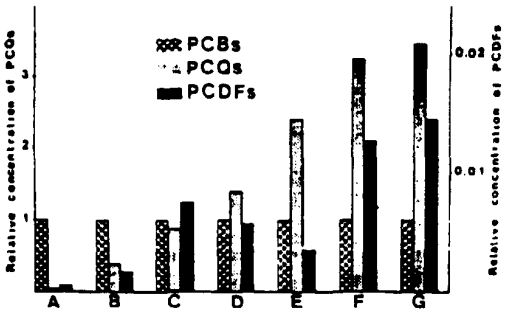


FIGURE 4. Relative concentrations of PCQs and PCDFs to PCBs (= 1) in deodorized rice bran oils and Yusho oils. (A) Nondeodorized rice bran oil; (B) rice bran oil deodorized at 200—210°C; (C) a sample of Yusho oil manufactured on February 5, 1968; (D and E) rice bran oils deodorized at 240—250 and 260—270°C, respectively; (F and G) samples of Yusho oil manufactured on February 9 and 10, 1968, respectively. Fifty *ml* of rice bran oil, which was spiked with PCBs, PCQs, and PCDFs (2375, 90, and 1.35 ppm, respectively) in similar proportions to that of a PCB product used as a heat exchanger, was deodorized for 1 hr at a reduced pressure (30 mmHg) using a laboratory deodorizer.

during the deodorization process because of the differences in vapor pressures (PCBs > PCDFs >> PCQs) or their respective individual isomers (lower chlorinated biphenyl isomers > higher chlorinated isomers and lower chlorinated dibenzofuran isomers > higher chlorinated isomers).

III. AMOUNTS OF RESIDUAL CHLORINATED COMPOUNDS IN PATIENTS WITH YUSHO, WORKERS OCCUPATIONALLY EXPOSED TO PCBs, AND HEALTHY PERSONS

As shown in Table 3, the concentrations of PCBs in the tissues of patients with Yusho (cases 2 and 3) who died within a few years following poisoning were higher than those in unexposed individuals.[36,37] The residual level, however, gradually decreased in the course of time following the incident and in a patient (case 6) who died in 1978, the concentration of PCBs was close to that of the control group. Most of the PCBs ingested by the patients, especially lower-chlorinated biphenyl congeners, disappeared rapidly from their tissues.[36-40] The residual PCBs had an almost constant composition in various tissues of the same individuals, being composed mainly of penta- to heptachlorinated isomers.[38,40] A year after the incident, PCB retained in the tissues of the patient (case 2) with severe dermal signs showed a so-called "type A" gas chromatographic pattern which is quite different from that observed in the unexposed normal person[37,40] (see Section V.A). This peculiar pattern is characteristic of severe cases of Yusho.[41,42] Five years after the poisoning, 61% of the living patients examined showed the type A gas chromatographic pattern, while only 9% showed the type C which was commonly noted in the unexposed normal person (control population), and 30% showed the type B pattern which was an intermediate one between the first and the second.[6,7] It has been established that the pattern persists and is still observed in most of the surviving patients (Figure 5).

On the other hand, the level of PCQs, as well as PCBs, in tissues of deceased patients

MONS 006164

Table 3
CONCENTRATIONS (ppb) OF PCBs, PCDFs, AND PCQs IN THE TISSUES OF YUSHO PATIENTS, UNEXPOSED INDIVIDUALS, AND IN THE MILK FAT OF A WORKER OCCUPATIONALLY EXPOSED TO PCBs

Case	Age	Sex	Date of death, surgical time, or sampling	Tissue (or fluid)	PCB level	PCDF level	PCQ level
				Yusho Patients			
1	0[a]	M	Oct. 1968	Intestine	29.7	0.4	83.6
				Liver	50.5	15.2	393
2	25	M	July 1969	Adipose tissue	5091	5.3	2400
				Liver	226	70.1	218
3	46	F	May 1972	Adipose tissue	6091	9.6	1444
				Liver	68.0	15.5	144
4	72	M	Apr. 1975	Intestine	3472	2.5	1770
				Liver	114	6.2	51.7
5	59	M	Mar. 1977	Intestine	3630	2.2	416
				Liver	68.4	6.1	6.3
6	69	M	Sept. 1978	Intestine	1273	0.2	24.5
				Liver	17.7	0.02	0.97
				Unexposed Individuals (av.)[b]			
	53	M,F	Sept. 1978	Adipose tissue	803	0.019	1.53
				Liver	32.5	0.006	0.41
				PCB Worker			
	37	F	Oct. 1977	Milk fat	6241	—	0.2

[a] A full-term stillborn baby.
[b] 14 patients with diseases other than Yusho.

gradually decreased subsequent to the incident (Table 3). The tissue level of PCQs, however, remained higher for 10 years compared to that of the control group. For example, a patient (case 5) who died 10 years after poisoning had PCQ level 272 times higher in his intestine and 15 times higher in his liver than did unexposed individuals. In addition, PCQs were detected at the level of, on the average, 2 ppb in the blood of 54 out of 56 living patients examined 11 years following intoxication (Table 4).[49] No PCQs, however, were found in the blood of any of the 69 workers occupationally exposed to PCBs despite having blood PCB levels as much seven times higher than those of the patients or in the blood of any of the 60 unexposed persons. Apart from one special case in which three workers exposed to PCBs used as a heat exchanger liquid, which might have contained both PCQs and PCDFs, were shown to have on the average 0.9 ppb of PCQs in their blood (Table 4), the high blood or tissue PCQ level is, therefore, considered to be characteristic of Yusho.

Compared with the original PCQs containing hexa- to octachlorinated isomers as the major components, PCQs in the liver of a deceased patient (case 2 in Table 3) gave a much broader gas chromatographic peak including higher-chlorinated isomers, while in his adipose tissue, there was a sharper peak composed mainly of lower-chlorinated isomers.[37] Following perchlorination, there was a change in the gas chromatographic patterns of the two tissues compared to those of the original PCQs, with an increase of the third peak in the liver and the first peak in the adipose tissue (Figure 6). The pattern of PCQs in the blood was also different from that of the liver or adipose tissue. These results suggest the possibility that PCQ congeners may distribute differentially within each tissue.

MONS 006165

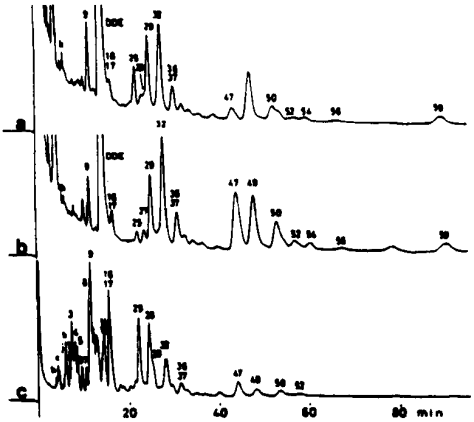


FIGURE 5. Typical gas chromatographic patterns of PCBs in the blood of a Yusho patient and an unexposed individual, and in Yusho oil (240°C, 5 m × 2.6 mm glass column containing 2% Apiezon L on Gaschrom® Q 100-120 mesh, carrier gas nitrogen, 40 ml/min). (a) PCBs from the blood of an unexposed individual; (b) PCBs from the blood of a Yusho patient 11 years after exposure, pattern A which contains relatively smaller amounts of peak no. k, 9, 25, and 28 components, and larger amounts of peak no. 47, 49 and 50 ones in comparison with that (a) of the unexposed person; (c) PCBs from a sample of Yusho oil manufactured on February 5, 1968.

Table 4
CONCENTRATIONS (ppb, MEAN ± SD) OF PCBs, PCDFs, AND PCQs IN THE BLOOD OF YUSHO PATIENTS, WORKERS OCCUPATIONALLY EXPOSED TO PCBs, AND UNEXPOSED INDIVIDUALS

Sample	No. of cases	Period after termination of exposure (year)	PCBs	PCDFs	PCQs
Yusho patients	56	11	6 ± 4	<0.01	2.0 ± 2.0
Workers occupationally exposed to unused PCBs[a]	69	9	45 ± 49	<0.01	<0.02
Workers occupationally exposed to used PCB[b]	3	9	19 ± 11	<0.01	0.9 ± 0.9
Unexposed individuals	60		2 ± 1	<0.01	<0.02

[a] Workers who engaged in charging unused PCB products (KC-300, -400 and -500) into the condenser.

[b] Workers who engaged in reclaiming PCB products used as a heat exchanger.



FIGURE 6. Gas chromatograms of PCQs in the blood and tissues of a Yusho patient after perchlorination (280°C, 0.5 m × 2.6 mm glass column containing 2% OV-210 on Gaschrom® Q 100-120 mesh, carrier gas nitrogen, 60 ml/min). (a, c, and d) PCQs from the blood, adipose tissue, and liver of a Yusho patient, respectively; (b) PCQs from a sample of Yusho oil manufactured on February 5, 1968.

Table 5
CONCENTRATIONS (ppm, MEAN ± SD) OF PCBs, PCDFs, AND PCQs AND THEIR RATIO IN JAPANESE AND TAIWANESE CAUSAL OIL

	No. of samples	PCBs level	PCDFs level	PCQs level	PCBs:PCDFs:PCQs
Japanese oil[47]	3	430 ± 391	3.85 ± 2.51	630 ± 167	100:0.90:147
Taiwanese oil[51]	3	44 ± 12	0.14 ± 0.03	17 ± 6	100:0.32:39
Taiwanese oil[48]	4	80 ± 13	0.29 ± 0.01	—	100:0.36:—

PCDFs were present at levels within the range from 0.02 to 70.1 ppb in the liver and 0.2 to 9.6 ppb in the adipose tissue or the intestine of the victims who died 1 to 10 years after the poisoning (Table 3). Similar patterns were reported by Kuroki and Masuda.[46] Most of PCDFs ingested by the patients, as well as in the case of PCBs, were eliminated relatively rapidly from their bodies. According to Rappe et al.,[45] compared to the original PCDFs which contained more than 40 PCDFs isomers, in the liver samples their numbers were markedly decreased to about 10, with the most numerous 1,3,6,8-tetra-, 2,3,7,8-tetra-, 1,2,4,7,8-penta-, and 1,2,3,4,7,8-hexachlorinated dibenzofuran. As shown in Table 3, PCDFs accumulated to a higher level in the liver than in the adipose tissue, which was quite different from the case with PCBs or PCQs. In the patients, the tissue levels of PCDFs as well as PCQs were extremely high for many years in comparison with those of the control group (Table 3). Even a patient (case 5) who died in 1977 had PCDFs 116 times greater in his intestine and 1017 times greater in his liver than did[10] the control group. However, it was impossible to detect PCDFs in the blood of the living patients 11 years following the poisoning at a detection limit of 0.01 ppb (Table 5), presumably due to their smaller intake of PCDFs (on the average 3.4 mg) compared to that of PCBs or PCQs (on the average 633 or 596 mg), respectively.[46]

Five years after intoxication, the concentrations of PCBs in the blood of the patients were reported to be similar to those of unexposed individuals.[6,7] Most patients, however, suffered from various clinical symptoms for more than 10 years.[8,9] On the other hand, many workers who had handled PCB products (Kanechlor® 300, 400, and 500 containing 42, 48, and 54% chlorine, respectively) in a condenser factory showed only mild clinical symptoms despite PCB blood levels as high as 100 to 1000 ppb.[10,11] They were estimated to have taken in 4

MONS 006167

to 12 mg of PCB daily over a period of a few years.[10] Their daily intake of PCBs was close to that (7.9 mg)[48] of Yusho patients. It was also reported that mild skin lesions quickly disappeared after PCB handling had been discontinued.[13] These facts unanimously indicated that a simple exposure to PCBs alone may not induce the severe and obstinate symptoms seen in Yusho patients.

Taking all the above-mentioned facts into consideration, it can be deduced that PCDFs and PCQs (other than PCBs) are strongly associated with the development of Yusho. Therefore, Yusho is considered to be symptomatically and etiologically different from PCB poisoning per se.

IV. PCB POISONING IN TAIWAN

In the spring of 1979, another Yusho-like PCB poisoning caused by consumption of a contaminated cooking rice bran oil occurred in the central part of Taiwan, the Republic of China[47-49] and affected about 1700 people.[50] All samples of the suspect oil examined were found to be heavily contaminated with PCBs, PCQs, and PCDFs.[49-52] The composition of the three chemicals, respectively, were almost constant in all oil samples. Both the PCBs and PCDFs present were composed of relatively larger amounts of their respective higher-chlorinated isomers compared with those in the Japanese Yusho oil manufactured on February 5, 1968, but their respective components were similar to those in the oil manufactured on February 9 or 10, 1968 (Figure 7 and 8). On the other hand, the PCQs present were predominantly hexa- to octachlorinated congeners and their composition was similar to that of the Japanese oil.[53] As shown in Table 5, Taiwanese oil samples had not only roughly one tenth of the contamination by PCBs, PCQs, and PCDFs but also three to four times lower ratios of PCQs or PCDFs to PCBs than the Japanese samples. This resulted in the Taiwanese daily intake of PCBs, PCQs, and PCDFs during the latent period (on the average, 3.7, 1.46, and 0.015 mg, respectively)[49] being much less than the Japanese (on the average, 7.9, 7.4, and 0.045 mg, respectively),[48] although the former patients were estimated to have consumed six times as much oil[49] than the latter.[54] The higher proportions of dermatologically light cases (grade 1 and 2) among Taiwanese victims[47] than among Japanese[3] might be attributed to the difference between their daily intakes of chlorinated compounds (Table 6).

Six months to 1 year after the poisoning, all patients examined had high PCB blood levels with ranges of, on the average, 39 to 73 ppb,[51,55-57] equivalent to 20 to 36 times as high as that (2.0 ppb)[51] of the Japanese control group.

As seen in the Japanese case, the blood PCBs were also mainly composed of penta- to heptachlorinated biphenyl congeners.[52,55,57] Various gas chromatographic types of PCBs were observed in the blood (Figure 7). Some patients showed a peculiar pattern resembling "type A" characteristic of most Japanese patients but it was more often observed in male patients than in females.[53] Thus, a sex difference in the gas chromatographic patterns indicates that males may have a stronger capacity to metabolize PCBs. In addition, such a pattern was also observed in the patients whose blood had a high level of PCDFs 1 year after poisoning.[58]

When 15 and 67 patients, respectively, were examined 6 months and 1 year following intoxication, PCQs were detected in all blood samples at high levels averaging 19.3[51] and 8.6 ppb,[58] respectively. As shown in Table 7, patients without dermal signs showed high PCQ blood levels (on the average 1.7 ppb), about 100 times that (<0.02 ppb) of the control group, although the average PCB blood level (12 ppb) of the former was only six times higher than that (2 ppb) of the latter, indicating the presence of PCQs to be a good mark of the ingestion of the toxic oil. Nakajima and Umeda[59] pointed out from 5 to 8 months after the termination of oil consumption, the biological half-life (on the average, 10.4 months) of PCQs in the blood of five patients was about three times longer than that (3.3 months) of PCBs. As observed in the Japanese case, after perchlorination, three peaks also

MONS 006168

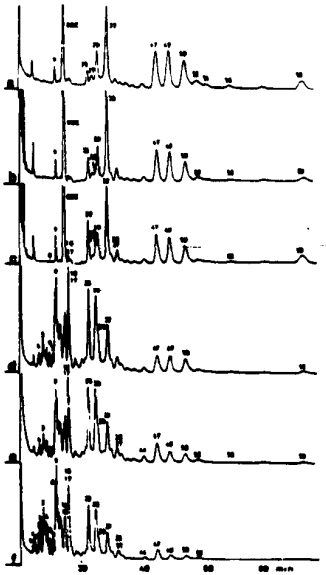


FIGURE 7. Gas chromatograms of PCBs in various materials (240°C, 5 m × 2.6 mm glass column containing 2% Apiezon L on Gaschrom® Q 100—120 mesh, carrier gas nitrogen, 40 mℓ/min). (a, b, and c) PCBs from the blood of Taiwanese patients 1 year after the poisoning; (d) PCBs from a sample of Taiwanese cassel oil; (e and f) PCBs from samples of Yusho oil manufactured on February 9 and 5, 1968, respectively.

appeared in the gas chromatograms of PCQs in the blood of the patients, showing a tendency for the third peak to increase compared to that of the original PCQs.[30,39]

Remarkably, highly toxic PCDFs were detected at the level of, on the average, 0.14 ppb in the blood of all 14 patients (6 months after the outbreak) except for one who had no dermal signs.[31] One year following the poisoning, all 67 patients examined also had high PCDF blood concentrations (average, 0.076 ppb)[39] (Table 7). Taking into account the larger daily intake of PCDFs by the Japanese patients, it is deduced that at the same time after the Yusho outbreak, they would have had higher blood levels of PCDFs than the Taiwanese patients. PCDF isomers in the blood samples had decreased in number and were similar to those seen in the tissue of a Japanese patient (case 2 in Table 3) who died 1 year following the Yusho incident (Figure 8).

A positive correlation was noted between the concentrations of PCBs, PCQs, or PCDFs in the blood of patients and the degree of severity of their dermal lesions (Table 7).

MONS 006169

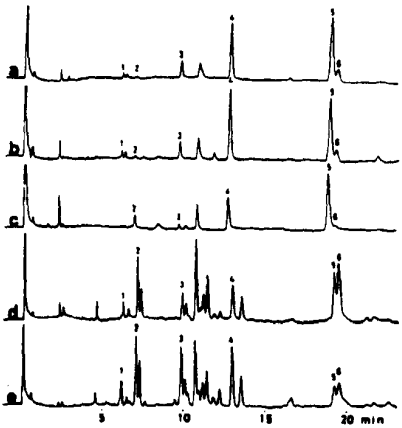


FIGURE 8. Gas chromatograms of PCDFs of various materials (225°C, 25 m × 0.23 mm OV-17 capillary column, carrier gas nitrogen, 1 ml/min). (a and b) PCDFs from the liver and adipose tissue of a Yusho patient (case 2 in Table 3), respectively; (c) PCDFs from the blood of Taiwanese patients 1 year after the poisoning; (d) PCDFs from a sample of Taiwanese oil; (e) PCDFs from a sample of Yusho oil manufactured on February 5, 1968. Peak no. 1,2,3,4,5, and 6: 2,3,7,8-tetra-, 1,2,4,7,8-penta-, 2,3,4,7,8-penta-, 1,2,3,4,7,8-hexa-, and 1,2,3,4,6,8-hexachlorinated dibenzofuran, respectively.

Table 6
DISTRIBUTION OF THE DEGREE OF DERMATOLOGICAL SEVERITIES IN JAPANESE AND TAIWANESE PATIENTS

	No. of patients	Degree of dermatological severities*			
		I	II	III	IV
Japanese patients[3]	138	25 (18%)	59 (43%)	28 (20%)	25 (18%)
Taiwanese patients[47]	122	32 (26%)	65 (53%)	13 (11%)	11 (9%)

* Classification according to the report of Goto and Higuchi;[3] grades increase with increasing severity.

V. BIOLOGICAL STUDY OF YUSHO

A. Investigation of Characteristic PCB Components Retained in Patients with Yusho

As already mentioned, most Yusho patients show a peculiar gas chromatographic pattern of PCBs, the so called type A pattern. This pattern, however, has rarely been observed in the workers occupationally exposed to PCBs or in normal people (controls).[11,48-52] Compared to the control group, the patients contained significantly smaller amounts of 4,2',4',-tri-

Table 7
CONCENTRATIONS (ppb, MEAN ± SD) OF PCBs, PCDFs AND PCQs IN BLOOD OF TAIWANESE PATIENTS 1 YEAR AFTER INTOXICATION

Degree of dermatological severities	No. of patients	PCBs level	PCDFs level	PCQs level
None*	5	12 ± 6	0.024 ± 0.018	1.7 ± 1.1
I + II	24	33 ± 13	0.062 ± 0.024	7.9 ± 3.7
III	14	43 ± 11	0.079 ± 0.030	8.2 ± 3.5
IV	24	49 ± 20	0.100 ± 0.040	11.0 ± 5.2
Total	67	42 ± 17	0.076 ± 0.038	8.6 ± 4.8

* Case without any dermatological signs.

(peak k), 2,4,3',4'-tetra- (peak 9), 3,4,2',4',5'-penta- (peak 25), and 3,4,2',3',4'-pentachlorinated biphenyl (peak 28) and on the contrary, larger amounts of 3,4,2',3',4',5'-hexa- (peak 47), 2,4,5,2',3',4',5'-hepta- (peak 49), and 2,3,4,2',3',4',5'-heptachlorinated biphenyls (peak 50) in their blood[65,69] (see Figure 5). It is noteworthy that a significant correlation has been observed between the gas chromatographic patterns of PCBs in the blood of the patients and their clinical manifestations such as the dermal signs,[7,41,42] ocular signs,[43] serum triglyceride levels,[44] etc.

Therefore, it was thought that to understand Yusho this peculiar pattern should be investigated. This peculiar composition of PCBs could be reproduced in the living rat by daily feeding Yusho oil containing 155 ppm of PCBs and 2 ppm of PCDFs, at a rate of 1 *mℓ* per rat for 10 days.[66]

The PCB pattern was recorded for a long period from the 8th to the 53rd week after the experiment began. However, the pattern was not also induced by supplying PCBs (KC-400) at the same or at a five times greater dosage.[66] A similar result was also reported in another rat experiment.[67] Therefore, it was deduced that the formation might be attributed to, as already mentioned, the unusual PCBs containing relatively larger amounts of higher-chlorinated congeners in the Yusho oil or the effect on their metabolism by a small quantity of PCDFs present in the oil.

Subsequently, the cause of this peculiar composition was studied by using PCBs and/or PCDFs, both of which had been separated from the toxic oil.[68,69] First, it was confirmed that the PCBs alone at a daily dosage of 15.4 μg for 7 days failed to induce the characteristic components in the mouse body.[68,69] The tissue PCBs showed a gas chromatographic pattern resembling that commonly seen in unexposed persons. On the other hand, a simultaneous treatment of the PCBs (15.4 μg/day) and the PCDFs (0.2 μg/day) in the same proportions as found in Yusho oil shortened the biological half-life of the 2,4,3',4'-tetra- (peak 9), 3,4,2',4',5'-penta- (peak 25), and 3,4,2',3',4'-pentachlorinated biphenyl isomers (peak 28) in both adipose and liver tissues of the rat. However, it had almost no effect on those of 3,4,2',3',4',5'-hexa- (peak 47), 2,4,5,2',3',4',5'-hexa- (peak 49), and 2,3,4,2',3',4',5'-heptachlorinated one (peak 50) (Table 8),[69] all of which are highly bioaccumulative compounds.[68,70,71] Consequently, the tissue PCBs showed the peculiar gas chromatographic patterns, type A, characteristic of Yusho.[68]

The above PCDFs, when applied separately, were more than 100 times more potent than the PCBs as inducers of drug-metabolizing enzymes such as cytochrome P-450, benzo(*a*)pyrene hydroxylase, and *p*-nitroanisol-*o*-demethylase in the rat liver.[72] Also, a greater difference in the ability to induce rat liver enzymes was reported between a synthesized PCDF mixture containing tetra- (12%) and pentachlorinated congeners (88%) and a commercial PCB product (Kanechlor® 500 with 54% chlorine content).[73] In addition, another PCDF mixture including

MONS 006171

Table 8
BIOLOGICAL HALF-LIFE OF PCB ISOMERS IN THE ADIPOSE TISSUE AND LIVER OF ICR STRAIN MICE

PCB isomers	Tissue	Duration (day)	Biological half-life (day)	
			PCBs treatment[a]	Mixture treatment[b]
2,4,3',4'-tetra	Fat	1—50	3.7	1.9
	Liver	1—30	3.7	1.6
3,4,2',4',5'-penta	Fat	1—50	8.1	5.5
	Liver	1—20	5.9	4.4
3,4,2',3',4'-penta	Fat	1—50	9.1	4.1
	Liver	20—50	9.1	5.5
3,3,2',3',4',5'-hexa	Fat	10—50	17.2	18.1
	Liver	1—50	13.6	17.0
2,4,5,2',3',4',5'-hepta	Fat	10—50	40.9	32.3
	Liver	1—20	13.4	17.5
		20—50	18.9	30.8
2,3,4,2',3',4',5'-hepta	Fat	20—50	7.6	10.5
	Liver	1—50	18.9	12.9

[a] Daily dosing of PCBs 15.4 μg per mouse for 7 days.
[b] Daily dosing of PCBs 15.4 μg and PCDFs 0.2 μg per mouse for 7 days.

tri- to pentachlorinated isomers was also shown to be 170 times more potent than a PCB product (KC-400) to induce reduction of the sleeping time of the rat after phenobarbital treatment.[70]

The above results unanimously indicate that the liver drug-metabolizing enzymes were more potently induced in the presence of PCDFs and would thus accelerate the selective elimination of some highly bioaccumulative PCB isomers (peaks 9, 25, and 28) and consequently, the PCB composition characteristic of Yusho patients would diminish.

B. Distribution of PCBs and Their Related Compounds

It has been established that after the exposure of the living body to PCB mixtures,[65,70,71] there is selective elimination and accumulation of certain isomers and that PCBs have a tendency to be deposited in the fatty tissues because of their lipophilic nature.[65,75-80] In general, the level of PCBs in the liver has been reported to be less than 10% of that in the adipose tissue, though some variation was observed according to dosage regime or animal species.[65,75-80] These facts can also be applied to Yusho patients, i.e., the ratio of PCB concentration of the liver to the adipose tissue ranged from 1.1 to 4.4% (Table 3).

On the other hand, PCDFs have been reported to show strong hepatotropism and in many experimental animals to have quite a different tissue distribution to that of PCBs.[38,77,81-85] In one outstanding example, more than 90% of total PCDF residues was detected in mouse liver.[85] This coincides with the analysis of the Yusho patients' tissue shown in Table 3. For example, in case 2, the ratios of liver to adipose tissue concentration for PCBs and PCDFs are 0.44 and 13.2, respectively. The accumulation, as well as in the case of PCBs[65,70,71] was indicated to be strongly related to both the number and position of the chlorine substitutions in the dibenzofuran molecule.[51,53] PCDF isomers with two vicinal hydrogenated carbon atoms in either of the two carbon rings of the dibenzofuran systems were shown to be easily eliminated from the Yusho patients' body.[43] On the contrary, an extremely highly toxic 2,3,4,7,8-pentachlorodibenzofuran was found to be a PCDF isomer that was preferentially accumulated in the livers of both rats and monkeys.[82] Such a phenomenon was also observed in the tissues of Yusho patients.[43]

PCQs were preferentially deposited in the livers of mice,[73] monkeys,[77] or rats[86] shortly

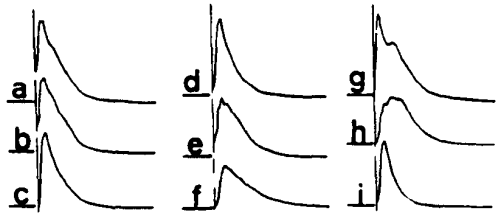


FIGURE 9. Gas chromatograms of PCQs in various tissues of the treated cynomolgus monkey (260°C, 0.5 m × 2.6 mm glass column containing 2% OV-210 on Gaschrom® Q 100—120 mesh, carrier gas nitrogen, 60 ml/min). (a to h) PCQs from the pancreas, skin, muscle, heart, kidney, adrenal, adipose tissue, and liver of monkey given PCQs at a daily dose of 5 mg per monkey for 20 weeks, respectively; (i) original PCQs.

after the termination of dosing. When the rat received a single oral dose of PCQs (44 mg), the liver contained about 50% of the total residual amount on the 6th day following the exposure.[86] In the rat given PCQs at a daily dose of 1.26 mg for 10 days, however, the ratio of PCQ concentration of the liver to the adipose tissue declined, showing 6.6, 3.0, and 0.9 on the 1st, 10th, and 50th days after exposure, respectively.[86] This suggests a possible transfer of PCQs from liver to adipose tissue. As observed in the case of Taiwanese patients,[39] the biological half-life of PCQs in a mouse whole body (86 days) was 2.5 times longer than that of PCBs (KC-400) (34 days),[75] indicating PCQs to be highly bioaccumulative compounds. This presumably explains why most Yusho patients had high blood PCQ levels for 10 years following poisoning.[27,43] In a monkey experiment[77,82] higher chlorinated PCQ congeners were confirmed to be preferentially deposited in the blood. After perchlorination, the third peak in the gas chromatogram of the blood PCQs gradually increased following treatment. A similar phenomenon was also noted in Taiwanese patients 6 months to 1 year following intoxication.[39]

In many species such as man,[30,40] rat,[86] and rabbit,[78] the chemical composition of PCB residues has been shown to be almost constant from tissue to tissue. In mouse dosed with PCDFs, the residual constituent was observed to be similar in all organs other than the liver.[81] There were also some differences in the components of PCDFs retained in the liver and the adipose tissue of Yusho patients (Figure 8).

The tissue distribution of PCQs, however, has been demonstrated to be rather different from that of PCBs or PCDFs.[27,77,86] In the monkey[27,77] and rat,[86] the gas chromatographic pattern varied from tissue to tissue (Figure 9). GC/MS analysis confirmed that when compared to the original PCQs containing hexa- to octachlorinated congeners as their major components, PCQs in the liver, kidney, and adrenal gland were mainly composed of higher-chlorinated congeners such as hepta- to decachlorinated ones, whereas in the adipose tissue they were composed mainly of lower-chlorinated congeners such as tri- to pentachlorinated ones, while in the heart similar ones.[27,77] After perchlorination, many patterns were also observed in the organs (Figure 10). These results indicate that the tissue distribution of PCQs may be related closely not only to the number and position of chlorine substitution but also to the skeletal structure.

C. Transfer of PCBs and Related Compounds from Mother to Fetus or Offspring

A full-term stillborn baby with dark pigmentation who had been delivered by a mother with Yusho was discovered to be rather heavily polluted with PCBs, PCQs, and PCDFs

MONS 006173

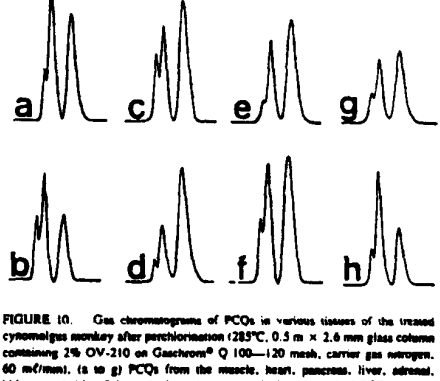


FIGURE 10. Gas chromatograms of PCQs in various tissues of the treated cynomolgus monkey after perchlorination (285°C, 0.5 m × 2.6 mm glass column containing 2% OV-210 on Gaschrom® Q 100—120 mesh, carrier gas nitrogen, 60 ml/min). (a to g) PCQs from the muscle, heart, pancreas, liver, adrenal, kidney, and skin of the treated monkey, respectively; (h) original PCQs.

(Table 3).[37,40] A recent study[40] has revealed that of five children delivered of a Yusho patient mother during the 7-year period following poisoning, PCQs could be detected in the blood of only the fourth son who was fed on mother's milk, but not in the blood of the others who were fed powdered milk. These facts indicate that chlorinated compounds can transfer from a mother to a fetus or baby via the placenta or the milk. Actually, Kuwabara et al.[91] and Yakushiji et al.[99] provided evidence with women occupationally exposed to PCBs and those who were not exposed that fairly large amounts of PCBs shift from the mother to the baby through milk during the feeding period. This was shown by analysis of samples of mothers' milk and blood and their children's blood.

Furthermore, placental and mammillary transfers of PCBs,[73,90-93] PCQs,[73,93] and PCDFs[90,94] from females to fetuses or suckling infants have been demonstrated in many experimental animals. In general, the quantity of these chemicals transferred via placenta was shown to be only 0.3 to 3% of that absorbed by the female's body.[73,91-93] Concerning such transference, a placental barrier against PCBs was surmised to exist because the PCB level in the blood of the umbilical cord was lower than that in the maternal blood.[93]

The amount moved via placenta was confirmed to relate closely to the maternal blood concentration but not to the maternal whole-body concentration.[93] The relative placental transferability in the rat was also confirmed to be PCBs (KC-400) > PCTs (Aroclor® 5460) > PCQs.[90]

In many animal experiments,[73,91,92,94-96] the amounts of PCBs, PCQs, or PCDFs transferred through the mammary gland have been proven to be overwhelmingly greater than amounts transferred via the placenta. PCBs, PCTs, PCQs, and PCDFs accumulated in the female body are transferred with little obstruction to the nursing infant. It was observed that most of the PCBs or PCDFs deposited in the nursing mouse body are transferred to the offspring within 1 to 2 weeks and PCTs or PCQs within 3 to 4 weeks after nursing.[96] The mammillary transferability of these chemicals tends to decrease with the increase in the number of phenyl nuclei in their molecules, namely, the relative transferability is hexachlorocyclohexane (HCH) > PCBs > PCDFs > PCTs > PCQs.[49,97] Compared to PCBs or PCTs, however, PCQs transferred through milk were confirmed to be more bioaccumulative in the body of the offspring.

MONS 006174

It is noteworthy that lower chlorinated biphenyl, terphenyl, or quaterphenyl congeners, respectively, preferentially moved from the female mouse to her suckling mouse through milk.[93] This warns us of the possible risk that heavily exposed women may cause acute poisoning of their suckling babies through such mammillary transfers.

D. Biological Effects of PCBs and Their Related Compounds

As already mentioned, there was a symptomatically great difference between Yusho patients and occupationally exposed workers, in spite of their similar daily intake of PCBs. Therefore, PCQs and PCDFs except for PCBs in the Yusho oil were deduced to be responsible for the Yusho condition.

In order to identify the causal agent of Yusho, the purity and the chemical composition of the compounds used in an experiment are considered to be very important. It has been indicated that a small amount of PCDFs present[15,21,22,96-100] as a by-product in PCB mixture products or individual PCB isomers strongly affects[14,101] the toxicity and promotes[102] the activity for inducing liver enzymes from the parent compounds, and that the biological effects of PCBs or PCDFs vary depending on the number and position of the chlorine substituents in their respective molecules.[102-106] PCBs in the samples of Yusho oil, as already described, have peculiar chemical compositions which are markedly different from those in commercial PCB products (Table 2). The composition of the PCDFs present are also different from those of commercially available PCDF mixtures. In addition, no PCQ products are available commercially.

In view of the above, PCBs, PCQs, or PCDFs containing similar compositions to those corresponding in Yusho oil (abbreviated as PY-PCBs, PY-PCQs, or PY-PCDFs, respectively) were prepared and used to discover the causal agents of Yusho.[30,72,77,108,109] PY-PCQs were confirmed to produce effects such as liver enzyme induction, liver hypertrophy, and immunosuppression to a somewhat slighter degree in the cynomolgus monkey or the SD strain rat than do PY-PCBs.[30,72,108,109] In monkey experiments,[30,109,110] no dermal lesions or body weight and hair loss were induced by daily feeding of 5 mg of PY-PCBs or 5 mg of PY-PCQs for 20 weeks. The PY-PCBs treatment, however, caused a mild liver hypertrophy and photomicrographs showed enlarged hepatocytes, interlobular inflammation, and epithelium proliferation of the bile ducts. As noted in liver biopsy specimens from a Yusho patient,[107] electron micrographs revealed a distinct reduction of the rough endoplasmic reticulum and marked proliferation of the smooth endoplasmic reticulum. In addition, mild damage to kidneys and a significant immunosuppression were observed (Figure 11). On the other hand, a 5-mg daily dose of a mixture containing PY-PCBs and PY-PCDFs (5 and 0.002 mg, respectively)[108,109] or 0.02 mg of PY-PCDFs alone[30,109] for 20 weeks induced a significantly higher degree of toxicity in the monkey compared to the above treatments. The dermal signs similar to those characteristic for Yusho (Figure 12) — ocular signs, severe body weight loss (18 to 20% of the initial body weight), and hair loss (finally spreading to the whole body area) were observed in the treated monkey.

Furthermore, the mixture or the PY-PCDFs caused more severe liver damage and immunosuppression (Figure 11) than did PY-PCBs or PY-PCQs. These results indicate that quantitatively PY-PCDFs can be hundreds to thousands of times more potent than PY-PCBs or PY-PCQs as inducers of the various clinical signs mentioned above. Therefore, the fact that secondary respiratory[4,109] and dermal infections[8] have been often observed in Yusho patients may be attributed to the severe immunosuppression caused by PCDFs. In rats,[72] no dermal lesions resembling those of Yusho were induced by daily feeding of 2.01 mg of a mixture including PY-PCBs, PY-PCQs, and PY-PCDFs (1, 1, and 0.01 mg, respectively) in proportions similar to those found in Yusho oil for 24 days, but retarded growth and caused enlargement of the liver and thymic atrophy. Similar adverse effects were induced by doses of 0.01 mg of PY-PCDFs but not by 1-mg doses of PY-PCBs or 1 mg of PY-

MONS 006175

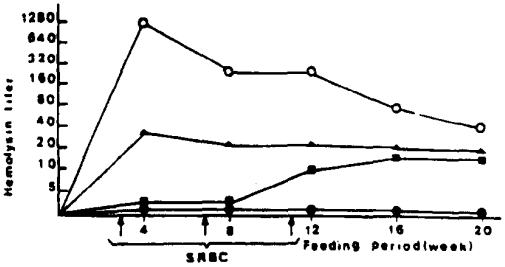


FIGURE 11. Effects of PY-PCBs, PY-PCQs, and PY-PCDFs feeding on production of anti-sheep red blood cell antibodies. Monkeys were immunized with sheep red blood cell on days 16, 44, and 72 of feeding. ⊙—⊙, A mixture containing PY-PCBs and PY-PCDFs (5 and 0.02 mg/day, respectively); ⊕—⊕, PY-PCBs (5 mg/day); ▲-▲, PY-PCQs (5 mg/day); ○—○, control.



FIGURE 12. Treated monkey on the left and control monkey on the right. The monkey was orally given a mixture containing of PY-PCBs and PY-PCDFs (5 and 0.02 mg/day, respectively) for 20 weeks. Note edema of the lips and eyelids, acne-form eruption of the malar region, pigmentation of the malar and nasal regions, and loss of facial hair.

PCQs, except for liver hypertrophy caused by dosing with PY-PCBs. These results confirmed that PY-PCDFs are also hundreds of times more toxic than PY-PCBs or PY-PCQs to the rat.

On the other hand, compared to the control rat group, serum triglyceride levels increased by 42 and 41%, respectively, in rats fed PY-PCQs in daily doses of 1 mg per rat and PY-

Table 9
SERUM TRIGLYCERIDE AND CHOLESTEROL LEVELS IN TREATED RATS

Experimental group	Triglyceride level (mg/dℓ, mean ± SD)	Cholesterol level (mg/dℓ, mean ± SD)
Control	36.7 ± 9.5	76.5 ± 4.5
Mixture	85.3 ± 20*	140.8 ± 4.5*
PY-PCBs	28.8 ± 6.6	87.2 ± 5.7
PY-PCQs	51.8 ± 9.9	70.6 ± 8.1
PY-PCDFs	52.2 ± 8.6	95.4 ± 6.2

Note: Each group of 6 male SD strain rats (5 weeks old) was orally given 0.5 mℓ of an olive oil solution containing a mixture at the level of 2.01 mg (1.0 mg PY-PCBs + 1.0 mg PY-PCQs + 0.01 mg PY-PCDFs/rat. PY-PCBs 1.0 mg/rat, PY-PCQs 1.0 mg/rat, and PY-PCDFs 0.01 mg/rat, respectively, for 22 consecutive days. Six control rats were similarly dosed with olive oil.

* $p > 0.001$.

PCDF doses of 0.01 mg per rat, but decreased in rats fed PY-PCBs 1 mg (Table 9).[72] In the monkey experiment,[100,108] a considerable increase of serum triglyceride levels was demonstrated only in the monkey given PY-PCQs. Consequently, it was deduced that the hyperglycemia observed in most Yusho patients during the long period (over 5 years) following intoxication[64] was principally induced by both PY-PCDFs and PY-PCQs.

VI. CAUSAL AGENTS OF THE YUSHO AND TAIWAN INCIDENTS

Taking all the facts described above into account, it has been concluded PCDFs are the primary causal agent of Yusho as well as of the Taiwan incident for the following reasons.

1. Both Taiwanese patients and Japanese workers occupationally exposed to PCBs had similar elevated blood levels of PCBs (Tables 4 and 7), but the former had severe clinical manifestations while few of the latter had any. Thus, PCBs do not seem to be responsible for the clinical manifestations. Since these two groups of subjects differed markedly in their exposure to PCDFs as well as in the PCDF concentrations in their blood,[31,22,99,108] differences in their clinical manifestations could be more reasonably explained by PCDFs.

2. Blood concentration of PCBs in the Japanese workers exceeded those of the Yusho patients, in spite of the fact that the former had far less severe clinical manifestations. Thus, the amounts of residual PCBs in their bodies do not explain this clinical difference. Furthermore, workers who had been exposed to PCB preparations used as heat transfer liquids showed similar blood levels of PCQs to those of Yusho patients (Table 4) but had few lesions. Thus, PCQs do not seem to be responsible for the observed marked difference in clinical manifestation.

3. Five years after the poisoning, PCB levels in the blood of Yusho patients were shown to be almost the same as those of unexposed individuals.[6,7] Here again, PCBs hardly explain their lingering suffering.[8,9] As already mentioned, we failed to detect PCDFs in the blood of Yusho patients 11 years after the outbreak (Table 4). However, it is quite certain that in the earliest stages of poisoning they would have had detectable levels of PCDFs in the blood because Taiwanese patients who ingested rice oil containing much less PCDFs than in the Japanese Yusho oils definitely had PCDFs in the blood when examined within 2 years of poisoning. It has also been confirmed that PCDFs were present in various tissues of Yusho patients 1 to 10 years after poisoning.[64]

MONS 006177

These facts indicate that the Taiwanese patients and the Japanese Yusho patients were heavily exposed to PCDFs and retained them in their body for long periods. Since PCDFs have been found only at extremely low levels in the tissues of unexposed people (Table 3), it seems more reasonable to consider this specific group of chemicals rather than PCBs is responsible for the obstinate symptoms and signs of Yusho patients.

4. As described above, exposed workers had fairly high blood PCB levels (45 ppb on average; Table 4) but no detectable amounts of PCQs and PCDFs 9 years after exposure ended. According to Watanabe et al.,[110] the concentration of PCBs in the blood of workers occupationally exposed to unused PCB preparations decreased at a rate of about 10%/year after exposure. If this is true, the subjects must have had a considerably higher (probably higher than 100 ppb on average) concentration of PCBs in the blood during exposure. Even so, they did not show such severe lesions as did Yusho patients.[12] Hasegawa et al.[19] also reported that many workers who had handled unused PCB products in an electrical condenser factory showed only mild clinical signs despite blood PCB levels as high as 100 to 1000 ppb and their estimated daily intake of PCBs was similar to those[46] of Yusho patients. It was also reported that the mild dermal lesions seen in some workers quickly disappeared after PCB handling was discontinued. Similar patterns have not been seen among Yusho and Taiwanese patients. All these facts unanimously indicate that a simple exposure to PCBs alone may not induce the severe lesions characteristic of Yusho, although the possible influence of the different routes of entry of PCBs on their toxicity should not be overlooked.

5. The PCDFs detected in the tissues of Yusho patients or in the blood of Taiwanese patients include highly toxic congeners[19,20] such as 2,3,7,8-tetra- and 2,3,4,7,8-penta-chlorinated ones.

6. In our animal experiments,[26,100,105] no dermal lesions resembling those characteristic for Yusho[3] were reproduced at all by feeding monkeys PY-PCBs or PY-PCQs each containing no PCDFs, even in doses about 13 times the average amount of PCBs or PCQs received by Yusho patients.[46] They were only induced when a mixture containing PY-PCBs and PY-PCDFs was fed. Other toxic effects were also evident only when the mixture was fed, but not with pure PY-PCBs or PY-PCQs. In rats,[26,72] no dermal lesions similar to those of Yusho were induced by feeding a mixture containing PY-PCBs, PY-PCQs, and PY-PCDFs but retarded growth, hypertrophy of the liver, and thymic atrophy were induced. Similar adverse effects were induced by feeding PY-PCDFs but not by feeding PY-PCBs or PY-PCQs, except for liver hypertrophy caused by feeding PY-PCBs. From these results, the chemicals in the Yusho oil could be ranked in the order PY-PCDFs ≫ PY-PCBs ≧ PY-PCQs in regard to toxicity.

7. As already mentioned, the so-called gas chromatographic pattern "A" which is considered to be characteristic of the PCBs retained in the body of Yusho patients was seen in Taiwanese patients whose blood had a high level of PCDFs 2 years after poisoning.[20] However, such a PCB pattern was never observed in any workers occupationally exposed to unused PCB preparations. These facts can be well explained by our animal observations[26,105] that the presence of PCDFs is necessary to yield such a peculiar gas chromatographic pattern in animals.

Now, we are able to say that Yusho is symptomatically and etiologically different from simple PCB poisoning.

MONS 006178

REFERENCES

1. Tsukamoto, H., Makinomi, S., Hirose, H., Kojima, T., Fukumoto, H., Fukumoto, K., Kuratsune, M., Nishinomi, M., Shibata, M., Nagai, J., Yao, Y., Sawada, K., Yoshimura, H., Tatsumi, K., Orugi, K., Shimono, H., Ueno, K., Kobayashi, H., Yano, T., Ito, A., Okada, T., Inagami, K., Koga, T., Tomita, Y., Koga, T., Yamada, Y., Miyaguchi, M., Sugano, M., Hori, K., Takeshita, K., Manako, K., Nakamura, Y., and Shigemori, N., The chemical studies on detection of toxic compounds in the rice bran oils used by the patients of Yusho. *Fukuoka Acta Med.*, 60, 496, 1969 (in Japanese).
2. Tanabe, H., Takeda, M., Ito, K., Suzuki, T., Kanda, H., Kanda, T., Uchiyama, S., Kurata, H., Netori, S., Terashima, T., Shimura, H., and Kanazawa, J., Ad Hoc Study on Prevention, Diagnosis and Treatment of Yusho. Study Report from Japanese Agency of Technology, 1970 (in Japanese).
3. Goto, M. and Higuchi, K., The symptomatology of Yusho (chlorobiphenyls poisoning) in dermatology, *Fukuoka Acta Med.*, 60, 409, 1969 (in Japanese).
4. Shigematsu, N., Norimatsu, Y., Ishibashi, T., Yoshida, M., Soetsugu, S., Kawatatsu, T., Ikeda, T., Saito, R., Ishimaru, S., Shirakusu, T., Kido, M., Emori, K., and Tashimitsu, H., Clinical and experimental studies on respiratory involvement in chlorobiphenyls poisoning, *Fukuoka Acta Med.*, 62, 150, 1971 (in Japanese).
5. Kaneda, M., Yusho and women — a study on sexual functions of women with the rice bran oil poisoning, *Sanka to Fujinka*, 38, 1963 (in Japanese).
6. Masuda, M., Kagawa, T., Shimada, K., Takeda, M., and Kuratsune, M., Polychlorinated biphenyls in the blood of Yusho patients and ordinary persons, *Fukuoka Acta Med.*, 65, 25, 1974 (in Japanese).
7. Takamatsu, M., Inoue, Y., and Abe, S., Diagnostic meaning of the blood PCB, *Fukuoka Acta Med.*, 65, 28, 1974 (in Japanese).
8. Asahi, M., Kada, H., Urabe, H., and Tashitani, S., Dermatological symptoms of Yusho alterations in the decade, *Fukuoka Acta Med.*, 70, 172, 1979 (in Japanese).
9. Kohno, T. and Yamano, Y., Ten-year follow-up study on ocular manifestations of "Yusho" (accidental polychlorinated biphenyls poisoning), *Fukuoka Acta Med.*, 70, 181, 1979 (in Japanese).
10. Hasegawa, H., Sato, M., and Tsuruta, H., The level of PCB in the blood of workers handling PCB in a factory, *Rodo Eisei*, 13, 50, 1972 (in Japanese).
11. Hirayama, H., A study of PCB contamination among industrial workers, *J. Kurume Med. Assoc.*, 41, 1, 1978 (in Japanese).
12. Hara, I., Hirao, M., Watanabe, I., Yakushiji, T., Takahashi, M., and Nishitani, N., Health status of the workers occupationally exposed to PCB at a paint manufacturing factory, *Ann. Rep. Osaka Pref. Inst. Pub. Health*, 17, 11, 1979 (in Japanese).
13. Hara, I., Yakushiji, T., Kashimoto, T., and Kunita, N., Follow-up studies on the health status of the workers occupationally exposed to PCB and their children, in *Proc. 8th Int. Conf. Occup. Health Chem. Ind.*, Takemura, N. and Yamamura, Y., Eds., Aikawa Shobo Publ. Co., Tokyo, 1980, 312.
14. Vos, J. G., Koeman, J. H., Van Der Maas, H. L., Ten Noever De Brau, M. C., and Vos, R. H., Identification and toxicological evaluation of chlorinated dibenzofuran and chlorinated napthalene in two commercial polychlorinated biphenyls, *Food Cosmet. Toxicol.*, 8, 625, 1970.
15. Bauer, H., Schulz, K. H., and Spiegelberg, U., Berufliche vergiftungen bei der herstellung von chlorphenol-verbindungen, *Arch. Gewerbepath. Gewerbehyg.*, 18, 538, 1961.
16. Miyata, H., Kashimoto, T., and Kunita, N., Detection and determination of polychlorodibenzofurans in normal human tissues and Kanemi rice oils caused "Kanemi Yusho", *J. Food Hyg. Soc. Jpn.*, 19, 260, 1977.
17. Miyata, H., Watanabe, I., Kashimoto, and Kunita, N., Studies of PCB and PCDF in Kanemi rice oils caused "Yusho", *Ann. Rep. Osaka Pref. Inst. Publ. Health*, 8, 11, 1977 (in Japanese).
18. Bonner, M. T., Polychlorinated dibenzofurans (PCDFs) found in Yusho oil and in used Japanese PCB, *Chemosphere*, 5, 439, 1978.
19. Moore, M. R., Comparative toxicity of three halogenated dibenzofurans in guinea pigs, mice and rhesus monkeys, in *Health Effects of Halogenated Aromatic Hydrocarbons*, Boland, B. and Hitchcock, J. M., Eds., Ann. N.Y. Acad. Sci., New York, 1979, 151.
20. Decad, G. M., Birnbaum, L. S., and Mathews, H. B., 2,3,7,8-Tetrachlorodibenzofuran tissue distribution and excretion in guinea pigs, *Toxicol. Appl. Pharmacol.*, 57, 231, 1981.
21. Miyata, H., Nakamura, A., and Kashimoto, T., Separation of polychlorodibenzofurans (PCDFs) in Japanese commercial PCBs (Kanechlors) and their heated preparation, *J. Food Hyg. Soc. Jpn.*, 17, 227, 1976.
22. Nagayama, J., Masuda, Y., and Kuratsune, M., Determination of chlorinated dibenzofurans in Kanechlors and "Yusho oil", *Environ. Contam. Toxicol.*, 15, 9, 1975.
23. Miyata, H., Kashimoto, T., and Kunita, N., Detection of unknown organochlorinated compounds in Kanemi rice oils caused "Kanemi Yusho", *J. Food Hyg. Soc. Jpn.*, 19, 126, 1978 (in Japanese).

MONS 006179

24. Miyata, H., Kashimoto, T., and Kunita, N., Detection and determination of unknown organochlorinated compounds in Kanemi rice oil caused the "Yusho". *J. Food Hyg. Soc. Jpn.*, 19, 365, 1978.
25. Kamps, L. V. R., Trotter, J., Young, S. J., Carson, L. J., Roach, J. A. G., Sphon, J. A., Tanner, J. T., and McMahon, B., Polychlorinated quaterphenyls identified in rice oil associated with Japanese "Yusho" poisoning. *Bull. Environ. Contam. Toxicol.*, 20, 589, 1978.
26. Maeda, K. and Kashimoto, T., Studies on quantitative analysis for polychlorinated quaterphenyls (PCQs). *Ann. Rep. Osaka Pref. Inst. Pub. Health*, 9, 89, 1978 (in Japanese).
27. Armour, J. A., Quantitative perchlorination of polychlorinated diphenyls as a method for confirmatory residue measurement and identification. *JAOAC*, 56, 987, 1973.
28. Miyata, H., Murakami, Y., and Kashimoto, T., Investigation on polychlorinated quaterphenyl in Kanemi rice oils caused the "Yusho". *J. Food Hyg. Soc. Jpn.*, 19, 233, 1978.
29. Miyata, H., Murakami, Y., and Kashimoto, T., Determination of polychlorinated quaterphenyl (PCQ) in Kanemi rice oil caused the "Yusho" and investigation on the PCQ formation. *J. Food Hyg. Soc. Jpn.*, 19, 417, 1978.
30. Kashimoto, T., Yusho and behavior of PCQs concerning the environmental pollution. *Furumaishu*, 17, 512, 1981 (in Japanese).
31. Miyata, H. and Kashimoto, T., Investigation on polychlorodibenzofuran formation. *J. Food Hyg. Soc. Jpn.*, 19, 78, 1978 (in Japanese).
32. Nakagawa, J., Morita, M., Akiyama, K., Higuchi, I., and Mimura, S., Formation of polychlorinated dibenzofurans through heating PCB mixture (Aroclor T-1248). *Ann. Rep. Tokyo Metr. Res. Lab.*, 28, 260, 1977 (in Japanese).
33. Morita, M., Nakagawa, J., Akiyama, K., Mimura, S., and Inoue, N., Detailed examination of polychlorinated dibenzofurans in PCB preparations and Kanemi Yusho oil. *Bull. Environ. Contam. Toxicol.*, 18, 67, 1977.
34. Buser, H. R. and Rappe, C., Formation of polychlorinated dibenzofurans (PCDFs) from the pyrolysis of individual PCB isomers. *Chemosphere*, 9, 157, 1979.
35. Yamaryo, T., Miyanishi, T., Masuda, Y., and Nagayama, J., Formation of polychlorinated quaterphenyls by heating polychlorinated biphenyls. *Fukuoka Acta Med.*, 70, 88, 1979 (in Japanese).
36. Miyata, H. and Kashimoto, T., Investigation on organochlorinated compounds formed in Kanemi rice oil caused the "Yusho". *J. Food Hyg. Soc. Jpn.*, 20, 1, 1979.
37. Kashimoto, T., Miyata, H., and Kunita, N., The presence of polychlorinated quaterphenyls in the tissues of Yusho victims. *Food Cosmet. Toxicol.*, 19, 335, 1981.
38. Kojima, T., Chlorobiphenyls in the sputa and tissues. *Fukuoka Acta Med.*, 62, 25, 1971 (in Japanese).
39. Kikuchi, M., Mihagi, Y., Hashimoto, M., and Kojima, T., Two autopsy cases of chronic chlorobiphenyls poisoning. *Fukuoka Acta Med.*, 62, 89, 1971.
40. Masuda, Y., Kagawa, R., and Kuroasawa, M., Polychlorinated diphenyls in Yusho patients and ordinary persons. *Fukuoka Acta Med.*, 65, 17, 1974.
41. Takamatsu, S., Maruta, H., Inoue, Y., Abe, S., and Takamatsu, M., Dermatological signs and blood PCB in the subjects having taken PCB-containing rice oil. *Fukuoka Acta Med.*, 68, 145, 1977 (in Japanese).
42. Toshitani, S., Ambi, M., and Kada, H., Alteration in dermatological findings of patients with Yusho (PCB poisoning) in general examination 1975. *Fukuoka Acta Med.*, 68, 152, 1977 (in Japanese).
43. Kashimoto, T., Miyata, H., Fukushima, S., and Kunita, N., Differences of residual chlorinated compounds between Yusho patients and persons exposed to PCB. *Fukuoka Acta Med.*, 72, 198, 1981 (in Japanese).
44. Kuroki, H. and Masuda, Y., Determination of polychlorinated dibenzofurans retained in patients with Yusho. *Chemosphere*, 7, 771, 1978.
45. Rappe, C., Buser, H., Kuroki, H., and Masuda, Y., Identification of polychlorinated dibenzofurans (PCDFs) retained in persons with Yusho. *Chemosphere*, 8, 259, 1979.
46. Hayabuchi, H., Yoshimura, T., and Kuratsune, M., Consumption of toxic rice oil by "Yusho" patients and its recession to the clinical response and latent period. *Food Cosmet. Toxicol.*, 17, 455, 1979.
47. Chang, P. C., Chen, C. J., Wong, C. K., and Chen, P. H. S., Dermatological survey of 122 PCB poisoning persons in comparison with blood PCB levels. *Clin. Med. (Taipei)*, 7, 15, 1981 (in Chinese).
48. Fu, Y. A., Ocular manifestation of PCB poisoning and its relationships between blood PCB levels and ocular findings. *Clin. Med. (Taipei)*, 7, 28, 1981 (in Chinese).
49. Lan, C. F., Chen, P. H. S., Shieh, L. L., and Chen, Y. H., An epidemiological study on polychlorinated biphenyls poisoning in Taichung area. *Clin. Med. (Taipei)*, 7, 96, 1981.
50. Chen, P. H. S., Chang, K. T., and Lu, Y. D., Toxic compounds in the cooking oil which caused PCB poisoning in Taiwan (I). *Clin. Med. (Taipei)*, 7, 71, 1981 (in Chinese).
51. Kashimoto, T., Miyata, H., Kunita, N., Tung, T., Hsu, S., Chang, K., Tung, S., Ohi, G., Nakagawa, J., and Yamamoto, S., Role of polychlorinated dibenzofuran in Yusho. 36, 321, 1981.
52. Chen, P. H. S., Lu, Y. D., Yang, M. H., and Chen, J. S., Toxic compounds in the cooking oil which caused PCB poisoning in Taiwan (II). *Clin. Med. (Taipei)*, 7, 77, 1981 (in Chinese).

MONS 006180

53. Kashimoto, T., Miyata, H., Fukushima, S., Kunita, N., Tung, T. C., Hsu, S. T., Chang, C. J., Tung, S. Y., Ohi, G., and Yamamoto, S., Chlorinated compounds in Taiwanese "Yusho" patients blood presented at 30th Annu. Conf. Mass *Spectrosc. Allied Topics*. Honolulu. June 6, 1982. 198.
54. Yoshimura, T., Epidemiological analysis of "Yusho" patients with special reference to sex, age, clinical grades and oil consumption. *Fukuoka Acta Med.*, 62, 104, 1971 (in Japanese).
55. Chen, C. H., Gaw, J. M., Wong, C. K., and Chen, C. J., Levels and gas chromatographic patterns of polychlorinated biphenyls in the blood of patients after PCB poisoning in Taiwan. *Bull. Environ. Contam. Toxicol.*, 25, 325, 1980.
56. Li, W. M., Chen, C. J., and Wong, C. K., PCB poisoning of 27 cases in three generations of a large family. *Clin. Med. (Taipei)*, 7, 23, 1981 (in Chinese).
57. Chen, P. H. S., Caw, J. M., Chen, C. J., and Tseng, H. H., Levels and gas chromatographic patterns of polychlorinated biphenyls in the blood of PCB-intoxicated patients after ingestion of the toxic cooking oil. *Clin. Med. (Taipei)*, 7, 40, 1981 (in Chinese).
58. Kunita, N., Kashimoto, T., Miyata, H., Fukushima, S., Hori, S., and Obana, H., Causal agents of Yusho. *Am. J. Ind. Med.*, 5, 45, 1984.
59. Nakashima, H. and Umeda, G., Changes in levels of blood polychlorinated biphenyls and quaterphenyls with time at the initial stage of PCB intoxication. *Med. Biol.*, 103, 237, 1981 (in Japanese).
60. Watanabe, I., Yakushiji, T., Kuwabara, K., Yoshida, S., Hara, I., and Kunita, N., Studies on PCBs in the blood of ordinary persons. Yusho patients and occupationally exposed workers. *Jpn. Soc. Publ. Health*, 24, 749, 1977 (in Japanese).
61. Kuwabara, K., Yakushiji, T., Watanabe, I., Yoshida, S., Koyama, K., Kunita, N., and Hara, I., Relationship between breast feeding and PCB residues in blood of children whose mothers were occupationally exposed to PCB. *Int. Arch. Occup. Environ. Health*, 41, 189, 1978.
62. Wolff, M. S., Fischbein, A., Lilis, R., and Selikoff, I. J., Disposition of polychlorinated biphenyls in occupationally exposed persons. *Toxicol. Appl. Pharmacol.*, 62, 294, 1982.
63. Oshibi, Y. and Yoshimura, T., Relationship between PCB concentrations or porterins in blood and ocular signs among people examined for "Yusho". *Fukuoka Acta Med.*, 68, 123, 1977 (in Japanese).
64. Ohnishi, M., Masuda, Y., and Nakamoto, S., Correlation between blood PCB and serum triglyceride levels in patients with PCB poisoning. *Fukuoka Acta Med.*, 65, 84, 1974 (in Japanese).
65. Koroki, H. and Masuda, Y., Structures and concentrations of the main components of polychlorinated biphenyls retained in patients with Yusho. *Chemosphere*, 6, 469, 1977.
66. Miyata, H., Watanabe, I., Yamamoto, H., Inoue, K., Hamano, Y., Oda, Y., Kuwano, A., and Kunita, N., Time course of PCB in rats which administered with KC-400 and Kanemi rice oil caused "Yusho". *Ann. Rep. Osaka Pref. Pub. Health*, 8, 93, 1977 (in Japanese).
67. Yoshida, S., Yakushiji, T., Watanabe, I., Kuwabara, K., Koyama, K., and Kunita, N., Studies on PCB pattern in rats administered KC-300. *Ann. Rep. Osaka Pref. Inst. Publ. Health*, 8, 59, 1977 (in Japanese).
68. Hori, S., Miyata, H., Maeda, K., Murakami, Y., and Kashimoto, T., Studies on the characteristic patterns of PCB residues in "Yusho" patients. *J. Food Hyg. Soc. Jpn.*, 20, 166, 1979 (in Japanese).
69. Hori, S., Kashimoto, T., and Kunita, N., Effect of polychlorinated dibenzofuran on the retention of polychlorinated biphenyl isomers in the liver and adipose tissue of mice. *J. Food Hyg. Soc. Jpn.*, 23, 167, 1982.
70. Jensen, S. and Sundstrom, G., Structures and levels of most chlorobiphenyls in two technical PCB products and in human adipose tissue. *Ambio*, 3, 70, 1974.
71. Yakushiji, T., Watanabe, I., Kuwabara, K., Yoshida, S., Koyama, K., and Kunita, N., Levels of polychlorinated biphenyls (PCBs) and organochlorine pesticides in human milk and blood collected in Osaka Prefecture from 1972 to 1977. *Int. Arch. Occup. Environ. Health*, 43, 1, 1979.
72. Hori, S., Obana, H., and Kashimoto, T., Unpublished data, 1982.
73. Kawano, S. and Hiraga, K., Potent inducers of rat hepatic drug-metabolizing enzymes. *Ann. Rep. Tokyo Metr. Res. Lab. Publ. Health*, 28, 175, 1977 (in Japanese).
74. Arishi, Y., Comparison of enzyme-inducing activities of chlorinated dibenzofuran and chlorinated dibenzodioxin. *Fukuoka Acta Med.*, 65, 61, 1974 (in Japanese).
75. Hori, S., Kashimoto, T., and Kunita, N., Difference of transfer among PCB, PCT and PCQ from mother to suckling mice. *Ann. Rep. Osaka Pref. Inst. Publ. Health*, 11, 103, 1980 (in Japanese).
76. Yoshimura, H., Yamamoto, H., Nagai, J., Yao, Y., Ueno, H., Ito, Y., Natsui, A., Mineikawa, S., Ito, A., Kato, K., and Tsuji, H., Studies on the tissue distribution and the urinary and fecal excretion of 14C-Kanechlor (chlorobiphenyls) in rats. *Fukuoka Acta Med.*, 62, 12, 1971 (in Japanese).
77. Hori, S., Obana, H., Yoshida, M., Yoshida, Y., Kashimoto, T., and Kunita, N., Biological effects of the compounds related to Yusho on female cynomolgus monkeys (*Macaca fascicularis*). *Ann. Rep. Osaka Pref. Inst. Publ. Health*, 12, 1, 1981 (in Japanese).
78. Tohyama, Y., Minagawa, K., Yokoyama, M., and Sakai, H., Studies on the distribution and the change of PCB and PCT in the living body. *Jpn. J. Hyg.*, 29, 143, 1974 (in Japanese).

MONS 006181

79. **Hansen, L. G.**, Selective accumulation and depletion of polychlorinated biphenyl components. in *Health Effects of Halogenated Aromatic Hydrocarbons*, Vol. 320, Nicholson, W. J. and Moore, J. A., Eds., Ann. N.Y. Acad. Sci., New York, 1979, 238.
80. **Kitamura, S., Somino, K., and Hirano, I.**, Studies on PCB decrease in various tissues of rats. *Jpn. J. Hyg.*, 29, 83, 1974 (in Japanese).
81. **Morita, M. and Otshi, S.**, Clearance and tissues distribution of polychlorinated dibenzofurans in mice, *Bull. Environ. Contam. Toxicol.*, 18, 61, 1977.
82. **Birnbaum, L. S., Decad, G. M., and Matthews, H. B.**, Disposition and excretion of 2,3,7,8-tetrachlorodibenzofuran in the rat, *Toxicol. Appl. Pharmacol.*, 55, 342, 1980.
83. **Kuroki, H., Masuda, Y., Yoshimura, S., and Yoshimura, H.**, Accumulation of polychlorinated dibenzofurans in the livers of monkeys and rats, *Food Cosmet. Toxicol.*, 18, 387, 1980.
84. **Birnbaum, L. S., Decad, G. M., Matthews, H. B., and McConnell, E. E.**, Fate of 2,3,7,8-tetrachlorodibenzofuran in the monkey, *Toxicol. Appl. Pharmacol.*, 57, 189, 1981.
85. **Nagayama, J., Tokudome, S., Kuratsune, M., and Masuda, Y.**, Transfer of polychlorinated dibenzofurans to the fetuses and offspring of mice, *Food Cosmet. Toxicol.*, 18, 153, 1980.
86. **Hori, S., Miyata, N., Kashimoto, T., and Kunita, N.**, Excretion, distribution and general biological effects of polychlorinated quaterphenyl (PCQ) in the rat, *Ann. Rep. Osaka. Prof. Inst. Publ. Health*, 9, 105, 1978, (in Japanese).
87. **Kuratsune, M., Yusho**, in *Topics in Environmental Health*, Vol. 4, Kimbrough, R., Ed., Elsevier/North-Holland, Amsterdam, 1980, 288.
88. **Takematsu, M., Oki, M., Masuda, K., and Kashimoto, T.**, Relations between PCQ level and PCB pattern in the blood of Yusho patients, *Fukuoka Acta Med.*, 72, 192, 1981.
89. **Yakushiji, T., Watanabe, I., Kuwabara, K., Kashimoto, T., Hara, I., and Kunita, N.**, Long-term studies on blood PCB levels of the children and their mothers occupationally exposed to PCBs, in *Proc. 8th Int. Conf. Occup. Health Chem. Ind.*, Takemura, N. and Yamamura, Y., Eds., Aikawa Shobo Publ. Co., Tokyo, 1980, 317.
90. **Allen, J. R. and Barsotti, D. A.**, The effects of transplacental and mammary movement of PCBs on infant rhesus monkeys, *Toxicology*, 6, 331, 1976.
91. **Takagi, Y., Otake, T., and Kataoka, M., Murata, Y., Aborade, S., Akaneka, S., Hashimoto, K., Uda, H., and Kitaura, T.**, Studies on the transfer and distribution of [^{14}C] polychlorinated biphenyls from maternal to fetal and suckling rats, *Toxicol. Appl. Pharmacol.*, 38, 549, 1976.
92. **Masuda, Y., Kagawa, R., Tokudome, S., and Kuratsune, M.**, Transfer of polychlorinated biphenyls to the fetuses and offspring of mice, *Food Cosmet. Toxicol.*, 16, 33, 1978.
93. **Masuda, Y., Kagawa, R., Kuroki, H., Kuratsune, M., Yoshimura, T., Taki, I., Kusuda, M., Yamashita, F., and Hayashi, M.**, Transfer of polychlorinated biphenyls from mothers to foetuses and infants, *Food Cosmet. Toxicol.*, 16, 543, 1978.
94. **Masuda, Y., Kagawa, R., Kuroki, H., Tokudome, S., and Kuratsune, M.**, Transfer of various polychlorinated biphenyls to the foetuses and offspring of mice, *Food Cosmet. Toxicol.*, 17, 623, 1979.
95. **Hori, S., Kashimoto, T., and Kunita, N.**, Transfer of PCB, PCT and PCQ from the mother to litters through the milk or placenta and their distribution in mother's body in rats and mice, *J. Food Hyg. Soc. Jpn.*, 22, 301, 1981 (in Japanese).
96. **Otshi, S. and Hiraga, K.**, Transfer of polychlorinated dibenzofuran and dibenzodioxin to the fetuses and sucklings of mice, *Ann. Rep. Tokyo Metr. Res. Lab. Publ. Health*, 30, 113, 1978 (in Japanese).
97. **Hori, S. and Kashimoto, T.**, Transfer of β-BHC from mother to suckling mouse, *J. Food Hyg. Soc. Jpn.*, 15, 446, 1976 (in Japanese).
98. **Bosch, J. A. G. and Pomerantz, I. H.**, The finding of chlorinated dibenzofurans in Japanese polychlorinated biphenyl sample, *Bull. Environ. Contam. Toxicol.*, 12, 338, 1974.
99. **Bowes, G. W., Mulvihill, M. J., Simoneit, B. R. T., Burlingame, A. L., and Risebrough, R. W.**, Identification of chlorinated dibenzofurans in American polychlorinated biphenyls, *Nature (London)*, 256, 305, 1975.
100. **Miyata, H. and Kashimoto, T.**, The finding of polychlorodibenzofurans in commercial PCBs (Aroclor, Phenoclor and Clophen), *J. Food Hyg. Soc. Jpn.*, 17, 434, 1976 (in Japanese).
101. **Vos, J. G. and Beems, R. B.**, Dermal toxicity studies of technical polychlorinated biphenyls and fractions thereof in rabbits, *Toxicol. Appl. Pharmacol.*, 19, 617, 1971.
102. **Goldstein, J. A.**, The structure-activity relationships of halogenated biphenyls as enzyme inducer, in *Health Effect of Halogenated Aromatic Hydrocarbons*, Vol. 320, Boland, B. and Hitchcok, J. M., Eds., Ann. N.Y. Acad. Sci., New York, 1979, 164.
103. **Mehlmney, J. D., Chee, K., Gupta, B. N., Moore, J. A., and Goldstein, J. A.**, Toxicological assessment of hexachlorobiphenyl isomers and 2,3,7,8-tetrachlorodibenzofuran in chicks, *Toxicol. Appl. Pharmacol.*, 36, 65, 1976.
104. **McNulty, W. P., Beeker, G. M., and Cory, H. T.**, Chronic toxicity of 3,4,3',4'-and 2,5,2',5'-tetrachlorobiphenyls in rhesus macaques, *Toxicol. Appl. Pharmacol.*, 45, 209, 1978.

MONS 006182

105. **Hori, S., Obana, H., Kashimoto, T., Otake, T., Nishimura, H., Ikegami, N., Kunita, N., Fukuda, Y., and Uda, H.**, Biological effects of the compounds related to Yusho on female cynomolgus monkeys (*Macaca fascicularis*). II. Studies on biochemical finding of blood, hepatic microsomal enzyme, immune response and histopathology, *Ann. Rep. Osaka Prof. Inst. Publ. Health*, 12, 9, 1981 (in Japanese).

106. **Hori, S., Obana, H., Kashimoto, T., Otake, T., Nishimura, H., Ikegami, N., Kunita, N., and Uda, H.**, Effect of polychlorinated biphenyls and polychlorinated quaterphenyls in cynomolgus monkey (*Macaca fascicularis*), *Toxicology*, 24, 123, 1982.

107. **Hirayama, C., Irie, T., and Yamamoto, T.**, Fine structural changes of the liver in a patient with chlorobiphenyls intoxication, *Fukuoka Acta Med.*, 60, 455, 1969 (in Japanese).

108. **Hori, S., Obana, H., Kashimoto, T., and Kunita, N.**, Unpublished data, 1982.

109. **Shigematsu, N., Ishimaru, S., Ikeda, T., and Masuda, Y.**, Further studies on respiratory disorders in polychlorinated biphenyl poisoning — relationship between respiratory disorders and PCB concentrations in blood and sputum, *Fukuoka Acta Med.*, 68, 41, 1969 (in Japanese).

110. **Watanabe, I., Yakushiji, Y., Yoshida, S., Tanaka, R., Kashimoto, T., Hara, I., and Kunita, N.**, The analysis of PCB in the blood of workers occupationally handling PCB preparation, *Jpn. Soc. Publ. Health*, 27, 769, 1980 (in Japanese).

MONS 006183

Chapter 2

PCB POISONING FROM TOXIC RICE-BRAN OIL IN TAIWAN

Paul H. Chen and Shu-Tao Hsu

TABLE OF CONTENTS

I. Introduction 28

II. Epidemiologic Studies 28
- A. Outbreak of Poisoning 28
- B. Discovery of PCBs in the Causal Oil 28
- C. Clinical Symptoms 28
- D. Geographical and Monthly Distribution of Patients 29
- E. Sources of the Toxic Rice-Bran Oil 30
- F. Deaths Among Yucheng Patients 30

III. Toxic Agents in the Toxic Oil 31
- A. PCBs in the Toxic Oil 31
- B. PCDFs in the Toxic Oil 32
- C. PCQs in the Toxic Oil 32
- D. Amounts of the Toxic Oil and Toxic Agents Ingested by Patients 33

IV. Toxic Agents in the Blood and Tissues of Yucheng Patients 33
- A. PCBs in the Blood of Patients 33
- B. Comparative Rates of Elimination of PCBs 34
- C. PCBs Retained in the Tissues 34
- D. PCDFs Retained in the Tissues 35
- E. PCDFs in the Blood 37
- F. PCQs in the Tissues 37

References 37

MONS 006184

I. INTRODUCTION

In the spring of 1979, an epidemic of a peculiar disease characterized by acne-form skin eruptions, pigmentation of the skin and nails, and hypersecretions of the Meibomian glands broke out in several townships in Taichung and Changhua counties in Central Taiwan. The cause of the disease was later identified as due to the ingestion of a brand of cooking rice-bran oil contaminated with polychlorinated biphenyls (PCBs), dibenzofurans (PCDFs), and quaterphenyls (PCQs).[1-4] The incident was called PCB poisoning or rice-bran oil poisoning in Taiwan. It was also called Yucheng (oil disease in Chinese) by some scientists in Taiwan. The total number of registered cases in the incident was more than 2000. This was one of the two most serious incidents of PCBs and PCDFs poisoning in humans. Another serious incident occurred in Western Japan in 1968 involving more than 1600 cases.[5]

II. EPIDEMIOLOGIC STUDIES

A. Outbreak of Poisoning

On May 21, 1979, a local health bureau in Taichung County was informed by Hui-Ming School for Blindness that a peculiar disease characterized by acne-like skin eruptions had occurred increasingly among students and staff from the end of March.[3] Almost at the same time, 85 of 150 workers from a nearby plastic shoe factory were also suffering from the same symptoms but did not report to the local health bureau until early September 1979. An extensive epidemiological investigation revealed that victims in both outbreaks consumed the same brand of cooking rice-bran oil purchased from a local oil retailer. The rice oil was strongly suspected of causing the disease. On September 18, 1979, two firms in a neighboring township of Taichung County reported that their workers were suffering from the same disease. In addition, cases were also reported in some families. All the victims in these patient groups in Taichung had consumed the rice-bran oil purchased from the Fong-Hsiang Oil Store and manufactured by the Chunghua Oil Company. In addition to Taichung County, cases of the disease were also reported in the neighboring Changhua County in the spring of 1979.

B. Discovery of PCBs in the Causal Oil

Dermal symptoms of the peculiar disease were very similar to those of chloracne, but the dermatologists in Taiwan consulted by the government health officials did not recognize chloracne at that time and thus did not provide any information suggesting PCBs or other related compounds as the possible causal agents. Then Yamamoto and Ohi of the University of Tokyo were consulted, and samples of the causal oil and patients' blood were sent to Japan for analysis. Both oil and blood samples were found to contain elevated levels of PCBs by Japanese scientists. After the discovery of PCBs in the causal oil in early October, 1979, health authorities in Taiwan immediately announced the cause of the disease and prohibited further distribution of the toxic oil.

C. Clinical Symptoms

The most common symptoms experienced by 122 poisoned patients were abnormal mucocutaneous pigmentation, acne-form eruptions, and deformity of nails.[6] Increased eye discharge and swelling of the upper eyelids were also experienced by many patients in the first stage of poisoning.[6] Abnormal pigmentation occurred on the conjunctivae, gingivae, finger and toenails, buccal mucosa, and nose. Acne-form eruptions, predominantly open comedones, papules, pustules, and pitted scarring, occurred not only on the classical sites for acne vulgaris but also on the extremities, axillae, and genital areas.[6]

MONS 006185

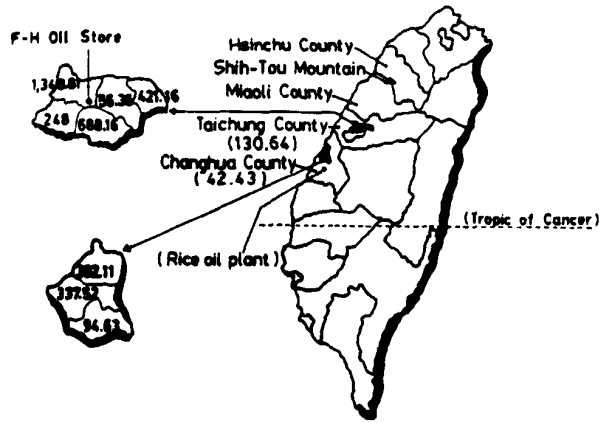


FIGURE 1. Locations of four counties and several townships in the counties in which the poisoning occurred. The numbers in the figure are the number of victims per 100,000 population in the counties or the townships outside the county. (From Hsu, S. T. et al., *Am. J. Ind. Med.*, 1983. With permission.)

D. Geographical and Monthly Distribution of Patients

Most of the poisoned victims were from several townships in Taichung and Changhua counties (Figure 1). Some cases were also reported in Maoli and Hsinchu counties (Figure 1), and they were from two groups. One group consisted of monks and nuns from the temples of Shih-Tou Mountain. The other group comprised students returning from technique-practicing courses in factories in Taichung county. The numbers in Figure 1 are the number of cases per 100,000 population. As shown in the figure, the morbidities are high in several townships in Taichung and Changhua. There are about 1300 cases in Taichung county, 500 cases in Changhua county, and 100 to 200 cases in Maoli and Hsinchu counties with a total of about 2000 cases in the whole of Taiwan. The poisoning in Taichung mainly occurred in the cafeteries of three factories and Hui-Ming School for Blindness as well as some sporadic cases in households and other communities. In Changhua, the poisoning occurred mainly in families of some communities.

Monthly distribution of new patients in Taichung and Changhua is shown in Figure 2. The earliest cases occurred at the end of 1978 and were identified by retrospective studies in Changhua. High frequencies of incidence occurred during the period from March to July 1979. It should be noted that after the health authorities announced the cause of the disease on October 6, 1979, new cases in October increased markedly in Taichung but not in Changhua. This can be explained as follows. Patients in Changhua consumed the toxic oil several months earlier than those in Taichung. At the time of announcement in October, most of the patients in Changhua had developed symptoms and had already registered in local hospitals or health bureaus. On the other hand, a number of victims in Taichung were in the early stage of poisoning or still in the latent period. They would not have known that they were PCB poison victims at that time if the health authorities had not announced the cause of disease in October.

MONS 006186

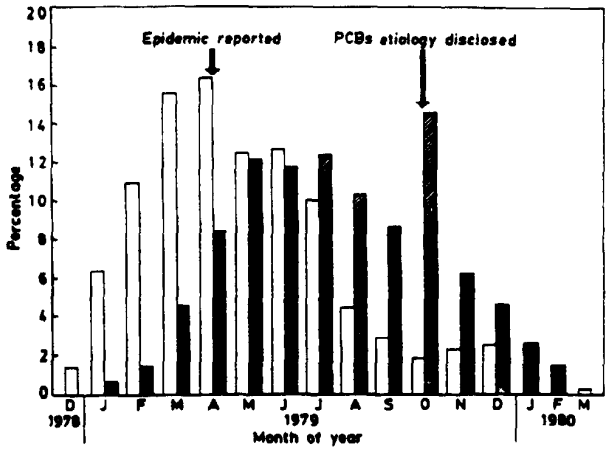


FIGURE 2. Monthly distribution of new patients in Taichung (shaded bar) and Changhua County (open bar). (From Hsu, S. T., et al., *Am. J. Ind. Med.*, 1983. With permission.)

E. Sources of the Toxic Rice-Bran Oil

All of the patients in Taichung as well as those in Miaoli and Hsinchu consumed the toxic oil purchased from the Fong-Hsiang Oil Store in Taichung and manufactured by the Chunghua Oil Company. At the time when the government health authorities announced the cause of the disease in early October 1979, PCBs were found in unsold oil in the Fong-Hsiang Oil Store and in unused oil in cafeterias or homes in Taichung where the patients were intoxicated. The poisoned victims in Changhua purchased the toxic oil from a few rice oil stores in Changhua which in turn bought the oil from the Changhua Oil Company. However, an extensive search for PCBs in hundreds of oil samples from the oil stores and victims' homes in Changhua failed to disclose any PCB contamination with the exception of one sample which was given to a patient by the Changhua Oil Company. It should be noted that no PCBs have been detected in recently refined oil from the Changhua Oil Company and the manager and the owner of the company insisted that they had not used PCBs in their manufacturing process since 1976. However, the fact that high levels of PCBs were found in the blood of the plant's workers as well as in the plant's soil seemed to suggest that PCBs had been used in the plant recently.[3] Furthermore, the elevated levels of PCQs and, to a lesser extent, PCDFs found in the toxic oil suggest that PCBs in the toxic oil had been subjected to heating at high temperature.[4] It was generally believed that PCBs in the toxic oil came from the accidental leak of the heat transfer medium during the manufacturing process in which PCB was presumably used as a heat transfer medium.

F. Deaths Among Yucheng Patients

By the end of February 1983, 24 deaths were reported among 2060 poisoned patients. Almost half of them died from hepatoma, liver cirrhosis, or liver diseases with hepatomegaly. The diagnoses were made from clinical symptoms and laboratory examinations. In addition,

MONS 006187

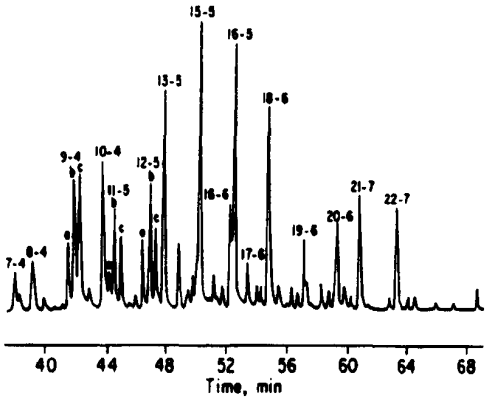


FIGURE 3. Gas chromatogram of PCBs in the toxic rice-bran oil obtained from Taichung using a DB-5 fused silica column. (From Chen, P. H. and Hites, R. A., *Chemosphere*, 1983. With permission.)

39 black-pigmented babies were born from the poisoned mothers. They showed very high infant mortality rate. Eight of them died from pneumonia, bronchitis, sepsis, and premature and congenital weakness.

III. TOXIC AGENTS IN THE TOXIC OIL

A. PCBs in the Toxic Oil

A typical gas chromatogram of PCBs in the toxic rice-bran oil obtained from Taichung is shown in Figure 3. In this figure, the number after a hyphen in each peak is the number of chlorine atoms in each PCB peak as determined by gas chromatography/mass spectrometry (GC/MS). The structural assignments of most of the major peaks as well as the percent distribution of each individual PCB components in the toxic oil have been published elsewhere.[4,7] The percentages of pentachloro-, tetrachloro-, hexachloro-, heptachloro-, and trichlorobiphenyls of PCBs in the toxic oil were calculated as 47.1, 33.8, 12.4, 4.5, and 2.2%, respectively. A comparison of GC patterns of PCBs in Taiwan and Japan toxic rice oil indicated that the former consisted of a larger percentage of PCB components with longer retention times.[3,8] This suggests that if the same amounts of PCBs were ingested by both Japanese and Chinese patients, then it would be expected that higher amounts of accumulative PCBs would be retained in the body of Chinese patients because it is difficult to excrete the highly chlorinated PCBs from the human body.

GC patterns of PCBs in the toxic oil obtained with a SE-30 packed column are similar to that of a one-to-one mixture of Kanechlor® 400 and 500 (KC-400 and KC-500) except that in the front portion of the chromatogram peaks are smaller in the rice oil.[3] This similarity does not necessarily mean that the toxic oil was actually contaminated with KC-400 and KC-500; it might be contaminated with another PCB preparation that gives a similar GC pattern.[4]

Concentrations of PCBs in 39 samples of unsold oil in the Fong-Hsiang Oil Store were

MONS 006188

Table 1
CONCENTRATIONS (ppm) OF PCBs, PCDFs, AND PCQs IN THE TOXIC RICE-BRAN OIL OBTAINED IN TAICHUNG[3]

Sample	PCBs	PCDFs	PCQs
A	53	0.18	25
B	99	0.40	40
C	78	0.25	—
D	77	0.21	43
E	65	0.30	53

reported as ranging from 5 to 205 ppm with a mean value of 52 ± 39 SD.[9] The sample that contained the highest level of PCB among these 39 samples was re-analyzed by one of us, and a much higher PCB level (405 ppm) was obtained. Concentrations of PCBs in the oil samples collected from the factory and school cafeterias and the families of poisoned patients in Taichung ranged from 53 to 99 ppm (Table 1). If PCB levels of these five samples in Table 1 are representative of the toxic oil ingested by the patients in Taichung, then PCB levels in the toxic oil consumed by the patients in Taichung was only about one tenth to one twentieth of that in the Japanese toxic oil.[4] This does not necessarily mean that the Chinese patients in Taichung ingested less PCBs than the Japanese Yusho patients because the former consumed about 15 to 20 times more toxic oil than the latter.[10] A more detailed discussion about the total oil consumption will be described later. The level of PCB in the toxic oil consumed by the patients in Changhua is not known. However, based on the severity of clinical symptoms for the patients in Changhua and the blood PCB analysis which showed that the patients in Changhua had in general higher PCB levels that those in Taichung, one can presume that the toxic oil ingested by the patients in Changhua contained higher levels of PCB than that consumed by the patients in Taichung.[3,6]

B. PCDFs in the Toxic Oil

A gas chromatogram of PCDFs in the toxic oil obtained from Taichung is shown in Figure 4. In this figure, all of the major peaks except peaks A and B are due to PCDFs. GC/MS analysis indicated that peaks 1 to 3 were tetrachlorodibenzofurans, peaks 4 to 9 were pentachlorodibenzofurans, and peaks 10 and 11 were PCDFs with 6 and 7 chlorine atoms, respectively. The structural assignments of most of these peaks are published elsewhere.[4,11] Using a DB-5 fused silica column for analysis, peak 3 is coincidental in retention time with that of the authentic standard of a very toxic PCDF, namely 2,3,7,8-TCDF. However, when a fused silica column coated with Supelco 2330 was used for analysis, we found that 2,3,7,8-TCDF was only a minor component in this peak. The major components of this peak are 2,3,4,8-TCDF and another unidentified TCDF. It should be noted that another very toxic PCDF, i.e., 2,3,4,7,8-PnCDF (peak 8 of Figure 4), is one of the major PCDFs in the toxic oil.

Quantification of PCDFs in the toxic oil was made by GC/MS operating in a selected ion monitoring mode.[2] The results are shown in Table 1. The ratios of PCDFs to PCBs in the toxic oil are roughly from 0.0025 to 0.005. These are much higher than PCDFs normally found in the commercial PCBs preparations. The formation of the elevated levels of PCDFs in the toxic oil is likely due to the heating of PCBs.[12]

C. PCQs in the Toxic Oil

In addition to PCBs and PCDFs, PCQs were also found in the toxic oil. The gas chro-

MONS 006189

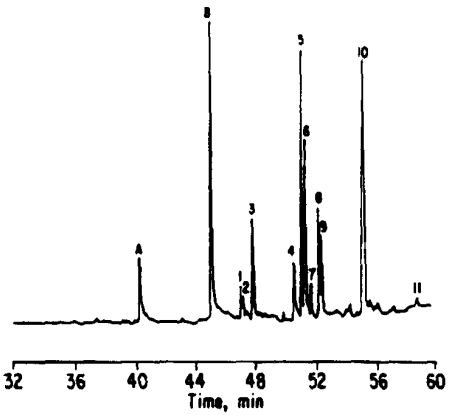


FIGURE 4. Gas chromatogram of PCDFs in the toxic rice-bran oil obtained from Taichung. (From Chen, P. H. and Hites, R. A., *Chemosphere*, 1983. With permission.)

matogram of PCQs in the Taiwanese toxic oil is similar to that of PCQs in the Japanese toxic oil.[4,13] GC/MS analysis of the PCQ fraction indicated that PCQs in the toxic oil contained 6 to 10 chlorine atoms. High levels of PCQs were found in the toxic oil (see Table 1). These elevated levels of PCQs are likely due to the heating of PCBs in the toxic oil because it had been demonstrated that PCQs can be produced by heating PCBs at high temperatures.[14]

D. Amounts of the Toxic Oil and Toxic Agents Ingested by Patients

The amount of toxic oil consumption by 98 patients from four patient groups was estimated on the average as 1.02 to 1.55 kg/month/adult.[10] The period of toxic oil taken for these patient groups was about 9 months.[10] Using these data, the total amount of toxic oil consumption by an adult for these patient groups is estimated on the average as 9 to 14 kg. This is about 15 to 20 times higher than the average total oil consumption by the Japanese Yusho patients which was estimated at 688 m*l*.[10]

An accurate estimation of total PCBs, PCDFs, and PCQs intake by Yucheng patients is difficult. However, it could be estimated roughly by the assumption that the concentrations of these toxic agents in the oil (see Table 1) which was collected for analysis at the end of 9-month period of toxic oil consumption represent the concentrations of these toxic agents in the oil taken in the whole 9-month period. Based on this assumption, the average toxic agents intake for these patient groups were estimated at 973, 3.8, and 586 mg for PCBs, PCDFs, and PCQs, respectively. These values are comparable to 633, 3.3, and 596 mg estimated for the Japanese Yusho patients for PCBs, PCDFs, and PCQs, respectively.[15]

IV. TOXIC AGENTS IN THE BLOOD AND TISSUES OF YUCHENG PATIENTS

A. PCBs in the Blood of Patients

A few laboratories in Taiwan have been engaged in blood PCB analysis since the outbreak

MONS 006190

Table 2
DISTRIBUTION OF BLOOD PCB LEVELS FOR 165 YUCHENG PATIENTS*

	PCB levels (ppb)					
	10—19	20—29	30—39	40—49	50—100	100—800
No. of patients	29	57	39	14	22	4
Percentage	17.6	34.6	23.6	8.5	13.3	2.4

* Blood samples were collected about 9 to 18 months after poisoning.

of Yucheng. A large range of variation in the blood PCB levels has been reported by these laboratories. The laboratory of one of the authors reported that blood PCB levels of 165 Yucheng patients sampled about 9 to 18 months after the onset of poisoning were in the range from 10 to 720 ppb with a mean value of 38 ppb.[6] The distribution of blood PCB levels of these patients is shown in Table 2. The blood PCB levels of these Yucheng patients are much higher than those of the Japanese Yusho patients, which had a mean PCB level of 5.9 ppb for 72 patients 5 years after poisoning. This great difference is largely due to the difference in time lags between PCB ingestion and sampling of blood for PCB analysis.[1]

B. Comparative Rates of Elimination of PCBs

The toxic oil ingested by the patients contained PCBs with 3 to 8 chlorine atoms. These PCB components are metabolized and eliminated from the patient's body at different rates depending on the number and position of chlorine substitutions. The laboratory of one author has investigated the comparative rates of elimination of some individual PCBs from the blood of patients. The results of this study were published recently.[7] The results indicate that tetra- and pentachlorobiphenyls with adjacent unsubstituted carbon atoms at *meta-para* positions are rapidly eliminated from the blood of patients, while PCBs with the same degree of chlorination but with adjacent unsubstituted carbon atoms at *ortho-meta* positions are eliminated more slowly. The results also indicate that most of the hexa- and heptachlorobiphenyls with adjacent unsubstituted carbon atoms at *ortho-meta* positions of the biphenyl ring are eliminated very slowly and would be expected to remain in the patient's body for a long time.

C. PCBs Retained in the Tissues

Various tissues from a Yucheng patient who died about 2 years after the onset of poisoning were available to us for the analysis. The tissues analyzed included intestinal fat, bronchus, large intestine, heart, stomach, liver, small intestine, kidney, lung, brain, and spleen. A gas chromatogram of PCBs retained in the bronchus of the deceased patient is shown in Figure 5. GC patterns of PCBs in other tissues of this patient are very similar to that in the bronchus shown here. A comparison of Figures 3 and 5 indicates that with the exception of 11-5-c, and to much lesser extents, 9-4-a and 15-5, PCBs with five or less chlorine atoms were almost completely excreted from the patient's tissues about 2 years after the ingestion of the toxic agents. In contrast, most PCB congeners with six or more chlorine atoms were still retained in the tissue. The major PCB congeners retained in the tissues are 2,3,4,2',4',5'-hexachlorobiphenyl (HxCB) (18-6), 2,4,5,2',4',5'-HxCB (16-6), 2,3,4,5,3',4'-HxCB (20-6), 2,4,5,2',4'-pentachlorobiphenyl (11-5-c), 2,3,4,5,2',4',5'-heptachlorobiphenyl (HpCB) (21-7), and 2,3,4,5,2',3',4'-HpCB (22-7). As reported in our study on the blood of Yucheng patients and described in the section above, these very slowly eliminated PCB congeners either do not have adjacent unsubstituted carbon atoms in the biphenyl ring or have a pair of adjacent unsubstituted carbon atoms at *ortho-meta* positions but not at *meta-para* positions.

MONS 006191

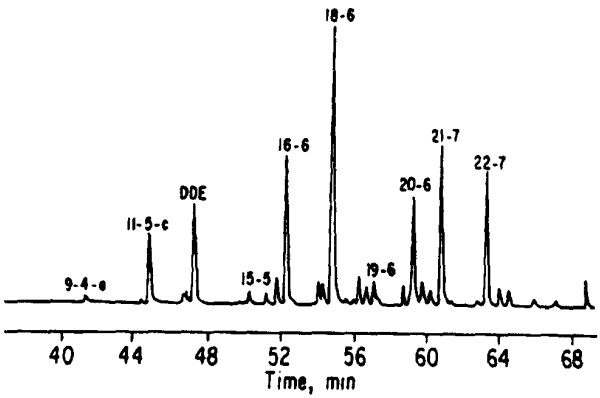


FIGURE 5. Gas chromatogram of PCBs retained in the bronchus of the Yucheng patient who died 2 years after the poisoning. (From Chen, P. H. and Hites, R. A., *Chemosphere*, 1983. With permission.)

