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POSITION PAPER ON

POLYCHLORINATED BIPHENYLS

(PCBs)

For National Air Quality Criteria Adv. Comm
vo Sept 73

U. S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460
JULY 1973

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PREFACE

This document was prepared by a Task Force convened under the direction of John F. Finklea, Director, National Environmental Research Center (NERC). The objective was to review and evaluate the current knowledge of polychlorinated biphenyls (PCBs) released into the environment as related to possible deleterious effects upon human health and welfare, with a view toward the preparation of a control strategy document, should such be required, in consonance with the provisions of the Clean Air Act as amended.

An extensive report prepared by an NIH Panel on Hazardous Trace Substances, chaired by Norton Nelson, served as a primary reference for the position paper. The report entitled "Polychlorinated Biphenyls - Environmental Impact," was published in Environmental Research, Vol. 5, No. 3, dated September 1972. Very recent data and information on PCB's in the marine environment were generously provided by Patrick L. Parker, Office of International Decade of Ocean Exploration (IDOE), NSF; and George R. Harvey, Woods Hole Oceanographic Institution.

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SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

A. Background Summary

Polychlorinated biphenyls (PCBs) have been shown to be toxic; however, the degree of toxicity appears to vary significantly among compounds. Some are highly toxic and others appear to be non-toxic. Some of the chemicals have been found to be contaminated with chlorinated dibenzofurans and chlorinated dibenzodioxins -- both of which are known to be highly toxic. Severe cases of chloracne and acute liver disease have been associated with occupational or accidental exposure to nigh concentrations of PCBs -- either via inhalation, contact, or ingestion with food. Biological experiments have produced similar results. The most serious incident occurred in Japan in 1968 as a result of large-scale contamination of cooking oil. There is an increasing body of evidence that PCBs, which are now widely distributed in the environment, have had a deleterious effect upon certain biological species. Particular attention has been devoted to birds and fish.

Polychlorinated biphenyls are a class of synthetic pollutants which have no known counterpart in the natural environment. The PCBs are manufactured by the chlorination of biphenyl with anhydrous chlorine using iron filings or ferric chloride as a catalyst. Two hundred and ten different chlorine-substituted biphenyls are possible, but the number observed in commercial formulations is much less. In their industrial applications, PCBs are relatively inert, stable chemicals with special dielectric properties. The higher-chlorinated species are nonflammable and have extremely low volatilities. Unfortunately, some of the characteristics which make PCBs so valuable in industrial

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applications also make them highly persistant in the environment.

PCBs were first produced commercially in 1929. They have since been used in many industrial products. The principal applications include: 1) non-flammable hydraulic and lubricating fluids, 2) heat-exchanger and dielectric-fluids, 3) plasticizers for plastics and coatings, 4) extenders for pesticides, and 5) ingredients for caulking compounds, adhesives, paint, printing inks, and carbonless duplicating paper.

The sole producer of PCBs in the U. S., and probably the worlds largest producer, is the Monsanto Company. PCBs also are produced in Great Britian, France, Germany, the U. S. S. R., Spain, Italy, Czechoslovakia, and Japan. Cumulative sales in the U. S., since the introduction of PCBs, are estimated at approximately 5 x 10^5 tons. Estimates for foreign production are not available. Loss to the environment figures are practically non-existent. Rough estimates based upon applications suggest that approximately 20% of the cumulative PCB production is still in service. It is assumed that the remainder has been discharged into the environment by the various routes.

Monsanto Company has restricted the sale of Aroclor based upon consideration of possible contamination of food products, or their ability to control or monitor possible losses into the environment. Since early 1972 sales of the liquid dielectric have been restricted to confined systems; i.e. capacitors and transformers. No sales are made to food processors. Similar controls, to our knowledge have not been established by foreign manufacturers.

Recommended procedure for thermal decomposition of PCBs is by burning in oil suspension with flame temperatures in excess of 1100°C - the products are CO_2, H_2O, and Hcl. Monsanto has established special disposal facilities

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for its customers.

Standard guidelines for handling and disposal of materials containing PCBs used in capacitors and transformers have been published by the National Electrical Manufacturer Association.

An extensive effort has been devoted to the development of methods for the analysis of PCBs and pesticides. Available metodologies are complex and require skilled analysts. Quantification is complicated by the many unidentified compounds in PCB preparation, as well as other contaminants in environmental samples. The principle analytical techniques involve the use of gas chromatography with electron capture detectors and mass spectrometry. Identification is accomplished by a "fingerprint matching" technique using a chromatogram of a known PCB standard. Quantification is accomplished by measuring chromatogram peak areas or peak heights. Sensitivity is about one part per billion; however, the accuracy is rather poor. Estimates of accuracy range from a factor of two to "impossible to quantify with reasonable confidence." A gas chromatogram of a given Aroclor will reveal many peaks, and any given peak may represent a number of different isomers and/or chlorine homologs of chlorinated biphenyls. Once released into the environment, the composition of the commercial preparation will change due to selective chemical and metabolic degradation. It is unlikely, for example, that Aroclor 1254 will be found in any environmental sample. A distribution of PCBs tending to match Aroclor 1254 may be detected. The many problems involved in the sampling and analysis of PCBs are treated in detail in Section IV.

Available evidence indicates that PCBs with a chlorine content of 42% or less are degraded in the environment within a reasonably short period of time -- possibly by microbial action. Higher isomers degrade more slowly. Some recent data indicate that the environmental degradation time for the PCBs with chlorine concentrations greater than 50%, for example Aroclor 1254, is greater than DDT. Laboratory studies conducted by Monsanto have shown that the degradation routes are quite variable depending upon the structure of the PCB. Non-biological degradation in the environment is expected to be slow. The conversion of DDT vapors to PCBs by irridation with ultraviolet light of sunlight wavelengths has been reported but not confirmed.

Environmental transport models for PCBs have not been developed. Conclusions regarding their behavior are based largely upon the results of DDT research. With some modification, models for DDT should be applicable to PCBs. The valadity of DDT measurements prior to 1969 is now being questioned due to the failure to correct for possible contamination by PCBs. The principal transfer routes for PCBs are: 1) aerial, 2) runoff, 3) sediments, 4) leaching from soil, or dumps, 5) uptake by organisms and plants, and 6) food transport. Little is known about specific pollutant dynamics. Recent data indicate that aerial transport is the most efficient route, although river runoff and dumping will contribute more effectively to local contamination. Measurable concentrations of PCBs have been found in rainwater. Recent measurements in the oceans by the Woods Hole Oceanographic Institution reveal that PCBs are widely distributed. No significant horizonal gradients were observed, except in areas where dredge spoils were dumped or in the immediate vicinity of known sources of river runoff. This evidence indicates that aerial transport is dominant. Only very curde estimates of the annual

losses of PCBs to the environment are available. These are: 1) 1.5 - 2.5 x 10^3 tons to the atmosphere, 2) 4-5 x 10^3 tons into fresh and coastal waters, 3) 6.8 x 10^4 tons into dumps and landfills, and 4) 10 tons into the soil as pesticide extenders.

Based upon our experience with DDT, and theoretical considerations, it has been postulated that PCBs would be found primarily on particulates in the atmosphere. Recent data do not support this conclusion. Atmospheric concentrations measured in the vapor phase at Bermuda in February 1973 ranged from 0.2 to 0.5 ng/m^3. No PCBs were found in the particulate analyses conducted during the Bermuda study. However, the sampling technique used does not differentiate conclusively between particulate absorbed and vapor phase PCBs. PCBs have been found in particulate samples taken in urban areas. Similar conclusions were drawn regarding PCBs in the aquatic environment; i.e., that they would be found primarily in the sediment and absorbed on suspended matter. Recent measurements in the North Atlantic by the Woods Hole Oceanographic Institution do not fully support this conclusion. Concentrations reported in solution in the open Atlantic surface waters averaged 35 ppt (parts per trillion).

There are essentially no data available on the concentration of PCBs in the soil. It is expected that the amount would be small, except in the vicinity of dumps and land fills, if the estimates on the use of pesticide extenders are correct. This may not be the case if aerial transport proves to be dominant resulting in wide disposal of emissions from incineration.

Data on the concentration of PCBs in food are sparse. Measurable quantities have been found in fish, milk, and eggs. None have been

found in fruits and vegetables, however, the search has not been extensive.

Based upon the few available measurements made in fresh water, it is estimated that concentrations might range from 0.5 ppt in unpolluted rivers and lakes to 500 ppt in highly polluted water. It is postulated that little or no PCBs will be found in ground water, since it is expected that they would be trapped or absorbed on soil particles. Concentrations ranging from 10 to 100 ppt were reported in tap water in Japan. If absorbed on airborne particulate or soil, it is postulated that there is an oil componentinvolved either from man-made causes or from vegetation, organisms. Similarly, it can be speculated that an oil or fat component in water is the vehicle carrying PCBs. This should be evaluated - particularly in soils and sea water by extracting and analyzing the oil and fat components for chemical hydrocarbons, DDT and PCB like compounds.

The oceans and the soil are probably the primary sinks for PCBs in the environment. PCBs were measured in soil in the Baltimore area. The concentration ranged from 0 to 0.9 ppm. Degradation times for these mediums have not been determined. The persistence of PCBs in the environment should be comparable to DDT. Both DDT and PCBs are relatively non-polar and consequently will not be readily absorbed, unless they have an oil component but also will not be washed out by polar molecules such as water.

Certain marine species are known to concentrate PCBs by factors of 10^4 or greater over that found in the ambient waters. Uptake by phytoplankton has been found to be very rapid. Concentrations of 1-3 ppm have been measured in phytoplankton samples taken from the North Atlantic. The concentrations measured in zooplankton were less than in phytoplankton, and even less in fish. Maximum concentrations found in the ocean environment

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were measured in sea birds - approximately 100 ppm. The chromatogram peaks closely matched that of Aroclor 1254. No evidence of lower isomers (four or fewer chlorine atoms) were found.

Data were only recently obtained from the North Atlantic by the Woods Hole Oceanographic Institution (See Preface). These studies are not yet complete, and the results have not been published. A paper on the sea water analyses has been approved for publication in Science: G. R. Harvey, W. G. Steinhauer, J. M. Teal, Polychlorobiphenyls in North Atlantic Ocean Water, Science in Press (April or May). The results are very significant in that they fail to support important conclusions offered by other investigators concerning the transport and behavior of PCBs in the environment, as well as previously established concepts regarding food chain magnification.

Information regarding toxicity threshold values is limited. PCBs are toxic to some aquatic invertibrates at levels as low as 1 part billion (ppb) in ambient water. As mentioned previously, they are known to be moderately toxic to fish. PCBs apparently are non-toxic to terrestrial insects, but act synergistically to increase the toxicity of several pesticides to insects. Experimental studies have shown that PCB concentrations of approximately 100 ppm adversely effect reproduction in birds and fish. There is suggestive evidence that adverse effects upon wild life populations, particularly birds and fish, may occur as a result of present levels of PCBs in the environment, although such effects are difficult to attribute solely to PCBs, because the wild animals are exposed to other pollutants.

During the Yusho incident in Japan, the minimum estimated toxic intake for humans was 200 µg/kg/day. This is a much higher level than that to which the general population is exposed. FDA has established

a maximum permissible level of 5 ppm in edible portions of fish, 5 ppm in separate milk fat (0.2 ppm in whole milk), and 0.5 ppm in animal feed. The American Conference of Governmental Industrial Hygienists has set a threshold limit value of 1 mg/m^3 for occupational exposure to vapors of Aroclor 1242 and Aroclor 1254.

Only very crude estimates of the mean daily intake for the general population are available. This would be highly variable depending upon the diet. The major intake would probably be from fish, milk, and eggs. Based upon available concentration data in air, water, and food, the mean daily intake for adults would probably be less than 100 µg/day.

Work on uptake, retention, and excretion of PCBs is incomplete. Very little work has been done on metabolism, and few metabolites have been identified precisely. There is circumstantial evidence that lower PCBs (tetrachloro and lower isomers) are metabolized very rapidly in the environment. Evidence suggest that differential metabolism is the primary mechanism in the environmental differentiation of isomers -- outweighing photolysis and mobility. Some higher PCBs appear to be metabolized by birds and mammals. The major storage tissue for PCBs is body fat - approximately 10-100 times the concentrations in other tissues. Mean levels of 1 ppm in human adispose tissue have been reported in the U. S., and Germany; respectively. However, in one study, 50% of the samples were negative.

Evidence regarding teratogenic, carcinogenic, and mutagenic effects of PCBs is incomplete. Little work has been done in these areas.

The Food and Drug Administration has taken action to control the contamination of food with PCBs, and has set temporary tolerances for PCBs in food-packing materials and certain foods. The Department of

Agriculture has taken action to prevent accidently PCB contaminated food from reaching the market. Passage of the Toxic Substance Control Act would provide authority to control import and restrict distribution and uses.

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B. CONCLUSIONS

Commercial production of PCBs began in 1929; however, these chemical compounds were not identified as environmental pollutants until 1966. Considerable research has been devoted to the toxicological properties of PCBs, but many important questions still remain unanswered. Critical research areas have been identified which will require several years for solution. In the meantime, it is important that action be taken to prevent further accumulation of toxic materials in the environment which may adversely effect the biota. Logical conclusions may be drawn from our present knowledge, which may serve as a basis for decisions regarding preliminary control actions. A number of conclusions expressed in the literature on PCBs are based upon extrapolation of our knowledge and experience regarding DDT, while others are well supported with reliable observations and experimental data. Recent data suggest that certain extrapolations based upon DDT properties and behavior may not be valid; therefore the risk of error must be accepted and weighed accordingly. The following conclusions represent the views of the members of the NERC/RTP Task Force on PCBs.

1) Certain PCBs are toxic to humans and certain animal species; however the degree of toxicity varies depending apparently upon the chlorine content of the molecular structure.

2) PCBs are synthetic pollutants with no counterpart in the natural environment; therefore observed environmental concentrations represent solely the contribution from anthropogenic sources. The rate of release of PCBs into the environment has been significantly greater

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than the rate of degradation.

3) PCBs now are widely distributed in the environment. Measurable concentrations have been found in air, water, soil, and biota components.

4) Certain species of marine life may concentrate PCBs by a factor of 10^3 - 10^5. Further concentration may occur within the vertibrate food chain. Concentrations found in sea birds have been 10^7 - 10^8 times greater than those in ambient water.

5) The principal exposure route for humans is via food -- primarily fish in the diet. Intake via air and water are small in comparison, except in cases of contamination or occupational exposure.

6) Reliable threshold values for PCBs have not been determined. The FDA has set an acceptable intake of 0.175 to 1.4 mg/day for an adult. The population involved in the Yusho incident in Japan had an intake of 200 µg/kg/day or greater. PCBs are moderately toxic to some marine invertibrates at concentrations as low as 1 ppb in ambient water. Growth of phytoplankton is inhibited at levels of 10-100 ppb.

why do they combine the results with more comparable units?

7) Reliable degradation times for PCBs in the environment have not been determined; however, there is some evidence that at least for some isomers, it may be greater than for DDT.

8) Lower isomers (tetrachloro and lower) appear to be degraded rather rapidly in the environment. Some pentachloro and hexachloro isomers appear to be metabolized by birds and mammals, but the metabolites have not been identified.

9) Work on teratogenicity, mutagenicity, and carcinogenicity is incomplete. Conflicting results have been obtained.

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10) The long term health and environmental effects of PCBs have not been clearly established. A decrease in certain bird and fish populations has been associated with PCBs.

11) Present PCB concentrations in ambient air do not pose a direct threat to human health and welfare; however, the total concentration accumulated in the environment does pose a threat to some components of the ecosystem.

12) Prudent action should be taken to control the further release of toxic PCBs into the environment. Priority should be given to the prohibition of the use of toxic PCBs in non-confined systems whose primary disposal route probably would be through open-burning dumps or other inefficient or uncontrolled incineration processes.

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C. Recommendations

Voluntary actions have been taken by Monsanto Company to restrict their sales of PCB and PCT formulations for use only in closed hardware systems--such as transformers and capacitors. Further, Monsanto has voluntarily withdrawn future sales to food processing plants and for paper and other applications that might contaminate the environment or result in exposure to persons using such products. These actions are highly commendable, but unfortunately do not eliminate the problem of long term effects that may result from PCBs which have already been released to the environment, or that may be released in the future through other routes which are not currently controlled. Manufacturers in several countries are continuing to produce and distribute PCBs without restrictions such as those imposed by Monsanto. Reliable estimates of the amount of PCBs produced by these countries, and the amount released into the environment is not known. Production, distribution, and disposal data should be obtained for all sources, foreign and domestic. It is recommended that action be taken to impose appropriate restrictions on all import items containing toxic PCBs. Control actions, such as those voluntarily imposed by Monsanto Company, should be formalized by responsible Federal authorities to ensure compliance by other manufacturers and users. PCBs should be restricted to essential non-replaceable uses. Estimates are that approximately 10^7 tons of PCBs and PCTs have been marketed in the U. S. since 1929. Only crude approximations have been made regarding the losses to the environment. We do not know the

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extent of the present environmental burden, nor do we know whether or not the trend is upward or downward. Only approximations have been made on how these chemicals are now distributed in the environment. They have been found in water, air, soil, and biological tissue; however, except for the biological tissue samples, the number of measurements have been extremely limited. In short, we really do not know the magnitude of the problem.

Information on the characterizations of PCBs in the atmosphere is very limited. Efforts to determine whether or not PCBs in the atmosphere are primarily in the vapor or particulate phase should be given a high priority, since this impacts directly on questions regarding the effects upon human health and ecosystems, the form of transport models, and control decisions.

Recent data indicate that aerial transport of PCBs is dominant. A high priority should be given to the verification of this postulate. Should this prove to be true, it would indicate that a significant portion of the environmental burden of PCBs was emitted by inefficient or uncontrolled incineration and vaporization.

The discharge into aquatic environments of waste items or materials containing toxic PCBs should be prohibited.

An adequate model to predict the future environmental impact of PCBs should be developed, and the monitoring system for environmental pollutants should be expanded to include PCBs, as well as more toxic materials such as chlorinated dibenzofurans and dibenzodioxins that may be important contaminants of PCBs.

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The problem of PCBs further emphasizes critical weaknesses in our research capability or objectives. The difficulties inherent in extrapolating from laboratory experiments to the ambient environment, from animal experiments to human response, from laboratory model ecosystems to field systems, and the myriad of problems associated with the determination of cause and effect, are common to most all pollutants. A concerted effort should be made to analyze and improve our position in this regard.

A system is urgently needed to identify potential pollutants which may have an adverse effect upon the environment and human health and welfare before such materials are produced and distributed in large quantities. A vast number of new synthetic products are introduced each year. An effective testing and screening system would minimize the risk of widespread, and possibly irreversible damage.

Research efforts on emissions control technology for polychlorinated biphenyls should initially be concerned with characterization of emission streams. Better data are needed on emission rates of PCB's to the atmosphere from the various sources that are suspected of being significant.

PCBs are synthetic pollutants which are now widely distributed in the environment. Solutions to problems relative to this class of pollutants will require a well coordinated multidisciplinary research effort on a national and international scale and will involve a number of Federal and Regional agencies. It is recommended that EPA conduct a core research program designed to determine the magnitude

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of the PCB environmental problem, and the effectiveness of current voluntary control actions, in order that prudent decisions regarding further control requirements might be made as early as practicable. The scope of the overall research effort would be altered depending upon the results obtained from the initial effort. It may be feasible to incorporate, at a minimum cost, PCB studies into ongoing research programs in EPA and other Federal Agencies, particularly in those programs involving ambient environmental monitoring. A number of recommended research projects are listed in Table S-1. An effort was made by the Task Force to order the recommended research projects in terms of priority relative to the specific problem of PCBs in the environment and the need for control. In an effort to encourage close interagency coordination, and where feasible active participation, suggested interested agencies are indicated for each project.