Table 3
CONCENTRATIONS OF TOTAL MAJOR PCBs AND PCDFs IN THE TISSUES OF THE DECEASED PATIENT WITH YUCHENG IN TAIWAN*

Tissue	PCBs (ppm)	PCDFs (ppb)
Intestinal fat	10.81	12.7
Bronchus	5.56	5.4
Large intestine	3.28	3.8
Heart	2.48	2.4
Stomach	0.66	0.68
Liver	0.65	35.1
Small intestine	0.27	0.60
Kidney	0.25	0.54
Lung	0.18	0.22
Brain	0.08	0.22
Spleen	0.07	0.19

* The patient died about 2 years after the poisoning.

The concentrations of total major PCBs retained in various tissues of the deceased patient are shown in Table 3. As expected, the intestinal fat contains the highest level of PCBs. Bronchus, large intestine, and heart also contain high levels of PCBs, while spleen and brain contain low levels of PCBs.

D. PCDFs Retained in the Tissues

Figure 6 shows that the major PDCFs retained in the liver of the patient are 1,2,3,4,7,8-

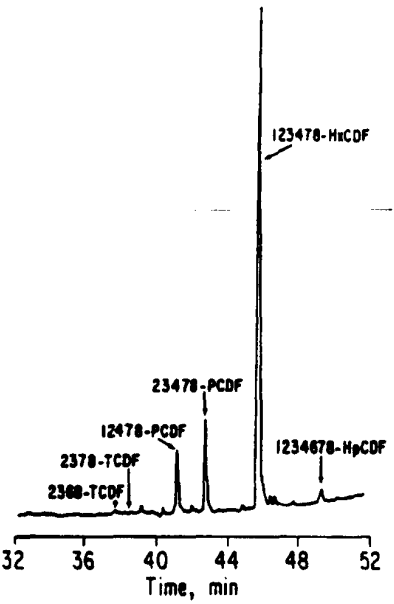


FIGURE 6. Gas chromatogram of PCDFs retained in the liver of the deceased patient. (From Chen, P. H. and Hites, R. A., *Chemosphere*, 1983. With permission.)

hexachlorodibenzofuran (HxCDF), 2,3,4,7,8-pentachlorodibenzofuran (PnCDF), and 1,2,4,7,8-PnCDF. Minor amounts of 1,2,3,4,6,7,8-heptachlorodibenzofuran (HpCDF), 2,3,6,8-tetrachlorodibenzofuran (TCDF), and 2,3,7,8-TCDF were also found in the liver. The PCDF congeners retained in other tissues are essentially the same as those retained in the liver. However, the relative amounts of each individual PCDF congener are somewhat different in the liver compared to other tissues.

In agreement with the findings by other workers in the study of Japanese Yusho patients,[16] we found that all PCDF congeners that were retained in the patient's tissues had no vicinal hydrogens in the dibenzofuran ring.[11] In contrast, all PCDF congeners that were excreted from the patient's body had at least two vicinal hydrogens in the ring.[11] These excreted PCDF congeners include 2,3,4,8-TCDF, 1,2,3,4,8-PnCDF, 1,2,6,7,8-PnCDF, 2,3,4,6,7-PnCDF, and 1,2,3,4,6,7-HxCDF which correspond to peaks 3,6,7,9, and part of 10 in Figure 4, respectively.

Table 3 shows that the concentration of PCDFs in the liver is about three times as much as in the intestinal fat, whereas the levels of PCBs in the liver are only about 1/17th of that in the intestinal fat. This high accumulation of PCDFs in the liver has been reported by other workers in an animal study[17] as well as for Japanese Yusho patients.[16]

MONS 006193

The most toxic PCDF congeners retained in the patient's tissues are 2,3,7,8,-TCDF and 2,3,4,7,8-PnCDF. Since 2,3,4,7,8-PnCDF is one of the major PCDFs retained in the tissues while 2,3,7,8-TCDF is only a very minor PCDF retained in the tissues and a minor PCDF present in the toxic oil, the former probably plays a much more important role in the etiology of Yucheng in Taiwan.[11] 1,2,3,4,7,8-HxCDF is the most abundant PCDF component retained in the tissues; it is also a toxic PCDF.[19] This PCDF, along with 2,3,4,7,8-PnCDF,[8] could play important roles in the etiology of Yucheng.

E. PCDFs in the Blood

The total PCDFs in the blood of ten patients ranged from 0.02 to 0.20 ppb. The major PCDFs found in the blood were 1,2,3,4,7,8-HxCDF and 2,3,4,7,8-PnCDF. Minor amounts of 1,2,3,4,6,7,8-HpCDF and 1,2,4,7,8-PnCDF were also found in the blood.

F. PCQs in the Tissues

The tissues from the deceased patients were also analyzed for PCQs. The bronchus and the intestinal fat were found to contain high levels of PCQs each amounting to 4.3 and 3.8 ppm, respectively. The large intestine and the heart also contained high levels of PCQs.

REFERENCES

1. Chen, P. H., Gow, J. M., Wong, C. K., and Chen, C. J., Levels and gas chromatographic patterns of polychlorinated biphenyls in the blood of patients after PCB poisoning in Taiwan, *Bull. Environ. Contam. Toxicol.*, 25, 325, 1980.
2. Chen, P. H., Chang, K. T., and Lu, Y. D., Polychlorinated biphenyls and polychlorinated dibenzofurans in the toxic rice-bran oil that caused PCB poisoning in Taichung, *Bull. Environ. Contam. Toxicol.*, 26, 409, 1981.
3. Hsu, S. T., Ma, C. I., Hsu, S. K. H., Wu, S. S., and Hsu, N. H. M., Discovery and epidemiology of PCB poisoning in Taiwan, *Am. J. Ind. Med.*, in press, 1983.
4. Chen, P. H., Luo, M. L., Wong, C. K., and Chen, C. J., Polychlorinated biphenyls, dibenzofurans, and quaterphenyls in the toxic rice-bran oil and PCBs in the blood of patients with PCB-poisoning in Taiwan, *Am. J. Ind. Med.*, in press, 1983.
5. Kuratsune, M., Yusho, in *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products*, Kimbrough, R. D., Ed., Elsevier/North-Holland, Amsterdam, 1980, 287.
6. Wong, C. K., Chen, C. J., Chang, P. C., and Chen, P. H., Mucocutaneous manifestations of polychlorinated biphenyls (PCB) poisoning: a study of 122 cases in Taiwan, *Br. J. Dermatol.*, 107, 317, 1982.
7. Chen, P. H., Luo, M. L., Wong, C. K., and Chen, C. J., Comparative rates of elimination of some individual polychlorinated biphenyls from the blood of PCB-poisoned patients in Taiwan, *Food Chem. Toxicol.*, 20, 417, 1982.
8. Masuda, Y., Kuroki, H., Yamaryo, T., Haraguchi, K., Kuratsune, M., and Hsu, S. T., Comparison of causal agents in Taiwan and Fukuoka PCB poisonings, *Chemosphere*, 11, 199, 1982.
9. Ko, Y. C., Chang, C. E., and Liu, S. S., Epidemiological study of PCB poisoning, *J. Formosan Med. Assoc.*, 80, 406, 1981.
10. Lan, C. F., Chen, P. H., Shieh, L. L., and Chen, Y. H., An epidemiological study on polychlorinated biphenyls poisoning in Taichung area, *Clin. Med. (Taipei)*, 7, 96, 1981.
11. Chen, P. H. and Hites, R. A., Polychlorinated biphenyls and dibenzofurans retained in the tissues of a deceased patient with Yucheng in Taiwan, *Chemosphere*, 12, in press, 1983.
12. Morita, M., Nakagawa, J., and Rappe, C., Polychlorinated dibenzofuran (PCDF) formation from PCB mixture by heat and oxygen, *Bull. Environ. Contam. Toxicol.*, 19, 665, 1978.
13. Kashimoto, T., Miyata, H., and Kunita, N., The presence of polychlorinated quaterphenyls in the tissues of Yusho victims, *Food Cosmet. Toxicol.*, 19, 335, 1981.
14. Yamaryo, T., Miyanishi, T., Masuda, Y., and Nagayama, J., Formation of polychlorinated quaterphenyls by heating polychlorinated biphenyls, *Fukuoka Acta Med.*, 70, 88, 1979.
15. Hayabuchi, H., Yoshimura, T., and Kuratsune, M., Consumption of toxic rice oil by Yusho patients and its relation to the clinical response and latent period, *Food Cosmet. Toxicol.*, 17, 455, 1979.

MONS 006194

16. **Rappe, C., Buser, H. R., Kuroki, H., and Masuda, Y.,** Identification of polychlorinated dibenzofurans (PCDFs) retained in patient with Yusho. *Chemosphere*, 8, 259, 1979.
17. **Kuroki, H., Masuda, Y., Yoshihara, S., and Yoshimura, H.,** Accumulation of polychlorinated dibenzofurans in the livers of monkeys and rats. *Food Cosmet. Toxicol.*, 18, 387, 1980.
18. **Kuroki, H. and Masuda, Y.,** Determination of polychlorinated dibenzofuran isomers retained in patients with Yusho. *Chemosphere*, 7, 771, 1978.
19. **Yoshihara, S., Nagata, K., Yoshimura, H., Kuroki, H., and Masuda, Y.,** Inductive effect on hepatic enzymes and acute toxicity of individual polychlorinated congeners in rats. *Toxicol. Appl. Pharmacol.*, 59, 580, 1981.

MONS 006195

Chapter 3

PCBs IN HUMAN POPULATIONS

Jos Mes

TABLE OF CONTENTS

I. Origin, Measurement, and Identity of PCBs in Humans 40

II. PCBs in Human Tissues and Fluids of Various World Populations 44
- A. Adipose Tissue 44
- B. Breast Milk 45
- C. Blood 46
- D. Miscellaneous Tissues and Fluids 46
- E. Infant and Fetal Tissues and Fluids 47

III. Trends in PCB Levels of Tissues and Fluids from Specific Human Populations 50
- A. Adipose Tissue 50
- B. Breast Milk 52
- C. Blood 53

IV. Some Parameters Which Can Affect PCB Levels in Human Populations 53
- A. Sampling 53
- B. Age 56
- C. Sex 57
- D. Race 57
- E. Population Density 57

References 58

MONS 006196

I. ORIGIN, MEASUREMENT, AND IDENTITY OF PCBs IN HUMANS

In general, polychlorinated biphenyls (PCBs) in human populations are probably the result of life-long exposure. Exposure to this ubiquitous contaminant begins *in utero* as shown by the presence of PCB residues in embryonic and fetal tissues and indirectly by their presence in placenta and amniotic fluid.[1-4] Postnatal exposure to PCBs will continue for those infants breast-fed with contaminated mother's milk.[5-8] After breast-feeding and in all other instances where contaminated food, water, and air are ingested or inhaled, the accumulation of the lipophilic PCBs likely continues from infancy to the end of adult life as shown by the relatively high levels of PCBs in fatty tissues.[9-12] Consequently, health authorities in many parts of the world are concerned about the PCB body burden in humans, because of its potential health hazard, especially in those instances where body lipids may be mobilized as during illness or nursing. At the same time regulatory agencies have been interested in PCB levels in human milk as an important element in their decision-making process to establish guidelines for physicians, who in turn must advise nursing mothers whether or not to breast-feed. The known PCB body burden of a given population may also affect the initiation and formulation of regulations with respect to environmental disposal of PCBs.

Monitoring programs of PCBs in human populations have mainly been restricted to the following substrates:

1. Adipose tissues, which can be obtained during biopsies or autopsies. Autopsy samples are normally available for all ages and sexes.
2. Breast milk, which is readily available and for which sufficient number of subjects can be found.
3. Blood, which can be taken at any age from healthy or diseased subjects by authorized personnel.

However, on occasion limited and local investigations on the levels of PCBs in liver, brain, hair, bone marrow, and other human tissues have been carried out.[11,13-15] The quantitation of PCBs in human tissues and fluids has left much to be desired, not because of the analysts in question, but because of the inherent complexity of the PCBs as illustrated by the large number of isomers, the relative poor separation by conventional gas liquid chromatography (GLC) on packed columns, and the different electron capture detector responses of the various isomers. In addition, investigators used PCB mixtures of different chlorine content and from various manufacturers as standards. The use of capillary GLC and the increasing number of commercially available isomers may improve future PCB measurements in human populations.

Table 1 shows the various commercial PCB mixtures used for the measurements of PCB residues in human tissues and fluids. This information indicates that most PCB residues were estimated as the higher chlorinated isomers. Nevertheless, recently, lower chlorinated biphenyls have been reported in some studies and they constituted a substantial percentage (≈30%) of the total PCB residues measured.

There are two main reasons why PCB residues in human populations are measured almost exclusively in terms of higher chlorinated biphenyls. First is the close resemblance of many GLC elution patterns of PCBs in human tissues and fluids to the higher chlorinated commercial PCB mixtures. Second is the knowledge that lower chlorinated biphenyls are more readily metabolized. It is noteworthy therefore, that PCB mixtures with low chlorine content have not been used to any great extent to measure PCBs in blood.

The data in Table 2 clearly accentuate the dilemma of choosing the proper standard PCB mixture. The composition of PCB congeners in human milk shows considerable variation among several countries. Some of the observed differences may be the result of the type of

MONS 006197

Table 1
VARIOUS COMMERCIAL PCB MIXTURES USED FOR THE DETERMINATION OF PCBs IN HUMAN TISSUES AND FLUIDS

Commercial PCB mixture	Human tissues and fluids[a]			
	Adipose	Milk	Blood	Other
Aroclor®	1242			
	1254	1254	1254	1254
	1260	1260	1260	
Clophen®		A-50		
	A-60	A-60	A-60	
Kanaclor®	200	200		
				300
				400
	500	500	500	500
	600	600	600	

[a] Only from literature sources, where the type of standard was specified.

Table 2
CONGENER DISTRIBUTION OF PCBs IN HUMAN MILK AND COMMERCIAL PCB MIXTURES

Sample	%							
	Cl_3	Cl_4	Cl_5	C_6	Cl_7	Cl_8	Cl_9	Cl_{10}
Aroclor® 1254[47]		1	21	48	23	6		
Clophen® A 50[48, 49]			16	42	21	3	<1	<1
Kanechlor® 500[50]	<1	3	9	60	22	6		
Aroclor® 1260[47]				12	38	41	8	
Clophen® A 60[49]				16	51	26	3	<1
Kanechlor® 600[50]	<1	2	2	5	36	45	10	<1
Japanese breast milk[16]		8	21	18	36	12		
Canadian breast milk[17]		4	25	12	15	36	8	
Swedish breast milk[20]			12	8	55	21		

[a] Reported congeners total only 82%.

PCB ingested, i.e., lower or higher chlorinated biphenyls. However, the effect of the use of different extraction solvents on individual isomer distribution may not be discounted.[17]

Some investigators chose to quantitate PCBs in human tissues and fluids by mixing commercial standards in proportions that would give GLC patterns closely resembling those found in the samples.[7-14] In many studies however, the basis of the PCB identification and quantitation was not specified.

With the development of capillary GLC, several successful attempts have been made to identify and/or quantitate individual isomers in human tissues and fluids.[18-21] At present a total of 80 PCB isomers have been identified in human adipose tissue, milk, and blood (Table 3). Other isomers not listed in Table 3 could be present in human tissues and fluids, but have as yet not been identified. PCB residues in adipose tissue and milk have two pentachloro-, eight hexachloro- seven heptachloro-, five octachloro-, and three nonachlorobiphenyl isomers in common, as well as the decachlorobiphenyl congener. All three

MONS 006198

Table 3
PCB ISOMERS IDENTIFIED IN SOME HUMAN TISSUES AND FLUIDS

Chlorine substitution pattern of biphenyl[a]	Presence in human tissues and fluids[b]		
	Adipose	Milk	Blood
Trichlorobiphenyls			
2,4,4'		+	
Tetrachlorobiphenyls			
2,2',3',4'	+		
2,2',3,5	+		
2,2',5,5'		+	
2,3,4,4'		+	
2,3',4,4'		+	
2,3,4,5'	+		
2',3',4,6	+		
2,4,4',5		+	
3,3',4,4'		+	
3,3',4,5'		+	
Pentachlorobiphenyls			
2,2',3,3',6'	+		
2,2',3,4,4'		+	
2,2',3,4,5'		+	
2,2',3,4',5		+	
2,2',3',4',5	+		
2,2',3,4,6'		+	
2,2',3,4,6		+	
2,2',3',5,5'	+		
2,2',3,5',6		+	
2,2',3',5,6	+		
2,2',4,4',5	+	+	
2,2',4,5,5'	+	+	
2,3,3',4,4'	+	+	+
2,3,3',4,5		+	
2,3,3',4,6'	+		
2,3,4,4',5'	+		
2,3',4,4',5		+	+
2,3',4,4',6		+	
2,3',4,5,5'		+	
Hexachlorobiphenyls			
2,2',3,3',4,4'	+	+	
2,2',3,3',4,5		+	
2,2',3,3',4,5'	+	+	
2,2',3,3',4,6		+	
2,2',3,3',4,6'	+	+	
2,2',3,3',5,6'	+	+	
2,2',3,4,4',5'	+	+	+
2,2',3,4,5,5'		+	
2,2',3,4',5,5'	+		
2,2',3,4,5,6'		+	
2,2',3',4,5,6	+	+	
2,2',3,4,5',6		+	
2,2',3,4',5,6		+	
2,2',3,5,5',6		+	
2,2',3',5',5',6'	+		
2,2',4,4',5,5'	+	+	+
2,3,3',4,4',5	+	+	+
2,3,3',4,5,5'		+	

MONS 006199

Table 3 (continued)
PCB ISOMERS IDENTIFIED IN SOME HUMAN TISSUES AND FLUIDS

Chlorine substitution pattern of biphenyl[a]	Presence in human tissues and fluids[b]		
	Adipose	Milk	Blood
2,3,3',4,5,6		+	
2,3,3',4',5,6		+	
2,3,3',5,5',6		+	
2,3',4,4',5,5'	+		
Heptachlorobiphenyls			
2,2',3,3',4,4',5	+	+	+
2,2',3,3',4,4',6	+		
2,2',3,3',4,5,5'	+	+	
2,2',3,3',4,5,6		+	
2,2',3,3',4',5,6		+	
2,2',3,3',4,5',6	+		
2,2',3,3',4,5,6'	+	+	
2,2',3,3',5,5',6	+	+	
2,2',3,3',5,6,6'		+	
2,2',3,4,4',5,5'	+	+	+
2,2',3,4,4',5',6	+	+	
2,2',3,4,5,5',6		+	
2,2',3,4',5,5',6	+	+	
Octachlorobiphenyls			
2,2',3,3',4,4',5,5'	+	+	
2,2',3,3',4,4',5,6	+	+	
2,2',3,3',4,4',5,6'	+	+	
2,2',3,3',4,4',6,6'		+	
2,2',3,3',4,5,5',6	+	+	
2,2',3,3',4,5,5',6'	+	+	
2,2',3,3',4,5,6,6'		+	
2,2',3,3',4,5',6,6'		+	
2,2',3,3',5,5',6,6'		+	
2,2',3',4,4',5,3',6	+		
2,3,3',4,4',5,5',6		+	
Nonachlorobiphenyls			
2,2',3,3',4,4',5,5',6	+	+	
2,2',3,3',4,4',5,6,6'	+	+	
2,2',3,3',4,5,5',6,6'	+	+	
Decachlorobiphenyl			
2,2',3,3',4,4',5,5',6,6'	+	+	

[a] For rules of nomenclature used, see Reference 47.
[b] References 18 to 20 and 84.

substrates contained the 2,3,3',4,4'-pentachlorobiphenyl, the 2,2',4,4',5,5'-, 2,2',3,4,4',5'- and 2,3,3',4,4',5-hexachlorobiphenyls, and the 2,2',3,3',4,4',5- and 2,2',3,4,4'5,5'-heptachlorobiphenyl isomers. The 2,2',4,4',5,5'- and 2,2',3,4,4',5'-hexachlorobiphenyl isomers are major components of all three substrates.

Masuda et al.[21] quantitated PCBs in blood of normal persons using the PCB isomers listed in Table 3. Yakushiji et al.[18] used 15 PCB isomers, including one tri- and one tetrachlorobiphenyl, to determine 95.5% of all human milk PCBs.

The similarities of the GC elution patterns for PCB residues in human adipose tissue, milk, and blood are illustrated for both packed and capillary columns in Figures 1 and 2

MONS 006200

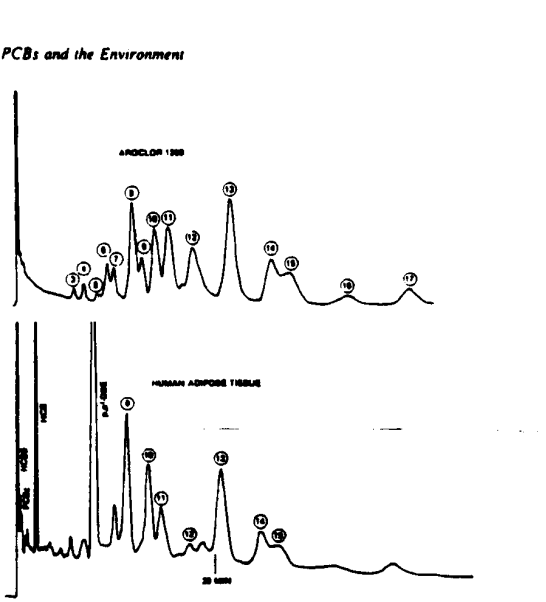


FIGURE 1. The GC elution pattern of PCBs in Aroclor® 1260, human adipose tissue, milk, and blood on a 0.6 × 183 cm glass column, packed with 6% OV-210 + 4% SE-30 on Chromosorb® W (AW). Retention times vary, since chromatograms were obtained from various projects with slightly different GLC conditions.

and are indicative of the many isomers in common as shown in Table 3. The numbering system for PCB peaks in both figures correspond to those used by Mes et al.[12]

II. PCBs IN HUMAN TISSUES AND FLUIDS OF VARIOUS WORLD POPULATIONS

A. Adipose Tissue

Investigators in many countries have determined PCBs in adipose tissue of their populations or parts thereof, as a convenient indicator of the PCB body burden. The results are tabulated in Table 4 (decimals were recorded in this and subsequent tables as reported in the literature) and indicate that the majority of the data were generated in the industrialized countries of the Western Hemisphere, while no information on African and little on Asian populations seems available. It may be postulated however, that results of some PCB monitoring programs were only locally reported and not further disseminated.

Comparison of results is made difficult because of the inconsistency in reporting the data on a fat or wet tissue basis, although the relative high fat content of adipose tissues should make an approximate conversion possible. The average PCB level on a fat basis for the populations listed in Table 4 is approximately 2.5 ppm with averages by country ranging from 0.51 to 8.3 ppm representing data from New Zealand and West Germany, respectively.

MONS 006201

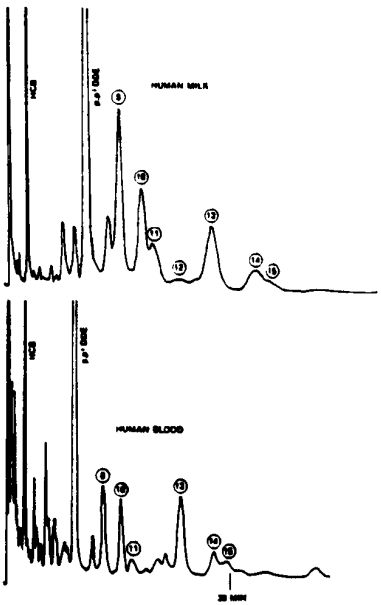


FIGURE 1.

B. Breast Milk

The reported PCB levels in the breast milk of several female populations are given in Table 5. The results, usually reported on both a fat and whole milk basis, indicate that PCB residues have been found in the breast milk of female populations on all continents.

Although most sampling sites were limited, extensive nationwide monitoring programs were undertaken in 1975 both in the U.S. and Canada. The results show a considerable difference in breast milk PCB levels between the two countries. The higher PCB level in the breast milk of the female population of the U.S. may be attributed to the fact that it represents only those samples containing more than 50 ppb or approximately 30% of the total number of samples analyzed.

Unless PCB levels were monitored on a nationwide basis, comparison of breast milk levels in various countries would be questionable. Therefore, high PCB levels in the breast milk of Spanish, German, or Australian women cannot be truly evaluated in terms of levels elsewhere in the world, notwithstanding the fact that the data were collected in different years.

No PCB residues were found in the breast milk of women from New Guinea in 1971, indicating a relatively clean environment with respect to PCBs. It would be interesting to determine the present status of PCB contamination in that population. The PCB level reported

MONS 006202

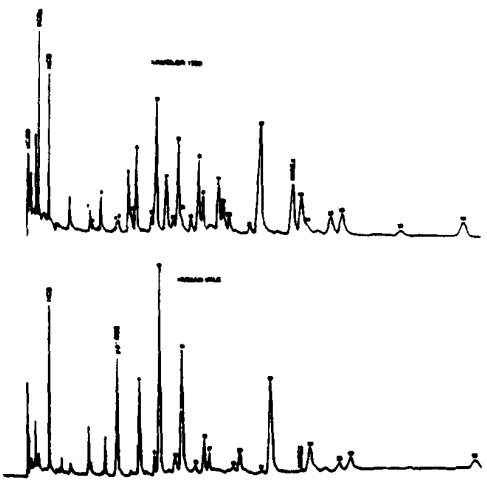


FIGURE 2. The isothermal GLC elution pattern of PCBs in Aroclor® 1260, human adipose tissue, milk, and blood on SP-2100 capillary columns (36 m × 0.5 mm, except blood PCBs, for which a 25 × 0.2 mm column was used).

for Australia in 1969 is based on a personal communication as quoted by Wasserman et al.[22] and therefore lacks background information. The latter would be important in order to evaluate the absence of PCBs in breast milk samples from four metropolitan hospitals in Australia in 1973.[23]

Geographically, the highest levels of PCBs (≥ 100 ppb) in human milk were found in Spain, Michigan (U.S), and Germany. The average PCB level in breast milk of all countries in Table 5 is 37 ppb on a whole milk basis.

C. Blood

PCB levels in blood have been reported in several studies from Israel, Japan, and the U.S.[24-28] Results are tabulated in Table 6 and indicate that most blood samples were taken from females, especially those who were pregnant or lactating. Major studies in terms of number of samples were carried out in South Carolina, Alabama, and Michigan and the results of these studies showed higher PCB levels than in whole blood collected in Japan. The average PCB level in blood derived from the data in Table 6 is 4.4 ppb. PCB levels in blood were often obtained as a result of local environmental problems, rather than nationwide surveys. Apparently no nationwide monitoring programs have been carried out. Of particular interest are the Israeli results, which show fetal PCB blood levels to be twice as high as those of the corresponding mothers.

D. Miscellaneous Tissues and Fluids

The PCB content of tissues and fluids other than adipose, milk, and blood have been determined in subjects from various countries (Table 7). The fact that these studies were

MONS 006203

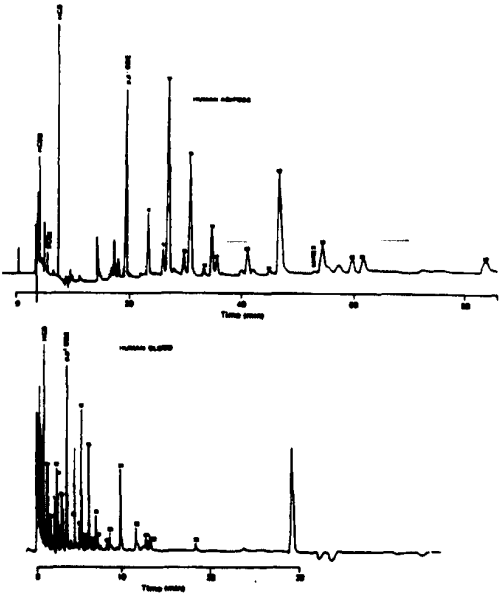


FIGURE 2.

conducted in different years and in many instances with a limited number of different samples makes comparison between populations difficult. Nevertheless, one can observe for example, a close agreement between PCB levels in liver samples from Finland and Denmark.

Polishuk et al.[7] found PCBs in uterine muscle, placenta, and amniotic fluid indicating *in utero* exposure. The bone marrow results closely resemble those found for adipose tissue in Germany in 1970-1971.

E. Infant and Fetal Tissues and Fluids

The PCB levels given in Tables 4 to 7 are all mainly related to adult populations, except for those in fetal blood in Table 6. A limited data base, however, is available for PCBs in infants up to 1 year of age from Japan and England. The results in Table 8, obtained during 1976-1977 are difficult to evaluate because of the limited number of samples used. The data do indicate however the presence of PCBs in many tissues at a very early and important stage of development.

It is known that PCBs cross the placental barrier.[3,27] This exposure of the fetus to PCBs is illustrated for Japanese women by the data in Table 9. The highest levels of PCBs were found in fetal skin, adipose, and liver which correlates with similar results found in infant tissues. Furthermore, an early exposure and accumulation of PCBs in human populations is

MONS 006204

Table 4
PCBs IN ADIPOSE TISSUES OF VARIOUS HUMAN POPULATIONS[a]

Country	Region	Year of sample collection	No. of samples	PCB (mg/kg) Fat Av.	Fat Max.[b]	Tissue Av.	Tissue Max.	Ref.[c]
Austria	Vienna	1971-72	32	3.5	8.5			9
Belgium		1978	73	1.45	21.4			10
Brazil	Sao Paulo	1978	15	1.50	2.12			15
Canada	Ontario	1969-70	29	1.2	2.0			48
	Ontario	1971-72	282	2.5	18.0			48
	All provinces	1972	168	1.1	8.12	0.907	6.603	35
	Ontario	1973-74	129	2.3	11.0			48
	All provinces	1976	98	1.0	7.56	0.944	6.801	12
Denmark		1972	38	3.40	11.30			49
		1972—73	82	5.1	49			34
	Funen	1976-78	22			2.221		50
	Odense	1978-79	44	2.489				51
	Greenland	1979	33	5.8[d]		4.3		52
	S. Denmark	1979	17	3.6[d]		3.5		52
East Germany	Rostock	1979	70	3.5	10			33
England		1976-77	236			0.7		53
		1976-77[e]	4			0.2	0.5	53
Finland	Pori	1974-75	41	3.55		2.40		13
	Jyväskylä	1974-75	32	2.04		1.54		13
Germany		1970	20			5.7	16.6	36
		1971	93	6.0	20.5			49
	Five cities	1975[f]	282	8.3				28
Hungary	Budapest	1978-79	46			0.37	2.0	42
	Budapest	1978-79	17[g]			0.29	1.0	42
	Zalaegerszeg	1978-79	10			0.26	0.39	42
Israel		1973		2.75				22
		1977	8	1.2049				2
Japan		1970	11	2.6	5.3	0.9	1.9	54
	Niigata	1970-71	9	1.6	2.3			36
	Kyoto	1971	19	4.7	13.3			36
	Tokyo	1971-72	27	2.1	5.1			36
	Kochi	1971-72	50	2.86	18.04			36
	Tokyo	1972	40	3	10			36
	Ehime	1972	16	1	1			36
	Yamagata	1972	15	1.73	3.9			36
	Chiba-ku	1973	25	0.8	1.48			55
	Fukuoka	1973-74	30	0.78	1.36	0.6	1.35	3
		1974	30	1.04	2.50			56
		1975-78	17			1.52	2.95	57
New Zealand	Upper Hut	1973	51	0.81	4.67			43
		1973-74	35	0.51				58
Norway	Oslo	1977	10	1.78	4.44			59
Poland		1979[f]	118	0.56	3.21			60
Switzerland		1973	13	1.0	2.2			44
U.S.	Texas	1971	88	1.7	9.9			32
		1982[f]		1.3	2.0			61

[a] Embryonic or fetal tissues not included.
[b] Maximum value observed.
[c] Reference.
[d] Median.
[e] Age <0.25 years.
[f] Year of publication.
[g] Children of 1.5 to 13 months.

MONS 006205

Table 5
PCBs IN BREAST MILK OF VARIOUS HUMAN POPULATIONS

Country	Region	Year of sample collection	No. of samples	Av. fat (%)	PCB (ug/kg) Fat Av.	Fat Max.[a]	Milk Av.	Milk Max.	Ref.[b]
Australia		1969					75.0		22
		1973	45				Nil		23
Austria	Vienna	1973	22		1,540	3,780	60	183	62
	Niederösterreich	1973	9		1,298	1,570	38	61	62
Canada	Ontario	1969-70	43	3.0	1,000	1,200	30		48
	All provinces	1970	90				6		63
	Ontario	1971-72	34	3.0	1,200	3,000	36[c]		48
	Ontario	1973-74	19	2.7	1,200	2,500	32[c]		48
	Alberta	1974	15	1.26	1,700		20	32	64
	All provinces	1975	100	2.20			12	68	8
	Alberta	1977-78	33	1.99	85	751	1.7		37
	Quebec	1978-79	154		837	4,340	29		65
	British Columbia	1980	49	1.32			8	51	38
Germany		1970	43		3,500	9,700	103		60
	Greifswald	1973	164		3,208	39,700	90	250	16
Ghana		1972					5		22
Israel		1977[d]	29		3,101		44.2		40
Japan	Tokyo	1971	671				35	200	36
		1971					3.4		22
		1972					3.1		22
	Fukuoka	1972	19		1,200	5,600	30	60	54
	Ishigaki	1972	12		400	700	14	20	54
	Osaka Pref[e]	1972	141	2.59	1,240	4,900	32	100	18
	Osaka Pref.	1972-73	402	2.75	1,150	4,900	29	123	6
	Kyoto Pref.	1973	35				46	101	14
	Osaka Pref.	1973	123	3.03	1,330	11,400	38	150	18
	Osaka Pref.	1974	119	3.03	1,360	4,800	40	190	18
	Fukuoka	1974-75	52		350	870	13	36	3
	Osaka Pref.	1975	113	3.14	1,140	4,080	36	140	18
	Osaka Pref.	1975	24				23	51	57
		1975-76	18				8	42	39
	Osaka Pref.	1976	100	3.30	1,040	5,400	33	100	18
	Osaka Pref.	1977	101	3.48	1,150	5,000	39	240	18
		1979	24				16		66
New Guinea		1971	32				0		67
Norway	Three cities	1969-70					11		68
	Four cities	1970	44	2.4			24		68
Poland		1979	179		360	1,400			60
Spain	Madrid	1981	70				250	320	69
Sweden	Stockholm	1967	[f]	3.2	450	700	14	20	5
	Stockholm	1968-69	51				18	20	70
	Stockholm	1971-72	18[g]	3.1			25	30	70
	Stockholm	1971-72		3.0	870	1,400	26	40	5
	Stockholm	1974		2.9		1,000	24	30	5
	Stockholm	1976-77		2.9	930	1,500	30	40	5
	Uppsala	1978-79	18		1,600	2,900	64	150	71
U.S.	Texas	1971	47				0		67
	Colorado	1971-72	40				49	100	72
	Arkansas	1973-74	37	3.0			T		73
	All states	1975	1,030[h]	4.49	2,308	16,920	89	563	46
	Michigan	1977-78	1,057		1,496	5,100	155	409	7
	Hawaii	1979-80	50	3.2	800	1,800	26		41
Yugoslavia		1973					103		74

Note: T = trace.

[a] Maximum value observed.
[b] Reference.
[c] Calculated on basis of fat content.
[d] Year of publication.
[e] Prefecture.
[f] 468 to 678 samples collected.
[g] Pooled samples.
[h] Based on 308 samples with PCB levels >30 ppb.

MONS 006206

Table 6
PCBs IN BLOOD OF SEVERAL HUMAN POPULATIONS

Country	Region	Year of sample collection	No. of samples	Sex	State of subject	Av. PCB content µg/kg Blood	Plasma	Serum	Lipid (mg/kg)	Max.[a] level	Ref.[b]
Israel		1977	24	F	Maternal[c]				2.7090		2
		1977	23		Fetal[c]				7.1097		2
		1977	29	F	Maternal		19.3		3.988		40
		1980	7	F	Pregnant			23.5			75
		1980[d]	12	F	Pregnant			17.8	3.15		76
Japan	Osaka Pref.[e]	1972	129	F	Lactating	3.0				8	18
	Osaka Pref.	1972-73	207			2.75					6
	Osaka Pref.	1973	123	F	Lactating	3.5				22	18
		1973-74	24	F	Maternal	2.8				7.6	4
		1973-74	24			1.1[f]				3.3	4
	Osaka Pref.	1974	117	F	Lactating	3.8				12	18
	Fukuoka	1974-75	56	F	Lactating	1.4				3.4	3
	Fukuoka	1974-75	42		Infant	2.5				6.2	3
	Osaka Pref.	1975	113	F	Lactating	3.7				12	18
	Kyoto	1975[d]	33				6.1				77
	Nagasaki	1975	28	M/F	Fishers		10.9				78
	Miyazaki	1975	40	M/F			12.2				78
	Fukuoka Pref.	1975	28	M/F			5.3				78
	Osaka	1975	24	F	Nursing	2.0				5.0	57
	Osaka Pref.	1976	100	F	Lactating	3.3				18	18
	Osaka Pref.	1976	16	F		2.8					79
		1976	17		Child	3.8					79
U.S.	South Carolina	1968	616	M/F			1.9			22.1	25
	Michigan	1973-74	1842	M/F		6.3[g]					24
	Alabama	1979	458	M/F		17.2[g]					26
		1982	19			12.0				27	61
Canada		1980[d]	4	M/F		2.6					80

[a] Maximum value observed.
[b] Reference.
[c] Related.
[d] Year of publication.
[e] Prefecture.
[f] Cord blood.
[g] µg/ℓ.
[h] Geometric mean.

evident. Whether there exists a relationship between the body burden of the mother and fetal PCB accumulation cannot be established at present. A relationship, however, was found between PCB levels in human milk and adipose tissue from various countries as shown in Figure 3. This relationship showed a 98% confidence level and therefore, in human populations with high PCB levels in their adipose tissues a high level of PCBs in the milk of their female populations may be expected. Assuming approximately 85% fat in adipose tissue, the average ratio of PCB levels in fat/milk fat can be approximated as 2.

III. TRENDS IN PCB LEVELS OF TISSUES AND FLUIDS FROM SPECIFIC HUMAN POPULATIONS

A. Adipose Tissue

The trends of PCBs in three specific populations in Canada, Denmark, and Japan are

MONS 006207

Table 7
PCBs IN MISCELLANEOUS TISSUES AND FLUIDS OF VARIOUS HUMAN POPULATIONS

Country	Region	Year of sample collection	No. of samples	Type of tissue or fluid	PCB(mg/kg) Fat Average	Fat Max.[a]	Tissue Average	Tissue Max.[a]	Ref.[b]
Brazil	Sao Paulo	1978	15	Gastric mucosa	5.72	11.32			15
				Epiploon	1.43	3.22			
Denmark	Funen	1976-78	22	Basal ganglia			0.080		50
				M. psoas			0.097		
				Spleen			0.038		
				Liver			0.144		
				Kidney			0.058		
				Ovary[c]			0.027		
				Testis[c]			0.069		
Finland	Pori	1974-75	41	Liver	3.44		0.17		13
				Brain	1.19		0.12		
	Jyväskylä		32	Liver	1.75		0.13		
Germany		1982	5	Bone marrow	6.4	11.8			11
Israel		1977	7	Uterine muscle	14.0968				2
			9	Placenta	5.0267				
			4	Amniotic fluid	124.7529				
Japan		1972	15	Hair			0.74	1.71	81
	Kyoto	1973	33	Hair			0.32	0.71	14
		1975-76	61	Hair	0.31	0.87			39
		1977	2	Cerebrum			0.027	0.043	1
			3	Heart			0.141	0.20	
			3	Kidney			0.037	0.076	
			2	Liver			0.058	0.099	
Norway		1977	10	Liver	1.87	2.29			59
U.S.		1976	4[d]	Hair			0.61	0.76	82

[a] Maximum value observed.
[b] Reference.
[c] Five samples.
[d] Seventeen samples.
[e] Composite samples of five or more individuals.

Table 8
PCBs IN INFANT (≤1 YEAR OF AGE) TISSUES FROM JAPAN AND ENGLAND

Infant tissue (autopsy)	No. of samples	PCB (μg/kg tissue) Av.	Range	Ref.
Cerebrum	2	7	4 and 9	1
Heart	1	16		
Kidney	2	11	10 and 11	
Liver	2	53	23 and 82	
Skin	1	140		
Adipose	3	267	100—500	53

MONS 006208

Table 9
PCBs IN FETAL TISSUES FROM JAPAN

Fetal tissue	Year of sample collection	Region	No. of samples	Fetal age (months)	PCB (μg/kg) Fat Av.	Fat Max.[a]	Tissue Av.	Tissue Max.	Ref.
Liver	1974—75	Fukuoka	16	7—T[b]	7.3	21			3
	1976	Kyoto	14	4—9			14	20	57
	1977		10	4—7			15	33	14
			4	T			34	90	
Skin	1976	Kyoto	12	4—9			84	448	57
	1977		7	4—7			57	120	14
			4	T			630	760	
Cerebrum	1977		10	4—7			7	23	14
			3	T			4	8	
Heart	1977		5	4—7			16	44	14
			4	T			7	11	
Kidney	1977		8	4—7			9	20	14
			4	T			8	10	
Adrenal	1974—75	Fukuoka	16	7—T	26	80			3
Adipose	1974—75		14	7—T	470	960			3

[a] Maximum value observed.
[b] Term.

followed in Figure 4. Only the decrease in PCB adipose tissue levels for the population of southern Honsū, the largest of the Japanese islands, could be interpreted with some confidence as a downward trend. The apparent decrease in PCB adipose tissue levels of southern Danes between 1973 and 1979 illustrates the difficulty in determining trends with only a limited number of data available over a long period of time. In Canada the industrialized province of Ontario showed a slight decrease in PCB adipose tissues levels of its population between 1974 and 1976, in agreement with the corresponding slight decrease for the entire nation between 1972 and 1976.

Figure 5 illustrates the world trend of PCBs in human adipose tissue for the available data. Although the number of data points are limited and the fact that these points are more often based on regional rather than national surveys in a given year, residue levels appear to have peaked and are on the decline. The high value for 1975 is the result of the highest reported average PCB level of 8.3 ppm.[28] Without this particular value, which was based on the population of five German cities, the 1975 average PCB world level would fall below 3 ppm.

B. Breast Milk

Figure 6 shows the trends of PCB levels in human milk from three distinct populations of three different continents. The Swedish results show a definite increase in PCB levels of the lactating population of Stockholm. On the other hand, an apparent decrease in PCB levels was observed in the milk of nursing mothers from Ontario (Canada). However, the results for Ontario in 1975 were generated by a different laboratory than those for 1972 to 1974. In Japan, between 1972 and 1977, PCB levels in the milk of lactating women from the Osaka Prefecture, fluctuated between 30 and 40 ppb on a whole milk basis.

The world trend of PCBs in human milk is shown in Figure 7. There appears to be no definite decrease in the worldwide PCB contamination of human milk, but rather a fluctuation between approximately 10 and 50 ppb on a whole milk basis. The high 1978 PCB average

MONS 006209

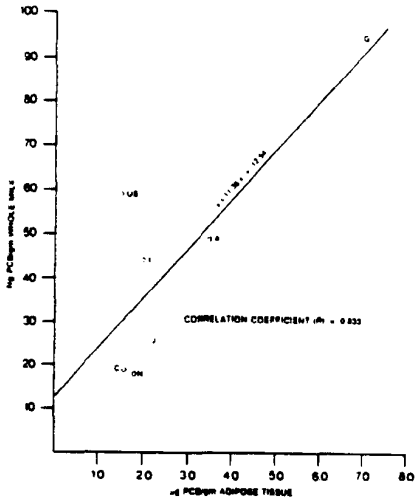


FIGURE 3. Relationship between PCB levels in adipose tissue and milk of human populations (A = Austria, C = Canada, G = Germany, I = Israel, J = Japan, N = Norway, US = United States).

resulted from a high average PCB level in human milk from Michigan which, after the Spanish results, was but one of the highest. The high average PCB level found in the milk of Spanish women from Madrid (1981) was not included in Figure 7. In general human milk and adipose tissue data seem to indicate that human exposure to PCBs is not on the increase.

C. Blood

The determination of PCBs in human blood has been limited to specific regions or studies in a given year. Therefore no data are available to establish the trend of PCBs in the blood of various populations, except for the Osaka Prefecture in Japan. In this prefecture the blood of lactating women was periodically examined for PCBs (Figure 8). PCB blood levels of these lactating Japanese women remained remarkably constant.

IV. SOME PARAMETERS WHICH CAN AFFECT PCB LEVELS IN HUMAN POPULATIONS

A. Sampling

The information in the literature on sampling of adipose tissue for PCB analysis is mostly limited to the anatomical region of the body together with the age and the medical state of the donor and the geographic area of sample collection. Statistical study designs are seldom reported. When anatomical details were provided, most adipose tissue samples seem to have

MONS 006210

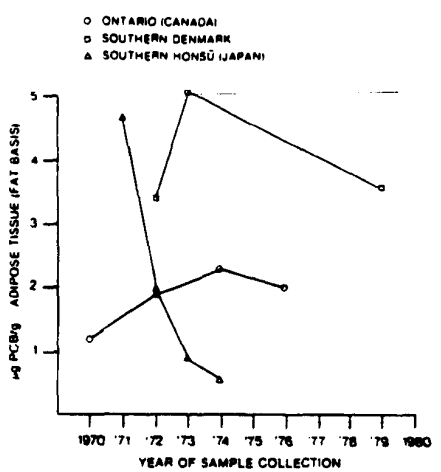


FIGURE 4. Trends in PCB levels of adipose tissue for specific human populations.

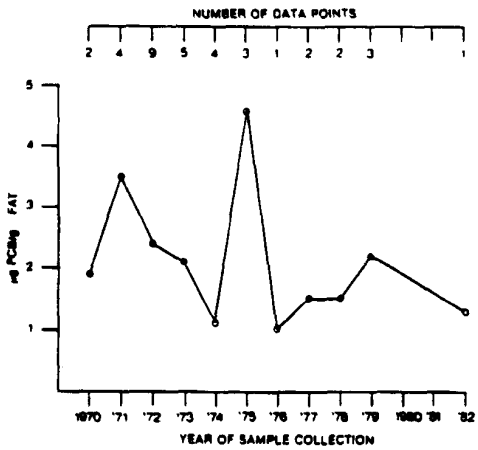


FIGURE 5. World trend of PCBs in human adipose tissue.

MONS 006211

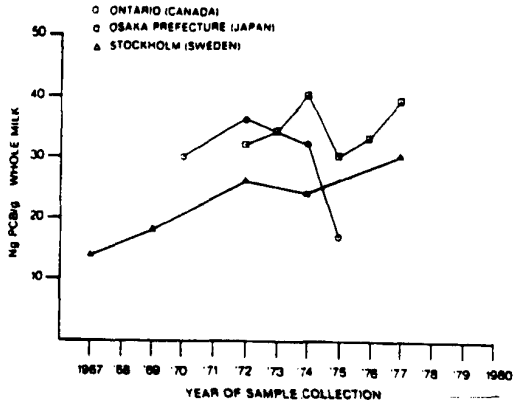


FIGURE 6. Trends in PCB levels of breast milk for specific human populations.

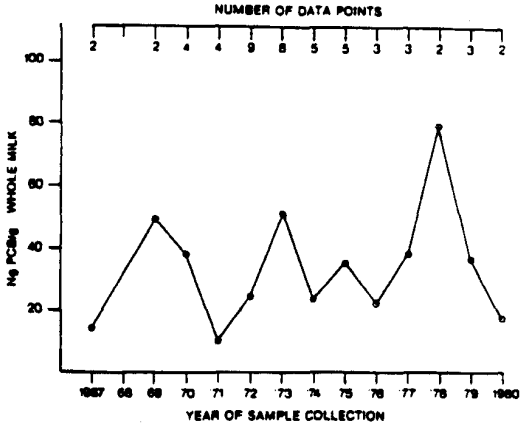


FIGURE 7. World trend of PCBs in human milk.

MONS 006212

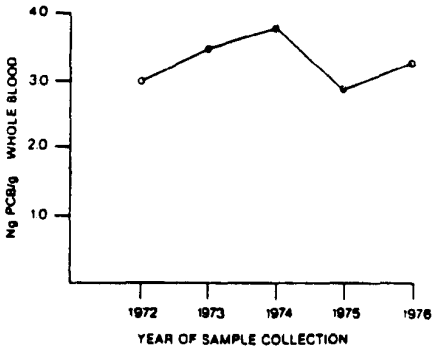


FIGURE 8. Trend of PCB levels in the blood of lactating women from the Osaka Prefecture in Japan.

been taken from the abdominal region of the body. Geographically, few attempts seem to have been made to carry out nationwide surveys and sampling has been mainly restricted to specific urban areas within a country.

The majority of samples were obtained during autopsies, but not necessarily from accident victims only. Sample collection could have included samples from chronically ill patients whose fat deposits may have been partially mobilized, thus affecting the homeostasis of PCBs.

In general, the age of donors range from 19 to 93 in those studies where ages were reported, with a very few donors below the age of 19. Therefore in this chapter, the reported results on PCBs in adipose tissue represent the adult population with little or no information on children.

The problems encountered in sampling of human milk for fat and PCB analysis as a consequence of the changing lipid content of breast milk during feeding and between feedings, have been outlined by Hytten and Mes and Davies.[29-31]

Hence, it appears that in the evaluation of the PCB human body burden, the absence of uniformity in sampling technique should be taken into consideration.

B. Age

In a study of PCBs in adipose tissue of a specific population segment of Texas (U.S.), Burns found that those people having PCB residues in their tissues were slightly older than those without PCB residues.[33] Van Haver et al.[10] reported an increase of PCBs in the adipose tissue of different age groups (0 to 20, 20 to 40, 40 to 60, and >60 years) and observed that for males the average value at 60 years of age or over, was twice the average value for the 0 to 20-year-old group. This increase in PCB levels with age was also observed by Luckas et al.[13] who found twice as much PCBs in the 80 to 89-year-old group than in the 20 to 29 year olds. Kraul and Karlog noted an increase in PCB levels of Danish subjects between the ages of 24 and 90, with a maximum level at approximately 67 years of age.[34] Although Mes et al.[12,35] in two nationwide surveys of PCBs in adipose tissue of Canadians found that PCB levels increased with age, the differences between their age groups (0 to 25, 26 to 50 and >51 years) were not statistically significant, notwithstanding that in their

MONS 006213

1976 survey the PCB level at the age 51 and over was approximately twice that for the 0 to 25 year age group. PCB levels in adipose tissue of a Japanese population apparently varied little between ages 20 to 90.[36]

Arbitrarily established age groups, varying number of samples, and different milieus may not be conducive in evaluating that effect of age on the PCB body burden. Besides, often one sample with a very high PCB content can easily affect the overall average of an age group.[10]

Some authors have reported an increase in PCB milk levels with age of the mother.[36-39] Polishuk et al.[40] however found that women in the age group of 20 to 29 years had higher PCB levels in their breast milk than 30 to 39-year-old group. This latter observation was corroborated in a recent study by Takahashi et al.,[41] who found that mothers in the 18 to 29 age bracket had higher average PCB levels in their milk than those mothers in the 30 to 37 year age group.

The effect of PCB contaminated breast milk on the PCB body burden of infants was investigated by Wickizer et al.[7] These investigators estimated an increase in PCB body burden from approximately 0.2 to 1 ppm (fat basis) between the age of 1 to 12 months. In an extensive study of 723 volunteers, Finklea et al.[25] could not demonstrate a definite trend in PCB levels in blood with age of the donor.

C. Sex

Many investigators reported higher PCB levels in adipose tissue of males than females.[9,13,32,36,42,44] In some instances adipose tissue of males contained almost twice as much PCBs as adipose tissue of females.[9,17,32,34] Kraul and Karlog found a statistically significant difference between male and female PCB adipose tissue levels in Denmark.[34] Although in 1972 Mes et al.[29] also observed that in the Canadian population PCB adipose tissue levels of males were higher than those of females, the difference was not statistically significant. Furthermore, in 1975, Mes et al.[12] in another nationwide survey of PCBs in adipose tissues of Canadians reported higher levels of higher chlorinated biphenyls (Aroclor®1260) and slightly lower levels of lower chlorinated biphenyls (Aroclor® 1242) in females than in males, while total PCB levels (Aroclor® 1260 + 1242) in males and females were 1.208 and 1.298 ppm (wet weight basis), respectively. Whether or not lower PCB levels in adipose tissue of females reflect their capacity to secrete significant quantities of PCBs in breast milk remains to be investigated.

PCB levels in liver tissues were found to be higher in males than in females, but PCB levels in brain tissues of females were sometimes higher and sometimes lower than their male counterparts.[15,36]

Finklea et al.[25] observed no sex difference in the PCB levels of blood plasma, although results in young males (>10 years) were lower than in the comparable female group: 3.8 vs. 4.8 ppb, respectively.

D. Race

From the limited data available it appears that approximate PCB levels in adipose tissues of the Mongoloid race (1.9 ppm) are lower than those of the Caucasian race (2.7 ppm). The same phenomenon was observed for breast milk of Mongoloid women (24 ppb PCB) vs. Caucasian women (45 ppb). The higher PCB levels in Caucasians may not necessarily be race related, but a consequence of higher environmental contamination in their habitats. Higher PCB levels in blood plasma of Negroids were reported by Finklea et al.[25] in a study of Negroid and Caucasian population in the U.S.

E. Population Density

The data in Table 4 were used to further evaluate the concept of a possible relationship

MONS 006214

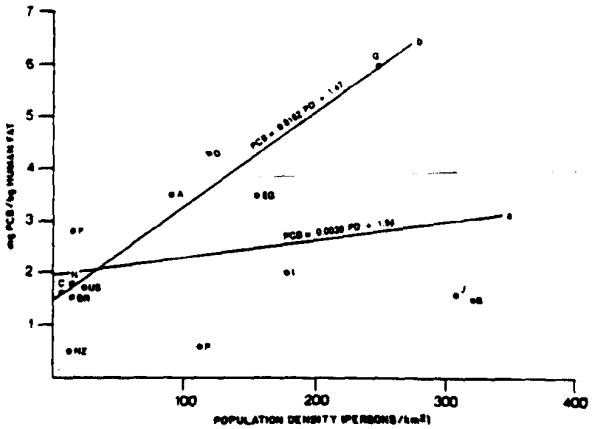


FIGURE 9. Relationships between PCB levels in adipose tissues of human populations and corresponding population densities. Equation a represents all data points. Equation b was computed without the data from Belgium, Israel, Japan, and Poland.

between PCB levels in human adipose tissue and population density as first reported by Zitko.[45] The result is shown in Figure 9, where the low coefficient of correlation ($r = 0.268$) indicates that A does not represent a strong linear relationship. If however, "outlying" observations such as the PCB values from Japan and Belgium, with high population densities are eliminated, an approach originally followed by Zitko, then an otherwise statistically weak relationship is strengthened (see B in Figure 9), but its usefulness limited.

In re-evaluating the possibility of such a relationship for a more defined sampling design and time, an attempt was made to correlate results of PCB analysis in breast milk of women in 41 states of the U.S. with the population density of their states.[46] At best a very weak relationship ($r = 0.10$) was observed. The same result was obtained when the statistical process was applied to PCBs in adipose tissue of Canadians in the various provinces vs. their provincial population densities.

REFERENCES

1. Nishimura, H., Shiota, K., Tanimura, T., Mimatani, T., Matsumoto, M., and Ueda, M., Levels of polychlorinated biphenyls and organochlorine insecticides in human embryos and fetuses, *Pediatrician*, 6, 45, 1977.
2. Pellizzari, E. W., Wassermann, D., Wassermann, M., Cucos, S., and Rea, M. Organochlorine compounds in mother and fetus during labor, *Environ. Res.*, 13, 278, 1977.
3. Masuda, Y., Kagawa, R., Kuroki, H., Kuratsune, M., Yoshimura, T., Tohi, I., Kusuda, M., Yamashita, F., and Hayashi, M., Transfer of polychlorinated biphenyls from mothers to foetuses and infants, *Food Cosmet. Toxicol.*, 16, 543, 1978.
4. Akiyama, K., Ohi, G., Fujikami, K., Yagyu, H., Ogino, M., and Kawana, T., Polychlorinated biphenyl residues in maternal and cord blood in Tokyo metropolitan area, *Bull. Environ. Contam. Toxicol.*, 14, 588, 1975.

MONS 006215

5. **Westöö, G. and Noren, K.**, Organochlorine contaminants in human milk. Stockholm 1967-1977. *Ambio*, 62, 1978.
6. **Yakushiji, T., Tanaka, R., and Kuwita, N.**, PCB and organochlorine pesticides in mother's milk, blood and food. *Perobstetrician*, 6, 28, 1977.
7. **Wickizer, T. M., Brilliant, L. B., Copeland, R., and Tilden, R.**, Polychlorinated biphenyl contamination of nursing mother's milk in Michigan. *Am. J. Publ. Health*, 71, 132, 1981.
8. **Mes, J. and Davies, D. J.**, Presence of polychlorinated biphenyl and organochlorine pesticide residues and the absence of polychlorinated terphenyls in Canadian human milk samples. *Bull. Environ. Contam. Toxicol.*, 21, 381, 1979.
9. **Von Passenderfer, H., Eichler, I., and Gloftke, E.**, Orientierende Untersuchungen uber Ruckstande an DDT, Anderen Organochlorpesticides and PCBs in Human Fettproben. *Wien Klin. Wochenschr.*, 85, 218, 1973.
10. **Van Haver, W., Vandezande, A., and Gerdts, L.**, Organochloor pesticiden in het menselijk vetweefsel. *Arch. Belg. Med. Soc. Hyg. Med. Trav. Med. Leg.*, 36, 147, 1978.
11. **Daschewitz, S. and Ballschmiter, K.**, Rückstand Analyse von Chlorkohlen Wasserstoffen in Human Knochenmark durch hochauflösende Gas-Chromatographie mit Elektronen-Einfang-Detektor. *Fresenius Z. Anal. Chem.*, 310, 6, 1982.
12. **Mes, J., Davies, D. J., and Turton, D.**, Polychlorinated biphenyl and other chlorinated hydrocarbon residues in adipose tissue of Canadians. *Bull. Environ. Contam. Toxicol.*, 28, 97, 1982.
13. **Hattula, M. L., Ihkala, J., Isomaki, M., Maasta, K., and Arstila, A. U.**, Chlorinated hydrocarbon residues (PCB and DDT) in human liver, adipose tissue and brain in Finland. *Acta Pharmacol. Toxicol.*, 39, 545, 1976.
14. **Mishera, S., Yountani, T., Duke, N., and Nagata, S.**, Polychlorinated biphenyl in human milk and in hair. *Annu. Rep. Kyoto Prefecture Inst. Publ. Health*, 19, 37, 1974.
15. **Wanvarnana, M., Nagasira, D. P., Cuesa, S., Mirra, A. P., Shibata, H., Arie, G., Miller, H., and Wanvarnana, D.**, Organochlorine compounds in neoplastic and adjacent apparently normal gastric mucosa. *Bull. Environ. Contam. Toxicol.*, 20, 544, 1978.
16. **Yakushiji, T., Watanabe, I., Kuwabara, K., and Yoshida, S.**, Identification of low chlorinated biphenyls in human milk by gas chromatography-mass spectrometry. *J. Chromatogr.*, 154, 203, 1978.
17. **Mes, J., Davies, D. J., and Lan, P.-Y.**, The effect of extraction technique on the fat content, polychlorinated biphenyl level and tri- to octachlorobiphenyl distribution in human milk., *Chemosphere*, 9, 763, 1980.
18. **Yakushiji, T., Watanabe, I., Kuwabara, K., Yoshida, S., Koyama, K., and Kuwita, N.**, Levels of polychlorinated biphenyls (PCBs) and organochlorine pesticides in human milk and blood collected in Osaka Prefecture from 1972 to 1977. *Int. Arch. Occup. Environ. Health*, 43, 1, 1979.
19. **Zell, M. and Ballschmiter, K.**, Baseline studies of the global pollution. III. Trace analysis of polychlorinated biphenyls (PCB) by ECD glass capillary gas chromatography in environmental samples of different trophic levels. *Fresenius Z. Anal. Chem.*, 304, 337, 1980.
20. **Mullin, M., Sovka, G., Safe, L., McCrindle, S., and Safe, S.**, Synthesis of the octa- and nonachlorobiphenyl isomers and congeners and their quantitation in commercial polychlorinated biphenyls and identification in human breast milk. *J. Anal. Toxicol.*, 5, 138, 1981.
21. **Masuda, Y., Kuroki, M., Yamaryo, T., and Haraguchi, K.**, Comparison of causal agents in Taiwan and Fukuoka PCB poisonings. *Chemosphere*, 11, 199, 1982.
22. **Wanvarnana, M., Tuntula, L., and Wanvarnana, D.**, Cartographie epidémiologique des résidus de composés organochlorés chez l'homme. *Bull. Med. Reg. Toxicol.*, 18, 255, 1975.
23. **Siyali, D. S.**, Polychlorinated biphenyls, hexachlorobenzene and other organochlorine pesticides in human milk. *Med. J. Aust.*, 2, 815, 1973.
24. **Kreiss, K., Roberts, C., and Humphrey, H. E.**, Serial PBB levels, PCB levels, and clinical chemistries in Michigan's PBB cohort. *Arch. Environ. Health*, 37, 141, 1982.
25. **Fishbein, J., Priester, L. E., Crumson, J. P., Hauser, T., Hinners, T., and Hammer, D. H.**, Polychlorinated biphenyls residues in human plasma expose a major urban pollution problem. *Am. J. Publ. Health*, 62, 645, 1972.
26. **Kreiss, K., Zack, M. M., Kimbrough, R. D., Needham, L. L., Smrek, A. L., and Jones, B. T.**, Association of blood pressure and polychlorinated biphenyl levels. *JAMA*, 245, 2505, 1981.
27. **Cortey, A., Burse, V. W., and Grim, M. E.**, Polychlorinated biphenyls: evidence of transplacental passage in the sherman rat. *Food Cosmet. Toxicol.*, 11, 471, 1973.
28. **Schulte, E. and Acker, L.**, Zur Kontamination des Menschen mit Chlorkohlen wasserstoffen, insbesondere durch PCB, in European colloquium problems raised by the contamination of man and his environment by persistent pesticides and organohalogenated compounds. *Commission Eur. Commun. Luxembourg Eur.*, 5196, 435, 1975.
29. **Hytten, F. G.**, Clinical and chemical studies in human lactation. *Br. Med. J.*, 175, 1954.

MONS 006216

30. Mes, J., Experiences in human milk analysis for halogenated hydrocarbon residues. *Int. J. Environ. Anal. Chem.*, 9, 283, 1981.
31. Mes, J. and Davies, D. J., Variation in the polychlorinated biphenyl and organochlorine pesticide residues during human breastfeeding and its diurnal pattern. *Chemosphere*, 9, 699, 1978.
32. Burns, J. E., Organochlorine pesticide and polychlorinated biphenyl residues in biopsied human adipose tissue — Texas 1969-72. *Pest. Monit. J.*, 7, 122, 1974.
33. Luckas, B., Predel, W., and Vieringhoff, U., Zurkontamination von Humanfett Rostocker Burger mit DDT und Polychlorierten Biphenylen im Jahre 1979, *Nahrung*, 25, 427, 1981.
34. Kreuzl, I. and Karlog, O., Persistent organochlorine compounds in human organs collected in Denmark 1972-73. *Acta Pharmacol. Toxicol.*, 38, 38, 1976.
35. Mes, J., Campbell, D. S., Robinson, R. N., and Davies, D. J. A., Polychlorinated biphenyl and organochlorine pesticide residues in adipose tissue of Canadians, *Bull. Environ. Contam. Toxicol.*, 17, 196, 1977.
36. Acker, L. and Schulte, E., Über das Vorkommen chlorierter Kohlenwasserstoffe im menschlichen Fettgewebe und in Human milch, *Dtsch. Lebensm. Rundsch.*, 66, 385, 1970.
37. Currie, R. A., Kadis, V. W., Breitkreitz, W. E., Cunningham, G. B., and Brown, G. W., Pesticide residues in human milk, Alberta, Canada 1966-70, 1977-78, *Pest. Monit. J.*, 13, 52, 1979.
38. Mes, J. and Davies, D. J., Polychlorinated biphenyl in human milk samples from British Columbian (Canada) women, in *Proc. 15th Annu. Workshop Pesticide Residue Analysis (Western Canada)*, Cessna, A. J., Ed., 1980, 99.
39. Takahashi, K., Ozawa, T., and Mishima, Y., Chlorinated organic compounds in human milk and hair, *Sendai-shi Eiseishiken-jo Shoho*, 6, 188, 1975.
40. Pellizzari, Z. W., Ren, M., Wassermann, M., Cucos, S., Wassermann, D., and Lernesch, C., Organochlorine compounds in human blood plasma and milk, *Pestic. Monit. J.*, 10, 121, 1977.
41. Takahashi, W., Saidin, D., Takai, G., and Wang, L., Organochlorine pesticide residues in human milk in Hawaii, 1979-80, *Bull. Environ. Contam. Toxicol.*, 27, 306, 1981.
42. Soos, K., Air, L., Bajnoth, J., and Kastyak, J., Poliklorozott benfenil (PCB) tartalom vizsgalata klorozott szenhidrogen szennyezettek mellett a hazai emberi zsirszovetben, *Egeszsegtudomany*, 24, 385, 1980.
43. Selby, S. R. B. and Shanks, V., Polychlorinated biphenyl and organochlorine pesticides in human fat in New Zealand, *N.Z. J. Sci.*, 17, 535, 1974.
44. Zimmerli, B. and Marek, B., Die Belastung der Schweizerischen Bevölkerung mit Pestiziden, *Mitt. Geb. Lebensmitteluntersuch. Hyg.*, 64, 459, 1973.
45. Zitko, V., PCB Levels in human adipose tissue and population density, *Chemosphere*, 2, 45, 1979.
46. Attachment D of Final report of September 1977 on PCBs in human milk as distributed at a conference on PCBs sponsored by the DHEW Committee to Coordinate Toxicology and Related Programs, Bethesda, Md., January 31, 1978.
47. Hutzinger, O., Safe, S., and Zitko, V., Commercial PCB preparations: properties and composition, in *The Chemistry of PCBs*, CRC Press, Cleveland, 1974, chap. 2.
48. Van Hove Holdrinet, M., Brunn, H. E., Frank, R., Stoppa, G. J., Smout, M. S., and McWade, J. W., Organochlorine residues in human adipose tissue and milk from Ontario residents, 1969-1974, *Can. J. Publ. Health*, 68, 74, 1977.
49. Dejonckheere, W., Steurbaut, W., Verstraeten, R., and Kips, R. H., Residues of organochlorine pesticides in human fat in Belgium, *Toxicol. Eur. Res.*, 1, 93, 1978.
50. Unger, M. O. and Nordberg, G. F., Distribution of PCB and DDT among human tissues, *Ark. Hig. Rad. Toksikol.*, 30, 537, 1979.
51. Unger, M. and Olsen, J., Organochlorine compounds in the adipose tissue of deceased people with and without cancer, *Environ. Res.*, 23, 257, 1980.
52. Jensen, G. E. and Clausen, J., Organochlorine compounds in adipose tissue of Greenlanders and southern Danes, *J. Toxicol. Environ. Health*, 5, 617, 1979.
53. Abbott, D. C., Collins, G. B., Goulding, R., and Hamilton, R. A., Organochlorine pesticide residues in human fat in the United Kingdom 1976-77, *Br. Med. J.*, 283, 1425, 1981.
54. Masuda, Y. and Kagawa, R., Comparison of polychlorinated biphenyl in Yusho patients and ordinary persons, *Bull. Environ. Contam. Toxicol.*, 11, 213, 1974.
55. Curley, A., Burse, V. W., Jennings, R. W., and Vallenasova, E. C., Chlorinated hydrocarbon pesticides and related compounds in adipose tissue from people in Japan, *Nature (London)*, 242, 338, 1973.
56. Fukano, S. and Deguchi, M., PCT, PCB and pesticide residues in human fat and blood, *Bull. Environ. Contam. Toxicol.*, 17, 613, 1977.
57. Watanabe, I., Yakushiji, T., and Kanita, N., Distribution differences between polychlorinated terphenyls and polychlorinated biphenyls in human tissues, *Bull. Environ. Contam. Toxicol.*, 25, 810, 1980.
58. Zabel, M. G. B., Analysis of polychlorinated biphenyl, DDE, and DDT in human fat *N.Z. J. Sci.*, 18, 627, 1975.

MONS 006217

59 **Bjerseth, A., Lunde, G., and Dybing, E.**, Residues of persistent chlorinated hydrocarbons in human tissues as studied by neutron activation analysis and gas chromatography. *Bull. Environ. Contam. Toxicol.*, 18, 581, 1977.

60. **Juszkiewicz, T.**, Toksykologia srodowiskowa zagrozen przed i paporodowych. *Ginekol. Pol.*, 2, 14, 1979.

61. **Chase, K. H., Wang, O., Thomas, D., Stat, D., Berney, B. W., and Simon, R. K.**, Clinical and metabolic abnormalities associated with occupational exposure to polychlorinated biphenyls (PCBs). *J. Occup. Med.*, 24, 109, 1982.

62 **Von Peerdorfer, H.**, Rückstande von Organochlorpestiziden (DDT u a.) und Polychlorierten Biphenylen (PCB's) in der Muttermilch. *Wien Klin. Wochenschr.*, 87, 732, 1975.

63 **Mes, J.**, Unpublished data, 1970.

64 **Mastai, C. J., Hutzinger, O., Zitko, V., and Crocker, J.**, Presence of PCB, DDE and DDT in human milk in the provinces of New Brunswick and Nova Scotia, Canada. *Bull. Environ. Contam. Toxicol.*, 12, 258, 1974.

65 **Dillon, J.-C., Martin, G. B., and O'Brien, H. T.**, Pesticide residues in human milk. *Food Cosmet. Toxicol.*, 19, 437, 1981.

66. **Sasaki, K., Watabe, K., Hayashi, S., and Sugaya, H.**, Residual quantities of organochlorine-type agricultural chemicals and PCBs in the human body. *Akita J. Rural Med.*, 26, 63, 1979.

67. **Dymond, P. G., Hebertson, L. M., Gomes, E. D., Wiseman, J. S., and Hornabrook, R. W.**, Absence of polychlorinated biphenyls in human milk and serum from Texas and human milk from New Guinea. *Bull. Environ. Contam. Toxicol.*, 6, 532, 1971.

68. **Brevik, E. M. and Bjerk, J. E.**, Organochlorine compounds in Norwegian human fat and milk. *Acta Pharmacol. Toxicol.*, 43, 59, 1978.

69 **Baluja, G., Hernandez, L. M., Gonalez, M. J., and Rico, M. C.**, Presence of organochlorine pesticides, polychlorinated biphenyls, and mercury in Spanish human milk samples. *Bull. Environ. Contam. Toxicol.*, 28, 573, 1982.

70. **Westöö, G. and Norén, K.**, Levels of organochlorine pesticides and polychlorinated biphenyls in Swedish human milk. *Var Foeda*, 24, 41, 1972.

71. **Hofvander, Y., Hagman, U., Linder, C.-E., Vaz, R., and Storach, S. A.**, WHO collaborative breast feeding study. *Acta Paediatr. Scand.*, 70, 3, 1981.

72. **Savage, E. P., Tessari, J. D., Malberg, J. W., Wheeler, H. W., and Bagby, J. R.**, A search for polychlorinated biphenyls in human milk in rural Colorado. *Bull. Environ. Contam. Toxicol.*, 9, 222, 1973.

73. **Strassmann, S. C. and Kutz, F. W.**, Insecticide residues in human milk from Arkansas and Mississippi, 1973-74. *Pestic. Mon. J.*, 10, 130, 1977.

74. **Anon.**, *Vyz. Zdravn.*, 18, 64, 1973.

75. **Borcovici, B., Wassermann, M., Wassermann, D., Cucos, S., and Ron, M.**, Missed abortions and some organochlorine compounds: organochlorine insecticides (OCI) and polychlorinated biphenyls (PCBs). *Acta. Med. Leg. Soc.*, 30, 177, 1980.

76. **Wassermann, M., Borcovici, B., Cucos, S., Wassermann, D., and Ron, M.**, Storage of some organochlorine compounds in toxemia of pregnancy. *Environ. Res.*, 22, 404, 1980.

77. **Inoue, Y., Abe, S., and Takemasa, M.**, PCB, DDT and BHC levels in human plasma as a measurement of tissue residue. *Fukuoka Igaku Zasshi*, 66, 64, 1975.

78. **Takemasa, M., Minegishi, K., Hirayama, H., and Inoue, S.**, Characteristics of PCB level and gas chromatogram pattern in blood plasma of Yusho patients among fishermen. *Fukuoka Acta Med.*, 70, 223, 1981.

79. **Kuwabara, K., Yakushiji, T., Watanabe, I., Yoshida, S., Koyama, K., and Kunita, N.**, Levels of polychlorinated biphenyls in blood of breast-fed children whose mothers are non-occupationally exposed to PCBs. *Bull Environ. Contam. Toxicol.*, 21, 458, 1979.

80. **Mes, J., Davies, D., and Tryslove, J.**, The determination of polychlorinated biphenyl in small samples of monkey milk and tissues. I. *Int. J. Environ. Anal. Chem.*, 8, 89, 1980.

81. **Miyahara, S. and Nagata, S.**, On the measurement of organochlorine compounds in hair. *Annu. Rep. Kyoto Prefecture Inst. Publ. Health*, 17, 43, 1972.

82. **Matthews, H. B., Dennstedt, J. J., and Gutherie, F. G.**, Hair and its associated lipids as an excretory pathway for chlorinated hydrocarbons. *Xenobiotica*, 6, 425, 1976.

83. **Yoshida, S. and Nakamura, A.**, The pattern of PCB in human milk among the Swedes. *Proc. Osaka Prefecture Inst. Publ. Health*, 8, 67, 1977.

84. **Jensen, S. and Sundström, G.**, Structures and levels of most chlorobiphenyls in two technical PCB products and in human adipose tissue. *Ambio*, 3, 70, 1974.

85. **Ugawa, M., Nakamura, A., and Kashimoto, T.**, Studies on a calculation method for polychlorinated biphenyl isomers (PCBs). in *New Methods in Environmental Chemistry and Toxicology*, Coulston, F., Korte, F., and Ooto, M., Eds., International Academic Printing, Tokyo, 1973, 253.

MONS 006218

Chapter 4

POLYCHLORINATED BIPHENYLS IN THE WORKPLACE

Alexander B. Smith and David P. Brown

TABLE OF CONTENTS

I. Introduction 64

II. Background Population PCB Levels 65

III. Occupational Standards for PCB Exposures 65

IV. Workplace PCB Exposure Levels 65
- A. Electrical Equipment Manufacturing 66
- B. Electrical Equipment Maintenance and Repair 69
  - 1. Maintenance at Sites of Transformer Installation 69
  - 2. Maintenance at Central Facilities 70
  - 3. Polychlorinated Dibenzofuran Exposures from Transformer Askarels 70
- C. Other Potential Occupational Exposures 71
- D. Summary of Workplace PCB Exposure Levels 71

V. Early Occupational Studies 72

VI. Epidemiological Studies, Post-Yusho 73
- A. Nonoccupational Studies 73
- B. Occupational Morbidity Studies 73
- C. Occupational Mortality Studies 77

VII. Discussion 78

References 79

MONS 006219

I. INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of chlorinated aromatic hydrocarbon compounds that have become widely dispersed in the environment. They were manufactured in the U.S. from 1929 to 1977 by the Monsanto Industrial Chemicals Company and marketed under the tradename Aroclor®.[1] Because of their remarkable physical characteristics, which include high stability, nonflammability, low volatility, low solubility in water, and high solubility in hydrocarbon solvents, PCBs have been used commercially for a wide variety of purposes, including insulating fluids for electrical capacitors and transformers, hydraulic fluids, heat transfer fluids, lubricants, plasticizers, and components of surface coatings and inks. However, these same properties contribute to their extreme stability and persistence in the environment, and result in their accumulation and concentration in the food chain, so that top predators in the food chain may have tissue concentrations of PCBs 10^7 to 10^8 times the level in the ambient environment.[2]

The nomenclature and chemistry of PCBs have been extensively reviewed. Briefly, commercial PCBs are mixtures of isomers of chlorinated biphenyl homologs of varying degrees of chlorination. Monsanto identified its commercial products by a four-digit numerical system "12xx", in which the last two digits ("xx") gave the percentage chlorination by weight. Thus, Aroclor® 1242, 1254, and 1260 were 42, 54, and 60% chlorinated biphenyls, respectively. The exception to this system was Aroclor® 1016, which was a 42% chlorinated biphenyl. PCBs used as dielectric fluids in transformers were designated "Askarel". Askarels generally contain a varying amount of chlorinated benzenes in addition to PCBs.[3,4]

PCBs have been in commercial use since 1929. However, it was not until the mid-1960s that analytical techniques were developed that allowed the identification and quantitation of PCBs in the environment.[5,6] The knowledge that measurable quantities of PCBs had contaminated the environment, and that PCB residues tended to accumulate and magnify in the food chain led to increasing speculation about their effect on the global ecology.[7] After a series of mishaps, including several industrial accidents which resulted in direct contamination by PCBs of human and animal food sources, attention was focused on their potential health hazard, and many countries placed increasingly stringent restrictions on their use. In the U.S., the recognition of the limit of the federal government's authority to cope with the problems of chemical contamination of the environment, coupled with increasing concern over environmental contamination by PCBs, contributed to pressure for passage by Congress of the Toxic Substances Control Act,[8] which took effect January 1, 1977. That act banned the use of PCBs in any manner that is not "totally enclosed" after January 1, 1978, the manufacture of PCBs after January 1, 1979, and the distribution in commerce of PCBs after July 1, 1979 except as may be exempted by the administrator of the U.S. Environmental Protection Agency.

Our intent in writing this chapter is to describe workplace PCB exposures and to use that description as a framework for discussing epidemiologic studies of workers occupationally exposed to PCBs. To provide points of reference for the information we shall present on workplace PCB exposures, we must first briefly document background PCB blood levels that prevail in the general population and summarize the standards that govern workplace PCB exposures. We will then present published and previously unpublished data documenting these exposures, obtained by ourselves and our co-investigators at the National Institute for Occupational Safety and Health (NIOSH). Where appropriate, we will refer to data from other published studies. Using these data as a basis for ranking magnitude of PCB exposures, we will then describe epidemiologic studies of workers occupationally exposed to PCBs. The epidemiologic studies will be discussed chronologically in two time periods: (1) early occupational studies from the 1930s to the 1950s and (2) epidemiological studies performed subsequent to the Yusho epidemic. Yusho will not be described, as it is documented else-

MONS 006220

where. We do not believe Yusho to be particularly relevant to the epidemiology of occupational PCB exposures. Yusho was caused by the accidental ingestion of rice oil, accidentally contamined by a leak from a heat exchanger used in the pasteurization of the oil.[9] The heat exchanger contained Kaneclor® 400, a 42% chlorinated biphenyl at a level of 1000 ppm. Five ppm of polychlorinated dibenzofurans (PCDFs), and 490 to 866 ppm of polychlorinated quarterphenyls (PCQs), not in the original chlorinated biphenyl placed in service as the heat exchange medium were also present.[10-13] It appears that the PCDFs and PCQs, as well as other unidentified chlorinated compounds were formed in the PCB during its commercial use. Since the Yusho epidemic was caused by the accidental ingestion of a mixture of chlorinated hydrocarbon compounds of varying toxicity, inferences about the human health consequences of occupational PCB exposure based upon extrapolation from the Yusho epidemic are best avoided. An epidemic similar to Yusho occurred in Taiwan in 1979 and was labeled "Yu-cheng".[14]

II. BACKGROUND POPULATION PCB LEVELS

PCB residues are detectable in various tissues of persons without known occupational exposure to PCBs. As summarized by Landrigan,[15] mean whole blood PCB levels range from 1.1 to 8.3 ng/mℓ (individual determinations ranging from 0 to 30 ng/mℓ), while mean serum plasma PCB levels range from 2.1 to 24.2 ng/mℓ (individual determinations ranging from 0 to 42 ng/mℓ). This summary includes data from Baker et al.[16] who studied residents of a community in which was located a capacitor manufacturing plant whose workers were studied by Smith et al.[17] Serum PCB levels were performed in either study using comparable methods, so that the Baker et al.[16] community data provide an appropriate reference for the serum PCB levels measured among PCB-exposed workers studied by Smith et al.[17]

III. OCCUPATIONAL STANDARDS FOR PCB EXPOSURES

The standard governing occupational exposure to PCBs in the U.S. is the 1968 American Conference of Governmental Industrial Hygiene (ACGIH) threshold limit value (TLV) for airborne contaminants, adopted in 1971 by the U.S. Occupational Safety and Health Administration.[18] Under this standard occupational exposure to PCBs is limited to 1 mg/m³ for 42% chlorinated biphenyl and 0.5 mg/m³ for 54% chlorinated biphenyl, as 8-hr time-weighted averages (TWA). The ACGIH TLV[19] appears to be based upon work by Drinker et al.[20,21] As of 1976, airborne contaminant limits for occupational exposure to PCBs in most countries were virtually identical.[22] In 1977, the National Institute for Occupational Safety and Health (NIOSH) recommended that occupational exposure to PCBs be limited to 1 μg/m³ as a TWA for up to a 10-hr work day, 40-hr work week.[23] This limit was selected as the minimum reliable detectable level for PCBs for the recommended sampling method. It was "based on the findings of adverse reproductive effects [among experimental animals and among Yusho victims], on its [NIOSH's] conclusion [from animal carcinogenesis bioassays] that PCBs are potential carcinogens in humans and on its [NIOSH's] conclusion that occupational and animal studies have not demonstrated a level of exposure that will not subject the worker to possible liver injury . . . "

IV. WORKPLACE PCB EXPOSURE LEVELS

Workplace PCB exposures have been documented in the published literature for industrial plants where PCBs were used in the manufacturing,[17,24-31] or encountered in the maintenance and repair[17,32] of PCB-containing electrical equipment. We will show that PCB exposures among workers in manufacturing operations were generally one to two orders of magnitude

MONS 006221

greater than PCB exposures encountered in the maintenance and repair of such equipment. Although substitutes for PCBs are now employed in manufacturing operations, studies of these exposures are not merely of historical interest. Studies of worker and nonworker groups with on-going but lower level PCB exposures may be considered in light of the results of studies at considerably higher exposure levels. Such on-going occupational exposures include the servicing, repair, and disposal of PCB-containing electrical equipment. Other exposures of interest include potential or actual exposures to the oxidation and/or pyrolysis products of PCBs that may occur during clean-up following electrical equipment failures and fires.

A. Electrical Equipment Manufacturing

Historically, the single largest use for PCBs in the U.S. (approximately 70% of production) was in the manufacturing of electrical equipment. Ninety-five percent of all capacitors produced through 1978 were PCB impregnated. In contrast, only 5% of electrical transformers produced used PCBs as the impregnant.[33]

The steps in capacitor and transformer manufacturing were conceptually similar. PCBs were shipped to the manufacturing site in heated tank cars. Both new and recycled (from later steps in the manufacturing process) PCBs were filtered, usually through Fuller's earth, prior to use (or reuse). The assembled electrical devices were placed under a vacuum to remove moisture and then filled and/or impregnated with PCBs at elevated temperatures under a vacuum. After excess PCBs were removed (for recycling or disposal), the units were sealed, possibly heat treated, degreased or washed, inspected for leaks, and electrically tested.[34-39]

All small capacitors and some large capacitors were impregnated by placing them in large ovens for direct immersion in PCBs at elevated temperatures, resulting in "flood-filling" through small fill holes in the capacitors' tops. After soaking for a specified period of time, the ovens were opened and the capacitors were transferred to other plant areas for sealing or crimping the fill holes. Small capacitors that failed to pass inspection were usually discarded; large capacitors that failed to pass inspection were usually salvaged by drilling a hole to drain the PCBs, opening the capacitor, and manually removing and repairing the wet components. Other large capacitors and all PCB-containing transformers were individually filled under a vacuum through a manifold. Individual filling appeared to generate less waste PCB from volatilization and condensation, spills, and drips.[35]

Actual worker PCB exposures among capacitor manufacturers varied according to specifics of the manufacturing processes as well as job assignments. For instance, we were told at two sites, and presume it to have been general practice, that in earlier years the impregnation ovens were opened while their temperatures were still elevated significantly above room temperature. The air exiting the ovens was saturated with PCBs volatilized at the elevated temperatures. Upon cooling, the volatilized PCBs condensed, depositing on surfaces not only adjacent to the ovens but also at some distance from the ovens, resulting in widespread areas of contamination where all exposed surfaces, including the skin and clothing of workers became wet with PCBs. With increasing concern about containment of PCB exposures and PCB loss to the environment, we were told it later became routine practice to allow the ovens to cool to room temperature prior to opening them. This apparently resulted in lower levels of PCB exposure than when the ovens were opened with their temperatures still elevated.

It was evident that within any particular capacitor manufacturing plant, workers involved in capacitor impregnation processes were likely to be most heavily exposed. However, all workers in a capacitor manufacturing plant must be considered to have had some level of PCB exposure. This conjecture is supported by data reported by Smith et al.[17] where the mean serum PCB levels of employees at a capacitor manufacturing plant (where large capacitors were impregnated by flood filling) who *never* had worked in the capacitor im-

MONS 006222

Table 1
PERSONAL AIR AND SERUM LEVELS OF PCB CONTAMINATION IN A CAPACITOR MANUFACTURING PLANT

Dept.	Job title	Mean personal[15] air levels ($\mu g/m^3$)	Mean serum levels L-PCB (ng/mℓ)	Mean serum levels H-PCB (ng/mℓ)
Capacitor impregnation	Capacitor repairman	154	1065	75
	Solderer/hanger	147	1458	81
	Power test operator	70	—	—
	Process controller	67	455	47
	Hesserman	59	220	25
	Painter	58	—	—
	Leak test operator	37	340	31
	Final assembly	31	130	20
Misc. assembly		127	—	—
Maintenance	Boilerhouse operator	4	106	38
	Plant serviceman	—	757	95
All "current" capacitor impregnation workers[17]			502	44
All "current" maintenance workers[17]			237	51
All plant workers not currently in capacitor impregnation or maintenance, but who *ever* had worked in either dept.[17]			149	27
All plant workers not currently in capacitor impregnation or maintenance, and who *never* had worked in either dept.[17]			89	22
Community background levels[16]			11.6	12.8

Note: — = not measured.

pregnation area had serum PCB levels two to eight times the background level[16] in the community in which the plant was located. Similar observations were made by Lawton et al.[20] at another such worksite.

In Table 1, we present personal (breathing zone) TWA PCB air levels, and corresponding serum PCB levels quantitated as lower and higher chlorinated biphenyls (L-PCBs and H-PCBs: see summary of Smith et al.[17]) for workers in and near a capacitor impregnation process at a time when it was the practice to allow the impregnation ovens to cool prior to opening them. The job titles in Table 1 are more fully described in Table 2. We noted that the serum L-PCB and H-PCB levels increased as personal air level exposures increased, although the rank correspondence was imperfect. Furthermore, the workers who repaired capacitors that failed to pass inspection (i.e., who drained, cut open, and worked on the wet components of failed capacitors), and who soldered the fill holes after the capacitors had been removed from the ovens, had the greatest PCB exposures, whether assessed as personal PCB air-level exposures or serum PCB levels. Among workers directly exposed to PCBs in capacitor impregnation, personal PCB air levels ranged up to 154 $\mu g/m^3$ for capacitor repairmen, well below the OSHA standard of 1000 μg (1 mg/m^3 but much in excess of the NIOSH recommended standard of 1 $\mu g/m^3$. Mean serum L-PCB levels were a minimum of 11 times and mean serum H-PCB levels were a minimum of 1.6 times community background levels determined by Baker et al.[16]

In Table 3 we present air sampling data from three other capacitor manufacturing facilities. Two of the facilities manufactured small capacitors; the third manufactured large, power capacitors by automatic, individual filling. One of the small capacitor manufacturing facilities and the large capacitor manufacturing facility were the subjects of the Lawton et al. and

MONS 006223

Table 2
DESCRIPTIONS OF JOB TITLES FOR TABLE 1, CAPACITOR MANUFACTURING PLANT

Job title	Description
Capacitor repairman	Worked on capacitors that failed to pass inspection
Solderer/hanger	Soldered fill holes; moved capacitors to degreaser; removed capacitors from degreaser and placed them on an overhead conveyor system
Power test operator	Checked finished capacitors for proper operation
Process controller	Ensured that the impregnation ovens worked properly
Heaterman	Pumped PCBs into and out of impregnation oven
Penner	Potted finished capacitors
Leak test operator	Tested capacitors for leaks
Final assembly	Prepared capacitors for shipping
Boilerhouse operator	In charge of boiler room, made sure furnaces were working properly

Table 3
PERSONAL (BREATHING ZONE) LEVELS OF AIRBORNE PCB CONTAMINATION, SUMMARY DATA

Facility	Operation	Range of av. TWA air exposure by job title ($\mu g/m^3$)	Mean serum levels		Ref.
			L-PCB (ng/ml)	H-PCB (ng/ml)	
2 Small capacitor manufacturers	Capacitor impregnation	161—1260			31, 38
			676	59	36
	Maintenance	150			
Large capacitor manufacturer	Capacitor impregnation	50—299	—	—	38
Transformer manufacturer		11—70	—	—	38
Utility co.	Transformer inspection	0.4—8.8	22	31	17, 39
	PCB nonexposed		21	8	
Utility co.	Transformer maintenance and repair	ND—215	14	24	17, 38
	PCB nonexposed		11	7	
Nonutility co.	Clean-up of transformer leaks	0.01—0.04			32
	Transformer repair operations	16.7—34	12*		
	PCB nonexposed		7*		
Nonutility co.	Transformer repair	ND	—	—	40
Utility co.	Transformer overhaul	3.1—82	22	26	17, 39
	PCB nonexposed		21	8	

Notes: ND = not detected; — = not measured.

* = Median total PCB, from Emmett et al.[41]

MONS 006224

associates report.[16] This same small capacitor manufacturing facility was also studied by Brown and Jones[21] and Fischbein et al.[17] At the two small capacitor manufacturing facilities, all personal PCB air levels examined by job assignment in the capacitor impregnation area exceeded the levels in the large capacitor manufacturing plant reported by Smith et al.[17] and presented in Table 1. Average PCB TWAs (by job title in the capacitor impregnation area) ranged from 161 to 1260 μg/m³. TWAs greater than 1000 μg/m³ were in excess of the OSHA workplace PCB exposure standard. One maintenance worker had a personal PCB air level exposure of 150 μg/m³. Similar to the data presented in Table 1, the highest personal PCB air levels were for the degreaser operator (TWA = 1260 μg/m³) and the solderers, who closed the capacitor fill-holes following impregnation (TWA = 1040 μg/m³). Although Brown and Jones[21] did not measure serum PCB levels among workers at this facility, Lawton et al.[16] reported that mean serum L-PCB and H-PCB levels among highly exposed workers at the plant measured 2 years after these PCB personal air levels were measured were 676 and 59 ng/mℓ, respectively. These levels are comparable in magnitude to those reported in Table 1 for workers studied by Smith et al.[17] At the capacitor manufacturing facility where large capacitors were impregnated individually by automatic filling, personal PCB air levels were much lower than at the facilities where impregnation was by flood filling, ranging by job title from 50 to 299 μg/m³. Again, however, the highest personal air levels were among persons who worked on capacitors that did not pass inspection (TWA = 299 μg/m³), followed by workers who soldered the fill holes after the filling valve had been removed (TWA = 169 μg/m³).[21]

At a transformer manufacturing facility where transformers were individually impregnated, personal PCB air levels ranged from 11 to 70 μg/m³. These levels were considerably less than those observed among capacitor manufacturers.[16] Similar to the capacitor manufacturers, the highest PCB personal level was for the worker who dismantled the equipment that failed to pass inspection.

B. Electrical Equipment Maintenance and Repair

Electrical equipment maintenance and repair are the activities which are likely to result in the greatest continuing PCB exposures. Transformer maintenance and repair operations range from inspections in which little PCB exposure potential appears to exist, to draining and complete dismantling of transformers in which extensive PCB exposure appears to occur. Nevertheless, such activities generally result in worker PCB exposures that are far less than those experienced in capacitor manufacturing operations as seen from the data that follows.

1. Maintenance at Sites of Transformer Installations

At one utility company, PCB personal air levels and serum PCB levels were measured during yearly inspection of distribution transformers in underground vaults.[17,20] The yearly maintenance operations included draining two pint samples of PCB-containing transformer oil which was tested for color and electrical properties and required approximately 40 min of potential PCB exposure. Personal air samples varied from 1.6 μg/m³ to 21.6 μg/m³ during the operations, which when averaged over an 8-hr work day resulted in TWAs from 0.4 to 8.8 μg/m³ (Table 3). Mean serum L-PCB and H-PCB levels were 22 and 31 ng/mℓ, respectively, among workers engaged in such activities,[12] compared to 21 and 8 ng/mℓ, respectively, among PCB nonexposed workers at the company.

At a second utility company, PCB personal air levels and serum PCB levels were measured during maintenance and repair of PCB-containing switches on distribution transformers in the vaults in which the transformers were located.[17,20] Personal PCB air levels were nondetectable during operations conducted during winter months. During operations conducted during the summer, personal PCB air levels varied from 37 to 166 μg/m³ for workers both inside and outside the transformer vault; from 47 to 215 μg/m³ for work on the switch inside

MONS 006225

the transformer vault; and 167 μg/m³ for the worker running the pump station. Mean serum L-PCB and H-PCB levels for workers employed in this line of work were 14 and 24 ng/mℓ, compared to 18 and 7 ng/mℓ, respectively, among PCB nonexposed workers at the company.

Moseley et al.[32] reported air levels of PCB exposure to electricians during repair and maintenance of PCB-filled transformers within their vaults. Eight-hour TWA exposures ranged from 0.01 to 0.04 μg/m³ for cleanup of a PCB leak only to 16.7 to 24 μg/m³ for repair operations that required draining the transformer, partial disassembly, refilling, and cleanup. Emmett et al.[41] reported the median serum PCB levels among these workers to be 12 ng/mℓ (range 0 to 300 ng/mℓ) among the "currently exposed", 7 ng/mℓ (range 0 to 30 ng/mℓ) among "past exposed" workers, and 6 ng/mℓ (range 0 to 15 ng/mℓ) among the "nonexposed".

In another survey in which workers at a nonutility company were monitored during the repair of a transformer in the substation in which it was located, NIOSH investigators detected no PCBs at a limit of detection of 0.05 μg per sample.[33] In a survey during clean-up of a ruptured transformer, the mean serum PCB level among 16 workers near the site of the leak was 6.44 ng/mℓ, measured as Aroclor® 1260,[42] which is well within reported background levels.

2. Maintenance at Central Facilities

Personal PCB air and serum levels were obtained at a utility company where transformers were removed from their vaults and transported to a building from limited overhaul.[17,39] Approximately nine transformers containing PCBs were overhauled at this facility during the previous year, with the time for overhaul varying from 3 to 6 weeks. Most potential PCB exposure occurred during the first 2 to 3 days of operation (draining of PCBs, opening the transformer, and decontamination) and during the last day of overhaul when the transformer was refilled.[39] Eight-hour TWA personal air levels ranged from 3.1 to 82 μg/m³ during the first 2 days of overhaul. PCB contamination of workroom surfaces, tools, and skin of exposed workers was noted. Mean serum L-PCB and H-PCB levels were 22 and 26 ng/mℓ,[12] compared to 21 and 8 ng/mℓ among the nonexposed.

At another company that repaired transformers under contract, the serum mean total PCB level among 16 workers was 58 ng/mℓ. At the time of the report, personal air levels had not been monitored.[43]

3. Polychlorinated Dibenzofuran Exposures from Transformer Askarels

Concern has been focused on PCDF exposures resulting from exposures to PCBs that have been in service for some period of time (i.e., "used" PCBs) and from the cleanup of electrical equipment failures and fires. Some toxic effects attributed to PCBs have been shown to be related to the presence of highly toxic impurities, especially PCDFs, which vary in amount between PCBs from different manufacturers, and between PCBs of differing percentage chlorination.[44-48] PCBs manufactured in the U.S. have been shown to contain fewer PCDFs than PCBs of the same degree of chlorination manufactured elsewhere.[49] The PCDF content of U.S. manufactured PCBs is below the level of detection for Aroclor® 1016 (a 42% chlorinated biphenyl), and increases with the degree of chlorination. For instance, samples of unused Aroclor® 1254 (typically used in transformer Askarels) have been shown to contain from 1.5 to 5.6 ppm (μg of PCDF per gram of sample).[46,47] PCDFs are formed during pyrolysis of commercial PCB products and pure PCB isomers.[46,48] PCDFs, dibenzodioxins, chlorinated phenols, and PCBs themselves are formed during pyrolysis of tri-, tetra-, and pentachlorobenzenes.[50] Tri- and tetrachlorobenzenes are components of some Askarels. Emissions from urban incinerators contain traces of chlorinated dioxins and dibenzofurans.[51-54]

MONS 006226

Samples of used transformer Askarel have been analyzed for PCDF content. Moseley et al.[32] found between 0.013 and 0.116 ppm of tetrachlorinated dibenzofurans (TCDFs) in bulk samples of used Askarel. At least 10 TCDF isomers were present, with 2,3,7,8-TCDF being quantitated at 0.031 ppm. Kominsky et al.[34] report TCDF levels in two other bulk Askarels at 0.013 and 0.030 ppm, respectively. Albro and Parker found used transformer oil to contain between 0.7 and 4.7 ppm of PCDF.[36] Unpublished analyses of used transformer oil, submitted in comments[37] to the U.S. Environmental Protection Agency in regard to proposed rule-making concerning the use of PCBs in electrical equipment[38] documented total PCDF concentrations to range from 0.62 to 1.86 ppm in used Askarels ranging from 32 to 40 years in age. Moseley et al.[32] measured TCDF levels in air samples obtained during transformer maintenance operations and found no TCDF in any of the samples at a limit of detection of 1 ng per sample.

All the above-reported analyses of PCDF content of used Askarels document PCDF levels no greater than those measured in unused Askarels. It would appear that routine maintenance and repair of Askarel-containing transformers pose no greater risk of PCDF exposure than that encountered during their manufacture. However, there does appear to be a risk for PCDF exposure from electrical equipment fires.

Jansson and Sundstrom[39] studied the aftermath of an electrical fire in which 18 PCB-containing capacitors were burned. Several weeks following the fire, environmental samples and blood samples from exposed firemen were obtained and analyzed for PCB and PCDF content. PCDF per gram of PCB increased from 1.1 to 1.3 ppm in two intact capacitors to 45 to 107 ppm in and on a burned capacitor. No PCDFs were detected in soot samples from a wire fence surrounding the capacitors or from downwind pine trees. Blood PCB levels among the exposed firemen were within the limits for the unexposed population, and serum PCDF levels were undetectable.

Kominsky et al.[35] document PCDF and TCDF levels in soot obtained from three transformer fires. Total PCDF concentrations ranged from 1.91 to 1185 ppm. Kominsky and Flesch[40] demonstrated surface contamination by PCB in a room where a fire involving a PCB-containing capacitor in an electric motor had occurred. Dibenzofurans were not detectable in samples showing the highest PCB concentration.

Boxer and Moody[41] examined 18 workers "exposed" to PCBs during clean-up following a transformer explosion, and 12 "nonexposed" workers. Median serum PCB levels among the exposed was 8.5 ng/mℓ, ranging from nondetectable to 36 ng/mℓ, and 7 ng/mℓ among the nonexposed, ranging from nondetectable to 30 ng/mℓ. Although these data do not pertain to PCDF exposure, they demonstrate similar to Jansson and Sundstrom[39] that workers who clean up following transformer explosions do not acquire serum PCB levels in excess of background levels.

NIOSH has recently reviewed the literature involving the health hazards from the pyrolysis of PCBs.[69] The reader is referred to this document for more detailed information on this topic.

C. Other Potential Occupational Exposures

Burn-outs of fluorescent light ballasts manufactured prior to 1969 can release measurable amounts of PCBs into the ambient environment. Staiff et al.[42] found approximately 0.1 μg/m³ of Aroclor® 1242 1 m below a fluorescent light ballast immediately after burn-out. MacLeod[43] demonstrated 5.74 μg/m³ of PCBs as Aroclor® 1242 and 5.86 μg/m³ as Aroclor® 1254 in laboratory air immediately following a ballast burn-out. Kominsky et al.[35] found 166 μg/m³ of PCBs as Aroclor® 1242 1 m below a ballast and 10 to 20 μg/m³ at 6 m from the ballast immediately after burn-out.

D. Summary of Workplace PCB Exposure Levels

PCB exposures were greatest in electrical equipment manufacturing[17,21,26] where impreg-

MONS 006227

nation was by flood filling. Exposures were less with individual impregnation through a manifold.[38] Within either impregnation process, the greatest PCB exposures were among workers who salvaged capacitors that failed to pass inspection, followed by workers who sealed the impregnation fill holes.[17,31,38] All employees at the facilities appeared to have some PCB exposure, to the extent that mean serum PCB levels among workers never assigned to capacitor impregnation were significantly greater than background levels in the community.[17] PCB exposures in capacitor manufacturing were generally greater than those encountered in transformer maintenance and repair,[17,32,39,41] whether evaluated by comparing PCB air levels or serum levels among exposed workers. Indeed, PCB air levels for workers in transformer maintenance and repair could be below the level of detection[33] and serum PCB levels could well be within what might be considered as background.[42]

Exposures to PCDFs associated with PCB exposures are of concern. There is no evidence, however, in used transformer Askarels, not subject to pyrolysis, that increased PCDF levels beyond the levels encountered in unused Askarels occur.[33,34,36,37] Evidence exists for increased PCDF levels in pyrolyzed PCBs and in soot from electrical fires in which PCBs were burned.[35,39] However, serum PCB levels among workers who have cleaned up pyrolyzed PCBs are not necessarily elevated,[39,61] suggesting that exposures in such clean-up do not necessarily result in PCB absorption.

V. EARLY OCCUPATIONAL STUDIES

Little information was accumulated on the toxicology of PCBs during the first 3 decades of its commercial use. That which was collected was almost exclusively in relation to the risks of occupational exposure to PCBs but invariably little distinction was made between the toxic effects of chlorinated biphenyls and those of other chlorinated hydrocarbon compounds that were also present, such as chlorinated naphthalenes.

The early occupational medicine literature generally described occupational acne (also termed chloracne) occasionally in association with systemic symptoms from exposure to various chlorinated hydrocarbon compounds. Chloracne was noted to result from open system manufacturing operations with exposure either to PCBs or to chlorinated hydrocarbon mixtures of which PCBs were but one component. Jones and Alden[64] published the first American report of an outbreak of an acne-like dermatosis in a group of workers employed in the manufacture of chlorinated biphenyl from benzene. The manufacturing process utilized "open stills and heating units" which allowed for extensive prolonged exposure to the fumes of the raw materials, intermediate, and end products. Acne began to appear among workers 1 month after the electrical properties of the chlorinated biphenyl product fell below specifications, and was attributed by the authors to chlorinated products of impurities present in a particular source of crude benzene. The outbreak subsided following enclosure of the distilling operation, improvement of ventilation, improvement of worker hygiene, and a change in the source of benzene used as a raw material in the manufacturing process.

Later reports generally described acne-like dermatoses from exposure to various chlorinated hydrocarbon waxes used as insulating materials in the manufacture of electrical cable, capacitors, and transformers.[20,65-69] These waxes, also termed "halowax" were mixtures of chlorinated naphthalenes and chlorinated biphenyls, in which the chlorinated biphenyls themselves were minor constituents. Systemic symptoms (e.g., headaches, nausea, and malaise) were frequently alleged to accompany the dermatologic findings and a number of deaths from liver disease were described among exposed workers.[20,67-69] Other chemical exposures were variously described, including exposure to solvents such as carbon tetrachloride, ethylene dichloride, and toluene.[65,66] Given the multiplicity of chemicals to which workers were exposed, these reports contribute little to an understanding of the health effects attributable specifically to PCB exposure.

MONS 006228

A later study by Meigs et al.[70] described an outbreak of chloracne involving 7 of 14 chemical operators exposed to chlorinated biphenyl from leaks in a heat exchange apparatus. This report detailed one of three outbreaks of chloracne attributed to leakage of PCBs in use as a heat transfer fluid published since the 1940s, the other outbreaks being the Yusho and Yu-cheng epidemics.

VI. EPIDEMIOLOGICAL STUDIES, POST-YUSHO

Following the Yusho epidemic, a number of epidemiological studies were undertaken in different countries of groups exposed to PCBs. We first briefly describe the nonoccupational epidemiologic studies since their findings are similar to and reinforce the findings of the occupational studies. We then describe the epidemiologic studies of occupationally exposed groups. In some countries (e.g., Italy and the U.S.), multiple independently conducted surveys were undertaken on the same worker populations. Since we do not believe this overlap in surveys to be readily apparent from the available literature, we have gone to some length to summarize the relationships between survey samples. Overall, workers exposed to PCBs accumulate serum PCB levels many times greater than background levels, yet a paucity of clinically apparent illness among study participants appears to be the rule. Clinical abnormalities range from none found to weak associations between blood PCB levels and serum liver enzyme levels and plasma triglyceride or cholesterol levels in the absence of any significant clinical abnormalities, to the presence of skin abnormalities including chloracne, and signs of liver enlargement. In general, the associations between PCB exposures and clinical abnormalities tend to be weak and inconsistent between investigations and their significance relative to the workers' health is unknown.

A. Nonoccupational Studies

Baker et al.[16] studied persons with potential exposure to PCBs through the use, as a garden fertilizer, of sewage sludge contaminated with PCBs. The survey was conducted in the same community as the electrical equipment manufacturing plant studied by Smith et al.[17] (described below). Serum PCB levels among community residents with no known occupational PCB exposure provided the background serum PCB levels to which Smith et al. compared the serum PCB levels measured among workers employed at the plant. Among community residents with no known unusual exposure to PCBs, the mean serum PCB level, measured as Aroclor® 1254, was 12.8 (ng/mℓ). Baker et al. noted no consistent pattern of clinical abnormalities on medical history or physical examinations. However, serum PCB level (as Aroclor® 1254) was positively correlated with plasma triglyceride level. Serum PCB levels did not correlate with sewage sludge use.

Kreiss et al.[71] studied 458 persons in Triana, Ala., where the population had "exceptional" exposure to DDT residues from eating locally caught fish. PCB levels in serum specimens, initially taken to determine DDT residues were measured. The geometric mean serum PCB level was 17.2 ng/mℓ with single specimens ranging from 3.2 to 157.9 ng/mℓ. Serum PCB levels increased with age, sex (males greater than females), fish consumption, and alcohol consumption. Log PCB was positively correlated with log serum GGTP, log serum cholesterol, and diastolic blood pressure when pertinent confounders were controlled for in the analyses. No correlation was found between serum PCB level and serum GPT or bilirubin, or triglycerides when log GGTP and log cholesterol were included as predictors in the analyses.

B. Occupational Morbidity Studies

In Japan, Hasegawa et al.[24] examined 99 persons at six plants handling PCBs. The average PCB blood level of workers was found to be 40 ng/mℓ, with a maximum of 920 ng/mℓ. No correlation was found between length of employment and blood PCB level. Several cases

MONS 006229

of acne-like eruptions and comedones were described. However, no significant clinical problems were identified. In a follow-up study 1 year following cessation of PCB use, Hara et al.[15] found the dermatologic complaints to have lessened. No correlation was found between PCB blood level and serum triglyceride. In a second follow-up study conducted 1 year later, Hara et al.[16] reported the skin problems to be primarily vestigial markings on a few persons. In contrast to the previous report, a significant correlation was demonstrated between PCB blood level and serum triglyceride levels.

In Finland, Karppanen and Kolho[72] determined blood PCB levels in 29 persons with varying occupational exposures. Despite blood PCB levels approximately 50 times greater in persons continually exposed to Aroclor® 1242 in a capacitor factory compared to controls, they were unable to detect any biological effect on clinical examination.

In Australia, Ouw et al.[27] studied 34 workers occupationally exposed to 42% chlorinated biphenyl in a capacitor manufacturing facility. Overall, clinical examinations revealed symptoms suggestive of irritation, and biochemical examinations identified scattered individual abnormalities of serum alkaline phosphatase and SGOT. Slight BSP retention was noted in four of seven workers judged to have the heaviest exposures. However, on a group basis each liver function test was within normal limits.

In the U.K., Crow[73] reported that in his survey of two thirds of the British capacitor industry, he had observed occasional chloracne in association with occupational exposure to pentachlorobiphenyl, although this was much less than that from penta- and hexachloronaphthalene. "Since the change to trichlordiphenyl, however, even this has entirely disappeared . . . Contact with cold liquid chlordiphenyls, although undesirable because of skin absorption, appears to pose no acnegenic hazard." Crow further stated that the complete absence in the literature of any reports of chloracne from PCB containing fewer than four chlorine atoms, had led him to conclude that PCBs with four or fewer chlorine atoms per molecule appeared to pose no acnegenic hazards.

In Italy, Marosi et al.[20,29] studied 80 workers at two plants. One plant manufactured electrical capacitors. Exposure was to 54% chlorinated biphenyl prior to 1964, a mixture of 42 and 54% chlorinated biphenyl from 1964 to 1970, and 42% chlorinated biphenyl thereafter. Three PCB area air samples[25] in 1954 were 5200, 5400, and 6800 μg/m³. PCB area air samples in 1977 ranged from 48 to 275 μg/m³. Workroom surface and worker skin contamination with PCBs were demonstrable. The mean blood PCB concentration among exposed workers was 379 ng/mℓ. The second plant was an experimental center. The mean blood PCB concentration among exposed workers was 200 ng/mℓ.

On physical examination, 10 of 80 workers, all of them from the capacitor manufacturing plant, had acne and folliculitis. Three were diagnosed "with certainty" as chloracne. Blood PCB concentrations of these ten workers did not differ significantly from other unaffected workers employed in the same job. Sixteen workers, none of them with acne or folliculitis, had some form of hepatic involvement, e.g., hepatomegaly and/or elevated serum GGTP, SOOT, or SOCT. The frequency of workers with abnormal liver findings correlated with increasing blood PCB levels quantitated as trichlorobiphenyl and as pentachlorobiphenyl.

In the U.S., Fischbein et al.[37] and Warshaw et al.[74] reported the results of a survey of 326 workers at two capacitor manufacturing plants with a total work force of approximately 800 persons. Lawton et al.[38] studied 194 persons from the same plants. Only 34 persons participated in both the Fischbein et al. studies and the Lawton et al. studies. Brown and Jones[31] included these two plants as one of their study sites, as described below. Various Aroclors® had been used at the plant since the 1940s, including Aroclor® 1242, 1254, and (at the time of the Fischbein et al. survey) 1016. PCB usage ceased in 1977. In 1977, Brown and Jones found TWA personal air samples to range from 24 μg/m³ to 393 μg/m³ and TWA area air samples to range from 3 μg/m³ to 776 μg/m³. Area air sampling in 1975, reported by Lawton et al.,[38] ranged from 260 to 2000 μg/m³ and "dropped steadily with time over the 1975—1980 period".

MONS 006230

Modes of survey participant selection were different for the Fischbein et al.[77] and Lawton et al.[36] studies. Lawton et al. note that Fischbein et al. "issued a call for volunteers through the union". The participant group was said to consist "predominantly of persons having occupational exposures to PCBs that were only indirect, although still above background". The Lawton et al. group was said to have been selected because of "direct (physical contact) occupational exposure to PCB at the time . . . " They were studied in 1976 and 1979. Due to analytical problems in serum PCB quantitation, the Lawton et al. report of clinical findings and correlations with measures of PCB body burden were based upon the 1979 data.

Blood PCB concentrations were quantitated by Fischbein et al. as "lower PCB homologs" (L-PCB) and "higher PCB homologs" (H-PCB), i.e., homologs eluting from the gas chromatograph before and after *p,p'*-DDE, respectively. In the Fischbein et al. study, mean plasma L-PCB concentration ranged from 73 ng/mℓ in "low" relative intensity exposure jobs to 266 ng/mℓ in "high" relative intensity exposure jobs. Mean plasma "higher PCB homologues" concentrations ranged from 25 ng/mℓ in "medium" relative intensity exposure jobs to 82 ng/mℓ in "high" relative intensity exposure jobs, and 84 ng/mℓ in retired persons. Blood PCB concentrations were quantitated by Lawton et al. as "Aroclor 1242" and "Aroclor 1260", which more or less corresponded to the Fischbein et al. "L-PCB" and "H-PCB" designations. In 1979, mean serum Aroclor® 1242 levels ranged from 50.4 ng/mℓ among workers with no direct PCB exposure to 676 ng/mℓ among workers with heavy direct PCB exposure. Mean serum Aroclor® 1260 levels ranged from 26 ng/mℓ among workers with no direct exposure, to 59 ng/mℓ among workers with heavy direct exposure.

Fischbein et al.[77] found no association between reported symptoms and either duration of employment or plasma levels of lower or higher PCB homologs. Forty-two of the 326 participants had one or more skin abnormalities thought to be related to PCB exposure, e.g., hyperpigmentation, hyperkeratosis, comedones, and chloracne. Serum L-PCB and H-PCB levels were higher in males and females among persons with "abnormal" skin status. However, the only statistically significant elevation was found for the mean H-PCB level among males.[78] A statistically significant positive correlation was found between plasma L-PCB and H-PCB levels and SGOT. No correlations were noted between plasma PCB and other biochemical tests (including SGPT, GGTP, bilirubin, and LDH). Pulmonary function tests were reported without regard to a valid comparison population, relative exposures, or plasma PCB levels[76] and therefore are not described here. Alvares et al.[76] reported studies of five asymptomatic workers from the plant who were exposed primarily to Aroclor® 1016 in the preceding 2 years. A statistically significant decrease in plasma half-life of antipyrine, administered orally, was found in the five "exposed" workers, compared to matched non-exposed controls. Acceleration of the elimination of antipyrine from plasma was attributed to increased metabolism secondary to liver microsomal enzyme induction, similar to the increased drug metabolism demonstrated in studies of workers occupationally exposed to DDT and lindane[77] and to DDT.[78]

Lawton et al.[36] examined 194 workers in 1976 and again in 1979, and noted the physical examinations to be unremarkable. In particular, no sign of chloracne past or present, pigmentation and thickening of the skin, discoloration of the fingernails, or enlargement of the meibomian glands, were noted. Significant positive correlations were noted between log serum PCB and log cholesterol, log triglycerides, and log GGTP. However, when PCB levels were expressed as calculated values for adipose tissue PCB levels, no correlation was found between this measure of PCB and those clinical tests.

Chase et al.[79] studied 120 male workers exposed to PCB-containing transformer fluids at a railroad maintenance facility. Mean plasma PCB levels ranged from 12 ng/mℓ among the nonexposed to 33.4 ng/mℓ among the exposed. A review of survey participants' medical histories and physical exams "failed to reveal evidence of organ toxicity in the exposed group, although several cases of chloracne were encountered in this group . . . Other der-

matological findings were more prevalent in the exposed group as well, but no significant association between these and PCB levels could be demonstrated within the group." A significant correlation was noted between length of employment and both plasma and fat PCB levels, the correlation with fat PCB levels being greater than that for plasma PCB levels. Significant correlations between plasma PCB and SGOT were noted, but not between plasma PCB and SGPT or GGTP. No significant correlation between fat PCB and plasma triglycerides, SGOT, SGPT, or GGTP were noted.

Smith et al.[17] studied 321 workers at 3 sites: an electrical equipment manufacturing company where exposure was to 42% chlorinated biphenyl in the manufacture of electrical power capacitors and two utility companies where exposure was to 54% chlorinated biphenyl in the maintenance and repair of distribution transformers. TWA personal air samples for PCBs at the electrical equipment manufacturing company ranged from nondetectable to 264 $\mu g/m^3$. The TWA personal air samples for PCBs at the utility companies ranged from nondetectable to 215 $\mu g/m^3$. Smearable PCB skin contamination was demonstrated at all sites. Serum PCB levels were quantitated as lower or higher chlorinated biphenyl (L-PCB and H-PCB). Geometric mean L-PCB levels varied from 89 ng/mℓ among persons who never worked in capacitor impregnation or maintenance to 237 and 502 ng/mℓ among current workers in maintenance and in capacitor impregnation, respectively. The mean community level from data provided by Baker et al.[19] was 11.6 ng/mℓ. Geometric mean H-PCB levels varied from 22 ng/mℓ among persons who never worked in capacitor impregnation or maintenance to 44 and 51 ng/mℓ among current workers in capacitor impregnation and in maintenance, respectively. The mean community level was 12.8 ng/mℓ. At the two utility companies, the mean L-PCB level was 14 and 22 ng/mℓ among the PCB exposed and 18 and 21 ng/mℓ among the nonexposed. Mean H-PCB levels were 24 and 29 ng/mℓ among the PCB exposed and 7 and 8 ng/mℓ among the nonexposed. No clinical abnormalities attributable to PCB exposure were observed. Serum PCB levels were positively correlated with SGOT, GGTP, and plasma triglycerides and inversely correlated with plasma HDL-cholesterol across all study sites.

Emmett et al.[41] studied 55 electricians exposed to PCB-containing transformer fluids and a like number of nonexposed controls. Median serum PCB levels were 12 ng/mℓ among the currently exposed, 7 ng/mℓ among the previously exposed, and 6 ng/mℓ among the nonexposed. Chloracne was not observed on physical examination. One worker with hepatomegaly was noted. Findings suggestive of peripheral neuropathy among the PCB-exposed, e.g., abnormal sensory examinations with abnormal nerve conduction velocities were noted. After adjusting for confounders, a significant positive association between serum log PCB levels and log GGTP levels, and a significant negative association between serum log PCB and urinary 17-hydroxycorticosteroid excretion, were noted.

In summary, all cross-sectional studies demonstrate serum PCB elevations among exposed workers. Levels of PCB exposure and accumulation in workers' serum were much greater among workers exposed during capacitor manufacturing operations than among workers exposed during transformer maintenance and repair. The former type of exposure is now a matter of historical interest while the latter constitutes the type of PCB exposure that is likely to continue into the near future. Four studies[26,27,72,73] did not identify any significant clinical problem associated with PCB exposure. Four occupational studies[17,26,30,70] and two nonoccupational studies[16,71] found clinical abnormalities limited to correlations between blood PCB levels and one or more serum liver enzyme level, and plasma cholesterol or triglyceride levels. One study[27,70] found one or more skin abnormalities presumed related to PCB exposure in addition to an association between blood PCB levels and SGOT levels. One study[28,29] found chloracne and hepatomegaly and/or elevated serum liver enzyme tests associated with increasing blood PCB levels. One study[41] found signs of a peripheral neuropathy among PCB exposed workers and a significant positive correlation between serum PCB levels and serum GGTP.

MONS 006232

C. Occupational Mortality Studies

Bahn et al.[89] investigated a cluster of three cases of malignant melanoma among 72 employees at a U.S. petrochemical plant. These 72 employees included 31 research and development chemists alleged to be exposed to Aroclor® 1254 and 41 refinery workers with various exposures. Other chemical exposures were not defined, as pointed out in a more extensive unpublished report[91] and data on the duration and extent of actual exposure to Aroclor® 1254 were limited. These three cases of melanoma would have been a statistically significant excess compared to the expected, had the hypothesis been proposed *a priori*, as well as two cases of pancreatic cancer described in the unpublished report. However, in view of the multiple chemical nature of the study group's exposure, many of which are unknown, and the limited information on duration and extent of exposure to PCBs among the individuals in the cohort and the *a posteriori* recognition of the potential PCB exposure among the cluster, no inferences relating the occurrence of these cancer cases to a particular exposure are warranted.

Bertazzi et al.[92] studied the mortality of 1310 workers (290 males, 1020 females), who had worked at least 6 months in capacitor production between 1946 and 1970 at one of the plants studied by Maroni et al.[28,29] Follow-up was first reported through 1978 and was based upon 16,008-person years of observation. Expected deaths were based upon city rates in which the plant was located. Causes of death were analyzed separately for males and females. Males had a statistically significant increased number of deaths from all neoplasms. When analyzed separately by organ system, death from neoplasms of the digestive organs and peritoneum (3 observed vs. 0.88 expected) and from lymphatic and hematopoietic tissues (2 observed vs. 0.46 expected) were elevated. The numbers of observed deaths were small and not statistically significant. Among females, the all-causes-of-death SMR was significantly elevated. Deaths from all neoplasms were elevated although not significantly so. Within neoplasms, lymphatic and hematopoietic neoplasms (2 observed vs. 0.45 expected) were elevated, but not significantly so. Again, the number was small. No analyses were done by duration of exposure or latency.

Bertazzi et al.[90] have recently expanded this study to include all workers with 1 week or more of employment (N = 2100) with vital status follow-up updated through 1982. In the updated results there was a statistically significant excess in cancer among both females (12 observed vs. 5.3 expected) and males (14 observed vs. 7.6 expected). In both groups there were nonsignificant excesses in lymphatic/hematopoietic cancer and a statistically significant excess in digestive cancer among males (6 observed vs. 2.2 expected). Unfortunately, not enough information is provided to determine the risk specifically for liver cancer.

Brown and Jones[31] studied the mortality experience of 2567 workers at two capacitor manufacturing plants who were employed for at least 3 months between January 1940 and January 1976 in the areas of the plants where potential PCB exposure would occur. One of these plants included the groups studied cross sectionally by Fischbein et al.[37] and Lawton et al.[38] PCB air levels at the first plant are cited above. Personal PCB air levels at the second plant ranged from 280 to 1260 $\mu g/m^3$ as a TWA; area samples ranged from 50 to 810 $\mu g/m^3$. Follow-up through January 1, 1976 was based upon 39,018 person-years of observation. A greater than expected number of observed deaths from cancer of the liver and cancer of the rectum were noted. Neither increase was statistically significant for both study sites combined.

However, in a recent unpublished update[93] of this study, with follow-up through 1982, the excess in liver/biliary tract cancer was statistically significant (5 observed vs. 1.9 exposed), whereas the excess in cancer of the rectum was still elevated but not statistically significant. No excess mortality of liver cirrhosis, or of diseases of the circulatory system was observed. Despite the fact that the two plants were ranked among the five capacitor plants in the U.S. with the greatest PCB usage by weight,[33] the combined number of

MONS 006233

employees available for follow-up yielded a study with remarkably little power to detect an increase in disease occurrence, were such an increase postulated to exist.[83]

In summary, Bertazzi et al.[82] and Brown and Jones[31] studied capacitor production plants also studied on a cross-sectional basis. The studies remain inconclusive because they lack statistical power and the results are inconsistent when subdivided by plant and by sex; the results of the studies are inconsistent with each other. The liver cancer excess in the Brown and Jones update is very interesting because PCB has been shown to cause liver tumors in laboratory animals.

VII. DISCUSSION

Potential human PCB toxicity has been studied most extensively for electrical equipment manufacture at levels of exposure[17,24,27,28,30,31,36,82] unlikely to be encountered now or in the near future. Additional studies of human PCB exposures at levels considerably less than in electrical equipment manufacture, but greater than environmental exposures, have been undertaken in the maintenance and repair of such equipment.[17,79] Studies of the health effects of PCBs on individuals within communities with demonstrable levels of PCB contamination have also been reported.[16,71] The results of individual studies are remarkably consistent with each other. Among the cross-sectional studies of the occupationally exposed, a lack of clinically apparent illness in situations with high PCB exposure seems to be the rule.[17,24,27,29,36,72,73,79] Nonetheless, weak correlations of PCB exposure or serum PCB levels have been reported with various biochemical tests including positive correlations with SGOT,[17,27,30,37,80] GGTP,[17,29,36,61] and plasma triglycerides.[17,36,80] Correlations with plasma triglycerides[16] and with GGTP[79] were also found among community residents with low level PCB exposures. These studies were cross sectional, and as such causality cannot necessarily be imputed to PCBs. Although it has been suggested that the simultaneous changes in SGOT, GGTP, and plasma triglycerides with increasing serum PCB level are indicative of an effect on the liver of PCB exposure,[17] it has also been argued that the observed correlation of serum PCB level with plasma triglyceride is simply a manifestation of the second law of thermodynamics, e.g., the PCBs merely partition into plasma triglycerides the variation of which within individuals has nothing to do with PCB exposure.[36] PCBs are lipophilic. Akiyama et al.[84] noted for instance that a PCB concentration gradient between blood lipids and whole blood of 128:1 existed in 24 blood samples of mothers at delivery. The biological significance of these data is thus unclear.

The Brown and Jones[31] and Bertazzi et al.[82] studies and their subsequent updates[60,91] are equivocal in regard to an association between PCB exposure in electrical equipment manufacture and malignant neoplasms. Although the update of the Brown and Jones study demonstrated a statistically significant excess in liver/billary tract cancer, conclusions regarding these results are tentative because: (1) possible misclassification of cause of death due to primary liver cancer; (2) the category of liver/billary tract cancer includes organ sites that may not share a common etiology; (3) the pattern of risk by latency and duration of employment is not completely consistent with an occupational carcinogen; and (4) the analysis is based on a small number of deaths. It is frustrating to be forced to recognize that the Brown and Jones study, at two of the largest PCB users in the U.S. at exposure levels far in excess of those likely to be encountered from on-going PCB exposures and the Bertazzi et al. study, at a plant with exposures in 1954 stated[20] to exceed 5 mg/m^3, yield equivocal results. With time, as the two cohorts age, a more definitive conclusion regarding cancer mortality and PCB exposure may become evident.

Despite a growing body of published information, a human health hazard specifically due to PCB exposure is still largely unknown. A number of factors complicate the epidemiological studies and must be kept in mind when assessing such information. First, PCBs are not pure

MONS 006234

compounds but are mixtures of isomers of different chlorinated biphenyl homologs in which generally two or three PCB homologs predominate. Experimentally, observed effects may vary depending upon whether the PCB preparation contains predominantly lower or higher chlorinated PCB homologs.[83] Also, the metabolism of different PCB homologs and isomers varies and depends primarily upon the availability of adjacent unsubstituted carbon atoms in the biphenyl nucleus.[84] Second, some toxic effects attributed to PCBs have been shown to be related to the presence of highly toxic impurities, especially PCDFs which vary in amount between PCBs from different manufacturers and between PCBs of differing percent chlorination.[44-46] PCDFs themselves are suspected to cause chloracne and are strongly hepatotoxic, characteristics frequently attributed to PCBs.[87] Polychlorinated dibenzofurans do not appear to be present in used PCBs at levels greater than unused PCBs. However, PCDFs have been documented to be present in pyrolyzed PCBs at increased levels compared to nonpyrolyzed PCBs. Third, different animal species, including man, vary in their susceptibility to the toxic effects of PCBs and their pattern of biological response to PCB exposure.[88] Thus, the inability to identify a toxic effect from PCB exposure in one species (humans) ought not to be considered a testimonial to their safety. Clinical and epidemiologic methods at this time appear not to be sufficiently sensitive and specific to allow complete confidence, given the absence of unequivocal individual or group effects from PCB exposure that an adverse health effect still has not been overlooked.

REFERENCES

1. Lloyd, J. W., Moore, R. M., Woolf, B. S., and Stohr, H. P., Polychlorinated biphenyls, *J. Occup. Med.*, 18, 109, 1976.
2. Bradley, R. J., Jr., Polychlorinated biphenyls in man's food, *J. Milk Food Technol.*, 36, 155, 1973.
3. Hutzinger, O., Safe, S., and Zitko, V., *The Chemistry of PCBs*, CRC Press, Cleveland, 1974.
4. Kraybill, H. F., Chemical and physical properties of PCBs, in Polychlorinated Biphenyls and the Environment, Interdepartmental Task Force on PCBs, Washington, D.C., 1972, 23.
5. Jensen, S., Report of a new chemical hazard, *New Sci.*, 32, 612, 1966.
6. Widmark, G., Possible interference by chlorinated biphenyls, *J. Assoc. Offic. Anal. Chem.*, 50, 1069, 1967.
7. Risebrough, R. W., Reich, F., Peakall, D. B., Herman, S. G., and Kirven, M. N., Polychlorinated biphenyls in the global ecosystem, *Nature (London)*, 220, 1098, 1968.
8. Keugh, T. H., Chemical pollutants: polychlorinated biphenyls still a threat, *Science*, 190, 1189, 1975.
9. Kuratsune, M., Yoshimura, T., Matsuzaka, J., and Yamaguchi, A., Epidemiologic study on Yusho, a poisoning caused by ingestion of rice oil contaminated with a commercial brand of polychlorinated biphenyl, *Environ. Health Perspect.*, 1, 119, 1972.
10. Nagayama, J., Kuratsune, M., and Masuda, Y., Determination of chlorinated dibenzofurans in Kanechlors and "Yusho Oil", *Bull. Environ. Contam. Toxicol.*, 15, 9, 1976.
11. Morita, M., Nakagawa, J., Akiyama, K., Mimura, S., and Isono, N., Detailed examination of polychlorinated dibenzofurans in PCB preparations and Kanemi Yusho oil, *Bull. Environ. Contam. Toxicol.*, 18, 67, 1977.
12. Nagayama, J., Masuda, Y., and Kuratsune, M., Chlorinated dibenzofurans in Kanechlors and rice oil used by patients with Yusho, *Fukuoka Acta Med.*, 66, 393, 1975.
13. Masuda, Y. and Kuroki, H., Polychlorinated dibenzofurans and related compounds in patients with "Yusho", in *Chlorinated Dioxins & Related Compounds*, Hutzinger, O., Frei, R. W., Merian, E., and Pocchiari, F., Eds., Pergamon Press, Oxford, 1982, 561.
14. Wong, C.-K., PCB poisoning special issue, *Clin. Med. (Taipei)*, 7(1), 1981.
15. Landrigan, P. J., General population exposure to halogenated biphenyls, in *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products*, Kimbrough, R. D., Ed., Elsevier/North-Holland, Amsterdam, 1980, 267.
16. Baker, E. L., Jr., Landrigan, P. J., Glueck, C. J., Zack, M. M., Jr., Liddle, J. A., Burse, V. W., Housworth, W. J., and Needham, L. L., Metabolic consequences of exposure to polychlorinated biphenyls in sewage sludge, *Am. J. Epidemiol.*, 112, 553, 1980.

MONS 006235

17. Smith, A. B., Schloemer, J., Lowry, L. K., Smallwood, A. W., Ligo, R. N., Tanaka, S., Stringer, W., Jones, M., Horvin, R., and Glueck, C. J., Metabolic and health consequences of occupational exposure to polychlorinated biphenyls (PCBs), *Br. J. Ind. Med.*, 39, 361, 1982.
18. Occupational Safety and Health Administration, General Industry Standards, U.S. Department of Labor, Washington, D.C., 29 CFR 1910, revised, 1978.
19. American Conference of Governmental Industrial Hygienists, *Documentation of the Threshold Limit Values for Substances in Workroom Air*, 3rd ed., National Institute for Occupational Safety and Health, Cincinnati, 1971.
20. Drinker, C. K., Warren, M. F., and Bennett, G. A., The problem of possible systemic effects from certain chlorinated hydrocarbons, *J. Ind. Hyg. Toxicol.*, 19, 283, 1937.
21. Drinker, C. K., Further observations on possible systemic toxicity of certain of the chlorinated hydrocarbons with suggestions for permissible concentrations in the air of workrooms, *J. Ind. Hyg. Toxicol.*, 21, 155, 1939.
22. International Labour Office, *Occupational Exposure Limits for Airborne Toxic Substances*, Occupational Safety and Health Series No. 37, World Health Organization, Geneva, 1977.
23. National Institute for Occupational Safety and Health, Criteria for a Recommended Standard: Occupational Exposure to Polychlorinated Biphenyls, U.S. Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, 1977.
24. Hasegawa, H., Sato, M., and Tsuruta, H., Report on survey of work area environment where PCB is handled and of the health of workers handling PCB, in Special Report on Prevention of Environmental Pollution by PCB-like Substances, Research Coordination Bureau, Science and Technology Agency, Tokyo, 1972, 141.
25. Hara, I., Harada, A., Kimura, S., Endo, T., and Kawano, K., Follow-up study of condenser factory after use of PCB discontinued. I, *Jpn. J. Ind. Health*, 10, 365, 1974.
26. Hara, I., Harada, A., Kimura, S., Endo, T., and Kawano, K., Follow-up study of condenser factory after use of PCB discontinued. III, *Jpn. J. Ind. Health*, 17, 371, 1975.
27. Oaw, K. H., Simpson, G. R., and Styall, D. S., The use and health effects of Aroclor 1242, a polychlorinated biphenyl in the electrical industry, *Arch. Environ. Health*, 31, 189, 1976.
28. Maroni, M., Colombi, A., Cantoni, S., Ferioli, E., and Fea, V., Occupational exposure to polychlorinated biphenyls in electrical workers. I. Environmental and blood polychlorinated biphenyls concentrations, *Br. J. Ind. Med.*, 38, 49, 1981.
29. Maroni, M., Colombi, A., Arbosti, G., Cantoni, S., and Fea, V., Occupational exposure to polychlorinated biphenyls in electrical workers. II. Health effects, *Br. J. Ind. Med.*, 38, 55, 1981.
30. Puccinelli, V., Dell'acne clorica, *Med. Lavoro*, 45, 131, 1954.
31. Brown, D. P. and Jones, M., Mortality and industrial hygiene study of workers exposed to polychlorinated biphenyls, *Arch. Environ. Health*, 36, 120, 1981.
32. Moseley, C. L., Gerard, C. L., and Burg, J., Polychlorinated biphenyl exposure in transformer maintenance operations, *Am. Ind. Hyg. Assoc. J.*, 43, 170, 1982.
33. Durfee, R. L., Production and usage of PCBs in the United States, in Proc. Natl. Conf. Polychlorinated Biphenyls, EPA 560/6-75-004, U.S. Environmental Protection Agency, Washington, D.C., 1976, 103.
34. Versar Inc., Study of Regulatory Alternatives for PCBs, Draft Interim. Rep., EPA contract no. 68-01-3299, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., 1975.
35. Versar Inc. PCBs in the United States. Industrial Uses and Environmental Distribution, EPA/560/6-76/005, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C., 1976.
36. Lawton, R. W., Sack, B. T., Rees, M. R., and Feingold, J., Studies of Employees Occupationally Exposed to PCBs, General Electric Research and Development Center, Schenectady, N.Y., 1981.
37. Fischbein, A., Wolff, M. S., Lilis, R., Thornton, J., and Selikoff, I. J., Clinical findings among PCB-exposed capacitor manufacturing workers, *Ann. N.Y. Acad. Sci.*, 320, 703, 1979.
38. Jones, M., Unpublished data, 1977.
39. Horvin, R. and Smith, A. B., Health Hazard Evaluation Rep. No. 77-7A and 7B, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, 1977.
40. Daniels, W. J. and Orris, P., Health Hazard Evaluation Rep. No. 81-064-1035, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, 1982.
41. Emmett, E. A., Agnew, J., Bleiker, M. L., Ferrara, J. M., Levin, B. K., Jeffreys, J., and Maroni, M., Health Effects of PCB Exposure of GSA Switchgear Employees, NIOSH Technical Assistance Request #80-7, The Johns Hopkins University School of Hygiene and Public Health, Baltimore, 1983.
42. Apol, A. G., Baxter, P., and Skinner, M. D., Technical Assistance Rep. No. 79-58, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, 1980.

MONS 006236

43. Lipscomb, J., Interim Report #2. Health Hazard Evaluation #81-415. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, 1982.
44. Vos, J. G. and Koeman, J. G., Comparative toxicologic study with polychlorinated biphenyls in chickens, with special reference to porphyria, edema formation, liver necrosis, and tissue residues. *Toxicol. Appl. Pharmacol.*, 17, 656, 1970.
45. Vos, J. G., Koeman, J. H., van der Maas, H. L., ten Noever de Brauw, M. C., and de Vos, R. H., Identification and toxicological evaluation of chlorinated dibenzofuran and chlorinated naphthalene in two commercial polychlorinated biphenyls. *Food Cosmet. Toxicol.*, 8, 625, 1970.
46. Bowes, G. W., Mulvihill, M. J., Simoneit, B. R. T., Burlingame, A. L., and Risebrough, R. W., Identification of chlorinated dibenzofurans in American polychlorinated biphenyls. *Nature (London)*, 94, 125, 1975.
47. Morita, M., Nakagawa, J., Akiyama, K., Nimura, S., and Isono, N., *Bull. Environ. Contam. Toxicol.*, 18, 67, 1977.
48. Buser, H. R., Bosshardt, H.-P., and Rappe, C., Formation of polychlorinated dibenzofurans (PCDFs) from the pyrolysis of PCBs. *Chemosphere*, 7, 109, 1978.
49. Buser, H. R. and Rappe, C., Formation of polychlorinated dibenzofurans (PCDFs) from the pyrolysis of individual PCB isomers. *Chemosphere*, 8, 157, 1977.
50. Buser, H. R., Formation of polychlorinated dibenzofurans (PCDFs) and dibenzo-p-dioxins (PCDDs) from the pyrolysis of chlorobenzenes. *Chemosphere*, 8, 415, 1979.
51. Olie, K., Vermeulen, P. L., and Hutzinger, O., Chlorodibenzo-*p*-dioxins and chlorodibenzofurans are trace components of fly ash and flue gas of some municipal incinerators in the Netherlands. *Chemosphere*, 6, 455, 1977.
52. Eiceman, G. A., Clement, R. A., and Karasek, F. W., Analysis of fly ash from municipal incinerators for trace organic compounds. *Anal. Chem.*, 51, 2343, 1979.
53. Buser, H. R., Bosshardt, H.-P., Rappe, C., and Lindahl, R., Identification of polychlorinated dibenzofuran isomers in fly ash and PCB pyrolyses. *Chemosphere*, 7, 419, 1978.
54. Choudhry, G. G., Olie, K., and Hutzinger, O., Mechanisms in the thermal formation of chlorinated compounds including polychlorinated dibenzo-p-dioxins, in *Chlorinated Dioxins & Related Compounds*, Hutzinger, O., Frei, R. W., Merian, E., and Pocchiari, F., Eds., Pergamon Press, Oxford, 1982, 275.
55. Kaminsky, J. R., Mellus, J. P., and Flesch, J. P., Assessing PCB contamination from electrical equipment failures, presented at the 62nd Annu. Massachusetts Safety and Health Conference, Foxboro, Mass., 1983.
56. Albro, P. W. and Parker, C. E., Comparison of the compositions of Aroclor 1242 and Aroclor 1016. *J. Chromatogr.*, 169, 161, 1979.
57. National Electrical Manufacturers Association, reply comments on notice of proposed rulemaking concerning polychlorinated biphenyls (PCBs) use in electrical equipment, EPA docket no. OPTS-62015B, U.S. Environmental Protection Agency, Washington, D.C., 1982.
58. U.S. Environmental Protection Agency, Polychlorinated biphenyls (PCBs); use in electrical equipment, *Fed. Reg.*, 47, 17426, 1982.
59. Jansson, B. and Sundstrom, G., Formation of polychlorinated dibenzofurans (PCDF) during a fire accident in capacitors containing polychlorinated biphenyls (PCB), in *Chlorinated Dioxins & Related Compounds*, Hutzinger, O., Frei, R. W., Merian, E., and Pocchiari, F., Eds., Pergamon Press, Oxford, 1982, 201.
60. Kaminsky, J. R. and Flesch, J. P., Health Hazard Evaluation Report HETA 81-237-915, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, 1981.
61. Boser, P. A. and Moody, P. L., Health Hazard Evaluation Report HETA 81-414-1047, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health, Cincinnati, 1982.
62. Stauff, D. C., Quinby, G. E., Spencer, D. L., and Starr, H. C., Polychlorinated biphenyl emission from fluorescent lamp ballasts, *Bull. Environ. Contam. Toxicol.*, 12, 455, 1974.
63. MacLeod, K. E., Sources of Emissions of Polychlorinated Biphenyls into the Ambient Atmosphere and Indoor Air, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1979.
64. Jones, J. W. and Alden, H. S., An acneform dermatergosis, *Arch. Dermatol. Syphilol.*, 33, 1022, 1936.
65. Schwartz, L., Dermatitis from synthetic resins and waxes, *Am. J. Publ. Health*, 26, 586, 1936.
66. Fulton, W. B. and Manthews, J. L., A Preliminary Report of the Dermatological and Systemic Effects of Exposure to Hexachloro-Naphthalene and Diphenyls, Bull. 43, Department of Labor and Industry, Harrisburg, Pa., 1936.
67. Mayers, M. R. and Silverberg, M. G., Skin conditions resulting from exposure to certain chlorinated hydrocarbons, *J. Ind. Hyg. Toxicol.*, 20, 244, 1938.
68. Good, C. K. and Penahy, N., Halowax acne ("cable rash"), A cutaneous eruption in marine electricians due to certain chlorinated naphthalenes and diphenyls, *Arch. Dermatol. Syphilol.*, 48, 251, 1943.

MONS 006237

69. Strauss, N., Hepato-toxic effects following occupational exposure to Halowax (chlorinated hydrocarbons). *Rev. Gastroenterol.*, 11, 381, 1944.
70. Meigs, J. W., Albers, J. J., and Kartin, B. L., Chloracne from an unusual exposure to Aroclor, *JAMA*, 154, 1417, 1954.
71. Kreiss, K., Zack, M. M., Kimbrough, R. D., Needham, L. L., Smrek, A. L., and Jones, B. T., Association of blood pressure and polychlorinated biphenyl levels, *JAMA*, 245, 2505, 1981.
72. Kerpponen, E. and Kolho, L., The concentration of PCB in human blood and adipose tissue in three different research groups, in PCB Conference II, National Swedish Environmental Protection Board, Stockholm, 1973, 124.
73. Crow, K. D., Chloracne. A critical review including a comparison of two series of cases of acne from chloronaphthalene and pitch fumes, *Trans. St. John's Hosp. Dermatol. Soc.*, 56, 79, 1970.
74. Warshaw, R., Fischbein, A., Thornton, J., Miller, S., and Selikoff, I. J., Decrease in vital capacity of PCB-exposed workers in a capacitor manufacturing facility, *Ann. N.Y. Acad. Sci.*, 320, 277, 1979.
75. Fischbein, A., Wolff, M. S., Bernstein, J., and Selikoff, I. J., Dermatological findings in capacitor manufacturing workers exposed to dielectric fluids containing polychlorinated biphenyls (PCBs), *Arch. Environ. Health*, 37, 69, 1982.
76. Alvares, A. P., Fischbein, A., Anderson, K. E., and Kappas, A., Alterations in drug metabolism in workers exposed to polychlorinated biphenyls, *Clin. Pharm. Ther.*, 22, 140, 1977.
77. Kolmodin, B., Azarnoff, D. L., and Sjoqvist, F., Effects of environmental factors on drug metabolism: decreased plasma half-life of antipyrine in workers exposed to chlorinated hydrocarbon insecticides, *Clin. Pharm. Ther.*, 10, 638, 1969.
78. Poland, A., Smith, D., Kuntzman, R., Jacobson, M., and Conney, A. H., Effect of intensive occupational exposure to DDT on phenylbutazone and cortisol metabolism in human subjects, *Clin. Pharm. Ther.*, 11, 724, 1970.
79. Chase, K. H., Wang, O., Thomas, D., Bernay, B. W., and Sloan, R. K., Clinical and metabolic abnormalities associated with occupational exposure to polychlorinated biphenyls (PCBs), *J. Occup. Med.*, 24, 109, 1982.
80. Bahn, A. K., Rosenwaike, I., Herrmann, N., Grover, P., Stellman, J., and O'Leary, K., Melanoma after exposure to PCBs, *N. Engl. J. Med.*, 295, 450, 1976.
81. Bahn, A. K., Report on Paulsboro, N.J. Mobil Oil plant study, unpublished report, Mobil Oil Corp., Paulsboro, N.J., 1976.
82. Bertazzi, P. A., Zocchetti, C., Guercilena, S., Foglia, M. D., Pesatori, A., and Riboldi, L., Mortality study of male and female workers exposed to PCBs, presented at the Int. Symp. Prevention of Occupational Cancer, Helsinki, Finland, April 1981.
83. Beaumont, J. J. and Breslow, N. E., Power considerations in epidemiologic studies of vinyl chloride workers, *Am. J. Epidemiol.*, 114, 725, 1981.
84. Akiyama, K., Obi, G., Fujitani, K., Yagyu, H., Ogino, J., and Kawana, T., Polychlorinated biphenyl residues in maternal and cord blood in Tokyo metropolitan areas, *Bull. Environ. Contam. Toxicol.*, 14, 588, 1975.
85. Panel on Hazardous Trace Substances, PCBs — environmental impact, *Environ. Res.*, 5, 249, 1972.
86. Matthews, H. B. and Kato, S., The metabolism and disposition of halogenated aromatics, *Ann. N.Y. Acad. Sci.*, 320, 131, 1979.
87. Kimbrough, R. D., Toxicity of chlorinated hydrocarbons and related compounds, *Arch. Pathol.*, 94, 125, 1972.
88. Vos, J. G., Toxicology of PCBs for mammals and for birds, *Env. Health Perspect.*, 21, 29, 1969.
89. National Institute for Occupational Safety and Health, Current Intelligence Bulletin 45, Polychlorinated Biphenyls: Potential Health Hazards from Electrical Equipment Fires or Failures, Publ. No. 86-111, U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH, Cincinnati, 1986.
90. Bertazzi, P. A., Riboldi, L., Pesatori, A., Radice, L., and Zocchetti, C., Cancer mortality of electrochemical workers exposed to PCB, *Am. J. Ind. Med.*, in press, 1986.
91. Brown, D., Mortality of workers exposed to polychlorinated biphenyls—an update, *Arch. Environ. Health*, submitted, 1986.

MONS 006238

Chapter 5

DISPOSAL AND DESTRUCTION OF WASTE PCBs

Jack D. Lauber

TABLE OF CONTENTS

I. The Long-Term Risks of Landfilling PCBs 84

II. Nonthermal Methods for PCB Disposal 91
- A. The Sun Ohio PCBX Process™[12] 92
- B. Acurex Waste Technologies Inc. (AWT) PCB Destruction Process 94
  - 1. AWT Process Chemistry[14] 94
    - a. PCB Dechlorination 94
      - i. Side Reactions 96
      - ii. Reagent and Chemistry 97
      - iii. Process Tests and Analyses 97
      - iv. Mass Balance and Stoichiometry 97
      - v. Sampling and Analysis 98

III. High Temperature PCB Incineration 99
- A. Summary of U.S. EPA Toxic Substance Control Act (TSCA) Regulation Requirements and Guidelines 99
- B. Energy Systems Company (ENSCO) El Dorado, Arkansas[17,18] 101
- C. PCB Trial Burn — Rollins, Deerpark, Texas[17,18] 105
- D. Case Study: Kommunekemi Hazardous Waste Incinerator, Nyborg, Denmark[19] 105
- E. Case Study: General Electric Co., Pittsfield, Massachusetts[20] 106
  - 1. Description of Thermal Oxidizer 107
  - 2. Thermal Oxidizer Operating History 108
  - 3. Research on the Oxidizer 108

IV. Burning Low Level PCB/Mineral Oil Wastes in High Efficiency Boilers 109
- A. Summary of the U.S. EPA TSCA Regulation Requirements 109
- B. Case Study — General Motors Corp., Warren, Michigan[21] 110
  - 1. Boiler Operating Conditions 113

V. Burning PCB Wastes in Cement Kilns[22] 113
- A. Cement Kiln Technology 113
  - 1. Burning Chemical Wastes (Including PCBs) and Chlorinated Wastes at St. Lawrence Cement Company, Mississauga, Ontario, Canada[23] 115
    - a. Ambient Air Monitoring for PCBs at Mississauga 116
  - 2. Burning PCBs at Peerless Cement Company, Detroit, Michigan[22] 116
  - 3. Burning Chemical Wastes at the Stora Vika Cement Plant in Sweden[22] 117
  - 4. Burning PCBs at the Degerhamn Dry Cement Kiln in Sweden[20] 117
  - 5. Burning PCBs at Norcem Cement Company, Norway[20] 117
  - 6. California Office of Appropriate Technology Recommendations for Burning PCBs 121

MONS 006239

B. Recommended Environmental Controls for Storage, Handling, and Process Disposal of Toxic Chemical Wastes in Cement Kilns[29] 122
C. Conclusion 126

VI. Burning PCBs at Sea[11,34] 127

VII. New Technologies for High Efficiency Destruction of PCBs 132
A. U.S. EPAs Mobile Incinerator[6,27,29] 132

VIII. Future PCB Waste Disposal Concepts 138
A. Arc Technologies Company Arc Pyrolysis Project[40] 139
1. Description of the Project 139
2. Process Engineering Information 140
3. Destruction Process 143
4. Arc Furnace 144
a. Electrodes 146
b. Gass Handling Duct Work 146
c. Capacitor Charging Units 147
d. Gas Handling System 147
e. Electric Power Supply System 147
i. DC Power Supply System 147
ii. AC Auxiliary Power System 148
iii. Emergency Power System 148
f. Instrumentation and Control Equipment 148
g. Closed-Circuit Cooling Water System 149
h. Hydraulic System 149
i. Furnace Tapping Equipment 149

References 149

I. THE LONG-TERM RISKS OF LANDFILLING PCBs

In 1980 about 41 million tons of hazardous wastes were generated by various sources in the U.S.[1] and almost 80% of these wastes were deposited in lagoons, landfills, and open dumps.[2] These environmentally unsound hazardous waste disposal practices have resulted in the contamination of land, water, and air throughout many areas in the U.S. The tragedy of Love Canal has illustrated that hazardous wastes deposited in improper landfills, decades ago, have become toxic time bombs for future generations. Numerous examples of environmental contamination from inadequate hazardous waste landfilling practices exist today. The resultant contamination of local community water supplies, lands, and airsheds have demonstrated that such practices are a serious threat to public health and welfare.

Of the roughly 1.25 billion lb of PCBs introduced into commerce in the U.S. since 1929 only approximately 55 million lb have been destroyed by incineration or by degradation in the environment; 290 million lb are under varying degrees of control in landfills and dumps and 150 million lb are free in the environment; 750 million lb of PCBs are still apparently in service.[3] These statistics are not highly accurate, and there have been other estimates of PCBs distributed in the U.S. Table 1[4] also gives an estimated distribution of PCBs in the U.S.; it shows that about 47% of the 1.25 billion lb of PCBs used are either in storage, in landfills, are currently in the environment, or have been destroyed. Table 2[4] gives a breakdown of the estimated 404 million lb of PCBs still in use and accessible. Table 3[4] is an

MONS 006240

Table 1
ESTIMATED DISTRIBUTION OF PCBs IN THE U.S.

1.25 Billion lb Used

Still in use and accessible	Still in use and generally not accessible	In storage, landfills, environment, destroyed
404 million lb (32%)	262 million lb (21%)	585 million lb (47%)

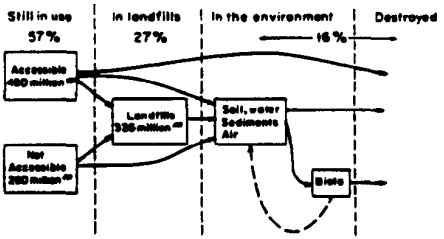
Table 2
PCBs STILL IN USE AND ACCESSIBLE

Use	Estimated millions of lb of PCBs
Askarel transformers	300
Power capacitors	103
Mineral oil transformers	1
Other Askarel-filled electrical equipment	0.1
Total	404

Table 3
PCBs IN "ALL OTHER" CATEGORIES

Estimated millions of lb of PCBs	
"Mobile" environment —	
Freshwater sediments	8.8
Soil	12.8
Vegetation	2.2
Atmosphere, water, biota	0.2
Subtotal	24
In the oceans	13
In landfills, in storage	385
Degraded	162
Total	584

Table 4
PCBs — DISTRIBUTION AND FATE (1980)



estimate of the quantities of PCBs currently in the environment; i.e., PCBs in water, soil, air, vegetation, and in oceans; plus PCBs in landfills, storage, and those which have been degraded. Of the estimated 584 million lb of PCBs in this category, one can see that a large fraction, 385 million lb, are estimated to be in landfills and in storage at the present time. Table 4[4] is an estimate of the distribution and fate of PCBs in 1980 showing 27% in landfills and 16% either in the environment or having been destroyed. Consequently, we can see that PCBs in the environment are very significant and that we must take further steps to ensure that these environmentally persistent materials are fully destroyed and are not further reintroduced into the environment by improper waste disposal practices.

MONS 006241

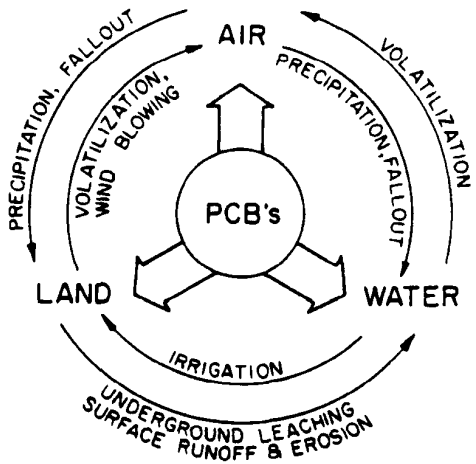


FIGURE 1. PCB environmental cycle.

The quantities of PCBs in landfills are substantial, and although PCBs are considered to have low volatility, landfilling such waste is certainly not the complete answer to solving PCB waste disposal problems. New evidence has shown that significant quantities of PCBs can migrate from landfills into the ambient air.

In order to assess the problems of hazardous organic wastes migrating from a landfill under varying physical conditions it is necessary to determine the rate of waste volatilization which is dependent on the physical and chemical properties of the waste, site design, operation, surrounding environment, and meteorological conditions. When hazardous organic wastes volatilize from a landfill, hazardous vapors may not be removed from the atmosphere for a relatively long period of time; such emissions may contribute to existing air pollution problems, especially when hazardous gases may be adsorbed or absorbed on small particles in the atmosphere, which then can eventually fall out on land and on surface waters. Consequently, hazardous wastes that have been deposited in landfills can volatilize, and can be re-emitted into the atmosphere by cyclic processes which can transfer PCBs from the air to bodies of water and other media as shown in Figure 1.[3]

At present thousands of landfills and surface impoundments used for disposal and treatment of hazardous wastes are operating under interim status provisions of Section 3005-E of the U.S. EPA Resource Conservation and Recovery Act (RCRA). These regulations were designed primarily to protect against contamination of surface and underground water supplies and do not adequately address air pollution aspects from hazardous waste landfills. The RCRA regulatory requirements[4] attempt to reduce hazardous air emissions from hazardous waste sites by requiring that:

1. Waste piles containing hazardous waste must be covered or otherwise managed to prevent wind erosion.

MONS 006242

2. Migration of air contaminants from the site must be controlled.
3. The vertical and horizontal escape of gases must be controlled by a gas collection and control system if one is present in the landfill.
4. Bulk or noncontainerized liquid waste must not be placed in a landfill, with few exceptions such as use of liners or pretreatment of the waste.

The air monitoring requirements for new hazardous waste sites under RCRA rules include:

1. An air monitoring system to yield samples for analysis and to provide sufficient ambient air quality data to perform the required comparisons and evaluations.
2. An air emission sampling and analysis plan which describes the sampling and analytical techniques and procedures.
3. An air emission evaluation to compare the anticipated effect of the waste site on ambient air quality within the provision of the site permit.
4. Records of all analyses and evaluations of ambient air quality, wind direction, and speed.

Summary of U.S. EPA 40 CFR 761 TSCA PCB Regulations Annex II Chemical Waste Landfills for PCBs:

1. Impermeable soils (clay, clay-silt, low permeability) required.
2. Synthetic membrane liners required.
3. Acceptable hydrological conditions required.
4. Flood protection provisions.
5. Acceptable topography.
6. Monitoring systems — ground water monitoring wells required.
7. Leachate collection system required.
8. Chemical waste landfill operations:
   a. Segregation of PCB items from incompatible materials, e.g., organic solvents.
   b. Operation plan required:
      - Liquid PCBs >500 ppm prohibited in landfills.
      - Bulk liquids <500 ppm to be pretreated and/or stabilized to increase solid content.
      - Ban on ignitable wastes (flash point <60°C) in landfills.
      - Extensive record-keeping requirements.

Practical experiences in implementing the U.S. EPA 40 CFR 761 PCB regulatory requirements have shown that there is a need for better pretreatment of discarded PCB transformers prior to landfilling. A new transformer solvent degreasing facility is planned in the Niagara Frontier in New York State. However, the ultimate success of this operation also depends on adequate PCB incineration facilities to dispose of the spent degreasing fluids.

Some environmental engineers do not favor the solidification of liquid PCBs less than 500 ppm, and as a preventive measure would ban all liquid PCBs from landfills.

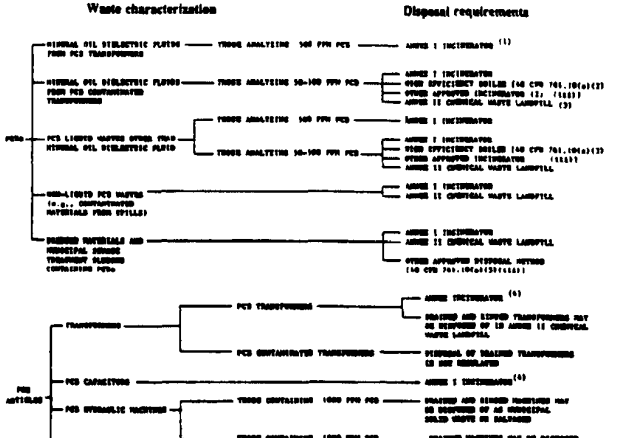
PCB wastes have to be fully segregated in landfills. Volatile organic solvent wastes, such as chlorinated, oxygenated, organic solvents must be similarly banned from landfills because they have the potential to mix with PCBs and enhance the mobility of PCBs in ground water.

Tables 5[11] and 6[12] present a summary of the U.S. EPA TSCA disposal requirements for various types of PCB wastes.

The New York State Department of Environmental Conservation has required that hazardous waste land disposal facilities have five cells based on chemical properties of the waste to be disposed.[7] These cells are to be hydrologically isolated and composed of:

MONS 006243

Table 5
U.S. EPA TSCA 40 CFR 761 DISPOSAL REQUIREMENTS FOR PCBs AND PCB ITEMS



1. General cell
2. Flammable waste cell
3. Pseudometal cell
4. Heavy metal cell
5. Halogenated organic cell

The primary reason for subdividing landfills into cells is to match the construction material used in the receiving cell with the corrosive and other physical characteristics of the waste. Subdivision in the landfill also promotes safe handling during operations, permits accurate record keeping of waste disposition, and facilitates environmental monitoring for leakage

MONS 006244

Table 6
SUMMARY OF EPA DISPOSAL REQUIREMENTS FOR PCB LIQUID AND PCB CONTAMINATED WASTES[a] [b]

	Disposal options				
	Chemical waste landfill	Destruction in high efficiency boiler	Incinerator	Municipal refuse disposal	Other
PCBs					
Mineral oil from PCB contaminated transformers (50—500 ppm)	Yes[c]	Yes	Yes	No	
PCB liquids other than mineral dielectric fluid (50—500 ppm) (including flushing solvents)	Yes[c]	Yes	Yes	No	
Any nonliquid PCB (rags, soil, & other debris)	Yes	No	Yes	No	
All dredge materials, sewage sludge, etc.	Yes	No	Yes	No	Yes[d]
All other PCB liquids (>500 ppm)	No	No	Yes	No	
PCB articles					
PCB transformers (drained)	Yes	No	Yes	No	
PCB-contaminated[e] transformers (drained)	NR[f]	NR	NR	NR	NR
PCB capacitors					
Small	NR	NR	NR	Yes	
Small[g]	No	No	Yes	No	
Large (high and low voltage)	No	No	Yes	No	
PCB hydraulic machines	NR	NR	NR	Yes	
PCB containers (drained)	Yes	No	Yes	Yes[h]	Yes[i]
All other PCB articles (drained)	Yes	No	Yes	No	
Any waste material contaminated with less than 50 ppm PCB (e.g., lighting ballast)	NR	NR	NR	Yes	

[a] For incineration EPA requires a destruction efficiency of 99.9999% for PCB nonliquids and a combustion efficiency of 99.9% for PCB liquids.
[b] Waste must not be ignitable (F.P. <140°F).
[c] Alternative disposal of these materials can be made upon approval of the EPA regional administrator.
[d] PCB contaminated transformer means the transformer previously contained 50—500 ppm of PCBs.
[e] Not regulated.
[f] Only small capacitors owned by persons who manufactured capacitors or PCB equipment are subject to special EPA disposal requirements.
[g] Yes, only if they previously contained PCBs of a concentration less than 500 ppm.
[h] PCB containers can be decontaminated by solvent rinsing.

and emission. Furthermore, the use of cells can reduce the rate of gas generation within the entire landfill and correspondingly diminish overall hazardous air emissions.[3]

It is difficult to predict emission rates of organic compounds from industrial landfills; however, certain predictive techniques can be used, assuming that diffusion in the vapor phase is the only transport process operating. If transport in moving water and degradation of the organic compound in the site are considered insignificant, the emission rate of a specific organic compound based on Fick's law, may be estimated using the following equation:[3]

$$E_i = D_i C_a A P_t^{m/2} W_i(I/L)$$

MONS 006245

where: E_i = emission rate of a specific compound in the waste (g/sec); D_i = diffusion coefficient of a specific compound (cm^2/sec); C_{v_i} = saturation vapor concentration of the compound (g/cm^3); A = exposed area (cm^2); P_t = total soil porosity (dimensionless); L = effective depth of soil cover (cm); and W_i = weight fraction of a specific compound in the waste.

The soil porosity may be calculated by the following equation:

$$P_t = 1 - d_b/d_p$$

where: d_b = soil bulk density (g/cm^3); and d_p = particle density (g/cm^3).

Open dump sites and hazardous waste disposal lagoons can be evaluated using other modified techniques noted in Reference 5.

Control of landfill gas emissions is more difficult than control of leachate because prediction of the migration route for landfill gas is more complicated and difficult than for leachate. At present, landfill gas is generally vented directly to the atmosphere. This practice may cause significant adverse effects on air quality. Unless the quantity and composition of gaseous emissions are known to be insignificant, gas collection and control systems should be installed to prevent hazardous air emissions.[5]

To determine if gas collection and control systems will operate efficiently, one should first investigate whether the gas migration is primarily a pressure or diffusion problem. If the predominant mechanism is pressure flow, one would normally choose a passive venting system with adequate control to remove the pressure gradient, assuming the landfill cover is relatively impermeable. On the other hand, if the primary gas migration process is a diffusion flow, a passive venting system would probably not be effective and the gas will eventually escape from landfill cracks unless a forced venting system is installed to maintain a slightly negative pressure within the landfill.[5]

A practical and effective control of gas generation and emission for new landfills is pretreatment of the wastes. The usual objectives of pretreatment are to destroy, recover, or convert hazardous components of the wastes into forms suitable for reuse, or innocuous forms that are acceptable for land disposal. Gas generation can also be reduced by eliminating all volatile organic wastes and liquids from landfills; keeping waste liquids from entering and leaving landfills would eventually minimize gas generation and gas emissions. This can be accomplished by using liners that may be concrete, asphalt, certain plastics, or a mixture of natural soil and sodium bentonite. Sodium bentonite swells more than ten times its original size when it comes into contact with water. When combined with natural soil, it creates an impermeable layer.[5]

As a remedial action at existing landfills, the use of covering materials, known as "capping", can be a fair control method for the temporary solution of a problem that needs immediate action. An example of such remedial action was the Caputo disposal site located near South Glens Falls, N.Y.

The Caputo land disposal site was an open dump, which was used until 1968 to receive PCB wastes from two electrical capacitor plants. The in place wastes were estimated to contain about 5000 ppm of PCBs as Arochlor® 1242 in soil. Ambient air sampling for PCBs was begun in November 1977. Tenax adsorbtion tubes were used for sampling, for 24-hr cycles. The maximum ambient concentration of PCBs was 5.9 $\mu g/m^3$ in November 1977, 300 $\mu g/m^3$ in August 1978, and 540 $\mu g/m^3$ in April 1979. After covering with layers of 6 in. of manure, 12 in. of paper mill sludges, and 2 in. of topsoil beginning in May 1979, the ambient concentration of PCBs was greatly reduced to less than 1.0 $\mu g/m^3$ in June 1979.[9] Reference 9 also gives a complete set of diffusion calculations illustrating the estimation of potential PCB air emissions from this PCB waste disposal site.

The proper design and operation of landfills may minimize PCB emissions to the envi-

MONS 006246

ronment now, but can never eliminate them in the future. Predictive diffusion calculations indicate that even properly controlled PCB waste landfills will have trace PCB air emissions which can continue for thousands of years.

To illustrate these points, the New York State Department of Environmental Conservation staff approximated PCB air emissions from an open dump, a covered dump site, and a cement kiln burning PCBs which are summarized as follows:[10]

Example 1: Assume 1 million gal of 500 ppm PCB wastes are stored in a 40 × 40 m open dump site at a depth of 5 m. PCB evaporation rate is 580 g/year for 4568 years.

Example 2: If the Example 1 PCB dump site is covered with 10 cm of topsoil the PCB emission rate is reduced to 25.2 g/year for 100,000 years.

Example 3: If the 1 million gal of 500 ppm PCB wastes are burned in a cement kiln at a minimum level of 99.999% PCB destruction for 1 year, the resultant one time PCB emissions would be 26.3 g/year. In reality this PCB emission value may be much lower, since 99.9999% + PCB destruction in cement kilns has been proven (see further references in cement kiln section of this chapter).

Consequently, landfilling PCB wastes should only be used as a last resort for PCB articles that cannot be effectively degreased, dechlorinated, or destroyed permanently by high temperature incineration methods.

II. NONTHERMAL METHODS FOR PCB DISPOSAL

Section 761.10 of the U.S. EPA TSCA PCB regulations,[8] the requirements of which are summarized in Tables 5[31] and 6,[32] require that the disposal of PCBs and PCB items must be accomplished in Annex I incinerators, except where Annex II chemical waste landfills or high efficiency boilers can be used for disposal, such as in the case of mineral oil dielectric fluids for PCB contaminated transformers containing 50 to 500 ppm PCBs, and for liquids other than dielectric oil fluids also containing up to 500 ppm PCBs.

Section 761.10(e) provides for alternate disposal methods for PCBs or PCB items that must be incinerated. The basis for technically evaluating an alternate, nonthermal, method for PCB disposal is at the moment relative to the equivalency of thermal disposal methods.

Any person who is required to incinerate any PCBs or PCB items under the U.S. EPA TSCA regulations and who can demonstrate that an alternative method for destroying PCB and PCB items exists, and that such an alternative method can achieve a level of performance equivalent to Annex I incinerators, or high efficiency boilers, as provided in Section 761.10 may submit a written request to the regional U.S. EPA administrator for an exemption to the incineration requirements for Annex I. The applicant must show that his method of destroying PCBs will not present an unreasonable risk of injury to health or the environment. On the basis of such information and any other available information, the regional administrator may, at his discretion, approve the use of an alternate method if he finds that the alternate disposal method provides PCB destruction equivalent to disposal in an Annex I incinerator, and will not present an unreasonable risk of injury to health or the environment. Any approval must be stated in writing, and may contain such conditions and provisions as the regional administrator deems appropriate. The persons to whom such waiver is issued must comply to all limitations contained in such determinations.[8]

The primary basis for evaluating an alternative method for PCB disposal is its relative performance compared to thermal methods. However, the TSCA regulations allow certain flexibilities. For example, the PCB regulation uses the term "destruction efficiency" as a measure of the difference of the amount of PCBs fed to a combustion system and the amount emitted into the air. This definition is relevant to the evaluation of boilers and incinerators

MONS 006247

but is irrelevant to the evaluation of a chemical process which has no air emissions. Thus, the regional administrator must be able to evaluate whether an alternative PCB disposal process system provides PCB destruction equivalent to Annex I incineration, and whether the alternative will not present an unreasonable risk to injury, health, or the environment before he grants a waiver request and issues an approval for a nonthermal PCB waste disposal process.

There are several commercial processes in current use that are capable of dechlorinating PCBs, breaking down PCB molecules into two primary components, biphenyl and chlorine. Examples of these processes are the Sun Ohio PCBX Process™ and Acurex* process.

A. The Sun Ohio PCBX Process™[12]

Sun Ohio has developed a PCB waste disposal process to break down PCB wastes into two primary components, biphenyl derivatives and chlorides. Chlorine atoms in PCBs are converted to naturally occurring chlorides. The biphenyl molecule is converted to polymeric solids. As the chemical reactions occur, the biphenyl nuclei polymerizes and chlorine is removed from PCB wastes. The PCBX Process is a Sun Ohio trademark. A full scale stationary model is now completed as well as an operational mobile unit which is designed to perform the following functions:

1. It treats transformal oil by filtering it, removing moisture, acids, and other contaminants.
2. It removes and destroys all PCBs contained in the transformer oil but not the oil itself.
3. It destroys pure PCBs.

The equipment needed to process the PCB oil is contained in a large tractor-trailer. It is self-contained and can either generate its own power or be hooked up to an external electrical power source.

The initial mobile processing unit was designed to handle about 1.9 thousand gal/hr of transformer oils containing up to 1000 ppm of PCBs. The general process description is as follows (see Figure 2):[12]

1. A gas chromatograph analysis is run to determine PCB content.
2. The contaminated oils are passed through a conventional facility to remove moisture and contaminants.
3. A vacuum degasser elevates the temperature of the oil. Oil is passed through the entire apparatus and reagent is added at a rate that is consistent with the flow rate of the oil and the PCB content.
4. The oil is heated to reaction temperature and goes through the mixing chamber where the reagent is thoroughly kneaded and mixed. The reagent is proprietary.
5. The oil then enters the reaction vessel. After leaving the reaction vessel, it goes through a heat exchanger and exchanges heat with the oil that will enter the vacuum degasser. This cools the PCB oil to the correct temperature. It next goes through two stages of filtration. Next it becomes the counterflow in the first heat exchanger. After the vacuum degassing step, it is returned to the transformer or held in the retention tank.

The degradation of pure PCB is similar to the above process. A quantity of oil is retained in the retention tank and continued to be recycled. Pure PCBs can be destroyed at an approximate rate of 19 ℓ/hr.

Overall the process depends on the use of a commercially available reagent which abstracts chlorine atoms from the biphenyl nucleus. The specific chemical reactions are carried out

* This process was recently sold to SCA and may have a new name, not known at press time.

MONS 006248

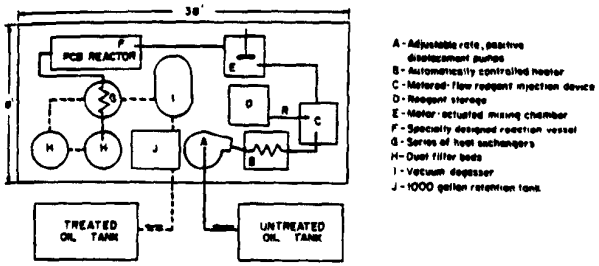


FIGURE 2. Schematic flow diagram for the Sun Ohio Mobile PCBX Unit.

under controlled conditions of process time, temperature, and reagent amounts. Selective filtrations remove any excess reagent and all the products. Transformer oils can be removed from fully charged transformers and after treatment, can be returned to the same transformer in minutes by this continuous flow process. The goal in developing this process was to remove all the PCBs from the fluids treated. Fluids used in laboratory studies contained from 100 to 10,000 ppm PCBs. The treated fluids contained 0 and 40 ppm PCBs, respectively, after one treatment.

Optimum reaction conditions have been established for the following primary variables:

1. The temperature is well below the flash point for hydrocarbon fluids.
2. Reaction times. A few minutes retention time is adequate to meet process requirements.
3. Reagents. Reagent amounts of about four times the theoretical amounts are optimum.

This process has also been applied to silicone oil. The PCBs were destroyed by the process and the silicone oil appeared to be unchanged. More testing is required to prove the reliability of the PCBX Process for application to all silicone fluids.[11]

The Sun Oil firm does not believe that the reaction products of the PCBX Process are objectionable from an environmental point of view. The chloride produced in the reaction is a naturally occurring chlorine type compound, being nontoxic. The polymeric solid is similar, but not identical, to polyphenyls that have been studied by many research groups, including the U.S. Air Force, NASA, etc. The firm has searched the literature for information pertaining to the toxicity of the solids, and to date has found nothing specifically adverse for these polymers. They claim that these materials are nonsoluble in water, transformer fluids, or other common solvents, and, therefore, should not migrate in the soil by means of ground water. Similar solubility characteristics have been confirmed by other investigators of polyphenyls. The firm also reports that the literature describes that both biphenyl and terphenyl compounds are biodegradable and infers that the polymeric reaction products of the PCBX Process will also be biodegradable and should not present a hazard to the environment.[12]

The PCBX Process has been approved by U.S. EPA Regions I, IV, VII, VIII, IX, and X for destroying PCB compounds in transformer oils. This process is capable of treating PCBs from any PCB concentration down to 2 ppm in transformer oils. The process transformer oils may be reclaimed to a normal condition and thus would be acceptable for transformer reuse.

The Tennessee Valley Authority (TVA) tested the Sun Ohio PCBX Process™ treatment

MONS 006249

unit in December 1981 at the TVA power service shops in Muscle Shoals, Ala.; 30,290 gal of transformer oils were processed. The untreated oils contained PCB concentrations ranging from 51 to 1100 ppm and had a great variety of dielectric properties. The treatment was carried out from the oil storage tanks and in the DM transformers. The decontaminated oil was evaluated to determine its suitability for reuse according to American Society for Testing and Materials (ASTM) and TVA criteria. The effectiveness of the PCBX Process was examined on the process of PCB concentrations and the following selected parameters: color, neutralization number, dielectric strength power factor, interfacial tension, water content, and oxidation stability index. TVA test results indicated that the PCBX Process effectively removed PCBs through concentrations of 2 ppm or less; in addition only two of the treated oil quality parameters, interfacial tension and color, exhibited a statistical improvement from the untreated state.[12]

During the test of the PCBX Process ambient air quality was monitored and found not to be hazardous to public health and the PCBX Process had negligible air emissions.

The TVA staff compared the economics of treating transformer oils by the PCBX Process to incinerating PCBs at the Energy Systems Co. (ENSCO), El Dorado, Ark. They found that the unit cost for each gallon of oil treated based on 30,290 gal treated, was $6.44/gal. The total cost for incineration by comparison was $6.03/gal. Consequently, the total cost for oil treatment by the Sun Ohio PCBX Process™ and incineration by the ENSCO incinerator appeared to be comparable. However, if the decontaminated oil processed by the Sun Ohio PCBX Process™ is reused, then the economics of the PCBX Process become more favorable because new oil costs $1.06/gal. Consequently, reusing transformer oils processed by the PCBX Process in this example can result in an additional saving of $36,000. On the contrary, if the decontaminated oil cannot be reused, the oil must be sent for disposal by incineration and the PCBX Process would be more expensive. In this case, although the process oils did not meet all the ASTM recommended standards for new oils, the processed oils did comply with the TVA classifications for reconditioned oils (category A). One can assume, if reused, that reprocessed transformer oils have a normal service life of 15 to 20 years.[13]

B. Acurex Waste Technologies Inc. (AWT) PCB Destruction Process

The AWT PCB destruction process is a mobile unit that chemically detoxifies PCBs. The unit includes five process vessels, a laboratory, and the necessary controls mounted on a 35-ft long flat bed trailer. Figures 3 and 4 describe the process equipment and its chemical process flow configurations. PCB treatment is carried out in a batch process, where contaminated oil enters the surge tank for batch sizing at 250 gal. A 250-gal batch of PCB laden oil is then pumped to one of the parallel reactor tanks through a filter that traps any excess water. Once the oil is in the reactor tank, the proper amount of sodium reagent is added and the mixer is turned on. After 30 min a sample of the oil is taken from the reactor and analyzed for PCBs using standard gas chromatography methods. If the PCB level is not below 2 ppm the reaction is allowed to continue. If the level is below 2 ppm the oil is transferred to the quench tank where water is added to destroy excess reagent in the oil. After quenching the oil is pumped to a final coalescing filter to remove aqueous solutions. The PCB-free oil is pumped to receiving tanks or drums. Table 7 indicates typical operating conditions of the AWT PCB waste destruction process.[14]

1. AWT Process Chemistry[14]

a. PCB Dechlorination

PCB is a molecule consisting of two attached aromatic rings and a varying amount of chlorine substitutions. In this state, the molecule is extremely stable and will remain in the environment for very long periods. PCB is known to concentrate in body tissue and can cause serious illness and organ disorders. A typical PCB molecule may look like this:

MONS 006250

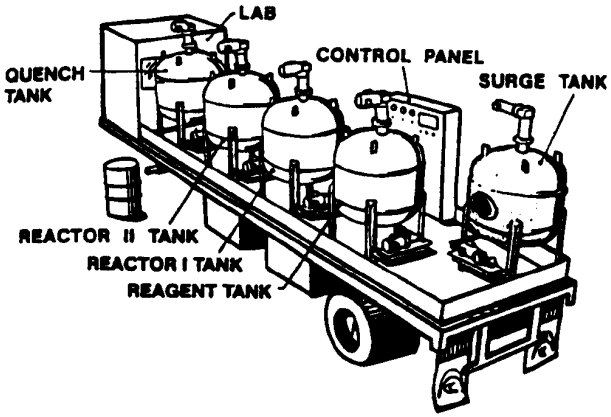


FIGURE 3. AWT PCB process mobile unit.

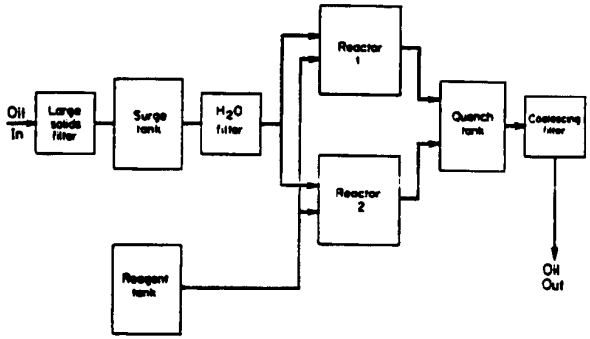
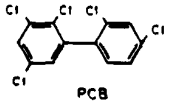


FIGURE 4. Flow diagram of the AWT PCB process.

MONS 006251

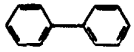
Table 7
TYPICAL OPERATING CONDITIONS OF AWT PCB WASTE DESTRUCTION PROCESS

Batch size	250 gal
Processing rate	250 gal/hr
Pumping rate	7 gal/min
Temp in	Ambient
Temp out	Ambient + 5°C (from quenching)
Vessel nitrogen pressures	6-in. H_2O
Reagent to PCB ratio	10:1 to 100:1 (Na:PCB)
Reagent conc.	0.75 to 2.0 *M* Na
Quench water to Na ratio	1.1:1 to 1.5:1
Reaction time (e.g., 1000 to 2 ppm)	20 min
PCB gas chromatograph analysis	Carrier gas — 10% methane, 90% argon at 30 ml/min Deflector temp — 300°C Oven temp — 200°C Injection body temp — 300°C Sample — 10 µl



PCB

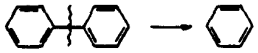
Incineration methods aim at completely destroying the total molecule, breaking it down to noncyclic by-products of combustion. To detoxify it, however, it is only necessary to completely dechlorinate the PCB molecule. The AWT sodium-based process does just that. The chlorine molecules are removed leaving the cyclic compound intact, thus:


Biphenyl

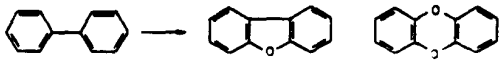
At this point, PCB health hazards are nonexistent.

1. Side Reactions

It is important that the dechlorination reaction be controlled so as to not form any unwanted by-products. Two possibilities exist for which the AWT process has controls. First, the biphenyl molecule above could be cleaved to form benzene and other similar derivatives:


Biphenyl Benzene

The second possible side reaction involves breaking the cyclic chain and forming an oxidation product such as furans or dioxins:



Styrene Dibenzofuran Dibenzodioxin

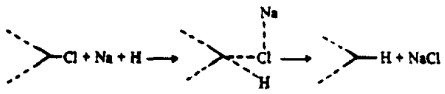
MONS 006252

These by-products and their derivations have their own associated hazards, and are therefore undesirable.

These two side reactions require excess energy to proceed. To break the biphenyl bond heat must be added. The AWT process avoids this by performing all dechlorination steps at ambient temperature. To form an oxygen by-product, oxygen must be present in the reaction vessel. The AWT process proceeds under a positive inert nitrogen atmosphere. Thus, none of these unwanted by-products can form.

ii. Reagent and Chemistry

The reactive agent in the AWT process is sodium. The sodium "displaces" the chlorine atom and allows a hydrogen atom to take its place. The sodium by-product is sodium chloride, salt:



PCB Sodium Intermediate (schematically) Biphenyl Salt

The sodium is mixed in a solution of tetrahydrofuran and a proton donor agent to form the reagent. This reagent is the vehicle whereby the sodium comes in contact with the PCB molecule in the oil.

Excess sodium is used to ensure complete PCB destruction. After the reaction, water "quenches" the remaining sodium forming sodium hydroxide:

$$Na + H_2O \longrightarrow NaOH + H_2$$

Sodium Water Sodium hydroxide Hydrogen

The small amount of hydrogen that forms is displaced by the positive nitrogen pressure on the quench tank. The sodium hydroxide and sodium chloride solution are filtered from the oil in the final filter step.

iii. Process Tests and Analyses

Tests and analyses have confirmed the process chemistry and PCB destruction. During an EPA-observed test of the AWT unit, samples were taken before, during, and after processing of the PCB-laden oil.

Overall, the results show that:

- PCB was completely destroyed.
- No harmful by-products are formed.
- Essentially no emissions are emitted.

iv. Mass Balance and Stoichiometry

The basic PCB destruction chemistry requires one sodium atom for each chlorine atom displaced. To positively ensure complete destruction, AWT uses adequate excess sodium. The sodium reagent is made up at 0.75 to 2.0 *M* with tetrahydrofuran and a small amount of another proprietary chemical. The excess sodium is quenched with water using 110 to

Table 8
AWT PCB PROCESS MASS BALANCE

Substance	Mol wt	g/cm³	Contaminated oil mol/ℓ	g/ℓ	lb/gal
Chlorine	35.45	—	6.85×10^{-3}	0.24	2.0×10^{-3}
Sodium	23.00	0.97	3.43×10^{-3}	7.9	6.6×10^{-2}
Tetrahydrofuran	72.1	0.889	—	113.8[d]	0.95
Transformer oil	—	0.83 to 0.91[c]	—	900	7.5

[a] Based on contaminated oil at 500 ppm PCB containing 54% Cl (w/w)..
[b] Based on 50:1 ratio of sodium to chlorine (w/w).
[c] Average 0.9 g/cm³.
[d] Based on 14.4:1 ratio of THF to sodium (w/w).

Table 9
AWT PROCESS TEST RESULTS

	Run 1	Run 2	Composite
Initial PCB conc., ppm	425	989	To be supplied
Initial TCDD[a] conc., ppt			
Final PCB conc., ppm	<1	<1	
Final TCDD conc., ppt			20
Final TCDF[b] conc., ppt			0
Final THF conc., %			2
Final Na conc., ppm			120
Final Cl ppm			<6
Final filter residue[c] PCB conc., ppm			Not detectable
PCB emissions[d], mg/kg			0.0091
Process temp increase[e]	<5°C	<5°C	

[a] TCDD — tetrachlorodibenzodioxin.
[b] TCDF — tetrachlorodibenzofuran.
[c] Only detectable component 100 ppm biphenyl by GC/MS.
[d] Incinerator standard is 1 mg/kg.
[e] Temperature increase after PCB destruction step; results from H_2O addition.

150% stoichiometric quantities. A complete mass balance of the process is shown in Table 8. The AWT process test results are shown in Table 9.[14]

v. Sampling and Analysis

The method and schedule of AWT sampling an analysis ensures that initial PCB concentration is known, and thus, proper amounts of reagent can be added. Final PCB concentration is shown to be less than 2 ppm before transfer out of the system.

The standard operating procedure includes a pretreatment site inspection. At this time, samples of the client's PCB-laden oil are taken and sent to the analytical laboratory of AWT for analysis. The samples are checked for PCB and suspect samples are further checked for competing contaminants. On-site, each batch of oil processed is analyzed before being

MONS 006254

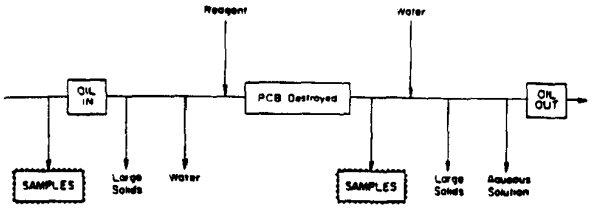


FIGURE 5. Process line flow diagram of the AWT process.

transferred out of the reactor tank. Only after complete PCB destruction is shown is the oil pumped from the reactor tank. Figure 5 shows a line flow diagram including analysis points in the process.

On September 9, 1981, AWT demonstrated its mobile PCB destruction process for the U.S. EPA, the Ohio EPA, and other interested observers. The demonstration was conducted at the Cincinnati Gas and Electric Company's facility in Hamlet, Oh.; two runs were conducted. In the first test, 200 gal of waste transformer oil containing 440 ppm PCB content was treated; in the second test, 100 gal of waste transformer oil containing 1062 ppm PCBs were treated. In both cases the PCB was destroyed to below the level of detectability (1 to 2 ppm) within 30 min. Other analytical results were equally negative indicating that the AWT PCB destruction process is both effective and environmentally safe. During these tests, a fluorisil tube which is a standard PCB sampling tube, used as part of the PCB sampling train, was attached to the gas vent from the reactor. The complete gas emission stream from the reactor was put through the tube; the test tube was analyzed for PCBs by Battelle Columbus Laboratories. No PCBs were found in the emissions.[13] At the current time the AWT process has been approved in U.S. EPA Regions I, VII, and VIII, with approvals pending in other U.S. EPA regions.

III. HIGH TEMPERATURE PCB INCINERATION

A. Summary of U.S. EPA Toxic Substance Control Act (TSCA) Regulation Requirements and Guidelines

The U.S. EPA Toxic Substances Control Act provisions (see Tables 5 and 6) for controlling the disposal of PCBs and PCB items are given in Sub-part B, Section 761.10 of the U.S. EPA TSCA regulations.[4] Mineral oil dielectric fluids containing PCB wastes and having PCB concentrations of between 50 and 500 ppm must be disposed of by either: (1) an incinerator that complies with Annex I, Section 761.40 requirements; (2) chemical waste landfills that comply with Annex II, Section 761.41 requirements; (3) a high efficiency boiler.

PCB articles such as transformers must be disposed of either in an incinerator that complies with Annex I requirements or in a chemical waste landfill which complies with Annex II provisions, providing that the transformer is first drained of all free-flowing liquid and flushed with a solvent to minimize PCB contamination.

PCB containers unless decontaminated in compliance with Annex IV provisions shall be disposed of either in an incinerator which complies with Annex I requirements or in a chemical waste landfill that complies with Annex II provisions also requiring that PCB containers shall first be drained and PCB liquids disposed of by U.S. EPA approved incineration or equivalent disposal methods.

MONS 006255

Table 10
INCINERATION SYSTEM SUMMARY FOR PCB WASTES

Type	Applicability	Reasons
Rotary kiln	Liquids — yes Solids — yes	Good system for PCB items; requires an afterburner
Liquid injection	Liquids — yes Solids — no	Best system for liquid PCBs; may be used as afterburner following a solids incinerator
Multiple hearth	Liquids — yes Solids — yes	Design is suitable, but may require operation at higher temperatures than currently used; afterburner required; scrubber may be required
Fluidized bed	Liquids — potential Solids — no	Future consideration warranted for liquids; hard to remove shredded noncombustibles; temperatures probably too low
Multiple chamber	Liquids — yes Solids — no	Liquids may be suitable if liquid burner is installed above grates; insufficient air/solid mixing
Catalytic combustion	Liquids — no Solids — no	Primarily designed for gases and vapors
Pyrolysis	Liquids — no Solids — no	High probability of forming toxic combustion products
Starved air combustion	Liquids — no Solids — no	High probability of forming toxic combustion products
Molten salt	Liquids — potential Solids — no	Future consideration warranted for liquids; proven commercial PCB removal technology; temperatures probably too low; hard to remove shredded noncombustibles
Cement kiln	Liquids — yes Solids — no	Best system 99.999990% PCB destruction proven

There are several types of process systems capable of destroying PCBs such as various high temperature incinerators and cement kilns. Table 10 presents a summary of various incineration methods and comments on their applicability for destroying PCB liquid and solid wastes.

As noted previously in discussion of nonthermal PCB waste destruction processes, U.S. EPA allows the demonstration of alternate methods of destroying PCBs and PCB items providing that such an alternate method can achieve a level of performance equivalent to Annex I incinerators or high efficiency boilers.

Annex I: PCB incineration requirements — The combustion criteria for basic compliance with the provisions of Section 761.40 of the TSCA regulations[4] are (1) maintenance of the introduced liquids for a 2-sec dwell time at 1200°C (± 100°C) at 3% excess oxygen in the stack gas or (2) maintenance of the introduced liquids for a $1^1/_2$-sec dwell time at 1600°C (± 100°C) at 2% excess oxygen in the stack gas. (3) Combustion efficiency shall be at least 99.9% computed by: combustion efficiency = $CO_2/CO_2 + CO \times 100$.

The owner and operator must monitor the rate and quantity of PCBs fed to the combustion system at regular intervals no longer than 15 min as well as monitoring temperatures of the incineration process continuously by either direct pyrometer or indirect wall thermocouple-pyrometer temperature readings. The U.S. EPA regulations require automatic control of the incinerator so that the flow of PCBs to the incinerator will stop automatically whenever the combustion temperature drops below temperatures specified.