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Table S-1

RECOMMENDED NEW RESEARCH

Task Description	Priority*	Years to Complete	Agency Coordination
1. Conduct a detailed international inventory of PCB products and uses, and the amount released to the environmental stratified by source.	1	1	Dept. of Commerce Dept. of State WHO
2. Determine a preliminary estimate of the present and predicted environmental burden, the principal environmental sinks, and residence times for PCB's.	2	3	NSF NOAA WHO USDA U.S. Navy U.S. Coast Guard Dept. of Interior
3. Conduct an ambient survey of selected urban areas to determine the distribution and effects of PCBs in air, soil, and water. Consideration should be given to including PCBs in the Regional Air Pollution Study in St. Louis.	1	2	NSF NIEHS Dept. of Interior
4. Determine the partioning of PCBs between the vapor phase and the particulates in the atmosphere; between water and sediment; and the biota uptake. Determine PCBs in organic components in water including oil and sewage pollutants.	1	3	NSF NOAA Dept. of Interior USDA
5. Develop a reliable routine procedure for sampling and measurement of total PCBs in the atmosphere, dustfall, precipitation, soil, water, and biological tissue.	1	2	NBS NIEHS FDA NOAA NSF USDA

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*Recommended priorities are based upon a scale of 1 to 4.

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Table S-1 (Continued)

RECOMMENDED NEW RESEARCH

Task	Description	Priority*	Years to Completion	Agency Coordination
6.	Develop sensitive techniques for analysis of highly toxic PCDD and PCDF.	3	2	NSF NBS, FDA NIOSH
7.	Establish standards and quality control procedures for sampling and analysis of PCBs in food and biological tissues.	3	3	NBS FDA NIOSH WHO
8.	Conduct a detailed study of the qualitative and quantiative composition of large composite airborne particulate samples for the various industrial members of the various families of organohalo compounds.	4	2	NSF NBS
9.	Determine the PCB human body burden levels in high exposure situations and in relatively clean areas for control.	2	2	NIEHS NIOSH WHO FDA
10.	Conduct a study using available evidence of human exposure (occupational or accidental) involving PCBs, PCTs, and contaminants such as PCDD and PCDF and related chemicals, to determine direct or synergistic efforts relative to cancer, teratogans, mutagens, chloracne, and hepatomas and other adverse liver effects.	1	3	NIEHS National Cancer Institute NIOSH FDA WHO
11.	Conduct studies using primates to determine acute and chronic effects, to simulate Yusho effects and to attempt to duplicate the increase in the occurrence of gastric cancer reported in Yusho victims.	3	3	NIEHS National Cancer Institute NIOSH FDA WHO

*Recommended priorities are based upon a scale of 1 to 4.

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Table S-1 (Continued)

RECOMMENDED NEW RESEARCH

Task	Description	Priorities*	Years to Completion	Agency Coordination
12.	Conduct studies to determine products of microbial PCB metabolism and their effects upon selected climates of the ecosystem.	3	3	USDA Dept. of Interior NOAA
13.	Sample and analyze for both gaseous and particulate PCB's (i.e., as condensation aerosols or as adsorbates on other particulates) from (a) combined ventilation gases from a PCB manufacturing plant; (b) stack gases from a PCB waste incinerator; (c) ventilation gases from a capacitor assembly plant; (d) ventilation gases from a transformer assembly plant; (e) stack gases from two or more sewage sludge incinerators, and (f) stack gases from two or more municipal incinerators. Sampling to be done both before and after any existing emissions control devices (e.g., fly ash scrubbers at municipal incinerators).	2	1	

*Recommended priorities are based upon a scale of 1 to 4.

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I. INTRODUCTION

The purpose of this document is to summarize the current knowledge regarding polychlorinated biphenyls (PCBs) in relation to their effects upon human health and welfare, and the environment; and to evaluate this knowledge base with a view toward the need to control the release of PCBs into the environment.

Sources of PCBs and their subsequent concentrations, transport, and behavior in the environment are reviewed. Sampling and analytical techniques are examined in order that the validity of the available data may be evaluated. Toxicological and epidemiological appraisals are presented and estimates of threshold values are stated when justified by available data. The total human body burden results from intake via breathing ambient air; and ingestion of water, and food. The relative importance of these intake routes are examined. Food chain magnification of PCBs may have an important impact upon human health and certain ecosystem components. Data are presented which reflect our knowledge, or lack thereof, concerning this aspect of the problem as related to human body intake, and the biological effects upon man and other species.

The status of technology applicable to the control of the release of PCBs into the environment is assessed. Monsanto Company, the principal producer of PCBs in the United States has voluntarily restricted the sale of PCBs for certain applications which do not involve closed systems. The Company also makes available to its customers a disposal facility for closed-system products. This should result in a decrease in environmental

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contamination by PCBs. The effectiveness of this approach coupled with other control techniques is discussed.

Specific research projects are recommended where significant knowledge gaps have been identified. These research projects would be designed to provide the knowledge required for control decisions at the earliest practical date.

The references cited in this document do not constitute a bibliography on the subject of PCBs. The information presented in the report prepared by the NIH Panel on Hazardous Trace Substances, which served as a primary reference, was accepted as being representative of the current state of knowledge unless contradicted by later data, or unless there was a difference in professional opinion by members of the NERC/RTP Task Force. These differences are specifically noted in the text of this document.

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II. ENVIRONMENTAL APPRAISAL

A. Environmental Sources and Physical Effects

1. Sources

Monsanto Company is the sole producer of PCBs in the U. S. Production figures for the period 1957 thru 1972, with estimated values for 1973, are shown in Table II-1.

Although loss figures for PCBs are practically nonexistent, a number of possible routes into the environment do exist. These include:

· Spills and losses during manufacture - Production of PCBs began in 1929 and since then total cumulative sales in North America through 1970 has been about 500,000 tons. Spills and losses are a part of all manufacturing operations.

· Leaks from sealed systems - Major sealed systems are electrical capacitors and transformers, and heat exchangers. Presently, almost all industrial capacitors contain PCBs. Two important types are phase correction capacitors on power lines and ballast capacitors for fluorescent lighting. Phase correction capacitors have been developed to the point that failures are considered negligible (1). Because of fire and explosion hazards, many distribution type transformers, especially those installed underground, use PCB liquids and other askarels. The use of PCBs as heat transfer fluids is mainly because of their fire resistance.

· Leaks from partially sealed systems - Such systems mainly make use of PCBs as nonflammable hydraulic fluids and lubricants.

· Vaporization or leaching from PCB-plasticized products - A multitude of products contain PCBs as a plasticizing agent. These include various plastics, adhesives, sealing and caulking materials, and surface coatings.

Table II-1

PCB MANUFACTURE AND SALES

MONSANTO INDUSTRIAL CHEMICALS COMPANY

1957 thru 1964

(Thousands of Pounds)

	1957	1958	1959	1960	1961	1962	1963	1964
U.S. PRODUCTION	(1)	(1)	(1)	37919	36515	38353	44734	50833
DOMESTIC SALES (LBS.)	32299	26061	31310	35214	37538	38043	38132	44869
U.S. EXPORT SALES	(2)	(2)	(2)	(2)	(2)	(2)	3647	4096
DOMESTIC SALES BY CATEGORY								
Heat Transfer	-	-	-	-	-	157	582	929
Hydraulics/Lubricants	1612	1549	2685	2523	4110	3915	3945	4374
Misc. Industrial	704	755	1569	1559	2114	1681	1528	1692
Transformer	12955	5719	5984	7921	6281	7984	7290	7997
Capacitor	17028	14099	16499	16967	15935	15382	15606	19540
Plasticizer Applications	(1)	3939	4573	6244	9098	8924	9181	10337
Petroleum Additives	-	-	-	-	-	-	-	-
DOMESTIC SALES BY PCB GRADE								
Aroclor 1221	23	16	254	103	94	140	361	596
Aroclor 1232	196	113	240	155	241	224	13	13
Aroclor 1242	18222	10444	13598	18196	19827	20654	18510	23571
Aroclor 1248	1779	2559	3384	2827	4023	3463	5013	5238
Aroclor 1254	4461	6691	6754	6088	6294	6325	5911	6280
Aroclor 1260	7587	5982	6619	7330	6540	6595	7626	8535
Aroclor 1262	31	184	359	326	361	432	414	446
Aroclor 1268	-	72	102	189	158	210	284	190
Aroclor 1016	-	-	-	-	-	-	-	-

(1) Production figures and Plasticizer Applications figures unavailable during year indicated.
(2) U.S. Export Sales figures unavailable during year indicated.

(3) Source - Monsanto Company

Table II-1 (Continued)

PCB MANUFACTURE AND SALES

MONSANTO INDUSTRIAL CHEMICALS COMPANY

1965 thru 1972

(Thousands of Pounds)

	1965	1966	1967	1968	1969	1970	1971	1972	Est. 1973
U.S. PRODUCTION	60480	65849	75309	82854	76389	85054	34994	38600	
DOMESTIC SALES (LBS.)	51796	59078	62466	65116	67194	73061	34301	26408	
U.S. EXPORT SALES	4234	6852	8124	11231	10624	13651		6388	
DOMESTIC SALES BY CATEGORY									
Heat Transfer	1237	1766	2262	2529	3050	3958	3060	752	
Hydraulics/Lubricants	4616	4258	4643	5765	8039	7403	1552	0	
Misc. Industrial	1841	1779	1426	1283	1079	1627	1155	0	
Transformer	8657	8910	11071	11585	12105	13828	11134		
Capacitor	23749	28884	29703	29550	25022	26708	14141	25676	30000
Plasticizer Applications	11696	13481	13361	14404	16460	19537	3259	0	
Petroleum Additives	-	-	-	-	1439	-	-	0	
DOMESTIC SALES BY PCB GRADE									
Aroclor 1221	369	528	442	136	507	1476	2215	171	100
Aroclor 1232	7	16	25	90	273	260	171	0	0
Aroclor 1242	31533	39557	43055	44853	45491	48588	21981	728	900
Aroclor 1248	5565	5015	4704	4894	5650	4073	213	807	0
Aroclor 1254	7737	7035	6696	8891	9822	12421	4661	3495	5000
Aroclor 1260	5831	5875	6417	5252	4439	4890	1725	305	0
Aroclor 1262	558	768	840	720	712	1023	1	0	0
Aroclor 1268	196	284	287	280	300	330	-	0	0
Aroclor 1016	-	-	-	-	-	-	3334	20902	24000

· Disposal of waste PCBs and materials containing PCBs - Disposal can take many forms: incineration, open burning dumps, discharge into sewers or directly into water systems, and use as antidusting agents on roads and as pesticide extenders. PCBs were detected in incinerator residue fines, incinerator fly ash, and compost samples. Efficiently operated high temperature incinerators will destroy PCBs. Anything less will result in various degrees of vaporization and/or leaching.

2. Gross Loss Estimates

The distribution of PCBs into the environment is based largely on deductive reasoning and provide at most order-of-magnitude estimates.

(a) Annual Loss Estimates - Annual loss estimates based on 1970 production (33,000 tons) are as follows (2):

From sources	tons/year
· Manufacturing	not estimated
· Spills, leaks and disposal of hydraulic fluids, lubricants, and heat-transfer and transformer oils	4000 - 5000
· Evaporation of plasticizers	1000 - 2000
· Disposal (especially ballast capacitors) in incinerators, dumps, and sanitary landfills	22,000

Into the environment

	tons/year
· Atmosphere	1500 - 2500
· Fresh and coastal waters	4000 - 5000
· Dumps and landfills	18,000

(b) Cumulative Loss Estimates - Over the period 1930-1970 cumulative

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sales of PCBs in North America were about 500,000 tons. Estimated losses into the environment for this same period are as follows (2):

· Atmosphere	30,000 tons
· Fresh and coastal waters	60,000
· Dumps and landfills	300,000

3. Future Losses

In September, 1970, Monsanto, the sole U. S. producer of PCBs, voluntarily restricted sales to closed system applications, primarily electrical capacitors and transformers (2). Furthermore, sales will be restricted mostly to PCBs containing 4 chlorine atoms or less; some evidence indicates that the lower isomers more easily decompose. To meet the problem of scrap disposal for their customers, Monsanto has also set up a disposal system with a capacity of 4500 tons per year.

Assuming close cooperation between Monsanto and its customers, the combination of restricted sales and an available disposal system should result in future PCB losses being reduced to a minimum. The results of these actions should be monitored closely.

4. Physical Effects

Since PCBs are highly stable, chemically inert compounds, they should have no effect on non-biological matter.

B. Concentrations

1. Air

Measurements of PCB levels in air for all practical purposes do not exist. One researcher (3), however, has reported that air over Bermuda in February 1973 contained 0.2-0.5 ng/m^3 - all in the vapor phase. No PCBs were detected on the particulate matter.

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2. Water

(a) Fresh Water - Scattered PCB measurements have been made on fresh water samples, mainly from relatively polluted rivers and bays (2). Industrial rivers in Maine, Massachusetts, Wisconsin, and Japan contained levels ranging from 200 to 2800 ppt. Levels in Green Bay and Milwaukee Harbor, Wisconsin, ranged from 20-120 ppt. Tap water in Kyoto, Japan contained 10-100 ppt PCBs.

(b) Sea Water - Few measurements of PCBs in sea water have been made. Harvey (3) found that surface levels of PCBs in the North Atlantic averaged 35 ppt; at depths of 200 meters PCB levels averaged 10 ppt. PCBs measured in northeast U. S. coastal surface waters ranged from 50-4150 ppt (3). North Atlantic open ocean samples ranged from 10-150 ppt. Nearshore Pacific Ocean samples average 1 ppt PCBs.

3. Soil

No measurements of PCB levels in soils have been reported. Unlike insecticides, however, PCBs will be distributed primarily around industrial areas, unless aerial transport proves to be dominant.

4. Food

The FDA has analyzed raw agricultural commodities sampled under the pesticide surveillance program for PCBs. PCBs were encountered most frequently in fish. Some results are presented in Table II-2.

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Table II-2

PCBs in Selected Food Commodities
7/1/70 to 9/30/71 (7)

Commodity	No. of Samples Examined	No. of Samples Positive	Percent Positive	PCB Levels (ppm) Low	High	Average
Fish	670	363	54	T*	35.29	1.87
Cheese	1344	91	6	T	1.00	.25
Milk	941	69	7	T	27.80	2.27
Shell Eggs	550	161	29	T	3.74	.55
Fish Byproduct	--	13	--	T	5.00	1.17
TOTAL (Excluding Fish Byproducts)	3505	684	19			1.14

* T indicates "trace."

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C. Transport and Modeling

Once sufficient data on PCBs becomes available, transport models must be developed to describe the global distribution of these pollutants. The main function of these models will be to provide a mass balance for PCBs in order that the emission of these substances into the environment can be related to the various transformations that these pollutants undergo and to the ultimate fate of these substances. The models developed must be able to account for the present levels of these pollutants and must be able to predict the impact that may be caused by a change in input. In addition, these models must be able to assess the long-term effects that these substances may have on the environment.

A necessary input into these models will be the rates of emission of PCBs into the environment. While the major paths by which PCBs enter the environment are known, definitive measures of the total loss of PCBs by the various escape routes is unknown. Accurate and up-to-date measurements of the rate of loss of these substances into the environment and the distributions of these emissions among the various compartments of the environment are needed before PCBs can be modeled.

The transport of PCBs through the atmosphere is subject to speculation. Nisbet and Sarofin in the Nelson Report (2) assume that PCBs behave like DDT. The transport mechanism they postulate for PCBs is analogous to that proposed for DDT. They assume that the vaporized PCBs, discharged from urban areas, are absorbed on particulate surfaces and transported with the prevailing winds. The PCB-containing particulates are then

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deposited on land or water by particle sedimentation or rain-out. If this mechanism is correct, large amounts of the PCBs may be absorbed on particulate surfaces. The half-life of these particulates in air will depend greatly on size and the amount of atmospheric precipitation. The large particles will be deposited near the source and only the fine particulates will be transported to remote areas.

Nisbet et. al. further assume that the PCBs deposited in the soil will continue to vaporize into the atmosphere, reattach themselves to particulates, and be redeposited until eventually they reach the coast. Additional amounts of PCB can be expected to be deposited in the ocean through dumping or leakage from ships and small quantities deposited in rivers may eventually find their way to the ocean. This latter contribution is expected to be small since the solubility of PCBs in water is so low that most of the deposited material will be absorbed in the sediment at the bottom of lakes and rivers and will not be transported further.

Not only is there some doubt as to whether or not PCBs are analogous to DDT, but there is also some doubt as to whether the transport mechanism postulated for DDT is correct. There is some evidence to suggest that substantial quantities of DDT released into the atmosphere may be transported in the gas phase rather than on particulate surfaces. If this is the case, even if PCBs should be analogous to DDT, the main aerial transport route of these pollutants may not be by attachment to particulates.

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If the transport of PCBs through the atmosphere does occur on particule surfaces, particulate samples collected from the atmosphere should contain large amounts of PCBs. Some PCBs have been detected in selected samples of total suspended particulates collected in urban areas. However, in general, PCBs are usually not detected in most particulate samples. This indicates that the main aerial transport route of PCBs may not be by attachment to particulates.

G. R. Harvey et al. (3) have uncovered other evidence to suggest that PCBs are not transported through the atmosphere on particulate surfaces. The data collected by these researchers from the waters of the Atlantic Ocean strongly suggest that PCBs are transported freely in the atmosphere. These workers found that there is no significant concentration gradient of PCBs in ocean organisms with distance from shore indicating that coastal dumping or runoffs from fresh water bodies are not significant transport routes of PCB's. In addition, as many PCBs was found in waters off the poorly developed countries of the Southern Hemisphere as in waters off the highly industrialized countries of the Northern Hemisphere. Because the half-life of particulates is short due to rain-out and because PCB is usually undetectable in marine air particulate samples, these workers believe that their data can only be explained by assuming that PCBs are transported with an air mass in the vapor phase. More atmospheric measurements of PCBs from both gas phase samples and particulate samples collected in remote areas are necessary before this theory can be accepted.

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Once transport mechanisms have been developed for PCBs, it will be necessary to determine the ultimate fate and degradation products in order to model these pollutants. The following sinks should be considered for the PCBs:

1) Dissolution in the oceans

The evidence presented by Harvey indicates that significant quantities of PCBs are deposited in the oceans. There is strong evidence to indicate that quantities of PCBs are also taken up by marine life.

2) Washout by rain

In urban areas where loading of total suspended particulates is high, large quantities of PCBs may attach themselves to particulates and subsequently be washed out near the source of entry.

3) Microbiological utilization at the earth's surface

There is evidence to indicate that the lower isomers of PCBs may be efficiently degraded by microorganisms.

4) Metabolism

The higher isomers of PCBs appear to be readily taken up by animal life. In Monsanto, experiments lower chlorinated homologs present in all products were preferentially excreted and/or metabolized.

5) Uptake by soil and plants

No studies have been made to determine the importance of soil and plants for the uptake of PCBs. It is anticipated, however, that such a sink for these pollutants would be of minor importance.

6) Photochemical and/or thermal reactions in the lower atmosphere

Very little information on the chemistry of PCBs is available. Hutzinger et al. (4) have studied the photolysis of a number of

PCBs in hexane. They found that 67% of 2,2', 5, 5' tetrachlorobiphenyl reacted with irradiated at 3100 Å in hexane. Both dechlorination and formation of polymers occurred. From the results of their studies they concluded that higher isomers of PCBs are more easily broken down than lower isomers. It is difficult to extrapolate the results of this solution study to gas phase reactions that may be occurring in the atmosphere.