As a minimum U.S. EPA requires monitoring for: (1) oxygen, (2) CO, (3) CO_2, (4) NO_x, (5) HCl, (6) total chlorinated organic compounds (RCl), (7) PCBs, (8) total particulate matter.

Monitoring for oxygen and CO shall be continuous and the monitoring for CO_2 in the exhaust gases shall be periodic as specified by the agency; additional monitoring and recording equipment is also required.

The requirements for incinerating nonliquid PCB waste are similar to those for thermal

MONS 006256

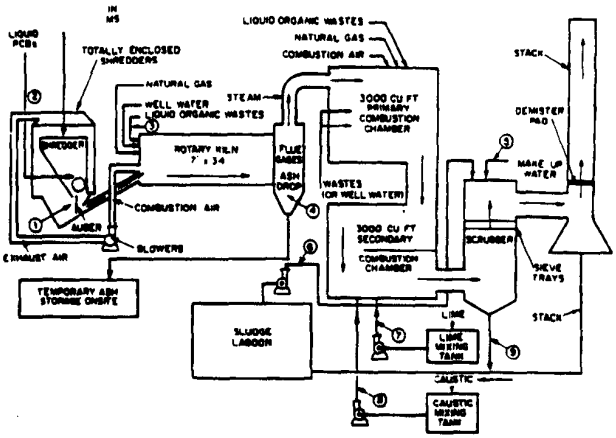


FIGURE 6. Process flowchart of ENSCO facilities.

destruction of PCB liquids: in addition the mass air emissions from such an incinerator burning such wastes shall be no greater than 0.001 PCB per kilogram of the PCB introduced in the incinerator (99.9999% destruction and removal efficiency).

The U.S. EPA PCB incineration requirements also require an extensive trial burn in order to demonstrate compliance with the Annex I incineration requirements of this regulation. Those desiring further complete details of U.S. EPAs TSCA PCB waste incineration technology requirements, especially administrative, environmental, technical, and monitoring provisions should specifically consult the "U.S. EPA Guidelines for the Disposal of PCBs and PCB Items by Thermal Destruction".[16]

B. Energy Systems Company (ENSCO) El Dorado, Arkansas[17,18]

ENSCO submitted an application for the incineration of PCB waste to U.S. EPA Region VI on March 8, 1978. The first PCB trial burns were conducted at ENSCO in October 1979. Test results revealed the possibility that very low levels of two toxic organic compounds, tetradibenzo-*p*-dioxin and tetradibenzo-*p*-furan were present in the samples. In order to evaluate if dioxins and furans were being emitted from the stack in significant quantities additional tests were conducted at ENSCO in August 1980. The PCB waste destruction tests carried out at ENSCO in El Dorado, Ark. were the first commercial attempts to destroy PCBs in accordance with the U.S. EPA regulation 40 CFR Part 761[4] *process description.* ENSCOs hazardous waste incineration system is shown in Figure 6. The shredder structure houses two hammermills that operate in series. The primary hammermill shreds smaller electronic capacitors which then drop into the secondary hammermill and are reduced to $^1/_2$-in. square pieces, referred to as "fluff". These capacitors are contained in weighed 55-gal drums. The contents of these drums are manually dumped into the primary shredder. The capacitors only contain about 31 ± 5% oil, having about 80% by weight of Arochlor® 1016. The average feed rate of capacitors for the three PCB tests was 980 lb/hr. PCBs

MONS 006257

accounted for 243 lb/hr of this total amount. No large electrical utility capacitors were incinerated during this trial burn. Liquid PCBs containing about 80% by weight of Arochlor® 1016 are gravity fed to the hopper under the secondary hammermill where they mix with the fluff and adsorb onto the fluff which is then transported to the rotary kiln; the average feed rate during this trial burn of this material is 486 lb/hr. The hoppers of the hammermills are maintained under slight negative pressure to prevent the release of PCBs into the ambient air during the shredding operation; this exhaust air is used as combustion air for the rotary kiln.

The rotary kiln is 34 ft long and has an internal diameter of 7 ft. The kiln is refactory lined and rotates at about 0.5 rpm which results in a retention time of approximately 60 min for solids and about 3.7 sec for gaseous material. There are lifters protruding from the refractory to ensure that the solid material is turned over as it passes through the kiln. The temperature inside the kiln at the front end is measured by a thermocouple, temperatures of 1200 to 1500°F were maintained in the front section during this test. Liquid organic wastes such as chlorinated aliphatic hydrocarbons, well water, and natural gas are also injected into the front of the rotary kiln. About 75% of the total natural gas is consumed in the rotary kiln to ignite the waste material being fired; the remaining 25% of the natural gas is used in the primary combustion chamber through two burners. About 10% of the total organic liquid waste, averaging 590 gal/hr was injected into the rotary kiln, compared with 90% burned in the primary combustion chamber. A drag train is used to remove the ash remaining in the kiln after destruction of all the combustible matter.

The gases leaving the rotary kiln are injected with steam and fed into the primary combustion chamber of the afterburner; this refractory-lined chamber is approximately 3000 ft^3 in volume, into which most of the liquid organic waste is fired; it has a residence time of approximately 2.19 sec. The temperature of this chamber is measured by a thermocouple in the crossover duct. The average temperatures in this section, measured during the tests were approximately 2300°F. The secondary combustion chamber is baffled to promote mixing of the combustion gases; temperatures measured in this chamber were approximately 1900°F during the tests. The retention time in this chamber is approximately 2.11 sec. Total retention time of both chambers and the crossover duct is approximately 4.53 sec.

Combustion gases leaving the secondary combustion chamber enter a refractory lined duct which provides additional residence time of about 0.18 sec to complete combustion of the gases. The gases are quenched as they enter the bottom of the venturi jet scrubber. The quench gases are drawn through two sets of sieve trays which are irrigated with recycled scrubber liquor, lime, and caustic solution to remove particulates and neutralize acid gases such as HCl and SO_2. This spent scrubber liquor falls to the bottom of the scrubber and drains into a tank which overflows to the sludge lagoon for recycling. The gases and fine particulates not removed by the sieve trays are passed through a venturi section of duct work into which recycled scrubber water is sprayed through a jet. Make-up well water is also injected to compensate for the loss of moisture of the stack.

Samples of these clean gases were extracted for analysis by continuous stack gas monitors for CO, O_2, and by Orsat for CO_2, to determine combustion efficiency. ENSCO has a electrolytic fuel cell type CO analyzer to measure the CO content of the gases. The set point for the CO monitor alarm is 50 ppm, and when combustion efficiency drops exceeding this CO value, the PCB feed to the rotary kiln would be shut off. The average CO value measured during these tests was less than 10 ppm, indicative of high combustion efficiency. Oxygen levels are also measured during the trial burns and averaged 13.4%.

The gases leaving the scrubber pass through a demister pad to remove entrained water droplets, and travel up the stack discharging to the atmosphere. The stack is equipped with a drain to collect the condensate which eventually returns to the lagoon. There were problems with the mesh demister pad during these tests and an improved demister pad was later installed in the system.

MONS 006258

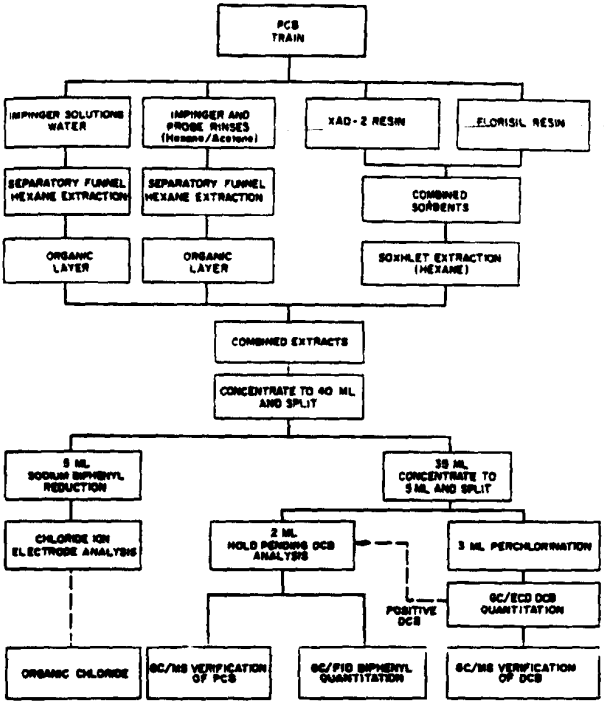


FIGURE 7. Analytical scheme of PCB stack gas sampling train. ENSCO & Rollins PCB trial burn.

Figure 7 shows the analytical scheme for the PCB stack gas sampling train using the modified U.S. EPA method 5 sampling train for the ENSCO PCB trial test burn. The sampling train incorporated two resin cartridges to adsorb the organic vapors; the resin cartridges contained XAD-2 resin and Florisil resin. The sampling train is shown in Figure 8. The stack gases were sampled isokinetically for a period of 4 hr. At the completion of each sampling period the stack samples were transported to the laboratory for analysis. Stack samples were extracted with an appropriate solvent, and analyzed using capillary column gas chromatography and high resolution mass spectrometry. The results of the ENSCO El Dorado, Ark. PCB trial burns performed in October 1979 and August 1980 are shown in Table 11; as can be seen, these results indicate complete compliance with the U.S. EPA PCB incineration requirements.

From results of the first test showing the possible presence of dioxins and furans, EPA concluded that additional testing was necessary to determine if the operation of the incin-

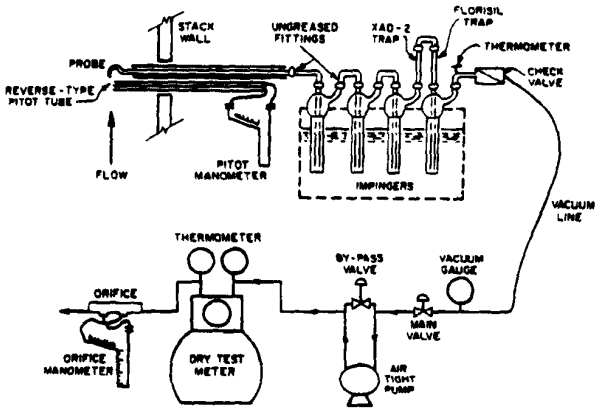


FIGURE 8. Stack sampling train of ENSCO & Rollins PCB trial burns.

Table 11
ENSCO, EL DORADO, ARKANSAS
RESULTS OF PCB TRIAL BURN

	October 1979	August 1980
PCB feed rate, lb/hr	636	722
Temp, °F (av.)	2,289	2,236
CO, ppm (maximum)	10	7
Excess O_2, % (minimum)	13.4	9.5
CO_2, %	5.5	8
Particulate, lb/hr	149	23
HCl removal efficiency, %	98.9	99.8
PCB destruction efficiency, %	99.9998	No PCB analysis
Combustion efficiency, %	99.98	99.99
Dioxin, ng/dscf*	Not analyzed	0.005
Furan, ng/dscf*	Not detected	0.060

Note: The detection limit for the 1979 furan results was 1000 times greater than the 1980 furan results.

* ng/dscf = nanogram per dry standard ft³.

eration operations would present an unreasonable risk of injury to health or the environment from PCBs. EPA reassed the incineration process in August 1980 and verified the existence of very low levels of dioxins and furans in the exit gas stream. EPA used the emissions data to predict ambient concentrations which then became the input for an upper limit of risk estimate. Special attention was given to the 2,3,7,8-TCDD dioxin isomer and its analogous furan compound 2,3,7,8-TCDF. A complete description of the computer dispersion modeling techniques used to predict ambient air concentrations from this facility and all the assumptions regarding risk elements and cancer risk projections are given in Reference 18.

MONS 006260

In evaluating the level of risk for the ENSCO facility many worst-case conservative assumptions which were made, such as, that the total amount of TCDD found had the same toxicity and carcinogenicity as the 2,3,7,8-TCDD isomer; a similar assumption was made for the TCDF materials. Other assumptions were made, such as that there would be a 70-year average exposure at 24 hr a day, 7 days a week which would never happen in reality. The study also assumed that the total population within the affected area would be exposed to the highest ambient TCDD and TCDF levels predicted by the dispersion model, which is not the case. The conclusion reached by EPAs carcinogen assessment group[17] was that the resulting individual risk for ENSCO was 3.9×10^{-7} which translates into less than one increased case of cancer in 2.5 million exposed persons. This risk assessment does not represent an estimate of the actual individual risk from operation of the hazardous waste incinerator but rather an estimate of the upper level of risk possible, including many worst-case assumptions which could not happen in reality.

C. PCB Trial Burn — Rollins, Deerpark, Texas[17,18]

Similar PCB trial burns were conducted at Rollins, Deerpark, Texas in November 1979 and 1980, similar to the previously mentioned test at the ENSCO facility. The Rollins incinerator complex consists of a rotary kiln and a modified liquid burner, both discharging into a common afterburner chamber. The flue gas from the afterburner goes to a venturi scrubber which operates on a dilute lime slurry and a bubble tray absorber where particulates and acidic gases are scrubbed with water. The scrubbed flue gas leaves through the stack. The combustion conditions for this rotary kiln were monitored using a continuous carbon monoxide infrared analyzer set to automatically shut off the PCB feed whenever the carbon monoxide concentration exceeded 80 ppm. Oxygen in the exhaust gases was also continuously measured during these tests and the automatic controls were set to automatically cut off the PCB feed whenever the oxygen concentrations dropped to below 3%.

The PCB fuel used for the three PCB tests was prepared by blending 25,700 kg of auxiliary fuel with 52,900 kg of PCB waste in a blend feed tank. During each test, grab samples were taken from the feed line every 15 min and composited by consecutive 2-hr periods. Each composite sample was analyzed for PCB concentration and other parameters. During all tests auxiliary fuel was fed to the kiln at an average rate of 840 kg/hr; the PCB fuel was fed at about 3000 kg/hr. While the tests were being made, no other fuels were fed to either the kiln or the liquid burner. Temperatures attainable in the Rollins Environmental Services' rotary kiln liquid injection burner and the common afterburner are normally 1300 to 1500°C, the overall retention time of the incineration system is 2 to 3 sec.[18] Various tests were performed in this hazardous waste incinerator using various process wastes, liquid chlorinated hydrocarbon wastes such as vinyl chloride, still bottoms, liquid PCB waste, and mixtures of liquid PCB wastes and clean fuel oil. A complete series of environmental tests were performed at this facility similar to those previously mentioned which were performed at the ENSCO facility. The Rollins Environmental Services, Deerpark, Texas PCB trial burn results are summarized in Table 12 which show excellent destruction of PCB waste in full compliance with the U.S. EPA 40 CFR 761 PCB incineration criteria for Annex I incinerators.[17]

Quantitative carcinogen risk assessments were also performed for the Rollins facility, similar to those previously described for the ENSCO facility;[18] the resulting individual cancer risk for Rollins is 1.8×10^{-5}. Again, these numbers do not represent an estimate of the actual individual risk from operation of the incinerator and are an estimate of the upper level of risk possible including many worst-case assumptions which could not happen in reality.

D. Case Study: Kommunekemi Hazardous Waste Incinerator, Nyborg, Denmark[19]

The Kommunekemi hazardous waste disposal center is a joint enterprise established by local authorities in Denmark to regionally dispose of waste oils and chemical wastes. This

MONS 006261

Table 12
ROLLINS ENVIRONMENTAL SERVICES, DEERPARK, TEXAS RESULTS OF PCB TRIAL BURN

	November 1979	August 1980
PCB feed rate, lb/hr	2,438	2,502
Temp. °F (av.)	2,161	2,147
CO, ppm (maximum)	11	38
Excess O_2, % (minimum)	8.9	9.8
CO_2, %	9	8.1
Particulates, lb/hr	39	24
HCl removal efficiency, %	98.4	99.9
PCB destruction efficiency, %	99.99999	No PCB analysis
Combustion efficiency, %	99.98	99.95
Dioxin, ng/dscf*	Not analyzed	0.018
Furan, ng/dscf*	Not detected	0.281

Note: The detection limit for the 1979 furan results was 1000 times greater than the 1980 furan results.

* ng/dscf = nanogram per dry standard ft³.

regional hazardous waste disposal center is located in an industrial area of Nyborg, Denmark and consists of two types of incinerators. The main incinerator I is a rotary kiln incinerator described in Figure 9 which is used to dispose of oil and solvent wastes, solid organic chemical waste, and medical wastes that are generally halogen free.

In 1978 the Swedish boiler association investigated the destruction efficiency of this rotary kiln incinerator which has a waste heat boiler to recover energy. The combustion efficiency was determined by measuring CO, CO_2, and oxygen at various points of a cross-sectional sampling area in the secondary combustion chamber. PCBs were added to the wastes that are fed into the rotary kiln in drums and the destruction efficiency for PCB was measured. Kommunekemi A/S also tested the combustion efficiency of the facility in September 1978. This rotary kiln incinerator is capable of meeting the U.S. EPA PCB incineration criteria of 1200°C and 2 sec residence time; however, we do not have the full technical details of this preliminary PCB waste destruction test, only a summary. The PCB test results for this facility indicate that 13.5 kg of PCBs were introduced into the rotary kiln with a destruction efficiency for PCBs of 99.996%, using the spiezon sampling method, where less than 16 mg/kg of PCB were found. Destruction efficiency (99.999%) was determined, and less than 9 mg/kg of PCB were found using a freezeout sampling method. In certain cases high temperature incineration can achieve 99.9999% PCB destruction, which in some cases is difficult to prove in terms of sample collection and limits of analytical methods. The overall combustion efficiency based on CO_2 and CO measurements was 99.96% during the stack test.[19] A gas chromatograph with an electron capture detector was used for the determination of PCBs in the samples.

These PCB test results performed at the Kommunekemi hazardous waste disposal incinerator at Nyborg, Denmark, which is one of the most advanced hazardous waste disposal centers in the world, also verify that high temperature rotary kiln incinerators can adequately destroy PCB laden wastes.

E. Case Study: General Electric Co., Pittsfield, Massachusetts[20]

A high temperature chemical waste incinerator, or thermal oxidizer is located at General Electric Co., Pittsfield, Mass., in the heart of the beautiful Berkshire Hills. Since the early 1970s, GE-Pittsfield has recognized that incineration of liquid PCB wastes (such as those

MONS 006262

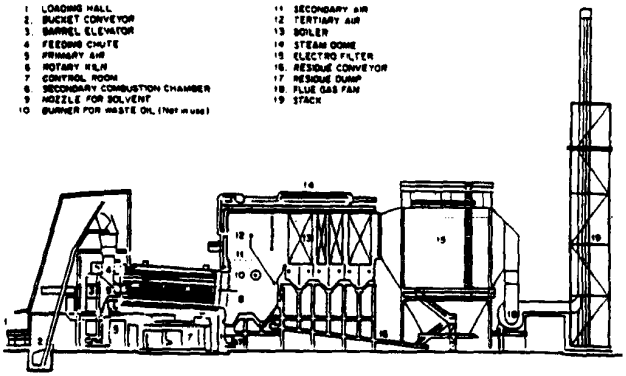


FIGURE 9. Incinerator I.

resulting from its own transformer operations) is the most environmentally sound method of PCB disposal. In 1972, therefore, GE purchased a liquid-waste incinerator from the John Zink Co. which was specifically designed to incinerate PCBs. GE subsequently modified the incinerator and added additional monitors and fail-safe systems to make the oxidizer one of the safest and most successful devices of its kind in the world.

1. Description of Thermal Oxidizer

Unlike most PCB waste incinerators which use forced draft combustion, GEs thermal oxidizer utilizes an induced draft system for the control of combustion gases within the unit. PCB-contaminated liquid enters the oxidizer through either one or two burner guns into the burner section. The liquid is atomized by steam and is mixed with combustion air that is supplied by a 40-hp forced-draft fan. Secondary air, if required, is directed downstream in the primary combustion chamber. The mixture of air to fuel is controlled by a split-range proportional controller.

The outer shell of the oxidizer is composed of welded steel plate. Inside the steel shell, the refractory consists of a combination of high-alumina firebrick and castable materials, varying in thickness from 7 to 8 in. (18 to 20 cm). Gases are conducted through the afterburn section and a refractory-lined water spray quench section by a Hastelloy-C induced draft fan. The oxidizer itself is maintained at slightly below atmospheric pressure to prevent the loss of hot corrosive gases to the environment in the event of an opening of the unit (to change burners, for example).

The final portion of the thermal oxidizer system is a vertical countercurrent gas scrubber. Quenched combustion gases are forced upward through 12 (3.7 m) of polypropylene saddle packing. As the gases flow upward, a solution of approximately 10% sodium or potassium hydroxide is sprayed over the packing section at a rate controlled by a proportional pH controller. The discharge from this system is continuously monitored for PCB loading and other parameters in accordance with conditions issued to GE-Pittsfield by the federal government.

While incinerating PCB wastes, the oxidizer is continuously monitored for over 15 con-

MONS 006263

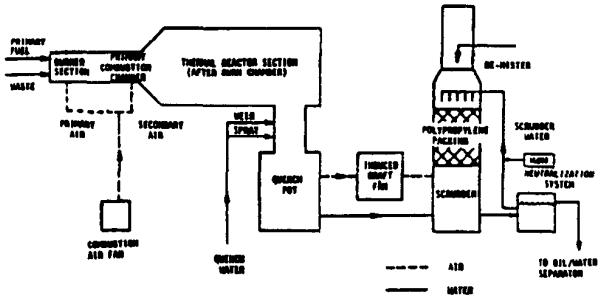


FIGURE 10. Thermal oxidizer schematic. General Electric Co., Pittsfield, Mass.

ditions and parameters. Any violation of predetermined operating conditions or federal government incineration regulations automatically shuts the oxidizer down immediately, with complete safety. Figure 10 shows the configuration of this process incinerator.

2. Thermal Oxidizer Operating History

Since the oxidizer was made operational in 1973, it has logged thousands of hours and burned tens of millions of kilograms of a variety of liquid wastes. Such wastes have included aromatic and aliphatic solvents from GE-Pittsfield's plastics business operations, hydrocarbon wastes from its ordinance systems, and PCB and non-PCB wastes from its power transformer department on-site. As it gained experience with the unit, GE began to diversify its list of candidate wastes, accepting materials for contract incineration from across the entire U.S. GE also gained confidence in its ability to operate the oxidizer safely, even if the unit was left completely unattended.

PCB incineration operations continued until July 2, 1979, when federal regulations governing the incineration of PCB-contaminated materials took effect. Non-PCB materials were incinerated until a thorough study of the oxidizer leading to federal PCB incineration approval was accomplished. PCB incineration operations were approved in 1980 and resumed in 1981, and continue today to incinerate millions of kilograms of PCB wastes for GE, government agencies, and anyone else with a liquid PCB waste problem.

3. Research on the Oxidizer

The unique balanced-draft system which keeps the oxidizer below atmospheric pressure not only provides safety for GE operators and the general public, but also permits the safe and successful testing of the unit. Such research was begun by the U.S. EPA and GE in 1974, when an experimental mixture of pesticides (DDT) and PCBs was burned and results qualified in a nationally recognized report by EPA officials. Subsequently, in April 1979, GE prepared a unique program to meet impending federal PCB disposal regulations. The program was conducted in two phases. First, in late 1979, an experiment was performed which served to demonstrate that the oxidizer could meet EPA regulations and combustion criteria. Temperature and combustion gas measurements were made at various points within the incinerator, that enable GE to predict operational results within extremely close tolerances (5% or less) with great confidence. Additional automatic shutdown and purge controls were added in 1981 and the flue gas monitoring system was tested using EPA procedures for response time and drift.

MONS 006264

Table 13
GENERAL ELECTRIC COMPANY PITTSFIELD, MASSACHUSETTS SUMMARY OF TRIAL BURN RESULTS[20]

Item	Trial burn results	Federal standard
Temp inside afterburn chamber	1,262—1,141°C (2,303—2,085°F)	1,200 ± 100°C (2,192 ± 180°F)
Residence (dwell) time of combustion products	4.01 sec	Minimum of 2.0 sec
Combustion efficiency	99.993%	Minimum of 99.9%
Oxygen conc. during PCB incineration	9.5—10.5%	Minimum of 3.0%
PCB conc. in oil	18.4—20.0%	
Av. PCB destruction and removal efficiency	99.999982%	
HCl scrubber efficiency	99.82%	
Particulate emissions @ 12% CO_2	0.543 lb/hr (0.0361 g/dscf)	
NO, emissions	18.3 ppm - 0.43 lb/hr)	
HCl emissions	0.000304 ppm (0.00002542 lb/hr)	
HCl emissions	0.2752 lb/hr	

Note: dscf = dry standard ft³.

Finally, in 1981, GE undertook a successful trial burn of PCBs in the oxidizer which met or surpassed all federal and state criteria for operation of the PCB incinerator. Table 12 shows GE-Pittsfield's trial burn results. Sophisticated tests of oxidizer discharges showed that over 99.99998% of the PCBs which were admitted to the incinerator were destroyed. Operating temperatures and gas residence times were determined within 5°F (3°C) and 0.1 sec, respectively. The temperature at the point where the gas residence time was 2.0 sec was 2225°F (1218°C). At the discharge point of combustion gases from the afterburn section, the average gas temperature during all tests was 2085°F (1141°C). GE calculation of average combustion gas residence time (using a method more conservative than recommended by trial burn guidelines) was 4.01 sec during the test period. Tests of the combustion gas stream showed that the flue gas was well-scrubbed of acid gases (with HCl over 99.8% removed), and was largely free of other types of pollutants. The levels of nitrogen oxides (18 ppm), carbon monoxide (6 ppm), and organic chlorides (0.000304 ppm) indicate the stable, thorough nature of the combustion within the oxidizer. Interestingly, over 83% of the organic chlorides found in the flue gas stream may be attributed to the generation of such materials during the sparging of natural substances from water used in quenching combustion gases.

The culmination of GEs research and development work was federal approval of its thermal oxidizer for the incineration of PCB. Table 13 shows a summary of these PCB waste destruction test results.

IV. BURNING LOW LEVEL PCB/MINERAL OIL WASTES IN HIGH EFFICIENCY BOILERS

A. Summary of the U.S. EPA TSCA Regulation Requirements

The U.S. EPA TSCA regulation requirements as they apply to burning PCBs in high efficiency boilers[9] requires that:

1. The boiler must be rated at a minimum of 50 million Btu/hr.
2. If the boiler uses natural gas or oil as the primary fuel, the carbon monoxide concentration in the stack must be 50 ppm or less, and the excess oxygen is at least 3% when PCBs are being burned.
3. The waste does not comprise more than 10% on a volume basis of the total fuel feed rate.
4. The waste fluid is not fed into the boiler unless the boiler is operating at its normal temperature. This prohibits feeding these waste PCB fluids during either start-up or shut-down operations.
5. The owner/operator of the boiler continuously monitors and records the carbon monoxide concentration and excess oxygen percentage in the stack gas while burning waste fluids.
6. The primary fuel feed rate, waste fluid feed rate, and total quantities of both primary fuel and waste fluids fed to the boiler are measured and recorded at regular intervals of no longer than 15 min while burning waste fluids.
7. The carbon monoxide concentration and the excess oxygen percentage are checked at least once every hour that waste fluid is burned; if either measurement falls below the levels specified in this rule the flow of waste to the boiler shall be stopped immediately.

In summary, the U.S. EPA TSCA combustion efficiency requirements are 50 ppm CO for oil firing and 100 ppm CO for coal, 3% excess O_2 for all PCB operations.

B. Case Study — General Motors Corp., Warren, Michigan[21]

In May 1980 waste oil contaminated with PCBs was burned in a high efficiency industrial boiler owned by the Chevrolet Motor Division of General Motors at Warren, Mich. In accordance with the U.S. EPA TSCA 40 CFR 761 regulations[6] the PCB burn was monitored by GCA Corp., U.S. EPA, the Michigan Department of Natural Resources, and by General Motors to ensure compliance with federal regulations and to document the PCB destruction efficiency of the test burn.

Measurements of PCB levels in the waste oil feed and in combustion exhaust gases were performed to establish PCB destruction efficiencies; combustion parameters (CO, O_2) were monitored to evaluate boiler performance to establish compliance with federal regulations governing the burn. PCBs were also sampled in ambient and in-plant air, and in the workers' bloodstreams, before, during, and after the test burn in order to evaluate all environmental and occupational health parameters. Stack tests were performed using EPA method 5 stack sampling techniques, modified to capture PCBs, with additional secondary sampling trains to capture organic compounds and chlorinated hydrocarbons, in order to assess hazardous combustion by-products. GCA, in conjunction with these tests, also operated four ambient air monitors, one upwind and three downwind, of this boiler to verify the presence or absence of significant PCB loadings in the ambient air during this PCB trial burn.

Three separate PCB tests were conducted with the boiler operating under normal load conditions. The normal boiler fuel, number 6 residual fuel oil, was cofired with 10% waste oil prepared to contain approximately 500 ppm PCBs; thus the PCB concentration in the fuel being burned was about 50 ppm.

The General Motors boiler used for this test burn was a Wickes type K 65-4K-7 package boiler with a 60,000 lb/hr steam generation capacity at 8 gal/min of number 6 fuel oil.[21] CO and O_2 were continuously monitored as per the previously noted EPA regulations. Provision was made for shutting down the supply of waste fuel to the boiler unless the following criteria were met: flame temperature normal, at approximately 2500°F; CO concentration less than 50 ppm; and excess O_2 greater than 3%. An additional requirement for this test was steady state operation with 4 gal/min fuel feed rate being maintained. Figure

MONS 006266

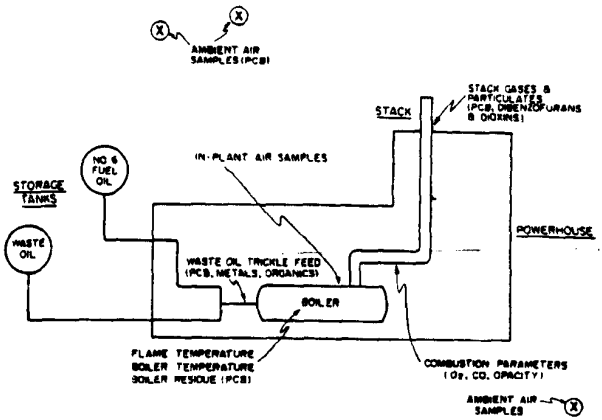


FIGURE 11. Schematic diagram of General Motors high efficiency boiler PCB trial burn.

Table 14
DESTRUCTION EFFICIENCY OF PCB GENERAL MOTORS BOILER TESTS

Run no.	PCB in fuel[a] conc. range (mg/kg)	PCB[a] in (mg/min)	PCB out (mg/min)	PCB[a] destruction efficiency (%)
PCB-2	34—72	480—1000	$<5.8 \times 10^{-1}$	≥99.99[d]
PCB-3	34—76	480—1100	$<5.6 \times 10^{-1}$	≥99.99[d]
PCB-4	34—75	480—1100	$<5.6 \times 10^{-1}$	≥99.99[d]

Note: Density of 1:10 dilution of waste oil: No. 6 fuel oil is 3.4 kg/gal.

[a] Based on GM and OCA reported results.
[b] Fuel combustion rate: 3.43 kg/gal × 4 gal/min fuel flow = 14 kg/min.
[c] Percent destruction = 100 [PCB in − PCB out/PCB in].
[d] This assumes 100% sample collection efficiency. A validated test of sample collection efficiency was not conducted as part of this verification burn.

11 gives a schematic view of the boiler plant layout and shows where samples were taken throughout this PCB test burn.

The results obtained during this worst case trial burn of PCBs indicated that greater than 99.99% destruction efficiency of PCBs was achieved. No PCBs were found in the stack exhaust gases within the detection limits of the instruments used.

Table 14 gives the destruction efficiency of PCBs as determined during the tests; Table 15 indicates the stack emission rate of PCBs which verify that there were no PCBs detected within the analytical range of sensitivity of these measurements.[11]

Tests for hazardous combustion by-products, for example, chlorinated dioxins and dibenzofurans were also performed using the modified U.S. EPA method 5 sampling train in

Table 15
STACK EMISSION RATE OF PCBs

Run no.	Test day	Gas vol. sampled (DSCM)[a]	Aroclor® 1242 detected (mg)[b]	Stack gas conc. of Aroclor® 1242 (mg/m)	Stack flow (DSCMM)[c]	PCB (mg/min)
PCB-1[d]	1	4.898	<0.001	$<2.0 \times 10^{-4}$	274	$<5.6 \times 10^{-2}$
PCB-2	2	5.380	<0.001	$<1.9 \times 10^{-4}$	307	$<5.8 \times 10^{-2}$
PCB-3	3	5.785	<0.001	$<1.7 \times 10^{-4}$	328	$<5.6 \times 10^{-2}$
PCB-4	3	5.964	<0.001	$<1.7 \times 10^{-4}$	346	$<5.6 \times 10^{-2}$
PCB-5	4	3.207	NA[e]	NA	264	—

[a] Dry standard m^3.
[b] Based on GC/ECD results (1.0 µg Aroclor® 1242/extract).
[c] Dry standard m^3/min.
[d] This was a run to measure background levels of PCBs in the stack gas. No PCB contaminated waste oil was burned during this run.
[e] NA — sample extract was inadvertently spilled during analysis sequence. This loss was not integral to calculating destruction efficiency with confidence because of redundant sampling.

Table 16
STACK EMISSIONS DATA FOR DIBENZOFURANS AND DIOXINS

Run no.	Test day	VMSTD (DSCM)	Weight in particulate extract (mg)	Conc. in particulate (mg/m³)[a]	Weight in resin extract (mg)	Conc. in resin extract (mg/m³)
MS-1[b]	1	4.808	$<1.0 \times 10^{-3}$	$<2.1 \times 10^{-4}$	$<8.8 \times 10^{-4}$	$<1.8 \times 10^{-4}$
MS-2	2	5.446	$<5.0 \times 10^{-4}$	$<9.2 \times 10^{-5}$	$<8.5 \times 10^{-4}$	$<1.6 \times 10^{-4}$
MS-3	4[c]	3.290	$<5.0 \times 10^{-3}$	$<1.5 \times 10^{-4}$	$<8.5 \times 10^{-4}$	$<2.6 \times 10^{-4}$

[a] MS-1 particulate is 50% aliquot. MS-2 and MS-3 are 100% aliquot.
[b] This was a run to measure background levels of dibenzofuran and dioxins in the stack gas. No PCB contaminated waste oil was burned during this run.
[c] No dibenzofuran or dioxin data were taken on day 3. On day 3 two trains were run simultaneously for PCB sampling to test reproducibility. Dioxin and dibenzofuran sampling was resumed on day 4.

order to collect such trace hazardous combustion by-products. Table 16 gives the stack emission data for dioxins and dibenzofurans, which shows that essentially no dioxins or dibenzofurans were detected in these samples at the limits of detectability.

The ambient tests were designed to measure PCB concentrations in the ambient air on the firms' property and in the immediate populated area downwind of the stack during the test burns. Meteorological conditions on the date of each test burn were used to position the monitors in areas on the plant property where maximum concentrations were predicted. Sampling was accomplished using high volume samplers modified with a series of two precleaned polyurethane foam plugs. Ambient and background sampling were performed in four runs, each 3 hr in duration. Analysis of ambient samples indicated that ambient concentrations of PCBs at the downwind test sites were less than the upwind concentrations by factors which range between 200 and 400%, indicating that emissions from the test burn did not increase the ambient air loading of PCBs in any significant manner.

Tests for PCBs performed in the in-plant employee workplace areas by General Motors industrial hygiene department personnel, using National Institute for Occupational Safety and Health (NIOSH) procedures, indicated nondetectable levels of PCBs, considerably lower than current Occupational Safety Health Administration (OSHA) 8-hr workplace exposure standards for PCBs.

MONS 006268

Table 17
FLUE GAS ANALYSES FOR O_2, CO_2, CO, THC

Date sampled	O_2 (%)			CO_2 (%)			CO (ppm)			Total hydrocarbons (ppm)		
	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.	Min.	Max.	Av.
Day 1	5.6	6.7	6.3	11.2	13.4	12.3	12.3	16.7	14.2	1.3	3.1	2.2
Day 2	5.3	7.3	6.1	12.0	21.3	14.1	6.8	9.7	8.7	0.2	0.8	0.4
Day 3	3.9	8.0	5.6	8.3	12.6	11.3	8.0	11.0	9.6	0.7	2.4	1.4
Day 4	5.3	>10.23*	6.5	6.7	13.12	11.3	7.2	12.4	8.0	0.5	2.3	0.8

* This reading was off scale for the O_2 meter used.

Tests performed on the powerhouse employees showed PCB blood levels essentially comparable to office employees with the least exposure to environmental PCBs.

1. Boiler Operating Conditions

For the duration of the PCB verification burn, continuous monitors were installed to measure CO and O_2 as prescribed by federal regulations. CO_2, and total hydrocarbons (THC). These instruments were installed to monitor flue gas from the stack above the boiler. Provisions were made to shut down the waste fuel feed to the boiler unless the boiler flame temperatures were normal (2500°F), CO concentrations were less than 50 ppm, excess oxygen was greater than 3%, and opacity was less than 5%. Steady-state operation was maintained during testing by setting the boiler at a base load and compensating for fluctuating steam demand with another boiler. Table 17 shows the flue gas analyses for O_2, CO, CO_2, and THC. O_2 concentrations were determined using a paramagnetic O_2 analyzer and CO_2 concentrations were determined using an infrared CO_2 analyzer. CO concentrations were determined using a nondispersive infrared CO analyzer. The data in Table 17[21] indicate that the carbon monoxide levels were significantly less than the 50 ppm federal regulatory requirement, further illustrating very high combustion efficiencies. Although there is no direct correlation between combustion efficiency and PCB or other hazardous organic waste component destruction efficiency, there is reason to believe that high efficiency boilers having sufficiently high temperatures and residence times will have high waste component destruction efficiencies if combustion efficiencies are kept high by proper operation and maintenance.

Other physical parameters were also measured during these tests such as flame temperature, which was found to be between 2500 to 2700°F. The furnace temperatures measured at the back wall of the boiler were 1500 to 1700°F. Smoke density or opacity was found to be 0 to 2%.

This test at the General Motors Warren, Mich. facility was a significant demonstration of compliance with the U.S. EPA TSCA PCB disposal requirements, proving that 99.99% or greater PCB destruction efficiency can be achieved in a high efficiency boiler without generating hazardous combustion by-products such as chlorinated dioxins or dibenzofurans. Extensive monitoring of stack emissions, in downwind ambient air, the workplace environment, and employee blood levels indicated that PCB destruction test burns can be conducted with no measurable adverse effects on workers or on the surrounding environment.[21]

V. BURNING PCB WASTES IN CEMENT KILNS[22]

A. Cement Kiln Technology

The wet process cement kiln shown in Figure 12 is the major type of Portland cement

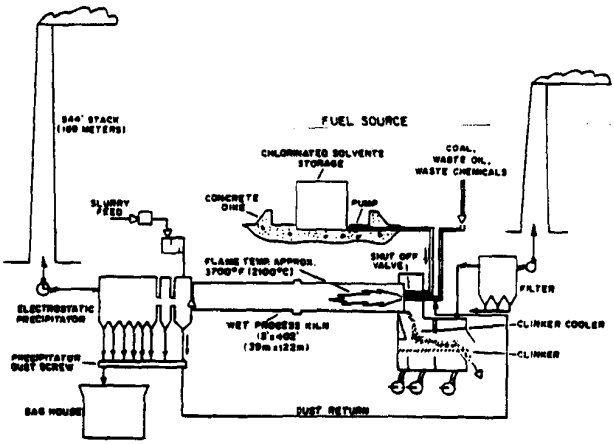


FIGURE 12. Burning toxic, organic chemical wastes in cement kilns.

kiln used in New York State. The newer dry type suspension preheater cement kilns may play a future role in chemical waste incineration. However, since dry cement kilns have not been significantly used for burning toxic chemical wastes, other than lubricating oils, and may experience system pluggage when burning halogenated wastes, such processes will not be reviewed in this chapter.

The cement kiln is the heart of the cement process. A cement kiln is a large steel horizontal tube with refractory linings. Such kilns may be up to 25 ft in diameter and over 500 ft long. The kiln rotates slowly and has a gentle slope to allow material to pass through by gravity. Cement kilns are counter current, i.e., solid materials travel in one direction and gases plus dust emissions travel in the opposite direction. A slurry of 30 to 40% water and crushed rock is fed into the kiln at the left. At the opposite end of the kiln is a powerful oil or coal fire. As the raw material passes slowly through the kiln (1 to 4 hr), it first dries, then approaches the hot burning zone of the kiln. In the burning zone, 2700°F (1500°C) temperatures calcine and fuse, and the raw materials create a complex calcium silicate aluminoferrite mineral substance called "clinker" which is discharged from the lower end of the kiln at the right and cooled in the clinker cooler.

In a typical wet cement process, formation of the key calcium silicate components of the clinker does not begin until temperatures of approximately 2300°F (1260°C) are reached; consequently, in order to get a good quality cement clinker, the rotary kiln must reach (and maintain) temperatures of between 2500 and 2650°F (1370 to 1450°C) in the kiln burning zone. Control of cement quality requires that the clinker be heated to a minimum temperature of 2600°F. It is impossible for a cement plant to allow temperatures to fall to the point where the efficiency of waste destruction is compromised.

If waste liquid organic chemicals are fed into the firing end of the cement kiln, it can be readily seen that they will be subject to the high temperatures and long residence times of the cement clinker production process. Consequently, they will be completely destroyed by a combination of pyrolysis and oxidation.

MONS 006270

1. Burning Chemical Wastes (Including PCBs) and Chlorinated Wastes at St. Lawrence Cement Company, Mississauga, Ontario, Canada[22]

From 1974 to 1976 the St. Lawrence Cement Co. burned waste chemicals in two separate cement kilns at their Mississauga, Ontario plant.

Waste chlorinated hydrocarbons, consisting of approximately 45% PCBs, 12% aliphatics, and 33% chlorinated aromatics were burned in a wet process cement kiln, shown in Figure 12. Stack tests performed during trial burns indicated a destruction efficiency of at least 99.986% for the chlorinated hydrocarbons. About 50 ppb of volatile low molecular weight compounds (e.g., CCl_4) were found in the emission samples. It appears that these low molecular weight compounds found in the kiln emissions are not materials that have escaped destruction; rather they may originate in the feed water used to blend the clinker constituents. There were no detectable quantities of high molecular weight chlorinated compounds in the stack gases as determined by gas chromatography/mass spectroscopy tests. PCBs were not found in the cement clinker.

A mass balance was carried out for chlorine and essentially all the chlorine was reacted with the process solids. This demonstrated that acid gases such as hydrochloric acid, which are generated by the pyrolysis and oxidation of chlorinated hydrocarbons are effectively neutralized by process lime in the cement kiln. This provides an additional benefit. Some cement plants have a need for a low alkali cement. In such cases, the burning of chlorinated hydrocarbons directly results in the lowering of the alkalinity of the cement products.

The test burns of chlorinated hydrocarbon wastes and PCBs at St. Lawrence Cement Co. indicated increased potential emission rates of particulates. "Increased emission rates were not unexpected since combustion of the chloride wastes produces HCl (hydrochloric acid) and Cl_2 (chlorine), which react with the alkali components in the raw feed to form volatile alkali chlorides. At the precipitator, the particulate loading is therefore increased and, since the condensed alkali chlorides are very fine and have a different resistivity, the amount of material passing through the collector increases."[22]

Even though potential particulate emissions can increase when burning halogenated chemical wastes, the actual particulate emissions should not significantly increase if the cement kiln air cleaning system is operating properly. The St. Lawrence experience involved the burning of some very concentrated halogenated waste streams, which in some cases caused alkali halogen rings in the kilns, which also can increase particulate emissions. However, even in such cases, McDonald et al. concluded that "the higher emission rates did not significantly add to the suspended particulate in the ambient air in the vicinity of the plant".[22]

Based on the St. Lawrence Cement plant tests, most cement plants now planning to burn halogenated chemical wastes plan to limit the burning of such wastes to less than 10% of the waste fuel stream. This will minimize kiln ring formation and particulate emissions. It is thus advisable to limit the burning of waste chemicals to cement plants that have highly efficient, reliable, and well-maintained cement kiln particulate air cleaning systems.

During the chlorinated waste burning tests, the average fuel replacement value was about 12%, while the heating value of these wastes averaged about 10,000 Btu/lb of waste. Fuel requirements for the kiln were reduced by about 65% of the actual energy content of the wastes burned. It was estimated from these tests that chlorine can be added to a typical wet process kiln at rates of about 0.4 to 0.7% without disrupting kiln operations.

The burning of halogenated PCB wastes at St. Lawrence Cement Co. was a technical success. For about 2 years, PCB containing wastes of up to 10,000 ppm of PCBs were burned successfully and completely without any adverse environmental effects or chemical accidents. The general public was, however, never informed about these practices and when they learned about the destruction of these PCB wastes in their community, they became outraged despite the fact that in most cases chemical wastes injected into the cement kilns were destroyed to below analytical limits of detection. Public emotion and fear may have

MONS 006271

clouded rational scientific facts. The PCB waste burning operations were later suspended pending extensive environmental public hearings.

a. Ambient Air Monitoring for PCBs at Mississauga

During the early PCB test burns at St. Lawrence in 1977, PCB ambient levels were monitored in residential areas near the plant. Levels of PCBs in the air ranged from 0.1 to 6 ng/m³,[24] typical of background levels found in other urban areas.

Three studies of PCB ambient levels were performed near the St. Lawrence Cement plant in 1978 before and during incineration of PCBs in the cement kiln. These studies were carried out by the Ontario Research Foundation for the Ontario Ministry of Environment and Environment Canada. Some of these measurements were made by the Sciex TAGA 2000 Mobile Monitor which contains a mini mass spectrophotometer. The three 1978 ambient air surveys for PCBs indicated average concentrations of 10 ng/m³ for residential sites and 18 ng/m³ for industrial sites, for 533 collected samples.

Toxicologists at the New York State Department of Health have previously advised the New York State Department of Environmental Conservation that maximum no-adverse effect ambient levels for human exposure to PCBs are in the order of 10 μg/m³ of air for intermittent exposures.[22] This value is designed to prevent acute and chronic human systemic health effects, such as liver damage. Newer guidelines for acceptable ambient levels of PCBs are based upon 1/300 TLV or approximately 2 μg/m³ or 2000 ng/m³ on an annual basis.[23]

The PCB average ambient levels found at Mississauga were about 1/1000 of the maximum recommended ambient PCB levels for human exposure in residential areas. Slightly higher ambient PCB levels near the plant site were about 3/1000 of this recommended maximum no-adverse effect PCB ambient concentration value.

These trace ambient PCB levels were mainly due to storage and handling vapor losses, not cement kiln emissions.

2. Burning PCBs at Peerless Cement Company, Detroit, Michigan[22]

Because of the lack of suitable industrial incinerators to destroy PCB wastes, there was a pressing need to find other PCB waste incineration options to dispose of Michigan's PCB wastes. In December 1976 Amcord, Inc. carried out a test burn of PCBs at its Peerless Cement plant facility in Detroit. PCB material was obtained from Detroit Edison Co. as Arochlor® 1260 drained from transformers. A mixture of 40% Arochlor® 1260 PCBs was pumped at a rate up to 0.75 gal/min through a specially designed auxiliary burner directly into the main coal flame of the kiln. Combustion temperatures in the burning zone of the cement kiln were 2650°F, with residence times of about 10 sec. The cement kiln was a large modern, wet process kiln 19.5 ft in diameter and 580 ft long. The kiln burns 20 tons of coal per hour at a heat load of approximately 500 million Btu/hr. Feed rate of materials was 140 tons/hr of a typical limestone-clay raw mix. Emission control is provided by an electrostatic precipitator.

Stack tests showed complete destruction of PCBs injected into the cement kiln at normal kiln flame temperatures and residence times. However, when background stack tests were performed with no PCBs being injected into the kiln, some low level PCB emissions were detected in the kiln emission stack. The paradox was that these PCB emissions were from the raw material feed slurry, and there was no evidence of any PCBs actually penetrating the length of the kiln.[26]

The plant's raw material slurry contains about 30% water and about 45 tons of water per hour are evaporated in the process. Any PCBs in the plant's feed water would be stripped out in the cold end of a process cement kiln and would be emitted. The Rouge River in Detroit did contain PCBs to the extent of approximately 9 ppb. Consequently, there always was a trace emission of PCBs from the cement kiln stacks, even without the process burning of PCB wastes, as long as PCBs were present in the raw slurry feed water.

MONS 006272

Following these successful PCB waste destruction tests, several public hearings were held. Despite the support of U.S. EPA, Michigan Department of Natural Resources, Wayne County Health Department, and later the International Joint Commission, there was considerable public opposition to this project. Some people tried to equate this PCB waste disposal project with the hazards of nuclear waste and termed it "lethal" and "very dangerous". Perhaps the scientific facts about the safety of such operations revealed in the St. Lawrence Cement Co. and Peerless Cement Co. environmental reports were also clouded by emotional reactions.

3. Burning Chemical Wastes at the Stora Vika Cement Plant in Sweden[22]

Between February and July 1978 various chlorinated chemical wastes were burned at the Stora Vika Cement Plant, near Stockholm. This firm operates a 620 tons/day coal-fired wet process cement kiln, where chlorinated aliphatics, PCBs, chlorophenols, and phenoxyacids were burned during these tests. The average chlorine concentration while burning these chemical wastes was 17%. Chlorine addition averaged 0.35% of clinker weight. At up to 0.6 to 0.7% chlorine input, there were no kiln operational problems; at higher rates alkali halogen rings began forming in the kiln, which later disappeared when chlorine feed rates were reduced.

During the burning of chlorinated aromatic wastes, tests showed no analytically detectable concentrations of chlorinated organics in the flue gases, with the exception of small quantities of chloroform.[26] Chloroform was also found in samples taken when no wastes were being burned, which appears to be similar to the Peerless Cement Co. case where it seems likely that the materials (chlorinated organics) detected in the stack, entered the kiln in the make-up water used to blend the raw feed slurry.

Waste destruction efficiencies of chlorinated aliphatics were 99.995 to 99.9998%. The destruction of PCBs was greater than 99.99998%.[26]

Analyses were also conducted for dioxins and furans. This investigation did not find any detectable quantities of dioxins or furans containing four or six chlorines, the more toxic forms of these contaminants.[27]

Dust emissions from this plant increased during the experiments, as in the Canadian tests due primarily to an increase in potassium chloride concentrations in the kiln dust. It appears that alkali chlorides generated when chlorine is added to the kiln may have a higher resistivity than typical kiln dust; this may require "tuning" the precipitator stages to reduce emissions to normal.

4. Burning PCBs at the Degerhamn Dry Cement Kiln in Sweden[28]

In October and December 1982 new PCB tests were performed in the dry cement kiln at the Degerhamn Cement Plant in southern Sweden.

These PCB test burns indicated that PCB emissions were less than 0.1 mg/kg of PCB wastes burned, with a PCB waste destruction efficiency in excess of 99.99999%.

Trace chlorinated benzenes and dibenzofurans were found however, at ultra-low concentrations lower than those found at the accepted detection limits in the Stora Vika PCB test burns. The trace concentrations of chlorinated dibenzofurans were of the same order of magnitude as levels of this contaminant found burning highly chlorinated non-PCB wastes at the U.S. EPA sponsored test burn at the San Juan, Puerto Rico cement plant.[28,29]

The Swedish researchers also reported that there were no essential differences in the trace concentrations of chlorinated dibenzofurans found in these latest cement kiln waste burning tests, with or without the introduction of PCB wastes.[28]

These experiments at Degerhamn show that dry Portland Cement kilns can also effectively destroy highly chlorinated and PCB wastes.

5. Burning PCBs at Norcem Cement Company, Norway[30]

The Norwegian government, unlike others that have either been neutral or not fully

MONS 006273

Table 18A
ENERGY REQUIREMENTS FOR CEMENT KILNS

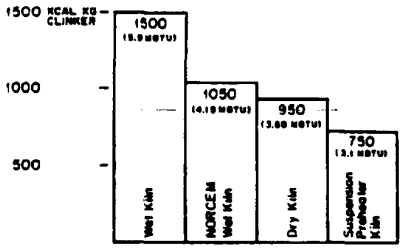
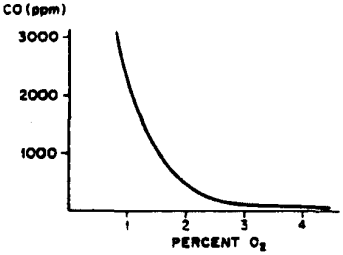


Table 18B
CO CONCENTRATION IN RELATION TO THE EXCESS OF AIR



supportive of burning wastes in cement kilns, has encouraged the efficient burning of hazardous wastes in cement kilns in order to effectively dispose of such wastes by destroying them completely, and to lower the fuel consumption of cement industries to save valuable fossil fuels.

For several years the Norcem Cement Co. in Slemmestad, Norway has had an ongoing program to reduce energy consumption. Tables 18A and 18B illustrate the energy requirements for cement kilns which are typically 1500 kcal/kg of clinker that has been reduced to approximately 1000 kcal/kg of clinker at the Norcem Cement Co.'s wet process cement kiln by reducing the water content in the slurry to 24%. The economical results have been further improved by effectively burning waste fuels to replace part of their fossil requirements.

Cement kilns have very high process temperatures, greater than 1400°C, which ensure the complete destruction of hazardous waste components such as PCBs. Figure 13 illustrates a *test cement kiln temperature profile, showing* that the ordinary process conditions for the manufacture of cement require high temperatures and long residence times, which are fully adequate to destroy PCBs and that other difficult to burn hazardous waste such as PCBs are neutralized by the alkalinity of the cement kiln process materials.

Norcem decided to burn waste chemicals in their cement kilns and developed a coordinated

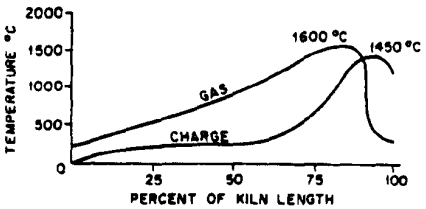


FIGURE 13. Test kiln temperature profile.

management plan to carry out this project. A project group was organized with representatives from labor and government; equipment specifications and emission control programs were established. Detailed emergency plans were prepared to deal with potential accidents. The responsibility for waste transportation was clearly assigned to the waste supplier. Adequate safety procedures were developed involving fire and police officials and the firm's environmental and safety staff. Adequate waste storage and transport procedures were developed. The organic vapors from the waste storage tanks are ventilated to the cement kiln where the organic gases are completely burned. The tanks are pressurized by an inert gas, and water drainage from the storage tanks is connected to the kiln slurry feed system for destruction purposes.

The Norcem Cement kiln, where PCB wastes were first burned in carefully controlled tests in Norway, is 155 m long and has a diameter of 4 m. Normal fuel consumption is 92 tons of fuel oil for a production of 860 tons of clinker a day. A separate waste burner was installed in order to properly atomize the liquid waste by ultrasound techniques. The incineration of hazardous wastes such as PCBs is controlled by carefully monitoring kiln temperatures and by monitoring the oxygen and carbon monoxide exhaust gas concentrations.

A special emission test program was arranged with the Norwegian Institute of Industrial Research, the Norwegian Institute of Air Pollution Research, and the Steam Users Association.[39] A complex chemical analytical program was developed in order to analyze all chemical emissions from the kiln stack gases. The quantities of the exhaust gases in all the tests were approximately 100,000 normal m^3/hr during these two tests: first for the incineration of organic tar wastes, second for the incineration of PCBs.

As previously discussed in the sections referring to high temperature incineration of PCBs, high combustion efficiency is important; while there is no direct correlation of combustion efficiency to waste destruction efficiency, there is an empirical relationship. Table 18B shows the relationship of the carbon monoxide exhaust gas concentration in relation to excess air, as excess oxygen, in cement kilns.

At oxygen levels of 3% or more the carbon monoxide concentrations are minimal, and the highest combustion efficiency will be achieved, correlating with high waste destruction efficiencies. Consequently, it is important to continuously monitor excess oxygen and carbon monoxide in a cement kiln, or in any hazardous waste incinerator or boiler burning hazardous wastes such as PCBs, to ensure efficient operation and high degrees of waste destruction.

During the Norcem waste tar test, 70 different organic components were detected in the stack gases. Tar was fed to the cement kiln at a rate of 900 kg/hr based on extensive stack tests, and due to the concentration of polynuclear aromatic hydrocarbons (PAH), a destruction efficiency of 99.99999% was achieved. No organics were detected in the dust from the electrostatic precipitator or in the clinker.[39]

PCBs were incinerated in the Norcem cement kiln at a rate of 50 kg/hr; using a PCB

MONS 006275

Table 19
STACK GAS ANALYSIS, SLEMMESTAD WORKS, NORWAY (NORCEM)

	Heavy oil normal oper. (O_2 > 2%)	Heavy oil abnormal oper. (O_2 < 1%)	Heavy oil + tar	Heavy oil + PCB	Threshold values (Norwegian government)
Benzene	0.45		0.2	0.1	15
Toluene			0.04	1	280
C_7-alkylbenzenes			0.1	0.023	435 ethylbenzene
Xylene			0.2		435
C_9-alkylbenzenes			0.080	0.007	120 trimethylbenzene
C_{10}-alkylbenzenes	0.001	0.002	0.034	0.008	
Alkanes	0.014	0.021	10	0.054	360 *n*-hexane
Ketones	0.006	0.016	0.023	0.007	230 ethylbutylketone
Aldehydes	0.004	0.012	0.096	0.022	1.2 formaldehyde
Phenols			0.02		19 phenol
PAH	0.014	0.025	0.014	0.002	0.04
TOH	9.3		40.5		
Chloroform $CHCl_3$				0.0012	10
Carbon tetrachloride				0.0012	13
Trichloroethylene				0.0009	160
Tetrachloroethylene				0.0012	200
Chlorobenzenes				0.0075	230
Dichlorobenzenes				0.0016	300
3—6 Chlorobenzenes				0.00016	40 trichlorobenzenes
PCB	0.00004[a]			0.00017[a]	
Mercury (Hg)	0.0044				0.05
Lead (Pb)	0.150				0.05
Cadmium (Cd)	0.085				0.05

Note: All figures are given in mg/nm$_3$. Stack-gases are diluted 40—70,000 times in the atmosphere.

[a] PCB DRE = 99.99997%

containing 48% chlorine; the destruction efficiency determined from these tests based on a feed of 50 kg/hr PCBs to the cement kiln was greater than 99.99997%. No polychlorinated dibenzodioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs) were detected. Special efforts to identify these compounds were undertaken but there was no trace of these toxic air contaminants in these tests.[30,31] These PCB burning tests are summarized in Table 19.

No PCBs were observed in the cement clinker or dust. A slight increase of stack particulate emissions from 5.2 kg/hr to 6.8 kg/hr was detected similar to that previously noted in the Canadian tests. The physical quality of the cement clinker was not affected but a slight increase of chloride and a slight reduction of the alkaline content was observed.[29]

Emission analysis was supplemented by biological testing using the Ames test for mutagens. No increase in carcinogenic activity in the stack gas emission was detected.[29]

Sulfur hexafluoride (SF_6) was sprayed into the stack gas as a tracer. Twenty-six (26) ambient air sampling stations were located downwind of the cement kiln stack during these tests. The maximum ambient concentration was found to occur at a distance of 1 km from the stack, and was 1:40,000 of the stack gas concentration. Theoretical calculations gave a dilution factor of 1:70,000, proving the calculations to give a reasonably good picture of the stack's dilution efficiency. A maximum hourly concentration of 1 µg PCB per normal m^3 in the ambient air at a distance of 1.5 km from the stack was estimated based on wind measurements and diffusion calculations; the actual ambient PCB levels based on test data (Table 19) were far lower.[29]

These 1980 PCB test results were very promising and the company proceeded with further tests in 1981, burning other wastes containing heavy metals, other chlorinated organics,

MONS 006276

wastes from vinyl chloride monomer processes, and waste tars from the aluminum electrochemical industries.

The Norcem cement kiln test burning PCBs and other waste chemicals was very successful and again illustrated the complete destruction of PCBs without any resultant significant emissions of toxic air contaminants that could be harmful to the environment or to public health. An approximate 20% saving of conventional fuels was realized, making this wet cement kiln competitive to a modern dry cement kiln using conventional fuels. The Norcem PCB waste disposal destruction test again demonstrated that cement kilns are superior to the use of hazardous waste incinerators in destroying PCBs and other hazardous organic wastes because of their ultrahigh temperatures and long residence times, and the fact that acid gases such as HCl, produced by burning chlorinated wastes and PCBs are effectively neutralized by the alkaline materials within the cement kiln.

6. California Office of Appropriate Technology Recommendations for Burning PCBs

In March 1981 the State of California Air Resources Board developed a proposed policy regarding incineration as an acceptable technology for PCB disposal. A report on this subject was drafted, which was reviewed and discussed at a public meeting to review all aspects of PCB incineration.[33] This extensive report reviewed the state of the art for hazardous waste incineration and incineration of PCBs, and made health risk projections based on the U.S. EPA PCB incineration studies of the Rollins Environmental Services, Deerpark, Tex., and ENSCO, El Dorado, Ark., hazardous waste incineration studies previously referred to in this chapter. The appropriate health risk factors determined in the Rollins and ENSCO case studies by the EPA were used to make projections for cement kiln incineration of PCBs. Table 20[33] gives a comparison of combustion parameters for various incinerator types and cement kilns and their estimated PCB destruction efficiency. We can see that the PCB destruction efficiency of 99.99998% for the Rollins and ENSCO hazardous waste incineration systems are identical to the PCB waste destruction value for cement kilns, which is based on previous studies in Scandinavia. Figure 14[33] shows a typical wet process cement kiln burning after burning, and wet zones, illustrating the high residence times of up to 10 sec present in a Portland cement kiln, which make it ideal for the incineration and destruction of PCB wastes.

The California Air Resources Board report on their proposed air resources policy regarding incineration as an acceptable technology for PCB disposal concluded that:[33]

1. At present, proper cement kiln incineration appears to the staff to be the best way of eliminating the threat which PCBs now pose to our air, land, and water environments.
2. Cement kilns have been shown in test burns to destroy PCBs to the limits of analytical detectability (99.99998% destruction).
3. Cement kilns also have an intrinsic safety factor; the conditions for making cement are such that the kiln must maintain operational temperatures, dwell, and oxygen parameters which far exceed those for PCB destruction.
4. Using worst case analyses (based on the previous Rollins and ENSCO hazardous waste incineration studies) the predicted ambient values for PCBs range from 0.013 to 0.45 ng/m³ over 24 hr which are values well below background (0.5 to 14 ng/m³) and home (39 to 620 ng/m³) levels.
5. The predicted worst case ambient exposures to PCBs from cement kiln PCB incineration is lower than background, and the air concentrations of PCBs found in homes or offices. These important conclusions are summarized in Table 21.
6. Similarly, dioxin and furan emission rates and concentrations are also predicted to be so low as to be without adverse affects to public health.
7. At present, none of the other types of incinerators and some chemical methods for

MONS 006277

Table 20
COMPARISON OF COMBUSTION PARAMETERS FOR VARIOUS INCINERATOR TYPES AND THEIR ESTIMATED PCB DESTRUCTION EFFICIENCY

Incinerator or study author	Temp. (°C)	Dwell time (sec)	Exit O_2 (%)	Destruction efficiency (%)
Cement kilns	1,200—1,700	1.7—10	>2	≥99.99998
Rollins rotary kiln	1,090—1,200	2.6	7	≥99.99998
ENSCO, 2 boilers in series	1,090—1,200	3.2		≥99.99998
Carey (1978)	1000	1		99.995
Komamiya (1978)	1300	2.0—2.9	8—37	99.999994
Ackerman (1977)	1230	3.2 (2.3 in afterburner)		99.999
Electrical utility boilers	1200	2	— — —	N/A
Sludge incinerators (multiple hearth)	310—540 (top stage) 760—980 (deodorizing stage) 200—320 (cooling stage)			N/A
Liquid-injection incinerator	650—1650	0.5—2		N/A
Typical rotary kiln	870—1650	2—120		N/A
Typical fluidized kiln	1200	2—3		N/A
MoChelan incinerator	1300	0.8	4	N/A
Dow incinerator	1265	2	7.5	≥99.998
	1390	1.6	7.5	≥99.997
	1385	1.6	7.6	≥99.997

Note: N/A = not available.

PCB destruction can match the cement kiln's advantages, including energy conservation, ability to accept PCB liquid wastes in various strengths, proven destruction efficiency, and economic incentives.

These conclusions developed by the California Air Resources Board are very impressive; they point out the fact that existing cement kilns appear to be the best hazardous waste disposal method for disposing of liquid PCBs known to exist today. There has been much concern about proper environmental controls for the safe storage, handling, and disposal of toxic wastes and PCBs in cement kilns. The following recommended environmental controls for cement kiln hazardous waste disposal operations were taken from the author's previous studies of burning hazardous waste as fuels in cement kilns, and represent the state of the art for practically controlling such operations.

B. Recommended Environmental Controls for Storage, Handling, and Process Disposal of Toxic Chemical Wastes in Cement Kilns[29]

The following recommended engineering controls and safeguards are designed to ensure that toxic waste chemicals will be properly handled and destroyed in cement kilns, without any appreciable environmental discharges that could affect public health or safety.

1. Chemical wastes should be stored in an isolated area, preferably well fenced and locked to provide good security from intruders and vandals.

2. All ground area within diked storage areas will be sealed so that spills will not penetrate the ground. Sealed concrete surfaces are recommended.

MONS 006278

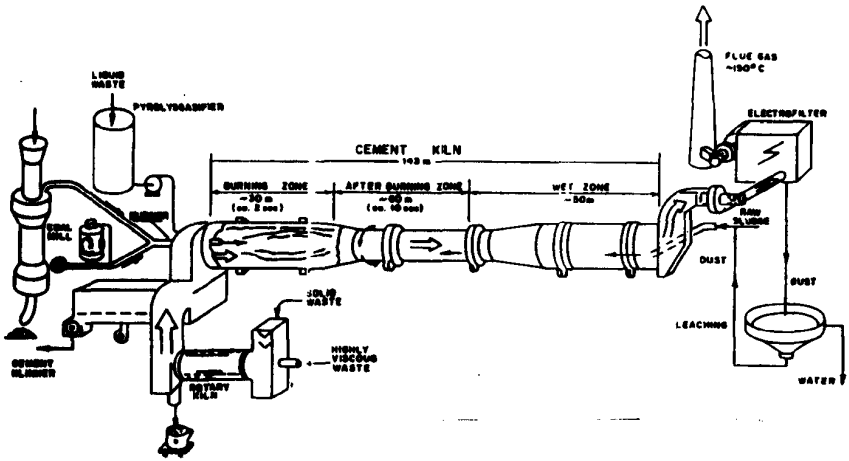


FIGURE 14. Kiln gas residence time in a cement kiln.[7]

MONS 006279

Table 21
PREDICTED MAXIMUM GROUND LEVEL PCB CONCENTRATIONS FROM CALIFORNIA CEMENT KILNS AND TYPICAL MEASURED PCB BACKGROUND CONCENTRATIONS

Maximum ground level conc. range PCBs (ng/m^3)			Typical background PCBs (ng/m^3)	
1-hr av.	24-hr av.	Fumigation	Home-indoors	Community ambient air
0.052—0.606	0.013—0.152	0.282—3.42	39—620	0.5—14

3. Well controlled drainage — all leaks, spills, rain water, etc., should be easily collected and saved for destruction. Receiving area spills is particularly important.

4. All liquid storage should be in closed tanks, not open lagoons.

5. Methods to contain and recover piping leaks without environmental contamination should be provided.

6. Adequate alarms for abnormal conditions should be provided.

7. Leak-free design should be specified whenever possible.

8. The waste liquid storage sump area will be enclosed and all vent gases from such area and storage tank shall be vented to an emission control system.

9. No runoff water from the waste chemical storage area shall be discharged to city sewers. Any such runoff will be redirected into storage tanks for subsequent high temperature destruction in the kiln.

10. Emergency equipment, such as fire extinguishers, selfcontained breathing masks, sorbent materials, and shower stations shall be sited in the immediate vicinity of the waste chemical storage area. Employees shall be trained in their proper use.

11. No double-bottom tank trucks will be permitted for delivery of waste liquids to the plant.

12. The company will be required to have specially trained and authorized personnel at the chemical waste storage and pumping site for unloading and storage of chemical waste/synthetic fuels.

13. When authorized operating personnel are not on site, the storage and pumping area shall be made sufficiently secure to prevent site access and operation of the storage and unloading system.

14. All volatile organic emissions from waste chemical storage and handling facilities should be exhausted and piped to the cement kiln for incineration and complete destruction. Explosion-proof safety valves shall be provided, similar to those used in burning noncondensable organic gases in lime kilns at Kraft pulp mills.

15. As an alternate to condition 14, a closed vapor line between the storage tank vents and the tank trucks should be provided to return the displaced volatile organic vapors from the storage tanks to the tank truck when loading the tanks.

16. In conjunction with condition 15 to control organic emissions, a back-up carbon adsorption vapor control system should be provided to control volatile organic compound storage tank breathing emissions.

17. A management control and record-keeping system shall be established identifying the source, chemical composition, and quantity of all waste materials received for destruction. These management and record-keeping systems shall be submitted to the environmental control agency for review and approval prior to initiating any liquid waste storage or destruction. Such records shall be available for inspection by the environmental control agency at all times.

MONS 006280

18. The kiln will be operated at all times in an oxidizing atmosphere. Oxygen in the kiln exhaust gases will be maintained at a level of not less than 0.5% and continuously recorded. Additionally, a monitor shall continuously measure and record combustible content of exhaust gases. CO shall be continuously monitored and shall not exceed a 100 ppm value (new).

19. No waste liquid burning shall take place unless the cement kiln is operating at normal temperatures in the range of 1260 to 1650°C as a kiln flame temperature. The waste liquid materials shall be provided to continuously record the rate of flow of these wastes. Burning shall not be permitted during periods of kiln start-up, shut-down, major upset, or coal fuel interruption. Kiln coating temperature will be measured by a recording optical pyrometer and coal fuel flow shall be continuously measured and recorded.

20. System controls shall provide for automatic shutdown of introduction of waste liquid materials into the kiln in the event any of the following conditions occur:

- Cement kiln temperatures fall below 1200°C
- Coal flow interruption
- Kiln speed decrease to below 60 RPH
- Loss of draft in the firing hood
- Exhaust gas combustible content in excess of 0%
- Exhaust gas oxygen content less than 0.25%
- Kiln coating temperature below 1090°C
- CO exhaust gas concentration greater than 100 ppm

21. Upon request of the control agency, the firm shall perform stack particulate emission tests to determine the extent, if any, of increase in emissions due to waste liquid destruction. The proposed facility shall not cause an increase in the particulate emission rate specified by the environmental control agency's regulations. If emissions are found to exceed such standards due to waste liquid destruction, the company shall outline and implement an acceptable abatement program to bring these emissions within the stated limit.

22. Special attention is directed to the specific requirements for handling, storage, and disposal of PCB waste liquid materials noted in federal rules governing the disposal and storage of PCBs (40 CFR 761) (demonstration of 99.9999% waste destruction and 99.9% combustion efficiency).

23. The firm burning chemical wastes as synthetic fuels in cement kilns shall demonstrate compliance with the following conditions:

- 99.99% or greater waste conversion and removal efficiency
- 99.9% combustion efficiency
- No detectable residual total organic halogens in the air emissions (using gas chromatography/electron capture or equally sensitive analytical methods)
- An acceptable ambient air impact analysis, demonstrating that all trace toxic air contaminants are within acceptable ambient limits[29]

24. If the outside skin temperature of the kiln exceeds 480°C, the feed of waste chemicals shall be shut off from introduction into the kiln, and shut-down shall be initiated for repair of the refractory. Reintroduction of chemical waste liquids will not take place until such lining repairs are completed.

25. Chemical waste liquid introduction into the kiln shall cease in the event of midkiln ring formation. Reintroduction of chemical waste liquids into the kiln shall not take place until such ring is eliminated.

26. Automated monitors should be employed to alert operators in the event of a waste-fuel handling problem. A pressure transducer located in the waste piping at the entrance of

the kiln shall be provided to automatically turn off the waste fuel pump in the event of a sudden pressure drop due to pipe rupture or pump failure.

27. Interlocks should be provided to automatically stop the flow of waste fuels if either normal fuel supply or combustion air flow are interrupted or if carbon monoxide levels indicate less than 99.9% combustion efficiency.

28. Monitoring systems capable of detecting volatile organic vapors shall be placed at key process locations to signal accidental waste fuel leaks. Periodic monitoring for volatile organic compound emissions shall be provided.

C. Conclusion

In several states in the U.S. and in Europe, especially Scandinavia, cement kilns are now burning hazardous waste as alternate fuels, completely destroying such wastes and reaping the economic benefits by burning such materials as low cost supplemental fuels. However, in other areas, environmental control agencies are still studying the use of cement kilns for hazardous waste and PCB destruction because of political opposition to this concept. The burning of hazardous wastes and PCBs in cement kilns is now in the second decade of proven effectiveness and reliability. To some, 99.9999% or greater proven destruction of PCBs and other hazardous wastes in cement kilns is not enough; others may want to literally count the molecules coming out of a cement kiln stack to ensure zero emissions and zero risks. Such extreme attitudes, and the fact that local politicians can gain much personal attention by opposing such projects in their jurisdiction, can prevent the sound, safe, effective disposal of PCBs in cement kilns.

The foregoing technical examples of burning liquid PCB chemical wastes in cement process kilns in Canada, Michigan, Norway and Sweden have demonstrated the ability to completely destroy such wastes without significant environmental emissions of these materials. Such operations are preferable to landfilling toxic wastes which could escape into the environment if the integrity of the landfill is ever disturbed due to unforeseen future conditions. The process incineration of hazardous liquid organic wastes or the use of such wastes as synthetic process fuels is the only way to ensure that such materials are properly destroyed and do not ever come back to haunt us in the future.

The energy crisis of the 1970s has placed a premium on fossil fuels. The ability to burn waste chemicals as supplemental fuels in the mineral products industries can save large quantities of virgin fuels that can be used elsewhere to ease fuel shortages.

The burning of waste chemicals in cement kilns is not only economically beneficial to cement companies but to the public as well. Cement companies can save large quantities of fossil fuels and will be able to operate older cement kilns more economically and be able to better compete with newer plants elsewhere. The burning of waste chemicals may extend the economic life of older wet process cement kilns by as much as 10 years or more. This could mean more jobs for the public, not only in the cement industry but in numerous other firms in the private sector which are economically related to these industries.

The burning of hazardous organic chemical wastes as synthetic fuels in cement plants has been proven to be safe. The U.S. EPA has concluded that the risks incurred in burning toxic wastes in cement kilns appear to be very low. Given proper controls, emissions of organic compounds are likely to be at or below analytical limits of detection.

The public must ultimately pay the cost of environmental cleanup of toxic chemicals whether directly by public funding or indirectly by increased costs of goods and services. The use of toxic organic chemical wastes as synthetic fuels in cement kilns and other mineral products industries will greatly lower the cost of disposing of these toxic wastes by realizing their potential as supplemental fuels. If these practices are implemented, the public, industry, and government will reap significant environmental and economic benefits.

MONS 006282

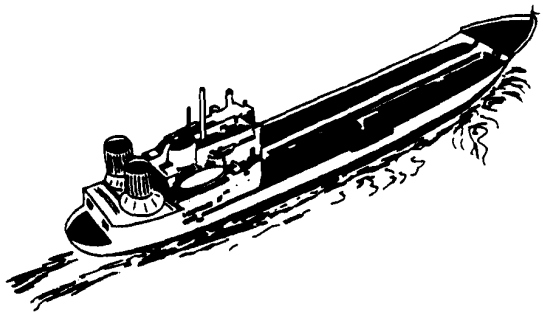


FIGURE 15. *MIT Vulcanus* — incineration vessel.

VI. BURNING PCBs AT SEA[33,34]

Thermal destruction of combustible hazardous waste at sea is recognized as an alternative to land-based incineration and has been successfully performed in Europe since 1969. In late 1974 and March of 1977 organochlorine wastes were incinerated in the Gulf of Mexico by the *MIT Vulcanus*. These tests were evaluated by the U.S. EPA and provided a technical basis for concluding that at-sea incineration of hazardous waste is a viable alternative to other means of disposal. These tests burning the herbicide, Agent Orange, having toxic waste components containing 2,4-D, and 2,4,5-T, as well as some tetrachlorodibenzo-*p*-dioxins were very successful and formed the basis for future PCB waste destruction tests using the *MIT Vulcanus*. Generally, the waste destruction efficiencies achieved during these tests were greater than 99.99%. These tests were performed in an isolated area of the South Pacific Ocean, approximately 120 mi west of the Johnson Atoll.

The operation of the *MIT Vulcanus* in U.S. waters is permitted by the U.S. EPA under a research permit which allows up to 3000 gal of PCB waste to be burned at sea, and provides for proper monitoring and testing for combustion efficiency and waste destruction efficiency. The *MIT Vulcanus* can carry slightly less than 1 million gal of waste, so the U.S. EPA research permit essentially covers three test burns; the first test burn was at the end of December 1982, and the second in July of 1983. The complete environmental assessment of the research permit for incineration at sea of PCB waste on the *MIT Vulcanus* is given in Reference 33.

The *MIT Vulcanus* was originally a cargo ship and was converted in 1972 to a chemical tanker fitted with two large incinerators located on the stern of the vessel. This incinerator ship successfully burned chemical wastes from both the U.S. and European chemical industries, and is now owned by the Chemical Waste Management Company. The vessel currently meets all applicable requirements of the Intergovernmental Maritime Consultive Organization (IMCL). The specifications of the *MIT Vulcanus* are shown in Figure 15 and Table 22.[34]

The *MIT Vulcanus* incinerators may be preheated with fuel oil and gradually brought up to a temperature of 1100°C, then waste may be injected and burned.

However, waste cannot be injected into the incinerator until this temperature is maintained, and the ship is within the specified burn zone. Once in the zone, the captain selects a point

MONS 006283

Table 22
SPECIFICATIONS OF THE *M/T VULCANUS*

Length overall	101.95 m
Breadth	14.40 m
Draft maximum	7.40 m
Dead weight (DWT)	4,768 t
Speed	10—13 knots
Tank capacity	3,503 m³
No. of tanks	15, ranging in size from 115 to 574 m³
Tank coating	No coating in tanks, pipes, pumps, etc., all equipment consists of low carbon steel
Loading equipment	Not available, but can be placed on board, if required
Hose connection	10.2, 15.2, and 20.3 cm (4, 6, 8 in.) in diameter
Safety equipment	Specially designed for this task and in accordance with latest regulations of IMCO, Scheepvaart-Inspectie (The Hague)
Waste to be processed	Must be liquid and pumpable; may contain solid substances in pieces up to 5 cm in size; must not attack mild steel
Incinerators	2
Per incinerator	
Overall height	10.45 m
Combustion chamber	
O.D.	5.5 m
I.D.	4.8 m
Stack (top)	
O.D.	3.8 m
I.D.	3.4 m
Waste feed (max.)	12.5 t/hr
Combustion air (max.)	90,000 m³/hr
Burners (vortex type)	3
Volume	120 m³
Residence time	1.0 sec at 1500°C (calc.)

at which to anchor close to the center of the burn zone; upon reaching this point the anchor is dropped, the engine is shut down, and the ship naturally heads itself into the wind. The crew maintains an angle to the wind so that the plume from the incinerators will be discharged aft at an angle of 45° from the ship's center line. The procedure in U.S. waters is somewhat different; the incineration site is located in the central part of the western part of the Gulf of Mexico and was selected on the basis of studies and an environmental impact statement done by the oceanography department of Texas A&M. It is 160 mi from the nearest land, which is near Galveston, Tex. The site is in an area of low biological activity and is far from normal shipping lines.

The specifications for the *M/T Vulcanus*' on board incinerators generally require that the waste burned must have a minimum heating value of about 5769 Btu/lb pound (3200 kcal/kg); such waste may have a halogen content of up to and over 70% and a maximum viscocity of approximately 50 cp. The system is not designed to burn heavy residual-type wastes; the water content should be kept low for best burning conditions; however, in actual operation an aqueous layer tends to settle or separate in the storage tanks. If the hydrocarbon layer has a high Btu content, the aqueous layer can be sprayed into the incinerator to one of the burners and completely evaporated with all hydrocarbons destroyed at the same time. The controlling factor is the incinerator temperature.[34]

Each incinerator combustion chamber consists of two main sections, a combustion chamber and a stack shown in Figures 16 and 17, the lower chamber employing three rotary cup burners of the forced draft type for combustion of the waste. Each chamber has an overall height of 10.45 m with an outside diameter of 5.5 m and an inside diameter of 4.8 m. The

MONS 006284

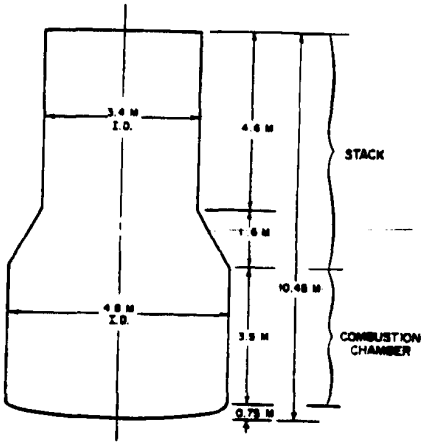


FIGURE 16. Incinerator configuration.

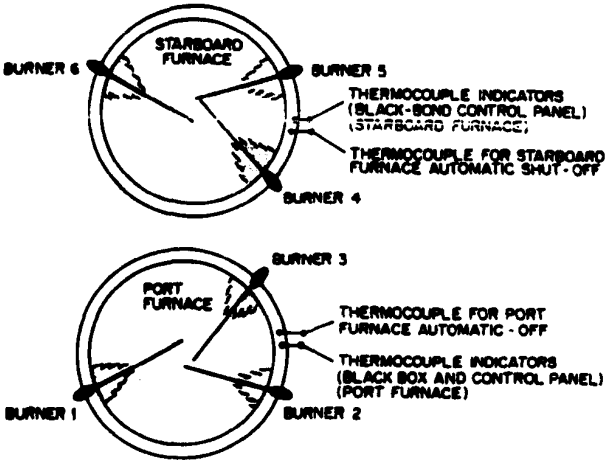


FIGURE 17. Incineration system — burner and thermocouple locations.

MONS 006285

combustion capacity is 12.5 tons/hr; however, this is under ideal conditions when the heating value of the waste is optimum. When high heating value wastes are burned, the capacity can drop off to 7 or 8 tons/hr in order to maintain a temperature of approximately 1200°C in the chamber. The volume of each incinerator is 120 m^3 and residence time is approximately 9/10 of a second.

The air for combustion is supplied by large fixed-speed electric motor driven blowers with a rated maximum capacity of 90,000 m^3/hr for each incinerator.

The liquid waste is fed to the combustion system by means of electrically driven pumps; the pumps pass from the storage tanks through a supply pump which reduces the solids and the wastes to pumpable slurry. This is known as a gorator which also acts as a mixing pump by recirculating the wastes back through the various waste tanks. The power for the blowers, pumps, and other parts of the incinerator system is supplied by two diesel generators with a total capacity of 750 kW at 440 V and 60 Hz. The waste burners deliver waste or fuel oil through a central tube to an atomization nozzle where it meets high velocity air delivered through an annulus. From time to time the burners require cleaning and are normally cleaned one at a time while the remaining two burners continue to fire waste. Each burner has a three-way valve which can provide waste feed, fuel oil, or shut-off conditions. Waste and fuel oil cannot be valved into a burner simultaneously under the present piping arrangements of the *M/T Vulcanus*.[34]

The *M/T Vulcanus* is capable of monitoring the stack gases from each incinerator as to operating temperature, CO_2 content, O_2 content, and CO concentration. Samples are taken from the incinerator stack and passed through a line through scrubbing equipment instrumentation on the bridge. A "black box" with a camera continuously monitors these four elements of incineration capability. The ship also has an optical pyrometer which is a portable device to measure incinerator flame temperature/temperatures during operation. A more sophisticated sampling system designed by TNO of Holland was used for the first PCB test burn in U.S. waters; this system was modified even further in the second test burn as suggested by U.S. EPA.[34]

The following fact sheet summarizes the results and conclusions of the first PCB test burn on the *M/T Vulcanus*.[33]

Fact Sheet — First Vulcanus Test Burn[33]

- *M/T Vulcanus*, owned and operated by Ocean Combustion Service, B.V., Rotterdam, The Netherlands, now a subsidiary of Chemical Waste Management, Inc., Oak Brook, Ill., was used to incinerate approximately 700,000 gal of PCB wastes and rinsate in the EPA-designated incineration site in the Gulf of Mexico.
- The incineration site is located in the central part of the western Gulf of Mexico and was selected on the basis of studies and an environmental impact statement done by the Oceanography Department of Texas A&M. It is 160 mi from the nearest land which is near Galveston. The site is in an area of low biological productivity and is far from major shipping lanes.
- The *M/T Vulcanus* is fully certified under the international regulations for transportation of hazardous cargo and the international regulations for incineration at sea. The international regulations for incineration at sea were developed under the London Dumping Convention, to which both the U.S. and Mexico are signatories.
- International regulations for incineration at sea require minimum combustion efficiency of 99.93 ± 0.03%. On-board monitoring of CO, O_2, and CO_2 yielded combustion efficiencies ranging from 99.93 to 99.99%, with an average of about 99.98% throughout the duration of the first burn. Calculated destruction efficiency based on laboratory analysis of samples taken on board and analyzed on shore exceeded 99.9999%.
- Two EPA observers were aboard the *M/T Vulcanus* during the burn. They had authority to stop the burn if the conditions of the permit were not being met.
- Existing air quality models were used to predict the concentration of unburned PCB residues and hydrogen chloride emissions at various distances from the incinerator vessel, and for worst-case conditions show the following:

MONS 006286

Distance (mi)	PCB(ng/m³)*	HCl(mg/m³)**	Wind speed (mph)
0.4	22	13	1
40	1.1	2.2	5
60	0.3	0.17	15

* Averaged over 10 hr
** Averaged over 8 hr

- The comparable safe exposure standard for PCB is 1000 ng/m³, and for HCl is 7 mg/m³. It may therefore be concluded that there will be no adverse impact on the atmosphere from the stack emissions from incineration at sea of PCB wastes under the conditions permitted by the U.S. EPA.
- The requirements of the permit are that combustion efficiency and destruction efficiency values must be in excess of 99.9%. The results of this burn demonstrate conclusively that these requirements have been met and exceeded by a considerable amount. It is therefore the conclusion of the U.S. EPA that the *M/T Vulcanus* has demonstrated its ability to destroy PCB wastes in accordance with applicable regulations.
- EPA is proposing designation of an additional incineration site in the North Atlantic about 100 mi from shore, and is considering designation of an additional site in the Pacific Ocean.

The PCB waste destruction test burns aboard the *M/T Vulcanus* demonstrated the advantage of burning chemical wastes, especially highly contaminated, very toxic organohalogen wastes which are difficult to handle aboard an incineration ship. The obvious advantage of such operations is that no scrubbing device is needed to clean HCl gases from the plume. The incinerator stacks emit a high concentration of HCl, which is heavier than air, and descends very rapidly to the surface of the sea, which is alkaline, and quickly reacts with the HCl, neutralizing the acids, and forming common salt, sodium chloride. Tests which have been run both in Europe and in the U.S. burn zone in the Gulf of Mexico indicate that high temperature combustion of chlorinated hydrocarbons under strictly observed regulations has no provable negative environmental effects on the sea water near the burn site and causes no evident ecological damage.[36]

It is interesting to note that an international convention for the prevention of marine pollution has developed rules for the incineration of hazardous wastes at sea.[37] Generally, these proposed international regulations do not permit the incineration of substances and materials for which practical alternative land-based methods of treatment, disposal, or elimination are available. Generally, incineration at sea is considered an interim method of waste disposal, to encourage the further development of alternative land-based methods of treatment, disposal, or elimination of hazardous wastes. These proposed international rules have sections governing incineration permits, control over the nature of wastes to be incinerated, and specific requirements for facilities for incineration of hazardous wastes at sea, which are generally similar to the U.S. EPA PCB interim incineration requirements that govern the *M/T Vulcanus* tests, such as a required combustion efficiency of 99.9% with the waste destruction efficiency being equivalent to other approved high efficiency PCB destruction methods.

The incineration of PCB wastes at sea certainly has political advantages, especially when there is local political resistance to incinerating PCB wastes in areas of local jurisdiction; however, the economics of burning wastes at sea must be carefully evaluated when compared to land-based methods in order to determine the most economically advantageous incineration or waste treatment method.

Historically, six incineration ships were designed and built in Europe, three of which are now operating. Two additional ships are under construction by At Sea Incineration Co. and are expected to soon be operational. U.S. EPA will be conducting further research on ocean incineration under provisions of the Marine Sanctuary Act to assess hazards to the environment; this will be part of U.S. EPAs efforts to promulgate new regulations for ocean incineration of hazardous wastes.[38]

MONS 006287

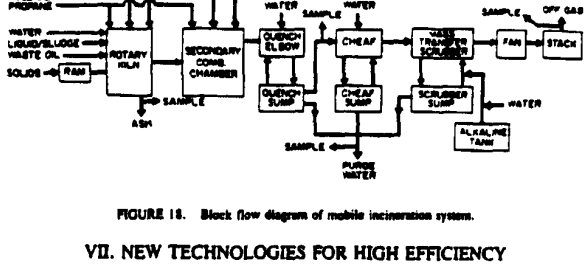


FIGURE 18. Block flow diagram of mobile incineration system.

VII. NEW TECHNOLOGIES FOR HIGH EFFICIENCY DESTRUCTION OF PCBs

A. U.S. EPAs Mobile Incinerator[36,37,39]

U.S. EPAs Office of Research and Development has developed a mobile incineration system designed for field use to destroy hazardous organic substances collected from clean-up operations at spills or at uncontrolled hazardous waste sites. It is the policy of U.S. EPA to encourage the development of cost-effective advanced technologies for the disposal of hazardous waste. After testing, U.S. EPA intends to make the details of this system available to the public for the purpose of encouraging commercial development of such new technologies.

The mobile incineration system is designed to U.S. EPAs PCB destruction specifications to provide state of the art thermal detoxification of long-lived refractory organic compounds, as well as for debris from clean-up operations; hazardous substances that could be incinerated include compounds containing chlorine and phosphorus; e.g., PCBs, kepone, dioxins, and complex pesticides which may be in pure form, in sludges, or in soils.

The mobile incinerator consists of four trailers with specialized equipment consisting of three major subsystems: (1) combustion and air pollution control, (2) continuous flue gas monitoring systems, and (3) support equipment (see Figures 18 to 22). In the rotary kiln, organic wastes are fully vaporized and completely or partially oxidized at 1800°F. Incombustible ash is discharged directly from the kiln, while the off gases are passed through the secondary combustion chamber at about 2200°F; here, the thermal decomposition of the contaminants is completed. The flue gas exits from the secondary combustion chamber, and is then cooled from 2200°F to approximately 190°F in the quench elbow; excess water is collected in the quench elbow sump. The exhaust gases then pass into the third trailer's air cleaning system; here, submicron particulates are removed from the gas train as it passes through a cleanable, high efficiency air filter (CHEAF: acid gases are neutralized in the mass transfer, MX scrubber). The exhaust gases are drawn through the system by an induced draft fan and are discharged from the stack. A monitoring system is used to analyze the stack gases for combustion components, such as CO, CO_2, O_2, and emission components such as oxides of nitrogen (NO_x), sulfur dioxide (SO_2), and total hydrocarbons (THC).[36,37]

A 15-hr test burn with fuel oil has been completed and the system has undergone priority modifications identified during this burn. A PCB trial burn has been performed and represents a systematic approach to evaluate and demonstrate the ability of the incinerator to meet and exceed the performance requirements established by federal, state, and municipal regulations.[36,37]

The mobile incineration system which has about 1/3 the capacity of large fixed industrial installations is specifically designed to be taken to a spill or release area for on-site clean-up to permanently destroy hazardous waste materials and to eliminate the need for trans-

MONS 006288



DESCRIPTION

OVERALL LENGTH: 45.7 m (150 ft)
STACK HEIGHT: 9.1 m (30 ft)
OVERALL HEAT DUTY: 15 MILLION BTU/h
ELECTRICAL REQUIREMENTS: 100 KW

DESIGN SUMMARY

	KILN	SCC	APC
TEMPERATURE:	1000°C	1200°C	80°C
PRESSURE:	- 1000 PASCAL*	- 1500 PASCAL*	- 10K PASCAL*
GAS RESIDENCE TIME	2 SEC	2 SEC	
EXCESS OXYGEN:	4%	4%	4%

FEED RATES (AT 20% XS AIR)

AIR:	68 m^3/min	34 m^3/min	NONE
FUEL OIL:	295 l/h	150 l/h	NONE
WASTE SOLIDS:	60 kg/min	NONE	NONE
WASTE OIL:	227 l/h	NONE	NONE
WATER:	680 l/h	NONE	•

DISCHARGES

ASH:	•	NONE	PARTICULATE FILTER MEDIA
WASTE WATER:	NONE	NONE	•

* 1000 PASCAL = 4 in. H_2O
• DEPENDENT UPON FEED MATERIAL

FIGURE 19. EPA mobile incineration system

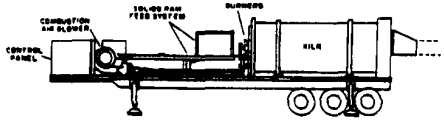
MONS 006289

DIMENSIONS

TRAILER LENGTH · 15.7 m (45 ft)
KILN LENGTH · 4.9 m (16 ft)
KILN I.D. · 1.32 m (52 in)
KILN VOLUME · 6.7 m^3 (236 ft^3)

DESCRIPTION

KILN: CARBON STEEL SHELL, REFRACTORY LINED (KAST-O-LITE 30)
DUCT: INCONEL 601
BURNERS: 2 · MAXON FUEL OIL BURNERS — WITH PROPANE PILOT (6.5 MILLION BTU/h TOTAL)
1 · NORTH AMERICAN WASTE OIL NOZZLE (7.6 MILLION BTU/h)



DESIGN KILN FEED RATES

AIR · 84.9 m^3/min (3000 ACFM)
FUEL OIL · 285 l/h (75 gal/h)
WASTE SOLIDS · 68 kg/min (9000 lb/hr)
WASTE OIL · 227 l/h (1 gal/min)
WATER · 680 l/h (180 gal/h)

DESIGN OPERATING CONDITIONS

TEMPERATURE · 1000°C (1832°F)
PRESSURE · -1000 PASCAL (-4 in H_2O)
FLUE GAS RESIDENCE TIME · ≈ 2 SEC

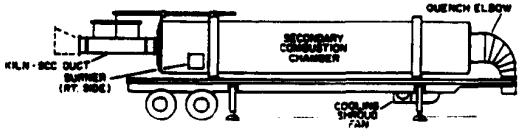
FIGURE 20. Rotary kiln.