Only the scantiest information is available for gas phase photolysis of PCBs. In a preliminary investigation Lillian (6) studied the photolysis of 1.5 ppm of a low isomer of PCB in air at 3100 Å. This researcher found that all of the PCB disappeared after 48 hours of irradiation. To date, the decomposition products of this photolysis have not been determined. Much more work in this area must be undertaken before conclusions can be drawn regarding the chemistry of PCBs in the lower atmosphere.

7) Primary degradation

The rate of primary degradation increases as the degree of chlorination of the Aroclor product decreases (5).

8) Escape from the tropopause into the stratosphere

If chemical reactions in the lower atmosphere are unimportant sinks for PCBs and if it is determined that aerial transport of these pollutants occurs in the gas phase, it is possible that these potentially long-lived species could diffuse into the upper atmosphere. Because of the highly reactive species present in the stratosphere, such as single oxygen, chemical reactions in the upper atmosphere, could be a sink for substantial amounts of PCBs.

Once the emission rates, transport phenomena and sinks for PCBs have been established, a global transport model can be developed to assess the impact of these substances on the environment. If PCBs

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are transported through the atmosphere on particulate surfaces, it should be possible to use the models developed for DDT, with slight modifications, to describe the fate of PCBs. If it is determined that gas phase aerial transport is the predominant transfer mode for PCBs, these pollutants can then be modeled using the techniques developed to describe the diffusion of other gas phase pollutants. No modeling can be attempted until it is determined whether the PCBs are transported through the atmosphere in the gas phase or by attachment to particulate matter.

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5. Monsanto Company, Presentation to the Interdepartment Task Force on PCBs. Washington, D. C. May 15, 1972.

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III. BIOLOGICAL EFFECTS

A. Human Health

1. Introduction

Toxic properties of the widely used groups of industrial chemicals, chlorinated bi and terphenyls (PCB and PCT) follows well defined patterns in humans. These chemicals are widely disseminated in our environment and are also present in some of the foods we eat (1,2). In the body, these chemicals reside primarily in the adipose tissue where the mean level is approximately 1 to 2 ppm (5). At these levels, any observed chronic effects are masked by the chronically similar pesticide DDT and its metabolites that are present in fatty tissues in amounts 3 or 4 times greater than PCB and PCT.

Our most reliable information on the human effects has been developed from documented exposures of 1001 Japanese to rice oil contaminated with a chemical grade of PCB and PCT. This rice oil used as a cooking oil and salad dressing contained up to 2000 ppm of PCB and PCT. Results from epidemiology studies on this incident occurring in Yusho Japan are in three reports issued by a medical group from Kyusho University (9-19,22).

The symptoms observed in those afflicted were similar to those reported in occupational exposures to chlorine and its compounds. Chlorace, skin and darkening and abnormal eye discharge were observed in infants, children and adults. Those symptoms abated slowly and residual effects are still apparent four years after exposure. Some

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concern has been expressed for delayed effects such as gastric cancer that has been reported in several of those afflicted (25). Whether those incidents being reported on gastric cancer are above the average rate for the Japanese population as a whole remains to be determined. At any rate persons and communities receiving subacute and acute levels of these chemicals should be carefully observed for periods of at least 5 years to determine the possible development of latent effects. PCB ingestion experiments on Rhesus monkeys produced gastric hyperplasia (9).

It is recognized that the acute levels of PCB and PCT are high for both animals and humans. For rats, the acute toxic level range between 5-10 g/kg of body weight.

Ingestion of PCBs have produced embryotoxicity in both animals and humans.

Interference with reproduction has been observed in chickens (8 ppm in foods) and fish (0.9 ppb) in water.

In humans, two stillbirths occurred in 13 cases of pregnancy in the Yusho incident and marked skin pigmentation and eye discharge were observed in 11 infants from Yusho afflicted mothers.

Impurities in commercial grades of polychlorinated biphenyls such as chlorinated dibenzofurans complicate efforts to obtain accurate toxic levels of these chemicals, particularly at the higher exposure levels.

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A. Animal feed establishments.

Under 21 CFR Part 3, the rule making includes the following provisions:

1. Coatings or paints for use on the contact surfaces of feed storage areas shall not contain PCB's.

2. New equipment or machinery for handling or processing feed in or around an animal feed producing establishment shall not contain PCB's.

3. The management of establishments producing animal feed shall eliminate to the fullest extent possible commensurate with current good manufacturing practice the following: heat exchange fluids formulated with PCB's, any PCB-containing feed contact surfaces and lubricants, and any other PCB-containing materials that reasonably could be expected to cause animal feed to become contaminated with PCB's. The management of such establishments shall eliminate the use of any feed-packaging material containing PCB's in excess of 10 ppm. Paper feed-packaging material containing PCB's in excess of 10 ppm can be used, provided this material is separated from the packaged feed by a functional barrier impermeable to PCB migration.

4. The use in these establishments of electrical transformers and capacitors that contain PCB's are not expected to cause the contamination of animal feed in these establishments and are exempt from the above-mentioned provisions.

B. Food-packaging material establishments.

Under 21 CFR Part 3, the rule making includes the following provisions:

1. New equipment or machinery for manufacturing food-packaging material shall not contain or use PCB's.

2. The management of establishments manufacturing food-packaging material shall eliminate to the fullest extent possible commensurate with good manufacturing practice the following: heat exchange fluids formulated with PCB's and any other PCB-containing materials that reasonably could be expected to cause food-packaging material to become contaminated with PCB's.

3. Electrical transformers and capacitors that contain PCB's are not expected to cause the contamination of food-packaging material in these establishments and are exempt from the above-mentioned provisions.

C. Food establishments.

Under 21 CFR Part 128, the rule making includes the following provisions:

1. New equipment, utensils, and machinery for handling or processing food in or around a food plant shall not contain PCB's.

2. The management of food plants shall eliminate to the fullest extent possible commensurate with good manufacturing practice the following: heat exchange fluids formulated with PCB's, any PCB-containing food-contact surfaces and lubricants, and any other PCB-containing materials that reasonably could be expected to cause food to become contaminated with PCB's. The management of such

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establishments shall eliminate the use of any paper food-packaging material containing PCB's in excess of 10 ppm. Paper food-packaging material containing PCB's in excess of 10 ppm can be used, provided this material is separated from the packaged food by a functional barrier impermeable to PCB migration.

3. Electrical transformers and capacitors that contain PCB's are not expected to cause the contamination of food in these establishments and are exempt from the above-mentioned provisions.

D. The amendment to food additive resulation 121.2546 does not allow the use in food-packaging material of pulp from industrial waste or salvage that bears or contains any poisonous or deleterious substance which is retained in the recovered pulp and that migrates to the food.

E. Temporary tolerances are established under the authority of section 406 of the Federal Food, Drug, and Cosmetic Act the establishment of temporary tolerances for PCB's would permit unavoidable PCB residues in paper food-packaging material and in certain foods. These temporary tolerances are established for a sufficient period of time to permit the elimination of such contaminants at the earliest practicable time and are based on currently available information regarding the toxicity and the analytical behavior of PCB's, and the background levels of PCB's in these products. Where appropriate and necessary, new or additional information on PCB toxicity, analytical behavior, and background levels may serve as the basis for changing the temporary tolerances. These tolerances are

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established because the FDA recognizes that total, immediate elimination of PCB's in these articles is not possible and that controls in uses of PCB's will reduce unavoidable contamination of foods. The temporary tolerances, expressed as parts per million, to be included in a new Part 122 are as follows:

(1)	Milk (Fat basis)	2.5
(2)	Dairy products (Fat basis)	2.5
(3)	Poultry (fat basis)	5.0
(4)	Eggs	0.5
(5)	Complete and finished animal feeds	0.2
(6)	Animal feed components	2.0
(7)	Fish and shellfish (edible portion)	5.0
(8)	Infant and junior food	0.2
(9)	Paper food-packaging material	10.0

The tolerance for paper food-packaging material shall not apply to such material separated from the packaged food by a functional barrier impermeable to PCB migration.

The Food and Drug Administration will provide upon request the analytical methods it will use for enforcing the temporary tolerances (11).

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2. Exposures to PCB

a. Food

Twenty-two of 720 composite samples from the FDA's market-basket surveys have contained PCB's ranging in concentrations from a trace to 0.36 ppm (1). The 0.36 ppm value was caused by migration of PCB from grayboard containers and dividers into packaged shreaded wheat. Estimates of the mean daily intake of PCB's in the American diet range from 5 to 10 µg/day. PCB occurrence in certain foods is shown in Table III-1.

Long-term effects upon human health from exposure to low levels of PCB's have not been studied extensively. An intake of 1-3 µg/kg/day has been suggested as a safe level. A daily intake of 1 µg/kg is thought to be 1/100 of the smallest "no effect" dose found in animals (2,2a,2b). The acceptable daily intake for an adult set by the Food and Drug Administration (FDA) is from 0.175 to 1.4 milligrams/day (2a).

The description of the rule making published by the FDA included a number of significant control measures. The following is an extraction from reference 2a.

It is evident that PCB residues are found most consistantly in fish, and that the concentrations of the material in fish vary substantially. In a study being conducted by the Department of Public Health, State of Michigan, the PCB concentration was higher than the DDT concentration in most all fish analyzed from the Great Lakes.* Thus, it is possible that individuals consuming above the average amounts of fish could have a dietary intake of PCB several times greater than the estimated mean of 5-10 µg. In addition, reported instances

*Unpublished data

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Table III-1 (1a)

	Number of samples examined	Number of samples positive	Percent positive	Low	PCB levels (ppm) high	Average
Fish	670	363	54	T	35.29	1.87
Cheese	1344	91	6	T	1.0	.25
Milk	941	69	7	T	27.8	2.27
Shell eggs	550	161	29	T	3.74	.55
Fish by-product	--	13	--	T	5.0	1.17
Total (excluding fish by-product)	3505	684	19			1.14

Above results reflect both surveillance and compliance*samples. Average residue levels do not include values indicated as "trace." T indicates "trace", which in normal analyses would be less than approximately 0.1 ppm fish; 1-1.5 ppm milk or cheese fat; 0.2 ppm eggs.

*Compliance samples reflect followup of violative samples hence biased towards high levels.

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of local contamination of food products by PCB could have resulted in large intakes of PCB's by individuals consuming the food. The one known human epidemic of PCB poisoning was caused by an episode of local contamination of rice oil by PCB's leaking from a heat exchanger.

b. Air Inhalation

Measurements of PCB's in the air are limited at this time. There is varying opinion as to the physical state of the material in the air (i.e. liquid or solid particulate versus vapor). In any event intake from the air can be calculated when the concentration in the air are known. If PCB's are present in the atmosphere as particulates, retention of the material in the lung would depend in part on the particle size distribution of the aerosol.

3. Absorption

There are no data which defines the relative efficiencies of absorption of PCB's from the human gastro-intestinal tract and lung. Since it is more likely that PCBs exist in the atmosphere as monomolecular vapors, a study needs to be initiated on the effectiveness of the lung as a scavenger of airborne PCB's.

a. Distribution and Metabolism

There is no accurate information on the distribution among various tissues and metabolism of PCB in humans. However, in rats fed a single 1600 ppm dose of Aroclor 1254, the PCB was found in all tissues examined 24 hours later. In order of descending concentration, the material was present in fat, kidney, liver, brain, muscle, lung and plasma. In chronic feeding experiments, rats fed 100 ppm of Aroclor 1254 in the diet continued to cumulate PCB in body fat for the 240 days of the study. In another experiment in which the feeding of PCB was continued for

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58 days, the concentration of PCB in the fat dropped 20% in 71 days after the cessation of PCB in the diet. Unfortunately, similar data for other tissues were not reported (3).

4. Excretion

Information concerning the excretion of PCB's by humans is currently not available.

5. Human Tissue Concentrations of PCB's

Several studies have determined the concentrations of PCB's in samples of human adipose tissue obtained at autoposy. Price and Welch reported on 196 samples of human adipose tissue. Eleven (5.6%) of the samples contained more than 2 ppm of PCB. One of these autopsy samples (from a 77 year old white man who died of pulmonary embolism) contained 100 ppm of PCB in the adipose tissue. PCB levels in the liver and kidneys of this individual were 2 and 0.75 ppm respectively. The authors showed that, at least in this man, the distribution of PCB in the liver, kidney and fat correlated with the distribution of extractable lipid. Seventy two (36.7%) of the samples contained between 1 and 2 ppm of PCB, and 109 (55.6%) of the samples contained between a trace and 1 ppm of PCB. The remaining 4 (2%) samples contained no PCB. Yobs (5) (TableIII-2) reported 165 of 637 (25.9%) samples of human adipose tissue contained 1-2 ppm of PCB. Thirty three (5.2%) of the samples contained more than 2 ppm; 125 (19.6%) contained between a trace and 0.99 ppm, and the remaining 314 (49.3%) were negative.

Finklea et.al. (6) studied the concentrations of PCB in the plasma of urban and rural dwellers in Charleston County, S.C. and found them present in 43% of 616 samples. The highest concentration found was 29 ppb and the mean concentration for the entire 616 measurements was 2.1 ppb. A study by Hammer et. al. (7) examined PCB concentrations in the plasma and hair of refuse workers. It was found that 32/37 (81%) of the refuse workers had detectable concentrations of PCB's

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Table III-2. INCIDENCE OF POLYCHLORINATED BIPHENYLS IN ADIPOSE OF THE GENERAL POPULATION OF THE NATION (5).

	Reported		Analyzed	
	No.	%	No.	%
Total	637	100.0	688	100.0
Negative	314	49.3	235	34.2
Trace-<1.0 ppm	125	19.6	229	33.3
1-2 ppm	165	25.9	188	27.3
>2 ppm	33	5.2	36	5.2

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in their plasma (median of 32 detectable values = 2.6 ppb) while only 6 of 54 (11%) controls had detectable PCB's (median of detectable values = 3.7 ppb).

The mean concentrations of PCB in human milk found by Risebrough and Brodine (8) was approximately 60 ppb.

A number of abnormalities of physiology and biochemistry have been noted in patients suffering from "rice oil disease" in Japan.

Changes in the Blood - Four of nine patients who were seriously poisoned in the Yusho incident had reductions in hemoglobin of greater than 30 percent (9). In addition, the average RBC count of the seriously effected individual was significantly less than the less severely effected group (grading of clinical severity was on the basis of dermatologic changes).

Hypertriglyceridemia (serum triglycerides between 200 and 600 mg %) was noted in 12 of 24 patients with "rice-oil disease" (10). Changes in total cholesterol were not noted, but low values of total serum phosopholipids were found in 14/24 patients. The triglycerides in these patients was shown to be associated with pre-beta lipoproteins (endogenous triglyceride). Analysis of the fatty acid composition of serum lipid in three patients with triglycerides in excess of 400 mg % showed that there was an increased concentration of oleic acid and a diminished concentration of palmitic acid. The authors suggested that this pattern might be the result of the discharge of free fatty acids from adipose tissue.

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The bromosulfophthalein (BSP) excretion was abnormal in three subjects. Other abnormalities of liver functions noted in the patients include: 1) diminished serum albumen, 2) increased α_2 globulin and, in the group of severely affected patients, 3) slightly elevated serum alkaline phosphatse.

The serum copper concentration of seriously affected patients was increased.

Other abnormalities noted in the patients with "Yusho" included: 1) diminished post-heparin plasma bipoprotein lysase activity, 2) diminished lecithin-cholesterol acyltransferase activity, 3) increased ratio of urinary etiocholanolone/androsterone, 4) increased 17-ketosteroids and 17-hydroxycorticosteroids in the urine (11), 5) markedly increased excretion of taurine, b-amino-isobutyric acid, glycine and histidine in the urine (12).

6. Morbidity

The first reports of human disease associated with exposure to PCB's concerned workers exposed in their jobs. Affected workers developed small dermal cysts and comedos on the face and ears, most commonly, but the abdomen, back, thighs, forearms, buttocks and scrotum were affected as well. The disease (known as chloracne) was thought to result from direct contact of the effected skin with the PCB. In severely intoxicated workers, nausea, lassitude, anorexia, impotence and hexmaturia were noted. A long latent period (7 mos.) between onset of exposure to PCB and onset of disease as well as a prolonged course of the chloracne was also noted in these initial cases.

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An outbreak of skin disease resembling chloracene was noted in the Fukuoka prefecture of Japan in 1968. It was eventually discovered that most of the effected individuals had consumed rice oil shipped from a particular company in early February of 1968. Of the 325 cases found in the epidemiological study, 166 used canned rice oil shipped on Feb. 5 and 6 and 143 used bottled rice oil shipped between Feb. 6 and Feb. 15. A PCB, Kanechlor 400 (chlorine content - 48%) was found in samples of the rice oil in concentrations of 2,000-3,000 ppm

The initial symptoms noted by patients with Yusho are shown in TableIII-3.It is evident that the most frequent presenting symptoms were increased eye discharge with associated swelling of the upper lids, acne-like eruption, and abnormal pigmentation of the nails, gingival buccal mucosa and face (14). TableIII-4 summarizes the symptoms of 189 patients with Yusho.

A rough estimate of the total quantity of contaminated rice oil that each patient in the subgroup that used canned oils and the immediate members of his family consumed was made. It was found that for those who consumed less than 720 ml of rice oil, the attack rate of Yusho was 88% while those who consumed more than 720 ml of the oil had a 100 percent attack rate. Furthermore, it was shown that the proportion of severe cases of Yusho increased as the amount of rice oil consumed increased. Since the concentration of Kanechlor 400 in the rice oil was 2,000-3,000 ppm and the average quantity of rice oil consumed by members of the subgroup was 800 ml., the average dose of PCB ingested by effected individuals was 2 g. The smallest dose ingested by a patient was estimated to be 0.5 g.

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Table III-3. Initial Symptoms of Yusho (14)

Initial symptoms	Patients No.	Patients %
Swelling of upper eyelids, increase eye discharge	52	38.3
Acne-form eruption, follicular accentuation	45	33.1
Edematous swelling of limbs	9	6.6
Languishment	4	2.9
Disturbances in digestive canal	4	2.9
Numbness and other neurological signs	9	6.6
Pigmentation of skin	13	9.6
Total	136	100.0

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Table III4. Symptoms of Yusho Reported by 189 Patients (14).

Symptom	% Reporting Symptom	
	Males	Females
Increased eye discharge	88.8	83.0
Acne-like skin eruption	87.6	82.0
Brown pigmentation of nails	83.1	75.0
Pigmentation of skin	75.3	72.0
Swelling of upper eyelids	71.9	74.0
Hyperemia of conjunctiva	70.8	71.0
Distinctive hair follicles	64.0	56.0
Feeling of weakness	58.4	52.0
Transient visual disturbance	56.2	55.0
Pigmented mucous membrances	56.2	47.0
Increased sweating of palms	50.6	55.0
Itching	42.7	52.0
Numbness in limbs	32.6	39.0
Headache	30.3	39.0
Stiffened soles in feet and palms	24.7	29.0
Vomiting	23.6	28.0
Red plaques on limbs	20.2	16.0
Swelling of limbs	20.2	41.0
Hearing difficulties	18.0	19.0
Fever	16.9	19.0
Jaundice	11.2	11.0
Spasm of limbs	7.9	8.0

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Of 13 babies born to 10 patients with Yusho, two non-patients and one woman whose status was unknown, two were stillborn. Of the 11 liveborn children, ten had grayish, dark-brown skin and five had similarly colored gingiva and nails. Increased eye discharge was noted in 9 infants. The rice oil consumption of nine of the thirteen mothers was estimated to be from 0.3 to 2.6 liters.

The growth of school children afflicted with Yusho has been studied (17). Both height and weight gain of boys (N=23) with the illness were significantly less than a control group. Also, sixteen of nineteen girls with Yusho had a smaller gain than the average noted for the control group.