DIMENSIONS

TRAILER LENGTH · 13.7 m (45 ft)
SCC LENGTH · 11 m (36 ft)
SCC INTERNAL DIAMETER · 1.32 m (52 in)
SCC VOLUME · 15 m^3 (531 ft^3)

DESCRIPTION

SCC: CARBON STEEL SHELL WITH FORCED DRAFT COOLING ANNULUS REFRACTORY LINED (KAST-O-LITE 30)
BURNERS: 2 · MAXON FUEL OIL BURNERS WITH PROPANE PILOT (6.5 MILLION BTU/h TOTAL)
QUENCH DUCT: INCONEL 625 WITH INTERNAL WATER SPRAY COOLING (60 gal/min H_2O)



DESIGN SCC OPERATING CONDITIONS

TEMPERATURE · 1200°C (2200°F)
PRESSURE · -1000 PASCALS (-4 in. H_2O)
FLUE GAS RESIDENCE TIME · 2 SEC
REYNOLDS NUMBER · 30,000

AIR · 34 m^3/min (1200 ACFM)
FUEL OIL · 190 l/h (40 gal/h)
NO WASTE ADDITION TO SCC

ESTIMATED FLUE GAS COMPOSITION (AT 20%XS AIR)

O_2	4 %	NO_x	50 - 500 ppm
CO_2	10 %	CO	40 - 200 ppm
H_2O	20 %	SO_2	< 2000 ppm
N_2	64 %	HCl	0.2 - 2.0%

FIGURE 21. Secondary combustion chamber and quench.

portation and or landfilling such wastes. This system was designed to meet the requirements for PCB incineration previously noted in the U.S. EPA 40 CFR 761 regulations, namely a minimum 2 sec residence time at 1200°C, with 3% excess oxygen, and a combustion efficiency of at least 99.9%. In addition to the previously mentioned contaminants that are routinely monitored in this system, other measurements and analyses are conducted as required by other regulations and operating protocols; other significant contaminants such

MONS 006290

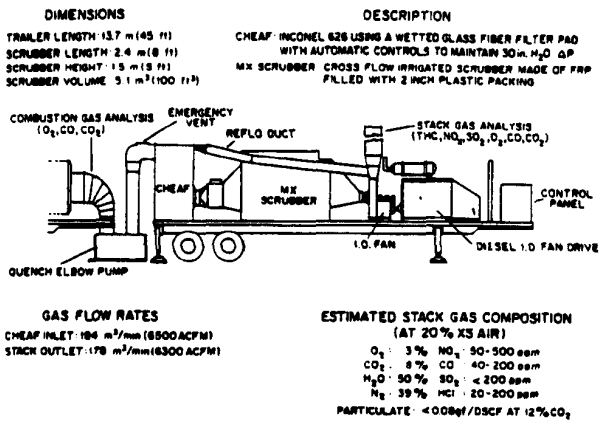


FIGURE 22. Air pollution control.

as principal organic hazardous components (POHCs), hydrochloric acid (HCl), and trace, toxic, hazardous combustion by-products such as dioxins (PCDDs), and dibenzofurans (PCDFs) are monitored in this system on an ad hoc basis, depending on the wastes being burned. For the destruction of PCBs it is usually necessary to monitor for all these contaminants, since PCBs can be considered precursors to trace toxic air contaminants, such as PCDDs and PCDFs. Table 23 presents a summary of the trial burn scope and activities for the U.S. EPA mobile incinerator. As can be seen in this table, the analytical requirements for the test burn will vary depending on the type of waste that is burned, as shown in the examples concerning burning baseline oil, particulates, orthodichlorobenzene (ODCB), and PCBs.[36,37]

Safety interlocks and emergency process controls are quite important in the operation of any hazardous waste incinerator or process burning hazardous waste as fuels. Section V on cement kiln incineration of PCBs presents the many types of process interlocks that are necessary in order to ensure a *failsafe* operation and protection of the public from unburned emissions that can occur during process upsets. Figure 23 shows the safety interlock system for the U.S. EPA mobile incinerator. Adequate safeguards are provided to allow for almost any type of equipment or process failure in order to prevent the uncontrolled emission of hazardous contaminants to the environment.

The three-phase U.S. EPA testing program for the EPA mobile incinerator was designed to minimize the risk of any undesirable emissions to the environment, and involved the incineration of the following liquids:

Phase I: Diesel oil only

Phase II: A blend of 20 to 23% carbon tetrachloride (CCl_4) and 25 to 31% orthodichlorobenzene (ODCB) dissolved in diesel oil

Phase III: A blend of 2% tetrachlorobenzene, 11% trichlorobenzene, and 18 to 22% PCBs such as Arochlor® 1260 dissolved in diesel oil

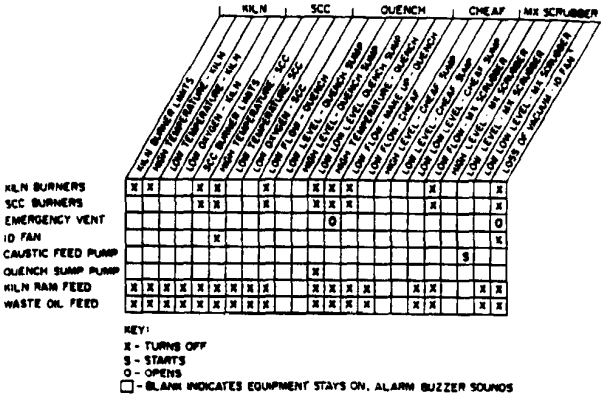
MONS 006291

Table 23
SUMMARY OF TRIAL BURN SCOPE AND ACTIVITIES FOR THE U.S. EPA MOBILE INCINERATOR

					Tests								
					Removal			Exclusion					
Category	Surge[a]	Test phase	Test pts.	Test day[b]	DRE[c]	HCl[d]	Particulate	PCDD[e]	PCB[f]	PCDF[g]	Other POHC[h]	Total RCF[i]
Baseline	Oil	1	1	1				x		x		
Particulate	Oil + Fe_2O_3	1	2	2			x					
ODCB	1% Cl	1	2	2	x	x		x		x	x	
ODCB	5% Cl	2	4	13	x	x		x		x	x	
ODCB	25% Cl	3	5	14	x	x		x		x	x	
PCB	0.05% PCB	2	6	15	x	x		x	x	x		x
PCB	1% PCB	3	7	25	x	x		x	x	x		x
PCB	10% PCB	3	8	26	x	x		x	x	x		x
PCB	20% PCB	3	9	27	x	x		x	x	x		x

[a] All concentrations are on a weight basis, i.e., % (w/w) of total chlorine in fuel oil mixture, % (w/w) total PCB (Askarel) in fuel oil mixture.
[b] Days between tests are used for analysis (see Table 2).
[c] Destruction and removal efficiency.
[d] Hydrochloric acid.
[e] Polychlorinated dibenzodioxins.
[f] Polychlorinated biphenyls.
[g] Polychlorinated dibenzofurans.
[h] Principal organic hazardous component.
[i] Chlorinated organic.

MONS 006292



KEY:
X - TURNS OFF
S - STARTS
O - OPENS
☐ - BLANK INDICATES EQUIPMENT STAYS ON, ALARM BUZZER SOUNDS

FIGURE 23. Safety interlock system.

Table 24
CONTINUOUS COMBUSTION AND STACK GAS ANALYZERS FOR THE U.S. EPA MOBILE INCINERATOR

Analysis	Component	Sample location	Analyzer	Analysis range	Analysis time
Combustion gas	CO	SCC	Methanizer — GC/FID Bendix model 9220	0—350 ppm	4—5 min
Combustion gas	CO_2	SCC	GC/TC Bendix model 9120	0—10%	5—6 min
Combustion gas	O_2	SCC	GC/TC Bendix model 9120	0—6%	5—6 min
Stack gas	NO_x	Stack	Chemiluminescence Bendix -model 8102	0—500 ppm	On-line
Stack gas	SO_2	Stack	GC/TC Bendix model 9120	0—2000 ppm	5—6 min
Stack gas	THC	Stack	GC/FID Bendix model 9220	0—200 ppm	4—5 min

The Phase II evaluations were completed and showed waste destruction and removal efficiencies for all principal organic hazardous constituents (PHOCs) well above 99.99%.

Table 24 illustrates the continuous combustion and stack gas analyzers that were used for these U.S. EPA mobile incinerator hazardous waste burning tests. Table 25 lists the U.S. EPA trial burn sampling program and Table 26 gives analytical methods for these tests. Table 27 shows the average combustion chamber operating conditions which indicate exceptionally high combustion efficiencies, some of the highest values noted for hazardous waste incinerators operating to meet U.S. EPA TSCA PCB incineration requirements.

Table 28 presents the summary of the PCB waste test burns, generally indicating 99.9999% PCB destruction and removal efficiency and compliance with TSCA regulations.[39]

The U.S. EPA mobile incinerator is also being tested on burning dioxin containing wastes in Missouri. This system is also expected to meet the destruction and removal efficiency for dioxin wastes as per recent U.S. EPA RCRA requirements as it has been proven to comply with TSCA regulations for PCB disposal.

Table 25
SAMPLING PROGRAM FOR TRIAL BURN

Sample	Sampling method and frequency	Analysis
Waste feed	1 composite sample per run (3 grabs)	Elemental (C, H, O, N, S, organic Cl), Density, ash, moisture Conc. of POHCs[a] Presence of PCDD[b], PCDF[c]
Diesel fuel	1 composite sample per lot	Elemental (C, H, O, N, S, organic Cl) Density, ash., moisture
Make-up water	1 sample per test phase	Presence of POHCs, PICs[d]
Alkaline scrubber solution	1 composite sample per test phase	Presence of POHCs, PICs
Purge water	1 composite sample per DRE run, one sample per test	Presence of POHCs, PICs Presence of PCDD, PCDF
	Daily composite	Total organic carbon, pH, temperature
	Weekly grabs	Petroleum hydrocarbons Total suspended solids Volatile organics Total dissolved solids
	Weekly composite	Presence of POHCs
Kiln ash	1 sample per DRE run	Presence of POHCs, PICs Presence of PCDD, PCDF
CHEAF media	1 sample per DRE run	Presence of POHCs, PICs Presence of PCDD, PCDF
Stack sample	EPA, modified method 5; 1 sample per DRE run (3 samples per test)	EPA particulate emission rate POHC emission rate HCl emission rate PIC identification and estimated conc. PCDD, PCDF emission rates
	N.J. incineration method; 3 samples test	N.J. particulate emission rate
	Gas bag, 1 per run	ORSAT for O_2, CO,
	VOST RCI[e] sample; 2 samples per DRE run	Chlorinated organic emission rate
	Visual inspection; 4 6-min observations per DRE run, 30-min observation per particulate run	Opacity (tests 1, 2, and 3)
Site monitoring	1 set of samples per DRE test	PCBs, TCBs (tests 4 and 5)
Personnel monitoring	1 set of samples per DRE test (6 locations)	PCBs, TCBs (Tests 4 and 5)

[a] POHC = Principal organic hazardous constituents (test compounds).
[b] PCDD = Polychlorinated dibenzo-*p*-dioxin.
[c] PCDF = Polychlorinated dibenzofuran.
[d] PIC = Product of incomplete combustion.
[e] VOST RCI = Volatile organic sample train, chlorinated organics.

VIII. FUTURE PCB WASTE DISPOSAL CONCEPTS

Plasma arc high temperature destructors are now under development for PCB and other complex hazardous waste disposal applications. A unique plasma arc destructor is now being developed by the Chemical Waste Management Co. This arc technology process[10] utilizes

MONS 006294

Table 27
AVERAGE COMBUSTION CHAMBER OPERATING CONDITIONS

Parameter	Test no.				
	1[a]	2[b]	3[c]	4[d]	5[e]
Rotary kiln					
Temp. (°C)	900	890	900	980	960
Pressure (kPa)	102	102	102	102	101
Combustion air flow (m^3/min @ STP)	37.1	35.8	35.2	33.7	34.3
Atomization air flow (m^3/min @ STP)	0.7	0.9	0.9	0.9	1.1
Waste flow (kg/hr)	88	92	147	94	98
Diesel fuel flow (kg/hr)	13	15	17	11	14
Injection water flow (ℓ/min)	6.4	5.3	5.7	6.4	5.3
Atomization steam flow (kg/hr)	29	44	45	45	44
Gas residence time (sec)	1.96	2.10	2.06	1.97	2.03
Excess air (%)	104	86	63	92	119
Secondary combustion chamber					
Temp. (°C)	1180	1180	1190	1220	1250
Pressure (kPa)	101	102	102	101	101
Combustion air flow (m^3/min @ STP)	27.5	31.8	31.6	22.4	25.5
Diesel fuel flow (kg/hr)	109	132	137	94	110
Gas residence time (sec)	2.22	2.17	2.14	2.43	2.28
Excess air (%)	69	55	42	59	65
O_2 (dry vol %)	7.54	8.79	8.0[f]	7.21	6.93
CO_2 (dry vol %)	10.6	9.81	10.0[f]	11.1	11.4
CO (dry vol ppm)	<1.0	<1.0	<1.0	<1.0	<1.0
THC (dry vol ppm)	<1.0	<1.0	<1.0	<1.0	<1.0
NO, (dry vol ppm)	41	52	67	51	51
Combustion efficiency (%)	>99.9991	>99.9990	>99.9990	>99.9991	>99.9991

[a] Average results from 2 particulate and 2 DRE test runs.
[b] Average results from 3 particulate test runs.
[c] Average results from 3 particulate and 3 DRE test runs.
[d] Average results from 3 particulate and 3 DRE test runs.
[e] Average results from 3 particulate and 3 DRE test runs.
[f] Average ORSAT analysis at this sampling location.

program is known as the Arc Pyrolysis Project (APP). The project is part of a demonstration project jointly funded by ATC and the Electric Power Research Institute (EPRI). ATC is a joint venture firm formed by Chemical Waste Management, Inc. of Oak Brook, Ill., and Electro-Pyrolysis, Inc. of Wayne, Pa., for the development of this thermal pyrolytic destruction technology.

The facility proposed meets the U.S. EPA definitions of (1) an alternate disposal method and (2) a facility design that is intended for use in more than one EPA region as defined under the regulations promulgated under the Toxic Substances Control Act (TSCA). In accordance with federal regulations, a demonstration test of the process is conducted, under the supervision of the EPA, prior to the issuance of an operating permit. The start-up of the facility involves detailed system tests on nonhazardous materials prior to feeding PCB capacitors.

2. Process Engineering Information

The general arrangement for the APP is shown in Figure 24.

MONS 006295

Table 26
ANALYTICAL METHODS SUMMARY

Analysis	Sample matrix	Methods summary
Ash	Diesel & waste feed oils	Thermal gravimetric analysis
Density	Diesel & waste feed oils	Gravimetric analysis
Elemental analysis	Diesel & waste feed oils	ASTM D-3178, D-3179, E-258, D-3176, D-3177, D-129, D-2361, D-808
HCl	Stack gas (MM5)[a]	EPA method 325.3, specific ion electrode, ion chromatography
Heavy metals	Waste feed oil	Atomic absorption, inductively coupled argon plasma
Moisture	Diesel & waste feed oils	Karl Fisher titration
Opacity	Stack gas	Visual by certified observer
ORSAT	Stack gas	EPA method 3
pH	Purge water	Method 150.1, EPA-600/4-79-020
Particulate, EPA	Stack gas (M5)[a]	EPA method 5
Particulate, NJ	Stack gas	N.J. air test method 1 and incinerator methods
PCDD, PCDF	Waste feed oil	GC/MS[c]
	Make-up & purge water, scrubber solution	Solvent extraction, conc., GC/MS
	Kiln & CHEAF ash	Solvent extraction, conc. GC/MS
	Stack gas (MM5)	Solvent extraction, conc. GC/MS
Petroleum hydrocarbons	Purge water	Method 418.1, EPA-600/4-79-020
PIC	Make-up & purge water, scrubber solution	Solvent extraction, conc., GC/MS
	Kiln & CHEAF ash	Solvent extraction, conc., GC/MS
	Stack gas (MM5)	Solvent extraction, conc., GC/MS
POHC	Waste feed oil	GC/MS
	Make-up & purge water, scrubber Sols.	EPA method 617
	Kiln & CHEAF ash	Solvent extraction, conc., GC/MS
	Ambient air (site & personnel monitors)	NIOSH method P&CAM 244 and S135
	Stack gas (MM5)	Solvent extraction, conc., GC/MS
RCL	Stack gas (VOST)	Thermal desorption, GC/MS
Total dissolved solids	Purge water	Method 160.1,EPA-600/4-79-020
Total organic carbon	Purge water	Method 415.1,EPA-600/4-79-020
Total suspended solids	Purge water	Method 160.1,EPA-600/4-79-020
Volatile organics	Purge water	EPA method 624

[a] Sample collected with EPA modified method 5 sample train.
[b] Sample collected according to EPA method 5 sampling procedure.
[c] Gas chromatography/mass spectrometry.

a direct current electric arc furnace with a molten steel bath maintained at temperatures near 3000°F into which hazardous materials such as PCB-contaminated capacitors can be fed. At these temperatures the capacitors melt immediately and the PCBs pass through the electric arc plasma at ultrahigh temperatures and are destroyed. The gases formed from the destruction of the organic material pass up through a hollow electrode and then through a conventional treatment process. Scrubbed gases containing residual hydrogen are flared using conventional techniques.[39]

A. Arc Technologies Company Arc Pyrolysis Project[40]

1. Description of the Project

Arc Technologies Company (ATC) proposes to construct commercial size facilities (Figure 24) for the thermal destruction of whole PCB capacitors. The facility design and construction

Table 28
TESTS 4 AND 5 STACK EMISSIONS

Parameter	Test no 4[a]	Test no 5[a]
Waste feed		
Trichlorobenzenes (kg/hr)	3.8	15.1
Trichlorobenzenes (kg/hr)	0.6	2.9
Aroclor® 1260 (kg/hr)	6.6	22.7
Stack emissions		
Temperature (°C)	78	78
Flow rate (m^3/min)	200	208
Flow rate (m^3/min @ STP, dry)	86.2	90.5
Particulate matter (g/hr)[b]	140	165
Particulate matter (mg/m^3)[b]	35.2	42.7
HCl (ppm)	0.13	0.18
HCl (mg/m^3 @ STP, dry)	0.20	0.26
HCl (g/hr)	1.12	1.50
HCl removal efficiency (%)	99.98	99.99
Trichlorobenzenes (ppb)	<0.15	<0.23
Trichlorobenzenes (µg/m^3 @ STP, dry)	<1.1	<1.6
Trichlorobenzenes (g/hr)	<0.006	<0.010
Trichlorobenzenes DRE (%)	>99.9998	>99.99993
Tetrachlorobenzenes (ppb)	<0.07	<0.07
Tetrachlorobenzenes (µg/m^3 @ STP, dry)	<0.63	<0.59
Tetrachlorobenzenes (g/hr)	<0.004	<0.004
Tetrachlorobenzenes DRE (%)	>99.9994	>99.99985
Aroclor® 1260 (ppb)	<0.15	<0.23
Aroclor® 1260 (µg/m^3 @ STP, dry)	<2.1	<3.3
Aroclor® 1260 (g/hr)	<0.013	<0.020
Aroclor® 1260 DRE (%)	>99.9998	>99.99991
Total HCl (µg/m^3 @ STP, dry)	<66	<66
Total HCl (g/hr)	<0.39	<0.41

[a] Average results from 3 DRE test runs.
[b] Average results from 3 separate particulate test runs.
[c] Corrected to 7% O_2 in accordance with RCRA.

The process proposed utilizes direct current (DC) arc furnace technology for the destruction of whole utility capacitors containing PCBs. Figure 25 is a block flow diagram of the process.

The destruction system concept may be summarized as follows.

PCBs have high thermal stability and to assure total destruction, federal regulations require combustion temperatures of 1200 to 1600°C (2192 to 2912°F) depending on residence time. Conventional combustion systems have several problems which include difficulty in continually maintaining temperatures as high as 1600°C (2912°F), generation of large gas volumes to be scrubbed, and difficulty in handling solids at these high temperatures.

Destruction of PCB capacitors presents additional problems in that PCB liquids are absorbed in the capacitor core and are retained on the metal surfaces. Present disposal methods require opening the capacitor and handling the PCB-contaminated solids and fluids separately or, alternatively, shredding the capacitors.

The proposed capacitor destruction system eliminates all of the above problems. The system concept, based on arc furnace technology, has been specifically directed to destruction of PCB capacitors by designing a sealed system operating under pyrolytic conditions (low oxygen levels) and utilizing materials compatible with the ultrahigh temperature environment

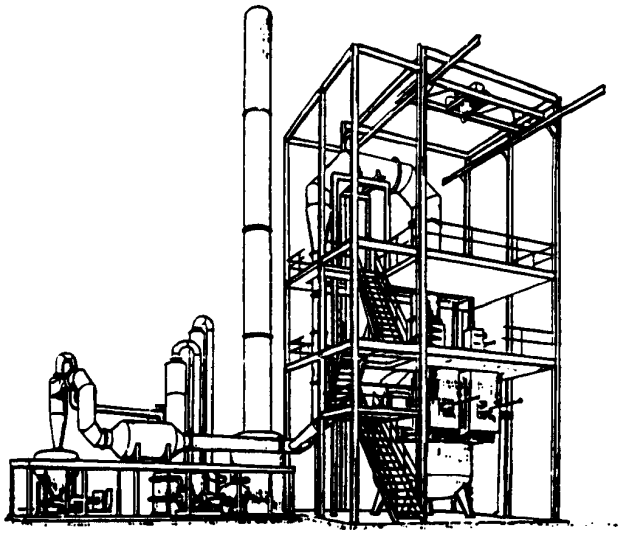


FIGURE 24. Arc pyrolysis system — general arrangement.

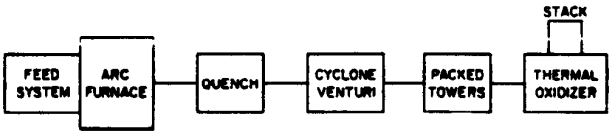


FIGURE 25. Process flow diagram — Arc pyrolysis system.

found in the plasma zone of the arc furnace. Figure 26 presents a sketch of the arc furnace, identifying the different temperature destruction zones.

Basically, the process is one in which the whole unopened PCB capacitor will be fed into a molten metal bath (zone 1). The capacitor shell will melt and the internal organic components will pyrolize. In the region above the molten bath (zone 2), the released gases will be subjected to intense UV radiation and heat from the arc plasma. The decomposition products will then be directed through the arc plasma (zone 3) to the vicinity of the high current DC arc (zone 4). EPA guidelines indicate that PCBs are totally destroyed at 1600°C (2912°F) in the absence of oxygen and are converted to environmentally acceptable gases. The direct current arc pyrolysis approach decomposes liquid PCBs and other organic components to CO, H_2, HCl, and solid carbon. The action on the inorganic materials in capacitors will produce an inert solid residue from which the metals may be recovered, if desired.

MONS 006298

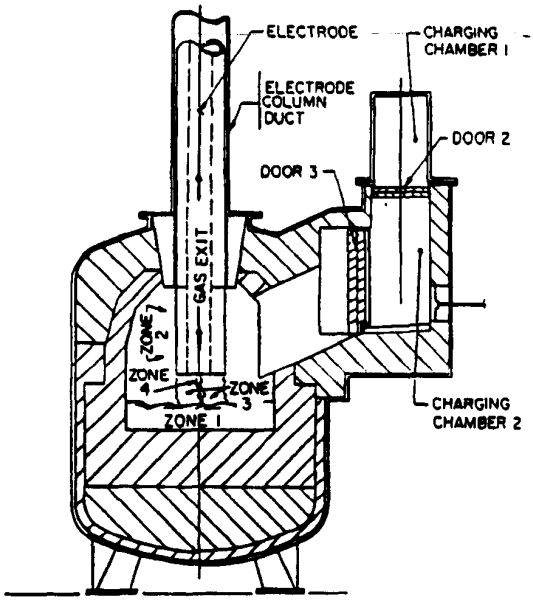


FIGURE 26. Furnace cross section.

The pyrolysis process converts the organic constituents to by-products that will be removed/destroyed from the exit gas stream before release to the atmosphere. The gas products of the process are cleaned and treated by a gas cleaning system to produce environmentally acceptable air emissions.

3. Destruction Process

The capacitor destruction facility will consist of three major equipment systems:

- Arc furnace system
- Gas handling system
- Power supply system

Additionally, the facility will include a number of support systems required for material handling and various ancillary functions:

MONS 006299

- Capacitor handling system
- Tapping system
- Cooling water system
- Nitrogen gas supply
- Propane gas supply
- Scrubber liquid and waste solid handling
- Personnel support

4. Arc Furnace

The arc furnace is designed, utilizing a blend of existing and new technologies as a sealed thermal waste destruction unit. DC electrical power will be utilized as the energy source to form a high energy electric arc which will supply thermal and other types of energy to melt the capacitors and destroy the PCB compounds they contain.

The furnace will utilize DC power, rather than AC, because it offers greater stability as a continuous rather than a pulsed arc and better process control characteristics, resulting in reduced operating costs for consumables such as electrodes. A sealed furnace design was selected to create pyrolytic thermal destruction with the exclusion of oxygen. The gas volume emitted from the furnace will be relatively small, since no CO_2 and only small amounts of N_2 will be present. This feature represents a substantial savings in both equipment and operating costs for the gas-handling equipment if compared to those required for a conventional incinerator with equivalent destruction capacity. Additionally, the pyrolytic process prevents the formation of NO_x.

The furnace shell will be constructed of 1-in. thick carbon steel and will be of all welded construction. It will be lined with refractory materials specially selected to resist the high temperature gaseous and liquid conditions inside the furnace. The furnace shell will have a number of sealed openings which will be for:

- Capacitor charging
- Tapping (molten material removal)
- Electrode entry and exit gas duct
- Emergency pressure relief
- Monitoring instruments

Regular inspections with a combustible gas detector will be performed on the externally accessible seals.

A design requirement of the arc furnace is to equal or exceed the destruction performance requirements established by the EPA for PCB incineration processes. The EPA has established minimum acceptable guidelines for temperature and residence time to assure a 99.9999% thermal destruction efficiency for PCBs.

Table 29 provides a comparison of the EPA requirements for alternative technology processes to the design performance of the arc furnace. Considerations evaluated during the design of the arc furnace that determine destruction efficiency include interior cavity volume, system pressures, volume of gas produced during decomposition, and interior temperatures.

The volume of gas produced by the destruction of the capacitor is dependent on the physical size of the capacitor (see Figure 27). The total gas produced by pyrolysis consisting of H_2, CO, and HCl gas ranges from 10.34 to 10.785 standard ft^3/lb of capacitor. The variability in the range is dependent on the type of core used in the capacitor, with paper core having the lower and film core having the higher gas production rates. Therefore, generated gas would range from 310 to 1833 ft^3 for capacitors that range in weight from a minimum of 30 lb to a maximum of 170 lb.

The internal cavity temperature is estimated to be equal to or greater than 1600°C and

MONS 006300

Table 29
DESIGN OF THERMAL DESTRUCTION CONDITIONS[a]

Parameter[b]	Design	EPA requirement alternative technology	Incineration
Destruction temp. (°C)	>1,600	N/R[c]	1,200
Residence time (sec)	[d]	N/R	[e]
Destruction removal efficiency (DRE)	≥99.9999%	99.9999%	99.9999%
Excess O_2(%)	0	N/R	[f]
HCl removed (%)	99.95	N/R[d]	Scrubber
Emissions			
CO	1.76 lb/hr	N/R	N/R
Particulates	0.0	N/R	N/R
Opacity	<20%	N/R	N/R

[a] Approval of alternative thermal destruction process (40 CFR 761.60(e)) requires a demonstration that the method can achieve a level of performance equivalent to EPA-approved incinerators or high efficiency boilers as defined in 40 CFR 761.70.
[b] Only the common parameters between the APP and EPA criteria are listed.
[c] N/R identifies no requirement for alternative technology processes.
[d] EPA requires use of scrubber for removal of HCl.

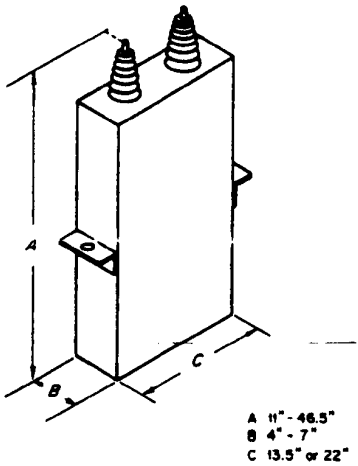


FIGURE 27. Typical capacitor shape.

MONS 006301

will be controlled by the temperature of the molten bath. Prior to exiting the furnace, the gases will have to pass through zones of higher temperature representative of the arc plasma and the arc itself. The arc will emit UV radiation which will assist in the breakdown of PCB gas molecules.

a. Electrodes

Both a positive and a negative electrode will be required to form the electric arc. The furnace's positive electrode (anode) is an integral part of the furnace shell design and will be formed by the molten metal/interior lining combination of the furnace hearth.

The negative electrode (cathode) will be a 30-in. O.D. (outer diameter) cylinder having a 15-in. I.D. (inner diameter) opening running through the center. It will be constructed from graphite in 6-ft long sections with male and female threaded ends. The electrode will be inserted into the furnace through a sealed opening in the furnace top. A hydraulically activated assembly above the furnace will grip the electrode and automatically move it up and down to control arc length (and energy input) as commanded by the furnace's automatic control system. This assembly will also allow precise, gradual advancing of the electrode sections as the electrode is consumed in the thermal destruction process. Besides its electrical importance, the hollow-centered electrode will also serve as the exit duct for gases produced in the thermal destruction process.

The portion of the electrode above the furnace top will be surrounded by a water-cooled, sealed conduit which will prevent the escape of furnace gases into the atmosphere. The conduit will be constructed of telescopic sections which will maintain the gas-tight seal while moving to compensate for movement of the electrode. As an additional safety measure, the annulus between the exterior wall of the electrode and interior wall of the conduit will be continuously purged with nitrogen to minimize any furnace gases reaching the seal area. A flammable gas detector will be located in this vicinity to assure the continued integrity of these seals.

b. Gas Handling Duct Work

A sealed duct work system directs the hot gases from the top of the electrode column to the downstream gas cleaning system. In addition, the refractory-lined duct acts as a cooling section, allowing the hot furnace gas to cool by radiation to approximately 1000°C (1800°F) prior to reaching the gas cleaning system.

The arc furnace's emergency pressure relief duct, which will provide overpressure protection to the furnace shell is connected to the main duct upstream of the gas cleaning train. As described in the previous section, gases generated during capacitor destruction normally exit the furnace through the center of the electrode. If the electrode center passage becomes blocked, the pressure inside the furnace will begin to increase as gases are generated. Prior to the emergency pressure relief duct opening, a high pressure condition will first activate an alarm which will allow the operator to discontinue capacitor charging and shut down DC power supply until the problem is rectified. If the furnace pressure continues to rise and reaches 10 psi, the emergency pressure relief valve will automatically open to vent gas directly to the gas handling system. The opening of this bypass will automatically sound an alarm and shut down the capacitor charging and DC power supply systems (if not already accomplished by the operator). The gases vented during emergency bypass operation will be at elevated temperatures. The emergency gas handling system is designed to handle the exposure to these temperatures without damage.

Since the gases will be exposed to the ambient temperatures of the arc furnace destruction chamber, approximately 1600°C (2912°F), bypassing the blocked electrode will not adversely affect the minimum PCB destruction efficiency.

MONS 006302

c. Capacitor Charging Units

Since the arc furnace is a sealed pyrolysis unit, capacitors will be added to the furnace while excluding the entrance of outside air. Two capacitor addition, or "charging" units will be used to maintain a balanced feed to the system.

The two capacitor charging units will be mounted side by side and will be identical in construction and performance (see Figure 25). Each unit consists of two chambers, one chamber mounted above the other, designed to accept the smallest to the largest capacitors known to be in use in the U.S. Each two-chambered feed unit will have three doors. Door 1 will be opened to allow a capacitor to be fed into the first (upper) chamber by the charging unit operator. Door 2 is intermediate and will allow automatic transfer of the capacitor from the upper chamber to the lower chamber. Door 3 will open the lower chamber to the furnace interior and allow the capacitor to be automatically fed into the furnace.

The flow of outside air into the furnace and release of furnace gases through the capacitor charging units is eliminated by the use of a nitrogen (N_2) purging system.

After the capacitor is loaded into the first compartment, the door is closed and nitrogen is automatically introduced into the compartment. At this point, the blower is shut off and nitrogen continues to pressurize the compartment. When the pressure reaches 4 psi, the nitrogen is automatically shut off and the capacitor charging sequence is continued.

The lower chamber of each charging unit will have a hydraulically activated "iron maiden", a set of specially designed steel spikes, which will automatically puncture each capacitor while it is inside the lower chamber prior to charging into the furnace. Perforation of the capacitor will prevent the formation of pressure inside the casing, capable of rupturing the capacitor when it is transferred into the molten bath of the furnace, and will also decrease the decomposition time of the capacitor.

Additionally, each charging unit will have a hydraulically operated ram to automatically push the capacitor from the lower chamber into the furnace. The three doors, iron maiden, and ram will be equipped with limit switches to sense that the devices have operated properly. These switches, along with the rest of the charging unit's control system, will be designed to achieve automatic operation in a prescribed sequence which will not be allowed to continue if one item in the sequence operates improperly.

d. Gas Handling System

The gas handling system (Figure 28) will receive the pyrolysis gases from the arc furnace system. The system will cool the gas, remove HCl, remove particulates, and combust the CO and H_2 gas produced in the pyrolysis process. The system is a skid-mounted modular design and will require minimal field installation. Fabrication, assembly, and initial testing will be performed in the manufacturer's shop. The gas-handling system consists of the following units: quench chamber, dry separator, cyclonic separator, venturi scrubber, packed towers, scrubber recycle tank, and afterburner.

e. Electric Power Supply System

There are four electrical power systems associated with the overall arc furnace system: the high voltage AC power system, the main DC power supply system, the low voltage AC auxiliary power system, and the low voltage emergency power system.

i. DC Power Supply System

The DC power supply system receives high voltage AC electric power from the supplying utility and converts and delivers DC electric power to the arc furnace.

Control of the power output of this DC power conversion equipment will be performed automatically by the arc furnace electrode regulator and/or manually by the furnace operator from the control panel in the instrumentation and control house. Electrical interlocks on the

MONS 006303

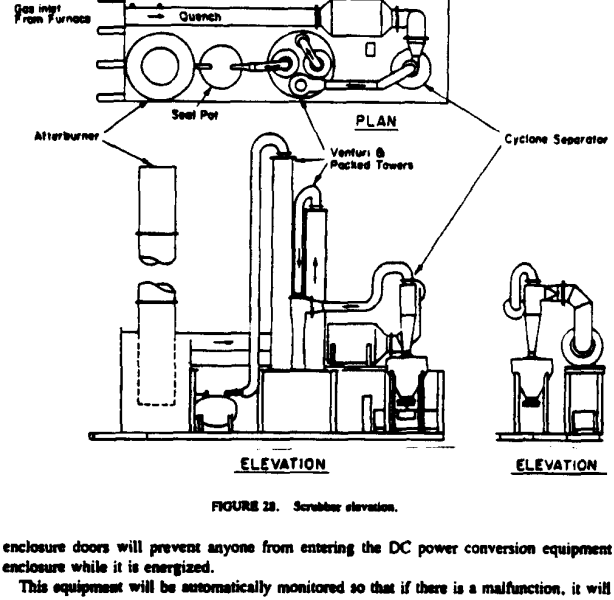


FIGURE 28. Scrubber elevation.

enclosure doors will prevent anyone from entering the DC power conversion equipment enclosure while it is energized.

This equipment will be automatically monitored so that if there is a malfunction, it will be quickly and safely shut down by its own automatic controls. An annunciator will alert the operator that there is a problem and pinpoint the reason for the alarm.

ii. AC Auxiliary Power System

Transformers will be provided for 480-V three-phase AC power for motors and other use where required. A dry type 120/240 V, 480 V transformer will provide lower voltage power for lights, control circuitry, and other components requiring lower operating voltages.

iii. Emergency Power System

A 100-kW emergency diesel generator with automatic open circuit transfer switches will be employed in order to ensure that essential emergency power is available in the event that utility power is lost. The generator will automatically start when utility power is lost. When utility power is restored, synchronizing equipment will be provided so that a closed transfer of auxiliary power may be made by the operator.

f. Instrumentation and Control Equipment

Instrumentation and control equipment will be located in a prefabricated control house containing everything that is necessary to operate, control, and monitor the arc furnace system. Control and power feed wiring will be run in a weatherproof conduit from the

MONS 006304

control house to the arc furnace, gas handling equipment, high voltage switchyard, DC power conversion equipment, and other required areas.

g. Closed-Circuit Cooling Water System

Cooling water will be supplied by means of a closed-loop system with a fin-type heat exchanger. This system will recirculate 650 gal/min to provide cooling to equipment such as the DC power cables, the conduit enclosing the electrode, the recycle scrubber liquids, heat exchanger, etc.

In the event of a power failure, the cooling water system will be powered by the emergency generator to ensure that cooling water continues to be provided.

h. Hydraulic System

An integrated hydraulic system will be provided to supply hydraulic fluid to the various cylinders which raise and lower the electrode or operate the doors, iron maiden, and ram in the capacitor charging units.

The system will be designed with sufficient accumulator capacity to close the furnace charging units' doors and automatically place the entire system in an environmentally safe condition in case of emergency shutdown.

i. Furnace Tapping Equipment

Approximately once every 8 hr the molten metal and slag material inside the arc furnace will be removed by a procedure known as "tapping", utilizing equipment arising from standard metal industry techniques.

The mold cart will ride on rails and is specially designed for easy removal of the cooled "ingot". This mold cart will be lined with refractory material and have an additional graphite lining for protection in the metal and slag impact area. Prior to each tap, the mold cart will be relined with mold sand in key areas in accordance with modern steel mill practice.

When tapping is complete, the tap hole will be replugged with a carbon tap plug. The mold car will be towed into a cooling area. A crane will be used to move the ingot when solidified, into a lay-down yard from which ingots will be loaded onto trucks for transport to disposal or reuse. The tapping and mold preparation areas will be roofed.

REFERENCES

1. USEPA activities under the Resource's Conservation and Recovery Act of 1976, Annu. Rep. to the President and the Congress for Fiscal Year 1978, SW-755, U.S. Environmental Protection Agency, Washington, D.C., March 1979.
2. USEPA Hazardous Waste Generation and Commercial Hazardous Waste Management Capacity, P. #III-3, Appendix C-2, SW-894, U.S. Environmental Protection Agency, Washington, D.C., December 1980.
3. PCB Waste Disposal at Peerless Cement International, Semiannual Report, Michigan-Ontario Air Pollution Board, April 3, 1978.
4. MacDonald, B. L., PCB Perspectives, paper given to the Eastern New York chapter of the Air Pollution Control Association, Colonie, New York, November 16, 1982, General Electric Co., Corporate Environmental Issues Project, Fairfield, Conn.
5. Shen, T. T. and Sowell, G. H., Air pollution problems of uncontrolled hazardous waste sites, presented at the 3rd Natl. Conf. Hazardous Waste Sites, Washington, D.C., November 29, 1982.
6. USEPA interim status standards for hazardous waste incinerators and hazardous waste and consolidated permit regulations, *Fed. Regist.*, Part 265, December 18, 1978; May 19, 1980; January 23, 1981; June 24, 1982.
7. New York State Environmental Facilities Corporation, Technical Marketing and Financial Findings for the NYS Hazardous Waste Management Program, prepared by Camp, Dresser & McKee Environmental Consultants, #III-12, 1980.

MONS 006305

8. *Federal Register*. 44(106), 31514, 1979.
9. Shen, T. T., Air quality assessment for land disposal of industrial wastes. *Environmental Management*. Vol. 6. Springer-Verlag. New York, 1982, 297.
10. NYSDEC memo to Hovey, H. from Lauber, J., PCB Emissions from Landfills and Cement Kilns. February 26, 1980, based on diffusion calculations by Shen, T. T., Cement Kiln PCB Emission Values Updated, Lauber, J., New York State Department of Environmental Control, Albany, December 22, 1982.
11. Sworsyn, E. M. and Ackermann, G., Jr., Draft Interim Guidelines for the Disposal/Destruction of PCB's and PCB Items by Non-Thermal Methods, TRW Environmental Engineering Division for USEPA Industrial Engineering Research Laboratory, U.S. Environmental Protection Agency, Washington, D.C., 1980.
12. PCBX, chemical destruction of PCB's, May 16, 1980 report, PCBX is a Better Environmental Solution, Sun Ohio Oil Co., Canton, Oh.
13. Chen, K., The Reclamation of PCB-Contaminated Transformer Oils by the Sun Ohio PCBX process, Report No. TVA/OP/EDT-82/45, Tennessee Valley Authority Office of Power, Division of Energy, Demonstrations and Technology, Chattanooga, Tenn., March 1982.
14. PCB Destruction Process — Executive Summary, a report to R. T. Dewling, Acting Regional Administrator — USEPA Region II, Acurex Waste Technologies Inc., Mountainview, Calif., November 13, 1981.
15. Test Report for PCB Destruction Process — September 9, 1981 — Hamlet, Ohio, Reported October 16, 1981 to USEPA by Acurex Waste Technologies Inc., Mountainview, Calif.
16. Guidelines for the Disposal of PCB's and PCB Items by Thermal Destruction, prepared by USEPA Industrial Environmental Research Laboratory, EPA-600/2-81-022, NTIS# PB81-182339, U.S. Environmental Protection Agency, Washington, D. C., February 1981.
17. Incineration of PCB's — Summary of Approval Actions, Energy Systems Co. (ENSCO), Eldorado, Ark., *USEPA Region VI Air & Hazardous Materials Section, Solid Waste Branch, Dallas, Tex., February 6,* 1981.
18. PCB Disposal by Thermal Incineration — USEPA Region VI, EPA-906/9/82/003, NTIS# PB82-241860, Dallas, Tex., February 1982.
19. Determination of Destruction & Combustion Efficiencies of a Land Based Incineration Plant, Report of the National Agency of Environmental Protection Ministry of the Environment, Copenhagen, 1979.
20. Thayer, J. H., Grandfield, A. C. et al., Introduction to the unique thermal oxidizer at General Electric Company, Pittsfield, Mass., Paper 83-51.6, Air Pollution Control Assoc. Annu. Meet., Atlanta, June 21, 1983.
21. Evaluation of PCB Destruction Efficiency in an Industrial Boiler, General Motors Corp., Warren, Mich., OCA Corp., OCA Technology Division, Bedford, Mass., Study for USEPA Official Research & Development, Contract #68-02-3168, U.S. Environmental Protection Agency, Washington, D.C., November 1980.
22. Lauber, J. D., Burning chemical wastes as synthetic fuels in cement kilns, presented at the Air Pollution Control Assoc. Annu. Meet., Philadelphia, June 21, 1981.
23. McDonald, L. P., Skinner, D. J., Hopton, F. J., and Thomas, G. H., Burning Waste Chlorinated Hydrocarbons in a Cement Kiln, Canadian Environmental Protection Service Report No. EPS-WP-77-2, Toronto, March 1977.
24. Director's Report to the Environmental Assessment Board Regarding Burning of Polychlorinated Bi-phenyls at St. Lawrence Cement, Mississauga, Ontario Ministry of the Environment, Toronto, December 1978.
25. Application of 6 NYCRR-Part 212-Toxic Air Contaminants, Air Guide 1, New York State Department of Environmental Conservation, Albany, November 15, 1982.
26. Bluh, M. W. and Asher, D., Safe disposal of PCB's Nat. Conf. Treatment and Disposal of Industrial Waste Waters and Residues, Houston, Tex., April 26, 1977.
27. Ahling, B., Destruction of Chlorinated Hydrocarbons in a Cement Kiln, Vol. 13, No. 11, Swedish Water and Air Pollution Research Institute, Environmental Science and Technology, Stockholm, November 1979.
28. Letter to Lauber, J. from Ahling, B., Swedish Water and Air Pollution Research Institute, Stockholm, March 11, 1983.
29. Lauber, J. D., Burning chemical wastes as fuels in cement kilns, *Air Pollution Control Assoc.*, 32(7), July 1982.
30. Wenga, P., The role of cement kilns in hazardous waste management, the Norwegian experience, 1st Int. Conf. Industrial Hazardous Waste, Toronto, Ontario, Canada, October 18, 1982.
31. Rappe, C., Marklund, S. et al., Polychlorinated dioxins (PCDD's), dibenzofurans (PCDF's) and other polynuclear aromatics (PCPNA's) formed during PCB fires, *Chem. Scripts*, 20, 56, 1982.
32. California Air Resources Board, Agenda items #81-4-1, Public meeting to discuss proposed air resources board policy regarding incineration as an acceptable technology for PCB disposal, date of release — February 23, 1981, scheduled for consideration March 25, 1981, California Air Resources Board, Sacramento.

MONS 006306

33. Preliminary Report Research Permit for Incineration at Sea of PCB Waste. Hg 81-002 Results of Test Burn on *M/T Vulcanus*. U.S. Environmental Protection Agency. Washington, D.C., May 20, 1982.
34. **Ross, R. D.,** Hazardous waste incineration aboard the *M/T Vulcanus*. NSWMA 11th Annu. Conf. Waste Technology. October 13, 1982.
35. Annex IV rules on incineration at sea. Convention for the Prevention of Marine Pollution by Dumping from Ships & Aircraft. 7th Meet. Oslo Commission. Brussels, Belgium, June 10, 1981.
36. USEPA Fact Sheet, U.S. Environmental Protection Agency. Washington, D.C., April 1982.
37. **Brugger, J. E., Yezzi, J. J., et al.,** The EPA-ORD Mobile incineration system: present status. Proc. Hazardous Material Spills Conf., April 19, 1982.
38. **Sweet, W. E., Ross, R. D., and Vanderveide, G.,** Hazardous waste management. *J. Air Pollution Control Assoc.*, February 1985.
39. **Yezzi, J., Brugger, J. et al.,** Results of the initial trial burn of the EPA-ORD mobile incineration system. Proc. Natl. Waste Processing Conf., American Society of Materials Engineering. New York, 1984.
40. **Wittle, J. K.,** personal communication. Electro-Pyrolysis, Inc., this work was conducted by Arc Technologies Co. and was co-funded by the Electric Power Research Inst. and Chemical Waste Management, Inc.

MONS 006307

Chapter 6

THE GREAT LAKES ECOSYSTEM — MODELING OF THE FATE OF PCBs

Robert V. Thomann, John P. Connolly, and Nelson A. Thomas

TABLE OF CONTENTS

I. The PCB Problem in the Great Lakes 154
A. Concentration in the Fish 154

II. Inputs of PCBs to the Great Lakes 155
A. Atmospheric Input 157
B. Tributary Input 159
C. Municipal and Industrial Inputs 160
D. Total PCB Load 160

III. Model of Physical-Chemical Fate of PCBs 161
A. Theory 161
B. Data and Model Results 164

IV. Model of Fate of PCBs in Aquatic Ecosystems 167
A. Theory 167
B. Application to Lake Michigan 169
1. Basic Model 169
2. Inclusion of Benthic Component 170

V. Effect of Solids-Dependent PCB Partitioning and Sediment Diffusion on PCBs 171
A. Introduction 171
B. Sensitivity of PCBs Calculation for Great Lakes 172

VI. Human Exposure Through Fish Consumption Contaminated with PCBs 177

Acknowledgments 178

References 178

MONS 006308

I. THE PCB PROBLEM IN THE GREAT LAKES

A. Concentration in the Fish

The Great Lakes represent one of the most significant inland freshwater systems of the world and one of sizeable economic and ecological importance to both the U.S. and Canada. Figure 1 shows the location of the lakes and Table 1 details their principal physical limnological features. The concentration of polychlorinated biphenyls (PCBs) in the water, sediment, and aquatic ecosystem of the Great Lakes has been a matter of concern for a number of years.[18] For example, the elevated concentrations of PCB in the fishes of Lake Michigan, particularly the lake trout *(Salvelinus namaycush)* were a matter of significant regulatory action. Concentrations of PCBs in the lake trout in 1971, for example, ranged from 5 to 20 μg/g (weight), substantially above the U.S. Food and Drug Administration (FDA) guideline of 2 μg/g in the edible portion of fish. Several fishing bans have been issued concerning the consumption of fish contaminated with PCBs. In 1978, commercial fishermen in Lake Michigan harvested more than 43 million lb of alewife for fish meal. But in 1980, the catch dropped dramatically because of recognition that the PCB concentration of alewives exceeded the FDA guideline of 2 μg/g for fish meal.[2] This particular chemical had been in use within the Lake Michigan drainage basin for more than 20 years when it was restricted in sales (except for minor uses) in 1971. A full ban was instituted several years later.

Neidermeyer and Hickey[20] analyzed the PCB concentration in museum specimens of small fish from Lake Michigan and observed a marked increase beginning in the 1950s. Their results are shown in Figure 2 together with additional data on PCB concentration from the U.S. Fish and Wildlife Service (USF & WLS). Concentration appears to peak in the early 1970s at the approximate time when a ban on the use of PCBs was initiated.

The PCB concentration in lake trout for several Great Lakes is shown in Figure 3. As shown for the period indicated, the PCB concentration of the lake trout for Lake Michigan was the highest followed by Lake Ontario. The uppermost Great Lake, Lake Superior, and Lake Huron each has reported concentrations of less than 1 μg/g.

The PCB concentration in the lake trout of Lake Michigan also displayed a relationship with age as shown in Figure 4. For 1971 and 1975, there is a decided trend toward increasing concentration with age. The initial high concentrations of 10 to 12 μg/g for the 2- to 3-year-old age class followed by a decline in the 4-year-olds may be the result of exposure to higher water concentration in near-shore areas.

The PCB concentrations for other fish in Lake Michigan during 1971 as measured by Veith[42] are shown in Figure 5. Thirteen species of fish were taken from 14 regions and analyzed for PCBs. Additional parameters included the weight, length, and percent fat of the fish. As shown in Figure 5, there is an apparent relationship between weight and concentration (with the exception of the principal detrital feeders such as carp and the suckers). The apparent relationship with weight may reflect differing positions in the food chain. The highest concentration reported was for the lake trout (#8). The redhorse sucker (#5), white sucker (#6), whitefish (#7), and carp (#9) all have relatively low concentrations of PCBs. This undoubtedly reflects the simple food chain structure of these primarily herbivorous and bottom feeding species. Analysis also indicated that there was no apparent relationship between the PCB concentration and the mean species percent lipid. This probably reflects a confounding of lipid concentration and trophic level position. Thus, although the bloater (#4) has the highest mean species percent lipid (20 ± 5.9%), the mean PCB concentration is only 6 μg/g.

The time variation of PCB in the smelt of the five Great Lakes is shown in Figure 6 and indicates an apparent declining trend in PCB concentration in lakes such as Michigan and Ontario.

MONS 006309

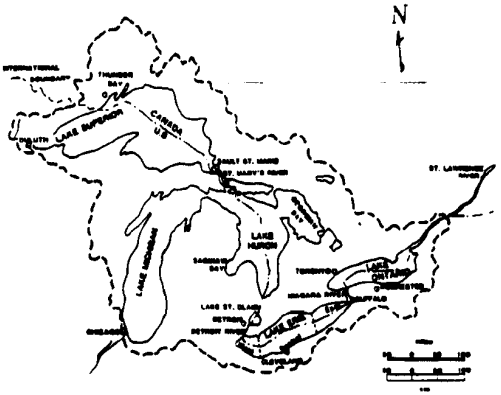


FIGURE 1. The Great Lakes.

Table 1
PHYSICAL LIMNOLOGICAL CHARACTERISTICS OF THE GREAT LAKES

Lake or region	Volume (km^3)	Depth (m)	Surface area (km^2)	Flow	
				In (m^3/sec)	Out (m^3/sec)
Superior	11,326	137	82,882	2,033	2,033
Michigan	4,717	82	57,772	1,470	1,470
Huron	3,278	56	61,659	3,303	4,967
Erie	496	18	24,996	4,967	5,692
Ontario	1,666	86	19,485	5,692	6,740

All of these data show the distribution of PCBs in important fish species in the Great Lakes, the accumulation to high concentration in the upper trophic levels, especially in Lakes Michigan and Ontario, and the apparent decline or beginning of a decline from the early 1970s to the late 1970s.

II. INPUTS OF PCBs TO THE GREAT LAKES

The principal external sources of PCBs to the Great Lakes are

1. Atmospheric input from precipitation and dry deposition
2. Tributary inputs representing up-basin discharges of PCB and subsequent transport to the Lakes
3. Direct inputs of municipal and industrial PCB loads to the Lakes

Thomann and Di Toro[41] have summarized the expected loads from these sources.

MONS 006310

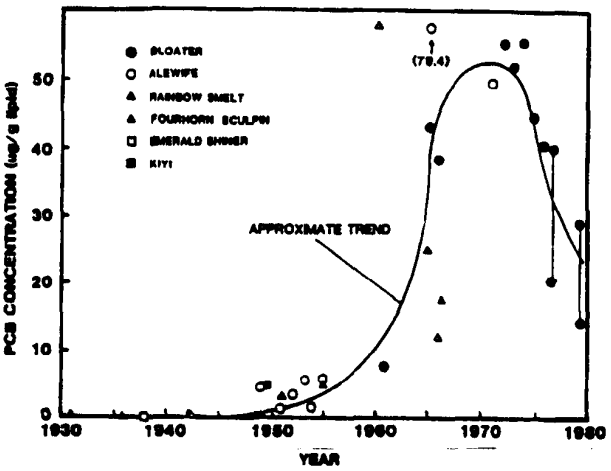


FIGURE 2. Historical trend of PCB concentration in small fish of Lake Michigan.[29]

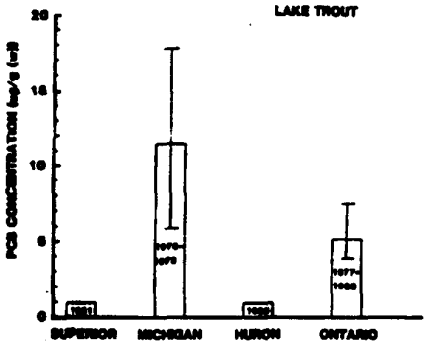


FIGURE 3. Recent (1975 to 1980) PCB concentration in lake trout for different Great Lakes. Bar is approximate mean over period indicated, range shown for Lakes Michigan and Ontario is annual mean variability.

MONS 006311

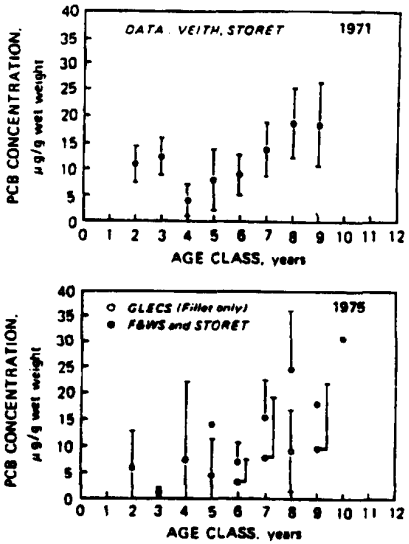


FIGURE 4. PCB concentration in Lake Michigan lake trout as a function of age class for 1971 and 1975.

A. Atmospheric Input

The concentration of PCBs in precipitation over the Great Lakes has been determined by Murphy and Rzeszutko[37] and Strachan and Huneau.[38] These results and the data reported by Wells and Johnstone[40] are summarized in Table 2.

As seen, the mean concentrations differ by almost a factor of five which may reflect sampling or analytical variations. (The reported concentration for the east coast of Scotland is included for reference.) Strachan and Huneau[38] reported significantly different levels for the various stations located in the lake's basins, i.e., mean values of 26 ng/ℓ for Superior, 11 ng/ℓ for Huron, 9 ng/ℓ for Erie, and 32 ng/ℓ for Ontario. Because of the variability in reported values of PCB precipitation concentration, a range of 10 to 100 ng/ℓ was chosen for an input load estimate.

Dry deposition has been estimated by Eisenreich et al.[9] for Lake Superior. In their estimate, 10% of the measured PCB air concentrations (range 0.1 to 10 ng/m³) was assumed to be in the particulate form and a deposition velocity of 0.005 m/sec was used. The input of PCBs to Lake Superior then from dry deposition was estimated at 0.1×10^3 to 1×10^3 kg, which for a surface area of 8.21×10^{10} m² is an areal loading of from 1.2 to 12 g PCB/km²/year. This range in the areal dry deposition rate was used for the calculations described below. On an areal basis, the total atmospheric input due to wet and dry deposition is then in the range of 9 to 90 g PCB/km²/year.

MONS 006312

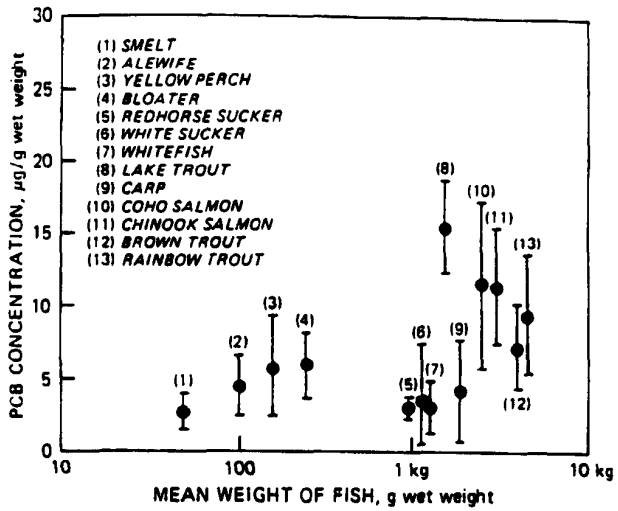


FIGURE 5. PCB concentrations (whole fish) for Lake Michigan as a function of weight.[48]

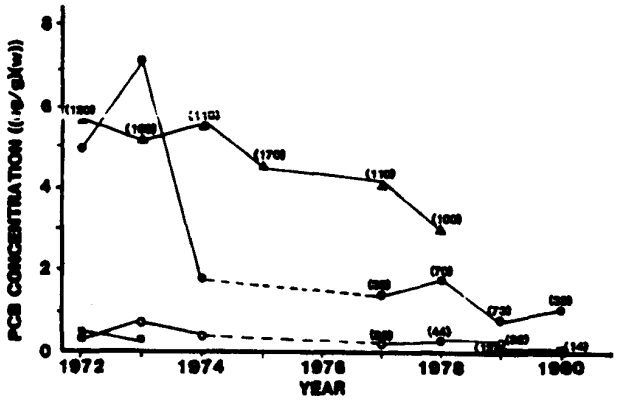


FIGURE 6. Time variation of PCBs in smelt for the Great Lakes. Numbers in parentheses indicate number of fish. Key: (closed square) Superior, (closed triangle) Michigan, (open square) Huron, (open circle) Erie, (closed circle) Ontario.

MONS 006313

Table 2
CONCENTRATIONS OF PCBs IN PRECIPITATION

Location	Mean	Conc. (ng/ℓ); no. of samples	SD	Range	Ref.
Lake Michigan	111	35			27
Lakes Superior, Huron, Erie, and Ontario	21		30		35
East coast Scotland	15	—	—	1.8—74	45

Table 3
PCB CONCENTRATIONS IN GREAT LAKES TRIBUTARIES[a]

Lake or region	Total water (ng/ℓ)	PCB conc. on susp. solids (ng/g)	Remarks	Ref.
Superior	27		Calc. from reported tributary load of 1740 kg/year	21
		20 (10—30)	Mean and range of Canadian tributaries (1975)	14
Michigan				
Platte River	15		Aroclor® 1254	21
Huron				
Cheboygan River	500			21
Saginaw River	74		1979 mean and range*	
		84 (20—370)	Mean and range of Canadian tributaries (1974)	14
		20 (8—30)	Mean and range of Canadian tributaries (1975)	14
Erie		60 (10—30)	Mean and range of Canadian tributaries (1975)	14
Grand River	2.6 ± .65		Mean ± 95% limits, 9 samples, (1976)	21
Cuyahoga River	39—589		1973 data	21
Tributaries to Cuyahoga River	48—482		1973 data	21
Agricultural plots	38			
	ND—110		1975—1976 data	10
	25		1976—1977 data	21
Ontario		194 (2—1800)	Mean and range of Canadian tributaries (1974)	14
Oakville Creek	3.5 ± 1.2		Mean ± 95% limits, 9 samples (1976)	21

* U.S. EPA Grosse Ile Laboratory (private communication).

B. Tributary Input

Konasewich et al.[21] have summarized a variety of isolated data on concentration of PCB in tributaries to the Great Lakes and that work, together with work on the Saginaw River and the Canadian rivers is summarized in Table 3. The range is quite large for any given tributary and reflects transient events associated with suspended solids resuspension, probable differences in analytical techniques throughout the Great Lakes regions, and of course, variable point and nonpoint source loadings to the tributaries. In view of the range in the

MONS 006314

Table 4
ESTIMATED RANGE OF CONTEMPORARY TOTAL PCB LOADING (g/km²/year) TO THE GREAT LAKES[a]

Lake	Tributary[b]	Direct municipal & industrial	Total[b]	Atmospheric load as % of total
Superior	8—23	0.1—1	17—114	26—92
Michigan	8—24	1—12	18—126	20—91
Huron	11—33	0.2—2	20—125	20—89
Erie	9—28	9—87	27—205	7—84
Ontario	17—51	7—65	33—206	7—80

[a] Not including PCB load from upstream Great Lakes.
[b] Including 9 to 90 g/km²/year from wet and dry deposition to each lake.

data and the difficulty of determining, in detail, the effect of each upon basin loading, a range of concentration from 10 to 30 ng/ℓ was assigned to the tributary flows into each lake. The resulting range of tributary loading for the lakes on a lake surface area basis, is shown in the first column of Table 4. In general, the net loading due to this input on an areal basis is approximately equal except for Lake Ontario which has a relatively higher tributary area/lake surface area ratio.

C. Municipal and Industrial Input

Data on the concentration of PCBs in municipal and industrial point sources throughout the Great Lakes have been summarized by Konasewich et al.[21] Again, the range of reported concentrations is wide (from about 0.1 to 100 μg/ℓ). Also, Mueller and Anderson[26] in a survey of data on PCB in municipal plants (including Canadian plants in the Great Lakes basin) reported a range in average concentration from <0.2 to 1.2 μg/ℓ. Given the range in reported concentrations and the unavailability of any detailed reliable data base on individual point source inputs directly to the lakes (as opposed to the tributary inputs which include up-basin point sources), a range of concentration of PCB from 0.1 to 1.0 μg/ℓ was used. This range was applied to the estimated municipal point source discharge flows directly entering the model segments and the result is shown in the second column of Table 4. Lakes Erie and Ontario are seen to have the highest loading rate from this source due to the increased municipal direct point sources to these lakes.

D. Total PCB Load

Table 4 and Figure 7 show the total load range estimated for the lakes including the range of 9 to 90 g PCB/km²/year from atmospheric sources. Figure 7 also includes an approximate loading from the upstream lakes to Huron, Erie, and Ontario at about 2 ng/ℓ in the incoming flow from the upstream lake. (This is discussed further below.) The ranges are large, reflecting the uncertainty in the estimates but, in general, show the increased loading on the downstream lakes Erie and Ontario. The magnitude of upstream load is not great when compared to the upper bound direct load to the lakes but can be significant when compared to the lower bound of the external load. Also as indicated in Table 4, the atmospheric input could account for as much as 80 to 90% of the total load to the lakes. It should be stressed that these load estimates are for contemporary conditions (i.e., approximately 1975 to 1980) and do not reflect any discharges of PCBs prior to the banning of PCBs in the basin.

MONS 006315

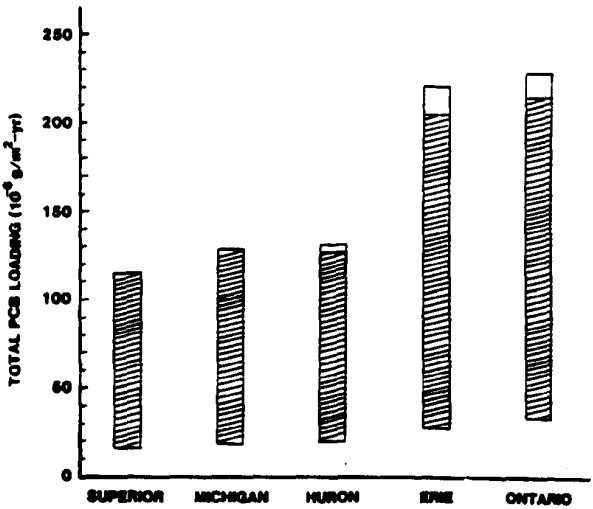


FIGURE 7. PCB loading to the Great Lakes. Cross-hatched bar indicates range of external loading; open bar indicates approximate loading from upstream lake at 1 to 2 ng/ℓ.

III. MODEL OF PHYSICAL-CHEMICAL FATE OF PCBs

A. Theory

The above review of the PCB problem in the Great Lakes and the incoming PCB loading indicates the need to construct a framework that would provide a basis for predicting the response of the Lakes to external PCB load reduction. In addition, the PCB distribution in the lakes, as observed, is an archetypal situation that can provide insights into the mechanisms of fate and transport of other toxic chemicals. Hence, a model of the physical-chemical fate of PCBs in the Great Lakes has been constructed and is discussed in this section. The subsequent uptake of the chemical and bioaccumulation in the food chain is discussed in the next section. A detailed discussion of the fundamental structure of the physical-chemical PCB model is given in Thomann and Di Toro.[40,41]

The model of the physical-chemical fate of a toxic substance such as PCB must recognize the partitioning of the chemical between the particulate and dissolved phase. Thus, let

$$c_T = c_p + c_d \qquad (1)$$

where c_T is the total concentration of PCB (ng/ℓ), c_p is the concentration of PCB associated with the particulates either in the water column or the sediment (ng/ℓ), and c_d is the porosity corrected concentration of PCB in the dissolved form (ng/ℓ). The volume in each of these concentrations is the bulk volume, i.e., the volume of the water plus the solids. Assuming that the kinetics of the reaction between the particulate and dissolved concentrations are

MONS 006316

"fast" (order minutes-hours), then a porosity corrected partition coefficient (π') can be defined as

$$\pi' = r/c_d \qquad (2)$$

where convenient units for π' are μg PCB per kg solids ÷ μg PCB per ℓ (bulk) and r is the concentration of PCBs on a solids basis (μg PCBs per kg solids). The particulate toxicant concentration relative to the bulk volume is then

$$c_p = rm \qquad (3)$$

where m is the concentration of solids (mg/ℓ[bulk]). From these equations, the fractions of PCB in the dissolved form (f_d) and particulate from (f_p) are given respectively by

$$f_d = (1 + \pi'M)^{-1} \qquad (4)$$

$$f_p = \pi'M(1 + \pi'M)^{-1} \qquad (5)$$

The mass balance equation for PCB can best be understood by considering a single completely mixed lake. The extension to the multidimensional water body is direct and discussed by Thomann and Mueller (1983).

For a single completely mixed lake of volume, V, the mass balance for the total toxicant is given by

$$V\,dc_T/dt = W_T - Q\,c_T - w_s f_p c_T + w_m f_{pn} c_{T_n} + K_L A(f_{dn}c_{T_n}/\phi_n - f_d c_T/\phi) - KV c_T + k_v A(c_g/H_n - f_d c_T/\phi) \qquad (6)$$

where W_T is the PCB load to the lake (g PCB per day), Q is the out flow (m^3/day), A is the interfacial area between water and air and water and sediment, w_s is the particulate settling velocity (m/day), w_m is the particulate resuspension velocity (m/day), c_{T_n} is the sediment total toxicant concentration (ng/ℓ), K_L is the sediment water diffusive transfer coefficient (m/day), k_v is the volatilization transfer coefficient (m/day), c_g is the toxicant concentration in the atmosphere overlying the water (ng/m^3), H_n is the Henry's constant (ng/m^3 ÷ ng/ℓ), i.e., the partitioning between the gaseous and aqueous phase, and K is an overall loss rate (per day) given by

$$K = K_d f_d + K_p f_p \qquad (7)$$

In Equation 7, K_d and K_p are the loss rate of the dissolved and particulate forms, respectively, due to mechanisms such as biological degradation and photolysis. The first four terms of Equation 6 represent respectively: (1) the external input of toxicant, (2) the transport of PCBs out of the lake due to flow, (3) the loss due to particulate settling, and (4) the gain due to particulate resuspension. The fifth term is the flux of chemical from (to) the sediment due to interstitial diffusion of the dissolved form. The sixth term is the overall loss of the chemical due to decay and the seventh term is the flux of the dissolved form of PCBs to the atmosphere due to volatilization.

Following a similar procedure, the equation for the total toxicant in the sediment segment is

$$V_s \frac{dc_{T_n}}{dt} = w_s A f_p c_T - w_m A f_{pn} c_{T_n} + K_L A(f_d c_T/\phi - f_{dn} c_{T_n}/\phi_n) - w_b A c_{T_n} - K_r V_s c_{T_n} \qquad (8)$$

MONS 006317

where

$$K_s = K_{ds} f_{ds} + K_{ps} f_{ps} \quad (9)$$

All the terms of Equation 8 represent similar mechanisms as in the water column, i.e., in order on the right, influx due to settling, loss due to resuspension, diffusive exchange of interstitial dissolved chemical, loss due to net sedimentation (at velocity, w_s (m/day)) and loss due to decay processes in the sediment. A similar equation can be written for sediment segments below the surface sediment layer. Equations 6 to 9 represent the time variable chemical mass balance for a completely mixed lake for turbulent mixing and advective transport.

In the fully time variable form, it is difficult to obtain insight into the nature of the solution. However, at steady state, further understanding of the behavior of PCBs can be obtained. (The fully time variable equations are used below for model calibration.) With the derivatives in Equations 6 and 8 set to zero, the solution for the water column is

$$c_T = \frac{W_{T_0}}{q + w_T} \quad (10)$$

where W_{T_0} is the areal loading rate of (g PCB/m²/year), w_T (m/year) is the overall net loss of PCBs from the lake and $q = Q/A_s$, for A_s, (m²) the surface area of the lake. The overall net loss of PCB (w_T) incorporates all of the sediment-water, air-water, and decay interactions. Di Toro et al.[3-7] express the net loss rate as

$$w_T = \left(K_1 + \beta \frac{r_2}{r}(K_2 + K_3)\right) H \quad (11)$$

where

$$K_1 = (K_a + K_r/H) f_a + K_p f_p \quad (12)$$

$$K_2 = K_{ds} f_{ds} + K_{ns} f_{ps} \quad (13)$$

$$K_3 = \frac{w_s f_{ps}}{H_s} \quad (14)$$

and

$$\beta = \frac{M_s H_s f_p}{M H f_{ps}} \quad (15)$$

$$\frac{r_2}{r} = \frac{(w_n + w_s) f_{ds} + K_s(\pi/\pi) f_{ds}}{(w_n + w_s) f_{ps} + K_s f_{ds} + K_2 H_s} \quad (16)$$

These results show that for steady state, the concentration in the water column given by Equation 10 is identical to the simple water quality constituent for a completely mixed case but the net loss rate includes sediment interactions. If data are available on the load and resulting water column concentration of a chemical, the net loss rate can be computed from Equation 10. Further simplification under conditions of no decay in the sediment and equal

MONS 006318

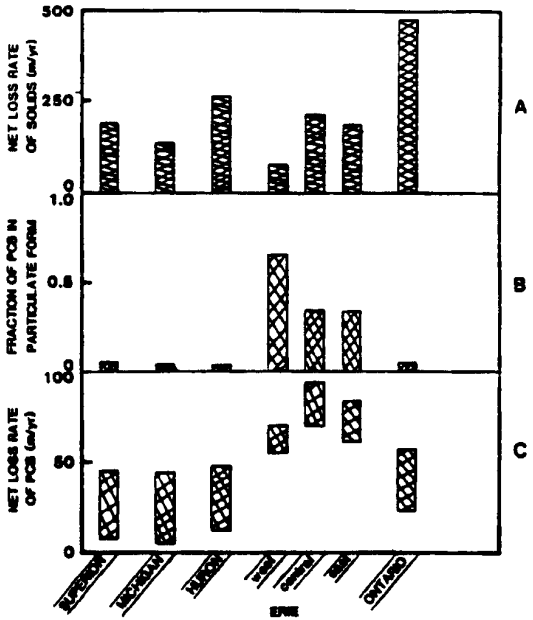


FIGURE 8. (A) Net loss rate of solids from lake water column to sediment. (B) portion of PCBs in the water column as particulate form, (C) net loss rate of PCBs from water column to sediment.

partitioning between the water column and sediment are discussed in References 5 to 7 and 40.

B. Data and Model Results

The time variable version of the preceding model (Equations 6 and 8) has been applied to the Great Lakes using the physical characteristics given in Table 1 as described in Thomann and Di Toro.[39] The analysis includes a mass balance of the suspended solids in the lakes and an accompanying calibration of the model to time variable behavior of plutonium-239 in the lakes. For PCBs using a partition coefficient of 100,000 ℓ/kg, settling and resuspension velocities from the solids-plutonium calculation, estimates can be made of the PCBs in the water column and sediment for a given external load. Figure 8[39] shows the net loss rate of solids for the lakes, the fraction of PCBs in the particulate form, and the net loss rate of PCBs to the sediments. As shown, the net loss of solids in m/year (i.e., the net depositional velocity) varies from less than 100 m/year in the shallow western basin of Lake Erie to 500 m/year for Lake Ontario, the last lake in the chain. The fraction of PCB estimated to be in the particulate form in the water column varies less than 0.1 for all lakes except Lake Erie.

MONS 006319

Table 5
CALCULATED PCB CONCENTRATION IN WATER COLUMN AT END OF 20-YEAR PERIOD

	PCB concentration (ng/ℓ)							
	Upper PCB loads				Lower PCB loads			
	Volatilization = 0.0		Volatilization = 0.1 m/day		Volatilization = 0.0		Volatilization = 0.1 m/day	
Lake	Total	Diss.	Total	Diss.	Total	Diss.	Total	Diss.
Superior	6.6	6.3	2.1	2.0	0.67	0.64	0.29	0.27
Michigan	9.1	8.6	2.5	2.4	0.80	0.76	0.31	0.29
Huron	6.1	5.8	1.9	1.8	0.67	0.64	0.26	0.25
Erie								
West	7.3	2.5	5.3	1.8	0.91	0.31	0.70	0.23
Central	2.9	1.9	2.0	1.3	0.36	0.23	0.25	0.17
East	2.8	1.8	1.9	1.2	0.36	0.23	0.25	0.16
Ontario	6.8	6.5	3.1	3.0	0.93	0.89	0.47	0.45

Table 6
CALCULATED PCBs IN SURFACE SEDIMENT (0 TO 3 cm) AT END OF 20-YEAR PERIOD

	PCB in sediment (ng/g)			
	Upper PCB load		Lower PCB load	
Lake	Volatilization = 0.0	Volatilization = 0.1 m/day	Volatilization = 0.0	Volatilization = 0.1 m/day
Superior	526	147	42	18
Michigan	714	182	50	19
Huron	501	138	44	17
Erie				
West	246	178	30	23
Central	192	131	24	17
East	177	120	23	16
Ontario	594	236	66.0	31

For this lake because of the higher solids concentrations, the fraction particulate increases to 0.3 to 0.7. As a result, the net loss rate of PCBs from the water column to the sediment is highest in the more shallow Lake Erie than in the deeper lakes as shown in Figure 8.

Water column data for the open waters of the Great Lakes are sparse and range from about 1 to 10 ng/ℓ of total PCBs[32-36] during the late 1970s. Recent (1980-1981) open lake samples that have been analyzed with improved evaluation using capillary gas chromatograph techniques indicate PCB concentrations of 1 to 3 ng/ℓ for Lake Superior.[10]

Surface sediment data vary widely ranging from about 3 ng/g for Lake Superior in 1973[13] to about 100 to 300 ng/g for Lake Erie in 1971.[14]

The input loads, as shown in Table 4, were applied for a 20-year period and the resulting calculation for the range of loads and with and without volatilization at 0.1 m/day is shown in Table 5 for the water column and Table 6 for the surface sediment.

The calibration of the PCB model to these ranges of data indicated that volatilization of PCBs was probably taking place at about an overall exchange rate of about 0.1 m/day. The results of the calculation for each of the lakes using this volatilization rate and the range of

MONS 006320

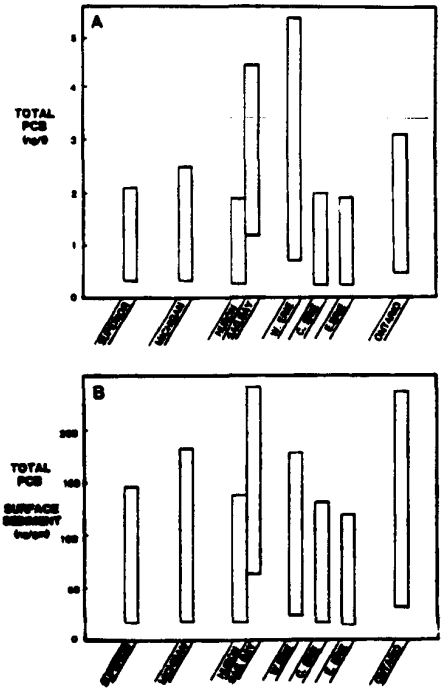


FIGURE 9. Calibrated PCB concentrations with volatilization for upper and lower load ranges (A) water column (B) surface sediment.

loadings shown in Table 4 are shown in Figure 9. The figure shows that on a lake to lake basis, it is calculated that the highest total PCB in the water column is in western Lake Erie, but because of high solids concentrations there, the dissolved PCB is estimated to be lower than the other lakes (see also Table 5). As a result, the PCB fish concentration in Lake Erie would be expected to be lower than upstream lakes even though the total PCB concentration is calculated to be higher. This is supported in a very general way by Figure 6.

Figure 9 also indicates that the calculated water column concentrations are in approximate agreement with the reported ranges cited earlier but that the sediment concentrations appear high, especially for Lake Superior where, as noted previously, concentrations of about 3 ng/g have been reported.[19] This is due in part to the PCB partition coefficient relationship with solids concentration described later in this chapter where it is shown that the PCB partition coefficient apparently decreases with increasing solids concentrations. At the higher

MONS 006321

solids concentration in the sediment then, one would generally expect a lower PCB particulate concentration. This effect is not included in the calculations described here.

IV. MODEL OF FATE OF PCBs IN AQUATIC ECOSYSTEMS

A. Theory

Significant contamination of the Great Lakes fishery has resulted from exposure to PCBs both in the water and in ingested food. PCBs are taken up directly from water either through transfer across the gill as in fish or through surface sorption and subsequent cellular incorporation as in plankton. It is taken up from food through absorption across the gut. The significance of the former uptake route has been demonstrated by laboratory experiments indicating an equilibrium bioconcentration of PCBs from water of approximately 10^5 ($\mu g/g_{dry} \div \mu g/g_{wet}$).[37] The latter uptake route is significant for higher trophic levels because of food chain accumulation.[38-40] The equilibrium concentration resulting from exposure to PCBs in food is additive to that from water so that a higher trophic level species exposure to PCBs in food reflects the prey's exposure to PCB in both food and water. A compounding effect results that is responsible for the observed increase in PCB concentration with species size (Figure 5). A model of PCBs in an aquatic food chain, therefore, must consider both uptake routes.

For fish, the primary mechanism for uptake directly from water is through transfer of the chemical across the gill surface. The rate of transfer can be calculated from the rate of transfer of oxygen from water to the blood of the fish.

The rate of mass transport of a substance is given by

$$M = \frac{DA}{10^3 \delta} c \tag{17}$$

where M is the mass transport (μg/day), D is the diffusivity of the substance (cm^2/day), A is the effective surface area of gill for transfer (cm^2), δ is the effective thickness of the gill (cm), and c is the concentration of the substance in the water ($\mu g/\ell$). If it is assumed that the mechanism for uptake of the chemical, e.g., PCB is identical to oxygen uptake, then

$$\frac{M_{PCB}}{M_{O_2}} = \frac{D_{PCB}\, c_{PCB}}{D_{O_2}\, c_{O_2}} \tag{18}$$

where the subscripts PCB and O_2 are for the chemical PCB and dissolved oxygen, respectively. From Equation 18

$$M_{PCB} = \left(\beta \frac{M_{O_2}}{c_{O_2}}\right) c_{PCB} \tag{19}$$

where $\beta = D_{PCB}/D_{O_2}$, the ratio of the diffusivity of PCB to that of oxygen. From Equation 19

$$M_{PCB} = k_1' c_{PCB} \tag{20}$$

where

$$k_1' = {}^{\beta}M_{O_2}/c_{O_2} \tag{21}$$

The quantity k_1' represents the mass uptake for the whole fish and has units, ℓ/day. Dividing k_1' by the fish weight gives the uptake rate per unit weight, i.e.,

MONS 006322

$$k_u = \frac{k_2}{w} = \beta \frac{M_{O_2}/w}{c_{O_2}} \tag{22}$$

The quantity M_{O_2}/w is the respiration rate, r, of the fish, i.e.,

$$r = M_{O_2}/w$$

where r has units (g O_2/g (weight) − day). The uptake rate for the chemical is therefore related to the respiration rate of the organism by

$$k_u = \beta \frac{r}{c_{O_2}} \tag{23}$$

The uptake of PCBs due to ingestion of contaminated food depends on (1) PCB concentration in the food, (2) rate of consumption of food, and (3) the degree to which the ingested PCBs in the food is actually assimilated into the tissues of the organisms.

For a food chain level i preying on lower level individuals indexed as j this uptake (μg PCB/day) may be written as:

$$\sum_j \alpha_{ij} p_{ij} C_i w_i \nu_j$$

where α_{ij} is the chemical assimilation efficiency of i on j (μg chemical absorbed/μg chemical ingested), p_{ij} is the fraction of the consumption of i that is on j, C_i is the weight-specific consumption of i (g prey/g predator/day), w_i is the weight of i, and ν_j is the chemical concentration (μg PCB/g) in j.

The general mass balance equation for the whole body burden of level i includes the uptake forms given above and an excretion or depuration term. It has been presented by Thomann and Connolly[36] as:

$$\frac{d\nu_i'}{dt} = \frac{d(\nu w)_i}{dt} = \frac{w_i d\nu_i}{dt} + \frac{\nu_i dw_i}{dt} = k_{ui} w_i c - K_i \nu_i' + \sum_j p_{ij} \alpha_{ij} C_i \nu_j w_i \qquad i = 1 \ldots m \tag{24}$$

where ν_i' is the chemical whole body burden (μg PCB) and k_{ui} and K_i are the uptake rate from water and excretion rate, respectively. The quantity $(1 - \alpha)$, represents that portion of ingested chemical which is immediately or rapidly egested by the organism and never accumulated in body tissue. The excretion rate in Equation 24 is interpreted as excretion and desorption of the chemical that has been sorbed onto or into the organism.

The individual organism weight is related to species bioenergetics as

$$\frac{dw_i}{dt} = (a_i C_i - r_i) w_i \qquad i = 1 \ldots m \tag{25}$$

where a_i is the biomass assimilation efficiency (g predator/g prey) and r_i is the respiratory weight loss (per day) due to routine metabolism, swimming, and other activities. The weight change is therefore

$$G_i = \frac{dw_i}{dt} / w_i = a_i C_i - r_i \tag{26}$$

MONS 006323

Equation 24 can then be written as

$$\frac{dv_i}{dt} = k_w c + \sum_j \alpha_{ij} p_{ij} C_j v_{ij} - K_i' v_i \qquad i = 1...m \qquad (27)$$

where

$$K_i' = G_i + K_i \qquad (28)$$

The first term of Equation 27 represents the direct uptake of the chemical by the organism from the water. The second term represents the flux of the chemical into the organism through feeding. Note that the units of this term are gram of chemical assimilated per gram predator per day. The third term is the loss of chemical due to desorption and excretion from body tissue at a rate K_i plus the change in concentration due to growth of the individual.

In the analysis of a food chain each species or level is separated into discrete age classes to which Equation 27 is applied using predator-prey relationships and bioenergetic information specific to that age class.

B. Application to Lake Michigan

Use of Equation 27 requires that a specific food chain be chosen and that the bioenergetic parameters (growth rate, respiration rate, food assimilation efficiency) and PCB related parameters (assimilation efficiency, excretion rate) be specified for each age class. In addition, the predator-prey relationships must be established.

1. Basic Model

In the application of the above model to Lake Michigan by Thomann and Connolly,[38] a four-species food chain was chosen consisting of phytoplankton, *Mysis relicta*, alewife (*Alosa pseudoharengus*), and lake trout (*Salvelinus namaycush*). This species linkage constitutes the major energy transport route to the lake trout. Both *Mysis* and alewife are viewed as representative species of the middle levels of the food chain acknowledging that other invertebrates and small fish also contribute to the observed PCB levels in lake trout. The phytoplankton component of the model is assumed to represent nonliving particulate organic material as well as living plankton.

The model was calibrated against 1971 observed alewife and lake trout PCB concentrations reported by Veith[42,43] and shown in Figure 5 for lake trout. A constant dissolved PCB concentration of 5 ng/ℓ was assumed. A constant value implies that the alewife and lake trout sampled in 1971 were exposed to a constant PCB concentration for their entire lives, which for the oldest trout represented is 10 years. The values assigned to the PCB assimilation efficiency were adjusted to reproduce the observed PCB distribution. This parameter was chosen as the calibration variable because of the uncertainty of its value relative to the other parameters in the model.

The data and the model calculations both indicate that PCB concentrations in lake trout are three to four times those in alewife. The computed increase results from the higher PCB concentration in lake trout prey (alewife) relative to alewife prey (*Mysis*). All species in the model accumulate similar PCB concentrations from dissolved PCB because of the constant relationship maintained between uptake rate from water and excretion rate (i.e., constant bioconcentration factor). Some variation does occur depending on the influence of growth rate as a concentration loss mechanism. The increase in computed PCB concentration with increasing trophic level is a direct consequence of the transfer of accumulated PCB from one level to the next.

Including uptake of PCB from food results in over an order of magnitude higher biocon-

MONS 006324

centration factor for juvenile trout increasing with the concentration in the prey to an approximately two orders of magnitude higher BCF for the oldest trout. Expressing PCB accumulation in terms of concentration, the calculations indicated that greater than 99% of the PCBs in adult trout is taken up in food.

2. Inclusion of Benthic Component

An interesting question regarding PCB contamination of the Lake Michigan food chain is the contribution to the PCBs in the lake trout from organisms that interact with the sediment. Benthic species may have higher PCB concentrations than pelagic species and thereby contribute to the PCB body burden of top predators. To account for this PCB transfer pathway, the food chain model was modified to include *Pontoporeia affinis*, a benthic invertebrate that is an alternate prey species to *Mysis* for middle level fish in Lake Michigan.

Little bioenergetic information on *Pontoporeia* is available. Growth rate ranges from 0.0056 to 0.012/day[48] which is consistent with that calculated for *Mysis* (0.0056 to 0.019/day).[39] Dry weight and length of *Pontoporeia* are approximately one third that of *Mysis*.[24,25] In the model, the initial weight of each of the four 4-month age classes was assumed to be one third that of *Mysis*. The growth rate of each age class was assumed to be the same as that of *Mysis*.

The relationship between *Pontoporeia* weight, w (grams) and respiration, R(g/g/day), was the same as the experimentally determined relationship for *Mysis*.[25]

$$R = 0.015\, w^{-0.25} \tag{29}$$

which is consistent with the general relationship found to hold for all poikilotherms and homoiotherms.[38]

Pontoporeia food assimilation efficiency was the same as that of *Mysis* which was computed from observed consumption rates[4] and calculated growth and respiration rates.

Alewife predation on *Pontoporeia* relative to *Mysis* was based on stomach content examinations of alewife from Lake Michigan.[20] *Mysis* were found to be the predominant diet of alewife with *Pontoporeia* significant only during the early evening, possibly during migrations from the sediment. In the model, *Pontoporeia* were assumed to be available for predation 6 hr each day during which time alewife preyed equally on *Pontoporeia* and *Mysis*. Sediment-associated bacteria were assumed to comprise the total diet of *Pontoporeia*.

The assimilation efficiency of PCBs from ingested food by *Pontoporeia* was set at 0.35. Excretion rate was directly related to uptake rate to maintain a constant bioconcentration factor from water of 2.5×10^5 $\mu g/g \div \mu g/g_{water}$.

Computed PCB concentrations with *Pontoporeia* included are shown in Figure 10. Note that at the assigned PCB concentrations of 5 ng/ℓ in the water column, 0.038 μg/g of bed sediment, and 3.8 ng/ℓ in the surface sediment interstitial water (representative of 1971) the *Mysis* and *Pontoporeia* have similar computed PCB concentrations. These species are therefore equivalent prey for the upper trophic levels.

The impact of the benthic food chain link in a load reduction scenario was assessed using the limiting case of an instantaneous decline of water column PCBs from 5 ng/ℓ to 1 ng/ℓ and no decline in sediment PCBs. The model without a benthic component is linearly dependent on the dissolved PCB concentration and an 80% decline in this concentration will reduce food chain concentrations by 80%. For lake trout the average computed PCB concentration at 5 ng/ℓ of 12.9 μg/g is therefore reduced to 2.6 μg/g at 1 ng/ℓ. Under the assumption of no decline in sediment PCBs, the computed lake trout PCBs is reduced by 74% to 3.4 μg/g. A mitigating effect is evident although the benthic component does not significantly alter the response of the food chain. The sediment associated PCB is not an important component in the model because the *Pontoporeia* is a small component of the

MONS 006325

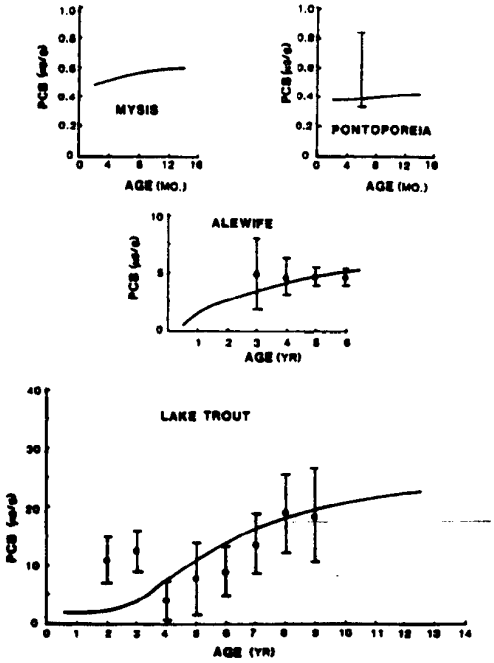


FIGURE 10. Calculated and observed PCB concentrations for Lake Michigan food chain including *Pontoporeia*.

diet of the alewife (12.5%) and its PCB concentration is similar to that of the pelagic invertebrate, *Mysis*.

An analysis of the response of the food chain without a benthic component has been published elsewhere.[20] This analysis indicated that a criterion specifying that PCB concentrations of all ages of lake trout be at or below 5 µg/g (wet weight) in the edible portion requiring that dissolved PCB concentrations be reduced to somewhere between 0.5 and 2.5 ng/ℓ.

V. EFFECT OF SOLIDS-DEPENDENT PCB PARTITIONING AND SEDIMENT DIFFUSION ON PCBs

A. Introduction

It has been noted by O'Connor and Connolly[20] in a summary of the literature that there is for some chemicals an apparent dependence of the partition coefficient on the concentration

MONS 006326

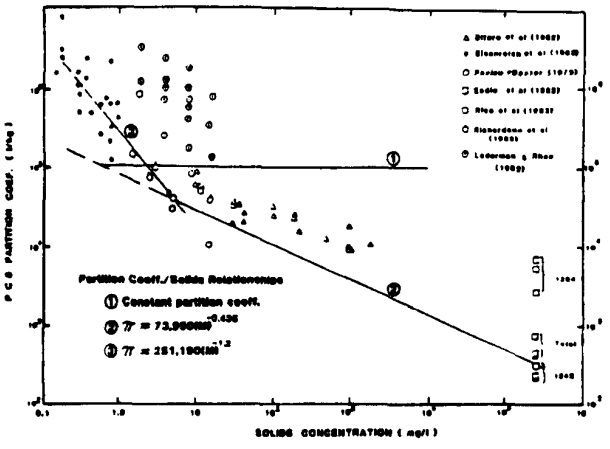


FIGURE 11. Summary of reported PCB partition coefficients and solids concentrations and relationships assumed in sensitivity analyses.

of solids. The mechanisms for this dependence are not clear but may be related to some interaction between solids which affects the available sites for sorption.

O'Connor and Connolly[39] analyzed a variety of data relating partition coefficient to solids concentration using the general form of

$$\pi = \pi_\infty + \frac{b}{m_o + m^a} \tag{30}$$

where π_∞ is the lower limiting partition coefficient at high solids and m_o bounds the upper limiting partition coefficient at low solids concentration. Assuming that π_∞ and m_o are zero and generally over the range of solids from 10 to 10^6 mg/ℓ, O'Connor and Connolly[39] computed values for a ranging from 0.19 to 0.92.

If a chemical such as PCB displays an inverse dependence of partition coefficient on the concentrations of solids, then at the high solids concentrations found in bed sediment, the partition coefficient would be expected to be lower than for the water column. Less chemical would then be sorbed onto sediment particles and an increase in interstitial dissolved chemical would occur. A gradient between the dissolved chemical in the bed and the dissolved chemical in the overlying water would then develop and depending on the magnitude of the exchange between the sediment and water column, a flux of the chemical from the sediment to the water may occur. In this section, the sensitivity of the previous PCB calculations to this effect is calculated and discussed.

B. Sensitivity of PCBs Calculation for Great Lakes

Figure 11 shows a compilation of PCB partition coefficient as a function of solids concentration ranging from approximately 0.1 mg/ℓ as reported for Lake Superior[10] to Lake

MONS 006327

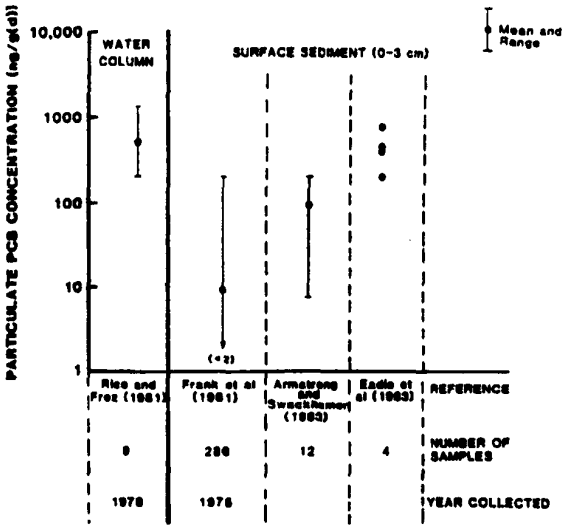


FIGURE 12. Comparison of measured particulate PCB concentration in water column and surface sediment, Lake Michigan.

Michigan sediment solids of 200,000 mg/ℓ as reported by Eadie et al.[9] The data indicate a dependence of the PCB partition coefficient on solids concentration where for concentrations at about 10 mg/ℓ and higher, the partition coefficient declines logarithmically at a slope of about −0.435. This depends heavily, however, on the one point of a sediment partition coefficient reported by Eadie et al.[9] The data of Di Toro et al.[7] indicate for Saginaw Bay sediments, that the partition coefficient may be leveling off at about 10^6 ℓ/kg at solids concentrations greater than about 1000 mg/ℓ. The data of Eisenreich et al.[10] for Lake Superior extend into the concentration of solids at less than 1 mg/ℓ and show a steep increase in partition coefficient at the lower solids concentration. The data from Lederman and Rhee (1982) are for Great Lakes algae and the higher partitioning may reflect the presence of lipids in the algae.

If the partition coefficients differ between the water column and the sediment, then one would expect the particulate PCB concentration in the water column to be higher than that of the sediment. There is some evidence to indicate that this may be the case for Lake Michigan as shown in Figure 12. Rice and Frez[20] reported water column particulate PCB concentrations ranging from 213 ng/g (day) to 1147 ng/g (day) with indications of a decrease of the concentration with depth. The average of their data is 537 ng/g (day). The surface sediment PCB data as shown in Figure 12 vary by an order of magnitude although it should be recognized that the data of Frank et al.[16] represent 286 samples throughout the lake while Armstrong and Swackhamer[3] and Eadie et al.[9] represent only 12 and 4 samples, respectively. If the data of Frank et al.[16] are used then there is about a two-order of magnitude decrease

MONS 006328

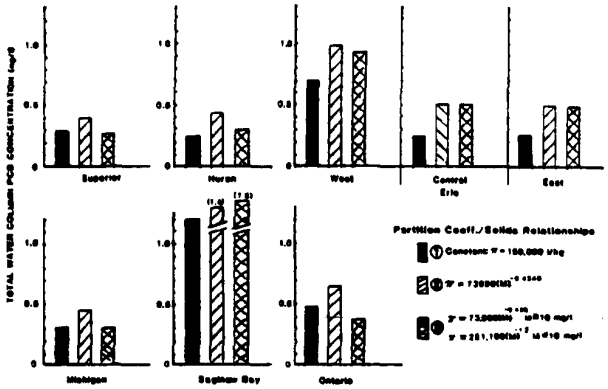


FIGURE 13. Comparison of calculated total water column PCB concentration (ng/ℓ) using different solids-dependent partitioning; low load level with volatilization.

in the particulate PCB concentration between the water column and the sediment. In the model used here, the only way that such a decrease can be calculated is through a solids-dependent partition coefficient.

Two cases of solids-dependent partitioning of PCBs were therefore examined:

$$\text{(a)} \quad \pi = 73.990\, M^{-0.433} \quad \text{and}$$

$$\text{(b)} \quad \pi = 25.120\, M^{-1.2} \quad \text{for solids} < 10\ mg/\ell$$
$$\pi = 73.990\, M^{-0.439} \quad \text{for solids} \geq 10\ mg/\ell$$

Figures 13 to 16 summarize the results under the lower level of loading of PCBs and including volatilization. Several points can be noted. As shown in Figures 13 and 14, the total and dissolved water concentrations are not sensitive in a significant way to the assumption on partitioning. The principal effect on the dissolved component is in western Lake Erie where the dissolved concentration increases by a factor of three. In all other lakes, however, for practical purposes, the total and dissolved concentrations are unaffected by the partitioning assumption. Figure 15 shows that the surface sediment concentration is also not markedly affected (to order of magnitude) by the partitioning assumption although a decline of about 50% is evident in the lake sediment and a decline of about 70% is calculated for the surface sediment of Saginaw Bay.

These reductions in sediment PCB particulate concentration reflect the assumed reduced partitioning at the high solids concentrations and are, therefore, subsequently reflected in the PCB concentration of the interstitial water of the surface sediment as shown in Figure 16. It is in the interstitial water that the effect of the solids-dependent partitioning is most pronounced. Here, increases in the dissolved PCB concentration of about two orders of magnitude are calculated as seen in Figure 16.

For Lake Michigan, as an example, the interstitial concentration of PCBs as calculated for a constant partition coefficient is about 0.25 *ng/ℓ*. For a variable partition coefficient

MONS 006329

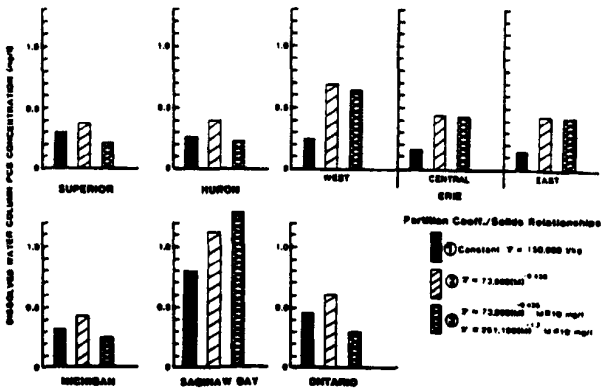


FIGURE 14. Comparison of calculated surface sediment PCB concentration (ng/g) using different solids-dependent partitioning; low load level with volatilization.

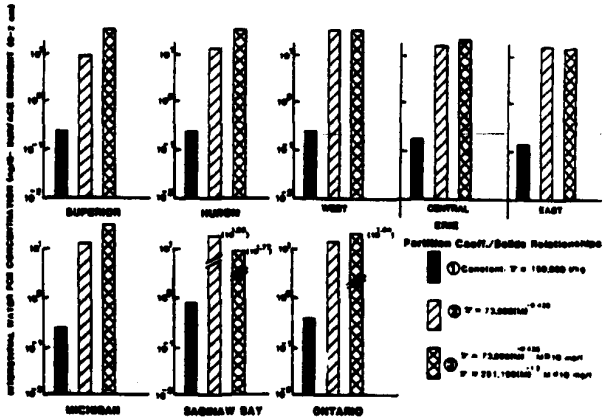


FIGURE 15. Comparison of calculated dissolved water column PCB concentration (ng/l) using different solids-dependent partitioning; low load level with volatilization.

MONS 006330

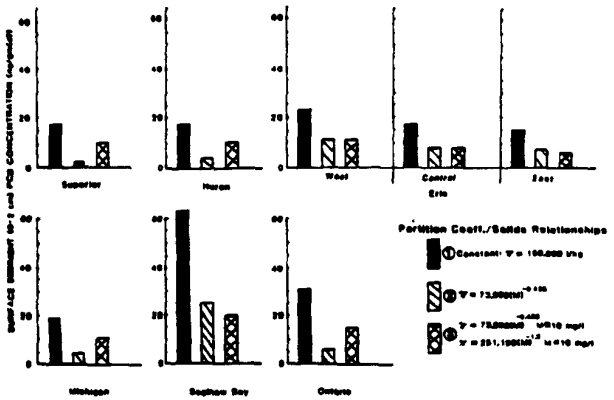


FIGURE 16. Comparison of calculated interstitial PCB concentration (ng/ℓ) in surface sediment using different solids-dependent partitioning; low load level with volatilization.

(relationship No. 3 in Figure 16), the concentration increases to about 30 ng/ℓ. Eadie et al.[4] reported values of pore water PCBs at three stations in southern Lake Michigan of 159, 214, and 342 ng/ℓ, which is about one order of magnitude higher than that calculated in Figure 16. However, the estimate shown in Figure 12 represents a lake-wide average including regions of nondeposition. One would, therefore, expect an observed lake-wide average to be less than individual core samples. Indeed, the high value of 342 ng/ℓ reported by Eadie et al.[4] is for a station off Benton Harbor, Mich. with the highest recorded accumulation rate in Lake Michigan of 3 g/m²/day. This accumulation is 16 times the lake-wide average net deposition as used in the preceding solids balance calculation. It can also be noted that the calculation shown in Figure 15 is for the low loading condition for PCB. The higher loading condition would result in an increase in interstitial water PCB concentration approximately proportional to the load or a factor of about 7 over the lower load condition.

It appears from this calculation on the sensitivity of the PCB distribution in the Great Lakes to a sediment-dependent partition coefficient that:

1. Such a relationship is more representative of the observed particulate and sediment PCB data in Lake Michigan.
2. Total and dissolved PCB concentration in the water column and sediment PCB concentration are not affected significantly (i.e., by at least one order of magnitude) under a solids-dependent partitioning assumption.
3. Interstitial PCB concentration in the sediment is affected markedly by such an assumption and an increase of about two orders of magnitude is calculated.
4. Since the increased interstitial PCB concentration in the sediment is about two orders of magnitude higher than the overlying water dissolved PCB concentrations, one would expect benthic organisms to carry a significantly higher body burden than organisms exposed solely to the water column and as a result would be a potential significant source of PCBs to top predators in the food chain.

MONS 006331

VI. HUMAN EXPOSURE THROUGH FISH CONSUMPTION CONTAMINATED WITH PCBs

The potential for impact of PCBs on human health has been recognized through the establishment of fish advisories by the Great Lakes states and Province of Ontario. Fish advisories related to PCBs exist for various species of fish for all of the Great Lakes.

Health effects on human infants have been related to PCB dose obtained through the consumption of fish by expectant mothers and through the consumption of breast milk by the infants.[36] The major route of exposure is through consumption of contaminated fish by women. PCBs in the maternal serum are then transferred to the prenatal infant through the umbilical cord blood. The postnatal infant receives exposure from maternal milk. The effects on the infant are measured by both physical and behavioral tests.

Studies by Humphrey[17] and Kreis et al. (1981) concluded an almost linear direct relationship between amounts of fish consumption and PCB concentration in the blood of those individuals consuming fish. This relationship was further substantiated in the examination of blood in nursing mothers who had consumed various quantities of Lake Michigan fish.[17,33] The results indicated that for every pound of contaminated fish ingested by the mother, the PCBs in their serum increased about 0.15 ng/mℓ on a whole blood basis or 23.6 ng/g on a fat basis. These studies showed a significant correlation between quantity of fish consumption and PCB levels in neonatal breast milk.

A study by Allen et al.[1] reported higher concentrations of PCBs in the tissue of the offspring of exposed rhesus monkeys, further indicating the passage of PCBs to the fetus. The offspring born to animals exposed to PCBs by injection also were often stillborn or had lower birth weights.

The major finding from the study by Humphrey[17] of people who have consumed large amounts of Lake Michigan fish was that no acute disease had been identified in exposed individuals. However, Sonzogni and Swain[34] pointed out that the real concern is in the exposure to infants. The exposure to infants is through two routes: passage across the placental barrier and through consumption of breast milk. The studies by Fein et al.[12] and Schwartz et al.[33] showed that PCBs in maternal blood and milk can be predicted from fish consumption, but not in umbilical cord serum. The concentration of PCBs increased in maternal serum and milk at the rate of 0.15 ng/mℓ and 0.12 ng/g, respectively, for every 0.5 PCB-kilogram of contaminated fish consumed. The significance of fish consumption shown by the Schwartz et al.[33] study was that for fish eaters who consumed only between 6 and 12 meals per year, the PCB body burden is higher than for those who did not consume fish. Also, of breast milk samples supplied by nursing mothers consuming fish at that rate, 7.5% equaled or exceeded the Food and Drug Administration's present tolerance level of 1.5 ppm (fat weight basis for PCBs in cow's milk and dairy products). The maternal serum PCB levels in turn predicted the umbilical cord serum levels for these compounds[19] whereas the umbilical cord serum level could not be predicted from fish consumption. This correlation between the maternal and cord serum indicates the high probability of transplacental passage by the PCB molecule.

Intrauterine exposure to PCBs is clearly associated with reduced size at birth and shorter periods of gestation.[12] Infants with umbilical cord blood PCB concentrations greater than 5 ng/ℓ averaged 194 g lighter than those infants having umbilical cord blood concentrations below the laboratory detection limit of 3 ng/ℓ. Higher umbilical cord blood levels were also associated with poor autonomic and reflex functioning and more limited lability of states in the newborn infant. These subtle neonatal behavioral deficiencies may have ominous implications for subsequent development. The higher cord blood PCB levels were also correlated with poor performance at 7 months of age on visual recognition memory tests (Flaganan and Singer, 1983). This visual recognition memory test has been shown[11] to predict reliably

MONS 006332

for ages 4 and 7. Recognition memory performance was not correlated to postnatal exposure from breast milk, however, suggesting that the cord serum PCB effect may be to the central nervous system prior to the formation of the blood-brain barrier.

The above studies clearly indicate the potential for adverse effects on infants born to mothers consuming PCB-contaminated fish, with exposure prior to birth via the placenta having a different mode of action than that after birth via consumption of breast milk.

ACKNOWLEDGMENTS

Although the research described in this chapter has been funded wholly or in part by the U.S. Environmental Protection Agency through Cooperative Agreements CR805916 and 807853 to Manhattan College, it has not been subjected to the Agency's required peer and probing review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

Thanks are extended to Mr. William Richardson, U.S. Project Officer of the U.S. EPA, Large Lakes Research Station at Grosse Ile, Mich. for his helpful encouragement. Also, thanks are gratefully acknowledged to Mrs. Eileen Lutomski and Ms. Cynthia O'Donnell for their fine and careful typing of the manuscript.

REFERENCES

1. **Allen, J. R., Barsotti, D. A., and Carstens, L. A.,** Residual effects of polychlorinated biphenyls on adult nonhuman primates and their offspring. *J. Toxicol. Environ. Health.* 6, 55, 190, 1980.
2. **Anon.,** Sea grant today, *Utilizing Airwaves.* 11(2), 10, 1981.
3. **Armstrong, D. E. and Brunkhammer, D. L.,** PCB accumulation in southern Lake Michigan sediments: evaluation from core analysis, in *Physical Behvior of PCBs in the Great Lakes*, Mackay, D., Paterson, S., Ann Arbor Science Press, Ann Arbor, Mich., 1983, 229.
4. **Cooper, S. D. and Goldman, C. R.,** Opossum shrimp (*Mysis relicta*) predation on zooplankton, *Can. J Fish. Aquat. Sci.*, 37, 909, 1980.
5. **Di Toro, D. M., O'Connor, D. J., Thomann, R. V., and St. John, J. P.,** *Analysis of Fate of Chemicals in Receiving Waters*, phase I, Chemical Mfg. Assoc., Washington, D. C., prepared by HydroQual, Inc., Mahwah, N. J., 1981.
6. **Di Toro, D. M., Horzempa, L. M., Casey, M. M., and Richardson, W.,** Reversible and resistant components of PCB adsorption-desorption: adsorbent concentration effects, *J. Great Lakes Res.*, 8(2), 336, 1982.
7. **Di Toro, D. M., O'Connor, D. J., Thomann, R. V., and St. John, J. P.,** Simplified model of the fate of partitioning chemicals in lakes and streams, in *Modeling the Fate of Chemicals in the Aquatic Environment*, Dickson, K. L., Maki, A. W., and Cairns, J., Jr., Eds., Ann Arbor Science, Ann Arbor, Mich. 1982, 165.
8. **Eadie, B. J., Rice, C. P., and Frez, W. A.,** The role of the benthic boundary in the cycling of PCBs in the Great Lakes, in *Physical Behavior of PCBs in the Great Lakes*, Mackay, D., Paterson, S., Eisenreich, S. J., and Simmons, M. S., Eds., Ann Arbor Science, Ann Arbor, Mich., 1983, 213.
9. **Eisenreich, S. J., Hollod, G. J., and Johnson, T. C.,** Accumulation of polychlorinated biphenyls (PCBs) in surficial Lake Superior sediments, Atmospheric deposition, *Environ. Sci. Technol.*, 13, 569, 1979.
10. **Eisenreich, S. J., Capel, P. D., and Looney, B. B.,** PCB dynamics in Lake Superior water, *Physical Behavior of PCBs in the Great Lakes*, Mackay, D., Paterson, S., Eisenreich, S. J., and Simmons, M. S., Eds., Ann Arbor Science Press, Ann Arbor, Mich., 1983, 181.
11. **Fagan, J. F., III and McGrath, S. K.,** Infant recognition memory and later intelligence, *Intelligence*, 5, 121, 1981.
12. **Fagan, J. F., III and Singer, L. T.,** Infant recognition memory as a measure of intelligence, in *Advances in Infancy Research*, Vol. 2, Lipsitt, L. P., Ed., Ablex, Norwood, N. J., 1983.
13. **Fein, G. G., Jacobson, J. L., Jacobson, S. W., and Schwartz, P. M.,** Intrauterine Exposure of Humans to PCBs: Newborn Effects, Final Grant Report, University of Michigan, Ann Arbor, Mich., 1982.

MONS 006333

14. **Frank, R., Holdrinet, M., Braun, H. E., Thomas, R. L., and Kemp, A. L. K. W.,** Organochlorine insecticides and PCBs in sediments of Lake St. Clair (1970 and 1974) and Lake Erie (1971). *Sci. Total Environ.*, 8, 205, 1977.
15. **Frank, R., Thomas, R. L., Braun, H. E., Rasper, J., and Dawson, R.,** Organochlorine insecticides and PCB in the surficial sediments of Lake Superior (1973). *J. Great Lakes Res.*, 6(2), 113, 1980.
16. **Frank, R., Thomas, R. L., Braun, H. E., Gross, D. L., and Davies, T. T.,** Organochlorine insecticides and PCB in surficial sediments of Lake Michigan (1975). *J. Great Lakes Res.*, 7(1), 42, 1981.
17. **Humphrey, H. E. B.,** Population studies of PCBs in Michigan residents, in *PCBs: Human and Environmental Hazards*. D'Itri, F. M. and Kamrin, M. A., Eds., Ann Arbor Science, Ann Arbor, Mich., in press.
18. International Joint Commission, Environmental Management Strategy for the Great Lakes System, Final Report to the IJC from the Int. Ref. Group on Great Lakes Pollution from Land Use Activities, Windsor, Ontario, Canada, 1978.
19. **Jacobson, J. L., Fein, G. G., Jacobson, S. W., Schwartz, P. M., and Dowler, J. K.,** *The Transfer of Polychlorinated Biphenyls Across the Human Placenta and into Maternal Milk*, in press.
20. **Jansson, J. and Brandt, S. B.,** Feeding ecology and vertical migration of adult alewives (*Alosa pseudoharengus*) in Lake Michigan, *Can. J. Fish. Aquat. Sci.*, 37, 177, 1980.
21. **Kennesevich, D., Traverey, W., and Zar, H.,** States Report on Organic and Heavy Metal contaminants in the Lakes Erie, Michigan, Huron, and Superior Basins, Appendix E, International Joint Commission, Great Lakes Water Quality Board, Windsor, Ontario, Canada, 1978.
22. **Kreis, K., Roberts, C., and Humphrey, H. E. B.,** Serum PBB levels, PCB levels, and clinical chemistries in Michigan's PBB cohort, *Arch. Environ. Health*, 37(3), 141, 1982.
23. **Lasenby, D. C. and Langford, R. R.,** Growth, life history, and respiration of *Mysis relicta* in an Arctic and temperate lake, *J. Fish. Res. Board Can.*, 29, 1701, 1972.
24. **Mansell, J. W. and Nordon, C. R.,** Food habits of the alewife, *Alosa pseudoharengus* (Wilson), in Lake Michigan, Proc. 11th Conf. Great Lakes Res. 1968, 96.
25. **Mosley, S. C. and Hewwaller, R. P.,** *Environmental Status of the Lake Michigan Region*, Vol. 6, Argonne National Laboratory, Argonne, Ill., ANL/ES-40, 1977.
26. **Mueller, J. A. and Anderson, A. K.,** Municipal sewage systems, in The Impact on Marine Coastal Water of the Ocean Discharge of Municipal Wastewater and its Consituents, Prepared for U.S. Department of Commerce, NOAA, Boulder, Colo. by Hydroscience, Inc., Westwood, N.J., 1978, chap. 2.
27. **Murphy, T. J., and Rasmussen, C. P.,** Polychlorobiphenyls in Precipitation in the Lake Michigan Basin, EPA-600/3-78-071, U.S. Environmental Protection Agency, Washington, D.C., 1978.
28. **Neldermeyer, W. J. and Hickey, J. S.,** Chronology of organochlorine compounds in Lake Michigan fish, 1929—66, *Pest. Monitor. J.*, 10(3), 92, 1976.
29. **O'Connor, D. J. and Connolly, J. P.,** The effect of concentration of adsorbing solids on the partition coefficient, *Water Res.*, 14, 1517, 1980.
30. **Rice, C. P. and Frea, W. A.,** Application of Capillary Chromatography to the Study of the Cycling of PCBs on Suspended Particles, Great Lakes Res. Div., University of Michigan, Ann Arbor, 1981.
31. **Rice, C. P., Eadie, B. J., and Ernstfeld, K. M.,** Enrichment of PCBs in Lake Michigan surface films, *J. Great Lakes Res.*, 8(2), 265, 1982.
32. **Schmidt-Nielsen, K.,** Energy metabolism, body size, and problems of scaling, *Fed. Proc.*, 29(4), 1524, 1970.
33. **Schwartz, P. M., Jacobson, S. W., Fein, G. G., Jacobson, J. L., and Price, H. A.,** Lake Michigan fish consumption as a source of polychlorinated biphenyls in human cord serum, maternal serum, and milk, *Am. J. Public Health*, 73, 293, 1983.
34. **Sonnegal, W. C. and Swain, W. R.,** Perspectives on U.S. Great Lakes chemical toxic substances research, *J. Great Lakes Res.*, 6(4), 285, 1980.
35. **Strachan, W. J. J. and Huneault, H.,** Polychlorinated biphenyls and organochlorine pesticides in Great Lakes precipitation, *J. Great Lakes Res.*, 5(1), 61, 1979.
36. **Swain, W. R.,** Chlorinated organic residues in fish, water and precipitation from the vicinity of Isle Royale, Lake Superior, *J. Great Lakes Res.*, 4(3-4), 398, 1978.
37. **Thomann, R. V.,** Equilibrium model of fate of microcontaminants in diverse aquatic food chains, *Can. J. Fish. Aquat. Sci.*, 38(3), 280, 1981.
38. **Thomann, R. V. and Connolly, J. P.,** A model of PCB in the Lake Michigan lake trout food chain, *Environ. Sci. Technol.*, 18, 65, 1984.
39. **Thomann, R. V. and Di Toro, D. M.,** Physico-Chemical Model of the Fate of Toxic Substances in the Great Lakes, Final Draft Report, U.S. Environmental Protection Agency, Washington, D.C., 1983.
40. **Thomann, R. V.,** Physico-chemical and ecological modeling of the fate of toxic substances in natural water systems, in Proc. ISEM Conf. on Modeling Fate and Effect of Toxic Substances in the Environment, Jorgensen, Ed., Copenhagen, 1983.
41. **Thomann, R. V. and Di Toro, D. M.,** Physico-chemical model of the fate of toxic substances in the Great Lakes, *J. Great Lakes Res.*, 9(4), 474, 1983.

MONS 006334

42. Veith, G. D., Chlorinated Hydrocarbon in Fish from Lake Michigan, Project No. 16020 PBB, U.S. Environmental Protection Agency Water Quality Office, 1973.
43. Veith, G. D., Baseline concentrations of polychlorinated biphenyls and DDT in Lake Michigan fish, 1971, *Pest. Monitor. J.*, 9(1), 21, 1975.
44. Weininger, D., Accumulation of PCBs by Lake Trout in Lake Michigan, Ph.D. thesis, University of Wisconsin, Madison, 1978.
45. Wells, D. E. and Johnstone, S. J., The occurrence of organochlorine residues in rainwater, *Water Air Soil Pollut.*, 9, 271, 1978.
46. Zaika, V. E., *Specific Production of Aquatic Invertebrates*, John Wiley & Sons, New York, 1973.

MONS 006335

Chapter 7

PCBs IN THE BALTIC ENVIRONMENT

Mats Olsson

TABLE OF CONTENTS

I. A Short Presentation of the Baltic Sea — Brackish Water System 182

II. The Early Findings and PCB Alarms 182

III. Pollution Levels in the Baltic 183

IV. PCB Levels in Locally Polluted Regions 185

V. Seasonal Variations of PCB Levels in Fish 186

VI. Effects of PCBs 187
- A. Field Studies on Effects of Organochlorines on Birds 188
- B. Field Studies on Effects of Organochlorines on Mammals 190
  - 1. Decreasing Seal Populations 191
  - 2. Lowered Reproductive Rate Among Seals 191
  - 3. Closed Uteri 193
  - 4. Can We Compare PCB Levels in Various Seal Populations? 195
  - 5. Otter 195
  - 6. Mink 196
  - 7. Porpoise 196

VII. What Impact Have Legislation and Changes in the Use of PCBs Had on the Baltic Biota Levels? 198

VIII. What Experiences Have We Gained from the Baltic PCB Studies and What Can We Learn for the Future? 202

References 205

MONS 006336

I. A SHORT PRESENTATION OF THE BALTIC SEA — A BRACKISH WATER SYSTEM

The Baltic represents a marine environment with some very specific characteristics. It comprises the Bothnian Bay, the Bothnian Sea, the Gulf of Finland, and the Baltic proper. The Bothnian Sea and Bay together are named the Gulf of Bothnia (Figure 1). All over the Baltic the water is brackish with a salinity in the surface water varying from 1% in the south to about 0.2% in the north. It is a cold area, and during winter ice normally covers the archipelagos and even the open sea in the Gulfs of Bothnia and Finland. In some years the ice cover will also extend into the northern areas of the open Baltic proper, and during extreme winters all the Baltic area is ice covered.

In some areas (deeper parts of the Baltic proper) there is a well-developed halocline separating a water volume of high salinity on the bottom from a surface volume of less salinity. These two volumes have separate exchange times. Since the Sound and the Belt Sea are shallow and narrow waters, the exchange of water between the North Sea and Baltic is limited, and normally only surface water is exchanged. Occasionally, with strong western winds, high water levels, etc., water of a high salinity will be pressed over the threshold into the Belt Sea and the Sound, and new fresh marine water of a high salinity will be pushed into the Baltic and press the old bottom water up to the surface volumes and a water exchange of the bottom water will then take place. Normally, the bottom water has less interim time than the surface water. Tidal movements in the Baltic are very small — only a few centimeters.

All nations around the Baltic are industrialized countries, which creates pollution problems caused by multitudinous disposals of waste material. There are three reasons why the Baltic area is very sensitive to pollution: (1) it is a heavily industrialized area with many kinds of disposals; (2) there is a slow water exchange, not only caused by a narrow connection area in the Belts and Sound, but also by stratification layers such as the halocline and thermocline, which prevents vertical movement in the water; and (3) it has a low temperature, implying slow biological turnover and low metabolic activity.

The fish fauna of the Baltic are a mixture of fresh water fauna such as perch, pike, roach, etc., and marine fauna such as cod, sprat, herring, flounder, etc. The freshwater fish dominate in the north and in the archipelagos, while the marine fish fauna dominate in the south, and especially in the open sea. However, in all areas, there is a mixture of fresh and marine water species.

II. THE EARLY FINDINGS AND PCB ALARMS

The first study of the serious DDT and PCB pollution of the Baltic was presented in 1969.[1] The research behind the publication was a result of the discovery of PCBs as an environmental pollutant by Jensen.[2] It is worth mentioning that this happened shortly after a long, intense discussion about mercury as an environmental pollutant in Sweden. Both the agricultural use of mercury as a seed dressing agent and the industrial use of mercury as in the pulp and paper industries has caused severe damage to the Swedish bird fauna and also led to limitations in the possibility to use the fish caught in locally polluted rivers, lakes, and coastal areas. The fish from these areas were blacklisted and it became forbidden to sell them on the market. Simultaneously, the book *Silent Spring*, by Rachel Carson made people aware of the DDT problems in the world. Later, the news that the whole marine environment of the Baltic was threatened, not only by the then-relatively well-known DDT substance, but also by an entirely "new", unknown substance called PCB, was more than slightly shocking.

Among the most striking results were the high DDT and PCB levels found in white-tailed

MONS 006337

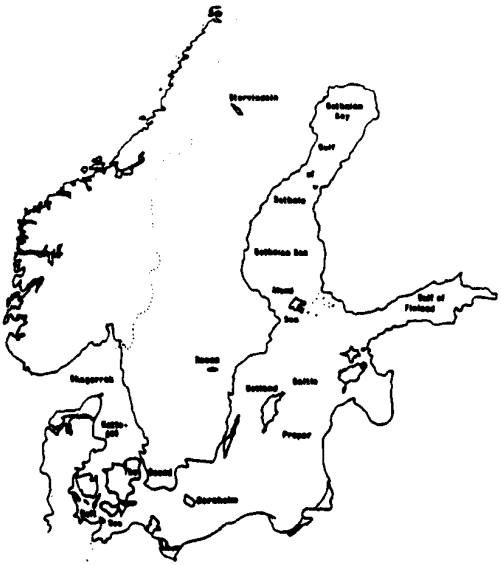


FIGURE 1. Map of the Baltic Sea. Geographical names used in the text have been indicated on the map.

sea eagles (*Haliaeetus albicilla*) which were found dead in the archipelago along the Swedish Baltic coast.[1] Levels of 10,000 mg/kg of both substances, or even more, were found in the fat of the sea eagles, implying that as a mean 3.9% of the eagle fat was a mixture of PCB and DDT. Many papers followed this report on the Baltic DDT and PCB pollution and confirmed the findings of a serious pollution.

III. POLLUTION LEVELS IN THE BALTIC

The work of Jensen and co-workers in 1969[1] was followed by a more comprehensive article presenting the geographical distribution of DDT and PCB measured in Baltic fish which were collected in the pelagic part of the Baltic.[2] Herring (*Clupea harengus*) was mainly used for environmental sampling, but cod (*Gadus morhua*), sprat (*Sprattus sprattus*), flounder (*Pleuronectes platessa*), and other species were also analyzed.

Simultaneously, littoral fish species such as pike (*Esox lucius*) and young eel (*Anguilla anguilla*), were collected along the Swedish coast and analyzed for presence of PCB and DDT. Both pike and young eel are more or less stationary species, making them representative for a specific area of the shoreline. The geographical distribution of DDT and PCB pollution was compared in the littoral fish fauna and the pelagic[4] (Figure 2). As a summary of the results, it can be said that based on the littoral fish fauna, local influences of PCB pollution

MONS 006338

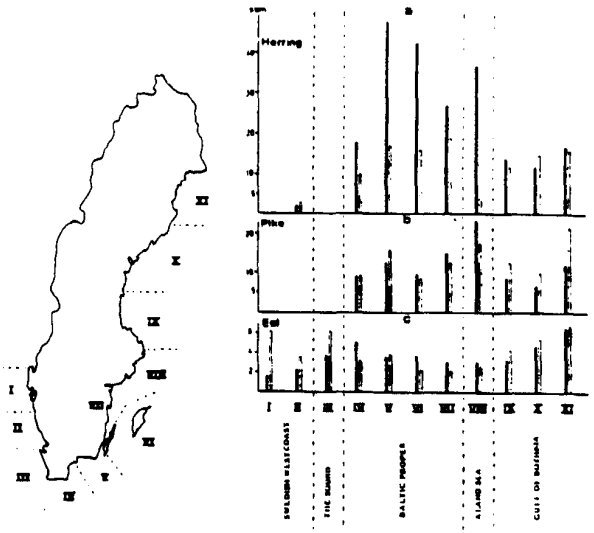


FIGURE 2. Levels of DDT substances (filled bars) and PCB substances (unfilled bars) in extractable fat of herring, pike, and eel collected in various parts of the Baltic environment. Observe that the scales on y-axis differ between eel and herring and pike. The map visualizes the collection areas.[1]

were found at several locations along the Swedish coast. However, no general gradient differences in PCB levels or DDT levels were found in materials collected from both the Gulf of Bothnia and the Baltic proper. Also, in pelagic fish such as herring, the PCB levels were of the same magnitude all over the studied area, but the levels of DDT substances (DDT + DDD + DDE) were substantially higher in the south of the Baltic proper than in the Gulf of Bothnia. Thus, the only major difference found between areas of the Baltic was found in DDT levels in pelagic fish, but not in littoral fish. This was explained by the presence of the distinct halocline in the deeper part of the central Baltic proper area, separating a deeper water volume from the surface water volume. The littoral fish, like pike and young eel are living in the upper water layers, while herring in the central Baltic proper have an essential feeding area in the stratification layers. In other areas, e.g., the Gulf of Bothnia and west of Bornholm where the levels of DDT were lower than in the central part of the Baltic proper — there is no halocline since these areas are too shallow. Thus, herring have no possibility to remain for a longer (or shorter) period in the halocline. It is believed that the bottom water below the halocline with longer interim time is more representative for an older period, while the surface water layers, which have a shorter interim time are more representative for the present period.

The western world production of DDT reached its maximum during the 1960s, while the maximum PCB production seems to have occurred later or in the beginning of the 1970s.[5-7] An older pollution situation ought to be found in the older water and thus one

MONS 006339

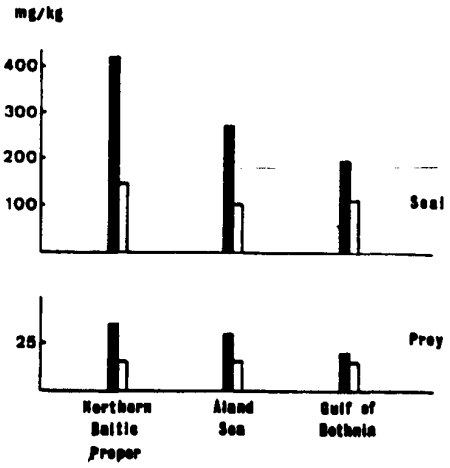


FIGURE 3. DDT substances (filled bars) and PCB substances (unfilled bars) in seal food and in seal blubber from different Baltic regions. All levels are given on a lipid weight basis.

expected to find more DDT in fish staying for some period of time in the deeper and older water layers which only herring (not pike and young eel) reach. Pike and eel in the entire Baltic and herring from areas where no halocline is developed, on the other hand, would represent the situation of the surface water, and a more recent period in time.

Another example of geographical variations in PCB and DDT in biota is contained in a study on seals. From earlier investigations the composition of the food for seals from different Baltic areas is fairly well known;[9] from data on levels of organochlorines in various fish species representing different areas of the Baltic, it was possible to calculate the mean levels of DDT and PCB in the fat of seal food and compare them to levels found in seal blubber.[9] An obvious conclusion is that the pollution pattern found in the calculated mean levels of the seal food coincides with those found in seals from various parts of the Baltic (Figure 3).

IV. PCB LEVELS IN LOCALLY POLLUTED REGIONS

In some areas and for some organisms the changes in PCB levels have been studied outside local discharges following a gradient from disposal point at the mainland out through an archipelago to open sea. In the archipelago of Turku in Finland high levels were found in pike form the inner part of the archipelago compared with pike from the outer parts.[10] A similar situation was also found in the archipelago outside Stockholm where pike were analyzed[11] (Figure 4). A third example of decreasing PCB levels in fish when moving away from the disposal point is found in cod from the Western Baltic.[12]

The first study of regional changes in PCB level near a disposal area in the Baltic was

MONS 006340

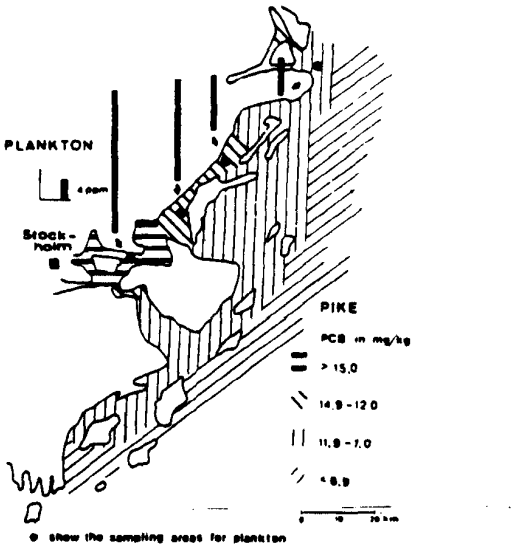


FIGURE 4. Levels of PCBs in pike and plankton collected in the archipelago outside Stockholm. All levels are given on a lipid weight basis.

carried out on plankton samples from outside Stockholm.[12] The levels decreased out to the periphery of the archipelago (Figure 4). The composition of the PCBs changed accordingly. The nearer the harbor and disposal area, the higher the percentage of tetrachlorobiphenyls were found in samples.[12]

In both the paper concerned with pike and the one with plankton from Stockholm,[11,12] it was stressed that the discrepancy between the outer and the inner part of the archipelago would have been larger if not for the simultaneous eutrophication taking place in the inner parts. The pollution with nutrients increases the biomass, implying a bigger biomass to "take care of" or dilute bioaccumulating substances such as PCBs and DDT.

V. SEASONAL VARIATIONS OF PCB LEVELS IN FISH

During a 7-year long study, roaches *(Rutilus rutilus)* were collected each month in Lake Roxen, which has an outflow of water into the Baltic (Figure 1). The fish were analyzed for the presence of PCBs, and substantial changes in PCB levels were found during the year.[14] All increases of PCB levels occurred during the winter and spring, even if the time of the year when the levels increase varied by some months. Furthermore, there were also years when no apparent increase occurred (Figure 5). A number of variables were tested against the PCB levels, such as fatness of the fish, snow melting, fish migration, spawning, and spring flow. It was discovered that the increase of PCBs in the fish was correlated to

MONS 006341

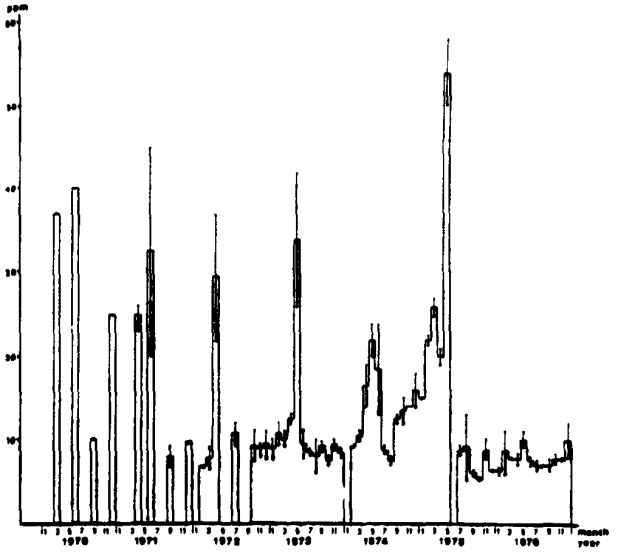


FIGURE 5. Mean levels of PCBs in extractable fat of roach muscles collected from Lake Rosen in different months during 1970 to 1976. Two tissue homogenates were normally tested on each occasion. Results from the individual homogenates are shown with dots.[14]

the spring flow of the contributing rivers of the lake. In 1 year there was no spring flow and consequently no increase in PCB levels occurred that year.

Also, perch collected in the archipelago of the Baltic show a dramatic change of both PCB and DDT levels in the spring after the spring flow.[15] These results stress the importance of avoiding sampling during the spring, when one collects material for annual monitoring studies. The best time seems to be the period of the most stable level during autumn and winter.[14]

VI. EFFECTS OF PCBs

Today, there are no reliable data showing an effect of PCBs upon Baltic fish. Some earlier data on salmon could be interpreted to mean that PCBs caused a low reproductive rate in Baltic salmon.[16] However, these data have not been confirmed. Much attention has been paid to the effects of organochlorine on Baltic birds as well as Baltic mammals, especially seals. Even in many other parts of the world, one important difficulty faced when interpreting field data is the presence, not of one pollutant, such as PCBs, but of a mixture of pollutants, including PCB, DDT, toxaphenes, and other organochlorines and heavy metals. Following is a short presentation of the field studies in the Baltic, aiming to correlate pollution burdens with reproductive capacities will be given.

MONS 006342

Table 1
DECREASE OF THE EGGSHELL THICKNESS IN SWEDISH BIRD POPULATIONS

Species	%
White-tailed sea eagle (*Haliaetus albicilla*)[20]	18
Marsh harrier (*Circus aeruginosus*)[21]	14
Osprey (*Pandion haliaetus*)[22]	11—13
Guillemot (*Uria aalge*)[23]	11
Razorbill (*Alca torda*)[24]	12

A. Field Studies on Effects of Organochlorines on Birds

It is a well-known fact that DDT substances affect the reproductive capacity of several bird species.[17,18] Much interest has been paid to eggshell thickness and levels of DDT in eggs. Also, Baltic bird populations have been studied[19] and a summary of recent changes in eggshell thickness is presented in Table 1.

A study of DDT and PCB residues in the eggs and the reproductive results of nesting Arctic terns (*Sterna paradisaea*) and hooded crows (*Corvus cornix*) in the archipelagoes of southwestern Finland did not confirm any decrease in the reproductive rate nor any developmental defects of the chickens.[25]

Among razorbills (*Alca torda*) studied in the archipelago of Stockholm, the decrease of the eggshell thickness was found to be more than 10% when comparing data from a period up until 1940 with data from 1970 to 1972.[24] The mean levels of DDT and PCBs in extractable fat of razorbill eggs collected during 3 consecutive years, 1970 to 1972 varied between 590 to 1600 mg/kg and 590 to 1300 mg/kg, respectively.[26] Despite the high levels found and the lessened eggshell thickness, the investigation failed to show any decreased hatching success, young survival, or nesting when compared to other razorbill data.[24]

Another study was concerned with the guillemot (*Uria aalge*) population nesting in the central part of the Baltic proper outside the island of Gotland. The population comprised about 6000 to 7000 nesting pairs and the reproductive rate was followed during the beginning of the 1970s.[26] The mean levels of DDT substances in egg lipids varied between 300 to 600 mg/kg during the investigated period, while the PCBs varied between 270 to 400 mg/kg (Figure 14). Nor for this population was there a significant decrease or reproductive capacity found. The eggshell thickness was, however, decreased by about 11% (Table 1).

The Baltic white-tailed sea eagle is a bird severely suffering from the serious organochlorine pollution of the Baltic environment. The number of nesting pairs along the Swedish Baltic coast is less than 70 pairs.[27] Normally, more than one young is produced per pair and year. In the Baltic area the corresponding figure has been less than 0.4.[28,29]

Based on individual analyses of unhatched eggs collected from 68 sea eagle clutches, critical ranges were estimated for PCBs and DDT.[28] The egg material was divided into three groups in accordance with their reproductive capacity: (1) fertile, successful, (2) fertile, unsuccessful, and (3) infertile. No significant difference was found in the studied levels between groups 1 and 2, but 3 was separated from the other two. The critical ranges for DDE were estimated to be 500 to 600 mg/kg and 800 to 900 mg/kg on a lipid basis for PCBs. The mercury levels could not be correlated to the reproductive capacity, nor dieldrin or hexachlorobenzene. Since there was a close correlation between residual levels of DDT and PCB, it was not possible, based on the Baltic material, to distinguish between an effect caused by DDT from an effect caused by PCBs. However, in a comparative study[30] including six sea eagle populations and six bald eagle populations, the productivity of the different populations showed the strongest negative correlation to DDE levels, and a weaker one to PCBs (Figure 6).

MONS 006343

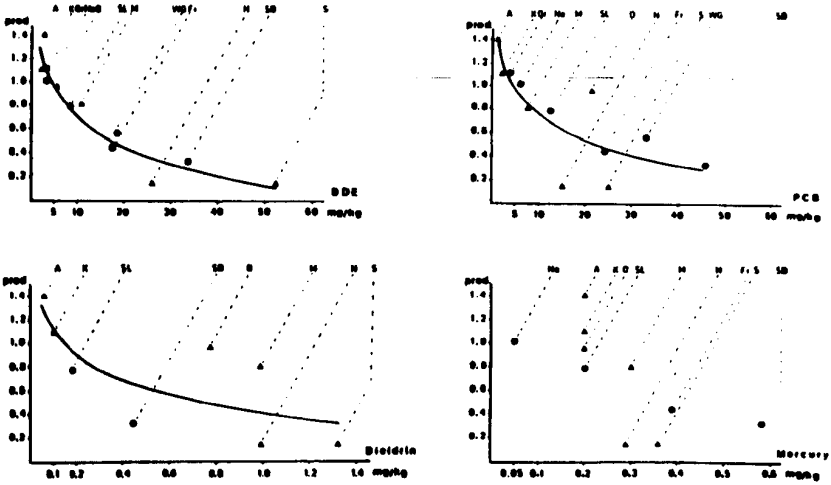


FIGURE 6. The productivity in six bald eagle populations and six white-tailed sea eagle populations plotted against their known mean levels of DDE, PCB, dieldrin and mercury. The following abbreviations have been used: ●, white-tailed sea eagle; ▲, bald eagle; SB, Swedish Baltic coast; SL, Swedish Lapland; Gr, Greenland; No, Norway; Fi, Finland; WG, West Germany; A, Admiralty Island, Alaska; K, Kodiak Island, Alaska; M, Minnesota; N, Lake Nipigon, Ontario; O, northwestern Ontario.[9]

MONS 006344

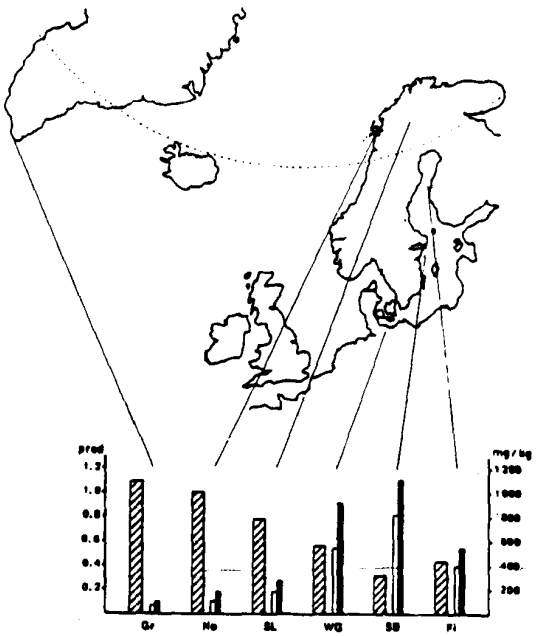


FIGURE 7. Reproductive rate (striped bars) and levels of DDT (unfilled bars) and PCB subcutaneous (filled bars) in European populations of white-tailed sea eagles. Levels are given on a lipid weight basis.[29]

In Figure 7, the number of young produced per pair and year and the mean levels of DDE and PCB in European sea eagle populations is visualized. As an attempt to summarize the results from the Baltic area, it seems that DDT has a major responsibility for the lowered reproductive rate among birds. However, it is still a possibility that PCBs cause an embryotoxic effect, even if this has not been clearly shown. A slight increase of the sea eagle productivity during the last years has been reported from the Gulf of Bothnia.[29] It is not surprising that the levels of DDT and PCB have simultaneously decreased (see following).

B. Field Studies on Effects of Organochlorines on Mammals

Besides man, six mammalian species inhabit and feed on Baltic marine fauna. The species are mink *(Mustela vison)*, otter *(Lutra lutra)*, ringed seal *(Pusa hispida)*, common seal *(Phoca vitulina)*, grey seal *(Halichoerus grypus)*, and common porpoise *(Phocoena phocoena)*. For all of these species the population numbers have decreased during the last 30 years, and for all except mink the changes have been dramatic.

MONS 006345

In the following, all analytical work for determination of PCB levels in Baltic mammals as well as in minks studied in Swedish laboratory tests are carried out at the same laboratory, namely the Swedish Environment Protection Board's Special Analytical Laboratory. This implies that even if data come from various reports they are still comparable.

1. Decreasing Seal Populations

In the beginning of the 20th century seals were common animals along the Baltic shores, even if the species varied from one area to another. Since then, drastic decreases in numbers have taken place as well as reductions of their geographical area of distribution.

Common seals were earlier found on the southern coasts and sandy beaches of Poland, Germany, Sweden, and Denmark, and also in the northern archipelagos of the Baltic proper. Today only some 200 specimens are left, most of which are found in southern Sweden and in Denmark.[30,31]

Ringed seal was earlier a common and widely distributed species in the central and northern Baltic area. The catch of ringed seals up until the 1960s in Finland and Sweden amounted to several thousand annually. Before 1940, often more than 10,000 individual seals were killed yearly. Today, the species is only rarely observed on the Swedish coast and has totally disappeared from the archipelagos where they earlier were well known. The number of individuals still left in the Baltic area is said to be 10,000.[32]

The number of grey seals in the Baltic in the early 1900s has been estimated to be at least several hundred thousand. Single flocks of over 10,000 individuals were reportedly seen in the Swedish archipelagos. The annual catch of grey seals in Sweden and Finland was about 2000 to 3000 after 1940, with maximum annual catches of over 10,000. Today, only about 1500 grey seals are left along the shores of Sweden, Finland, and the U.S.S.R.[30]

Three reasons for the rapid decline of grey seals have been discussed: namely hunting, disturbances and stress, and environmental pollution. There is no doubt that the extensive hunting, which took place during the beginning of the 20th century, caused a severe decrease of the seal stocks.[30,33] However, after World War II, the hunting ceased for several reasons and some reports indicated increasing stocks during the 1940s and 1950s.[34] After the 1950s the seal stocks decreased dramatically, despite the fact that by then hunting was very rare, and thus cannot explain the continued and rapid decrease.

Even if human disturbances can explain a disappearance of seals from some areas in the Baltic, there is no reason to believe that such disturbances in themselves have been so extensive that they alone can explain disappearances of seals from many parts of the Baltic coast.

Unintentional killing of seals, especially pups and young seals, is another effect of human activities. Ice breaking in breeding areas should not be too dangerous, as the ice breakers normally avoid the hard and thick ice of the seal breeding areas. Fishing, however, takes a heavier tribute. Of about 100 marked grey seal pups, 20 of them were found drowned in fishing gear within 6 months, indicating a great increase in juvenile mortality unintentionally caused by man.[35]

For the total body of populations, stress can hardly be a sole cause of their decline. Stress might, however, be important with regard to the local distribution pattern, and in increased susceptibility to pollutants.

2. Lowered Reproductive Rate Among Seals

Hook and Johnels[30] were among the first to stress the possibility of toxic effects of DDT and PCBs on seals. Results from laboratory and field investigations led to a preliminary hypothesis regarding effects of DDT and PCBs on the reproduction capacity of Baltic seal populations.[9,36] Findings of aborted seal pups in the Baltic area were correlated to similar reports from California.[9,37,38] The Baltic report[9] was presented at an International Baltic Seal

MONS 006346

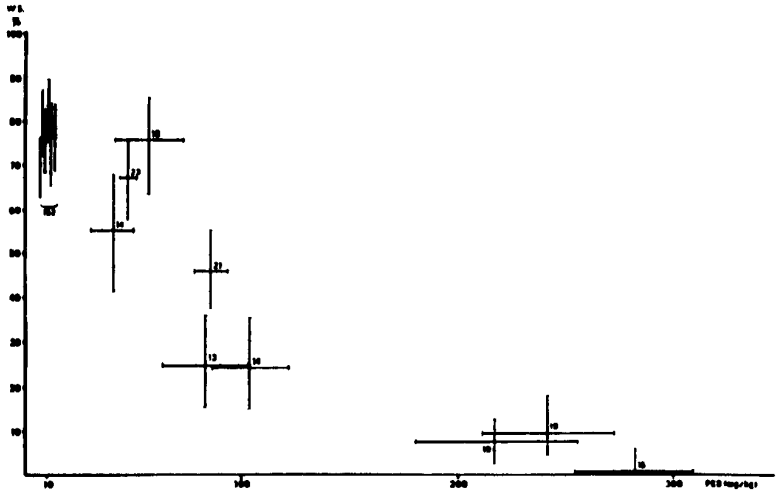


FIGURE 8. Whelping success in relation to PCB levels in musk bitches treated with PCBs for 2 to 3 months. Horizontal line visualizes the 95% confidence interval for PCB levels on a lipid weight basis and the vertical line gives the binomial distribution for whelping success. The figures in the diagram give the number of bitches analyzed per group.

MONS 006347

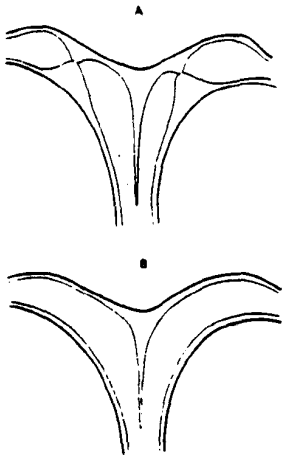


FIGURE 9. A schematic image of an occluded seal uterus (A) and a normal nonpregnant uterus (B).[39]

Symposium in Stockholm in 1979, and at the same meeting, a low reproductive rate was reported among the ringed seal of the northernmost part of the Bothnian Bay.[39] A cooperation between Finnish and Swedish scientists, who studied the ringed seal of the Bothnian Bay, revealed significantly higher levels of DDT and PCBs in nonpregnant females than in pregnant females.[40] All investigated Baltic specimens had corpora lutea and evidently the animals had ovulated. The low reproductive rate (only about 25%) was compared with corresponding figures from populations in the Arctic part of the Soviet Union[41,42] where 65 to 90% of the adult females were pregnant.

A comparison of levels of DDT and PCBs in Baltic seals with those found in aborting Californian sea lions led to the assumption that PCB was the noxious substance responsible.[40] Laboratory investigations have shown that the reproductive rates of mink decreased when exposed to PCBs, but not DDT, which was mixed into their feed.[43-47] PCB admixtured to the level in Baltic seal food was found to decrease the reproductive rate of mink significantly.[46,47]

Figure 8 presents a summary of the laboratory results from the Swedish mink investigation.[46,47] The levels of PCB in fat sampled from the bitches at the time of delivery, and after more than 2 to 3 months of PCB exposure are plotted vs. whelping success, e.g., the percentage of implanted ova grown to delivery or partus. As can be seen, the whelping success for minks decreases at about 50 mg/kg lipid and more or less ceases at 150 mg/kg lipid.

3. *Closed Uteri*

A remarkable finding in the Finnish-Swedish cooperation was the extremely high frequency of pathological changes of the uteri.[40] More than 40% of the investigated adult ringed seal females had occlusions or stenoses in one or both of the uterine horns (Figure 9). An increase of 10% in the frequencies was reported during the late 1970s.[40]

MONS 006348

Table 2
FREQUENCY OF ADULT SEALS WHICH WERE FOUND WITH NORMAL AND OCCLUDED UTERI IN MATERIAL OF SEALS FOUND DEAD OR DROWNED IN FISHING GEAR ALONG THE SWEDISH COAST

Species	n	Normal	Occluded
Grey seal (*Halichoerus grypus*)	32	16	16
Ringed seal (*Phoca hispida*)	23	8	15
Common seal (*Phoca vitulina*)	7	3	4

The occlusions and stenoses are not only found among ringed seals from the Bothnian Bay, but from all of the Gulf of Bothnia, the Baltic proper, and also from the Swedish west coast. This means that all areas around the Swedish coast have these changes, and furthermore, not only ringed seal but also grey seal and common seal have the pathological changes.[50] This implies that the changes are not species specific, nor geographically specific. Recent data on the frequencies of occlusions among seals found dead or accidentally caught by fishermen along the Swedish coast are shown in Table 2.

All occlusions or stenoses were found in an area on the uterus' horn where implantation normally occurs, and only adult females have such pathological findings. Furthermore, the frequencies of animals with occlusions or stenoses increase with increasing age and double-sided occlusions are more common among older females than younger.[49,51] This is to be expected if an occlusion has its origin in an earlier implantation with the following resorption since the animals must be older in order to have had two resorptions rather than one.[52]

Thus, from the localization of the occlusions and stenoses in the uterine horns, it is likely that the pathological changes occur at the place of an earlier implantation. Based on experimental data on minks and field data on seals, the hypothesis is put forward that PCBs or contaminants in the commercial PCB mixtures covarying with PCBs cause fetal death in seals as in minks.[36,48,68] The pinniped placenta differs from the mink placenta and being a diving animal, seals have some specific physiological problems, like the diving reflexes,[53] which can bring forth species-specific reactions during resorbtion or maceration processes, causing occlusions.[52]

To explain the mechanisms of occlusions, we need more information from both field research and laboratory experiments. Species variation in sensitivity for PCBs is a well-known fact. Laboratory experiments on seals within the Baltic area are, for both practical and ethical reasons, unsuitable. Furthermore, if the diving and the diving reflex is a specific process essential for genesis of the occlusions, giving specific physiological problems during a period when absorption, resorption, or maceration takes place, this phase of life will be even more difficult to simulate experimentally using laboratory conditions, even if seals can be used as test organisms.

Another way to study the process is to autopsy and examine organ preparates collected from seals from the Baltic in order to study the health and pathology of the seals suffering lessened reproduction.

These studies are carried out in Sweden and reports have been given from these investigations.[52-54] The studies are based on autopsies of 61 grey and 24 ringed seal females found dead at the shore or caught in fishing gear in the Baltic. Of these, 19 grey and 10 ringed seals were in such a fresh condition that the autopsies could be followed by histological examinations.

Uterine stenoses and occlusions were present in 30% of the adult grey seals. A corresponding figure for ringed seals was 70%. Uterine tumors (leiomyomas) were frequent in

MONS 006349

older grey seals being found in 46% of the animals more than 20 years old. No uterine tumors were found among ringed seals. Among the seals found in a fresh condition and where microscopical investigations could be carried out afterwards, lesions in other organs were found. When the frequency was found high among adult animals the frequency is given here within parentheses. Regional chronic intestinal ulcers were sometimes fatal (grey seal 77%, ringed seal 88%); bilateral adrenocortical hyperplasia (grey seal 83%, ringed seal 75%); arteriosclerosis; renal glomerulopathy (grey seal 92%, ringed seal 75%). In some grey seals regional bilaterally symmetric skin changes were observed with the character of a thin epidermis, hyperkeratosis, and cystic dilatations of hair follicles. Deformations and fractures of the claws were found in some grey seals.

The frequency of lesions found among Baltic seals seem very high when compared with earlier findings reviewed in a recent publication.[33]

Because of the high frequency and the character of the lesions which occurred in combination in the single individuals, influences of exogenous toxins such as PCBs and other organochlorines are believed to be part of a disease complex. This influence seems to interfere primarily with the endocrine system causing changes similar to those present in hyperadrenocorticism.

4. Can We Compare PCB Levels in Various Seal Populations?

There are many figures in the literature covering levels of PCBs in seals which can be used as comparison values between different areas. However, it is important to stress that this comparison must be made with caution. When trying to compare data for different populations, it is important to get values for the pollution burden from representative seals. Many parameters must be considered before the analytical values can be compared.[32] The methods used in the chemical analyses ought to be intercalibrated and the following biological parameters must be considered and discussed before any comparison can be made: species, age, sex, blubber thickness, health condition, sampling period of the year, and sampling methods.

A striking example from the Baltic on the difficulty to compare levels in actively killed animals with levels in animals found dead has been given.[32] From Table 3 it is apparent that the variation and range are much wider in the samples comprising animals found dead than in material composed of actively killed animals. The lower limit in the two samples is (which could be expected) much the same. Much of the data given in the literature are based on animals found dead *or* on a mixture of actively killed animals and animals found dead. These data must be interpreted with caution.

It is evident that scientists working with the Baltic seal populations and studying the effects of environmental pollution on seal reproduction have a grave suspicion that PCBs (or contaminants of the commercial PCB mixtures) are responsible for the decrease in population numbers and the high frequency of pathological changes.

5. Otter

The otter populations have decreased rapidly in Sweden, though all hunting has been forbidden.[20] There are several causes for the decreases in otters. Among causes mentioned are disturbances, fisheries, acidification of the water causing a killing of the otter feed, traffic accidents, and environmental pollutants. Obviously, all of these causes might partly and locally be responsible for the decreases in the otter populations. However, PCB is believed to be one important reason for the decline in Sweden and on the Baltic coast.[17,20]

More than 50 Swedish otters drowned in fishing gear or killed in traffic, etc., were analyzed for the presence of three of the most important environmental pollutants in Swedish nature. As a comparison value, 23 otters (shot in Norway) from a stable or increasing Norwegian otter population were analyzed. The levels of both mercury and DDT were

MONS 006350

Table 3
LEVELS OF PCBs (mg/kg) IN EXTRACTABLE FAT FROM SEAL BLUBBER

Species	n	M	Range
Grey seal (*Halichoerus grypus*)			
Males and females			
Killed	60	110	47—330
Found dead	54	820	84—4500
Ringed seal (*Phoca hispida*)			
Males			
Killed	24	100	35—270
Found dead	12	240	38—640
Females			
Killed	61	93	27—190
Found dead	6	270	125—710
Common seal (*Phoca vitulina*)			
Pups			
Killed	30	43	18—100
Found dead	43	100	12—500

Note: The material is divided into actively killed animals and those found dead; n = number of specimens analyzed; M = mean value.

comparatively low in both the Swedish and Norwegian material, whereas the Swedish otters had higher PCB levels (in mean 120 mg/kg lipid) and the Norwegian levels were low (in mean 17 mg/kg lipid) (Figure 10). As a comparison, the reproductive rate of mink, closely related to otter, decreased at a PCB level of 50 mg/kg lipid[46,47] see also Figure 8.

6. Mink

Little is known about "natural" numbers of mink, mainly because the species is a foreign fauna element for the Baltic escaped from farms, and consequently there is no real natural number. No census has been made, nor is there any traditional knowledge about the number in "earlier days". We thus have to face up to the fact that all data on mink are extremely uncertain and very difficult to interpret.

However, Gerell studied the hunting statistics of mink in Sweden,[59] and assuming that the numbers of captured minks reflect the population status, he found that the mink population after a rapid increase leveled off in the late 1950s and decreased during the early 1970s[60] (Figure 11). According to Gerell the Swedish mink population stabilized during the middle of the 1970s, and after 1977 there is a strong increase.[61] Monitoring results presented later in the chapter show that the PCB levels started to decrease after 1977. The indications that the mink population now increases might be the first important sign of a change in pollution impact on the Baltic environment. These results are, however, subject to many reservations.

7. Porpoise

A final remark shall be paid to the common porpoise. Levels of DDT and PCBs in porpoises drowned in fishing gear or found dead along the Swedish coast have been found to be high.[62] Many animals were found dead and as was the case for seals mentioned above, these levels might be too high for the normal population. The porpoise population has decreased since World War II, but the reason is not quite understood. Even if the levels of organochlorines sometimes are high, other ecological factors might also be important. For instance, the amount of suitable food supply for porpoise (herring and mackerel) has decreased severely on the Swedish western coast during the last decades. This might be one

MONS 006351

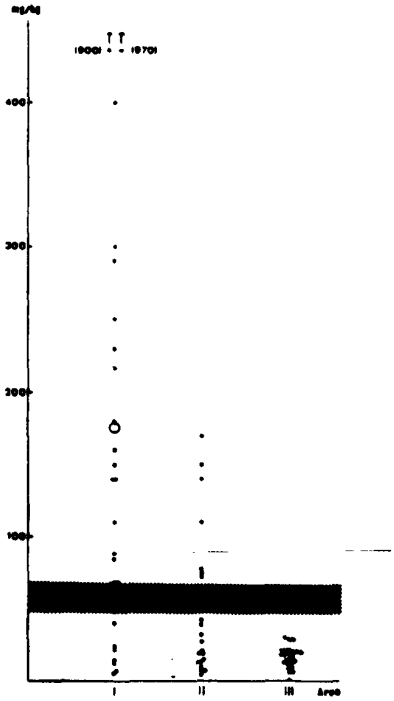


FIGURE 10. Levels of PCBs in extractable fat from muscles of otters from various parts in Scandinavia. Each dot represents an otter. The circles imply the mean level of the group. The lined area indicates the PCB level at which mink treated with PCBs in the laboratory decrease their ability to reproduce. The following areas are represented: (I) southern Sweden, (II) northern Sweden, (III) Norway.

important reason why porpoises today do not migrate to Swedish waters. Formerly, the Sound and the Belts were apparently an important area for porpoise hunting,[43] which might imply that these areas were migration routes.

Whether porpoises found in the Baltic belong to a separate and isolated population or are only visitors following shoals of mackerel, garfish, herring, and sprat from Skagerrak and Kattegat through the Sound and the Belts is not quite clear. If the latter is true one would not expect a large porpoise population in the Baltic during the last decades due to lack of fish suitable as food for porpoise along the Swedish west coast.

MONS 006352

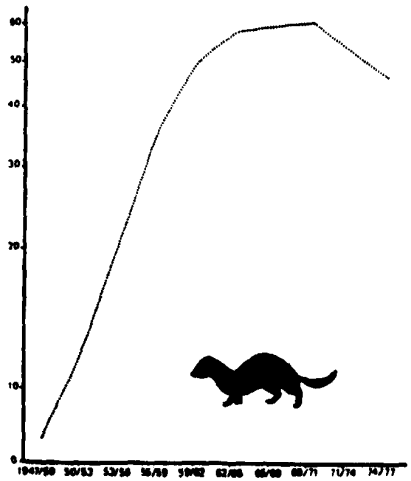


FIGURE 11. Number of mink caught in Sweden during the period 1947 to 1977. Figures on the y-axis indicate a × 1000.[45]

VII. WHAT IMPACT HAVE LEGISLATION AND CHANGES IN THE USE OF PCBs HAD ON THE BALTIC BIOTA LEVELS?

After the first reports on the serious DDT and PCB pollution of the Baltic, many steps have been taken by various countries in order to minimize or eliminate the use of both DDT and PCBs. Today, the use of both DDT and PCBs is more or less banned in all Baltic countries.[44] To what extent have these steps influenced the levels of organochlorines in Baltic biota? Several countries have contributed with series of analytical data providing us with the possibility to follow the situation.

There are two sets of data indicating earlier changes in pollution burdens in the Baltic. Data concerning levels of DDT and PCBs in dated sediments from the central Baltic have been presented[45] (Figure 12). Since DDT was not used until after World War II, it seems that DDT penetrates down through the sediments and is thus found in sediments from 1930 or even earlier. Also, PCBs are found in sediments from the 1930s, which is again probably caused by a late penetration of the substance down through the sediments.

Seal oil has been used as painting oil by seal hunters and fishermen. Older samples of seal oil have been analyzed and the results give us a rough idea of the changes in biota levels since the 1940s[9] (Table 4). Both the sediment samples and the seal oil samples indicate a rapid increase of environmental levels of pollution in biota.

Fish are, however, the samples normally used as monitoring material. Herring collected outside Finland during the period 1973 to 1975 show a significant decrease in DDT levels.[46] Decreasing DDT concentrations were also found in the southern Baltic in cod, herring, sprat, and garfish during the period 1975 to 1979.[47] In the Turku archipelago, the DDT

MONS 006353

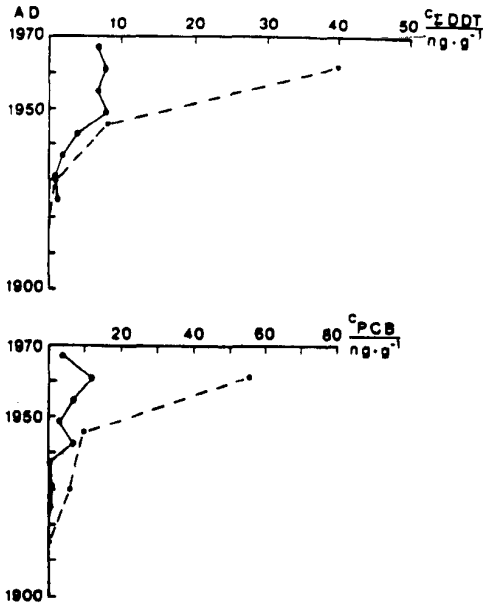


FIGURE 12. Levels of DDT and PCB in dated sediments from the Gulf of Bothnia (solid line) and the northern Baltic proper (dashed line).[48]

Table 4
LEVELS OF DDT AND PCB COMPOUNDS (mg/kg) IN EXTRACTABLE FAT-SEAL OIL OF SEALS FROM ÅLAND SEA SHOT DURING DIFFERENT PERIODS

Period	n	ΣDDT	ΣPCB
1940—1945	1	0	0
1950—1955	1	10	5.2
1968—1970	27	270 (68—850)	100 (20—320)

levels in pike were found to decrease between 1971 to 1978.[48] None of the cited reports were able to detect any PCB changes of significance.

In two series of herring samples covering a period from 1970 to 1981 collected in the southern part of the Baltic proper and the southern part of the Gulf of Bothnia, the levels

MONS 006354

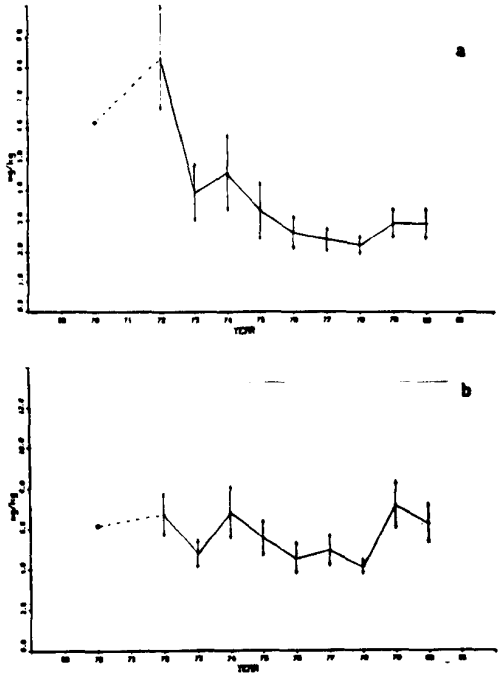


FIGURE 13. Levels of DDT substances (a, c) and PCB (b, d) in herring muscles collected in the southern part of the Gulf of Bothnia (a, b) and in the southern part of the Baltic proper (c, d). All levels given are on a lipid weight basis. Vertical line gives the 95% confidence interval.

of DDT decrease in both series while PCB only seems to decrease in the Baltic proper[49] (Figure 13).

In monitoring trend studies all environmental samples suffer in a more or less serious way by not being comparable in all respects with earlier collected samples. Samples of pelagic fish, even if using fish of the same age, sex, size, etc. and collected at the same locality and time of the year, will in one or many aspects differ in parameters of importance when comparing levels. For instance the migration route will vary between years implying different pollutant history for fish from different years. Reasons for varying body burdens for stationary species may be changes in water stream, temperature variation, variation in density of the biomass, etc.

When choosing a fish-feeding predator, a kind of integration can be possible, assuming

MONS 006355

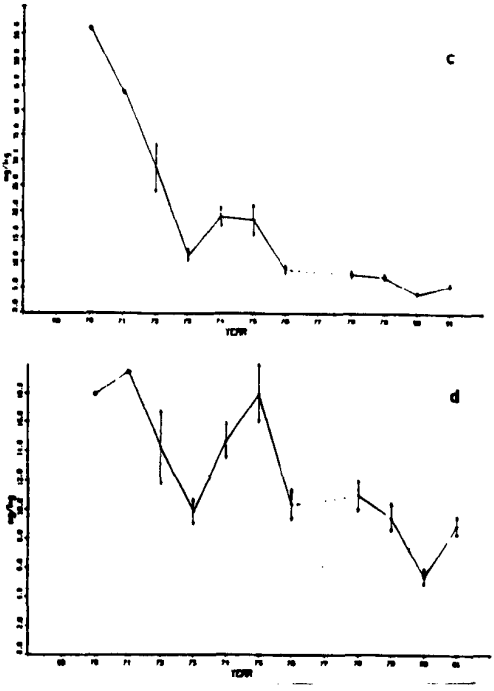


FIGURE 13.

the predator will select its food in a random way and will choose food from vagrant species covering a larger but still limited area. However, to be an ideal monitoring organism, the predator ought to stay all its life within the area to be monitored. The mammals of the Baltic are first of all very rare, which implies that active collection by hunting is not possible for both practical and ethical reasons. Furthermore, Baltic mammals have access to many possible food species, which implies that the individual specimens within the populations represent different food sources.

Among predatory birds, another problem predominates. Most of the species nesting in the Baltic leave the Baltic during the winter. Furthermore, most of the Baltic bird species are nesting in a scattered way along the coast, implying that the individual nests represent different local pollution burdens or local variations in availability of food species when different food species have different pollution burdens. However, the guillemot is in all of these respects more or less ideal, being a colony nesting bird, nesting on a small island in the central part of the Baltic proper far away from local discharges, over-wintering in the

MONS 006356

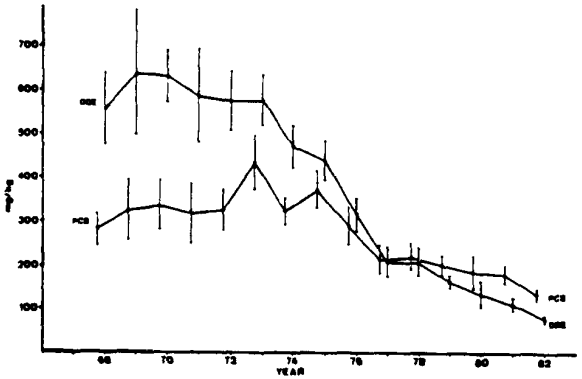


FIGURE 14. Levels of DDE and PCB on a lipid weight basis in guillemot eggs collected in the central part of the Baltic proper. Vertical line gives the 95% confidence level.

open part of the Baltic Sea, and feeding more or less exclusively on the vagrant clupeid fishes, as do herring and sprat. Guillemot eggs have been collected annually since 1968 at the island of Stora Karlsö west of Gotland. The eggs have been analyzed for the presence of DDT and PCBs[49] (Figure 14).

The 95% confidence limit for the annual samples is rather small, indicating a homogeneous population. Futhermore, the trend is more easily seen from the guillemot eggs (Figure 14) than Baltic fish samples (Figure 13). From the series in Figure 14, it is obvious that both the levels of DDT and PCB have decreased in the central part of the Baltic proper. The decreases of DDT came, however, earlier than PCBs, and the decrease of PCBs is less dramatic even if the levels today are only about 50% of the levels in the beginning of the 1970s.

The Baltic is a seriously polluted area. What has happened in a remote area of the Baltic environment can be seen in Lake Storvindeln, situated in the northern mountainous area of Sweden (Figure 1). Pike have been collected annually from the lake since 1967 and analyzed for both DDT and PCB levels[50] (Figure 15). Also, in this part of the surroundings to the Baltic area, the levels of both DDT and PCB have decreased. However, the PCB levels seem to have started to decrease earlier in the remote area than in the Baltic.

As a summary of the trends studied, one can conclude that the levels of both DDT and PCBs are now decreasing, even if the trend for PCBs is uncertain in the southern part of the Gulf of Bothnia.

VIII. WHAT EXPERIENCES HAVE WE GAINED FROM THE BALTIC PCB STUDIES AND WHAT CAN WE LEARN FOR THE FUTURE?

Looking back on the last 15 years during a time when the discussions about PCB pollution in the Baltic took place, it might be fruitful to find out what we have learned.

First of all, nations around the Baltic have become aware of the danger of environmental pollution in general, and that among the various pollutants, persistent bioaccumulative substances play an important role. The problem is no longer only the local problem outside

MONS 006357

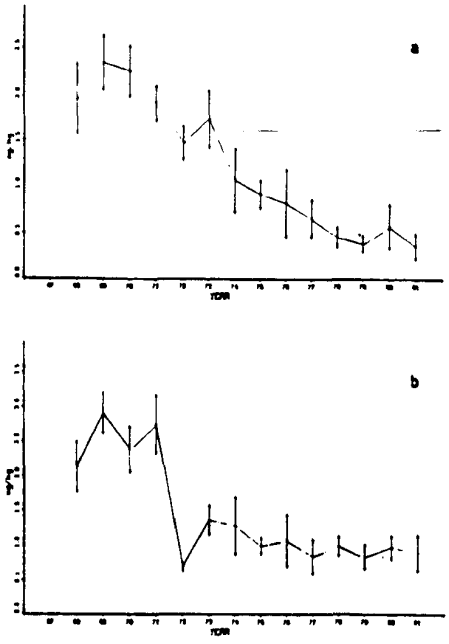


FIGURE 15. Levels of DDT substances (a) and PCBs (b) on a lipid weight basis taken from pike muscles collected in Lake Storvindeln in northern Sweden. Vertical line gives the 95% confidence interval.

the discharge area, but rather the whole Baltic area is contaminated by various substances in a way unbelievable only 15 years ago.

The biologists are now aware of the increasing risks with toxicants in the whole ecosystem, not only in locally polluted areas, but also in regions in the Baltic where reference areas (areas believed to be uninfluenced) were placed only a few years ago. We have to face the situation that there is no uncontaminated reference area to be found within the Baltic region. This situation is well demonstrated by the inability for the biologists, and chemists, representing various countries around the Baltic, to collect reference material of seals, otters, white-tailed sea eagles, peregrine falcons, etc. in the Baltic.

According to an earlier publication,[79] the total amount of PCBs in the water and biota of the Baltic is not more than about 6 tons. According to the same report, the stable levels of PCB in the Baltic during the early part of the 1970s were due to an airborne fallout of about 6 t/year. The transport of persistent and noxious substances by air has been demonstrated for mankind during the last decades, manifested in acid rains. DDT, PCB, toxaphenes, etc. Problems with these ecotoxins have to be solved internationally. Within the Baltic area,

MONS 006358

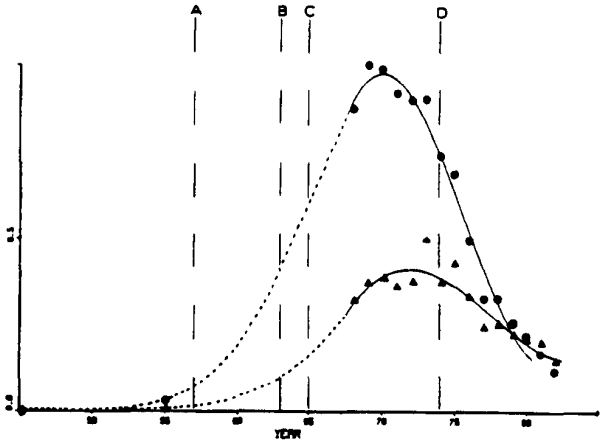


FIGURE 16. The relative amount of DDT and PCB substances during the period 1940 to 1982 in guillemot eggs from the Baltic. The values for 1940 and 1955 are calculated from seal oil data assuming a constant relation between seal and guillemot levels in 1940, 1955, and 1970. The following symbols are used: ●, relative amount of DDT; ▲, relative amount of PCBs; A, reproductive rate started to decrease among Baltic white-tailed sea eagles; B, reproductive failure among white-tailed sea eagles discovered; C, mink population leveled off after a period of continuous increase; D, seal reproductive failure reported.

international organizations such as the Helsinki Commission, ICES, and The Gulf of Bothnia Committee, are now concerned with environmental pollution problems. The need for international scientific exchange is fully understood when reports come out on "new" substances in Baltic environmental samples, today including chlordane compounds, chlorinated terpenes, dibenzofurans, dioxins, chlorinated naphthalenes, PAH, HCB, etc. Probably not one of these substances, for practical and economical reasons, can be studied as carefully as DDT and PCB. However, this is in all respects probably not necessary. Based on information collected during the research on DDT and PCBs, we have some comprehension of the behavior of nonpolar, bioaccumulating persistent chemicals in the Baltic environment and after 15 years, we know how it differs from a polar substance such as mercury. The difference in behavior in nature between nonpolar and polar substances was not easily understood 20 years ago.

We have pointed out critical species for study of nonpolar substances. During the period when mercury problems were discussed, pike and perch were fish species accumulating large amounts of mercury and animals feeding on these were within a risk group. For nonpolar substances, animals feeding on fat fish, such as herring, salmon, cod (liver), and turbot (liver), compose another risk group.

From an ecological point of view, the most important general information we obtained is, in my opinion, the sudden discovery of how rapidly a large marine area like the Baltic can be polluted, and how long a time it takes before the ecological inflictions are discovered. In Figure 16, the levels of PCB and DDT in guillemot eggs are plotted vs. time during the period 1968 to 1982, and a rough estimation of the levels in guillemot eggs in 1940 and

MONS 006359

1955, based on levels found in seal oil (Table 4), have also been plotted. It is obvious that both increases and decreases in levels of DDT and PCBs have occurred very fast (a process of decades). We know today that the reproductive rate of the Baltic eagles started to decrease in the late 1950s.[27] We have good reason to believe that the reproduction rate of the Baltic seals decreased during the same time.[24] The fact that the mink population curve leveled off[28] might be a sign of the same situation (Figure 11). Twenty years later, both the Baltic sea eagle and the Baltic seals are close to extinction. The severe situation for the seals was not discovered until the late 1960s, and that the reproductive rate was decreased was not discovered until 1974. In fact, it was not discovered until about 50% of the adult female seals were sterile.

One explanation for the delay in these discoveries is probably that the animals did not die physically, "only" biologically. The sterile animals were still, and are still, swimming around in the Baltic, concealing the fact that 50% or more of the Baltic females are non-reproductive and biologically dead.

We know today how difficult it is to interpret field data on pollution and its effects since field data never are simply "one pollutant" data but rather a mixture of several pollutants in nature. Laboratory data rarely produce information on synergism or effects of pollutant mixtures, but in nature mixtures and synergism can be "natural". We also know how difficult it is to apply laboratory data to explain field conditions. Can we compare a rat with a mink or a mink with a seal? Why do we have occluded seal uteri in the Baltic? Do we really know anything at all about chronic effects of environmental pollutants? Laboratory research gives quick answers upon rapid investigation. Even if we have long running experiments for 1 to 2 years, this is still a short period of time when one realizes that a Baltic seal's lifetime is 40 years and a man's is 70 years.

With this perspective in mind, it seems not to be an exaggeration to say that the time margins are very small in order to be able to discover and study, inform about, and legislate against, etc., a new environmental pollutant. We know that it takes years of work to develop analytical methods, years of work to find out the biological effects of a substance, and even more years to find out the ecological effects. Normally, it also takes a long time to make new laws, and still more to eliminate pollution nationally. Several years of information and international negotiations are necessary before there can be agreement on a worldwide limitation imposed on the use of any pollutant. Accordingly, hard work remains.

REFERENCES

1. Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G., DDT and PCB in marine animals from Swedish waters, *Nature (London)*, 224, 247, 1969.
2. Jensen, S., The PCB story, *Ambio*, 1, 123, 1972.
3. Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G., DDT and PCB in herring and cod from the Baltic, the Kattegat and the Skagerrak, *Ambio Spec. Rep.*, 1, 71, 1972.
4. Jensen, S., Olsson, M., and Vas, R., Levels of DDT and PCB in littoral fishes along the Swedish coast, *Ambio Spec. Rep.*, 5, 75, 1977.
5. Jensen, S., Tusalen — Nya globala miljöhot, *Kem. Tidskr.*, 5, 38, 1980.
6. Ames., DDT and its derivatives, in *Environmental Health Criteria*, Vol. 9, United Nations Environment Programme and the World Health Organization (WHO), Geneva, 1979, 11.
7. Hutzinger, O., Safe, S., and Zitko, V., *The Chemistry of PCBs*, CRC Press, Cleveland, 1974, chap 2.
8. Söderberg, S., Silene fångsvel och skadegörelse på laxfiskar i Östersjön, Report to Svenska Ostkustfiskarnas Centralförbund, Swedish Museum of Natural History, S 104 05, Stockholm, 1972.
9. Olsson, M., Johnels, A. G., and Vas, R., DDT and PCB levels in seals from Swedish water. The occurrence of aborted seal pups, in Proc. Symp. on the Seal in the Baltic, National Swedish Environment Protection Board, Stockholm, 1975.

MONS 006360

10. **Linko, R. R., Kaitaranta, P., Rantamaki, P., and Eronen, L.**, Occurrence of DDT and PCB compounds in Baltic herring and pike from the Turku archipelago, *Environ. Pollut.*, 7, 193, 1974.
11. **Olsson, M. and Jensen, S.**, Pike as the test organism for mercury, DDT and PCB pollution. A study of the contamination in the Stockholm Archipelago, *Inst. Freshw. Res. Drottningholm*, 54, 83, 1975.
12. **Schneider, R. and Osterroht, Chr.**, Residues of chlorinated hydrocarbons in cod livers from the Kiel Bight in relation to some biological parameters, *Meeresforschung*, 25, 105, 1977.
13. **Jensen, S., Reenberg, L., and Olsson, M.**, PCB contamination from boat bottom paint and levels of PCB in plankton outside a polluted area, *Nature (London)*, 240, 358, 1972.
14. **Olsson, M., Jensen, S., and Reutergårdh, L.**, Seasonal variation of PCB levels in fish — an important factor in planning aquatic monitoring programs, *Ambio*, 7, 66, 1978.
15. **Edgren, M., Olsson, M., and Reutergårdh, L.**, A one year study of the seasonal variations of DDT and PCB levels in fish from heated and unheated areas near a nuclear power plant, *Chemosphere*, 10, 447, 1981.
16. **Johansson, N., Jensen, S., and Olsson, M.**, PCB — indications of effects on fish, in *Proc. PCB Conference I*, Wenner-Gren Center, Stockholm, September 29, 1970, 39.
17. **Blus, L. J.**, Measurements of brown pelican eggshells from Florida and South Carolina, *BioScience*, 20, 867, 1970.
18. **Ratcliffe, D. A.**, Changes attributable to pesticides in egg breakage frequency and eggshell thickness in some British birds, *J. Appl. Ecol.*, 7, 67, 1970.
19. **Johnels, A. G., Odsjö, T., and Olsson, M.**, Miljögifter i Svensk natur, *Doc. Kungliga Vetenskapsakad.*, 18, 20, 1975.
20. **Odsjö, T. and Helander, B.**, Äggskalsförtunning hos havsörn häckande i Sverige, Bilaga 6, Report to the National Swedish Environment Protection Board, Stockholm, 1977.
21. **Odsjö, T. and Sandell, J.**, Populationsutveckling och häckningsresultat hos brun kärrhök *Circus aeruginosus* i relation till förekomst av DDT, PCB och Kvicksilver, *Var Fageluarld*, 36, 152, 1977.
22. **Odsjö, T.**, Eggshell Thickness and Levels of DDT, PCB and Mercury in Eggs of Osprey *Pandion haliaetus* L. and Marsh harrier *Circus aeruginosus* L. in Relation to their Breeding Success and Population Status in Sweden, Ph.D. thesis, University of Stockholm, Stockholm, 1982.
23. **Odsjö, T. and Edenstam, C.**, Effect of Toxic Chemicals on Bird Life, Swedish Research on Chemical Hazards to Birds, 12th Bulletin of the International Council for Bird Preservation, 1975, 114.
24. **Andersson, Å, Odsjö, T., and Olsson, M.**, Häckningsresultat hos tornfalk i Stockholms skärgård i relation till äggskalstjocklek och halter av DDT, PCB och kvicksilver i ägg, *Statens Naturvards.*, 483, 1, 1974.
25. **Lemmetyinen, R., Rantamäki, P., and Uusitalo, R.**, Saaristomerellä pesivien lapintiiroyen, kalasääskien ja varsten DDT — ja PCB-pitoisuuksista, *Linnuniet*, 12, 108, 1977.
26. **Hedgren, S.**, Reproductive success of Guillemots *Uria aalge* on the island of Stora Karlsö, *Ornis Fenn.*, 57, 69, 1980.
27. **Helander, B.**, Reproduction of the White-tailed Sea Eagle *Haliaeetus albicilla* (L.) in Sweden, in Relation to Food and Residue Levels of Organochlorine and Mercury Compounds in the Eggs, Ph.D. thesis, University of Stockholm, Stockholm, 1983.
28. **Helander, B., Olsson, M., and Reutergårdh, L.**, Residue levels of organochlorine and mercury compounds in unhatched eggs and the relationships to breeding success in white-tailed sea eagles *Haliaeetus albicilla* in Sweden, *Holarctic Ecol.*, 5, 349, 1982.
29. **Koivusaari, J., Nuuja, I., Palokangas, R., and Finnlund, M.**, Relationships between productivity, eggshell thickness and pollutant contents of addled eggs in the population of White-tailed Sea Eagles *Haliaeetus albicilla* L. Finland during 1969-1978, *Environ. Pollut.*, A23, 41, 1980.
30. **Almkvist, L.**, Baltic Marine Mammals — A Status Report, Report to ICES C.M. 1982/N:16, 1982.
31. **Heide-Jörgensen, M-P.**, Saelbestandene i de danske farvande, in Proc. Status over den danske plante-og dyreverden, Miljø-ministeriet, Copenhagen, 1980, 292.
32. **Helle, E.**, Reproduction, size and structure of the Baltic ringed seal population of the Bothnian Bay, *Acta Univ. Oulaensis (A)*, 106, 32, 1980.
33. **Almkvist, L., Olsson, M., and Söderberg, S.**, *Säler i Sverige*, Svenska Naturskyddsföreningen, Stockholm, 1980.
34. **Grunland, E.**, Säler i Bottniska Viken, *Österbotten*, 31, 57, 1975.
35. **Hook, O. and Johnels, A. G.**, The breeding and distribution of the grey seal (*Halichoerus grypus Fab.*) in the Baltic Sea, with observations on other seals of the area, *Proc. R. Soc. Lond. Ser. B.*, 182, 37, 1972.
36. **Olsson, M.**, Mercury, DDT and PCB in aquatic test organisms, Baseline and monitoring studies, field studies on biomagnification, metabolism and effects of some bioaccumulating substances harmful to the Swedish environment, *Report from the National Swedish Environment Protection Board*, 1977, 900.
37. **Le Boeuf, B. J. and Bonnell, M. L.**, DDT in California sea lions, *Nature (London)*, 234, 108, 1971.
38. **DeLong, R. L., Gilmartin, W. G., and Simpson, J. G.**, Premature births in California sea lions: association with high organochlorine pollutant residue levels, *Science*, 181, 1168, 1973.

MONS 006361

39. Helle, E., On the biology of the ringed seal *Pusa hispida* in the Bothnian Bay. in Proc. Symp. on the Seal in the Baltic Lidingö, Sweden, June 4, 1974. Report from the National Swedish Environment Protection Board. PM 591. 38. Stockholm. 1975.
40. Helle, E., Olsson, M., and Jensen, S., DDT and PCB levels and reproduction in ringed seal from the Bothnian Bay, *Ambio*, 5. 188. 1976.
41. Nazarenko, Y. I., Contributions to the Study of the Reproduction of the ringed seal (*Phoca hispida*) of the Chaska Inlet. *Morskie Mlekopitayushchie* (Marine Mammals), 171, 1965; Fisheries Research Board of Canada. Transl. Ser. No. 1461. 1970.
42. Fedoseev, G. A., On the embryonic and postembryonic growth and sexual maturation in *Phoca hispida* Ochotensis Pall. *Zool. Z.*, 43(7), 1230. 1964.
43. Ringer, R. K., Aulerich, R. J., and Zabik, M., Effect of dietary polychlorinated biphenyls on growth and reproduction of mink. 164th Natl. Meet. American Chem. Soc. 12, 149. 1972.
44. Aulerich, R. J. and Ringer, R. K., Current Status of PCB toxicity to mink, and effect on their reproduction. *Arch. Environ. Contam. Toxicol.*, 6, 279, 1977.
45. Bleavins, M. R., Aulerich, R. J., and Ringer, R. K., Polychlorinated biphenyls (Aroclors 1016 and 1242): effects on survival and reproduction in mink and ferrets. *Arch. Environ. Contam. Toxicol.*, 9, 627, 1980.
46. Jensen, S., Kihlström, J. E., Olsson, M., Lundberg, C., and Örberg, J., Effects of PCB and DDT on mink (*Mustela vison*) during the reproductive season. *Ambio*, 6, 239, 1977.
47. Kihlström, J. E., Olsson, M., and Jensen, S., Effekter på högre djur av organiska miljögifter. *Organiska miljögifter i vatten*, Nordforsk, 2, 567, 1976.
48. Helle, E., Olsson, M., and Jensen, S., PCB levels correlated with pathological changes in seal uteri. *Ambio*, 5, 261, 1976.
49. Helle, E., Lowered reproductive capacity in female ringed seals (*Pusa hispida*) in the Bothnian Bay, northern Baltic Sea, with special reference to uterine occlusions. *Ann. Zool. Fenn.*, 17, 147, 1980.
50. Olsson, M., PCB and reproduction among Baltic seals. *Finn. Game Res.*, 37, 40, 1978.
51. Helle, E., On the reproductive success in the Bothnian Bay population of the ringed seal and future prospects for the species. *Finn. Game Res.*, 37, 32, 1978.
52. Bergman, A., Olsson, M., and Reutergårdh, L., Lowered Reproduction Rate in Seal Population and PCB. A Discussion of Comparability of Results and a Presentation of some Data from Research on the Baltic Seals. Report to ICES C.M. 1981/N:10. 1981.
53. Harrison, R. J. and Young, B. A., Functional characteristics of the pinniped placenta. *Symp. Zool. Soc. London*, 15, 47, 1966.
54. Bergman, A. and Olsson, M., Pathology in baltic grey seal and ringed seal females with special reference to adrenocortical hyperplasia. Is environmental pollution the cause of a widely distributed disease syndrome?, *Fin. Game Res.*, 44, 1985.
55. Howard, E. B., Britt, J. O., Matsumoto, G. K., Itahara, R., and Nagano, C. N., Bacterial diseases. in *Pathobiology of Marine Mammal Diseases*, Vol. I, Howard, E. B., Ed., CRC Press, Boca Raton, Fla., 1983, 69.
56. Erlinge, S. and Nilsson, T., Utarn förtsatser att minska — Bara 1000-1500 utrar kvar, *Svensk Jakt.*, 116, 154, 1978.
57. Sandegren, F., Olsson, M., and Reutergårdh, L., Der Rückgang der Fischotterpopulation in Schweden, *Der Fischotter in Europa — Verbreitung, Bedrohung, Erhaltung*, Reuther, C. and Festetics, A., Eds., Selbstverlag, Göttingen, 1980, 107.
58. Olsson, M., Reutergårdh, L., and Sandegren, F., Var är utters?, *Sver. Natur.*, 6, 234, 1981.
59. Gorell, R., Dispersal and acclimatization of the musk (*Mussela vision Schreb.*) in Sweden. *Viltrevy*, 5, 1, 1967.
60. Gorell, R., Minken, en stabiserad nykomling i vår fauna, *Fauna Flora*, 1, 47, 1979.
61. Gorell, R., Personal communication, 1983.
62. Österlind, G., The harbour porpoise (*Phocoena Phocoena*) endangered in Swedish waters. Report to ICES C.M. 1976/N:16, 1976.
63. Mitchell, E., Porpoise, dolphin and small whale fisheries of the world. Status and problems, *IUCN Monogr.*, 3, 92, 1975.
64. Bertov, E., Baltic Environmental Commission, Helsingfors, personal communication, 1983.
65. Nilsmärk, L., Sedimen och sedimentation i Bottniska viken, in Kommunala för Bottniska viken, Årsrapport för år 1981, 9, 6, 1982.
66. Paasivirta, J., Kauranen, P., and Linko, R., OECD monitoring study in Finland 1973—1975, *Kemia-Kemi*, 12, 634, 1976.
67. Lackas, B., Wetzel, H., and Rechlin, O., Zur Kontamination von Ostseefischen mit polychlorierten Biphenylen, *Nahrung*, 24, 405, 1980.