In addition to the abnormalities of liver function mentioned in the section, physiological changes of uncertain significance, several changes were found in a liver biopsy specimen from a patient with Yusho. Reduction of the rough suffaced endoplasmic reticulum, hypertrophy of the smooth endoplasmic reticulum, increased numbers of lysosome and peroxisomes, (18) variation in mitochondiral size and form as well as filamentous mitochondrial inclusions (19) were found. The first two changes are particularly noteworthy since they are frequently observed in association with the induction of hepatic drug metabolizing enzymes. Although activity of the hepatic microsomal enzyme system has not been examined in Yusho patients, studies in animals have shown that PCB (specifically Aroclor 1254) is nearly equipotent with DDT as an inducer of microsomal enzymes (20).

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By analogy with DDT workers (21), individuals with sufficient intake of PCB would probably have abnormally increased activities of drug metabolizing enzymes.

Neurological alterations have been detected in individuals poisoned in the Yusho epidemic. Numbness, pain, hypoesthesia, or areflexia was present in eleven of 23 cases examined. Motor function was normal in the same patients. Measurements of motor nerve conduction velocity showed it to be normal in all but one case (ulnar and tibial nerves). Measurements of sensory nerve conduction velocity showed it to be abnormally slowed in radial and sural nerves in 5 of 23 and 9 of 23 cases respectively (22).

7. Delayed Effects - Acute Exposure

Some of the patients were still severely afflicted two years after the episode, although there have been no fatalities directly attributable to PCB.

Continuing observations of the effects of the Yusho incident on persons afflicted must be made for a number of years to determine whether there are latent effects of statistical significance. There is for example, some concern that the incidence of gastric cancer may show an increase above that normally occurring in the Japanese population. In the four years since the onset of the Yusho epidemic, there have been several occurrences of this disease in the 1001 persons afflicted (25).

Experiments with feeding subhuman primates (rhesus monkeys) has added some concern that PCB's and PCT's may be precursors of gastric carcinomas (9). Rhesus monkeys were fed 300 ppm PCB Aroclor 1248 and another fed 5000 ppm PCT (Aroclor 5460) for 3 months. Both sets

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lost weight and showed many of the symptoms of the Yusho patients including hair loss, acne form, subcutaneous edema, eye discharge and liver hypertrophy. In addition, a definite gastric mucosal response was demonstrated. Edematous thickening of the stomach wall and marked hyperplasia of the pyloric and fundic gastric mucosa was evident (23). Several investigators commented on the research and noted that the species of monkeys used in this study have responded similarly to Shale oil, organophosphates, parasitic infection and gastric bezoars suggesting that other species of primates should also be studied for this effect.

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1. Acute Lethal Toxicity

The available information indicates that polychlorinated biphenyls do not have a high acute toxicity. Fishbein (cited in Panel on Hazardous Trace Substances,(1), gives values for the oral and dermal toxicity of seven Aroclor mixtures to rats and rabbits, respectively. The oral LD_{50}s range from 3980 mg/kg for Aroclor 1221 to 11,300 mg/kg for Aroclor 1262. Koeman (cited in Backström, (26) fed Japanese quail a diet containing 2000 ppm of Phenochlor DP6 (a technical mixture) with all birds dying between 6 and 55 days after dosing began. Dahlgren et al. (27) reported that pheasants fed 210 mg of Aroclor 1254 daily died between 1.3 and 5.9 days, the average bird receiving 840 mg with a range of 420 to 1260 mg. Tucker and Crabtree (cited in Panel on Hazardous Trace Substances, (1) indicated that the acute oral LD_{50}s for Aroclors 1242, 1254, 1260 and 1268 were over 2000 mg/kg in the mallard duck. Stalling and Mayer (28) have shown that the acute oral toxicity of Aroclors 1242, 1248, 1254 and 1260 is greater than 1500 mg/kg in the rainbow trout.

2. Subacute Lethal Toxicity

Bennett et al (cited in Panel on Hazardous Trace Substances, (1) continually fed rats a PCB mixture with 65% chlorination. At 300 mg/rat/day, 7/10 animals died within eight days. At 25 mg/rat/day, 3/10 rats died within 12 days and 50% had died by seven weeks. The cumulative LD_{50} under these conditions was estimated to be between 1200 mg/kg and 7200 mg/kg. Tucker and Crabtree (cited in Peakall and Lincar, 1970) fed rats Aroclor 1254 at a dose level of 1000 ppm in the diet. They concluded that after 3/4 rats had died in 43 days, the total intake of 500-2000 mg/kg was the lethal level. The estimated cumulative lethal

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doses of Aroclors 1260 and 1254 are considerably lower than the single-dose oral LD_{50}s for the two PCB compounds; about 10,000 mg/kg.

McCune et al. (cited in Peakall and Lincer, (29) fed chickens 400 ppm - 800 ppm of Aroclor 1242 in the diet with a 50-90% mortality rate respectively after 4 weeks. Similarly, Flick et al. (cited in Peakall and Lincer, (29) found 13% mortality in chickens fed 400 ppm of Aroclor 1242 in the diet after 3 weeks. Dahlgren et al. (27) reported that 5/22 pheasants died after 5 weeks of receiving 50 mg of Aroclor 1254 every 3.5 days. Pheasants receiving double that amount displayed a 30% mortality rate after 5 weeks. Prestt et al. (cited in Dahlgren et al., (27) estimated that 254 mg/kg/day given to Bengalese Finches would give 50% mortality at 56 days. Heath et al. (cited in Dahlgren et al., (27) reported that Aroclor 1254 had an LC_{50} of 1090 ppm when fed to pheasants for 5 days. Vos and Koeman (cited in Dahlgren et al., (27) reported that of 20 chicks fed 400 ppm for 60 days, only 3 died.

The toxicity of a specific PCB compound appears to vary between different batches or sources. Vos (30) reported a comparison of the toxicity of three commercial PCB samples containing 60% chlorine: Phenoclor DP6, Clophen A60, and Aroclor 1260. It was shown that in a feeding experiment involving one-day-old chicks, 100% mortality, subcutaneous and abdominal edema, and centrolobular liver necrosis occurred in the groups that received Phenoclor DP6 and Clophen A60. The mortality in the Aroclor 1260 group was only 15%. It was felt that the greater toxicity of the Phenoclor DP6 and Clophen A60 was due to the presence of trace amounts of chlorinated dibenzofurans.

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3. Signs of Toxicity

Ataxia, blanched retinas, ptosis of eyelid, serous nasal exudate, withdrawal, and lack of preening are characteristics exhibited by rats poisoned with Aroclor 1254. Rats treated with Aroclor 1268 displayed reddish exudate on eyelids, ataraxia, possible blindness and withdrawal (Tucker and Crabtree cited in Panel on Hazardous Trace Substances, (1).

A study by Kohanawa et al. (cited in Panel on Hazardous Trace Substances, (1) showed that chicks poisoned with PCBs displayed dyspnea, gasping, waddling, ataxia, anorexia and lethargy. Prestt et al. (cited in Backstrom, (26) found that Bengalese Finches fed a diet containing various concentrations of Aroclor 1254 showed signs of acute poisoning which included balance disturbance at perching, paralysis in the legs, and trembling with shaking wings. Dahlgren et al. (27) showed that pheasants receiving one 210 mg capsule of Aroclor 1254 in the morning appeared weak that evening. After receiving the second capsule, the birds sat with feathers fluffed and slight tremoring. During the 24 hours preceding death they often showed tremors, particularly when disturbed. A similar effect was reported by Heath et al. (cited in the Panel on Hazardous Trace Substances, (1) in which a group of mallards, Japanese quail, bobwhites and pheasants were lethargic on the terminal day of survival. Mild tremor was observed during the last hour before death. Dahlgren et al. (27) have also shown that pheasant hens given 20 mg daily were hyperexcitable after 4 days of PCB treatment. After 10 days they sat with feathers fluffed. After 30 days of treatment they exhibited weakness with occasional tremors. The experimental group also appeared to have fewer body feathers after 30 days than controls.

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Pathological Findings

Koeman et al. (cited in Bäckström, (26) found that after feeding Japanese quail a diet containing 2000 ppm of Phenochlor DP6, large amounts of fluid were present in the pericardial sac. has also been observed in cockerels dosed with 400 ppm of Aroclor 1242 (Flick et al. cited in Bäckström, (26) and in Bengalese Finches fed a diet containing various concentrations of Aroclor 1254 (Prestt et al. cited in Bäckström, (26) Flick et al. (cited in Backstrom, (26) fed Aroclor 1242 to day-old cockerels (200 or 400 ppm) in the diet and found, besides hydropericardium, abdominal and subcutaneous edema, hemorrhagic and enlarged kidneys and adrenals, a reduced spleen, a cream-colored pale pancreas, increased hemoglobin values and dermatitis. In experiments with pheasants, Dahlgren et al. (27) found that PCBs decreased heart and spleen weights at all treatment levels used. Birds given 10-20 mg doses showed increased weights of kidney and liver and atrophy of the spleen.

Vos (30) in a comparative study of Phenoclor DP6, Clophen A60 and Aroclor 1260 on one-day-old chicks found that subcutaneous and abdominal edema and centrolobular liver necrosis occurred only in the first two groups. Hydropericardium was common with the first two compounds but was only occasionally seen in chicks fed Aroclor 1260. This difference was probably due to the presence of chlorinated dibenzofurans in the Phenoclor DP6 and Clophen P60. Hepatic porphyria was found in all groups.

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Vos and Notenboom-Ram (31) performed a comparative dermal toxicity study of 2,4,5,2',4',5' - hexachlorobiphenyl and Aroclor 1260 in rabbits. They found that after 3 days of treatment Arclor 1260 produced some redness on the skin and that after 14 days hyperkeratosis and transverse wrinkles existed. With the pure polychlorinated biphenyl some redness and slight hyperkeratosis was apparent after 14 days. They concluded that chloracne, a common anomaly associated with PCBs, is due primarily to chlorinated dibenzofuran contaminants. They also concluded that the liver damage caused by commercial PCB mixtures is due primarily to contaminants while hepatic porphyria is caused by the polychlorinated biphenyl itself.

Reproductive Effects

An FDA report cited by the Panel on Hazardous Trace Substances (1) indicates that Aroclor 1242 fed to rats at a level of 100 ppm had no effect on the first generation but decreased mating indices and survival of pups in the second generation. Aroclor 1254 administered at the same level showed no effects on the first generation but reduced the number of pups delivered and the number surviving to weaning in both the second and third generations. Aroclor 1260 at the 100 ppm level had no effect.

Risebrough et al. (cited in Bäckström, (26) have shown that PCBs in pigeons have the capacity to induce steroid hydroxylating liver enzymes to increase their breakdown of estrodial which is involved in the stimulation and maintenance of sex organs and breeding behavior. This could account for late breeding, the failure to lay eggs and the failure to lay eggs after the early loss of a clutch often seen in birds intoxicated with PCBs.

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Dahlgren et al. (27) have shown that pheasant hens given 12.5 mg/week of Aroclor 1254 displayed no differences in egg production when compared to controls. However, hens receiving 50 mg/week of Aroclor 1254 had a significantly lower egg production than controls. No differences were shown in egg fertility but hatchability was significantly lowered in the group receiving 50 mg PCBs. There were no significant differences in eggshell thickness. McLaughlin et al. (cited in Dahlgren et al., (27) injected both 10 and 25 mg of Aroclor 1242 in chicken eggs and found only 0-5% hatchability with growth retardation, edema, and beak deformities in embryos. Heath et al. (cited in Dahlgren et al., (27) fed 25 ppm of Aroclor 1254 to mallards through 2 breeding seasons and bobwhite quail 50 ppm PCBs and 25 ppm PCBs in conjunction with 15 ppm DDE for one reproductive season. They found no effects on egg production, cracked eggs, eggshell thickness, embryonation, embryos alive at 3 weeks, normality of hatchlings and normal hatchlings alive at 14 days. Scott et al. (cited in Dahlgren et al., (27) found a 10% reduction in egg production in chickens which had been fed 10 ppm Aroclor 1248 for 8 weeks and a 13% reduction associated with 20 ppm. The 10 ppm dose reduced hatchability of eggs by 8% after 4 weeks and 44% after 8 weeks. The 20 ppm level resulted in a very low hatchability. Bitman et al. (32) fed Aroclor 1242 and Aroclor 1254 to Japanese quail at a level of 100 ppm for 60 days. The 1242 group and controls exhibited similar egg production for the first 40 days but the PCB group declined to 71% during the next three weeks. The number of membranous and broken eggs in the Aroclor 1242 group exceeded that of the control group by a factor of 2. No effects were shown with Aroclor 1254.

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Tucker (cited in Peakall and Lincer, (29) demonstrated that a single oral dose of 500 mg/kg of Aroclor 1254 caused regular egg laying of Japanese quail to turn first to scattered egg production and then stop completely for one week. Mallards dosed with 1000 mg/kg of Aroclor laid one or no eggs before stopping for one to two weeks.

Peakall, Lincer and Bloom (33) fed ring doves 10 ppm Aroclor 1254 over two generations. Low hatching success of the second generation was due to heavy embryonic mortality which occurred mainly between 3-8 days. No eggshell thinning was observed. There was evidence that PCBs have a chromosome breaking action in dove embryos.

Toxic Interactions

Lichtenstein (cited in Panel on Hazardous Trace Substances, (1) has shown that PCBs at a dose level of 500 µg/g increased the toxicity of DDT and dieldren to house flies and Drosophila melanogaster. Friend and Trainer (cited in Vos, (30) fed 10-day-old ducklings a 54% chlorinated Aroclor mixture at levels of 25, 50 and 100 ppm. Five days later they were exposed to duck hepatitis virus with the result being a significantly higher mortality than birds which were not exposed to PCBs.

Toxicity as a Function of the Degree of Chlorination

There appears to be no consistent relationship between the toxicity of PCBs and the extent of chlorination that holds true for different species or routes of exposure. Acute oral toxicity decreases with increasing chlorine content in rats. Lethality in pheasants, quail and ducks increases with increasing degree of chlorination (Health et al. cited in the Panel on Hazardous Trace Substances, (1). Lethality in flies decreases with increasing degrees of chlorination (Lichtenstein, (30). Toxicity as related to reproduction in general decreases with

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increasing degrees of chlorination (panel on Hazardous Trace Substances, (1). It is pointed out that such generalizations are difficult to make in that research has been conducted using commercial preparations of PCBs which may vary in toxicity from batch to batch.

C. Ecological Effects

The effects of polychlorinated biphenyls on biological systems are not well understood, since a unified effort has not been made to determine their effects upon the biota of terrestrial or aquatic ecosystems. Therefore, the available information is scattered and in many areas sparse or non-existent.

PCBs enter the living organisms through the food webs, by absorption through the skin, and through the fills, and through the lungs by breathing. The chemicals may be adsorbed by mud and other solids which act as reservoirs and then gradually feed them into the water as theyare removed by organisms. It is possible, therefore, for living organisms to accumulate these chemicals from an environment which seems relatively uncontaminated. Living organisms, as well as the water, must be analyzed to monitor the contamination of a river, lake, estuary (44). The data of Harvey and Miklas (45) suggests that this is not necessarily true of oceans.

Once PCBs get into the food chain biological magnification seems to take place. Due to the concentration of the PCBs at each food level with a food chain, the concentration may become magnified by a factor of 10-100 at each step (1a,44). Food chain magnification does not occur in the oceanic fish probably because the lipid portions of oceanic organisms are in equilibrium with the water (45). However, aaquatic food chains involving such top predators as birds and mammals do accumulate PCB levels 10^7 times higher than those in the ambient water (1a). The concentration within an organism occurs because, though the food is digested, metabolized and excreted, the PCBs are retained in the lipids of the organism.

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Studies have shown that terrestrial birds of prey in five European countries had very high levels of PCBs (1a). In great Britain PCB levels in the liver were highest in the terrestrial bird-eating predators and lowest in the insectivorous birds. PCB levels reached 70. ppm in the predators.

Starlings and woodcocks are being used to monitor PCB levels in a nation-wide project. Woodcocks are considered to be a good indication of soil concentrations because they feed on earthworms (34). The half-life of PCBs in the soil is considered to be in the neighborhood of 5 years. No published data for soil levels of PCBs exist. In addition, there is no data dealing with uptake, effects or levels of PCBs in terrestrial plants.

In addition to the direct measurements of PCB levels in animals, especially fish and birds which are high in marine food chains, Risebrough and his coworkers have used the similarity in properties between persistent PCBs and the persistent metabolites of DDT to extrapolate PCB levels. PCBs and DDT, DDE and DDD are accumulated by aquatic animals to a similar degree from ambient water and measurements made in the same areas indicate the ratios of the sum of DDT, DDE and DDD (ΣDDT) are similar in animals on similar levels in a good chain.

In attempts to gain further insights into the movement of PCBs through the ecosystem, metabolism and excretion studies have been made. These studies indicate that rats and birds do not take up or retain the lower isomers of PCBs very efficiently. The pentachlors and lower isomers were generally present in lower proportions (1a). Differential metabolism is believed to have reduced the number of higher isomers.

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VII. CURRENT RESEARCH ACTIVITIES

A. Summary

Research and development has been conducted by the Quality Assurance and Environmental Monitoring Laboratory in-house and by contract with Syracuse University Research Corporation (SURC) over the past three and one-half years on efficient, high volume sampling methodologies for airborne pesticides and polychlorobiphenyls. A unique sampler was developed which collects particulate matter and organic vapors from the atmosphere at ten times the rate of other sampling devices designed for pesticides (1). QAEML has compared this sampler with the only commercial pesticide air sampler, the MISCO Sequential Pesticide Sampler (2). The SURC sampler operated at 10 cfm was found to have superior collection efficiency for chlorinated pesticides over the MISCO sampler operated at its maximum flow rate of 1 cfm. When the latter was run at 0.6 cfm, collection efficiencies were comparable (3). SURC sampler, is much simpler to maintain and operate than the MISCO sampler. Neither sampler has been evaluated for polychlorobiphenyls.

A task force committee was convened by QAEML on November 3, 1972, to prepare protocols for research and development and monitoring needs with respect to airborne pesticides and PCB's. A plan for a national and world-wide ambient trend monitoring network for airborne pesticides and PCB's was prepared by this task force committee on November 29, 1972 (4). At this time it appears that the program will not be funded for fiscal year 1974.

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The Pesticide Community Studies Division, Office of Pesticides Programs, EPA, operated an air monitoring network during 1970-72 using the commercial ethylene glycol sampler (2). In 1971, a total of 32 different pesticides were determined at 29 sites distributed throughout the United States (5). PCB's were added to the list of compounds sampled in 1972. The 1972 data are not yet available. The network was closed down at the end of 1972.

The Office of Pesticides Programs Ecological Monitoring Branch is undertaking a sampling study of pesticides and their photodegradation products in air during the summer of 1973 (6). The MISCO and SURC samplers will be compared as part of this study.

Another sampling device was developed by Tessari and Spencer of the Colorado State Department of Health in 1971 (7). It consists simply of a nylon chiffon cloth coated with ethylene glycol,and is difficult to use quantitatively. Work is presently underway to develop an improved system, however (8). Because of the large quantities of organic compounds collected by this sample, it is now being used to determine levels of airborne PCB's inside buildings utilizing fluorescent lighting (8). Similar measurements have been made by EPA's Wenachee Research Station. A report on the "preliminary study of PCB emissions from fluorescent light" is due in July 1973 (9).

The only significant investigation of PCB levels in the ambient atmosphere to date appears to be that being conducted by Dr. George Harvey of the Woods Hole Oceanographic Institute. Dr. Harvey and

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Dr. Robert Duce of the University of Rhode Island have measured PCBs in the atmosphere over the Atlantic Ocean near Bermuda at levels of 0.2 to 0.5 ng/m^3 (10). The collector which they used was a modified Hurricane sampler in which a bed of ceramic chips coated with silicone oil (OV-17) was placed behind the glass fiber filter to collect vapors. At a sampling rate of about 22 cfm, these investigators found no PCB's on the filter. It is recognized by Dr. Harvey, however, that particulate-adsorbed PCB's, if present, would likely have vaporized from the filter and have been trapped in the silicone oil (11). These studies are to be continued through the summer of 1973. Beyond that, new funding must be provided.

A study is being conducted to determine possible lower and upper atmospheric photochemical and thermal reactions of the PCBs. Dr. Daniel Lillian at Rudgers has a 3-year grant with EPA to study the fate of both atmospheric freons and PCBs. The expected completion date is August 1975. The emphasis of this work, however, is on the Freons, with only minor attention being directed to the PCBs.

A contract sponsored by the Chemistry and Physics Laboratory (NERC) is being processed on a task for the Development of Sampling Procedures for Polycyclic Organic Matter and Polychlorinated Biphenyls (DU-73-B395). The objectives of the contract are to design and test stationary sources sampling procedures for both POM and PCB. The procedures will be optimized based upon the physical and chemical characteristics of each group, and the conditions prevailing at the sources from which each is emitted. The estimated time for completion is fourteen months, the contract should be awarded in June 1973.

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A study is being conducted by the Department of Public Health, State of Michigan, in cooperation with the Food and Drug Administration, to determine the amount of PCB's ingested from fish by a selected exposed population. This investigation will be carried out by obtaining a dietary history of fish consumption of this select population group. The amount of PCB's ingested will be determined by measuring the PCB's in fish they consume and measurements made for PCB levels in human blood by this select group. An attempt will be made to correlate tissue levels with levels of PCB ingestion.

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Microorganisms have been shown capable of metabolizing chlorinated hydrocarbon pesticides (35-38) as well as chlorinated phenols (39,40). It has been suggested the reason that the proportion of higher isomers of Aroclor increase downstream in some Wisconsin Rivers (41) is because the lower isomers are being metabolized by microorganisms.

Using the information available, Nisbet and Sarofim, (1a) have developed diagrams suggesting the possible channel of PCB movement through terrestrial, fresh water, estuarine and oceanic ecosystems. Figures III-1, III-2, III-3, and III-4.

The ultimate question is, "What is the effect of the PCBs on the ecosystem?" The organisms at the tops of the food chain are most affected due to the occurrence of biological magnification. The concentration of PCBs in the raptorial and fish-eating birds has been reported to result in changes in the calcium physiology of these birds, and these changes have in turn resulted in thin-shelled eggs. Declining populations of these birds has been related to the thin egg-shells as eggs with thin shells break more readily. There is some evidence that PCB's contribute to embryonic mortality. The Asprey, Peregrin Falcon (42,43), sparrowhawks, Kittiwakes and Guillemots are among those being effected. As mentioned previously, woodcocks which feed on earthworms have shown higher PCB levels; however, the effect upon the earthworms themselves seems not to have been studied.

In freshwater ecosystems, amphipods have been shown to contain 30 times the amount of DDT that was found in the mud. Comparable levels of PCB's in amphipods could accumulate in predators and be passed up the food chain. Being carnivores, Coho Salmon were also shown to have accumulated DDT. Salmon fry from the contaminated eggs died

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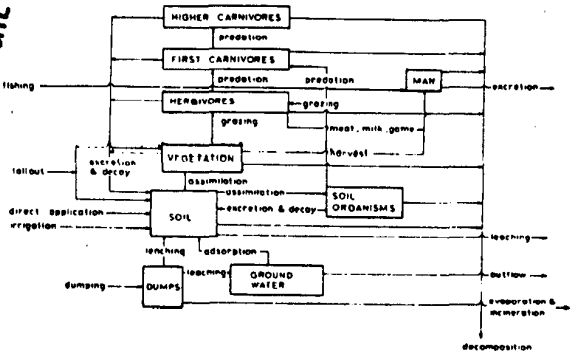

Figure III-1. Terrestrial submodel.

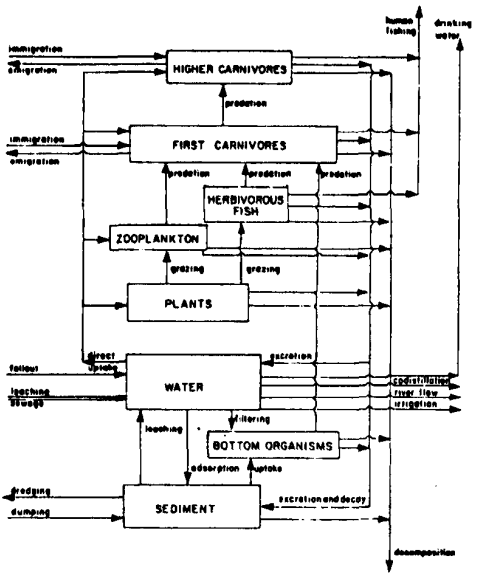

Figure III-2. Fresh-water submodel.

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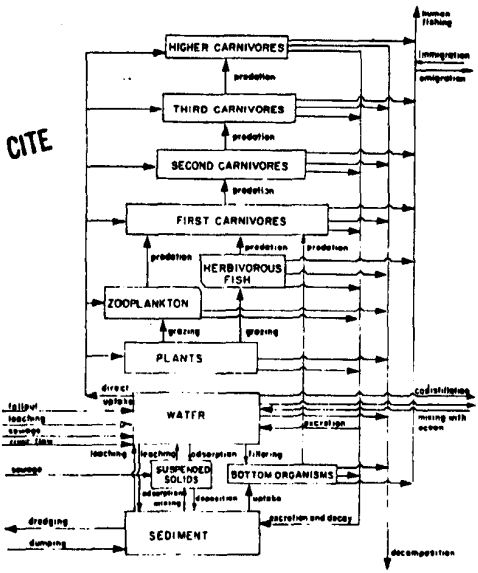
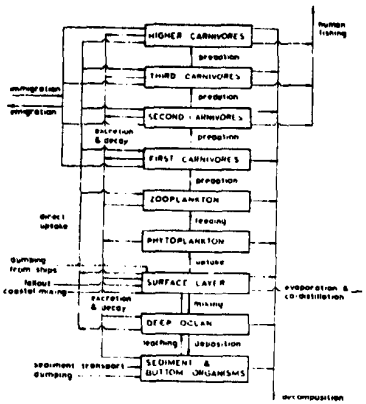


FigureIII-3. Estuaries submodel.



FigureIII-4. Ocean submodel.

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in large numbers (44). Studies seem not to have been made to determine PCB concentrations in these fresh water organisms. In the ocean, PCBs were found in every individual of every species examined (45).

Seals, porpoises and whales have been shown to have high levels of PCBs. The effect of the high levels upon the marine animals is not known though a high incidence of premature births has been reported in California sea lions (45).

The base of the food chain is also effected by PCBs. The growth of phytoplankton(1a,34,45) has been shown to be affected. The single celled algae found in phytoplankton are responsible for more than half of the world's photosynthesis. Changes in these algae could have a profound effect on the total world ecosystem.

Microorganismal metabolism of PCBs could also result in significant changes. Synthetic compounds are new and therefore decomposed by only a few species. These microorganisms increase in number because of the increased food source and are therefore selected out from the more common types. The population changes could therefore upset microbial processes which have been in existence for eons (36). The metabolic products of microbial metabolism could prove to be more toxic than the PCBs and bring about changes in several trophic levels (36,46).

The dearth of information concerning PCBs and their widespread presence makes studies of their effects upon the world ecosystem imperative.

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IV. REVIEW OF SAMPLING AND MEASURING TECHNIQUES

A. Introduction

1. Structures

In a previous task force document on the PPOM the analysis of the large polynuclear compounds (4 to 7 rings) were discussed. These included the polynuclear aromatic hydrocarbons (or arenes), the aza arenes, the imino arenes, and arenes with one or more ring carbonyl groups. In this document we will discuss the analysis of the polychloro derivatives of the di- and tricyclic hydrocarbons: biphenyl, I, p-terphenyl, II, naphthalene, III, dibenzofuran, IV, and dibenzo-p-dioxin, V. (See Figure IV-1). Two other terphenyls exist in addition to II; these are the o- and m- isomers. Most of the discussion will concern the polychlorobiphenyls (PCB).

Most of these compounds are marketed under a number of commercial trade names, e.g. Aroclor, Clophen and Phenoclor. The Aroclors from Monsanto Company are classified by a four digit number and consist of mixtures of polychlorinated biphenyls and terphenyls. The first two digits represent the hydrocarbon type, e.g. 12 are chlorinated biphenyls, 25 and 44 are blends of chlorinated biphenyls and terphenyls (75% and 60% biphenyl, respectively), and 54 are chlorinated terphenyls. The last 2 digits give the weight percent of chlorine, e.g. Aroclor 5460 is a chlorinated terphenyl containing 60% chlorine. Environmental PCB most often contains about 50% chlorine per molecule, that is from 4 to 8 chlorine atoms per molecule.

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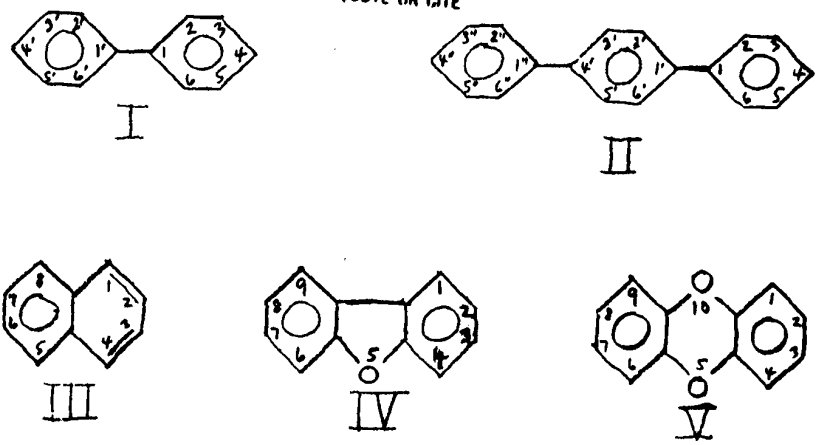

Figure IV-1. Structure of Polychloro Derivatives of Di- and Tricyclic Hydrocarbons.

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An example of the polychloronaphthalenes available are the Halowaxes from Koppers Co. Inc., e.g. Halowax 1014 is a mixture of tetra-, penta- and hexachloronaphthalenes; Halowax 1051 is octachloronaphthalene; Halowax 1099 is a mixture of trichloro- and tetrachloronaphthalenes (1). The percent chlorine values for the different Halowax numbers are 1031 - 22%, 1000 - 26%, 1001 - 50%, 1099 - 52%, 1013 - 56%, 1014 - 62%, and 1051 - 70%.

2. Intercalibration and standardization

Since 1966 when the PCBs were found to be an environmental pollutant, (2) PCBs, along with DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane), have been reported to be the most abundant chlorinated aromatic pollutants in the global ecosystem (3).

It is evident that appropriate recommended methods are necessary to make it possible and meaningful to compare the PCB values obtained in widely separated laboratories.

Some interlaboratory comparisons have been made for the PCB (4,5). Aroclor 1254 at the 1.1 and 2.1 ppm levels showed a percent recovery range of 63 to 95 (average 78) and 66 to 77 (average 73), respectively (4).

3. Contamination

Since the mixtures of PCBs, PCTs and PCNs (polychloronaphthalenes) are used as standard test mixtures, their contamination with polychloro derivatives of other ring systems becomes of some importance.

Polychlorodibenzofurans (PCDF) and PCN have been found in 2 commercial PCB, Clophen A60 and Phenoclor DP6 (6). These mixtures were chromatographed on a fluorisil column, the 25% diethyl ether in hexane fraction evaporated to 1 ml, and this separated by GLC. From the fragmentation patterns obtained with mass spectrometric analysis

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the impurities were identified as tetra- and pentachlorodibenzofurans and hexa- and heptachloronaphthalenes. The upper limits of pentachlorodibenzofurans were estimated to be 5 ppm and 20 ppm in Clophen A60 and Phenoclor DP6, respectively. The gas chromatogram of the third fraction of Clophen A60 (Fig. IV-2) and the mass spectrum of the pentachlorodibenzofuran (Fig. IV-3) are shown. Thus, with the help of mass spectrometry about one nanogram of contaminant can be detected in a 100 µg sample. This means that the lower limit of detectability of contaminants without prior concentration is 10 ppm (7).

The physical and chemical properties of the PCB and PCN are similar (1, 8). Consequently, the PCN, in addition to some of the pesticides, interfere in the gas chromatographic analysis of PCB. Techniques should be developed which would eliminate this interference. Preliminary studies indicate that PCN accompany PCB on silicic acid chromatography, but their presence can be detected from an absorption maximum at 306 nm, $A^{1\%}_{1cm} = 329$ (9).

Another family of contaminants which have been found in commercial chloroaromatic compounds are the polychlorodibenzo-p-dioxins (PCDD) (10 - 13). In addition, 2,4,5-trichlorophenol and 2,4,5-trichlorophenoxyacetic acids have been found to be contaminated with PCDF and PCDD (13). Commercial chlorophenols were analyzed for trace contaminants by solution in aqueous alkali, extraction with petroleum ether, fractionation on an alumina column, and followed by examination by electron capture gas chromatography and combined gas chromatography - mass spectrometry (12). The presence of PCDD, PCDF and polychlorodiphenyl ethers (PCDE) was confirmed. The 2,3,78-tetrachlorodibenzo-p-dioxin was found in half the samples of 2,4,5-trichlorophenol. Hexa-, hepta-, and octachlorodibenzo-p-dioxins as

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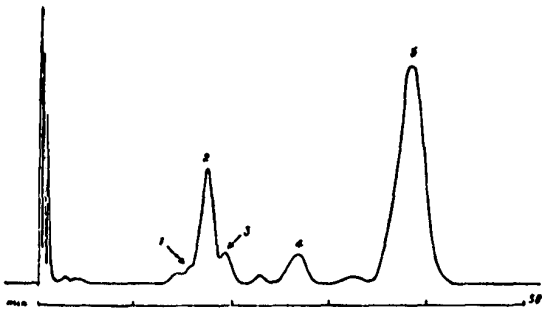

Figure IV-2. Gas chromatogram of third fraction of Clophen A60 (showing pattern identical to that for third fraction of Phenoclor DP6). Data for peaks 1-5 are given in Table 2.

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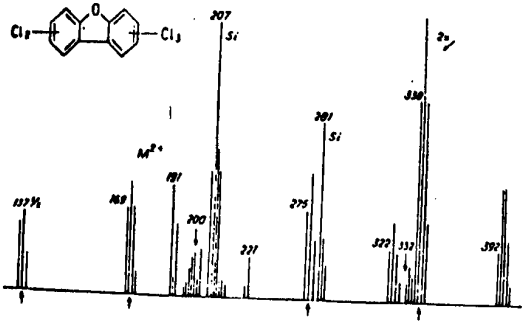

Figure IV-3. Mass spectrum of pentachlorodibenzofuran (mass no. 338) obtained from third fractions of Clophen A60 and Phenoclor DP6 (Peak 4 in Fig. 1). The spectrum of heptachlorobiphenyl (mol wt 392) is also present.

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well as a wide variety of PCDF and PCDE were present in most of the tetra and pentachlorophenols. In addition, the GC-MS data suggested that some of the chlorophenols contained methoxy and dimethoxy PCDF, and methoxy PCDE as well as hydroxy PCB.

4. Precursors

Some of the polychloro compounds are synthesized in the environment, or inadvertently as a byproduct in the preparation of some industrial chemical. The contamination described in the previous section is probably due to the latter type of synthesis.

Polychlorophenols have been stated to be precursors of the PCDD (14). Some of the PCDD found in polychlorophenols and their sodium salt are shown in Table IV-1. Some commercial grades of pentachlorophenol have been found to contain as high as 2500 ppm PCDD.

Since chloracne and liver damage may result from the handling 2,4,5-trichlorophenol, and this product is prepared by the alkaline hydrolysis of 1,2,4,5-tetrachlorobenzene, it has been concluded that byproducts which result during alkaline hydrolysis are the causative agents. These contaminants have been isolated and have been shown to be tetrachlorodibenzofuran and tetrachlorodibenzo-p-dioxin postulated to be formed by the type of reaction shown in Figure IV-4.

Similarly the tetrachloro DD could be a contamininant in the herbicide 2,4,5-T(2,4,5-trichlorophenoxyacetic acid), since this compound is produced by the interaction of sodium monochloroacetate with 2,4,5-trichlorophenol.

5. Artifact Formation

One of the difficulties in many types of trace analyses is the problem of the formation of test substances during the analytical

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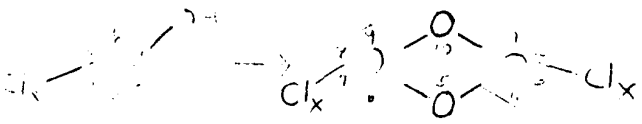
Table IV-1.

Polychlorodibenzo(p)dioxins in Polychlorophenols

by Electron Capture Gas Chromatography (12)



Position of Chlorine Atoms

Sample No.	Phenol	PCDD	Found ppm
5	2,4,5-	2,7-	0.72
		2,3,7,8-	1.4
6	2,4,5-	1,3,6,8-	0.3
		2,3,7,8-	6.2
7	2,4,5-	Pentachloro	1.5
8	2,4,5-	None	-
9	2,4,5-	2,3,7,8-	0.07
10	2,4,6-	2,3,7-	93
		1,3,6,8-	49
11	2,3,4,6-	Hexachloro-	15
		Hexachloro-	14
		Heptachloro-	5.1
		Octachloro-	0.17
12	2,3,4,6-	Hexachloro-	4.1

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Table IV-1 (Continued).

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Sample No.	Position of Chlorine Atoms Phenol	PCDD	Found ppm
13	2,3,4,6-	None	-
14	Pentachloro (PC)	Hexachloro-	14
		Heptachloro-	5.4
		Heptachloro-	9.1
		Octachloro-	3.8
15	PC	Hexachloro-	20
		Heptachloro-	1.3
		Heptachloro-	10
		Octachloro-	3.3
16	PC	Hexachloro-	0.96
		Hexachloro-	38
		Heptachloro-	10
		Heptachloro-	39
		Octachloro-	15
17	PC	Hexachloro-	35
		Heptachloro-	23
18	PC	Hexachloro-	0.03
		Hexachloro-	0.14
19	PC	Hexachloro-	13
		Hexachloro-	12
		Heptachloro-	35
20	PC	Hexachloro-	0.91
		Heptachloro-	0.50
		Heptachloro-	1.6
		Octachloro-	5.3

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Table IV-1 (Continued).

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Position of Chlorine Atoms

Sample No.	Phenol	PCDD	Found ppm
21	PC	Hexachloro-	15
		Heptachloro-	23
		Octachloro-	15

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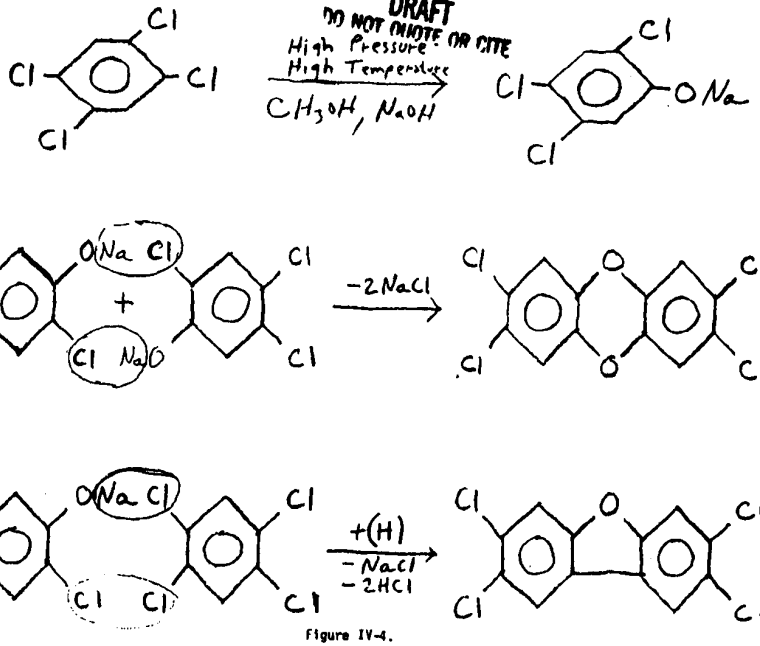

Figure IV-4.