MONS 006362

68. **Verta, M., Miettinen, V., and Erkomaa, K.,** Concentrations of chlorinated hydrocarbons in pike from the Turku archipelago in the years 1970—1978, *Publ. Wat. Res. Inst.*, 34, 108, 1979.
69. **Olsson, M. and Reutergårdh, L.,** Tidsserieundersökningar i Östersjöområdet. En undersökning av DDT — och PCB-halter i akvatiska miljöer 1967—1982. Kommitten för Bottniska viken. Årsrapport för år 1982, 10, 17, 1983.
70. **Kihlström, J. E. and Berglund, E.,** An estimation of the amounts of polychlorinated biphenyls in the biomass of the Baltic, *Ambio*, 7, 175, 1978.
71. **Olsson, M.,** Bioaccumulating substances — mainly DDT and PCB — in biota in the Gulf of Bothnia, *Finn. Marine Res.*, 244, 227, 1978.

MONS 006363

Chapter 8

PCBs AND THE ENVIRONMENT: THE MEDITERRANEAN MARINE ECOSYSTEM

Scott W. Fowler

TABLE OF CONTENTS

I. Introduction 210

II. Regional Sources, Usages, and Input 210

III. Levels in the Marine Environment 213
- A. Sea Water 213
  - 1. Coastal 213
  - 2. Open Sea 215
- B. Sediments 217
  - 1. Coastal 217
  - 2. Open Sea 218
- C. Biota 220
  - 1. Coastal 220
  - 2. Open Sea 227

IV. Vertical Flux and Removal Processes 232

V. Summary and Conclusions 233

Acknowledgments 236

References 236

MONS 006364

I. INTRODUCTION

Several oceanographic and geographic characteristics of the Mediterranean Sea render it potentially vulnerable to the effects of anthropogenic pollutants.[1] The sea is a relatively shallow, semi-enclosed body of water with only limited water exchange occurring at the narrow Straits of Gibraltar and the entrance to the Black Sea. Low salinity Atlantic surface water enters at Gibraltar and slowly circulates counter clockwise around the Mediterranean during which time it gradually becomes warmer and more saline due to increased insolation and intense evaporation. The general lack of tides combined with a regime of weak coastal currents act to reduce dispersion of pollutants entering coastal waters. Furthermore, increased construction of dams on major rivers feeding the Mediterranean may, in certain areas, have substantially reduced the spring runoff which tends to cleanse the shelf region of deposited contaminants. Besides these unique physical features of the Mediterranean Sea, there are several ecological factors which could also affect the sea's response to pollution insult. The Mediterranean is oligotrophic and significant perturbations of its limited potential productivity, especially in near-shore zones where productivity and pollutant levels are the highest, could cause long-term consequences on the ecosystem. In addition, Mediterranean flora and fauna display a high species diversity compared to the Atlantic and it is generally recognized that the recovery potential of a stressed ecosystem is inversely proportional to its species diversity index. Finally, the wide annual range in surface temperature (~ 12 to 26°C) can cause stress in stenothermic organisms living near their tolerance limits. For these reasons, it is generally regarded that the Mediterranean should be one of the first seas to register the effects of pollution arising from the high-density population centers situated along much of its coast.

Considering the precarious nature of the Mediterranean Sea as regards its resiliency to pollution insult, over the last 10 years there has been considerable effort expended on studying marine pollution in the region.[1,2] Most of the work has been aimed at establishing baseline data on levels of a number of pollutants in various components of the Mediterranean ecosystem. The PCB compounds are one group of the organic pollutants which has received considerable attention. Much of what is known about PCBs has come from coastal surveys; however, in recent years a very limited number of studies have obtained corresponding data from open Mediterranean waters. In the following sections, a summary of these findings is given as well as some tentative conclusions concerning the present health of the Mediterranean as regards PCB contamination.

II. REGIONAL SOURCES, USAGES, AND INPUT

Accurate figures on the production, usage, and environmental input of industrial contaminants such as PCBs are extremely difficult to obtain from most countries including the highly industrialized nations.[3-5] The Mediterranean region proves no exception to this rule especially when the diverse nature of the 18 countries surrounding the sea is considered. Such information regarding PCBs in the region is particularly difficult to gather. For example, a 1972 FAO report[6] stated that "PCBs are emerging as serious pollutants but no reports on their use in the Mediterranean countries and occurrence in the Mediterranean Sea are available". Furthermore, in the mid-1970s a coordinated program was initiated by UNEP[7] with the aim of inventorying all major pollutants originating from land-based sources in the Mediterranean region; it is perhaps significant that no information on PCB compounds resulted from that large-scale study. In fact the only published information[8-10] available on PCB production in the Mediterranean region pertains to figures[8,10] for France, Italy, and Spain (Table 1). As an added perspective, the amounts in Table 1 can be compared with the annual production figures for the following highly industrialized nations: U.S. 38,000

MONS 006365

Table 1
TOTAL PRODUCTION OF PCBs (MT) IN THREE MEDITERRANEAN COUNTRIES BETWEEN 1971 AND 1980[a,b,ss]

Year	France	Italy	Spain	Total
1971	7,600	1,500	1,500[c]	10,600
1972	NA[b]	NA	NA	—
1973	9,674	2,519	NA	—
1974	9,541	NA	1,935	—
1975	7,182	1,868	NA	—
1976	7,190[c]	1,933	NA	—
1977	7,640	2,343	1,504	11,487
1978	7,916[c]	1,767	NA	—
1979	NA	1,414	NA	—
1980	6,357	1,479	1,241	9,277

[a] Estimate.
[b] Not available.
[c] Includes T60 which is 100% triphenyl.

tons in 1970, 18,000 tons in 1971; Federal Republic of Germany 8000 tons in 1971; Japan 6800 tons in 1971; U.K. 5000 tons in 1971. Contrary to the situation elsewhere (e.g., North America) where PCB production dropped dramatically during the 1970s, the data in Table 1 indicate that there was little reduction in total PCB production during the same period for these three Mediterranean countries. The continued production of PCBs and, moreover, the continued use of these compounds for standard industrial purposes has ensured their eventual leakage into the Mediterranean environment. No information is available on the fraction of the PCBs that have actually entered the Mediterranean environment; however, it is assumed to be relatively large when one considers estimates[10] that of the 3.8×10^4 tons of PCBs produced in U.S. in 1970, roughly 80% was eventually released into the environment.

Two major routes would appear to be primarily responsible for the input of PCBs into the Mediterranean Sea. Most of the PCBs probably reach the coastal environment via discharge of industrial and municipal wastes into inland and coastal waters. Considering that both population density and industrial activities are highest along the northwestern Mediterranean shores,[11] the majority of PCB input should occur in this sector. In fact two of the largest rivers in this region, the Rhone and the Po, drain the most important industrial areas of the northern watershed and are generally considered to be the major point sources of land-based pollutants in the Mediterranean.[11] Although no quantitative data are available on PCB input loads from these two rivers, evidence is presented in the following sections which clearly underscores the importance of these and other Mediterranean rivers as input sources of PCBs.

Aside from rivers and local runoff, the most rapid route by which PCBs are injected into the open Mediterranean is via atmospheric transport of vaporized PCBs. Evidence for the effectiveness of this route comes from direct measurements of PCBs in coastal and over ocean air made during 1975[12] and 1977.[13] At a sea shore station in Monaco, PCB concentration (as DP-5) ranged from 0.5 to 0.9 ng/m^3 during the warmer months of 1975, declined during December with the onset of cooler temperatures, and reached a low level between 0.05 to 0.08 ng/m^3 during January/February 1976 when temperatures were at a minimum.[12] When the wind was predominantly from the north, a strong correlation between PCB concentration and temperature was evident; Villeneuve[13] observed an approximate order of

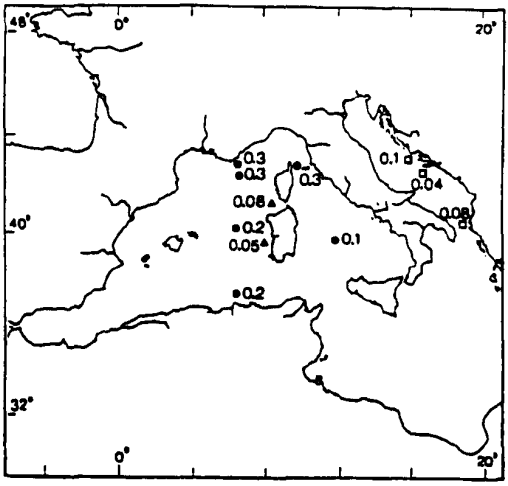


FIGURE 1. PCB concentrations (ng/m³ as DP-5) in marine air from the northwestern Mediterranean during September 1975[18] (●) and July 1977[19] (▲), and the Adriatic in November 1977[19] (□).

magnitude increase in PCB concentration between 5 and 12°C. Although the apparent correlation between PCB concentration in air and temperature is consistent with an increase in vapor pressure of PCBs with temperature; seasonal wind patterns in the region are also thought to affect the PCB concentration at the Monaco station. For example, during the late summer/early fall period, the winds are predominantly from the northwest and draw air through the industrialized Rhone Valley and along the French coast. During the winter, the winds shift to the northeast where they come either from offshore or over the Alps and through less industrialized areas.

Corresponding PCB concentrations in marine air sampled at several stations in the northwestern Mediterranean and Adriatic are shown in Figure 1. The air concentrations of PCBs in both years (0.04 to 0.3 ng/m³) are somewhat lower than those (0.3 to 1.6 ng/m³) reported for Bermuda and the Sargasso Sea in 1973[14] but are very similar to levels measured during 1980-1981 in the central Pacific (0.19 to 0.32 ng/m³) and Antarctic oceans (0.11 to 0.23 ng/m³).[15] Whereas strong onshore-offshore gradients have been noted for PCBs in air,[14,16] this apparently is not the case for the northwestern sector of the Mediterranean (Figure 1). In 1975 only slightly higher concentrations were found near the more heavily populated European coast; although the data from this single set of observations are limited, this finding suggests that the Mediterranean Sea is too small to exhibit large spatial concentration gradients of PCBs moving in air and that atmospheric input of PCBs to the entire sea is relatively uniform.

The results in Figure 1 are also of interest from a temporal standpoint in that the average concentration (ng/m³) for the 1977 samples (0.07 ± 0.02) is significantly less than that for

MONS 006367

the 1975 set (0.23 ± 0.08). This comparison suggests an approximate threefold reduction of PCBs in marine air during this 2-year period; however, it should be kept in mind that the number of observations are few and the stations at which air was sampled were not the same for the different years.

Clearly, PCB input data for the Mediterranean are extremely sparse. Until more information on production, usage, and important input routes of PCBs is available for the Mediterranean region as a whole, attempts at developing mass balance models for these compounds will be severely hampered.

III. LEVELS IN THE MARINE ENVIRONMENT

Although specific studies on PCBs are not as numerous for the Mediterranean as for many other areas of the globe, during the past decade there has been a substantial increase in the amount of information on environmental levels of PCBs in various matrices of the Mediterranean ecosystem. Much of what was published on PCBs prior to 1977 has been extensively reviewed by Bernhard;[17] therefore, in the following synthesis, emphasis has been placed on more recent information. Moreover, it should be kept in mind that, as is the case elsewhere, PCB data are often difficult to compare and interpret primarily because of the different sample preparation, pretreatment, and quantification techniques which have been used by many laboratories in the Mediterranean region.

A. Sea Water

Owing to the inherent difficulties in analyzing trace amounts of PCB compounds in sea water, data for the Mediterranean are accordingly few. Since inputs of PCBs to the Mediterranean Sea are expected to vary depending upon the region (Section II), it is instructive to examine the coastal and open sea sectors separately.

1. Coastal

The first reliable values for coastal waters are those of Elder[18,19] and Risebrough et al.[87] for the northwestern Mediterranean. In July 1974, PCB concentrations ranged from 0.68 to 0.95 ng/ℓ at coastal stations in the Golfe du Lion.[87] During the same month a somewhat higher concentration, 1.6 ng/ℓ was measured at Marseille.[87] Samples of surface and subsurface water taken in late 1974 about 1 km off Nice, France and Monaco contained PCB concentrations[18] ranging from 1.3 to 2.8 ng/ℓ. A more extensive survey was undertaken along the French coast in early 1975 (Figure 2). Elevated levels were found in the Rhone delta sector which is in the vicinity of major industrial and urban activities. The maximum value, 38 ng/ℓ measured 0.5 km from the mouth of the Rhone is good evidence that the river is an important source of PCBs for northwestern Mediterranean waters. Much lower values were noted in the northeastern sector and its was suggested[19] that this was most probably a result of the prevailing easterly currents which tended to concentrate PCBs entering the sea from local inputs toward the west in the Golfe du Lion. Furthermore, it was noted that at that time of year, northerly winds moving down the Rhone valley could also result in PCB input via atmospheric fallout in the region of the Rhone estuary.

A more recent study in 1981 by Burns and Villeneuve[20] examined the distribution of particulate and dissolved PCBs off the Var river estuary near Nice. They found that total PCBs decreased from 3.6 ng/ℓ near the mouth of the river to 1.7 ng/ℓ about 1 mi offshore. The offshore decrease in PCB concentration was correlated with a decrease in the fraction of particulate-associated PCBs (63 to 22%) over the same distance. Since the offshore decrease was not substantial, the authors concluded that while river inputs of PCBs could be important in localized areas, these inputs were likely to be merely superimposed on widespread PCB distributions that resulted primarily from atmospheric transport. A related

MONS 006368

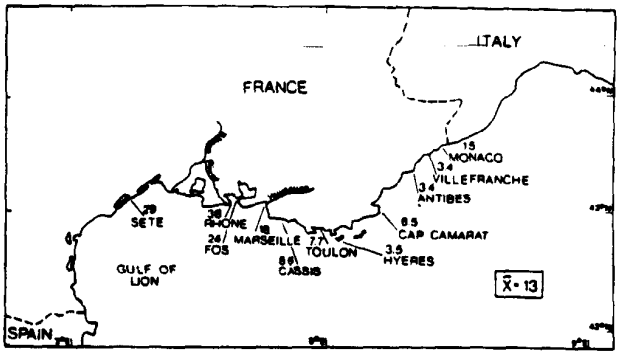


FIGURE 2. PCB concentration (ng/ℓ) in sea water from the French coast. Sampling sites were 3 to 5 km offshore except Rhone (500 m). All samples collected in February 1975 except Monaco (October 1974).[19]

series of measurements made off Monaco in the same year showed that 37 to 61% of the PCBs in near surface sea water were associated with particulate matter.[21] Total PCB levels ranged from 0.8 to 1.5 ng/ℓ, concentrations similar to values reported for the same site 7 years earlier.[19] Of particular interest were measurements of PCBs in the surface microlayer which demonstrated an average 32-fold enrichment of PCBs over that in near surface sea water.[21]

Low levels of PCBs (0.1 to 0.9 ng/ℓ) have been reported by Picer and Picer[22] for the north Adriatic Sea off the Istrian coast. While the authors fully acknowledge possible analytical problems with their measurements, relatively low levels may, in fact, be typical for the Yugoslav coastal region. For example, independent analyses of sea water from Split, Mljet Island, and Dubrovnik sampled during the same period (1977) resulted in PCB concentrations of 1.5, 1.4, and 0.9 ng/ℓ respectively.[23] Furthermore, low concentrations may be characteristic of other areas in the Mediterranean, particularly in more recent times. Two values of 0.17 (60% particulate) and 0.24 (15% particulate) ng/ℓ were measured in 1985 in an estuary of the Ebro River and 20 km east of Tarragona, Spain, respectively.[60]

The only other published data are those of Puccetti and Leoni[24] for Italian coastal waters near the Tiber River estuary. They reported very high levels averaging 297 ng/ℓ in 1976 and 135 ng/ℓ in 1977. Unfortunately, these data may not be directly comparable with those from the northwestern basin because of serious limitations with the perchlorination technique used to quantify PCBs in their samples (see Duinker et al.[25]). However, regardless of the reliability of the absolute numbers, their data are intriguing in that they indicate relatively lower PCB levels near the mouth of the Tiber than offshore. The authors hypothesize that microbial action in the heavily polluted estuary may result in rapid PCB degradation in this zone and, consequently, conclude that offshore concentrations principally originate from atmospheric transport. Nevertheless, in other areas of the Mediterranean where gradients near estuaries have been examined,[19,20] higher PCB levels were found in water near river mouths than offshore. Furthermore, the authors' sediment data which show a much higher PCB concentration near the river mouth than offshore are not in complete accord with the notion that the river is not a major source of PCBs to the environment; clearly the hypothesis of nearshore microbial biodegradation of PCBs needs verification.

MONS 006369

Table 2
PCB CONCENTRATIONS (ng/ℓ) IN SEA WATER (SURFACE AND DEEP) FROM THE OPEN MEDITERRANEAN[12,13,26,30,39]

Year	Month(s)	Region	No. of samples	Range	$\bar{X}$
1975	Feb.	Ligurian Sea	17	1.3—8.6	3.2
	Feb./May	Aegean Sea	7	<0.2—1.3	0.36
	Feb./May	Ionian Sea	10	0.2—2.0	1.0
	Feb./May	Tyrrhenian Sea & Algero-Provencal basin	34	0.2—5.9	2.0
	Sept.	Algero-Provencal basin	8	0.6—19	4.6
			(7)*	0.6—4.8	2.5
	Sept.	Tyrrhenian Sea	6	1.5—11.6	4.5
			(5)*	1.5—5.0	3.1
1977	June	Ionian Sea	2	0.7—1.9	1.2
	April/July	Central & Levantine basin	44	<0.1—1.9	0.73
	July	Algero-Provencal basin	7	0.2—0.6	0.29
	June/July	Tyrrhenian Sea	4	<0.1—2.5	0.94
	Nov.	Southern Adriatic	2	0.3—1.8	1.1
1979	June	Levantine basin	10	0.1—0.5	0.24

* Range and mean value computed without maximum value (11.6 and 19) which came from coastal areas and was probably a reflection of localized input.[13]

2. Open Sea

An extensive data set is available from a series of cruises taken throughout the open Mediterranean Sea between 1975 and 1979. In 1975 samples were collected in the Aegean, Ionian, and Tyrrhenian Seas and the western Mediterranean basins.[26] Several profiles taken down to 4000 m showed no regular trend in PCB concentration with depth indicating the relatively uniform distribution of these compounds in open Mediterranean waters. Aside from two high values at nearshore stations, PCB concentrations in open surface and deep waters ranged between 0.8 to 8.6 ng/ℓ ($\bar{X}$ = 2 ng/ℓ). The values were similar to concentrations measured in the North Atlantic[27] and Sargasso Sea[14] during the early 1970s.

An attempt was made by Elder and Villeneuve[26] to correlate PCB concentrations with demographic, oceanographic, and physical features of the Mediterranean. They found a trend for higher average concentration in the western basin and Tyrrhenian Sea compared to that for the Aegean and Ionian Seas but the differences were not statistically significant. This trend is consistent with the hypothesis of higher PCB input in the industrialized northwestern sector of the Mediterranean; however, the authors point out that the higher surface temperatures in the eastern basin and presumed evaporative co-distillation of PCBs could result in the same trend. For these reasons, it is difficult to draw any firm conclusions regarding spatial trends of PCB in water within the Mediterranean basin.

During 1977 and 1979 surface and subsurface sea water were similarly collected from the open Mediterranean and analyzed for PCBs by the same laboratory.[30] As in the 1975 survey, higher PCB levels were occasionally found in surface waters, although no systematic variation in PCB concentration was observed with depth. The concentrations for these years ranged between <0.1 and 2.5 ng/ℓ. The average value of 0.7 ng/ℓ was significantly lower than that computed for 1975[26] which suggests that PCB concentrations in open Mediterranean waters had diminished somewhat during the period 1975 to 1977/79. Open water PCB levels are summarized by regions and years in Table 2.

Recent detailed studies[39] on the partitioning of PCBs between particulate and soluble

MONS 006370

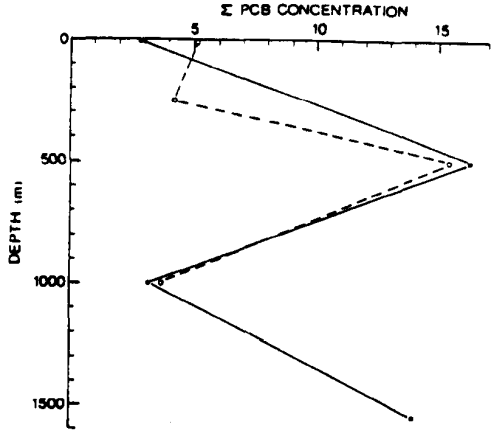


FIGURE 3. Depth profile of PCBs (ng/ℓ) in northwestern Mediterranean sea water, April to May 1982.[35] (O—O) 42°57'N, 5°15'E, depth 1050 m; (●—●) 42°29'N, 5°36'E, depth 2000 m.

phases in Mediterranean sea water have added to our general knowledge of the behavior of PCBs. Contrary to earlier observations,[20,28] two profiles taken in the northwestern basin showed a distinct subsurface maximum of total PCBs at 500 m (Figure 3). Plots of the individual isomers[23] confirmed the trends shown in Figure 3. The factors contributing to the maximum are at present unknown, but based on sedimentological and hydrodynamic knowledge of the region, Villeneuve and Burns[20] have suggested that the elevated PCB concentrations at 500 m may have their origin in a distinct layer of water moving laterally outward from the Rhone estuary. It is also noteworthy that in the deeper profile at 1500 m, a high PCB concentration (14 ng/ℓ) was also present. Since this sample was taken nearer the bottom (~2000 m), it is possible that resuspended particulates in the form of a nepheloid layer, known to occur in this region, could have contributed to the elevated PCB concentration.

Alternatively, these authors postulate that another possible mechanism contributing to these maxima could be the continuous sinking of fine particles enriched in PCBs with their subsequent release at that depth through degradation and resolubilization processes. For example, similar maxima for the particle-reactive radionuclides $^{239+240}$Pu and ^{241}Am have been observed at 250 and 500 m, respectively, throughout the open Mediterranean.[31] The occurrence of these maxima is attributed to differential adsorption-desorption kinetics of the radionuclides associated with different populations of sinking particles. Villeneuve and Burns[20] also measured PCB particle association with depth and found that particulate PCB decreased from 95% at the surface to 0% at 1000 m. The fact that the particulate fraction was low (19%) at 500 m where the PCB maximum occurred indicates that any PCBs originating from the downward vertical flux of particulate matter would have to be resolubilized at depth, most probably through biodegradative processes.

In water overlying a sediment core taken at the same station at approximately 1050 m, the particulate fraction of PCBs had increased to 60%. This observation may reflect input

MONS 006371

from the surface layers by large, rapidly sinking particles greatly enriched in PCBs (see Section IV).

In addition, related measurements of PCB partitioning in surface waters at various stations extending several kilometers off the coast of France[20] have demonstrated that the particulate PCB fraction decreases in the seaward direction, thus confirming the hypothesis based on nearshore studies[20] that particulate-soluble PCB partitioning is generally a function of particle load.

B. Sediments

Due to the strong affinity that PCB compounds have for particulate matter, it is generally recognized that sediments will serve as the final repository for PCBs entering the marine environment. For this reason many surveys in the Mediterranean have focused on measuring the levels of these compounds in surface sediments which integrate PCB input over time. Unfortunately, most studies have used grab samplers which often mix the PCB contaminated surface layer with lesser or uncontaminated underlying sediments, thus rendering the resulting PCB concentration questionable. This fact must be considered when comparing regional sediment data and more emphasis has been given to discerning major relative trends in a selected area rather than small or negligible interregional differences.

1. Coastal

Through analysis of sediments in the coastal zone, localized inputs have been readily identified. An early study in the Saronikos Gulf of Greece[21] pinpointed an Athens sewage outfall as the prime source of PCBs in the adjacent marine environment. Concentrations near the outfall approached 800 ppb dry and dropped off to less than 20 ppb in the offshore zone. By contouring sediment concentrations, it was possible to discern the flow patterns of the polluted waters and identify other sources of PCB input such as the highly industrialized Elefsis Gulf region. A similar survey in the vicinity of Naples[23] found extremely high levels (3200 ppb) in sediments from the Bay of Naples, presumably originating from local industries. Outside the bay levels were in the general range of 10 to 30 ppb. Furthermore, a core sample from the bay showed that PCBs were detectable to a depth of about 35 cm. Perhaps the most striking example of chronic PCB input from a point source comes from studies undertaken around the Marseille outfall at Cortiou.[24] In the vicinity of the outfall PCB concentrations in sediments from 20 to 50 m depth ranged between 3 and 16 ppm dry. By mapping concentrations in sediments over a distance of several kilometers, it was shown that PCB transport was predominantly toward the east and appeared to be controlled by association with fine suspended clays. Outside the immediate zone of contamination, concentrations in sediments dropped to background levels (10 to 30 ppb).

Two other PCB "hot spots" in the Mediterranean which have been identified through coastal sediment surveys are Agusta, Sicily (130 to 457 ppb dry)[25] and at 100 m depth just offshore the Casino at Nice, France (1165 ppb dry).[26] In the latter situation, concentrations in nearby sediments (Nice airport and Villefranche) from the same depth showed much lower concentrations (29 and 86 ppb, respectively); thus, a highly localized acute contamination was suspected.

Surveys of coastal sediments in the Adriatic Sea[27] during the early 1970s recorded high amounts of PCBs (although not quantified) primarily in the northern sector. The results indicated that the majority of these compounds originated from freshwater discharge in the north (e.g., Po River) and were transported in a southerly direction along the western shore; however, some lateral transport on fine particulates from Italian estuaries also occurred with subsequent deposition taking place near the Yugoslavian coast. Later studies verified the relatively low concentrations of PCBs (<1.0 to 28 ppb dry) in sediments from both the northern[22] and southern[28] regions of Yugoslavia.

MQNS 006372

Data on PCBs in sediments from the eastern Mediterranean are sparse. A Turkish survey[39] has shown that of seven sediments sampled along the eastern coastline near Mersin, only three contained detectable amounts of PCBs (2 to 4 ppb dry). Another study[40] reported levels ranging from 0.7 to 0.9 ppb in sediments from nearby Antalya. These very low levels are most likely a reflection of PCB background in the region arising from atmospheric transport and demonstrate the low degree of PCB contamination from land-based sources in this relatively undeveloped part of Turkey.

The only published data[40] on PCBs in sediments from the North African coast are those from spot samples taken on the circum-Mediterranean *Calypso* cruise in 1977. Levels in sediments from Tunisia and Egypt were in the range 0.5 to 2.0 ppb; significantly higher concentrations were noted off Algeria at Annaba (8 to 14 ppb) and Oran (325 ppb). Except for the PCB concentration at Oran, these values were generally lower than those measured on the European side of the Mediterranean and likely reflect the lower number of industrial and urban sources of PCBs along the north African shoreline. The results from these studies further support the hypothesis of a decreasing trend in PCB concentration from west to east in the Mediterranean basin.

Most of the above-mentioned baseline studies were not carried out over a sufficiently long period of time to establish temporal trends. However, in one area of the Golfe du Lion near Montpellier, sediments were sampled at the same site over a 3-year interval (1972 and 1975).[41,42] Although contamination of sediments (principally from two small rivers which drain the region) was evident, no temporal trends were noted during the study. PCB concentrations averaged 340 ppb in 1972 and 390 ppb in 1975.

A summary of PCB concentrations in coastal sediments is given in Table 3.

2. *Open Sea*

Several undisturbed cores were taken and sectioned during the Mediterranean cruises discussed above (Section III.A.2). PCBs were detectable in the top few centimeters of all cores, some of which were sampled at water depths as great as 4000 m. During a cruise in 1975 through the Ionian Sea and western basin, PCBs were only detectable in the top 1 cm of the sediment.[12] Furthermore, assuming an average deposition rate in the open Mediterranean on the order of 15 cm/1000 years, it is likely that all PCBs are located in the top centimeter of the sediments. The analyses also showed a preponderance of Phenochlor® DP 6 relative to DP 5 residues which suggested preferential adsorption and deposition of the more highly chlorinated biphenyls. An examination of the data[12,39] in relation to oceanographic features of the region was used to explain variations in PCB concentrations (Figure 4). The lowest values (0.8 ppb), found at the same depth on the sill slopes of the western basin were thought to be a result of surface scouring either by accelerated currents or turbidity flows moving down the slopes. On the other hand, the highest concentrations occurred in areas known to have a high sedimentation rate, *viz.*, the relatively shallow Siculo-Tunisian sill and the station near the Algerian margin of the Algero-Provencal abyssal plain (Figure 4, stations b and e).

Similar data[39] have been reported for a series of cruises undertaken in both eastern and western basins during 1977 and 1978. Concentrations of PCBs in the top centimeter of 12 cores ranged from 0.6 to 8.9 ppb dry. In most cores the highest levels were found in the top centimeter; however, in several of the sediments a subsurface maximum at about 3 cm was a regular feature. The factors responsible for these types of profiles are not understood; however, ruling out the possibility of a sampling artifact,[39] it would appear that PCB penetration in deep-sea sediments to depths greater than 5 cm is related either to specific behavior of these compounds in sediments and pore water or active bioturbation, or both.

MONS 006373

Table 3
PCB CONCENTRATIONS (ng/g DRY) IN COASTAL SURFACE SEDIMENTS FROM THE MEDITERRANEAN SEA

Region	Year	Sample no.	Range	$\bar{X}$*	Ref.
Northwest Mediterranean					
French coast	1973	12	0.8—1165	—	36
Ile des Embiez	<1979	1	12	—	43
Golfe du Lion	1972	9	40—1.200	340	41
	1975	21	120—780	390	42
Marseille	1978—79	50	5—15.815	—	34
Monaco	1981	3	11—61	34	21
Spain	1977	17	0.3—100	10	40
Tyrrhenian Sea					
Tiber estuary	1976—77	2	46—770	—	24
Tiber offshore	1976—77	2	28—73	—	24
Naples offshore	1980	38	9—170	33	33
Naples Bay	1980	38	6—3.200	248	33
Sicily	1980—81	36	0.6—82	12	35
Ionian Sea					
Sicily	1980—81	36	0.8—49	12	35
Augusta Harbor	1980—81	9	130—457	253	35
Adriatic Sea					
Yugoslavia (north)	1977—78	7	<1.0—2.8	—	22
Yugoslavia (south)	1977—78	3	13—17	—	38
Aegean Sea					
Greece	<1973	15	1.3—775	—	32
Eastern basin					
Turkey	<1980	7	2—4	3	39
Egypt	1977	1	1.9	—	40
Central & western basins					
Tunisia	1977	8	0.5—1.1	0.7	40
Algeria	1977	5	7—323	—	40

* Mean not computed: (1) ranges given as geometric means, (2) too few samples, or (3) range includes single exceptionally high value.

During 1976, deep-sea sediment was collected at a series of stations between Toulon, France and Corsica.[44] PCB concentrations ranged from 1.5 to 32.5 ppb dry with the maximum value found in the sediments nearest Toulon. This latter concentration is more typical of coastal sediments and probably is a reflection of local input. While several samples showed low values (1.5 to 4.0 ppb), it is questionable whether the concentrations are directly comparable with the undisturbed core data discussed above since the sediments were collected by grabs.

The finding of readily measurable PCBs in deep Mediterranean sediments attests to the rapidity with which these stable organochlorine compounds are transported to depth. PCBs entering coastal waters are rapidly scavenged and deposited near the source which results in overall higher concentrations in the near-shore zone. In the open Mediterranean, concentrations in the surface sediment layer reflect integrated deposition of PCBs delivered principally via the atmosphere. Hence, variations in PCB concentration in sediments within the open Mediterranean are likely to be strongly influenced by the sedimentation rate.

A summary of open Mediterranean surface sediments is given in Table 4.

MONS 006374

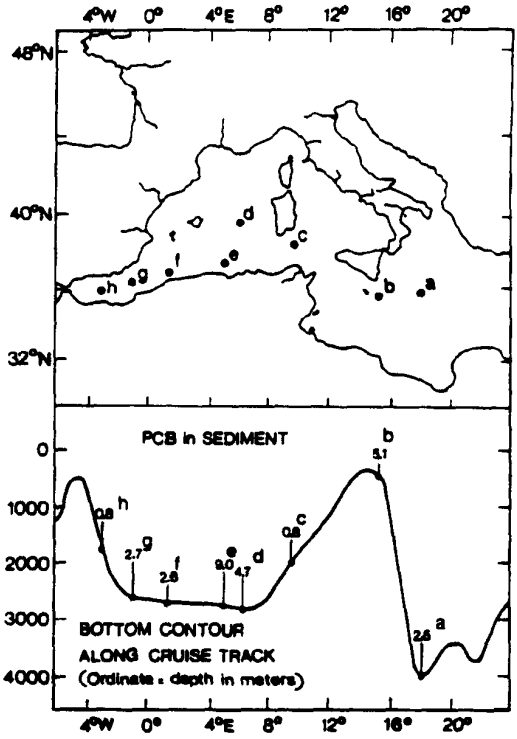


FIGURE 4. Concentration of PCBs (ng/g dry) in upper 1 cm of Mediterranean deep-sea sediments collected at a series of stations (letters) in 1975.[15,29]

C. Biota

More information is available on PCB levels in marine organisms because of the ease in sampling many species as well as the ease in measurement of the relatively high levels present in tissues. Furthermore, much of the recent data pertaining to marine species is a direct result of the UNEP Mediterranean Action Plan monitoring surveys which were initiated in the mid-1970s.

1. Coastal

Probably the organism most commonly analyzed for PCB compounds is the Mediterranean mussel *Mytilus galloprovincialis*. Mussels are widespread in the Mediterranean, except in

MONS 006375

Table 4
PCB CONCENTRATIONS (ng/g DRY) IN SURFACE SEDIMENTS FROM THE OPEN MEDITERRANEAN SEA

Year	Region	Sample no.	Range	$\bar{X}$	Ref.
1975	Algero-Provencal basin	5	0.6—9.0	4.0	12, 29
	Gibraltar sill & Siculo-Tunisian sill	2	0.8	0.8	
	Algerian margin	1	0.8	0.8	
	Ionian Sea	3	0.8—5.1	2.8	
1976[a]	Ligurian Sea	14	1.5—33	11	44
1977[b]	Tyrrhenian Sea	2	0.8—1.3	1.1	28
	Ionian Sea	3	1.2—1.6	1.4	
	Aegean Sea	2	0.6	0.6	
	Levantine & central basin	5	0.6—8.9	3.8	

[a] Grab samples.
[b] Undisturbed sediment cores (top 1 cm).

certain areas in the eastern basin, and are being used worldwide as biological indicators of marine contaminants including PCBs. Mussels have been particularly useful in the Mediterranean for identifying PCB "hot spots" arising from localized input. In a recent study in the Ebro delta of Spain,[48] levels in mussels (1100 ppb dry) from harbors near the mouth of the Ebro were about five times higher than concentrations (170 to 240 ppb) measured along the coast on either side of the delta, an observation signaling the Ebro River as an important source of PCBs. Risebrough et al.[49] pointed out that their lower values were comparable to levels recorded in relatively polluted Californian harbors and were an order of magnitude higher than those in mussels from relatively unpolluted areas of California. The fact that these relatively high levels were present as recently as 1980 would appear to reflect continued production and use of PCBs in Spain. Interestingly, if the concentrations measured by Risebrough et al.[49] are normalized to wet weight, the resultant values are substantially lower than those measured in mussels[48] from the Ebro delta 10 years earlier. A similar study[47] which took place earlier (1973—1974) along the northwest Mediterranean coast from the Spanish border to Genoa, Italy found the highest concentrations in mussels from Marseille and the Rhone estuary. This trend reflected that noted in coastal water samples from the region (see Figure 2) and clearly demonstrated that the Rhone River was a major source of PCBs. Marchand et al.[47] compared their concentrations with those measured at similar stations 2 years earlier[46] and concluded that there had been a general decrease (~twofold) in PCB concentration in mussels during that period. However the data of Marchand et al.[47] also show a strong seasonal variation in PCB content (>twofold), hence the significance of this 2-year trend is questionable. Nevertheless, Contardi et al.[46] analyzed mussels from Genoa sampled during 1977—1978 and found levels were 3 to 28 times lower than concentrations reported for the same area 4 years earlier. Although the data are not numerous, the trend for decreasing PCBs in mussels with time is consistent with the notion that PCB production and usage has declined somewhat during the last decade, and reflects the same decrease noted in open Mediterranean sea water (see Section A.2). Nevertheless, it should be kept in mind that because stationary sentinel organisms like mussels tend to reflect local input sources of PCB, temporal comparisons of concentrations in tissues, especially over the short term, may be of dubious value. For example, in contrast to the above examples, along the Greek coast in the northern Aegean Sea PCB concentrations in mussels doubled between 1975—1976 and 1979,[50] possibly as a result of increased urban industrial development in the Thessaloniki area.

MONS 006376

Table 5
PCB CONCENTRATIONS (μg/kg WET) IN MUSSELS[a] FROM THE MEDITERRANEAN SEA

Year	Region	PCB range	Ref.
1970	Ebro delta	400—1800	46
1980	Ebro delta	34—220[b]	45
1972	French coast	110—1920	48
1973—74	French coast	40—2700[b]	47
1974	French coast	200—1100	87
~1978	French coast	128[b]	43
1977—78	Ligurian Sea (Italy)	93—233[c]	49
1976—78	Tuscan Iss. (Italy)	20—59	51
1976—79	North Adriatic (Italy)	41—100[c]	52
1974—76	North Adriatic (Yugoslavia)	12—71	53
1977—78	Central Adriatic (Yugoslavia)	10—179	54
1977—78	South Adriatic (Yugoslavia)	2.2—148[b]	38
1976—77	Ionian Sea (Sicily)	61—100	55
1975—79	North Aegean (Greece)	261—575	50
1983	Algeria	7.3—630	56

[a] Refers to *Mytilus galloprovincialis* which are often considered to be the same species as *M. edulis*. In the case of Algeria some samples were *Perna perna*.
[b] Values calculated using 0.2 dry/wet weight ratio.
[c] Range of mean values.

Table 6
AVERAGE LEVELS OF PCBs (μg/kg WET) IN MUSSELS MEASURED DURING THE MED-POL III POLLUTANT MONITORING PROGRAM[57]

		PCB		
MED POL region	No. of samples	$\bar{X}$	σ	Range
Northwestern basin	17	307	266	22—1200
Tyrrhenian Sea	13	95	114	5—420
Adriatic Sea	159	84	221	5—2662
Aegean Sea	12	62	12	40—80

Published concentration ranges of PCBs in Mediterranean mussels are listed in Table 5. Ranges vary greatly and, among other factors, because of the wide dispersion it is difficult to drew any conclusions regarding spatial trends. The long-term Mediterranean Action Plan monitoring program has resulted in numerous measurements of PCBs in mussels throughout the region.[57] A summary of the results to date grouped by regions is given in Table 6. A trend for somewhat higher levels in the northwestern basin is evident but caution needs to be exercised in comparisons such as these since the number of data is relatively small and a strong bias can readily be introduced depending upon the exact location where mussels are collected. In general the concentrations reported in Tables 5 and 6 are of the same order of magnitude as those found during mussel surveys in the North Sea[58-60] during 1972—1976 and during the 1976 Mussel Watch program[61] which took place on the east and west coasts of the U.S.

Another commonly studied group of organisms is fish. PCB concentrations in edible flesh from a variety of pelagic and benthic species caught in coastal waters are presented in Table

MONS 006377

7. Levels vary over four orders of magnitude although surely not all the variation is related to environmental levels given the time span over which these surveys took place and the large number of laboratories involved. Nevertheless, very low values are found in less industrialized and populated regions such as the Yugoslav Adriatic, Turkey, and Libya. The highest levels tend to occur in the more industrialized sectors, e.g., the northern Italian coastline and in some cases near river mouths (Spain).

Some long-term studies with fish from single areas have proven useful in helping to establish spatial and temporal trends. For example, PCB concentrations in fish from the Adriatic generally tend to be lower on the lesser developed Yugoslav side.[28,32-36,62] Along the Italian coast in the northern Adriatic, Fossato and Craboledda[32] comparing PCB concentrations in anchovy with those measured in earlier surveys[60-67] found a 3.5-fold drop between 1970 and the period 1976—1979. They also concluded that although levels in north Adriatic fish suggested a moderate degree of PCB contamination, overall concentrations were similar to or lower than those in related species from the other urban and industrialized areas of the Mediterranean, a finding somewhat surprising considering that the northern Adriatic is usually regarded as a heavily stressed ecosystem.

Mullet (*Mullus barbatus*) have been used successfully in Greek waters to detect spatial trends in PCB concentrations. Samples collected from the most polluted area in the Saronikos Gulf near the Piraeus harbor contained roughly 15 times as much PCBs (~460 ppb dry) as those from the cleanest area.[64] The same species of mullet has also been used as an indicator organism for pollutants including PCBs in the MED POL program.[37] Hence, during the last few years a tremendous amount of data has been collected, the preliminary results of which are summarized in Table 8. As with values from the open literature, a large degree of variation is evident. The maximum values and highest mean concentrations are found in the coastal areas of the northwestern basin and the Tyrrhenian Sea. Statistical tests indicated that the mean concentration in the northwestern basin was significantly higher than the averages in all other areas except the Tyrrhenian Sea.[37] If the six samples from the north Levantine basin are considered representative of that area, the data indicate a near 100-fold drop in PCB concentration between the northwestern and less industrialized eastern regions of the Mediterranean.

Many other Mediterranean marine species have been analyzed for PCB content but not in a systematic manner as the examples cited above. For example, crustaceans, in particular the shrimp *Parapenaeus longirostris*, have received some attention.[37] PCB levels are generally low in these species with mean concentrations for various regions ranging from 1.5 to 31 ppb wet in shrimp muscle tissues. On the other hand, mean concentrations in crabs (*Carcinus mediterraneus*) are reported to be as high as 1448 ppb wet for the northwestern basin[37] and nondetectable[37] to 54 ppb wet[64] in the same species from the south Levantine basin.

At the lower end of the food chain, plankton and micronekton have been analyzed in a number of studies. Mixed microplankton collected in coastal waters in the Golfe du Lion during 1974 normally contained between 122 and 315 μg/kg dry of PCBs.[70] Two higher values (1350 and 1990 ppb dry) were measured in near-shore samples collected off Monaco during March 1973, a period of particularly heavy rainfall. Similarly high levels (4500 and 1800 ppb dry) were found in microplankton samples 5 km off Villefranche-sur-mer during November 1974 and March 1975, respectively.[70] During the November collection, plankton and nekton species forming a well-defined food chain were sampled from a single water mass and analyzed for PCBs. The PCB concentrations in Table 9 were examined by Fowler and Elder[71] and found not to differ markedly from those reported for similar species collected from the Atlantic and Pacific oceans during roughly the same period. More interesting, these data show an approximate 100-fold reduction in PCB concentration on a dry weight basis in going from lower trophic level microplankton to the top carnivorous myctophid fish, an

MONS 006378

Table 7
PCB CONCENTRATIONS (μg/kg WET) IN MUSCLE TISSUE OF FISH FROM THE MEDITERRANEAN

Species	Location	Date	PCB*	Ref.
Mullus barbarus	Ligurian Sea (Italy)	1977	188—1,486	49
	North and Central Adriatic (Italy)	1976-79	69—211	52
	Central Adriatic (Yugoslavia)	1975-79	<1—497	54
	North Adriatic (Yugoslavia)	1973	3	62
	Sicily coast	1976-77	17—373	55
	Augusta Bay, Sicily	1980	300	63
	North Aegean	1975-79	703	50
	Saronikos Gulf	1975-82	8—138*	64
		1975-76	4—1,100	65
	Eastern Turkey	~1980	2	39
	Israel	1975-79	60	86
M. surmuletus	Israel	1975-79	69	86
Mugil auratus	Eastern Turkey	~1980	10	39
M. cephalus	North and Central Adriatic (Italy)	1972	870	66
Sardina pilchardus	North and Central Adriatic (Italy)	1970	37—1,060	67
		1972	620	66
	North Adriatic (Yugoslavia)	1973	2—19	62
	France	1975	51—309	68
	Spain	1970	540—6,900	46
	Augusta Bay, Sicily	1980	2,300—6,100	63
Engraulis encrasicholus	Ligurian Sea (Italy)	1977-78	88—232	49
	Sicily coast	1976-77	9—176	55
	North and Central Adriatic (Italy)	1970	510—940	67
		1972	370	66
		1976-79	119—162	52
	North Adriatic (Yugoslavia)	1977	11—23	62
Thunnus thynnus	France	1975	95—407	68
		1977	6—89	69
	Sicily coast	1976-77	9—44	55
	North and Central Adriatic (Italy)	1976-79	344	52
	North Aegean	1975-79	2613	50
Euthynnus alletteratus	Ligurian Sea (Italy)	1977-78	191—1,029	49
Sarda sarda	Ligurian Sea (Italy)	1977-78	1,133—14,020	49
Xiphias gladius	North Aegean	1975-79	364	50
Boops boops	Israel	1975-79	74	86
B. salpa	Libya	1982	2.5	56
Scorpaena scrofa	Libya	1982	3.9	56
Sprattus sprattus	North & Central Adriatic (Italy)	1970	620—920	67
Gobius paganellus		1972	100	66
Pleuronectes flesus		1972	250	66
Squalus acanthias		1972	720	66
Esox lucius		1972	350	66
Anguilla anguilla		1972	720	66

MONS 006379

Table 7 (continued)
PCB CONCENTRATIONS (μg/kg WET) IN MUSCLE TISSUE OF FISH FROM THE MEDITERRANEAN

Species	Location	Date	PCB[a]	Ref.
	Augusta Bay, Sicily	1980	2,500	63
Saurida undosquamis	Israel	1975-79	236	86
Merluccius merluccius		1975-79	16	86
Trachurus mediterraneus		1975-79	63	86
Upeneus moluccensis		1975-79	151	86
Pagellus acarne		1975-79	151	86
P. erythrinus		1975-79	188	86
Mugil cephalus		1975-79	91	86
Dentex macrophthalmus		1975-79	195	86

[a] In some cases the ranges given are ranges of mean values. Single values represent either means of several determinations or a concentration based on a single measurement of a pooled sample containing tissues from several individuals.
[b] Computed from original data using 0.3 dry/wet weight ratio.

Table 8
AVERAGE LEVELS OF PCBs (μg/kg WET) IN MUSCLE OF THE MULLET *MULLUS BARBATUS* MEASURED DURING THE MED-POL III POLLUTANT MONITORING PROGRAM[87]

MED POL region	No. of samples	PCB		
		$\bar{X}$	σ	Range
Northwestern basin	33	813	1496	30—8000
Tyrrhenian Sea	33	477	770	50—3950
Adriatic Sea	86	234	473	<1—3117
Aegean Sea	51	113	204	0—1110
North Levantine basin	6	9	19	0.4—52
South Levantine basin	42	69	75	0—284

observation indicating that PCBs are not biomagnified in this particular food chain. The only other published surveys of PCBs in plankton appear to be those carried out in the Adriatic Sea during the late 1970s. Seasonal measurements made at two stations 3 and 7 km off the Italian coast[75] showed values ranged from 61 to 397 ppb dry. No onshore-offshore gradient was noted but the concentrations were highest during the summer months when the zooplankton was comprised mainly of cladocerans. PCB/DDT ratios were relatively high (1 to 3) in the plankton which confirmed the prevalence of pollution arising from industry rather than agriculture. In general, concentrations off Italy were similar to those which have been measured in plankton from Yugoslavian waters, *viz.*, 10.5 ppb wet, 59 to 287 ppb dry, and 400 ppb dry from the north, central, and southern Adriatic, respectively.[26,53,54]

The fact that zooplankton and their particulate products have been collected from a single area in the northwestern basin and analyzed for PCBs by the same analyst over a period of several years has allowed examining temporal changes in PCB concentration in this particular

MONS 006380

Table 9
PCBs AS DP-5 IN PELAGIC ORGANISMS COLLECTED IN NOVEMBER 1974 OFF VILLEFRANCHE-SUR-MER, FRANCE[71]

Organism	Weight ratio (wet/dry)	PCB (μg/kg dry weight)	PCB[b] C.F.
Microplankton[a]	10.4	4,500	170,000
Euphausiid			
Meganyctiphanes norvegica	5.0	620	50,000
Shrimp			
Sergestes arcticus	4.0	470	47,000
Pasiphaea sivado	4.2	210	20,000
Fish			
Myctophus glaciale	3.2	50	6,000
Surface water		2.5 ng/ℓ	

[a] Principally copepods, unidentified small crustaceans, chaetognaths, phytoplankton, and detritus.
[b] Concentration factor defined as ppb wet PCB in organism/ppb PCB in water.

Table 10
AVERAGE CONCENTRATIONS OF PCBs[a] (ng/g DRY) IN COMPONENTS OF THE PELAGIC ECOSYSTEM OF THE NORTHWESTERN MEDITERRANEAN BASIN[72]

Component	1974-78	1978-82	Reduction factor (approximately 5 years)
Zooplankton	1.5 ± 1.8 (× 10³) (6)[d]	0.23 ± 0.15 (× 10³) (14)[d]	6.5 X
Zooplankton fecal pellets	1.7 ± 1.4 (× 10³) (4)[d]	0.12 ± 0.09 (× 10³) (10)[d]	14 X
Sediment trap particles	4.6 ± 2.5 (× 10³) (4)[d]	1.3 ± 1.2 (× 10³) (44)[d]	3.6 X
Sea water[b]	3.2 ± 2.2 (9)[d]	1.0 ± 0.4 (6)[d]	3.2 X

Note: Number of samples are given in parenthesis below concentrations.

[a] PCB quantified as Aroclor® 1254 or Phenaclor® DP-5 equivalents.
[b] Concentration in ng/ℓ.
[c] References 70 and 71.
[d] Reference 73.
[e] Reference 74.
[f] Reference 26.

portion of the ecosystem. Average PCB concentrations in zooplankton, their fecal pellets, sedimenting particles, and sea water have been computed by Burns et al.[73] for two 4-year periods (Table 10). Their data show a clear decrease of PCB concentrations over a time span of approximately 5 years in all components analyzed, particularly in zooplankton and fecal pellets. Although the more recent measurements indicate that compared to other organochlorine compounds PCBs still remain an important class of pollutants in the Mediterranean, they appear to be declining in the northwestern basin reflecting reduced input as a result of national restrictions on their use.

MONS 006381

Amico et al.[75] measured PCBs in a variety of seaweeds from the east coast of Sicily. Concentrations ranged from 37 to 591 μg/kg dry and no major trends were noted between the various taxonomic groups of algae. The highest levels were found in samples from an area near Syracuse (Priolo) which is ostensibly polluted by nearby industrial activity. Concentrations in algae on a dry weight basis were lower than those measured in mussels from the same areas but were comparable or higher when normalized to extractable organic matter. Compared to mussels, higher amounts of the lesser chlorinated biphenyls were present in the algae, a difference due either to slower metabolic breakdown of PCBs or differential uptake of the individual compounds, or both.

Aside from fish, among top-level predators, sea birds have received the most attention with regard to PCB pollution. Bourne and Bogan[76] compiled existing information until 1979 and, although the database was not large, they concluded that fairly similar levels of PCBs (several parts per million wet) were present in sea birds throughout the Mediterranean. They also noted that these concentrations were typical for comparable species in the more developed regions of the world today and were of no cause for immediate concern. Later studies[77,78] pointed up the inadequacy of the Mediterranean database and furthermore stressed that certain gulls of the genus *Larus*, which contained high levels of PCB, were not ideal indicators of pollution due to their irregular and highly varied feeding habits. The results of these latter studies nevertheless corroborated the conclusions of Bourne and Bogan[76] in that with the exception of some terns and gulls nesting in very polluted lagoons in Sardinia and Venice, the levels of PCBs in the samples examined do not reach the high concentrations reported in the literature 10 to 15 years ago for the same or similar species living in North America or Europe. A compilation of PCB concentrations in tissues and eggs of representative coastal sea birds is given in Table 11. It is evident that the highest concentrations are found in gulls (up to 20 ppm) which forage over wide areas for food. In contrast, shore birds such as coots, stilts, and avocets typically contain one to two orders of magnitude less PCBs in their eggs and tissues. Although not unduly high, concentrations such as these present in all birds examined attest to the widespread occurrence of PCB in the Mediterranean environment.

2. Open Sea

Because of the migratory behavior of many marine species, particularly fish, it is often difficult to distinguish between organisms specifically inhabiting coastal or open oceanic waters. Some of the large predatorial fish discussed above, e.g., tuna, inhabit and forage in open waters but are fished in the near-shore zone. Hence, their contaminant load may be acquired in either or both environments. However, smaller pelagic species such as plankton and microplankton characteristically reside in a single water mass and, thus, if sampled in open waters, contaminant concentrations should be indicative of the organisms' immediate environment.

During the mid-1970s several cruises were made throughout the Mediterranean to measure contaminants in the open pelagic ecosystem. The data from these surveys were meant to serve as a baseline for comparison with monitoring studies undertaken in the coastal zone. The stations at which pelagic organisms were samples for PCB analyses are shown in Figure 5. In 1974 two different-sized fractions of microplankton (60 and 132 μm net mesh) were collected along a seaward transect running from 20 to 90 km offshore Monaco.[36] PCB concentrations normally ranged between 146 and 741 ppb dry and no onshore-offshore gradient was detected for either size fraction. PCB/DDT ratios in microplankton ranging between 2 and 20 were similar to those measured in mussels[36] during the same period; however, ratios in the larger euphausiids were much lower (0.87 to 0.95). One sample of microplankton from 60 km offshore contained approximately 75 ppm dry PCB; this exceptionally high value was explained by the fact that the sample was contaminated by oil originating from a surface slick.

MONS 006382

Table 11
PCBs (μg/g WET) IN EGGS AND TISSUES OF MEDITERRANEAN SEA BIRDS

Species	Location	Tissue	No. (n)	PCBs Range	PCBs $\bar{X}$	Ref.
Cory's shearwater (*Calonectris diomedea*)	Crete	Eggs	2	3.2—4.1	3.65	79
Manx shearwater (*Puffinus puffinus*)	Gibraltar	Muscle	2	0.99—1.1	1.02	79
Shag (*Phalacrocorax aristotelis*)	Gibraltar	Muscle	3	4.1—7.1	5.62	79
Lesser black-backed gull (*Larus fuscus*)	Gibraltar	Muscle	1		0.52	79
Herring gull (*Larus argentatus*)	Madeira	Muscle	1		0.4	79
	Gibraltar	Muscle	3	0.82—3.8	2.12	79
	Balearic Is.	Egg	1		11.0	80
	Rhone delta	Eggs	6	16—160	52	81
	Crete	Egg	1		5.32	79
	Cyprus	Eggs	2	1.2—4.2	2.7	79
	Tuscan Is.	Eggs	25		~8.4	77
	Po delta	Eggs	4		4.0*	78
Audouin's gull (*Larus audouini*)	Morocco	Eggs	3	3.1—4.2	3.82	80
	Balearic Is.	Eggs	4	12.8—20.6	16.8	80
Black-headed gull (*Larus ridibundus*)	Rhone delta	Eggs	4	1.6—7.8	5.45	81
	Po delta	Muscle	8	0.61—3.6	1.65	66
	N. Adriatic	Eggs	17		3.2*	78
Little gull (*Larus minutus*)	Malta	Liver	1		3.6	79
Common tern (*Sterna hirundo*)	Po delta	Muscle	2	0.43—8.0	4.21	66
	Po delta	Eggs	22		3.2*	78
	N. Adriatic	Eggs	13		4.1*	78
Little tern (*Sterna albifrons*)	Sardinia	Eggs	12		<4.0	77
	N. Adriatic	Eggs	16		2.6*	78
	C. Sardinia	Eggs	6		2.8*	78
	S. Sardinia	Eggs	6		4.9*	78
Black tern (*Chlidonias nigra*)	Po delta	Muscle	1		<0.01	66
Coot (*Fulica atra*)	Po delta	Muscle	1		0.21	66
	Malta	Liver	1		0.1	79
	Po delta	Eggs	3		0.19*	78
Gull-billed tern (*Gelochelidon nilotica*)	S. Sardinia	Eggs	7		1.1*	78
	N. Adriatic	Eggs	15		1.7*	78
Slender-billed gull (*Larus genei*)	S. Sardinia	Eggs	33		3.5*	78
Black-winged stilt (*Himantopus himantopus*)	N. Adriatic	Eggs	3		0.14*	78
Avocet (*Recurvirostra avocetta*)	N. Adriatic	Eggs	5		0.12*	78

MONS 006383

Table 11 (continued)
PCBs (μg/g WET) IN EGGS AND TISSUES OF MEDITERRANEAN SEA BIRDS

Species	Location	Tissue	No. (n)	PCBs Range	PCBs $\bar{X}$	Ref.
Little egret (*Egretta garzetta*)	Po delta	Eggs	9		2.3*	78
Night heron (*Nycticorax nycticorax*)	Po delta	Eggs	8		2.3*	78

* Computed from dry weight values using wet/dry ratio of 3 for terns, 4.3 for gulls, and 3.5 for others.[78]

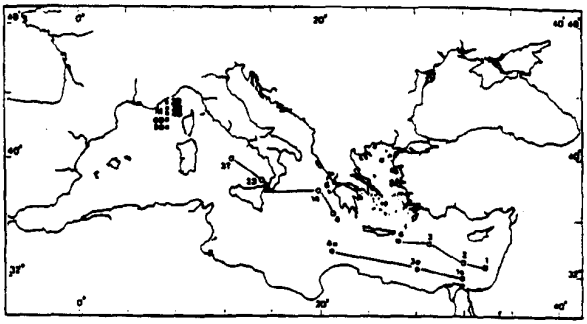


FIGURE 5. Cruise tracks and station numbers where open ocean plankton and nekton have been sampled for PCB analyses. R/V *Wimereux Singer*, 6/74 (x); R/V *Atlantis II*, 4/77 (⊕); USNS *Hayes*, 6/77 (○); R/V *Shikmona*, 7/77 (□).

On several occasions during 1977 pelagic organisms were collected primarily from open waters of the eastern Mediterranean (Figure 5). The results for these surveys are summarized in Table 12. Aside from samples collected at stations 3a and 6a, microplankton from the open Levantine basin generally contained less PCB residues than those samples in coastal waters of the northwestern basin and Adriatic sea (see Section III.C.1).

Euphausiids, the organisms most common to all stations, contained levels ranging from 10 to 110 ppb dry. These concentrations were somewhat lower than those measured in the euphausiid *Meganyctiphanes norvegica* ($\bar{X}$ = 302, range 38 to 620 ppb dry) sampled in French coastal waters[79] during 1974—1975. With the possible exception of the amphipod *Anchylomera blossevillei*, all other zooplankton and microplankton displayed relatively low concentrations of PCBs. The tunicate from the Ionian Sea contained approximately 6 to 20 times less PCBs than the same species living in the south Levantine basin. At one station in the Tyrrhenian Sea specimens of *Myctophum glaciale*, a vertically migrating fish, were separated into three size classes. Although no trends were noted for absolute concentration of PCBs in the different sized fish, the PCB/ΣDDt and PCB/DDE ratios decreased with increasing size of fish, suggesting differential uptake and/or metabolism of these compounds as the fish grow.

MONS 006384

Table 12
PCB CONCENTRATIONS (μg/kg DRY) IN MICROPLANKTON, ZOOPLANKTON, AND MICRONEKTON FROM DIFFERENT REGIONS OF THE OPEN MEDITERRANEAN; SAMPLES OF VARIOUS SPECIES OF ZOOPLANKTON AND MICRONEKTON WERE COMPOSITE SAMPLES OF SEVERAL INDIVIDUALS[24,25]

Organism	Region	Station[a]	PCB (DP-5)
Microplankton[b]	South Levantine	1a	30
		3a	100
		6a	230
		1	35
		2	19
		3	22
		4	15
	Northwestern basin	M20	272
		M30	232
		M40	266
		M60	24,500[c]
		M90	383
Euphausiids[a]	Tyrrhenian	37	25
		37	110[c]
		23	30
	Ionian	14	38
		14	57[c]
		4	23
	South Levantine	3a	26
		6a	65
		2	26
		3	18
		4	9.8
Siphonophora	Tyrrhenian	37	22
Abylopsis tetragona		23	41
	South Levantine	3a	37
Polychaeta	Ionian	14	96
Alciopa emiliani			
Amphipoda	Tyrrhenian	23	660
Anchylomera blossevillei			
Decapoda	Tyrrhenian	37	41
Sergestes arcticus[a]		23	56
Sergestes corniculum[a]	Ionian	4	21
Pollicaris (larva)		14	71
Tunicata	Ionian	4	6
Pyrosoma atlanticum			
	South Levantine	3a	49
		6a	150
Pisces	South Levantine	3a	35
Anguilla (leptocephalus)		6a	48
Myctophum glaciale[a]	Tyrrhenian	23	89
		37 (6—8 cm)	27
		37 (4—5 cm)	83
		37 (2—3 cm)	50
	South Levantine	6a	41

[a] See Figure 5 for station location and data.
[b] Dry weight averaged 11% of wet weight.

MONS 006385

Table 12 (continued)
PCB CONCENTRATIONS (μg/kg DRY) IN MICROPLANKTON, ZOOPLANKTON, AND MICRONEKTON FROM DIFFERENT REGIONS OF THE OPEN MEDITERRANEAN; SAMPLES OF VARIOUS SPECIES OF ZOOPLANKTON AND MICRONEKTON WERE COMPOSITE SAMPLES OF SEVERAL INDIVIDUALS[a,o,z]

[a] Dry weight averaged 18% of wet weight.
[d] Pure sample of *Meganyctiphanes norvegica*.
[e] Dry weight is 23% of wet weight.
[f] Dry weight is 27% of wet weight.
[g] Sample heavily contaminated with petroleum hydrocarbons.

Fowler and Elder,[82] after careful examination of the data, found no evidence for increased PCB concentrations with increasing trophic level. This observation was in agreement with their conclusions based on analyses of similar food chains sampled in the northwestern basin.[71] Where possible, these authors also compared PCB concentrations in individual species or groups of zooplankton and micronekton from their study with similar organisms from other areas. The limited data available for comparison indicated that concentrations were similar or in some cases lower than previously reported values.[82] In the case of mixed plankton far more data exist. Fowler and Elder[82] emphasized the difficulties involved in making valid comparisons between mixed plankton samples where variations in pollutant levels resulting from mixed species composition, different net mesh sizes used, sample contamination from abiotic particles etc., can become very important. Nevertheless, they showed that PCBs in mixed plankton from previous surveys in other geographical areas ranged between approximately 10^1 to 10^3 ppb wet with some values as high as 10^3, whereas levels in open Mediterranean microplankton were lower at 1 to 10^1 ppb wet. Direct comparison was limited by the fact that the previous studies were carried out several years prior to the Mediterranean survey and levels in Mediterranean plankton could have been higher during the early 1970s before certain restrictions on PCB usage came into effect in Europe. In view of the evidence from temporal studies of PCB in coastal zooplankton (Table 10), it is highly likely that PCB levels in open Mediterranean plankton have also decreased during the 1970s.

The only other report pertaining to PCBs in truly open Mediterranean animals appears to be that of Aizieu and Duguy[83] for cetaceans. Their comprehensive survey included a wide variety of open ocean species some of which are common to both the Mediterranean and Atlantic. Levels of PCBs in the striped dolphin *Stenella coeruleoalba*, which were stranded on the French shores of the Mediterranean and Atlantic are shown in Table 13. Although the number of specimens from the French Atlantic coast is small, the comparison shows a clear trend for higher concentrations in individuals from the Mediterranean. In a more limited comparison with Risso's dolphin *(Grampus griseus)* Aizieu and Duguy[83] reported higher PCB levels in three adults from the Mediterranean than in a very old individual found stranded on the Atlantic coast. In contrast, a single fin whale, *Balaenoptera physalus*, stranded on the Mediterranean coast in 1973 contained 5 μg/g lipid in the blubber whereas the corresponding concentration in a similar individual from the French Atlantic coast sampled in 1976 was 47 μg/g lipid. The authors pointed out that the concentration noted in the Mediterranean specimen was typical of those which have been reported for fin whales from other areas of the North Atlantic. Another baleen whale, *Balaenoptera acutorostrata*, stranded on Mediterranean shores in 1977 also displayed relatively low levels of PCBs; concentrations were 4.8, 4.6, 2.9, and 2.0 ppm dry in liver, stomach, kidney, and spleen, respectively.

MONS 006386

Table 13
CONCENTRATIONS OF PCBs (μg/g DRY)[a] IN TISSUES AND ORGANS OF THE STRIPED DOLPHIN *STENELLA COERULEOALBA* FROM THE MEDITERRANEAN AND ATLANTIC FRENCH COASTS[83]

Location	Sample no.	Liver	Kidney	Muscle	Blubber
Mediterranean	16				
Maximum		449	85.3	18.4	260
Minimum		6.6	4.1	3.3	172
$\bar{X} \pm \sigma$		83.2 ± 128	3 ± 30.1	—	—
Atlantic	4				
Maximum		9.2	8.5	3.3	47.7
Minimum		5.4	1.5	0.8	—

[a] PCB quantified as Phenoclor® DP-6.

Alzieu and Duguy[83] concluded that the lower concentrations found in the Mysticeti (fin whales) compared to other groups were probably a result of low PCB levels in zooplankton, their basic food.

Whereas no evidence for PCB biomagnification was evident in the lower trophic levels of the pelagic food chain (i.e., zooplankton and nekton), PCB concentrations in tissues of dolphins and whales from the Mediterranean (as is the case elsewhere) are clearly higher than levels in the organisms upon which they feed, a fact which may indicate PCB biomagnification at the top level of this pelagic food chain.

IV. VERTICAL FLUX AND REMOVAL PROCESSES

From knowledge of the strong affinity of PCB compounds for both biotic and abiotic particles, it follows that PCB removal from the surface layers will be partially governed by particulate formation and sinking processes. Nevertheless, measurements aimed at quantifying these processes are few. In the mid-1970s Elder and Fowler[70] studying PCBs in plankton from the northwestern basin found high levels of PCBs in euphausiid fecal pellets ranging from 4.8 to 38 μg/g dry. Furthermore, these concentrations were higher than those measured in either the euphausiids producing the pellets or their microplankton food source. Based on calculations of the euphausiid fecal pellet production rate, the authors concluded that roughly 1.4 to 4.1 μg PCB/m²/year would be transported to the benthos by sinking euphausiid fecal pellets alone. The importance of this mechanism was underscored by the good agreement between their estimate of the PCB deposition rate for the total zooplankton biomass and those (80 to 125 μg/m²/year) calculated from PCB measurements in undisturbed sediment cores from the Ligurian Sea.

Later Fowler et al.[76] directly measured PCB flux through the 100 m depth by deploying semipermanent sediment traps in the same region. Over a 5-month period between June to October 1978, PCB flux averaged 103 μg/m²/year (range 56 to 183 μg/m²/year); these values were also comparable with the aforementioned estimates of deposition rate based on surface sediment measurements. Examination of the particles collected by the traps showed that intact fecal pellets comprised at least 10% of the total dry weight. Furthermore, copepod fecal pellets of the type trapped at 100 m were found to sink at rates ranging from 20 to 260 m/day, speeds sufficiently high to ensure rapid transport of PCB residues to depth (250 m in the case of the Monaco sediment trap station).

More comprehensive studies at the same site[21,73] examined the seasonal aspects of PCB flux as well as assessed the importance of the biogenic particulate contribution to the flux.

MONS 006387

Time series measurements of trapped particulates between 1979 and 1982 showed that PCB flux varied seasonally by as much as two orders of magnitude with maximum fluxes occurring in late winter and the minima generally in late summer (Figure 6). While maximum PCB flux tended to correlate with periods of high mass flux, some differences were apparent primarily because PCB concentration in the sinking particles also varied with time. Moreover, PCB flux generally corresponded with regional zooplankton biomass and primary productivity cycles. The average PCB flux for the entire period was 37 $\mu g/m^2$/year, a value somewhat lower than the mean flux[76] measured during 1978. These studies also demonstrated that copepod fecal pellets were always an important component of the particulate flux (10^3 to 10^6 pellets/m^2/day) and that they contained higher levels of PCB than the copepods themselves. Similar PCB flux measurements were made in the Kiel Bight[64] during 1975 and 1977. Values were higher in the Kiel Bight ($\bar{X}$ = 146 $\mu g/m^2$/year, range 25 to 301 $\mu g/m^2$/year) than those that have been measured in the northwestern Mediterranean; however, this is not unexpected since Kiel Bight is extremely shallow (~20 m) and therefore subject to high rates of sediment resuspension.

Burns et al.[77] calculated residence times of PCBs in surface waters of the northwestern basin in accordance with recent partitioning models and compared them with those calculated from direct measurement of sediment trap particles. Good agreement was found between estimates based on direct measurement (2.6 years) and those using fluxes from sea water into sediments (4.0 years). The unrealistically short residence time (0.5 years) computed from PCB concentrations only in slow sinking suspended particles suggests that underestimates can arise if major contributions from the large particles which actually settle out are not considered. In this respect reliable estimates of residence times for PCBs in the nearshore zone of the northwestern basin probably lie in the range of 2 to 4 years. Most likely PCB residence times in the open waters of the Mediterranean, particularly in the eastern basin, will be much longer due to lower productivity and, hence, lower particle content in these waters. In addition, a relatively rapid PCB flux might be expected to occur in regions near the North African coast which are subject to eolian terrigenous input from the Sahara. However, at present, corresponding data on vertical PCB flux in other regions of the Mediterranean are lacking.

V. SUMMARY AND CONCLUSIONS

Because of unique oceanographic and geographic characteristics, the Mediterranean Sea is potentially vulnerable to the effects of anthropogenic pollutants such as PCBs. Despite this fact, until recently reliable information on inputs and existing levels of PCBs in various components of the Mediterranean ecosystem has been extremely limited. Published data on annual production of PCB compounds in France, Italy, and Spain indicate that there has been little decrease in production, and presumably usage, during the 1970s. While these three countries may be the most important producers and users of PCBs in the region, similar data from the remaining Mediterranean countries are needed to complete the picture. The major input sources are rivers in the northwestern sector, including the Adriatic Sea, and atmosphere fallout originating from industrial and urban areas of continental Europe. Measurements of PCBs in marine air have shown that onshore-offshore gradients are slight; this suggests that at least within the northwestern basin PCB input via the atmosphere is relatively uniform. Air measurements also indicate a threefold reduction in PCB concentration between the period 1975—1977; however, the data are few and more information is needed to confirm this trend.

PCB measurements in sea water have clearly demonstrated the influence of coastal source terms (e.g., the Rhone and other rivers as well as urban outfalls). Concentrations vary widely in coastal waters whereas offshore levels are lower and generally more uniform (e.g., $\bar{X}$ =

MONS 006388

2 ng/ℓ in 1975). These studies have also shown that levels in open waters of the western Mediterranean tend to be slightly higher than those in the eastern basins. Furthermore, the average PCB concentration in open waters for the period 1977—1979 dropped to 0.7 ng/ℓ, an observation which suggests a reduction in PCB input during the latter half of the 1970s. Throughout the Mediterranean, PCB concentrations have been found to be fairly uniform with depth except in the Golfe du Lion where a subsurface maximum was recently observed at approximately 500 m. The origin of the maximum is unknown but may be related to processes such as the Rhone river outflow and/or PCB resolubilization from sinking particles. More detailed profiles combined with sediment trap and nephelometry measurements would help to identify the process(es) involved.

The strong affinity of PCBs for suspended particulates in Mediterranean waters ensures their eventual deposition in the sediments. Concentrations in coastal sediments are high (10^3 to 10^4 ppb) near input sources such as urban and industrial outfalls, but rapidly drop off in a seaward direction displaying levels more typical of Mediterranean deep-sea sediments (1 to 10 ppb). PCB concentrations in coastal sediments from the eastern Mediterranean are low and fall within the range of values characteristic of levels in sediments from the open sea.

PCB measurements in certain organisms have proven instrumental in identifying local contamination "hot spots". For example, relatively high concentrations have been found in mussels from areas near major river outfalls (e.g., the Rhone and Ebro deltas) and large industrialized cities (e.g., Marseille and Genoa). There is also preliminary evidence emerging from comprehensive multinational mussel surveys which indicates higher PCB levels in the northwestern basin than in other Mediterranean regions. Nevertheless, PCB levels in mussels are generally comparable with similar measurements made in other regions of the world. Studies with various species of Mediterranean fish have demonstrated more or less the same trends, i.e., higher levels near river mouths and centers of industry, in certain areas a decrease in PCB concentrations between the early and late 1970s, and significantly higher levels in the northwestern basin than in the eastern sectors. Surveys using coastal zooplankton and marine birds, although far more limited in scope, have indicated that existing PCB levels are not unlike those measured in similar species from outside the Mediterranean. Furthermore, temporal studies with zooplankton and associated particulates have likewise demonstrated a decrease in PCB levels during the period between approximately 1975 to 1980.

Far less information is available from measurements of open Mediterranean species; however, evidence from a few plankton and nekton surveys carried out during the mid to late 1970s suggests that existing levels are the same or, in some cases, lower than those in similar species from other oceanic regions. Where examined, primarily in lower trophic level pelagic food chains, no evidence was found for the biomagnification of PCB compounds. On the other hand, although data are extremely limited, there is some evidence to show that PCB levels in Mediterranean cetaceans are higher than those measured in their relatives from the Atlantic. Furthermore, concentrations in the tissues of these top predators are significantly higher than levels measured in the organisms which serve as their prey. Given the fact that these data are patchy as well as oftentimes contradictory, more information on PCB levels in large carnivorous fish and mammals is particularly needed to clarify these points.

PCBs, entering Mediterranean surface waters by whatever means, are rapidly sequestered by fine suspended particles, packaged into larger ones, and subsequently transported downward. Zooplankton are instrumental in the repackaging process and their fecal pellets account for much of the rapid input of PCBs to the deep Mediterranean. Sediment trap studies in coastal waters of the northwestern basin have demonstrated that the vertical flux of PCBs is seasonally variable with the maximum fluxes occurring during late winter and the minimun in late summer. Moreover, there was a general correlation between PCB flux and the regional zooplankton biomass and productivity cycles, further underscoring the importance of small

MONS 006389

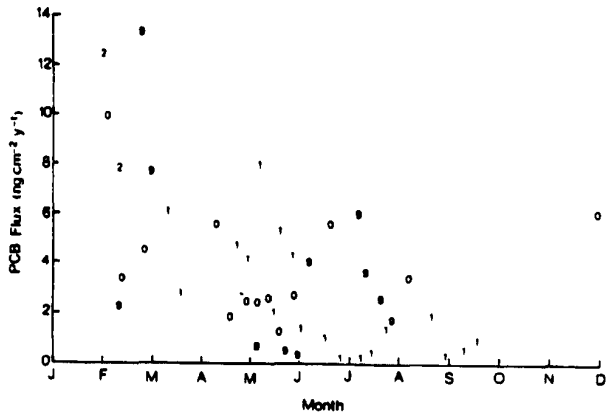


FIGURE 6. Composite plot of PCB particulate flux through 100 m vs. months of the year at a sediment trap station off the coast of Monaco. *Symbols refer to year of sample collection, i.e.*, 1979 (9), 1980 (0), 1981 (1), and 1982 (2).[78]

pelagic organisms in sequestering and removing PCBs from the upper layers. The average PCB flux through 100 m depth measured during the period 1979—1982 was 37 μg PCB/m²/year (Figure 6). These fluxes translate into a mean upper-layer PCB residence time of approximately 2.6 years. Although no comparable flux data are available from other regions of the Mediterranean including the open sea, PCB fluxes are expected to be lower in the less productive eastern and central basins. This hypothesis should, however, be examined in future studies.

It should be kept in mind that almost all PCB data for the Mediterranean originate from GC analyses that have used packed columns. In the future more sophisticated capillary column separation techniques will have to be used since scientific interpretation will rely increasingly on the ability to treat PCB transport and fluxes in terms of the principal PCB peaks in the mixtures.

Mediterranean PCB data are in many cases limited and of unequal reliability and any regional and temporal comparisons are thus open to question; nevertheless some general trends have emerged from this synthesis. First, there are several lines of evidence from both coastal and open Mediterranean studies which indicate that existing levels of PCBs are highest in the northwestern basin. This feature is certainly a result of the basin's proximity to the more highly industrialized and populated coasts of the northern European continent. Input to this region occurs via the major rivers and atmospheric fallout. With regard to atmospheric transport, at present marine air measurements are confined to the northwestern basin; thus, more synoptic coverage from both the western and eastern sectors is necessary to verify the importance of atmospheric transport from Europe in establishing the observed east-west trend.

Second, scattered data from several short-term temporal surveys suggest a general decrease in PCB levels in the Mediterranean over the last decade. This is particularly interesting considering that PCB production figures for France, Italy, and Spain during this period show

MONS 006390

little, if any, decrease. Although the overall reduction of PCBs in the Mediterranean ecosystem may simply be a reflection of the generally recognized diminution of PCB production and utilization in northern Europe as a whole, similar production and usage data from other Mediterranean countries may shed some light on the factors controlling the observed temporal trends. Most important, since more than a decade has passed since the initial measurements of PCBs in the Mediterranean were made, it is essential that measurements continue to be made with the same matrices at the same locations and by the same laboratories in order that long-term temporal trends be firmly established.

Third, where comparisons can be made, available data suggest that existing levels of PCBs in the Mediterranean ecosystem are generally similar to concentrations measured in the same matrices from other regions of the world ocean. From this observation we can conclude that aside from localized "hot spots" of PCB insult, PCB input concentration and removal processes in the Mediterranean appear to be operating in a manner similar to those in the larger, less-enclosed oceans.

ACKNOWLEDGMENTS

The International Laboratory of Marine Radioactivity operates under a tripartite agreement between the International Atomic Energy Agency, the Government of the Principality of Monaco, and the Oceanographic Institute at Monaco. I wish to especially thank Drs. A. Cruzado and G. P. Gabrielides, UNEP Co-ordinating Unit for the Mediterranean Action Plan, for their permission to cite some unpublished data from the MED POL Monitoring Programme, and J.-P. Villeneuve and K. A. Burns (ILMR) for use of their unpublished oceanographic results. I also thank J. La Rosa for his invaluable assistance in compiling references and drafting figures. Dr. S. R. Aston, R. W. Risebrough, and J.-P. Villeneuve for their critical reviews, and Bonny Taylor-Jones for her efforts in typing the manuscript.

REFERENCES

1. Osterberg, C. and Keckes, S., The state of pollution of the Mediterranean Sea. *Ambio*. 6, 321, 1977
2. UNEP, Mediterranean Action Plan. Report of the First Meeting of the Working Group for Scientific and Technical Co-Operation for Med Pol. UNEP/WG.62/7. United Nations Environment Program. Geneva. 1981.
3. Anon., The rising clamor about PCB's. *Environ. Sci. Technol.*, 10, 122, 1976.
4. Anon., The persistent PCB problem. *Environ. Sci. Technol.*, 16, 98A, 1982.
5. Richardson, B. J. and Wald, J. S., Polychlorinated biphenyls (PCBs). *Search*. 13, 17, 1982.
6. FAO, The State of Marine Pollution in the Mediterranean and Legislative Controls. GFCM Studies and Reviews, No. 51. Food and Agriculture Organization, Rome. 1972.
7. UNEP, Pollutants from Land-Based Sources in the Mediterranean, UNEP/WG.18/INF. 4. United Nations Environment Program. Geneva. 1979.
8. OECD, Polychlorinated Biphenyls, Their Use and Control, OECD, Paris, 1973.
9. Geyer, H., Freitag, D., and Korte, F., Polychlorinated biphenyls (PCBs) in the marine environment, particularly in the Mediterranean. *Ecotoxicol. Environ. Safety*. 8, 129, 1984.
10. Nisbet, I. C. T. and Sarofim, A. F., Rates and routes of transport of PCBs in the environment. *Environ. Health Perspect.*, 1, 21, 1972.
11. Helmer, H., Pollutants from land-based sources in the Mediterranean. *Ambio*. 6, 312, 1977.
12. Elder, D. L., Villeneuve, J. P., Paral, P., and Harvey, G. R., Polychlorinated biphenyls in sea water, sediment and over-ocean air of the Mediterranean. in *Activities of the International Laboratory of Marine Radioactivity*, 1976 Report, International Atomic Energy Agency, Vienna, 1976, 136.
13. Villeneuve, J. P., Polychlorinated biphenyls in near sea atmospheric samples from the Mediterranean in 1975 to 1977, in *VIIme Journées d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1985, 489.
14. Bidleman, T. F. and Olney, C. E., Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. *Science*, 183, 516, 1974.

MONS 006391

15. **Tanabe, S., Kawano, M., and Tatsukawa, R.,** Chlorinated hydrocarbons in the Antarctic, western Pacific and eastern Indian oceans. *Trans. Tokyo Univ. Fish.*, 5, 97, 1982.
16. **Harvey, G. R. and Steinhauer, W. G.,** Atmospheric transport of polychlorobiphenyls to the north Atlantic. *Annes. Environ.*, 8, 287, 1974.
17. **Bernhard, M.,** Heavy metals and chlorinated hydrocarbons in the Mediterranean. *Ocean Manage.*, 3, 253, 1978.
18. **Elder, D. L.,** Chlorinated hydrocarbons in the north western Mediterranean Sea. A preliminary report, in *IIème Journees d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1975, 175.
19. **Elder, D. L.,** PCBs in N.W. Mediterranean coastal waters. *Mar. Pollut. Bull.*, 7, 63, 1976.
20. **Burns, K. A. and Villeneuve, J. P.,** Dissolved and particulate hydrocarbons in water from a spring sampling of the Var river estuary (S. France), *Toxicol. Environ. Chem.*, 5, 195, 1982.
21. **Burns, K. A. and Villeneuve, J. P.,** Biogeochemical processes affecting the distribution and vertical transport of hydrocarbon residues in the coastal Mediterranean. *Geochim. Cosmochim. Acta*, 47, 995, 1983.
22. **Picer, N. and Picer, M.,** Monitoring of chlorinated hydrocarbons in water and sediments of the North Adriatic coastal waters, in *IVème Journées d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1979, 133.
23. **Villeneuve, J. P.,** Unpublished results.
24. **Pucconi, G. and Leoni, V.,** PCB and HCB in the sediments and waters of the Tiber estuary. *Mar. Pollut. Bull.*, 11, 22, 1980.
25. **Duinker, J. C., Hillebrand, M. T. J., Palmork, K. H., and Wilhelmsen, S.,** An evaluation of existing methods for quantitation of polychlorinated biphenyls in environmental samples and suggestions for an improved method based on measurement of individual components. *Bull. Environ. Contam. Toxicol.*, 25, 956, 1980.
26. **Elder, D. L. and Villeneuve, J. P.,** Polychlorinated biphenyls in the Mediterranean Sea. *Mar. Pollut. Bull.*, 8, 19, 1977.
27. **Harvey, G. R., Steinhauer, W. G., and Miklas, H. P.,** Decline of polychlorinated biphenyl concentrations in north Atlantic surface water. *Nature (London)*, 252, 387, 1974.
28. **Villeneuve, J. P., Elder, D. L., and Fukai, R.,** Distribution of polychlorinated biphenyls in seawater and sediments from the open Mediterranean Sea, in *Vème Journées d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1981, 251.
29. **Elder, D. L. and Villeneuve, J. P.,** Polychlorinated biphenyls in marine air, deep sediments and water of the Mediterranean Sea. *Thalassia Jugosl.*, 13, 59, 1977.
30. **Villeneuve, J. P. and Burns, K. A.,** Distribution of PCB isomers between dissolved and particulate phases in the Mediterranean sea: testing the sorption models (in preparation).
31. **Fukai, R., Ballestra, S., and Vas, D.,** Characteristics of the vertical transport of transuranic elements through the Mediterranean water column, in *VIème Journées d Etudes Pollutions*, C.I.E.S.M., Monaco, 1983, 95.
32. **Dexter, R. N. and Pavlou, S. P.,** Chlorinated hydrocarbons in sediments from southern Greece. *Mar. Pollut. Bull.*, 4, 188, 1973.
33. **Baldi, F., Borgagli, R., Fossardi, S., and Fossi, C.,** Mercury and chlorinated hydrocarbons in sediments from the bay of Naples and adjacent marine areas. *Mar. Pollut. Bull.*, 14, 108, 1983.
34. **Arnoux, A., Blanc, A., Jourjorin, A., Monod, J. L., and Tatoulian, J.,** Etat actuel de la pollution sur les fonds du secteur de Cortiou (Marseille), in *Vème Journées d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1981, 459.
35. **Amico, V., Chillemi, R., Impellitteri, G., Orlando, G., Piccitelli, M., Schato, S., and Tringali, C.,** Levels of chlorinated hydrocarbons in sediments from the central Mediterranean, *Sci. Total Environ.*, 24, 91, 1982.
36. **Marchand, M., Vas, D., and Duursma, E.,** Résidues de DDT et de polychlorobiphenyles (PCB) dans les moules, le sédiment et le plancton de las côte nord-ouest méditerranéenne, in *IIème Journees d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1975, 171.
37. **Stirn, J., Avsin, A., Cencelj, J., Derer, M., Gomiscek, S., Kveder, S., Malej, A., Malschner, D., Nedna, I., Paul, J., and Tomlin, P.,** Pollution problems of the Adriatic Sea, an interdisciplinary approach. *Rev. Int. Oceanogr. Med.*, 35/36, 21, 1974.
38. **Vilnic, D., Picer, N., Picer, M., and Nasensky, B.,** Monitoring of chlorinated hydrocarbons in biota and sediments of south Adriatic coastal waters, in *IVème Journées d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1979, 143.
39. **Basturk, O., Dogan, M., Saltoglu, I., and Balkas, T.,** DDT, DDE, and PCB residues in fish, crustaceans and sediments from the eastern Mediterranean coast of Turkey, *Mar. Pollut. Bull.*, 11, 191, 1980.
40. **Cousteau, J. Y.,** Rapport préliminaire de l'expedition C.I.E.S.M. — Cousteau Society effectuée par le navire *Calypso* pour concevoir à l'établissement d'un bulletin de santé de la Méditerranée, in *IVème Journees d'Etudes Pollutions*, C.I.E.S.M., Monaco, 1979, 21.

MONS 006392

41. **Mestres, R., Pegnon, M., and Dubosl-Razavet, C.,** Etude des résidues de pesticides et d'hydrocarbures organochlorés dans les sédiments du plateau continental Languedocien en Méditerranee. *Trav. Soc. Pharm. Montpellier*. 35, 181, 1975.
42. **Mestres, R., Dubosl-Razavet, C., and Cooper, J. F.,** Contamination par les diphenyles chlorés et les résidues de pesticides organochlorés des sédiments marins du Golfe d'Aigues-Mortes. *Trav. Soc. Pharm. Montpellier*. 40, 1, 1980.
43. **Monod, J. L. and Arneux, A.,** Etude des composés organochlorés (PCB-DDT) dans l'environnement marin de l'Ile des Embiez (Var, France), in *IVème Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1979, 147.
44. **Arneux, A., Bellan-Santini, D., Monod, J. L., and Tatoulian, J.,** Polluants minéraux et organiques dans les sédiments prélevés entre la Provence et la Corse (Mission BIOMEDE 1), in *Vème Journees d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1981, 423.
45. **Risebrough, R. W., De Lappe, B. W., Walker, W., II, Simonett, B. R. T., Grimalt, J., Albaiges, J., Garcia, J. A., Ballester, A., and Marino, M.,** Application of the mussel watch concept in studies of the distribution of hydrocarbons in the coastal zone of the Ebro delta. *Mar. Pollut. Bull.*, 14, 181, 1983.
46. **Beluja, G., Franco, J. M., and Morado, M. A.,** Contaminacion del medio por plaguicidas organoclorados. VI. Residuos de insecticidas y PCB en especies marinas, significado ecologico y su relation con la contaminacion litoral nacional. *Invest. Pesq.*, 37, 593, 1973.
47. **Marchand, M., Van, D., and Duursma, E. K.,** Levels of PCBs and DDTs in mussels from the N.W. Mediterranean. *Mar. Pollut. Bull.*, 7, 65, 1976.
48. **De Lappe, B. W., Risebrough, R. W., Mendola, J. T., Bowes, G. W., and Monod, J. L.,** Distribution of polychlorinated biphenyls on the Mediterranean coast of France, in *Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1972, 43.
49. **Contardi, V., Capelli, R., Pellizzari, T., and Zanicchi, G.,** PCBs and chlorinated pesticides in organisms from the Ligurian sea. *Mar. Pollut. Bull.*, 10, 307, 1979.
50. **Kilikidis, S. D., Psomas, J. E., Kamaritsous, A. P., and Panetsos, A. G.,** Monitoring of DDT, PCBs and other chlorinated hydrocarbons in marine organisms, in *Vème Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1981, 301.
51. **Bolognari, A., Ferro, R., Fossato, V. U., Pistolli, M., Rumossi, A., and Viviani, R.,** Monitorage de l'état de la pollution marine le long des côtes Italiennes avec l'emploi des indicateurs biologiques, in *IVème Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1979, 667.
52. **Fossato, V. U. and Crubeladdu, L.,** Chlorinated hydrocarbons in organisms from the Italian coast of the northern Adriatic Sea, in *Vème Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1981, 169.
53. **Nasnasky, B., Picer, N., Picer, M., and Ahel, M.,** Monitoring of chlorinated hydrocarbons in biota of the north and middle Adriatic coastal waters, in *IVème Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1979, 129.
54. **Dujmov, J., Vucetic, T., Picer, M., and Picer, N.,** Some results of the monitoring of chlorinated hydrocarbons in organisms from the Central Adriatic, in *IVème Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1979, 137.
55. **Amico, V., Impellitteri, G., Orlando, G., Piattelli, M., Scinto, S., and Triegali, C.,** Levels of chlorinated hydrocarbons in marine animals from the central Mediterranean. *Mar. Pollut. Bull.*, 10, 282, 1979.
56. **Fowler, S. W. and Villeneuve, J. P.,** Unpublished results.
57. **FAO/UNEP, MED-POL III:** baseline studies and monitoring of DDT, PCBs and other chlorinated hydrocarbons in marine organisms (FAO/GFCM/UNEP), in press, 1986.
58. **ICES,** Report of working group for the international study of the pollution of the North Sea and its effects on living resources and their exploitation, Coop. Res. Rep. No. 39, ICES, Denmark, 1974.
59. **ICES,** the ICES co-ordinated monitoring programme in the North Sea, 1974, Coop. Res. Rep. No. 58, ICES, Denmark, 1977a.
60. **ICES,** The ICES co-ordinated monitoring programmes 1975 and 1976, Coop. Res. Rep. No. 72, ICES, Denmark, 1977b.
61. **Goldberg, E. D., Bowen, V. T., Farrington, J. W., Harvey, G., Martin, J. H., Parker, P. L., Risebrough, R. W., Robertson, W., Schneider, E., and Gamble, E.,** The Mussel Watch, *Environ. Conserv.*, 5, 101, 1978.
62. **Revelante, N. and Gilmartin, M.,** DDT, related compounds and PCB in tissues of 19 species of northern Adriatic commercial fishes, *Invest. Pesq.*, 39, 491, 1975.
63. **Castelli, M. G., Martelli, G. P., Spagone, C., Cappellini, L., and Fanelli, R.,** Quantitative determination of polychlorinated biphenyls (PCBs) in marine organisms analysed by high resolution gas chromatography selected ion monitoring, *Chemosphere*, 12, 291, 1983.
64. **Vountsinou-Talladouri, F. and Sotiropoulos, J.,** Influence of metropolitan waste on the concentration of chlorinated hydrocarbons and metals in striped mullet, *Mar. Pollut. Bull.*, 13, 266, 1982.
65. **Stamatelis, J. and Gabrielides, G. P.,** Observations on the concentration levels of chlorinated hydrocarbons in a Mediterranean fish, *Mar. Pollut. Bull.*, 10, 109, 1979.

MONS 006393

66. Viviani, R., Criscuolo, G., Cortesi, P., and Carpenè, E., Résidus de polychlorobiphenyls (PCB) et de pesticides chlorés dans les poissons et les oiseaux du delta du Po. *Rev. Int. Oceanogr. Med.*, 33/36, 79, 1974.
67. Viviani, R., Criscuolo, G., Petruzzi, V., and Cortesi, P., Residui di pesticidi clorurati e di bifenili policlorurati nei clupeiformi Adriatico. in *Atti 3° Coll. Int. Oceanogr. Med. Messina*, 1973, 607.
68. Alzieu, C., Présence de diphényipolychlorés chez certains poissons de l'Atlantique et de la Méditerranée. *Sci. Peche*, 258, 1, 1976.
69. Fowler, S. W. and Elder, D. L., Unpublished results.
70. Elder, D. L. and Fowler, S. W., Polychlorinated biphenyls: penetration into the deep ocean by zooplankton fecal pellet transport. *Science*, 197, 459, 1977.
71. Fowler, S. W. and Elder, D. L., PCB and DDT residues in a Mediterranean pelagic food chain. *Bull. Environ. Contam. Toxicol.*, 19, 244, 1978.
72. Cattani, O., Cersi, M. G., Criscuolo, G., and Serrazanetti, G. P., Chlorinated hydrocarbon residues in zooplankton from the northern Adriatic sea. in *Ves Journées D'Etudes Pollutions*. C.I.E.S.M., Monaco, 1981, 353.
73. Burns, K. A., Villeneuve, J. P., and Fowler, S. W., Fluxes and residence times of hydrocarbons in the coastal Mediterranean: how important are the biota?. *Estuar. Coast. Shelf Sci.*, 20, 313, 1985.
74. Fowler, S. W., Small, L. F., Elder, D. L., Unlu, Y., and La Rosa, J., The role of zooplankton fecal pellets in transporting PCBs from the upper mixed layer to the benthos, in *IVe Journées d'Etudes Pollutions*. C.I.E.S.M., Monaco, 1979, 289.
75. Amico, V., Oriente, G., Piattelli, M., and Tringali, C., Concentrations of PCBs, BHCs and DDTs residues in seaweeds of the east coast of Sicily. *Mar. Pollut. Bull.*, 10, 177, 1979.
76. Bourne, W. R. P. and Bogan, J. A., Organochlorines in Mediterranean seabirds. *Environ. Conserv.*, 7, 277, 1980.
77. Focardi, S., Leonzio, C., and Renzoni, A., Idrocarburi clorurati e metalli in tracce in uova di *Larus argentatus michahellis* Naumann e *Sterna albifrons* Pallas. in *Atti Primo Congr. Naz. Soc. Ital. Ecol.*, 1981, 411.
78. Renzoni, A., Focardi, S., Leonzio, C., Fossi, C., Baldrighini, P., and Monti Demartis, A., Contaminants of resident and migratory birds of the Mediterranean sea, in VII Int. Symp. Chemistry of the Mediterranean, Primosten, Yugoslavia, May, 6, 1982.
79. Bourne, W. R. P. and Bogan, J. A., Estimations of chlorinated hydrocarbons in marine birds, in *Marine Pollution*, Johnston, R., Ed., Academic Press, New York, 1976, 482.
80. Bijleveld, M. F. I. J., Goeldlin, P., and Mayol, J., Persistent pollutants in Audouin's Gull (*Larus audouini*) in the western Mediterranean: a case-study with wide implications?, *Environ. Conserv.*, 6, 139, 1979.
81. Mendoza, J. T., Risebrough, R. W., and Blondel, J., Contamination de l'avifaune Camarguaise par des résidus organochlorés. *Environ. Pollut.*, 13, 21, 1977.
82. Fowler, S. W. and Elder, D. L., Chlorinated hydrocarbons in pelagic organisms from the open Mediterranean sea. *Mar. Environ. Res.*, 4, 87, 1980.
83. Alzieu, C. and Dugay, R., Teneurs en composes organochlorés chez les Cetaces et Pinnipedes frequentent les cotes francaises. *Oceanol. Acta*, 2, 107, 1979.
84. Osterroht, C. and Smetacek, V., Vertical transport of chlorinated hydrocarbons by sedimentation of particulate matter in the Kiel Bight. *Mar. Ecol. Progr. Ser.*, 2, 27, 1980.
85. OECD. Report on the Implementation by Member Countries of the Decision by the Council on the Protection of the Environment by Control of Polychlorinated Biphenyls, OECD, Paris, 1982.
86. Ravid, R., Ben-Yosef, J., and Herzberg, H., PCBs, DDTs and other chlorinated hydrocarbons in marine organisms from the Mediterranean coast of Israel. *Mar. Pollut. Bull.*, 16, 35, 1985.
87. Risebrough, R. W., De Lappe, B. W., and Walker, W., II, *Transfer* of higher molecular weight chlorinated hydrocarbons to the marine environment. in *Marine Pollutant Transfer*, Windom, H. L. and Duce, R. A., Eds., Lexington Books, Toronto, 1976, 261.
88. Risebrough, R. W., Personal communication, 1985.