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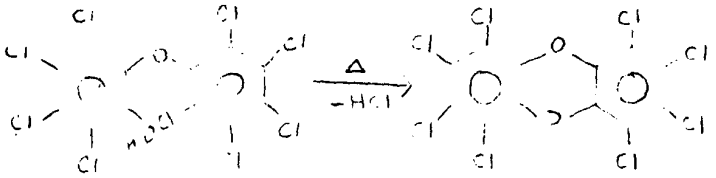

procedure. Thus, in searching for nitrosamines in cigarette smoke it has been found that substantial amounts can be synthesized from precursors in the test mixture during collection of the sample. An example of this frustrating problem is the synthesis of an octachlorodibenzo-p-dioxin on a gas chromatographic column during the separation of some isomeric nonachlorohydroxydiphenyl ethers (15), e.g.

6. Stability

Although the polychloro polynuclear compounds are believed to be very stable in the environment, there are indications that they could be broken down or modified in an appropriate environment. The extremely high physiological activity of 2,3,7,8-tetrachlorodibenzo-p-dioxin would seem to denote a high order of chemical activity in living tissue.

Under mild conditions light can promote reactions in so-called unreactive halides. Both PCDD and PCDF are very unstable to light in the presence of organic substrates (16, 17)

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B. General Methods

In the determination of the polychloro polynuclear compounds the following criteria are desirable - pure standards, a good calibration procedure, high collection efficiency (from air, water, etc.), complete extraction from the collected environmental mixture, no loss during cleanup, no degradation during the chromatographic steps, no artifact formation during the procedure, good overall recovery, reasonable sensitivity, no interferences, unequivocal characterization, as much simplification as possible, satisfactory intercalibration, capability of uninterrupted use in the automated or manual modes, and a high order of precision. With all this, all one can further ask for is accuracy.

1. Standards

For reasonably accurate work, pure standards or mixtures with a known amount of test substance(s) are necessary. A few commercial sources are Aldrich Chemical Co., Analabs, Burdick and Jackson Lab., Chemical Procurement Labs., Eastman, K and K Lab., Monsanto Co., Pfalz and Bauer Chemicals, and Sapon Lab. For example, Analabs is a source of the following 99% pure standards - 50 PCB, 3 PCT, an octachloronaphthalene, 2 PCDD and an octachlorodibenzofuran.

Standards for PCBs (Aroclors 1221, 1232, 1242, 1248, 1254, 1260 and 1262) and PCNs (Halowaxs 1000, 1001, 1013, 1014, 1051, and 1099) are available from the Technical Services Division, Pesticides and Primate Laboratory, EPA, Perrine, Florida. Standards for Aroclors 1242, 1248, 1254, and 1260 are available from Pesticides Reference Standards Section, Office of Pesticides Program, EPA, Washington, D. C.

In addition, synthesis procedures for PCBs have been reported (18, 19). All the PCBs were homogeneous on silica gel thin layer chromatogram plates developed with heptane and gave one peak when chromatographed on a 4% SE-30 column (18). The mass spectra of the compounds confirmed the molecular composition.

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The Aroclor mixtures can be used as standards for measuring environmental mixtures containing PCB. A thorough analysis of the mixture must be performed beforehand. Aroclor 1254 has been used as such a standard, but the levels of PCB obtained have been much too high (20). Because of impurities in an Aroclor being used as a standard, quantitation based on that one Aroclor will be erroneous.

However, semiquantitative measurements of PCB residues have been made using one peak of a commercial mixture as a standard (21). Quantitation has also been based on an average of 2 or more peaks.

The compositions of Aroclors 1242, 1254 and 1260 have been determined by elemental analysis, GC with a Coulson conductivity detector, and combined GC-MS (22). A procedure using these Aroclors is recommended for analyzing environmental samples containing more than one Aroclor mixture. In another GC procedure 6 Aroclor standards have been used so as to minimize the errors due to impurities (20). Chromatograms of six PCB standards were obtained for Aroclor 1232, 1242, 1248, 1254, 1260, and 1262. They were dissolved in hexane to concentrations of 2 ng/μl. A 4 ul injection placed peak heights on the linear portion of the standard curve for each Aroclor. Duplicate 4 ul injections were made. Total peak area for each Aroclor was determined by the cut and weigh method. Stock solutions of the Aroclors in isooctane are stable except when exposed to sunlight.

Another mixture which has been assayed by GC-MS to some extent is the French product, Phenochlor DP6 (19). Four of its major components are 2, 2', 4, 4', 5, 5' - hexachlorobiphenyl, the 2, 2', 3, 4, 4', 5' - isomer, and 2, 2, 3, 4, 4', 5, 5' - heptachlorobiphenyl and its 2, 2', 3, 3', 4, 4', 5 - isomer. This mixture could also be investigated as a standard.

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Of course, more accurate quantitation will be achieved when pure individual PCB components become available.

A polybromobiphenyl mixture for standard use is Firemaster BP6 (hexabromobiphenyl) which gives 7 peaks with retention times of 0.50, 0.88, 1.09 (major peak), 1.44, 1.77, 1.94 and 2.82 (major peak) relative to decachlorobiphenyl on the OV-210 column (23).

The highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin has been prepared from 2,4,5-trichlorophenol in pure form (10). Thirteen chlorinated dibenzo-p-dioxins containing from 1 to 8 chlorine atoms have been prepared for use as standards in the development of analytical methodology for the PCDD (24).

Internal standards are also of value in checking recovery. There is a definite need for these standards since it is difficult to measure accurately the small volumes remaining after evaporations and the less than 10 ul volume injected into the gas chromatograph. This standard must have a retention time different from those of the PCBs and must be in a clear area of the chromatogram. Where much dilution takes place and the internal standard could be diluted to the point of invisibility, dilutions can be accomplished by means of a standard solution of the internal standard. In this way the peak of the internal standard is referred to the corresponding peak in the standard solution. DPDE (1,1-diphenyldichloroethene) has been used as an internal standard in residue analysis. A standard injection of a standard such as p, p'-DDE can indicate whether detector sensitivity has changed from when the response curve was calculated (20) and so a simple factor can be applied to the entire curve and all isomers quantitated as before.

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2. Contamination

During the analysis for PCB and other polychloro polynuclear compounds, great care must be taken to avoid contamination of samples, since PCB may be present in a variety of products. PCBs of the 40% chlorine variety have been found in cardboard and in a wrapping plastic material. Glassware should be washed with chromic acid and liquid-chromatographic columns should be eluted with petroleum ether prior to use. The presence of aromatic hydrocarbons in pesticide-grade hexanes can affect the elution patterns of PCB and other chlorinated compounds from silicic acid columns (9). Several batches of silicic acid Silicar ^{R} (Mallinckrodt) were contaminated with 0.031 to 0.163 µg g of PCB expressed as Aroclor 1254. Hexane of satisfactory purity is difficult to obtain. It is reported to contain a significant amount of an impurity that has the same retention time as that of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Efforts to remove with fuming sulfuric acid, potassium permanganate or alkaline silver nitrate were fruitless. The only solution is the use of distilled batches of carefully selected hexane. The many usages of the PCB shows the wide extent of contamination possible (25).

3. Sampling

In sampling for PCB in air, water, soil and tissues different factors are involved. The collection efficiency and the physical state of the test substances are of importance in air analysis. The way the material is collected will depend on whether it is in the vapor and/or the particulate phase, the volume of air flowing through the samples per unit time, the temperature of the air, and the composition of the atmosphere in terms of its pollutants.

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The solubilities of the PCB in water and their attraction to the particulate phase will determine whether water, aqueous particulate, mud, etc. are collected.

Sampling of air, water, soil and tissues will be discussed more fully in the appropriate sections.

4. Interfacing - sampling to Separation

A cleanup procedure is necessary to concentrate the polychloro compounds and to eliminate all the interferences, if possible. One of the big problems has been that the PCB are extracted together with other hydrocarbons and their halo derivatives. Since many of the chloro compounds have retention times identical to the PCB on non-polar columns, their analysis presents a problem which is not completely soluble by gas chromatographic means alone. Accusations have been made that much of the data obtained in the past for the pesticides are unreliable because of this problem,and because of the lack of proper confirmatory techniques.

The use of the electron-capture detector in the analysis of the polychloro compounds has the advantage of high sensitivity and the requirement for small amounts of material for analysis. But, a vigorous cleanup procedure is necessary to prevent gross contamination of the detector by other chlorinated compounds present,and to remove interfering substances with the same retention times as the PCBs. No single cleanup procedure is adequate. Most of the cleanup methods used for this separation employ adsorption column chromatography and constitute a difficult and time-consuming step. Some of the problems associated with adsorption column cleanup methods are contamination of the adsorbent,involved procedures for adsorbent preparation, the

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large quantity of clean glassware required;and the errors that may be introduced by way of adsorptive loss of residues on glass, plastic surfaces, on the column, and from interfering substances present on the adsorbent or in the eluting solvent.

Separation prior to gas chromatography has been used by many researchers. Simpler chromatograms are obtained. Thin layer chromatography, reverse paper chromatography and column chromatography afford means of obtaining partial separations of chlorinated compounds from PCB and fractions can easily be obtained where only Aldrin, Heptachlor and p p' - DDE remain with the PCB. The former two show little interference with PCB bands, but p p' - DDE can emerge with the major PCB peaks using non-polar compounds. TLC has given this sort of separation using silica gel and alumina (26) as has column chromatography with alumina or silica gel (27), or Florisil (28). It is possible to carry out a separation leaving only Aldrin with the PCB (29). Column chromatography with silicic acid - celite and elution with petroleum ether is used. This type of separation is possible as long as the column is not overloaded and there is no trace of polar solvent in the sample. Double column systems have also been used, e.g. alumina partly deactivated with 5% water followed by silica gel.

Solvent partition methods also can be used prior to separation, e.g. acetonitrile or dimethylsulfoxide/hexane. The polychloro compounds can be extracted into hexane and then into dimethylsulfoxide or dimethylformamide, water is then added and they are re-extracted into hexane.

Another possible method is through chemical change of the test substances or of the interferences, and in so doing changing either their physical properties or retention time so they present no interference to the PCB. Thus, pesticides can be nitrated (30) in hopes that the PCB are unaltered while the DDT is essentially removed. Unfortunately some DDT derivative peaks emerge on the chromatogram and some of the lower chlorinated PCB are affected.

Alternatively, saponification with alcoholic potash leads to the dehydrochlorination of p p' DDT, p p' TDE, and Toxaphene with the derivative peaks appearing earlier in the chromatogram and the PCB reportedly unaffected. BHC is destroyed by this procedure. PCB can also be differentiated from DDT using carbon-skeleton chromatography.

Sulfuric acid can also be used as a cleanup agent (31). One modification involves shaking up the hexane extract with $H_2 SO_4$ (32). This treatment destroys dieldrin and organophosphate pesticides.

5. Separation

The standard method for analyzing the PCB fraction of an extract is by gas chromatography. We will first discuss the separation of the PCB from other interfering molecules. Because of their similar polarities and chemical properties the PCBs in a sample are carried through the usual pesticide extraction and screening procedures,and are frequently mistaken for DDT and analogs in routine monitoring. PCBs accompany chlorinated hydrocarbons in the usual extraction and cleanup techniques,and both groups must be separated before quantitation by gas chromatography. Column and thin layer chromatography are usually used for the separation. PCBs are eluted from Florisil columns with hexane, DDT and other pesticides with mixtures of ether and hexane (28).

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Other workers have shown that successful implementation of this method requires a preliminary examination of the elution behavior of the pesticides from Florisil (33). Column chromatography on silicic acid separates PCB from all common chlorinated hydrocarbon pesticides except p, p' - DDE (27), and under very carefully controlled conditions even from p, p' - DDE (29). DDE and PCB can be eluted on activated Florisil columns with n-hexane with dieldrin and endrin eluting with 10% diethyl ether in hexane (21). PCB can also be separated from the chlorinated pesticides by column chromatography on charcoal. The latter are eluted with 25% acetone in ethyl ether and PCB are subsequently recovered by elution with benzene. Column chromatography on alumina is used to separate PCB from PCDD (34).

The difficulty in most of these separations is the separation of PCB from p, p' - DDE. One way of canceling this problem is to oxidize p, p' - DDE to 4, 4' - dichlorobenzophenone without affecting the PCB (35, 36). Chromium trioxide was used as the oxidizing agent.

TLC on alumina with heptane as developing solvent has been used to separate PCB from the pesticides. The spots were extracted with methanol - hexane and analyzed by gas chromatography (37). Other TLC methods of this type include separations on silver - nitrate - coated alumina with 5% benzene in hexane, or hexane after CrO_3 oxidation of p, p' - DDE (35, 36), a two - dimensional technique (38), and reversed phase TLC (39).

Chromium trioxide has also been used to oxidize PCN in the presence of PCB and thus cancel this interference (40). Where both of these families exist together, or PCNs are found in the presence of the chlorinated hydrocarbon pesticides, this interference in GC analysis definitely exists (41). A silicic acid column chromatographic method

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has been used to separate PCN from the pesticides and permits GLC determination without interference (42).

Some PCDD have also been separated from the PCB with the help of alumina column chromatography (34) and alumina column chromatography (43). After isolation electron capture gas chromatography is used for analysis.

For the separation of individual members of the PCB or other polychloro compounds gas chromatography has been the method of choice. Column temperatures have usually ranged around 180° to 200°. A wide variety of chromatography packing has been used, e.g. DC-200 on Chromport 30, DC-200 on Chromosorb W, 10% DC-200 on Gas-Chrom Q, SF-95, QF-1, 1% SE30 on Chrom Q, OV-1 silicone oil, Silicone Epikote on Diatomite CQ, 6% QF-1,and 4% SE-30 on Chromosorb W. One of the most frequently encountered is the silicone grease SE-30, often mixed with other material such as QF-1. An example of some of the separations obtained and the detector response is given in Table II-2 (44). The separation was accomplished on a glass column (6 ft x 4 mm) containing 4% SE-30 on acid washed Chromosorb W (100 - 120 mesh) operated at 200°.

Thin layer chromatography can also be used to separate the PCB (39). Kieselguhr G saturated with 8 vol. % liquid paraffin in petroleum ether is developed with acetonitrile - acetone - methanol - water (40: 18: 40: 2) saturated with liquid paraffin. The type of separation is shown in Table IV-3. The reversed phase partition TLC system can be useful for the separation of the components of a PCB mixture and can be used in combination with GC for the study of the composition of PCB residues. Visualization of the TLC spots was accomplished by UV irradiation of the silver nitrate sprayed plate.

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Table IV-2

Retention time and electron-capture detector response of chlorobiphenyls

Compound	Relative retention time (p,p'-DDE=1.00)	Relative response per ng ± standard deviation (p,p'-DDE=1.00)
4-chlorobiphenyl	0.17	0.0033±0.00005
2- "	0.11	0.0030±0.00004
3- "	0.14	0.0006±0.00001
4,4'-dichlorobiphenyl	0.30	0.0152±0.0002
3,3'- "	0.25	0.0155±0.0001
2,2'- "	0.15	0.0131±0.0001
3,4- "	0.28	0.0388±0.0002
2,4- "	0.19	0.0450±0.0004
2,6- "	0.16	0.0815±0.0049
2,4,4'-trichlorobiphenyl	0.39	0.298±0.010
2,4,6- "	0.24	0.276±0.006
2,2',4,4'-tetrachlorobiphenyl	0.51	0.206±0.003
3,3',4,4'- "	0.96	0.770±0.027
2,2',6,6'- "	0.33	0.0403±0.0016
3,3',5,5'- "	0.70	0.625±0.045
2,3,4,5- "	0.69	0.715±0.010
2,3,5,6- "	0.51	0.505±0.010
2,3,4,5,6-pentachlorobiphenyl	1.00	1.30±0.017
2,2',4,4',6,6'-hexachlorobiphenyl	0.78	0.545±0.029
3,3',4,4',5,5'- "	2.98	1.15±0.064
2,2',3,3',4,4',6,6'-octachlorobiphenyl	2.62	1.5[illegible]±0.020
2,2',3,3',5,5',6,6'-octachlorobiphenyl	2.45	1.53±0.076
Decachlorobiphenyl	8.20	1.61±0.086
Aroclor 1254		0.910±0.008
Aroclor 1260		1.35±0.010

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Table IV-3

Relationship between Spots Obtained by TLC and Peaks Obtained by GC of Phenochlor DP6

Spot No.	Corresponding Peak No.
1	13
2	11
3	6, 9, 12
4	7, 8, 10
5	2, 4, 5
6	3, 6
7	1, 3

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PCT are not eluted from GLC columns used for PCB. They can be determined by GLC on a 6 ft x 4 mm glass column, containing 3% OV-210 on Chromosorb WAW 60/80 and operated at 200° (45) or on a glass column (6' x 1/4") packed with 3% Dexsil 300 on 100 - 120 mesh Gas - Chrom Q, operated at 310° (46).

PCDDs can be separated on a column of 2% OV-17 on Diatomite CQ or 1% Hi-Eff 8 BP on Gas Chrom 2 (10), or on a stainless steel column coated with Dexsil 300 and programmed from 150° to 215° with helium as carrier gas and flame ionization detection (11).

Examples of separations are shown for Aroclor 1260 (Figure IV-5), Aroclor 1254 (Figure IV-6), and for PCDD, PCDE and PCDF (Figure IV-7) (12).

6. Analysis

Some of the methods worth improving,which are believed to be gaining wide acceptance (47),include procedures developed by FDA (48), Official Methods of Analysis, 1970 (49), Armour and Burke (29) and Porter et al (50).

The many unidentified compounds in PCB preparations complicate the quantitation of PCBs. Assay has been by total peak area (29) or area under one (21), two (51) or more (52, 53) peaks, or peak heights (53 - 56). A method based on the average electron-capture detector response to PCB containing one to seven chlorine atoms also has been described (20). But since position of substitution affects the response, it is no more accurate than the others.

The dissatisfaction with the accuracy obtained is evident from the many methods of quantitation being used. Some people estimate that the quantitation of PCB is accurate only within a factor of 2 (57), whereas others assert it is impossible at the moment to quantitate PCB with any degree of confidence (58).

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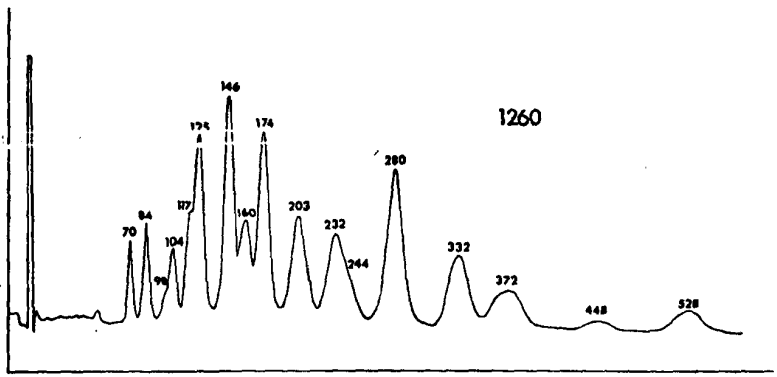

Figure IV.5. EC chromatogram of Aroclor 1260 chromatographed on SE-30 with a Ni-63 detector operated in the DC mode. The peak identification numbers correspond to the retention time relative to p,p'-DDE=100 (22).