MONS 006394

Chapter 9

CASE STUDY: THE AUSTRALIAN ECOSYSTEM

Bruce J. Richardson, Robert H. Smillie, and John S. Waid

TABLE OF CONTENTS

I. Introduction 242

II. Australian Usage of PCBs 242

III. PCBs in the Australian Environment 244
- A. New South Wales (NSW) 244
- B. Queensland 246
- C. Victoria 247
- D. Other Australian Data 256

IV. PCBs and the Australian Population 257

V. Disposal of PCBs in Australia 259

VI. Acknowledgments 260

References 261

MONS 006395

I. INTRODUCTION

Although polychlorinated biphenyls (PCBs) have been used fairly extensively in Australia, little attention has been paid to them as potentially hazardous environmental pollutants. The available evidence suggests that factors such as the size of the Australian continent, its geographic isolation, low population, and lack of major industries have resulted in isolated pockets of contamination associated particularly with urban centers. However, few detailed studies have been undertaken, and at present it is extremely difficult to assess the influence of PCBs on the Australian ecosystem.

II. AUSTRALIAN USAGE OF PCBs

No PCBs have been manufactured in Australia. Since 1975, all importations have been subject to restrictions imposed by the Department of Police and Customs.[1] In line with OECD recommendations,[2] the importation of PCBs and polychlorinated terphenyls (PCTs) is prohibited, except with the consent of the Minister for Customs, and then only for the following purposes:

1. "Dielectric fluids for transformers or large power-factor correction capacitors
2. Heat transfer fluid other than in installations for processing of food, drugs, feed and veterinary products
3. Hydraulic fluids in mining equipment"

The Australian government has adopted a "cradle to grave" policy in its attitude toward PCBs, ensuring that conditions must be met by importers with regard to the custody, use, and disposal of PCBs. Specifically, these regulations require that:

1. "The goods (PCBs) will not be used for any purpose other than that for which approval has been given
2. Records for receipt, use and/or disposal be kept in an approved manner
3. Evidence of use and/or disposal in respect of each shipment will be furnished, supported by statutory declaration"

PCBs imported in bulk must be in suitably labeled drums. PCB imports to Australia are also identified by modifications to the Customs and International Tariff Regulations, using a special tariff code for PCBs and PCTs.[3]

Essentially, the above regulations limit the use of PCBs in Australia to closed-system operations. However, only the use in transformers and large capacitors can be considered as "controllable closed systems". Heat transfer uses are uncontrollable closed systems, but Australian regulations at least specify that contact with most human food chains is unlikely. The use of PCBs as hydraulic fluids in mining operations, however, could be a difficult area to assess in this light: PCBs may escape, and this could bring them into contact with sensitive organisms in the environment, especially in the marine situation.

Table 1 indicates the amounts of PCBs imported by and consumed in manufactured products in Australia for the period 1971 to 1980 (the only figures available at the time of this writing). This usage is for bulk PCBs only, and contains no estimates of the amount of PCBs imported as an integral part of manufactured goods. The amounts of PCBs used in Australia have declined dramatically since 1975, due not only to import and handling restrictions, but also to the use of other compounds which may be substituted for PCBs in many applications. PCBs were put to a wide range of uses in Australia, including dissipative uses, but since 1975, usage has been limited almost exclusively to the electrical industry.

MONS 006396

Table 1
USAGE OF PCBs (T) IN AUSTRALIA AND NEW ZEALAND, 1971 TO 1980[a,c]

Year	Import/ consumption	Total consumption in manufactured products	Transformers	Capacitors (large/small)	Other uses[c]
1971					
Aust.	400	400	[d]	[d]	[d]
1973					
Aust.	160	NA	NB	NB	NB
N.Z.	20.5	22	7	10/0	14.7[e]
1974					
Aust.	NR	NR	NR	NR	NR
N.Z.	NA	NA	NB[f]	NA	0
1975					
Aust.	300	300	100	50/150	0[g]
N.Z.	NA	NA	0	NA	0
1976					
Aust.	60	60	7	34/19	0[g]
N.Z.	NA	NA	0	NA[h]	0
1977					
Aust.	13.5	14	0	13.5/0[i]	0
N.Z.	12.0	11.95	0	3.95/0	8[e]
1978					
Aust.	32.5	32.5	[b]	[b]	0
N.Z.	4.3	4.32	0	4.32/0	0
1979					
Aust.	NR	NR	NR	NR	NR
N.Z.	1.8	1.8	0	1.8/0	0
1980					
Aust.	0	0	0	0	0
N.Z.	0.2	0.2	0	0.2/0	0

Notes: NA = information not available; NB = no breakdown of statistics; NR = no report supplied to OECD.

[a] 87.5% used in dielectrics, heat transfer, hydraulic liquids, cutting oils and pumps; 12.5% used in paint, varnishes, inks, adhesives, sealing pastes, plasticizers, and paper.
[b] 11 and 3.7 t in plasticizers and vacuum pumps, respectively.
[c] The total amount of PCBs in transformers in N.Z. is 115 t, all of which were purchased prior to 1974.
[d] A small quantity used in microscope oils.
[e] The total amount of PCBs calculated to be present in capacitors throughout N.Z. is 28 t. Of these, 16 t were purchased prior to 1974 and 12 t since 1974.
[f] Manufacture of small capacitors ceased in Australia in 1976.
[g] 8 t used as plasticizers.
[h] Total consumption in transformers and larger capacitors 32.5 t.
[i] Heat transfer, hydraulic equipment, plasticizers, lubricants and cutting oils, vacuum pumps.

and then only when the risk of fire has been high. Table 1 also provides figures for the New Zealand usage of PCBs by way of comparison; it is interesting to note that the substances were still used as plasticizers in that country as late as 1977.

Most of the PCBs imported into Australia have been Aroclors® and Pyroclors® (Monsanto, U.S.), Phenoclor® and Pyralene® (Prodelec, France), Pyranol® (General Electric, U.S.), Clophen® (Bayer, Germany) and Clorestil® (a polychlorinated terphenyl produced by Caffaro, Italy). Although PCBs of all types have been used in the past, it would appear that in recent

MONS 006397

years there has been a trend toward the exclusive use of lower chlorinated varieties, such as Aroclor® 1016 and Pyroclor 5.[3-7]

In the past few years, there have been two importers of PCBs into Australia, Monsanto and May and Baker, who handle Prodelec's products. Monsanto has indicated that it stopped sales of PCBs from October 31, 1977.[8] According to a report by the NSW Metropolitan Waste Disposal Authority,[8] May and Baker were supplying only one customer in that state, who used 20 t/year from 1975 to 1977 in the production of capacitors. The Authority believes that customers requiring capacitors and transformers may import them from other states, or from abroad, but had no idea of the extent to which PCBs were imported in this fashion.

It would appear that PCBs have been used in all states in Australia, and certainly goods containing PCBs have been distributed throughout the country.[3] Apart from the manufacture of large transformers and capacitors, small capacitors containing PCBs have also been manufactured, for use in association with fluorescent lights, small electric motors, and compressors, such as the types used in refrigerators and air conditioners. Some electrical goods containing PCBs (e.g., transformers) have been exported to countries such as New Zealand and Vietnam.

III. PCBs IN THE AUSTRALIAN ENVIRONMENT

In 1974, the Australian Environment Council commissioned a major report on PCBs in Australia, the McMahon Report.[3] This document highlights the paucity of research into PCBs in the Australian environment up to that time. Information from Queensland and Victoria provided the only absolute values for PCB concentrations in waters, soils, and sediments; although there was some information on the amount of PCBs in biota, the evidence was fragmentary, making an overall assessment of environmental contamination impossible. McMahon indicated that many government and university laboratories reported finding PCBs in samples such as fish and birds undergoing analysis for other purposes (e.g., for pesticide residues), but although attempts were generally made to identify PCBs, the amounts were not generally measured. In many cases, only small numbers of individuals were analyzed.

The McMahon Report recommended that more comprehensive information should be gathered on the amount of PCBs in the Australian environment, and, since 1975, much more work has been performed.[3] By and large, this confirms a pattern of PCB contamination similar to that occurring in the Northern Hemisphere, in that highest concentrations have been recorded in the vicinity of large urban centers. There are still barely enough data, however, to make a thorough assessment of PCB pollution in Australia: to date, little sampling over time has been carried out, and there is still a lack of knowledge of "baseline" concentrations in areas of Australia remote from the influences of man. In order to place some degree of perspective on PCB contamination in the Australian ecosystem, the available evidence is summarized below on a state-by-state basis.

A. New South Wales (NSW)

McMahon provides details of work carried out by the two divisions of the Health Commission of NSW (Division of Analytical Laboratories and Division of Occupational Health and Radiation Control) prior to 1975, which indicates the presence of PCBs in local fish.[3] Data presentation makes interpretation difficult, but relatively large quantities of Aroclor® 1242 compounds were found in bream from Towra Bay, and mullet from Port Jackson (Table 2). Smaller quantities were detected in mussels and oysters from Quilbray Bay.

The Health Commission also undertook analyses of yogurt sold in plastic containers in 1973. In seven samples, they detected only very low concentrations of Aroclor® 1254 (mean 5 ng/g; range 2 to 12 ng/g). Aroclor® 1254 was also detected in samples of eggs during 1973 (mean 9 ng/g; range 7 to 10 ng/g), and in samples of dairy feeds (grass, pollard oatmeal, sunflower pods, and meatmeal containing 10, 12, 45, and 8 ng Aroclor® 1254/g, respectively).

MONS 006398

Table 2
QUANTITIES OF PCBs (AROCLOR® 1242-TYPE) IN FISH FROM THE SYDNEY AREA, PRE-1975[a]

Sample type	No. of samples and origin	Aroclor® 1242 (ng/g)[b] relative retention time to Aldrin® 1.00 mean[c] and (range)					
		0.69	1.31	1.47	1.96	2.34	2.62
Mussels	2. Quibray Bay	nd	22.5 (22—23)	nd	nd	nd	nd
Oysters	3. Quibray Bay, Towra Bay, mouth of Woolooware Bay	14 (7—22)	13 (8—24)	nd	nd	nd	nd
Blackfish	3. Sewage outfall, Malabar	147 (49—226)	145 (nd—434)	nd	nd	nd	nd
Bream	6. Towra Bay	3235 (nd—19,400)	1678 (400—3,570)	4945 (452—15,800)	5248 (525—16,300)	2161 (110—8,240)	nd
Mullet	3. Upper Clarence River	2 (nd—5)	3 (nd—8)	5 (nd—15)	3 (nd—9)	nd	nd
Mullet	3. Lower Clarence River	nd	nd	nd	nd	nd	nd
Mullet	2. Port Jackson	86 (35—136)	107 (36—177)	124 (37—210)	120 (37—202)	nd	nd

Note: nd = not detected (no detection limits provided).

[a] No indication given as to wet or dry weight.
[b] Mean calculated using nd = 0.

The results of fish samples detailed above reflect the difficulties experienced in measuring PCBs at that time. The first results of fish analyses from NSW which can be directly compared with international values were presented by Woollard and Settle.[9] Their investigation began following the discovery of PCBs accumulating in captive water rats. The most likely source of this contamination was thought to be mullet *(Mugil cephalus)* fed to the rats. The fish (obtained from the Sydney fish markets) were from three commercial fishing grounds in NSW; Clarence River, Wallis Lake, and waterways around metropolitan Sydney. Additional samples were also obtained from 13 localities in waters adjacent to Sydney.

No PCBs were detected in mullet obtained from Wallis Lake or the Clarence River (both some distance from Sydney). The fish caught in Sydney waters contained 0.02 to 1.0 μg/g PCBs (Aroclor® 1254 type). Of the 13 specimens obtained from Botany Bay and Port Jackson, 10 contained PCBs measured as Aroclor® 1254, and 6 of these contained PCBs measured as Aroclor® 1242 (Table 3). Values for PCB concentrations (wet weight basis) lay mostly in the range 0.25 to 3.1 μg/g; however, three of the fish contained PCBs in excess of the U.S. FDA recommended limit of 5 μg/g. Five of the 13 were above the new limit proposed by the U.S. FDA at the time (i.e., 2 μg/g).

More recently, the NSW State Pollution Control Commission has reviewed the PCB content of fish from Botany Bay.[10] Their results (Table 4) show considerably lower PCB concentrations in mullet than did Woollard and Settle.[9] A correlation between PCB and lipid content of the fish was noted. Highest concentrations (up to 0.4 μg Aroclors® 1242 and 1254/g) were noted in fish with the highest fat content (mullet and bream). The Commission attributed the lower concentrations of PCBs in comparison with those observed in earlier studies to a number of factors; these include the implementation of the Clean Waters Act,

MONS 006399

Table 3
CONCENTRATIONS OF PCBs (μg/g WET WEIGHT) IN MULLET FROM BOTANY BAY AND PORT JACKSON[a]

Locality	PCB concentration		
	Aroclor® 1254	Aroclor® 1242	Total
Port Jackson			
Hen and Chicken Bay	0.25	N.D.	0.25
Leichardt Bay	1.1	4.1	5.2
Burns Bay, Lane Cove River	0.23	N.D.	0.23
Snapper Island, Parramatta River	N.D.	N.D.	N.D.
Clifton Gardens, Chowder Bay	0.46	1.9	2.36
Middle Harbour	0.57	N.D.	0.57
Vaucluse Bay	N.D.	N.D.	N.D.
Botany Bay			
Quiley Bay	0.74	1.0	1.74
Kogarah Bay	1.6	N.D.	1.6
Georges River, Tasman Pt. Bridge	0.75	5.3	6.05
Woolooware Bay	0.77.	5.0	5.77
Towra Point	N.D.	N.D.	N.D.
Brighton Beach, near Baths	1.1	3.1	4.2

Note: N.D. = not detected (detection limit = 10 ng/g).

which progressively eliminated industrial discharges into local waterways; a combination of declining usage and greater care in the use and disposal of PCBs; and improvements in analytical techniques for PCBs.

B. Queensland

Within the metropolitan area of Brisbane (the capital city of Queensland), relatively high concentrations of PCBs have been encountered in a number of samples of waters, sediments, soils, and biota. McMahon reports results of PCB analyses conducted by the Water Quality Council of Queensland in three areas where concentrations of PCBs were significant (Table 5).[3] Details of other PCB analyses undertaken by the Water Quality Council during the years 1976 to 1984 are provided in Table 6.[12-20]

Shaw and Connell[11,21] have analyzed waters, sediments, and biota from the Brisbane River Estuary (Tables 5 and 7). They found PCBs in all species investigated, but no correlation was evident between total PCB concentrations on either wet or dry weight bases and trophic index. Although this suggested that biomagnification was not an important mechanism of PCB accumulation by most species, the PCB content of birds such as silver gulls and pelicans (which had among the highest trophic indices investigated) indicated a dependence upon food sources. Linear relationships were found between the lipid weight PCB concentrations in six sets of two invertebrate benthic species collected from different areas of the Brisbane River (the polychaete *Capitella capitata* and the crab *Sesarma erythrodactyla*). Shaw and Connell[21] believe, on the basis of these data, that the surrounding microhabitat of such organisms may provide a major influence upon PCB accumulation, irrespective of the route of PCB entry.

There is a sharp contrast between the relatively high PCB concentrations reported from Brisbane and other Queensland results. Olafson[22] surveyed corals, fish, and molluscs from 20 locations on the Great Barrier Reef in 1976 and 1977 but did not detect PCBs at all (detection limit 10 ng/g).[23] In contrast, Smillie and Waid[24] detected PCBs in all biota they sampled from the reef and the Gulf of Carpenteria, including sharks, coral trout, sea cucumbers, small fish (*Lutjanus* spp.), clams, soft corals, and one dugong. However, the

MONS 006400

Table 4
PCBs IN FISH AND SHELLFISH FROM PORT JACKSON, NSW[19]

Sample (no. of fish or homogenates analysed)	Date	Mean (range) of total PCBs (Aroclor® 1242 + 1254) µg/g wet weight	% Fat content
Oysters (2)	1973	8.9 (7.2—10.6)	
Oysters (7)	1977	0.08 (0.01—0.28)	
Oysters (5)	1978	tr (nd—tr)	0.06
Mussels (2)	1973	19.0 (11.6—26.3)	
King prawns (2)	1978	0.01	0.03
Crab (Blue Swimmers) (2)	1978	0.02 (tr—0.04)	0.11
Bream (5)	1974	7.9 (0.8—30.4)	
Bream (7)	1978	0.4 (0.01—0.9)	1.05
Tarwhine (2)	1974	4.5 (1.2—7.9)	
Blackfish (7)	1978	0.05 (tr—0.21)	0.42
Leatherjacket (6)	1978	0.01 (tr—0.02)	0.03
Flathead (5)	1978	0.01 (0.01—0.02)	0.05
Mullet (9)	1978	0.4 (0.1—0.8)	0.79
Trevally (1)	1978	0.1	0.66
Estuary perch (2)	1978	0.3 (0.2—0.3)	0.17
Flounder (1)	1978	0.2	0.34

Note: nd = not detected (detection limit = 0.01 µg/g); tr = trace (<0.01 µg/g).

concentrations encountered (Table 8) were typical of those from pristine habitats in other parts of the world, and indicated the low level of PCB contamination in areas of Queensland distant from large population and industrial centers.

C. Victoria

Up until the mid-1970s, little work had been done to detect PCBs in soils, waters, sediments, and biota in Victoria. McMahon[3] reports the analyses of waters and sediments from 17 streams in Westernport Bay, and indicates that no PCBs were found in any samples for the period February 1973 to May 1974. In a report by Dale and Pooley[25] on the same streams for the period May 1973 to May 1976, two streams showed positive results; in each case, detection above the limits of 100 ng/ℓ occurred only once in 11 samples taken from Toomuc Creek (100 ng/ℓ) and 13 samples from Watsons Creek (200 ng/ℓ). No follow-up work has been done on any of these sites.

Until 1978, there were few reports of PCBs in Victorian biota. McMahon[3] quotes from a report entitled "Polychlorinated Biphenyls (PCBs)" produced by the Victorian Environ-

MONS 006401

Table 5
CONCENTRATIONS OF PCBs IN QUEENSLAND WATERS, SEDIMENTS, AND SOILS[4,8]

Sample origin	Sample type	n	PCB conc. (μg/g wet weight)	Ref.
Water Quality Council				5
Plant using PCBs	Water	35	nd	
	Sediment	35	nd—250	
Drum wash plant	Water	25	nd	
	Sediment	25	nd—35,000	
Refuse tip	Water	43	nd	
	Sediment	43	nd—500	
Brisbane River				
Estuary	Water	8	nd—0.05[a]	11
	Sediment	8	nd—0.058	

Note: n = number of samples, nd = not detected (no detection limits provided).

[a] Results expressed as μg/ℓ.

Table 6
ANALYSES FOR PCBs IN QUEENSLAND WATERS AND SEDIMENTS, 1976 TO 1984[12-20]

Year	Total no. of sites	Total no. of analyses	Total no. of positive results	Positive site identity[a]	Maximum conc.[b]
1976—1977					
Waters	30	145	1	Bulimba Creek Estuary (1/2)	1.0
Sediments	37	183	8	Bulimba Creek Estuary (1/2)	300
				Norman Creek Estuary (5/10)	90
				Rocky Waterholes Creek, Brisbane (1/4)	2000
				Stable Swamp Creek, Brisbane (1/3)	16
1977—1978					
Waters	32	268	2	Cabbage Tree Creek, Sandgate (1/8)	1
				Oxley Creek, Brisbane (1/16)	2
Sediments	30	251	15	Brisbane River Estuary (1/19)	50
				Cabbage Tree Creek, Sandgate (2/8)	10
				Norman Creek Estuary (7/8)	200
				Oxley Creek, Brisbane (1/9)	10
				Rocky Waterholes Creek, Brisbane (3/3)	3800
				Stable Swamp Creek, Brisbane (1/3)	230
1978—1979					
Waters	29	231	1	Brisbane River Estuary (1/6)	0.02
Sediments	31	278	36	Blunder Creek (3/12)	20
				Breakfast Creek and Enoggera Creek (2/12)	25
				Brunner River (2/12)	5
				Brisbane River Estuary (6/16)	60
				Bulimba Creek Estuary (3/14)	350
				Cabbage Tree Creek, Sandgate (1/6)	10
				Moolabin Creek, Brisbane (3/4)	25
				Norman Creek Estuary (5/9)	200
				Oxley Creek, Brisbane (3/4)	40
				Rocky Waterholes Creek, Brisbane (4/4)	300
				Stable Swamp Creek, Brisbane (3/4)	25
				Tallebudgera Creek Estuary (1/16)	100
1979—1980					
Waters	29	239	1	Rocky Waterholes Creek, Brisbane (1/5)	0.25

MONS 006402

Table 6 (continued)
ANALYSES FOR PCBs IN QUEENSLAND WATERS AND SEDIMENTS, 1976 TO 1984[12-20]

Year	Total no. of sites	Total no. of analyses	Total no. of positive results	Positive site identity[a]	Maximum conc.[b]
Sediments	26	207	25	Blunder Creek, Brisbane (2/6)	110
				Breakfast Creek and Enoggera Creek (4/10)	90
				Brisbane River Estuary (2/16)	20
				Bulimba Creek Estuary (4/10)	180
				Cabbage Tree Creek, Sandgate (1/8)	5
				Norman Creek Estuary (3/6)	178
				Oxley Creek, Brisbane (2/7)	50
				Rocky Waterholes Creek, Brisbane (5/5)	335
				Stable Swamp Creek, Brisbane (5/5)	21
1980—1981					
Waters	28	275	1	Rocky Waterholes Creek, Brisbane (1/3)	0.27
Sediments	25	169	13	Blunder Creek, Brisbane (3/9)	106
				Bulimba Creek Estuary (1/6)	8.7
				Moolabin Creek, Brisbane (1/3)	7
				Rocky Waterholes Creek, Brisbane (3/3)	240
				South Pine River (1/6)	2.5
				Stable Swamp Creek, Brisbane (2/3)	35
1981—1982					
Waters	29	310	0		
Sediments	32	323	16	Albany Creek (1/3)	20
				Blunder Creek, Brisbane (2/15)	20
				Brisbane River Estuary (1/60)	10
				Bulimba Creek Estuary (2/14)	10
				Moolabin Creek, Brisbane (1/4)	21
				Norman Creek Estuary (3/12)	92
				Rocky Waterholes Creek, Brisbane (5/5)	390
				Stable Swamp Creek, Brisbane (1/3)	30
1982—1983					
Waters	29	299	1	Rocky Waterholes Creek, Brisbane (1/2)	2.5
Sediments	35	337	12	Albany Creek (1/3)	50
				Blunder Creek, Brisbane (5/22)	15
				Moolabin Creek, Brisbane (1/2)	25
				Norman Creek Estuary (3/10)	6.3
				Rocky Waterholes Creek, Brisbane (2/2)	100
1983—1984					
Waters	22	227	0		
Sediments	32	163	4	Blunder Creek, Brisbane (4/5)	30

[a] No. positive results/total no. analyses at each site.
[b] µg/ℓ for waters; detection limit, 1976-1977 0.5 µg/ℓ ; 1980-1984 0.5 µg/ℓ; ng/g for sediments; detection limit, 1976-1979 1.0 ng/g; 1980-1984 5.0 ng/g.

ment Protection Authority: "Fisheries and Wildlife have not reported its presence, and the Division of Agricultural Chemistry has not detected PCBs in any stock foods, eggs, milk or soil samples". However, McMahon also states that "many organisations indicated that they often come across PCBs during routine pesticide analyses, but normally PCBs were not quantified. For example, this was the case of the Fisheries and Wildlife Division of the Victorian Ministry for Conservation. This organization indicated that PCBs most often were detected when analyzing aquatic life, and birds which fed on aquatic life (e.g., pelicans), for organochlorine pesticides. Attempts are made to identify PCBs but their concentrations are not measured".[3]

MONS 006403

Table 7
TOTAL PCB CONCENTRATIONS AND TROPHIC DATA FOR ORGANISMS[a] FROM THE BRISBANE RIVER ESTUARY

Trophic index[a]	Species and no. analyzed	Dietary components[a]	Classification[a]	Av. conc. PCBs corresponding to Aroclor® 1260 (mg/kg)	
				Wet basis	Lipid basis
1.1	Mussel, *Mytilus corscus* Gould (2)	Microalgae and detritus	Herbivore group A	0.1	23
1.2	Sea mullet, *Mugil cephalus* Linnaeus (15)	Microalgae and detritus	Herbivore group B	0.5	16
1.4	Polychaete, *Capitella capitata* Fabricius (20)	Detritus and microalgae	Omnivore group A	0.2	10
1.4	Sleepy crab, *Sesarma erythrodactyla* Hess (19)	Detritus and small animals	Omnivore group A	0.1	5
1.4	Fiddler crab, *Uca* sp. (2)	Detritus and small animals	Omnivore group A	0.2	46
1.8	Striped burrfish, *Selenanace multipunctata* Richardson (1)	Algae and small animals	Omnivore group B	0.04	4
2.5	Mud crab, *Helicograpsus haswellianus* Whitelegge (1)	Small animals, crustaceans, and small fish	Lower carnivore	0.1	38
2.5	Whiting *Sillago ciliata* Cuvier (2)	Crustaceans and polychaetes	Lower carnivore	0.5	25
2.5	Bony bream *Nematalosa come* Richardson (2)	Polychaetes	Lower carnivore	0.2	27
2.5	Oyster blenny *Petroscirtes anolius* Cuvier and Valenciennes (5)	Crustaceans, polychaetes, and small animals	Lower carnivore	0.3	15
2.8	Catfish, *Neoarius australis* Gunther (1)	Assorted animals	Lower carnivore	2.1	16
2.8	Gull, *Larus novahollandiae* Stephens (3)	Crustaceans, polychaetes, isopods, and dead fish	Lower carnivore	2.6	58
2.8	Silli *Himantopus himantopus* Linnaeus (1)	Crustaceans, polychaetes, isopods, and dead fish	Lower carnivore	0.3	9
3.2	Flathead, *Platycephalus fuscus* Cuvier and Valenciennes (1)	Crustaceans, polychaetes, and fishes	Middle carnivore	0.1	41
2.5	Pelican, *Pelecanus conspicillatus* Temminck (6)	Fishes and crustaceans	Top carnivore	8.2	170

[a] Identification confirmed by the Queensland Museum.
[b] From examination of gut contents.
[c] Developed by the method of Odum and Heald.[35]

From Shaw, G. R. and Connell, D. W., *Aust. J. Mar. Freshw. Res.*, 33, 1057, 1982. With permission.

In 1978, the Victorian Ministry for Conservation Environmental Studies Group commissioned a review on the significance of PCBs in the local environment by Richardson and Waid[36] and a survey to determine the incidence of PCBs in the Port Phillip Bay marine system.[37-39] This survey adopted a similar plan of attack to the U.S. Mussel Watch, which used mussels as indicators of various types of pollutants, including PCBs.[38] Shellfish (*Mytilus*

MONS 006404

Table 8
PCB CONCENTRATIONS IN ORGANISMS FROM THE GREAT BARRIER REEF AND THE GULF OF CARPENTARIA[38]

Species	Tissue type	Locality	n	PCB concentration (ng/g) mean and (range) Wet weight basis	Dry weight basis	PCB type identified (Aroclor®)
Lutjanus spp.	Muscle	Heron Isl.	5	10.1 (7.9—12.7)	45.2 (35.4—54.6)	1254
Epinephelus sp. (Cod)	Muscle	Heron Isl.	1	21.2	98.8	1254:1260 (1:1)
	Liver			31.2	92.7	
Plectropoma sp. (Coral Trout)	Muscle	Rib Reef	2	10.5 (9.3—14.4)	45.5 (35.0—61.1)	1254
Shark (Gray Reef and Bronze Whalers)	Muscle		13	35.8 (6.5—85.8)	135.4 (32.7—274.0)	1248:1254 (1:1)
	Liver			67.9 (21.2—160)	125.0 (32.7—274.0)	1254:1260 (1:1)
Tridacna maxima (Clams)	Whole clams	Dip Reef	4	15.5 (12—19)	78.0 (65—103)	1254
Sillago sp.	Whole fish	Gulf of Carpentaria	6	9.0 (2.9—13.0)	37.0 (16.5—54.5)	1254
Arrhamphus sp. (Garfish)	Whole fish	Gulf of Carpentaria	5	9.0 (7.2—10.0)	39.6 (32.0—44.6)	1254
Dugong	Muscle	Magnetic Isl.	1	25.5	109.3	1248:1254 (2:1)
	Liver			40.3	167.9	1254
	Blubber			15.5	17.9	1254:1260 (1:1)

Table 9
PCB CONCENTRATIONS (μg/g DRY WEIGHT) IN SEDIMENTS

Location	Conc. range (μg/g)	No. of samples	Mean conc. (μg/g)	Ref.
South Puget Sound, U.S.	<0.01—0.3	18	0.02	37
Raritan Bay, lower New York Bay, U.S.	<0.01—2.03	19	0.02	36
Bahimore Harbor, U.S.	0.05—84.2	80	0.60	42
Corio Bay				27
In-shore	0.01—0.81	9	0.28	
Offshore	<0.01—0.09	9	<0.02	
Port Phillip Bay				27
In-shore	0.02—0.39	5	0.18	
Offshore	<0.01—0.06	4	<0.02	
Edwardes Lake				43
Drain	0.28—1990	10	256.59	
Lake	<0.01—3.33	35	<0.69	
Bass Strait	<0.01	36	<0.01	44

edulis and *Haliotis* sp.) and sediment samples were collected from Port Phillip and Corio Bays, adjacent to the cities of Melbourne and Geelong, respectively, and from Bass Strait, near the opening of Port Phillip Bay. PCBs were detected in every sample of shellfish analyzed (Figures 1 and 2).

The highest concentrations were found in localities adjacent to industrial activity, particularly for in-shore Corio Bay samples. Areas of heavy shipping traffic also showed relatively

MONS 006405

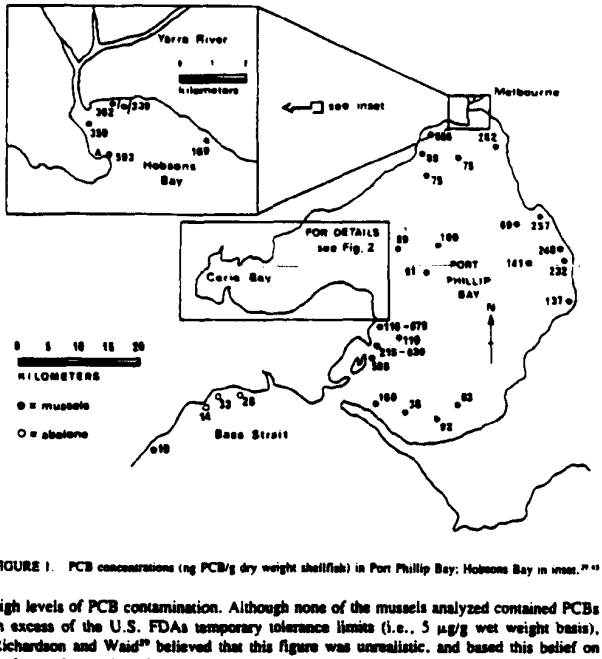


FIGURE 1. PCB concentrations (ng PCB/g dry weight shellfish) in Port Phillip Bay; Hobsons Bay in inset.[39,40]

high levels of PCB contamination. Although none of the mussels analyzed contained PCBs in excess of the U.S. FDAs temporary tolerance limits (i.e., 5 μg/g wet weight basis), Richardson and Waid[39] believed that this figure was unrealistic, and based this belief on analyses of mussels and other bivalves undertaken in contaminated regions overseas (Figure 3). For example, none of the PCB concentrations found during the Mussel Watch survey in the U.S. exceeded the tolerance limit,[39] but Richardson and Waid suggest that concentrations in excess of 600 ng/g dry weight (approximately 0.09 μg/g wet weight) were indicative of excessive pollution by PCBs. A total of six samples from Port Phillip Bay had higher concentrations than this, and a further six lay in the range 540 to 599 ng/g; this accounts for some 19% of the total samples analyzed.

The results of sediment analyses reinforced the mussel data and conformed to the patterns established in Northern Hemisphere research (Table 9). Highest concentrations were associated with areas closest to industry and high population density.

Recently, Murray and Richardson measured PCBs in mussels from two sites in Hobsons and Corio Bays (sites A, B, Figures 1 and 2, respectively).[40] Samples were collected quarterly between February 1983 and June 1984. Concentrations of PCBs in mussels from the Hobsons Bay site were similar to those recorded in 1979 by Richardson and Waid but at the Corio Bay site, concentrations had decreased in comparison with those recorded in 1979.[39] Seasonal effects were apparent at both stations (Figure 4), PCB concentrations increasing markedly during spring. The results indicate the need for continuing monitoring, particularly in areas deemed to be "hotspots" during the original 1979 work.

MONS 006406

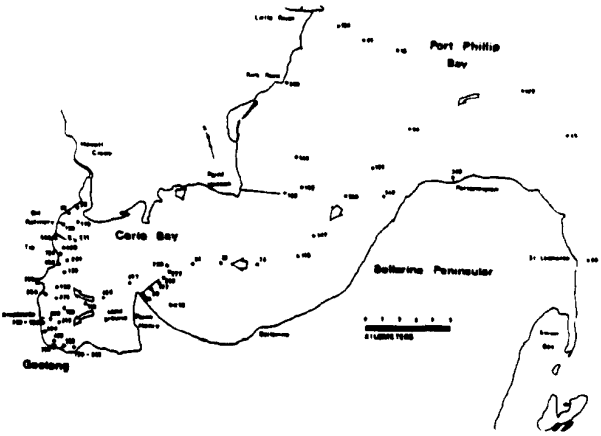


FIGURE 2. PCB concentrations (ng PCB/g dry weight shellfish) in Corio Bay.[39,40] Arrows indicate main routes taken by shipping.

Another major survey of PCB contamination in the Victorian environment has involved a small freshwater lake contaminated by an industrial accident.[42] In 1975, a scrap-metal merchant in Melbourne was responsible for the accidental discharge of a large quantity of PCB-containing dielectric fluid from a transformer into local storm-water drains. A quantity of this fluid reached Edwardes Lake, a man-made recreational reserve in the northern Melbourne suburb of Reservoir. The lake was developed from a marsh and municipal dump by damming the main tributary, Edgar Creek. The lake itself covers an area of approximately 7 ha, its depth varying from 1 to 4 m. Five major drains take water runoff from the surrounding urban and light industrial areas into the lake. Several cases of oil and solvent discharge from these drains have been reported.[46]

Clarke et al. surveyed PCB concentrations in the locality five years after the spillage.[42] Sediments were used as an indicator of contamination, to establish the distribution patterns of PCBs. The possibility of biological indicators providing this information in the lake was not considered feasible; no organism could be identified which fulfilled the necessary criteria in all the sampling stations examined. The use of sediment analyses, however, provided a direct, comparable link with the values recorded in the Port Phillip Bay and Bass Strait situations (Table 9).

The results of the survey (Figure 5) indicated the presence of considerable concentrations of PCBs in the lake 5 years after the spillage; indeed, some of the PCB concentrations encountered were among the highest reported internationally (Table 9). No comparable data were available on PCB concentrations in the lake sediments, either at the time of, or immediately following the accident. Clarke et al.[42] concluded that the movement of PCBs from the spillage site has been brought about largely in conjunction with oils and particulate matter, and that most of the spilled material, apart from that in soil at the spillage site itself had remained within the drainage system and the lake.[45]

MONS 006407

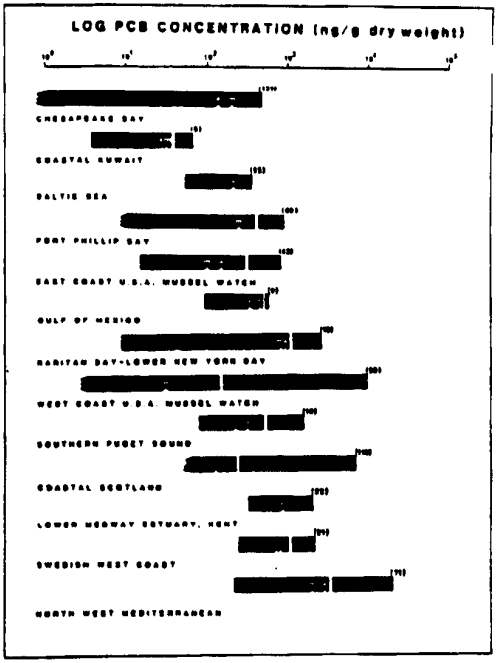


FIGURE 3. PCB concentrations (ng/g dry weight) in mussels (*Mytilus edulis*) and other marine bivalves from Chesapeake Bay,[39] coastal Kuwait,[32] Baltic Sea,[33-35] Port Phillip Bay,[36] U.S. Mussel Watch,[20] Gulf of Mexico,[37] Raritan Bay — lower New York Bay,[38] southern Puget Sound,[39] Scottish coastal waters,[40] lower Medway Estuary, Kent, England,[41] northern and central Swedish west coast,[42] and northwest Mediterranean.[43] Where appropriate, results have been calculated on a dry weight basis assuming the water content of bivalves to be 85%. Key: a = arithmetic mean, m = median, gap = upper quartile (lower limit), () = no. of samples.

During 1982 and 1983, core samples of sediments to a depth of at least 0.5 m were removed from selected sites in the lake (A to D, Figure 5), subsampled corresponding to depths 0 to 10, 10 to 30, and 30 to 50 cm, and analyzed for PCBs.[47] The results of these analyses (Table 10) showed that the surficial sediments (depth range 0 to 10 cm) contained PCB concentrations very similar to those reported by Clarke et al.[43] Near the mouth of the drain (core sample site A), fine silty sediment was found only to a depth of approximately 10 cm. Below this layer, the clay which was withdrawn by the sampler contained low concentrations of PCBs. It would appear likely that the clay represents the "base layer" of the lake in this region, and the silt overlaying it had been deposited since the PCB spillage.

MONS 006408

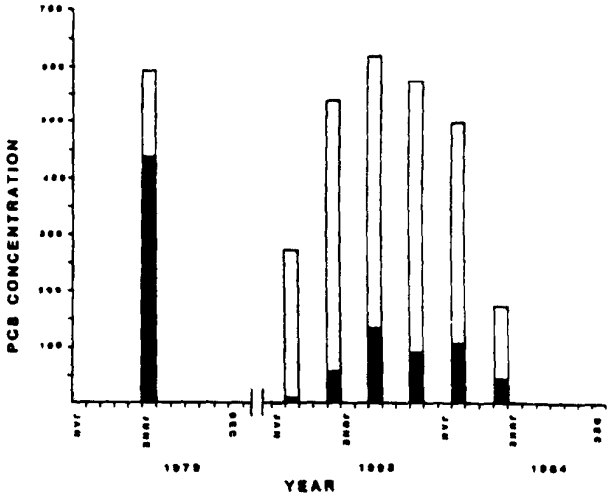


FIGURE 4. Concentrations of PCBs (ng PCB/g dry weight) in mussel samples from (A) Hobsons Bay (open histograms) and (B) Corio Bay (closed histograms).[48] See Figures 1 and 2 for sampling sites A and B, respectively.

In the cores toward the center of the lake (B and C), no clay was removed by the sampler. PCBs were found in higher concentrations in the deeper sediments of these cores (i.e., 10 to 30 and 30 to 50 cm segments) in comparison with surficial sediments. This is probably representative of the history of the spillage; large amounts of PCBs were probably deposited in the "older" (deeper) sediments in the period immediately following the spillage. The results suggest that the spillage may have occurred when the 30 to 50 cm sediments were deposited. However, detailed (centimeter by centimeter) analyses of the cores would be needed to confirm this hypothesis.

A similar pattern was evident in core D, although PCB concentrations at this site were considerably lower than in the center of the lake. The results of all four cores suggest that the surficial sediment areas designated by Clarke et al.[45] also reflected the relative amounts of PCBs in underlying sediments. The fact that lower concentrations of PCBs were found in the top layer of sediment (0 to 10 cm) as compared with the deeper (older) sediments suggests that the input of PCBs to the lake has diminished over the years since the spillage. It is likely that this phenomenon will continue, and could be assisted by the removal of highly contaminated soils near the spillage site.

Smillie and Waid determined PCB concentrations in algae from Edwardes Lake.[46] At the drain outfall, (site E, Figure 5) concentrations were highest (2.80 μg/g dry weight). Samples taken downstream of the outfall (sites F to K, Figure 5) showed lower average values (average = 0.26 μg/g dry weight; six samples); above the outfall (sites L to O, Figure 5), concentrations were lowest (average = 0.17 μg/g dry weight; four samples).

Apart from the major surveys described above, there are some figures available for the

MONS 006409

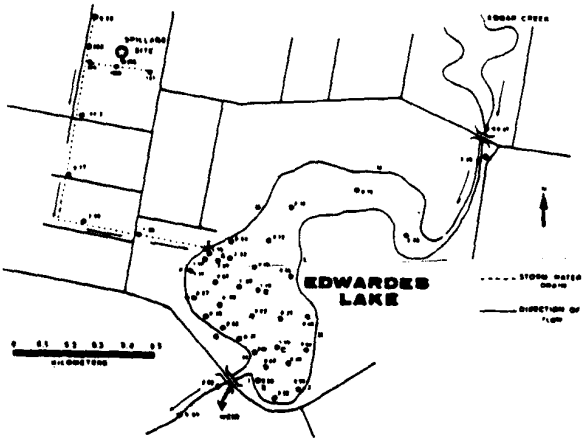


FIGURE 5. Sampling stations and PCB concentrations (ng PCBs/g dry weight sediments) in drainage system and Edwardes Lake.[47] Sites A to O represent sampling sites for core samples and algal samples (see text for explanation).

Table 10
RESULTS OF EDWARDES LAKE SEDIMENT ANALYSES[47]

	Core*			
Depth (cm)	A	B	C	D
0—10	2.8	1.1	1.2	0.5
10—30	0.2	6.3	6.8	0.7
30—50	<0.1	4.1	4.7	0.3

Note: PCB concentrations are expressed as micrograms per gram dry weight (PCB types; a mixture (1:2) of Aroclors® 1254 and 1260).

* See Figure 5 for locations.

concentrations of PCBs in higher trophic organisms from Victoria (Table 11), including fish, peregrine falcon eggs, and seals. However, to date no comprehensive surveys of such animals have been undertaken.

D. Other Australian Data

In other Australian states, there have been very few reports of PCBs in the environment. In Western Australia, fish samples from Cockburn Sound have been analyzed for PCBs, but all were below the limit of detection.[5] Olsen et al.[36] examined organochlorine residues

MONS 006410

Table 11
PCB CONCENTRATIONS IN SOME VICTORIAN BIOTA

Sample origin	Sample type	n	PCB conc. (μg/g wet weight)	Ref.
Victoria	Peregrine falcon eggs	32	0.10—4.30	49
Port Phillip Bay	Mullet	2	0.387—0.411	27
Bass Strait	Dogfish	5	0.01—0.07	48
	Flounder	6	0.03—0.05	
Seal Rocks (Westernport Bay)	Australian fur seals (male)	6 Muscle	<0.01—0.04	48
		7 Liver	0.02—0.08	
		7 Blubber	0.18—3.88	
		6 Gonad	<0.01—0.06	
	Australian fur seals (female)	4 Muscle	<0.01	
		4 Liver	<0.01—0.12	
		4 Blubber	0.05—0.54	

in the wings of ducks in southeastern Australia and found PCBs in low concentrations in only one sample of eight wild black ducks collected from the Barrenbox Swamp in NSW in 1979.

Smillie and Waid[46] have found PCB contamination of eucalyptus leaves collected from various sites in Australia. Leaves sampled in an area adjacent to an urban incinerator in Western Australia showed relatively high concentrations (mean of 9 samples, 5.4 μg/g; range 0.2 to 41.8 μg/g). In contrast, leaves from an area of intensive irrigation near Griffith, NSW, contained lower concentrations (mean of 5 samples, 0.16 μg/g; range 0.11 to 0.20 μg/g).

PCBs have been recorded by Tanabe et al.[51] in the atmosphere and surface waters near the Australian coastline. Highest concentrations (0.3 ng/m³ in air, 0.1 ng/ℓ in water) were found off the eastern Australian coastline. The authors note that the surface water PCB concentrations in the total region they surveyed (Antarctic, Western Pacific, and Indian Oceans) were generally lower than values reported for the Atlantic.[52-57] However, significantly high concentrations of PCBs were observed in coastal areas of both tropical and subtropical regions within the survey zone; here, higher chlorinated PCBs predominated, in comparison with localities more distant from shore where lower chlorinated PCBs were found.

IV. PCBs AND THE AUSTRALIAN POPULATION

Some research has been undertaken into PCB contamination of the local human population, but as with other aspects of the Australian situation, available results are inadequate to draw broad conclusions.

Siyali[58,59] found no PCBs in samples of human blood and breast milk from 45 women living in the NSW metropolitan area. In 1974, PCB concentrations in the blood of occupationally exposed people in NSW were examined.[60] The mean PCB level in the exposed group was 0.4 mg/ℓ; none was found in the controls. Several of the exposed workers complained of a burning sensation of the face and hands, nausea, and persistent body odor. One had chloracne, and several others had a rash on the legs and hands. The concentration of PCBs in the air at their work place was measured, and found to exceed the recommendations of the Australian National Health and Medical Research Council (1 mg/m³ for 42% chlorinated PCBs, 0.5 mg/m³ for 54% chlorinated PCB mixtures). The installation of a more efficient ventilation system lowered atmospheric quantities, but no significant lowering of blood levels was detected — either because the workers took no extra precautions in the

MONS 006411

course of their work, or due to the prolonged residence of PCBs in the body. Solly and Shanks[41] studied 51 body fat samples in New Zealand, where considerably less PCB is used (see Table 1). All of the samples contained PCBs, the average concentration being 0.28 μg/g.

There are no other Australian (or New Zealand) studies on human PCB exposure. A well-constructed survey of the Australian population is therefore needed to identify any groups suffering excess exposure. Additional knowledge of food contamination is also needed.

McMahon[3] noted that packaging materials were responsible for PCB contamination of several food and biota samples. PCB levels in packaging materials have been the subject of several Australian investigations. A national survey by the Department of Primary Industry indicated that PCBs were present in a variety of meat and dairy product packaging materials (probably because of the use of recycled paper in their manufacture).[42] The national average concentration was 8.5 μg/g. Although concentrations did not exceed international standards for packaging materials (10 μg/g), the amounts found were close to or exceeded the safety levels recommended by other countries.

The presence of PCBs in carbonless copy papers, and their influence on paper recycling is a problem which has received attention from the Australian paper industry. Production of this type of paper ceased in 1971, but a certain amount would have been in circulation for several years. Only negligible quantities of PCBs were found in plastic packaging materials. However, other analyses reported by McMahon[3] indicate that rather high quantities of PCBs (1.5 to 320 μg/g) in polythene bags were imported into Western Australia from Malaysia and Hong Kong.[3]

Several food materials have been analyzed in Australia for PCB content, but many analyses have been influenced by packaging contamination. From the very limited documentation, the amounts of PCBs appear to be relatively low. For example, yogurt in plastic containers was found to contain between 2 and 12 ng/g PCBs. As is the case in overseas studies, it would appear that the bulk of PCBs entering human food chains is via the aquatic environment.

Evidence for the presence of PCBs in the Australian environment up until 1975 was, therefore, very meager indeed. From the available data, and the work of other researchers since that time, it can be assumed that a baseline concentration must exist, as PCBs are global contaminants, capable of being spread over considerable distances by a variety of methods.[4,9,21,23,26-29,43,46-50] In addition, it would seem to be inevitable in the light of the information available from industrialized countries of the Northern Hemisphere, that higher quantities of PCBs would occur in and around major Australian cities. However, current evidence makes it impossible to assess the extent to which this has occurred, and a considerable amount of coordinated research is still needed to thoroughly clarify the situation.

Contamination of the Australian terrestrial and marine biota by PCBs may have been limited by the isolation of the bulk of the Australian land mass and coastal waters from internal and external sources of PCBs. Within Australia, the total amount of PCBs used would be insufficient to cause country-wide pollution, and the few major sources of PCB contamination are concentrated in widely separated and predominantly coastal urban centers.

Regional patterns of atmospheric circulation and ocean current flow, respectively, are unfavorable to the atmospheric or oceanic transport of PCBs from regions of high PCB usage and wastage in the Northern Hemisphere to Australia and its associated coastal waters. In many countries, PCB manufacture has ceased, and legal controls prohibit its release into the environment. We speculate that the bulk of PCBs present already worldwide in the environment will become immobilized in sediments and soils. Meanwhile, the current situation with respect to PCB contamination of most biota in Australia (especially that distant from large urban centres) might persist, or PCB concentrations may increase gradually as a result of deposition from the atmosphere but fail to reach the levels that exist at present in biota dwelling in the Northern Hemisphere.

MONS 006412

V. DISPOSAL OF PCBs IN AUSTRALIA

Perhaps the greatest area for concern is the means by which Australia will dispose of its present and future stocks of PCBs. This is a problem which has only recently been addressed, but has not yet been solved. Although the use of PCBs in Australia has been dramatically reduced (Table 1), the period when PCB waste reaches a maximum will most probably occur during the 1980s.[6] Already, considerable quantities await disposal. This highlights one of the most pressing concerns in Australia with regard to PCBs: the local inadequacy of available methods for disposing of these substances, and indeed, of other chlorinated hydrocarbons and intractable wastes. Three problems in combination may lead to a potentially dangerous environmental situation in this country:

1. Before 1972, most PCB-containing equipment had no attached label describing the hazards involved. Indeed, much equipment made after that date had no such warning.[63]
2. Most electrical equipment containing large amounts of PCBs has an extremely long life (30 to 50 years), and when it is ultimately scrapped, those involved may not know the dangers.
3. The recent practice of retro-filling PCB-containing transformers with substitute fluids may result in significant cross-contamination if drainage and cleaning of the units have not been carried out effectively. Insufficient disposal of the new dielectric, which may contain as much as 5% PCBs, could become a future source of PCB entry to the environment.

One of the most common, and arguably the most cost-effective methods for the complete destruction of PCBs is high temperature incineration.[64] Currently, no facilities exist in Australia for the destruction of PCBs (or other intractable wastes) by this means. While several alternatives to incineration exist, many incorporating relatively new technology, their relative advantages and usefulness to Australia are still being debated. However, some states have taken steps to resolve their problems.[65] The NSW government's Metropolitan Waste Disposal Authority has designed a high temperature rotary kiln incinerator with back burner, capable of handling waste from NSW with additional capacity for interstate waste. The cost of the plant was estimated at $15 million, and the anticipated completion date was 1985. However, recent information suggests that the building of the unit has been cancelled, due not only to siting problems, but also a recommendation of the federal government's House of Representatives Standing Committee on Environment and Conservation Inquiry into Hazardous Chemicals, favoring a national incinerator over regional plants.[65]

In Queensland and South Australia, disposal of PCBs in dumps is allowed under conditions imposed by the local authorities. Victoria has examined and rejected proposals by an inter-departmental task force to establish chemical disposal sites at Dargyle and Avalon,[4,66] and has recently published a draft strategy for the disposal of intractable waste.[67] In this, consideration is given to the establishment of a high temperature incinerator. A combination of installation and running costs of such a plant, especially in light of projected needs, and site location may prevent its construction, but the report assesses other means available, including interstate cooperation and the use of incinerator ships.[66]

In September 1982, Victoria planned to ship 18 t of PCBs to France for high temperature disposal. Although this initial operation was deferred due to concerns by environmental groups over shipping and handling, some 120 t were safely shipped to the U.K. for disposal during 1983. This practice, which is still continuing seems a reasonable stop-gap measure, given the lack of availability of local disposal methods for PCBs.[66] However, its continuation is dependent upon the cooperation of the receiving countries disposing of waste from abroad — an attitude which may change in the future.[68]

MONS 006413

Perhaps the best short-term solution to the disposal of stockpiled liquid PCBs is the use of an incinerator ship. During December 1982 and January 1983, the incinerator ship *MIT Vulcanus* visited Australia to dispose of (among other material) 215 t of waste containing 68% PCBs from Victoria, Tasmania, and Queensland.[64] Permission for this disposal was granted by the Australian Department of Home Affairs and Environment. However, the visit of the *MIT Vulcanus* took some 2 years to organize and future visits are also uncertain.[65] As the quantity of waste burnt was only a portion of the total chlorinated hydrocarbon waste held in Australia, urgent consideration must be given by both federal and state governments to ways and means of combatting the disposal problem.[65] A recent report to the Australian Environment Council and Confederation of Australian Industry strongly recommends the installation of a single, centrally located high temperature incinerator for Australia;[66] we are supportive of this initiative, particularly if the unit was capable of destroying solid as well as liquid wastes.

There is an obvious need for firm guidelines to be established in Australia for those involved with PCB wastes; Federal and State authorities should be encouraged to develop as soon as possible common procedures to monitor, regulate, store, and dispose of PCBs. The Victorian Environment Protection Authority is developing procedures for the disposal of PCB wastes,[66] but the situation in other states is unknown. Such procedures should be published in a manual (such as that produced by the U.K. Department of the Environment[70]), which should be distributed to all concerned with the handling of PCBs and PCB-containing goods.

It is essential that an environmentally acceptable solution to the problem of disposing Australia's intractable wastes be sought in the very near future. The installation of a high temperature incinerator in a central locality, capable of handling wastes from several areas within the country would seem a reasonable suggestion, and probably less costly in the long run than shipment overseas, particularly in view of its applicability to other types of waste. The use of an incinerator ship, either on regular hire from overseas, or constructed within Australia is another possibility. The recently reported New Zealand success in using a cement kiln for disposal of solid and liquid PCB wastes should also be thoroughly investigated.[71]

Perhaps the greatest potential threat posed by PCBs in Australia lies in delays in tackling the problem of finding efficient means of disposal. A large quantity of PCBs awaits disposal and more will become ready for disposal in the next decade. Because of inadequate storage methods, lack of labeling of old equipment, and a lack of knowledge on the part of those handling the waste, potentially harmful quantities may be unwittingly released into the environment. People must be educated about the dangers of indiscriminate handling of PCB waste and provision must be made for its adequate collection and disposal.

ACKNOWLEDGMENTS

We thank the following for financial and other support: La Trobe University, the Rural Credits Development Fund, the Ministry for Conservation — Victoria, The Marine Science Laboratories, Queenscliff, The Environment Protection Authority — Victoria, the Australian Marine Sciences and Technologies Advisory Committee, The Australian Institute of Marine Science and the Great Barrier Reef Marine Park Authority. Colleagues and other institutions that have assisted us in various ways are mentioned in the text; their help is appreciated.

MONS 006414

REFERENCES

1. Australian Department of Business and Consumer Affairs, Bureau of Customs, Customs (Prohibited Imports) Regulation 4AB. Customs General Order D/6/10 and Appendix D26 to Customs General Orders. Sydney, 1975.
2. OECD. Polychlorinated Biphenyls: Their Use and Control, Organisation for Economic Co-operation and Development. Paris, 1973.
3. OECD, Report on the Implementation by Member Countries of the Decision by Council on the Protection of the Environment by Control of Polychlorinated Biphenyls, ENV(82)5, Organisation for Economic Co-operation and Development, Paris, 1982.
4. Richardson, B. J. and Wald, J. S., Polychlorinated biphenyls (PCBs): an Australian viewpoint on a global problem, *Search*, 13, 17, 1982.
5. McMahon, R. G. P., *Environmental Behaviour of PCBs*, Amdel Report No. 1089, The Australian Mineral Development Laboratories, Adelaide, South Australia, 1975.
6. Monsanto Australia Ltd., Personal communication, 1982.
7. May and Baker Pty. Ltd., Personal communication, 1982.
8. NSW Metropolitan Waste Disposal Authority, Report on Disposal of Polychloro Biphenyl Wastes, Sydney, December 1976.
9. Woolford, P. and Settle, H., PCB residues in mullet, *Mugil cephalus*, fed to captive Eastern Australian water rats, *Hydromys chrysogaster*, *Bull. Environ. Contam. Toxicol.*, 20, 606, 1978.
10. NSW State Pollution Control Commission, Toxic Chemicals, Environmental Control Study of Botany Bay, Sydney, Australia, September 1979.
11. Shaw, G. R. and Connell, D. W., Polychlorinated biphenyls in the Brisbane River Estuary, Australia, *Mar. Pollut. Bull.*, 11, 356, 1980.
12. Water Quality Council of Queensland, Fourth Annu. Rep. for the Year Ending 30th June, 1976, Government Printer, Queensland, Australia, 1976.
13. Water Quality Council of Queensland, Fifth Annu. Rep. for the Year Ending 30th June, 1977, Government Printer, Queensland, Australia, 1977.
14. Water Quality Council of Queensland, Sixth Annu. Rep. for the Year Ending 30th June, 1978, Government Printer, Queensland, Australia, 1978.
15. Water Quality Council of Queensland, Seventh Annu. Rep. for the Year Ending 30th June 1979, Government Printer, Queensland, Australia, 1979.
16. Water Quality Council of Queensland, Eighth Annu. Rep. for the Year Ending 30th June 1980, Government Printer, Queensland, Australia, 1980.
17. Water Quality Council of Queensland, Ninth Annu. Rep. for the Year Ending 30th June 1981, Government Printer, Queensland, Australia, 1981.
18. Water Quality Council of Queensland, Tenth Annu. Rep. for the Year Ending 30th June 1982, Government Printer, Queensland, Australia, 1982.
19. Water Quality Council of Queensland, Eleventh Annu. Rep. for the Year Ending 30th June 1983, Government Printer, Queensland, Australia, 1983.
20. Water Quality Council of Queensland, Twelth Annu. Rep. for the Year Ending 30th June 1984, Government Printer, Queensland, Australia, 1984.
21. Shaw, G. R. and Connell, D. W., Factors influencing concentrations of polychlorinated biphenyls in organisms from an estuarine ecosystem, *Aust. J. Mar. Freshw. Res.*, 33, 1057, 1982.
22. Odum, W. P. and Heald, E. J., The detritus based food web of an estuarine mangrove community, in *Estuarine Research*, Vol. 1., Cronin, E. L., Ed., Academic Press, New York, 1975, 265.
23. Olafson, R. W., Effect of agricultural activity on organochlorine pesticides in hard corals, fish and molluscs from the Great Barrier Reef, *Mar. Environ. Res.*, 1, 67, 1978.
24. Sindlle, R. and Wald, J. S., Polychlorinated biphenyls and organochlorine compounds in Great Barrier Reef biota, in Workshop on Contaminants in Waters of the Great Barrier Reef, Workshop Ser. No. 5, Dunna, I. M., Ed., Great Barrier Reef Marine Park Authority, Townsville, Australia, 1985.
25. Dale, B. H. and Paisley, G. J., Wastewater Input Stream Assessment, Preliminary Report to May 1976, Environmental Studies Ser. No. 232, Ministry for Conservation, Victoria, Australia, 1978.
26. Richardson, B. J. and Wald, J. S., The Environmental Significance of Polychlorinated Biphenyls (PCBs), Environmental Studies Ser. No. 248, Ministry for Conservation, Victoria, Australia, 1979.
27. Richardson, B. J. and Wald, J. S., PCBs in the Port Phillip Region: Survey of Polychlorinated Biphenyls (PCBs) in Port Phillip Bay, Environmental Studies Ser. No. 249, Ministry for Conservation, Victoria, Australia, 1980.
28. Richardson, B. J. and Wald, J. S., Polychlorinated biphenyls in sediments and mussels from Port Phillip Bay, Victoria, Australia, in *Biogeochemistry of Ancient and Modern Environments*, Trudinger, P. A., Walter, M. R., and Ralph, B. J., Eds., Australian Academy of Science, Canberra, 1980, 423.

MONS 006415

29. Richardson, B. J. and Wold, J. S., Polychlorinated biphenyls (PCBs) in shellfish from Australian coastal waters. *Ecol. Bull. (Stockholm)*. 35. 511. 1983.
30. Goldberg, E. D., Bowen, V. T., Farrington, J. W., Harvey, G., Martin, J. H., Parker, P. L., Risebrough, R. W., Robertson, W., Schneider, E., and Gamble, E., The Mussel Watch. *Environ Conserv*. 5. 101. 1978.
31. Eisenberg, M., Mellman, R., and Tublash, H. S., Polychlorinated biphenyls in fish and shellfish of the Chesapeake Bay. *Mar. Fish. Rev*. 42. 21. 1980.
32. Andertini, V. C., Al-Hasmi, L., de Lappe, B. W., Risebrough, R. W., Walker, W., Simoneit, B. R. T., and Newton, A. S., Distribution of hydrocarbons in the oyster. *Pinctada margaritifera*, along the coast of Kuwait. *Mar. Pollut. Bull*., 12. 57. 1981.
33. Jensen, S., Johnels, A. G., Olsson, M., and Otterlind, G., DDT and PCB in marine animals from Swedish waters. *Nature, (London)*. 224. 247. 1969.
34. Klihstrom, J. E. and Bergland, E., An estimation of the amounts of polychlorinated biphenyls in the biomass of the Baltic. *Ambio*. 7. 175. 1978.
35. Rossins, M. T. L., Botello, A. V., Bravo, H., and Mandelli, E. F., PCBs and organochlorine insecticides in oysters from coastal lagoons of the Gulf of Mexico, Mexico. *Bull. Environ. Contam. Toxicol*., 21. 632. 1979.
36. Steinhoo, D. and Rollwagen, J., PCB residues in bivalves and sediments of Raritan Bay. *Bull. Environ. Contam. Toxicol*., 23. 690. 1979.
37. Mowrer, J., Calambokidis, J., Musgrove, N., Dreger, B., Beug, M. W., and Hermon, S. G., Polychlorinated biphenyls in canids, mussels and sediments in Southern Puget Bay, Washington. *Bull. Environ. Contam. Toxicol*., 18. 588. 1977.
38. Cowan, A. A., Organochlorine compounds in mussels from Scottish coastal waters. *Environ. Pollut. (Ser B)*. 2. 129. 1981.
39. Wharfe, J. R. and Van Den Broek, W. L. F., Chlorinated hydrocarbons in macroinvertebrates and fish from the Lower Medway Estuary, Kent. *Mar. Pollut. Bull*., 9. 76. 1978.
40. Dybern, B. I. and Jensen, S., DDT and PCB in Fish and Mussels in the Kattegat and Skagerrak Area. *Medd. Havsfiskelab. Lysekil*. 232. 1978.
41. Marchand, M., Van, D., and Duursma, E. K., Levels of PCBs and DDTs in mussels from N W Mediterranean. *Mar. Pollut. Bull*., 7. 65. 1976.
42. Morgan, R. P. and Sommer, S., Polychlorinated biphenyls in Baltimore Harbour sediments. *Bull. Environ. Contam. Toxicol*., 22. 413. 1979.
43. Clarke, R. G., Richardson, B. J., and Wold, J. S., Residence of polychlorinated biphenyls (PCBs) in a spoilage site. *Ecol. Bull. (Stockholm)*. 35. 533. 1983.
44. Richardson, B. J. and Wold, J. S., Unpublished data. 1982.
45. Murray, A. P. and Richardson, B. J., Unpublished data. 1984.
46. Preston City Council, Personal communication. 1982.
47. Richardson, B. J., Unpublished data. 1983.
48. Sanillo, R. and Wold, J. S., Unpublished data. 1982-1984.
49. Pruett-Jones, S. G., White, C. M., and Emison, W. B., Eggshell thinning and organochlorine residues in eggs and prey of peregrine falcons from Victoria, Australia. *Emu*. 80. 281. 1981.
50. Olsen, P., Settle, H., and Swift, R., Organochlorine residues in the wings of ducks in south-eastern Australia. *Aust. Wild. Res*., 7. 139. 1980.
51. Tanaka, S., Kawano, M., and Tatsukawa, R., Chlorinated hydrocarbons in the Antarctic, Western Pacific and Eastern Indian Ocean. *Trans. Tokyo Univ. Fish*., 5. 97. 1982.
52. Bidleman, T. F. and Olney, L. E., Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. *Science*. 183. 516. 1974.
53. Harvey, G. R., Miklas, H. P., Bowen, V. T., and Steinhauer, W. G., Observations on the distribution of chlorinated hydrocarbons in Atlantic Ocean organisms. *J. Mar. Res*., 32. 103. 1974.
54. Harvey, G. R. and Steinhauer, W. G., Transport pathways of polychlorinated biphenyls in Atlantic water. *J. Mar. Res*., 34. 361. 1976.
55. Harvey, G. R. and Steinhauer, W. G., Biogeochemistry of PCB and DDT in the North Atlantic. in *Environmental Biogeochemistry*, Vol. 1, Nriagu, J. D., Ed., Ann Arbor Science, Ann Arbor, Mich., 1976. 203.
56. Harvey, G. R., Steinhauer, W. G., and Teal, J. M., Polychlorobiphenyls in North Atlantic ocean water. *Science*. 180. 643. 1973.
57. Jones, R. B. and Pfluender, F. K., Chlorinated hydrocarbon pesticides in the western North Atlantic Ocean. *Environ. Sci. Technol*., 10. 770. 1976.
58. Styall, D. S., Hexachlorobenzene and other organochlorine pesticides in human blood. *Med. J. Aust*., 2. 1063. 1972.
59. Styall, D. S., Polychlorinated biphenyls, hexachlorobenzene and other organochlorine pesticides in human milk. *Med. J. Aust*., 2. 815. 1973.

MONS 006416

60. **Ouw, H. K., Simpson, G. R., and Siyali, D. S.,** Use and health effects of Aroclor 1242, a polychlorinated biphenyl, in an electrical industry. *Arch. Environ. Health*, 31, 189, 1976.
61. **Selby, S. R. B. and Shanks, V.,** Polychlorinated biphenyls and organochlorine pesticides in human fat in New Zealand, *N. Z. J. Sci.*, 17, 535, 1974.
62. **Seetoon, J. T.,** *Residues of Polychlorinated Biphenyls (PCBs) in Packaging Materials for Meat and Dairy Products*, Documents PB No. 271 and 271A, Australian Department of Primary Industry, Pesticides Section, 1976.
63. **Farugia, A. J.,** Report on the Usage and Disposal of Polychlorinated Biphenyls (PCBs) in New South Wales, Internal Report, N.S.W. State Pollution Control Commission, Sydney, February 1979.
64. **National Academy of Sciences,** Polychlorinated Biphenyls, A report prepared by the Committee on the Assessment of Polychlorinated Biphenyls in the Environment, Environmental Studies Board, Commission on Natural Resources, National Research Council, National Academy of Sciences, Washington, D.C., 1979.
65. Royal Australian Chemical Institute, Whither those environmentally hazardous wastes? Do we really care? An information report from the RACI Environment Committee, *Chem. Aust.*, 51, 105, 1984.
66. **Richardson, B. J. and Brenner, A. J.,** *Polychlorinated Biphenyls (PCBs): A Perspective on Human Health and Disposal Problems in Australia*, Tech. Report No. 33, Ministry for Conservation, Victoria, Marine Science Laboratories, Queenscliff, Australia, 1983, 28.
67. Environment Protection Authority, Disposal of Intractable Wastes in Victoria — A Draft Strategy, Publ. 119, Environment Protection Authority, East Melbourne, Australia, 1981.
68. Environment Protection Authority, Victoria, Australia, Personal communication, 1984.
69. **Maunsell and Partners,** Management and Disposal of Hazardous Industrial Wastes, Report prepared for the Australian Environmental Council and Confederation of Australian Industry, Australian Environmental Report No. 9, Australian Government Publishing Service, Canberra, 1983.
70. U.K. Department of the Environment, *Polychlorinated Biphenyls (PCB) Wastes, A Technical Memorandum on Reclamation Treatment and Disposal Including a Code of Practice*, Waste Management Paper No. 6, Her Majesty's Stationery Office, London, 1976.
71. **Holden, R., Tyson, M. O., and Hodgkinson, E. J.,** The destruction of polychlorinated biphenyl waste oils in a cement kiln, *Chem. N. Z.*, April, 31, 1983.

MONS 006417

INDEX

A

Accumulation of PCBs in human populations, 47
Acid rains, 203
Acurex Waste Technologies, Inc. (AWT) PCB destruction process, 92, 94—99
Adipose tissue, 44—48, 50, 52—54
Adrenocortical hyperplasia, 195
Adriatic Sea, 217, 229
Age groups, PCB levels affected by, 56—57
Airborne fallout, 203
Air emissions of PCBs from waste disposal site, 90—91
Air monitoring requirements, 87
Alca torda, see Razorbills
Alewife, 169—171
Algae, 255—256
Alosa pseudoharengus, see Alewife
American Conference of Governmental Industrial Hygiene, 65
Amniotic fluid, 47
Analytical methods summary, 139
Anchylomera blossevillei, 229
Antarctic Ocean, 257
Antipyrine, 75
Aquatic ecosystems, 167—171
Arc pyrolysis project (APP), 140—149
Arc Technologies Company arc pyrolysis project, 139—149
  arc furnace, 144—149
  description of the project, 139—140, 142
  destruction process, 143—144
  process engineering, 140—143
Arctic terns, 188
Aroclor 1016, 244
Aroclor 1242, 245—247
Aroclor 1254, 244—247, 256
Aroclor 1260, 256
Aroclors, 243, 251
Arteriosclerosis, 195
Asharels, 70—71
Atlantic Ocean, 257
Atmosphere, 257, 258
Atmospheric circulation, 258
Atmospheric fallout, 235
Atmospheric inputs of PCBs, Great Lakes, 155, 157, 159
Atmospheric transport, 211, 258
Australian Customs Regulations, 242
Australian ecosystem, 241—263
  disposal of PCBs, 259—260
  importation of PCBs, 242—244
  New South Wales, 244—247
  other Australian data, 256—257
  population, PCBs in, 257—258
  Queensland, 246—251
  usage of PCBs, 242—244
  Victoria, 247, 251—257
  Western Australia, 256—257
Autopsy, seals' pathological uterine changes, 194
Average PCB concentration in open waters, 234
Average PCB levels
  blood, 46
  breast milk, 46
  fat basis, 44

B

Balaenoptera acutorostrata, see Baleen whale
Balaenoptera physalus, see Fin whale
Bald eagle populations, 188—189
Baleen whale, 231
Baltic environment, PCBs in, see also specific topics, 181—208
  biota levels, 198—202
  birds, 188—190
  brackish water system, 182
  effects of, 187—198
    on birds, 188—190
    on mammals, 190—198
  experiences from studies, 202—205
  fish, 198—202
  locally polluted regions, 185—186
  mammals, 190—198
  mink, 196, 198
  otter, 195—197
  pollution levels, 183—185
  porpoise, 196—197
  seals, 191—195
  seasonal variations of levels of, 186—187
Baltic Sea, 254
Benthic species, 170—171, 222—225
Bilirubin, 75
Biodegradative processes, 216
Biological effects of PCBs, PCQs, and PCDFs, 18—21
Biological half life
  PCB isomers, 14—15
  PCQs, 11
Biological study of Yusho, 13—20
Biomagnification, 185, 232
Biota
  Australian ecosystem, 246—251, 257—258
  Baltic levels, see also Baltic environment, 185, 198—202
  Mediterranean marine environment, see also Mediterranean marine ecosystem, 220—232
Birds, effects of organochlorines on, 188—190
Bivalves, 252, 254
Blood level of PCBs, 44—47, 50, 53, 257
  fish consumption in relation to, 177
  occupationally PCB-exposed workers, 2, 9—10, 20
  Taiwanese patients, 11, 14, 20
  Yucheng patients, 33—34

MONS 006418

Yusho patients, 2, 8—10
Blood level of PCDFs
occupationally PCB-exposed workers, 9—10, 20
Taiwanese patients, 12, 14, 20
Yucheng patients, 37
Yusho patients, 8—10
Blood level of PCQs
occupationally PCB-exposed workers, 9—10, 20
Taiwanese patients, 11—12, 14
Yusho patients, 8—10, 20
Blood pressure, 73
Body burden, 44, 170, 200
Body fat, 258
Brackish water system, 182
Bream, 244—245, 247
Breast milk, PCBs in, 44—47, 49—50, 52—53, 55, 257
Burning low level PCB/mineral oil wastes in high efficiency boilers, 109—113
Burning PCBs at sea, 127—131
Burning PCB wastes in cement kilns, 113—126
cement kiln technology, 113—122
recommended environmental controls for storage, handling, and process disposal of toxic chemical wastes, 122—126

C

California Air Resources Board, 121—122
California Office of Appropriate Technology Recommendations for burning PCBs, 121—122
Californian sea lions, 193
Cancer, 77—78
Capacitors
dielectric fluids, 242—243
manufacturing, 66—69, 74—76, 244
PCB-contaminated, 139
Capitella capitata, 246, 250
Capuse land disposal site, 90
Carbonless copy papers, 258
Carcinus mediterraneus, see Crabs
Cement kilns, burning PCB wastes in, see Burning PCB wastes in cement kilns
recommended environmental controls for storage, handling, and process disposal of toxic chemical wastes in, 122—126
technology, 113—122
Cetaceans, 231
Chemical waste landfills, see Landfilling PCBs
Chesapeake Bay, 254
Chlorosis, 72—76
Chlorinated compounds
healthy persons, 7—11
occupationally PCB-exposed workers, 7—11
Yusho patients, 2—11
Chlorinated naphthalenes, 72
Cholesterol, 73, 75
Circus aeruginosus, see Marsh harrier
Clams, 246, 251
Claws, 195
Clophen, 243
Cloresil, 243
Clupea harengus, see Herring
Coastal waters
biota, 220—229
sea water, 213—214
sediments, 217—219
Cod, 183, 198
Commercial PCB mixtures, 40—41
Common porpoise, 190
Common seals, 190, 191, 194, 196
Composition of PCBs, 3—4
Congener distribution of PCBs, 40—41
Copepod fecal pellets, 232—233
Corals, 246
Coral trout, 246, 251
Corvus cornix, see Crows
Crabs, 223
Critical species for study of nonpolar substances, 204
Crows, 188

D

Daily intake of PCBs, PCQs and PCDFs, Taiwanese patients, 11
Dairy feeds, 244
Dairy products, packaging materials, 258
DDE, 188, 189, 202
DDT, in Baltic environment, see Baltic environment
Dechlorinating PCBS, 92—99
Degerhamn Dry Cement Kiln, Sweden, 117
Dermatological severities, 13
Destruction of waste PCBs, see Disposal of PCBs
Dibenzofurans, see PCDFs
Dieldrin, 188—189
Dielectric disposal, 259
Dielectric fluids, 242—243
Dimerization of PCBs, 6
Disposal of PCBs, 83—151
Arc Technologies Company arc pyrolysis project, 139—149
arc furnaces, 144—149
description of project, 139—140, 142
destruction process, 143—144
process engineering, 140—143
Australia, 259—260
burning at sea, 127—131
burning low level PCB/mineral oil wastes in high efficiency boilers, 109—113
burning PCB wastes in cement kilns, 113—126
recommended controls, 122, 124—126
technology, 113—124
dechlorination, 92—99
high temperature incineration, see also High temperature incineration, 99—109
landfilling, 84—91
nonthermal methods, see also Nonthermal methods for PCB disposal, 91—99

MONS 006419

plasma arc high temperature destructors, 138—139
U.S. EPA mobile incinerator, 132—141
U.S. EPA TSCA requirements, 87—89
Distribution of PCBs, Yusho, 15—17
Distribution of PCDFs, Yusho, 15
Distribution of PCQs, Yusho, 15—16
Ducks, 257
Dugong, 246, 251

E

Ecotoxins, 203
Eel, 184—185
Eggs, 244
Eggshell thickness, 188
Electrical equipment, 259
maintenance and repair, 69—71
manufacturing, 65—69, 76, 78
Elimination of PCBs in Yucheng patients, 34
Emission rates of organic compounds from industrial landfills, 89
Energy Systems Company (ENSCO), Eldorado, Arkansas, 101—105
England, Kent, 254
Environmental cycle, 86
Epidemiological studies, post-Yusho, see also Workplace, PCBs in, 73—78
Epidermis, 195
Estimated distribution of PCBs in U.S., 85
Eucalyptus leaves, 257
Euphausiids, 227, 229, 232
Eutrophication, 186

F

Fecal pellets, 226, 232—234
Fetal death, 194
Fetal PCB blood levels, 46
Fetal skin, PCB levels in, 47
Fetal tissues and fluids, PCBs in, 47, 50, 52
Fick's law, 89
Fin whale, 231—232
Fish
Australian, 244—247, 256
Baltic, 198—202
Great Lakes, 177—178, 186—187
Mediterranean marine environment, 222—227
Flounder, 183
Fluorescent light ballasts, 71
Food chain, 223
Food chain model, 167—171
Food materials, 258
French coast, 213—214
Future PCB waste disposal concepts, 138—149

G

Gadus morhua, see Cod
Garfish, 198
General Electric Co., Pittsfield, Massachusetts, 106—109
General Motors Corp., Warren, Michigan, 110—113
Geographical distribution of PCB and DDT, 183
GGTP, 73—76, 78
Gradient from disposal point, 185
Grampus griseus: see Risso's dolphin
Great Lakes ecosystem, 153—180
atmospheric inputs of PCBs, 155, 157, 159—161
concentration of PCBs, 154—158
human exposure through fish consumption contaminated with PCBs, 177—178
industrial input of PCBs, 155, 160
inputs of PCBs, 155, 157, 159—161
modeling of fate of PCBs, see Modeling of fate of PCBs
municipal input of PCBs, 155, 160
physical limnological characteristics, 155
sediment diffusion of PCBs, 171—176
solids-dependent PCB partitioning, 171—176
total PCB load, 160—161
tributary input of PCBs, 155, 159—160
Grey seals, 190, 191, 194, 196
Guillemot, 188, 201—202
Gulf of Mexico, 254
Gulls, 227

H

Hair follicles, cystic dilatations of, 195
Haliaeetus albicilla, see White-tailed sea eagles
Halichoerus grypus, see Grey seals
Haliotis sp., 251
Halocline, 184—185
Halowax, 72
Hatching success, 188
HDL-cholesterol, 76
Healthy persons, chlorinated compounds in, 7—11
Heat transfer fluid, 242—243
Herring, 183—185, 202
DDT levels, 198—201
Hexachlorobenzene, 188
High efficiency boilers, burning low level PCB/mineral oil wastes in, see Burning low level PCB/mineral oil wastes in high efficiency boilers
Higher trophic organisms, 256—257
High temperature incineration, 99—109, 259—260
Energy Systems Company (ENSCO), Eldorado, Arkansas, 101—105
General Electric Co., Pittsfield, Massachusetts, 106—109
Kommunekemi Hazardous Waste Incinerator, Nyborg, Denmark, 105—106
requirements, 100—101
Rollins, Deerpark, Texas, trial burn, 105—106
rotary kiln incinerators, 106
Toxic Substance Control Act, 99—101

MONS 006420

trial test burns, 103, 105—106, 138
Histological examinations, seals' pathological uterine changes, 194
Human exposure through fish consumption contaminated with PCBs, 177—178
Human milk, see Breast milk
Human populations, PCBs in, 39—61
  adipose tissue, 44—45, 48, 50, 52
  age, 56—57
  Australia, 257—258
  blood, 44—46, 50, 53
  breast milk, 44—46, 48—50, 52—53
  commercial PCB mixtures, 40—41
  fetal tissues and fluids, 47, 50, 52
  infant tissues and fluids, 47, 50—51
  measurement of residues, 40—41
  miscellaneous tissues and fluids, 46—47, 51
  monitoring programs of, 40
  parameters which affect levels of, 53, 56—58
  PBC isomers, 41—43
  population density, 57—58
  postnatal exposure, 40
  quantitation of, 40
  race, 57
  sampling, 53, 56
  sex, 57
  trends in levels, 50—56
Hydraulic fluids, 242—243
Hyperadrenocorticism, 195
Hyperkeratosis, 195

I

Importation of PCBs in Australia, 242—244
Incinerators, see High temperature incineration
Incinerator ships, 259—260
Incinerators, 257
  mobile, 132—138
  rotary kiln, 106
Indian Ocean, 257
Industrial input of PCBs, Great Lakes, 155, 160
Infant tissues and fluids, PCBs in, 47, 50—51
Insecticide wastes, 259
Intrauterine exposure to PCBs, 177—178
In utero exposure to PCBs, 40
Italian coastal waters, 214

K

Kent, England, 254
Kommunekemi Hazardous Waste Incinerator, Nyborg, Denmark, 105—106
Kuwait, 254

L

Lake Erie, 155, 159
Lake Huron, 154—155, 159
Lake Michigan, 154—159, 169—171
Lake Ontario, 154—155, 159
Lake Superior, 154—155, 157, 159
Lake trout, 169
Landfilling PCBs, 84—91
Larus, see Gulls
LDH, 75
Leiomyomas, 194
Levels of PCBs
  in humans, see also Human populations, 47, 53, 56—58
  marine organisms, 220
  Mediterranean marine environment, 213—232
  otters, extractable fat from, 197
  seal blubber, 196
  seasonal variations in fish, 186—187
Littoral fish, 184
Littoral fish fauna, 183
Liver, PCB levels in, 47
Lower trophic level, 223, 232
Lutjanus spp., 246, 251
Lutra lutra, see Otter

M

Malignant melanoma, 77
Mammals, see also specific types
  effects of organochlorines on, 190—198
Mammillary transfers of PCBs, PCQs and PCDFs, 17
Marine air measurements, 235
Marine organisms, levels of PCBs in, 220
Marsh harrier, 188
Meat packaging materials, 258
Mediterranean marine ecosystem, 209—239, 254
  biota, 220—232
    coastal, 220—229
    open sea, 227, 229—232
  coastal
    biota, 220—229
    sea water, 213—217
    sediments, 217—221
  fish, 222—227
  open sea
    biota, 227, 229—232
    sea water, 213—217
    sediments, 217—221
  regional PCB sources, usages, and input, 210—213
  sea water, 213—217
  sediments, 217—221
  vertical flux and removal processes, 232—233
Mediterranean mussel, 220—222
Meganyctiphanes norvegica, 229
Mercury, 188—189, 195
Micronekton, 223, 230—231
Microplankton, 223, 227, 229—231
Microsomal enzyme induction, 75
Mink, 190, 192—193, 196, 198, 204
Mobile incinerator, 132—138

MONS 006421

Modeling of fate of PCBs, 161—180
aquatic ecosystems, 167—171
physical-chemical fate, 161—167
Molluscs, 246
Monitoring programs of PCBs, 40
Monitoring trend studies, 200
Monkey, 16—19
Morbidity studies, occupational, 73—76
More highly chlorinated biphenyls, preferential adsorption and deposition of, 218
Mortality studies, occupational, 77—78
MT Vulcanus, 127—131
Mugil cephalus, see Mullet
Mullet, 223, 225, 244—247, 257
Mullus barbatus, see Mullet
Municipal input of PCBs in Great Lakes, 155, 160
Mussels
Australian ecosystem, 244—245, 247, 250—252, 254—255
Mediterranean marine ecosystem, 220—222, 227
Mussela vison, see Mink
Myctophid fish, 223
Myriophium glaciale, 229
Mysis relicta, see Phytoplankton
Mysticeti, 232
Mytilus edulis, see Mussels
Mytilus galloprovencialis, see Mediterranean mussel

N

National Institute for Occupational Safety and Health, 64—65
Nesting, 188
New hazardous waste sites, 86
New South Wales (NSW), PCBs in, 244—247, 257, 259
New technologies for high efficiency destruction of PCBs, 132—138
New Zealand, 243, 244, 258, 260
Nonoccupational studies, 73
Nonpolar substances, crucial species for study of, 204
Nonthermal methods for PCB disposal, 91—99
Norcem Cement Company, Norway, burning PCBs at, 117—121
Northern Hemisphere research, 252, 258

O

Occluded uteri, 193—195
Occupationally PCB-exposed workers, see also Workplace, PCBs in
Australia, 257
blood level of PCBs, PCDFs and PCQs in, 2, 9—10, 20
chlorinated compounds in, 7—11
symptomatic difference between Yusho patients and, 21
Occupational Safety and Health Administration, 65
Ocean current flow, 258
Oceanic transport, 258
Open Mediterranean plankton, PCB levels in, 231
Open sea,
biota, 227, 229—232
sea water, 215—217
sediments, 218—221
Osprey, 188
Otter, 190, 195—197
Oysters, 244—245, 247

P

Packaging contamination, 258
Packaging materials, 258
Pancreatic cancer, 77
Pandion haliaetus, see Osprey
Paper industry, 258
Parapenaeus longirostris, see Shrimp
Particulate PCBs, 216
Partitioning of PCBs between particulate and soluble phases, 215—216
Partitioning of PCBs in surface waters, 217
PCB, see specific topics
PCB components in Yusho patients, 13—15
PCB-contaminated capacitors, 139
PCB/DDE ratio, 229
PCB/DDT ratio, 227
PCB/ΣDDT ratio, 229
PCB exposures, workplace, 65—72
PCB isomers, 14—15, 41—43
PCB particulate flux, 235
PCB pattern in formation in Yusho, 14
PCB poisoning, 11—13
PCB products, 2—6
PCBs still in use and accessible, 85
PCDFs, 65
biological effects, 18—21
blood level in occupationally PCB-exposed workers, 9—10, 20
blood level in Taiwanese patients, 12, 14, 20
blood level in Yucheng patients, 37
blood level in Yusho patients, 8—10
changes of components and concentrations during deodorization process of Yusho oil, 6
components, residual, 15, 21
concentration ratios to PCBs in Yusho oils and PCB products, 3, 6—7
concentrations in Taiwanese incident oil, 10—11
concentrations in Yusho oil, 10
daily intake by Taiwanese patients, 11
distribution in Yusho, 15
exposure, Askarels, 70—71
formation, 6
gas chromatographic patterns, 13
mammillary transfers, 17
PCB products, 2—5
placental transfers, 17
rice-bran oil contamination, 28
tissue levels in Yusho patients, 8, 10

MONS 006422

tissue retention in deceased Yucheng patients, 35—37
toxic rice-bran oil, 32
PCQs, 65
biological effects, 18—20
biological half life, 11
blood level in occupationally PCB-exposed workers, 9—10, 20
blood level in Taiwanese patients, 11—12, 14
blood level in Yusho patients, 8—10, 20
changes of components and concentrations during deodorization process of Yusho oil, 6
components in Yusho patients, 8
concentration ratio to PCBs in PCB products, 3, 6
concentration ratio to PCBs in Yusho oils, 5—7
concentrations in Taiwanese incident oil, 10—11
concentrations in Yusho oil, 10
daily intake by Taiwanese patients, 11
distribution in Yusho, 15—16
formation, 6
gas chromatographic pattern in Yusho patients, 8, 10, 16
mammillary transfers, 17
PCB products, 2—5
placental transfers, 17
residual, 16—17
rice-bran oil contamination, 28
structure, 3
tissue levels in Yucheng patients, 37
tissue levels in Yusho patients, 7—8
toxic rice-bran oil, 32—33
Yusho oils, 4—5
PCQEs in Yusho oils, 5
Pearless Cement Company, Detroit, Michigan, 116—117
Pelagic fish, 170, 183—184, 200, 222—227
Pelagic food chain, 232
Pelicans, 246, 249—250
Perch, 187
Peregrine falcon, 256—257
Peripheral neuropathy, 76
Phenanthrene, 243
Phoca hispida, see Ringed seals
Phoca vitulina, see Common seals
Phocoena phocoena, see Common porpoise
Physical-chemical fate of PCBs, model of, 161—167
Physoplankton, 169
Pike, 184—186, 198—199, 202—203
Pinniped placentas, 194
Placenta, PCB levels in, 47
Placental transfers of PCBs, PCQs and PCDFs, 17
Plankton, 186, 223, 227
Plasma arc high temperature destructors, 138—139
Plaster packaging materials, 258
Pleuronectes platessa, see Flounder
Polychlorinated biphenyls (PCBs), see specific topics
Polychlorinated quaterphenyl ether, see PCQEs
Polychlorinated quaterphenyls, see PCQs
Polythene bags, 258
Pomaporeia affinis, 170
Population density, 57—58
Porpoise, 196—197
Postnatal exposure to PCBs, 40
Predatory birds, 201—202
Preferential adsorption and deposition, 218
Puget Sound, 254
Pusa hispida, see Ringed seals
Pyrolene, 243
Pyranol, 243
Pyrochemical reaction of PCBs, 6
Pyroclor 3, 244
Pyroclors, 243
Pyrolysis, 66, 71

Q

Quantitation of PCBs, 40
Quaterphenyls, see PCQs
Queensland, PCBs in, 246—251, 259, 260

R

Race affecting PCB levels, 57
Raritan Bay, 254
Rats, 18—20
Razorbills, 188
Recommended environmental controls for storage, handling, and process disposal of toxic chemical wastes in cement kilns, 122—126
Regional chronic intestinal ulcers, 195
Removal of PCBs, 232, 233
Renal glomerulopathy, 195
Residence times of PCBs, 233
Resorption, 194
Rice-bran oil, see Taiwanese patients: Yucheng patients; Yusho; Yusho oil
Ringed seals, 190, 191, 194, 196
Risso's dolphin, 231
Roaches, 186—187
Rollins, Deerpark, Texas, trial burn, 105—106
Rutilus rutilus, see Roaches

S

St. Lawrence Cement Company, Mississauga, Ontario, Canada, 115—116
Salmon, 187
Salvelinus namaycush, see Lake trout
Sampling methods, 195
Sampling of tissues for PCBs, 53, 56
Scottish coastal waters, 254
Sea birds, 227—229
Sea cucumbers, 246
Seal oil, 198—199
Seals, see also specific types, 185, 191—196, 204, 256—257

MONS 006423

Sea water, 213—217
Seaweeds, 227
Sediment-dependent partition coefficient, 176
Sediment diffusion of PCBs, 171—176
Sediments
  Australian ecosystem, 246—256
  Baltic environment, 198—199
  Mediterranean marine environment, 217—221
Sediment traps, 232—235
Sesarma erythrodactyla, 246, 250
Sewage sludge, 73
Sex affecting PCB levels, 57
SOOT, 74—76, 78
Sharks, 246, 251
Shellfish, 247, 250—253
Shrimp, 223
Silver gulls, 246, 250
Skin changes, 195
SOCT, 74
Soft corals, 246
Soils, 246—251
Solids-dependent PCB partitioning, 171—176
South Australia, 259
Spain, 221
Sprat, 183, 198, 202
Sprattus sprattus, see Sprat
Stenella coeruleoalba, see Striped dolphin
Sterna paradisaea, see Arctic tern
Stora Vika Cement Plant, Sweden, 117
Striped dolphin, 231—232
Subsurface maximum, 234
Sun Ohio PCBX process, 92—94
Surface waters, 257
Swedish west coast, 254

T

Taichung, 32
Taiwanese incident oil, see also Taiwanese patients; Yucheng patients, 11—13, 27—38
  amounts ingested by patients, 33
  concentrations of PCBs, PCDFs and PCQs in, 10—11
  discovery of PCBs in, 28
  epidemiological studies, 28—31
  gas chromatographic patterns, 12, 13
  PCBs in, 31—32
  PCDFs in, 32—33
  PCQs in, 32—33
  sources, 30
  toxic agents in, 31—33
  toxic agents in blood and tissues, 33—37
Taiwanese patients, see also Taiwanese incident oil; Yucheng patients, 11—14, 20, 21, 28
Tasmania, 260
Terns, 227
Thermal destruction, see Burning
Threshold limit value, 65
Tissue levels of PCBs, 7—8
Tissue levels of PCDFs, 8, 10
Tissue levels of PCQs, 7—8, 37
Tissue retention of PCBs, 34—35
Tissue retention of PCDFs, 35—37
Toxaphenes, 187, 203
Toxic rice-bran oil, see Taiwanese incident oil
Toxic Substance Control Act (TSCA), 64, 87, 99—101, 109—110
Transfer of PCBs and related compounds from mother to fetus or offspring, 16—18
Transformers, 69, 242—244, 259
Trends in PCB levels, 50—56
Trial test burns of PCBs, 103, 105—106, 138
Tributary input of PCBs, 153, 159—160
Triglycerides, 75—76, 78
Trophic index, 246, 250

U

Upper trophic levels, 170
Uria aalge, see Guillemot
U.S. EPA's mobile incinerator, 132—138
U.S. Mussel Watch, 250, 252, 254
Uterine horns, 193, 194
Uterine muscle, 47
Uterine stromas, 194
Uterine tumors, 194—195
Utility company, 69—70, 76

V

Vertical flux and removal processes, 232—233
Vertically migrating fish, 229
Victoria, PCBs in, 247, 249—257, 259, 260

W

Waste PCBs, disposal and destruction of, see Disposal of PCBs
Water Quality Council of Queensland, 246, 248
Waters, 246—251
Western Australia, PCBs in, 256—258
Western Pacific Ocean, 257
Whelping success in mink, 192—193
White-tailed sea eagles, 182—183, 188—190, 204
Whole body burden, 168
Workplace, PCBs in, see also Occupationally PCB-exposed workers, 63—82
  background population levels, 65
  capacitor manufacturing, 74—76
  early studies, 72—73
  electrical equipment manufacturing, 76, 78
  epidemiological studies, post-Yusho, 73—78
  exposure levels, see also PCB exposures, workplace, 65—72
  morbidity studies, 73—76
  mortality studies, 77—78
  nonoccupational studies, 73
  standards for exposures, 65

MONS 006424

utility company, 70
World production, 184
World trend of PCBs, 52—55

Y

Yogurt, 244, 258
Young bird survival, 188
Yucheng patients, see also Taiwanese patients, 28—31, 33—37, 65, 73
Yusho, 1—26, 65, 73
  biological effects of PCBs and their related compounds, 18—21
  biological study of, 13—20
  blood level of PCBs, PCDFs and PCQs in patients with, 2, 8—10, 20
  causal agents, 20—21
  cause of contamination, 6—7
  chlorinated compounds in patients with, 2—11
  distribution of PCBs and their related compounds, 15—16
  PCB components in patients, 13—15
  transfer of PCBs and related compounds from mother to fetus or offspring, 16—18
Yusho oil, 3—7, 9—10, 12—13

Z

Zooplankton, 225, 226, 229—231

MONS 006425