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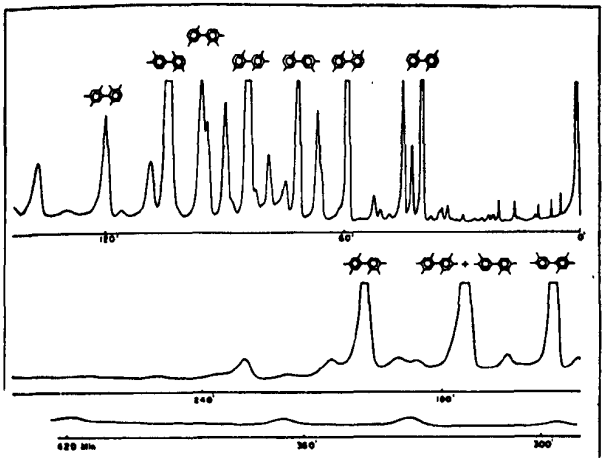

Figure IV-6. Separation of Aroclor 1254 by capillary column-gas chromatography. Conditions: 50 ft. x 0.02 in. SCOT Apiezon-L column; 205°; He flow 2.5 ml/min; flame-ionisation detector. Structures of isomers responsible for major peaks are indicated (60).

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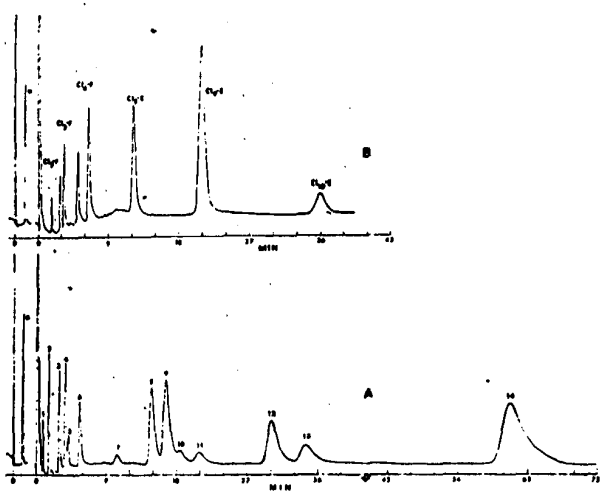

Figure IV-7. A, Gas chromatogram of a mixture of chlorodibenzo-p-dioxins (Cl_n-D): (1) 2-Cl-D; (2) 2,7-Cl_2-D; (3) 2,3,7-Cl_3-D; (4) 1,3,6,8-Cl_4-D; (5) Cl_4-D isomer; (6) 2,3,7,8-Cl_4-D; (7) Cl_5-D isomer; (8), (9), (10), and (11) Cl_6-D isomers; (12) and (13) Cl_7-D isomers; (14) Cl_8-D; a = aldrin standard. B, Gas chromatogram of a mixture of di-, tri, and tetrachlorodibenzofurans (Cl_n-F) (Cl_2-F, Cl_3-F, and Cl_4-F) and octa-, nona-, and decachlorodiphenyl ethers (Cl_n-E) (Cl_8-E, Cl_9-E, and Cl_{10}-E); a = aldrin standard.
EC-GLC conditions: 7' x 4 mm id glass coiled column packed with 3% XE-60 on 80-100 mesh Gas-Chrom Q; column temperature, 215°C; detector voltage, 80 v (tritium source); 1 x 10^{-9} AFS; nitrogen flow rate, 55 ml/min. Three µl containing 4-140 ng of each component was injected (12).

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Quantitation of PCB from electron capture chromatograms is complicated because the EC detector responds differently to each PCB isomer (44, 59). The wide response is demonstrated in Table IV-2. Quantitation by direct comparison of an unknown EC chromatogram with those of Aroclor standards is difficult because individual peaks in environmental samples are sometimes obscured by pesticide residues are completely missing, or have considerably different relative intensities.

The weight of PCB present in each GC peak of a given Aroclor can be calculated from two pieces of information: (1) the empirical formula of the compound represented by the peak, and (2) the absolute amount of chlorine represented by the peak. Combined GC - MS determines the first, and a GC equipped with an electrolytic conductivity detector can determine the second. The results are shown for Aroclor 1260 in Table IV-4 and Figure IV-5. The gas chromatograms of Aroclor 1254 and of a mixture of PCDD and PCDF are shown in Fig. IV-6 (60) and Fig. IV-7 respectively (12).

PCT can be determined by GC on a 6 ft. x 4 mm glass column containing 3% OV-210 on Chromosorb WAW 60/80 and operated at 200° (7). Eight major peaks are obtained.

It is also possible that the PCB can be analyzed by pulsed source-time resolved phosporimetry, as has been done with the monohalobiphenyls, Table IV-5(61). The limits of detection for the three 4-halobiphenyls are about 1 ng, for 2- and 4-chlorobiphenyls about 10 ng, and for 3-chlorobiphenyl about 10 μg. It also seems probable that time resolved phosphorimetry could be of value as a confirmation technique.

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Table IV-4

Composition of Aroclor 1260 (22).

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]
70	2.7	6.3	5
84	4.7	1.6	5
[98	3.8	3.5	] d
[104			5] 60%
			6] 40%
117	3.3	6.7	6
125	12.3	3.3	5] 15%
			6] 85%
146	14.1	3.6	6
160	4.9	2.2	6] 50%
			7] 50%
174	12.4	2.7	6
203	9.3	4.0	6] 10%
			7] 90%
[232			] e
[244	9.8	3.4	6] 10%
			7] 90%
280	11.0	2.4	7
332	4.2	5.0	7
372	4.0	8.6	8
448	.6	25.3	8
528	1.5	10.2	8
Total	98.6		

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of six results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[d]Composition determined at the center of peak 104.

[e]Composition determined at the center of peak 232.

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Table IV-5.

Phosphorescence Characteristics of Selected Halogenated Biphenyls (61)

Halogenated Biphenyl	Peak Phosphorescence Emission Wavelength,[a] nm	Phosphorescence Lifetime,[b] msec
2-Chlorobiphenyl	465	170.
3-Chlorobiphenyl	480	1300.
4-Chlorobiphenyl	477	570.
2-Bromobiphenyl	475	3.3
3-Bromobiphenyl	480	58.
4-Bromobiphenyl	480	17.
4,4'-Dibromobiphenyl	485	12.
2-Iodobiphenyl	490	3.0
4-Iodobiphenyl	480	3.2

[a]Solvent: ethyl alcohol.
[b]Relative errors in lifetimes are less than 10%.

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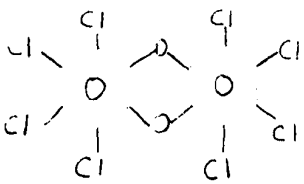
To avoid difficulties in quantitation, the PCB in a sample can be converted to decachlorobiphenyl and the EC signal from this derivative can be compared with that from conversion of a known amount of Aroclor 1254 to decachlorobiphenyl. This type of method is desirable for a monitoring program designed for rapid, inexpensive, and sensitive measurement of the total quantity of PCB without regard to composition. However, the development and usage of such a method would not preclude the need for the assay for individual PCBs.

Extracted PCB residues can be exhaustively chlorinated with chromous chloride or antimony pentachloride to decachlorobiphenyl and the electron capture signal of this compound can be compared to the EC signal of a known amount of a reference PCB mixture treated similarly (62). Aroclor 1254 has been chlorinated with antimony pentachloride and the resulting decachlorobiphenyl has been determined by GC (63).

Screening methods for PCDD residues based on their chlorination to octachlorodibenzo-p-dioxin, VI, have



VI

been developed (64, 65). The PCDD can be detected in the presence of PCB, PCN and PCDF. Chlorination with chlorine took place in the

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presence of iron filings and iodine. Ferric chloride - iodine (66) and antimony pentachloride (67) have been used as catalysts but were reported to give unsatisfactory results on the microgram scale (64). The recommended method consists of chlorination, liquid chromatography on alumina followed by electron capture GLC.

Another method of possibly quantitating the PCB as one entity involves carbon skeleton chromatography (68). The PCB residue is converted essentially into a mixture of cyclohexybenzene and biphenyl at a catalyst temperature of 300°, and into cyclohexylbenzene, and bicyclohexyl at 260°. The method needs further investigation and optimization. The technique may also be useful for confirmation purposes.

The formation of decachlorobiphenyl and its change into a measurable derivative by nucleophilic substitution reactions at the 4,4' - positions is another reaction that could be of value in developing an inexpensive monitoring method.

Confirmatory techniques are vital to assay methods for the environmental organic pollutants. The big problem is to identify component X in an environmental test sample. For the polychloro compounds assay is not enough; one must also be able to identify the pollutant unequivocally. In the majority of investigations one or more of four types of parameters have been used to identify trace amounts of organochlorine compounds: (1) GLC retention times using two or more stationary phases, (2) TLC R_f values using one or two systems, (3) preparation of derivatives and matching of the GLC retention times (and/or TLC R values) of the products with those of

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the known compounds, and (4) partition p-values. None of these procedures or their combinations are completely satisfactory to establish the identity of a component in an environmental sample. Since chemical identity at the submicro level is difficult, we will address ourselves to this problem.

The use of a double GC column system minimizes the risk of false identification, but GC alone cannot give an unequivocal identification. The use of GC with chemical treatment increases the certainty of the identification.

The uncertainties of identification are also confounded by the possibility that other halogens may be present in the PCB. Some of these compounds have been mentioned previously. Examples are trifluoropentachlorobiphenyls and trifluorotrichlorobiphenyls used in hydraulic fluids, and diaminopolyhalobiphenyls and dihydroxypolyhalobiphenyls used in the preparation of flame resistant polymers and reinforced plastics.

GLC has been the prime tool used in the analysis of organochlorine compounds, but it cannot give unequivocal characterization either with the help of retention indices, by the matching of retention time and peak height distribution with those of commercial products, by the use of halogen-specific microcoulometry to determine the presence of halogens in the compounds causing individual peaks, or by determining the resistance to attack by hot alcoholic KOH.

GLC-IR has also been used in identification studies (69). Identity was assumed if the synthetic PCB, when added to the Aroclor and chromatographed, enriched the appropriate peak and the IR spectrum

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of the synthetic isomer matched that of the isolated Aroclor isomer. Summary of the results are given in Tables IV-6 and IV-7.

With the help of carbon-skeleton chromatography PCB and biphenyl yield identical chromatograms that are different from those of DDT or other polychloro compounds (68).

Confirmation of identity can be achieved by combined GC-MS (70-72) which, in addition, yields the number of chlorine atoms per molecule (71). However, rearrangement of chlorine atoms on phenyl groups occurring in the electron-impact-induced fragmentation (7) limits the use of MS for structural studies. GC-MS does offer an excellent means of distinguishing PCN from pesticides and PCB (41). Identification of PCN has been made with the GC-MS system.

Mass spectrometric analysis has been used,even in the early work,to confirm the presence of PCB suggested by GLC data (21, 72). Although commercial PCB mixtures are complex, the mass spectra are relatively simple, since all isomers of a particular molecular composition give identical molecular ions (60), Figure II-8. The mass spectrum also reveals the typical isotope distribution pattern which is highly characteristic of the number of chlorine atoms present in the PCB isomers. The presence of these patterns facilitates identification of small quantities of PCB which may be present in a contaminated environmental mixture. The mass spectra of each set of isomeric compounds are similar and the fragmentation pattern of all the compounds from the dichlorobiphenyl isomers to decachlorobiphenyl feature successive expulsion of chlorine atoms and molecules, Fig. IV-9,

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Table IV-6. Summary of Aroclor GLC retention times and identities.

Retention Time[a]	Synthetic Chloro-biphenyl	Aroclor 1221	1232	1242	1248	1254
10	Biphenyl	X[b] C[c]	X	X	X	
13	2	X C	X	X	X	
16.9	1	X D[d]				
17	4	X C	X			
17.7				X		
18.6	2,2'	X C	X	X C	X	
21.3		X	X	X		
21.6		X	X	X		
23.5	2,3'	X C	X	X	X	
24	2,4'	X C	X	X C	X	
26	2,5,2'		X	X D	X	
29	2,5,2'		X	X C	X	
29.2	2,4,2'	X	X	X C	X	
29.9	4,4'	X C	X	C		
34	2,3,2'		X	X C[e]	X	
38	2,4,3'		X	X C	X	
38.8	2,4,4'		X	X C	X	
38.7	2,5,4'		X	X C	X	
41.5				X	X	
42.5	3,4,2'			X C	X	
43				X	X	
44				X	X	
44.5					X	
48	2,5,2',5'			X C	X	X C
49.5	2,4,2',5'			X C	X	X C
58.5	2,4,2',4'			X D	X	
61.5				X	X	
66	2,3,2',5'			X	X	X C
67				X	X	
69	2,3,6,2',6'			X	X	X D

(Continued)

Table IV-6 (Continued)

Retention Time[a]	Synthetic Chloro-biphenyl[b]	Aroclor 1221	1232	1242	1248	1254
80				X	X	
84				X	X	
89				X	X	
89.5					X	X
70	2,5,3',4'			X C[c]	X	
70.5	2,3,6,2',5'					X C
71	2,4,3',4'			X C[c]	X	
72				X	X	
76	2,3,6,2',4'					X C
82					X	
83	2,3,6,2',3'				X	X C
84					X	
95	2,4,5,2',5'				X	X C
97	2,4,5,2',4'				X	X C
98	[illegible]					X
99	2,4,5,2',3'				X	X C
101					X	X
104					X	X
107	2,3,6,3',4'				X	X
115						X
117					X	X
119						X
125	2,4,6,2',3',5'					X C
126	2,4,5,3',4'				X	X C
135						X
147						X
148	2,4,5,2',4',5'					X C
149						X
152						X
165						X
170						X

[a] Relative to p,p'-DDE at 190°C on 180' × 0.02" SCOT SE-30 column.

[b] X indicates a GLC peak in this Aroclor at this retention time.

[c] C means that the synthetic compound in the second column was confirmed by GLC and IR in this Aroclor. Because of the labor involved, most compounds were only confirmed in one Aroclor. For example, biphenyl is probably present in 1232-1248 as well as 1221.

[d] Only GLC data available.

[e] Something else also present.

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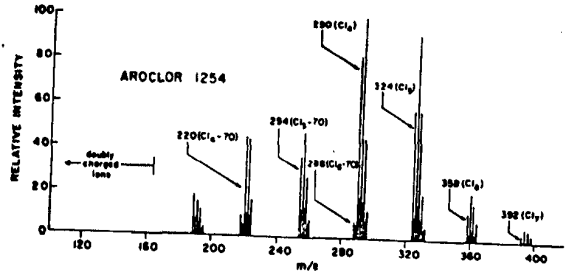

Figure IV-8. Mass Spectrum of Aroclor 1254.

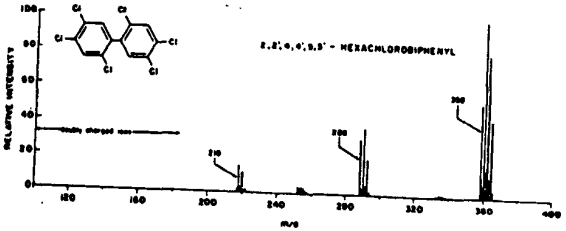

Figure IV-9. Mass Spectrum of 2,2',4,4',5,5' - Hexachlorobiphenyl.

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with elimination of HCl from the less chlorinated homologues also evident (60).

The molecular-ion peaks of the major biphenyl components are easily distinguishable from those of the most common chlorinated pesticides (73). For mixtures, it is possible to obtain separate spectra by using a controlled temperature probe and by operating at the temperature at which the components fractionally sublime; for the PCB and DDT these are 24^{0} and 67^{0}, respectively.

Nuclear-magnetic-resonance spectroscopy has also been used to resolve the structures of some of the PCB isomers (74). Unequivocal characterization of the components of technical PCB mixtures has also been claimed based on the criteria of the availability of the pure standard, GLC retention times on three different GLC columns, infrared spectra and NMR spectra (75).

Some of the reactions of the fully chlorinated PCB, etc. could be developed into confirmatory tests (76). Thus, decachlorobiphenyl reacts at the 4,4'-positions in nucleophilic substitution reactions. The halogens in these positions are activated so that they can be substituted by more eletropositive groupings.

Ultraviolet absorption spectra are also useful in confirming the basic ring structure. The PCN can be differentiated from the other polychloro compounds by the long wavelength band at 305 nm. The PCDF have a very characteristic UV spectrum. The spectra of the PCDD are given in Table IV-8 (24). In addition, the PCDDsgive a blue color reaction in concentrated H_2SO_4 when treated with an oxidizing agent such as potassium nitrate (66,77). This

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Table IV-8. Ultraviolet Spectral Data for Chlorinated Dibenzo-p-dioxins

$CHCl_3$

Dibenzo-p-dioxin	λ	ε	λ	ε'	ε/ε'
Unsubstituted	248	1020	293	3680	0.278
1-Chloro-	248	1320	294	3190	0.414
2-Chloro-	248	1140	299	3700	0.308
2,7-Dichloro-	247	1340	302	4590	0.292
2,8-Dichloro-	247	1180	299	4690	0.252
2,3-Dichloro-	247	1830	304	3190	0.573
1,2,4-Trichloro-	253	5290	294	2250	2.36
1,2,3,4-Tetrachloro-	257	6290	317	2290	2.75
2,3,7,8-Tetrachloro-	248	2970	310	5593	0.532
1,3,6,8-Tetrachloro-	250	5540	305	3440	1.61
1,2,3,4,7-Pentachloro-	259	5920	306	2690	2.20
1,2,3,4,7,8-Hexachloro-	259	5370	316	3660	1.47
1,2,4,6,7,9-Hexachloro-	259	4450	310	1480	3.01
Octachloro-	261	13150	318	2400	5.48

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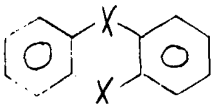
formation of a highly colored cation radical is characteristic of compounds of structure VII, where X can be O, S, Se or Te.



VIII

The PCDDs also show widely varying phosphorescent spectra which can be used in characterization studies, (See Table II-9). In addition, all of the isomers are distinguished easily from one another by their infrared spectra and the PCDDs can be distinguished from the PCDF and PCDE by their characteristic mass spectral fragmentation patterns.

Confirmation of the structure of the PCB isomers could also be accomplished with the help of pulsed source-time resolved phosphorimetry (61).

C. Air

The vapor pressures, boiling points and distillation ranges of PCB technical mixtures give an indication which of these compounds will be found in the vapor phase and or in the particulate phase in the air (78). Thus, the distillation ranges of the Aroclors vary from 275 - 320° for Aroclor 1221 to 435 - 450° for Aroclor 1268. Anthracene and phenanthrene boil at 341 and 338°, respectively, and are probably present in the atmosphere in the vapor phase since

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Table IV-9. Phosphorescence Spectral Data for Chlorodibenzo-p-dioxins

Dibenzo-*p*-dioxin	Excitation, λ (nm)	Emission bands, λ (nm)
Unsubstituted	294	386, 395,[a] 410, 418, 426,[b] 438
1-Chloro-	296	396, 402,[a] 422, 430[a]
2-Chloro-	295	400,[a] 420
2,7-Dichloro-	300	404,[a] 412, 426, 433, 458, 465
2,8-Dichloro-	304	400,[a] 404,[b] 412, 420, 428, 432, 440, 450, 458
2,3-Dichloro-	312	408, 418, 435[a]
1,2,4-Trichloro-	304	412,[b] 418,[b] 427, 439[a]
1,2,3,4-Tetrachloro-	304	485[a] (very broad)
2,3,7,8-Tetrachloro-	305	411,[a] 418, 422, 436, 440, 448, 468
1,3,6,8-Tetrachloro-	300	410,[a] 418, 433, 438, 465
Octachloro-	310	433,[a] 458, 490

[a] Strongest peak. [b] Peak not resolved.

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they are not usually collected on glass fiber paper with a high volume sampler. Anyway, as far as this type of collection is concerned, they are atmospheric vapors. This would mean that Aroclor 1221 also could not be collected in this fashion. Fluoranthene, pyrene and chrysene have boiling points of 384°, 394° and 441°, respectively, and are probably mainly collected as particulate with a large portion not collected by the filter. This means that Aroclor 1268 could be only partially collected as particulate.

The importance of PCB in the atmosphere derives from the spread of the PCB by air transport. The following sources are of importance - (a) Manufacturing in the Sauget, St. Louis and Anniston, Alabama plants of the Monsanto Co., (b) Evaporation from incineration of refuse that contains PCB, (c) Use and wear of PCB containing materials, (d) Leakage from closed systems, (e) Open air burning, (f) Fine spray mist from the concentrated monomolecular layer of the oceans and other bodies of water.

In a study of air over the North Atlantic ocean and in Bermuda PCB could only be found in the vapor phase (79). None were found in the particulates, although PCBs have been reported in selected urban airborne particulate samples. A large amount of PCBs must get into the air since it has been shown that 81% of incinerator workers have PCB in their blood plasma (81).

Collection of PCBs has been accomplished by passage of air at 20-30 CFM through ceramic chips coated with 0.1% OV-17 (79). PCB were not

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detected in a sample of marine air taken off the California coast (82). However, PCB fallout has been reported in southern Sweden. PCBs also have been detected in black snow in southern Sweden.

Certainly, a variety of good analytical techniques are now available for the PCBs which could easily be applied to air analysis, but a good sampling method for atmospheric PCBs needs to be developed

D. Water

The solubilities and the partition coefficients of the PCB are of prime importance in understanding the distribution of the PCB in aqueous systems. These physical constants have been discussed (84). Because of their low solubility and high adsorbability most of the PCB could be expected to be present in aqueous sludges or sediments. Similarly, tetrachloro DO, like DDT and higher PCB is soluble to the extent of 0.2 ppb and is strongly adsorbed on clay and organic matter. The solubilization of PCB in water by non-ionic surfactants as well as the determination of concentration of the solubilized PCB by UV spectrophotometry, fluorescence and GLC has been described (85).

Sampling of water solutions of the PCB has been accomplished by extraction with organic solvents (86), adsorption on activated carbon (87), collection by reversed phase liquid-liquid partition (88), collection on a porous polyurethane foam (89), and passage through a 3g. filter containing a mixture of n-undecane and Carbowax 4000 monostearate on Chromsorb W (88). Extraction is time-consuming and needs to be done in the laboratory. However, the process can be

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considerably speeded up and made more efficient by means of ultrasonic extraction. Recovery from charcoal is variable and inefficient and the recovered material may be significantly different from the initial PCB. The reversed liquid-liquid partition filter gives excellent recoveries but is limited by low flow rates and requires elaborate preparation.

A recent method for collection and elution of PCB (89a) from seawater utilizes Amberlite XAD-2 Resin (XAD-2) (89b), a synthetic polymer of styrene and divinylbenzene which is further crosslinked and formulated into 20-50 mesh white beads. The claimed advantages of this material as compared to polyurethane and reversed phase liquid-liquid chromatography are that: (a) it is not compressible even at a depth of 1000 m, (b) there is no organic coating on the XAD-2 so that after elution of the column, it is ready to be reused, (c) chlorinated hydrocarbons are readily adsorbed from seawater, and (d) they are readily eluted quantitatively by 4 bed volumes of acetonitrils or ethanol.

Material collected on a solid material can be eluted with petroleum ether, cyclohexane or with acetone and hexane or ether and hexane. If necessary ultrasonics can be used to speed up the extraction. Another possibility is direct sublimation into the GC. Ultrasonic extraction and sublimation have been found to be useful in our laboratories in the analysis of atmospheric PAH.

Although the extraction of PCB from sewage solids using a mixture of n-hexane and isopropanol is probably less efficient than extraction from water, many sludge samples were found to

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give gas-liquid chromatograms similar to those of PCB mixtures (90). Aliquots of concentrated extracts of California coastal waters contaminated by PCB from urban sewage outfalls have been analyzed by GLC using a ^{63}Ni electron capture detector and a 3% QF-1 column on 80 - 100 mesh, acid-washed, DMCS-treated Chromosorb (91).

The occurrence and distribution of the PCB in the River Rhine and the coastal areas of The Netherlands have been studied with the help of GC-MS (21). Computer-controlled GC-MS has been used to identify tetrachlorobiphenyls in a Los Angeles sewer extract (92). The sensitivity of the method for aqueous PCB based on reversed phase liquid-liquid partition between water and Chromosorb W (coated with n-undecane and Carbowax 4000) is in the ppt range (88).

Highly sensitive and reliable methods are needed for analysis of water samples especially those obtained from the ocean since it has been reported that aqueous concentrations in the North Atlantic are 35 ppt at the surface, 10 ppt at 200 meters and traces at 3000 meters (79). The lack of systematic analytical procedures for the characterization and determination of PCB in natural waters has been pointed out in a recent review (93).

E. Soil

Very little work has been done in the study of the contamination of soil with PCB. It has been estimated that the half life of PCB soil is of the order of five years while tetrachlorodibenzo-p-dioxin appears to have a long life in soil. The persistence of pesticides

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in soil has aroused considerable interest in recent years, as evidenced by soil monitoring activities at local and national levels (94 - 98). The extraction of residues from soil is as important as their determination since residues not extracted are not measured. The usual extraction methods make no provision for rupturing cells and liberating bound residues. Ultrasonic extraction has been used to obtain insecticides from soil (99) and polynuclear aromatic hydrocarbons from air particulate samples (100) efficiently and quickly. The PCB could be extracted in the same way from the various types of soil samples and further cleanup, characterization and assay would be by some of the procedures previously described.

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F. Food and Biological Tissues

1. Introduction

The sampling and analysis of polychlorobiphenyls in biological tissues is essential for the establishment of the extent of their deposition and distribution in the biosphere. The food chain probably represents the major source of man's exposure to PCB's. This supposition can only be confirmed when the levels of PCB's in the environmental media, in man's food and in man himself can be accurately determined and correlated. The deposition, retention and metabolism of PCB's in the human body must be determined before the potential hazard to human health can be assessed. Measurement of PCB residues in wildlife is likewise necessary to ascertain what biota serve as "sinks" for PCB's and to what extent PCB's are a threat to the ecosystem.

While different sampling methods may be required for different biological specimens, the isolation, cleanup and analysis methodologies for PCB's in foods and in plant, animal and human tissues and fluids will be essentially similar. For this reason, these laboratory procedures will be discussed in general and pertinent information regarding specific sampling and analysis techniques will be discussed separately.

2. Isolation, Cleanup and Analysis

Polychlorobiphenyls are chemically similar to organochlorine insecticides. The methods of extraction, cleanup

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and determination developed over many years for organochlorine pesticides are, for the most part, also satisfactory for PCB's. PCB's readily pass through the analytical schemes designed for the recovery of pesticides from plant and animal tissues and when present in sufficient quantities interfere with the determination of many of the chlorinated pesticides. In fact, the existence of PCB's in the environment was first discovered in this way[2] and PCB "contamination" continues to plague the pesticide residue chemist. Several means of eliminating this mutual interference have been developed in recent years.

(a) Pesticides Residue Analysis

The most generally accepted methods for determination of organochlorine pesticides in biological tissues are those published by the U.S. Department of Health, Education and Welfare, Food and Drug Administration, in their Pesticide Analytical Manual(101). There are essentially two procedures:

(1) For fatty tissue (both animal and plant), the pesticides are extracted (along with lipids) from the ground or chopped specimen with an organic solvent such as hexane. The pesticides are then separated from the lipids by liquid-liquid partitioning into acetonitrile. Column chromatography on activated Florisil (a magnesia-silica gel adsorbant manufactured by the Floridin Company, Pittsburgh, Pennsylvania) is then utilized to remove remaining lipids and to fractionate the pesticides into groups to facilitate their identification. Finally fractions from the Florisil column are analyzed by gas chromatography coupled with an appropriate detector.

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Organochlorine pesticides can be identified and quantitatively measured by either of two chlorine-specific detectors, the electrolytic conductivity detector (102) or the microcoulometric titrator (103). However, due to the relatively low sensitivity of these detectors (10-50 ng minimum detection limits), the non-specific electron capture detector (5 to 100 pg minimum detectability, ref. 104 is more often used.

(ii) Non-fatty tissues (less than 10% fat) are usually extracted directly with acetonitrile or some other solvents. Otherwise, the methodology is the same as that for fatty tissues.

(b) Separation of PCB's from Pesticides

In these procedures, polychlorobiphenyls are extracted from plant and animal tissues along with any pesticides present. Some losses may result on acetonitrile partitioning, however. Risebrough (105) cautioned that as much as 30% of the rather nonpolar PCB's may remain behind in the hexane layer. Reports of nearly quantitative recoveries of Aroclors from fatty foods (29) suggest that efficient partitioning is possible. It should be noted that the FDA procedure (101) calls for partitioning four times. Recoveries of nonpolar pesticides such as aldrin are only about 70% after the first partitioning. Chromatography on Florisil will not allow separation of PCB's from many organochlorine insecticides. The PCB's are eluted in the first fraction (6% diethyl ether in petroleum ether or 20% methylene

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chloride in hexane, depending on the method used) along with most of the organochlorine pesticide group. Initial elution with n-hexane has been used to effect a partial separation (21,28) but for the complete separation required for analysis further steps are necessary.

The problem of separating PCB's from chlorinated pesticides has been approached successfully from several directions. The separation may be accomplished either by physical or chemical means.

(i) Physical separations have been primarily accomplished by liquid-solid absorption chromatography, often in conjunction with Florisil cleanup chromatography. Holden and Marsden reported success with alumina and silica gel (27). Synder and Reinert found silica gel to be effective in separating Aroclors 1254 and 1260 from DDT and its metabolites (106). Gel permeation chromatography has been recently reported to be efficient and reproducible for both cleanup and separation of PCB's from organochlorine pesticides (107). A still more recent paper describes the use of activated charcoal (63). Extracts are adsorbed in a column of cocoanut charcoal. An ether-acetone mixture is used to remove the DDT group of pesticides (with 91-94% efficiency) and benzene serves to elute PCB's (90% efficiency). Oils or fatty extracts can be removed by Florisil cleanup after the charcoal separation.

A technique developed by Armour and Burke of the FDA (29) has now been incorporated into the Pesticide

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Analytical Manual (108). This technique employs column chromatography on silicic acid-Celite after the Florisil cleanup.

Thin-layer chromatography has also been used to separate PCB's from pesticides. Probably the most widely used method is that of Mulhern et al. (35). After Florisil cleanup, the 6% ether-pct ether fraction is thin-layer chromatographed on alumina G impregnated with silver nitrate. The PCB's accumulate in one spot, visible after exposure to ultraviolet light, and are estimated semi-quantitatively by visual comparison to a standard of Aroclor 1260. Another method is based on two-dimensional thin-layer chromatography (38).

Reversed-phase paper chromatography has also been used successfully to separate PCB's from chlorinated pesticides and their metabolites (109). The former exhibit much lower R_f values.

(ii) The other means by which interferences by some organochlorine pesticides can be eliminated is by chemical alteration. The PCB's resist alteration due to their high chemical stability. The most common methods used are nitration (28,110) and dehydro-chlorination of the pesticides (111). Both of these methods have draw-backs in that they do not eliminate all chlorinated pesticides; the products produced may have long GC retention times and thereby cause analytical problems; and some of the PCB isomers may also be altered. Treatment with fuming nitric

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acid is known to nitrate some of the lower chlorinated biphenyls and will not affect some pesticides, such as toxaphene, lindane, γ-BHC or strobane (112) Dehydrochlorination with alcoholic potassium hydroxide will eliminate DDT and DDD, but not the important interferent DDE (in fact, it may produce it). Fuming sulfuric acid can also be used to eliminate interference by aldrin, DDT, DDD and DDE, but not lindane or heptochlor epoxide (88).

A recently reported method takes advantage of the high thermal stabilities of PCB's to eliminate them as interferences in the determination of organochlorine pesticides (113). In the Coulson electrolytic conductivity detector chlorine-containing organic compounds are pyrolyzed in a hydrogen atmosphere as they exit from the gas chromatograph. The hydrogen chloride produced is passed through de-ionized water and measurement of electrical conductivity is used to determine the initial amount of compound present. Under the normal operating conditions (850°C), both PCB's and chlorinated pesticides are pyrolyzed. However, at 600°C, the PCB's are not burned and will, therefore, produce no response. In this manner, PCB's may be determined by differences.

c. Quantification

Once PCB's have been isolated from biological media and interfering organochlorine pesticides, the problem then arises as to how to quantify them. There are 210 possible compounds of mono- to decachlorinated biphenyl (72).

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Commercial preparations, such as the Aroclors, are complex mixtures of many chlorinated biphenyls. A gas chromatogram of a given Aroclor will reveal many peaks and any given peak may represent a number of different isomers and/or chlorine homologs of chlorinated biphenyls. Once released into the environment, the composition of a commercial preparation will change since the different PCB compounds contained therein have different volatilities, solubilities and stabilities to chemical and metabolic breakdown. It is highly unlikely, for example, that Aroclor 1254 will be found in any environmental sample. A distribution of PCB's tending to match an Aroclor 1254 standard may be detected, but that would not mean that the sample was exposed to that particular Aroclor. In fact, even the composition of Aroclor 1254 (or any other Aroclor) will vary slightly from batch to batch. Yet, for lack of better methodology or lack of understanding, nearly all residue analysts in the United States try to identify and quantify PCB residues as particular Aroclors.

Estimation is usually accomplished by:

(i) "Fingerprint matching" with a known PCB standard and summation of all components detected (114);

(ii) Using the average of two peaks (28);

(iii) Comparison to p,p'-DDE using electron capture detection (30); or

(iv) Comparison to the peak in Phenoclor DP6 which has a retention time relative to dieldrin of 1.45 (21).

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Electron capture detection (ECD) is most often used in each case. Another method which is perhaps better is that of Rote and Murphy (20). These investigators prepared electron capture response curves of total peak area per nanogram for six Aroclors versus the average number of chlorine atoms per molecule for each Aroclor. Unknowns were then compared to this response curve for identification and quantification. Of course, such response curves would have to be prepared frequently to assure accuracy.

In all of these methods, as well as in the thin-layer chromatographic methods previously mentioned, the PCB's are determined as an Aroclor (or its European or Japanese counterpart), which has no real meaning.

Isomeric groups of polychlorobiphenyls can be detected by mass spectroscopy. It is possible, therefore, to determine the amounts of tetrachloro-, pentachloro-, hexachlorobiphenyls, etc. in a PCB mixture (92,115). By combined gas chromatography-mass spectroscopy (GC-MS), the molecular weight and chlorine number associated with each peak can be ascertained. Elucidation of the structures of the many individual isomers is a very difficult task, particularly since chromatographic separation prior to analysis is not possible.

Perhaps the most valuable application of mass spectroscopy to PCB and pesticide residue analysis is as a confirmatory tool. Although GC-MS is one or more orders of magnitude less sensitive than GC-ECD for PCB's, it has sensitivity

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as good or better than other chlorine-sensitive detectors and it is far more specific. Mass spectroscopy is often the only way by which the identity of a trace pollutant can be established. Mass spectrometers are not, however, simple to operate. Computer operation and data interpretation is usually required, with very expensive instrumentation the result.

The problem of the multi-component nature of PCB's can be circumvented by chemical conversion to a single compound and at the same time a large increase in sensitivity can be achieved. There are two methods: dechlorination to biphenyl (63,116,68) and perchlorination to decachlorobiphenyl (63). By these methods all isomers and chlorine homologs are converted on one chemical entity which allows determination of the total PCB content of the sample. Problems with identification, interference and detection limits are reduced since one peak instead of many is obtained from the gas chromatograph. Dechlorination (usually with hydrogen over platinum or palladium) is less advantageous in that the product is a hydrocarbon and can be measured only at a relatively low level of sensitivity. Perchlorination with antimony pentachloride yields fully chlorinated biphenyl for which chlorine-specific and electron capture detectors should be most sensitive. At the microgram level yields are reported to be 85 ± 5% (63). On gas chromatography using SE-30, the decachlorobiphenyl peak is well removed from those of common chlorinated pesticides (44). The perchlorination procedure, therefore, offers

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much promise for the solution of the complicated problems of analysis and quantification of PCB's. Confirmatory analysis, usually very difficult at the residue level, is also greatly simplified.

3. Foods

Extraction and cleanup methodologies suitable for analysis of PCB residues in food products are provided in detail in the FDA's Pesticide Analytical Manual (101); the USDA's Chemistry Laboratory Guidebook (117), the "Guide to the Analysis of Pesticide Residues" published by the U. S. Public Health Service (118), the Canadian Food and Drug Directorate's "Analytical Methods for Pesticide Residues in Foods" (119), and the Official Methods of Analysis of the Associates of Official Analytical Chemists (120).

Instructions for the collection of food and feed samples for pesticide residue analysis are given in the FDA Inspectors Programs Manual. Total composite samples of approximately 20 pounds are collected from retail units, warehouses and transport vehicles. Additional specifications are given for sample sizes for selective samples such as raw agricultural products, milk, eggs, meat, etc.

The Manual also covers sample preparation, as does the Pesticide Analytical Manual (ref.101,Section 141). Inedible and decomposed parts, soil, waxes, etc., are removed from raw agricultural products and discarded. In the case of processed foods, packing liquors are analyzed only if

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normally consumed and dehydrated or concentrated foods are not reconstituted prior to analysis. Meats and other fatty foods are ground or blended, usually with anhydrous sodium sulfate for drying, and extracted with petroleum ether. The extract is dried to recover the fat. The fat is then redissolved in a minimum quantity of petroluem ether and the pesticides (or PCB's) are partitioned out into acetonitrile. Cleanup and separation procedures described previously are utilized. Sweep-codistillation of pesticidal compounds from edible fats and oils is sometimes employed (121). Non-fatty foods (fruit, green vegetables, berries, corn meal, potatoes, wheat, etc.) are analyzed in much the same manner. The primary difference is that extraction and partitioning are done in one step. The commodity is usually blanded with acetonitrile, filtered, sodium chloride solution added, and then extraction with petroluem ether is carried out. Milk requires some special treatment. Whole milk is mixed with an equal volume of ethanol or methanol and sodium or potassium oxalate is added. After further dilution with aqueous sodium chloride, it is extracted with a 1:1 mixture of petroleum ether and diethyl ether. Partitioning into acetonitrile and Florisil cleanup follows this treatment.

The latest addition to Volume I of the FDA Pesticide Analytical Manual describes a method for exhaustive extraction of organochlorine residues in foods and feeds (Section 253, September 1, 1972). Soxhlet extraction is employed in place of cold extraction for solid foods. A 1:1 mixture of chloroform and methanol is substituted for petroleum ether.

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The method was first reported by Porter et al. (50) for fish, meat and poultry.

Cold extraction with a 1:1 mixture of hexane and isopropanol, followed by benzene, was used by Skrentny et al. (122) to recover PCB's from homogenized corn silage. Florisil chromatography was employed for cleanup, with elution by hexane used to partially separate the PCB's from chlorinated pesticides.

Bellman and Barry (123) applied combined gas chromatography-mass spectroscopy to the determination of PCB's in several food products. The standard FDA isolation and cleanup methodologies were utilized. However, these investigators were unable to detect PCB's in any samples.

In the examination of food commodities as sources of polychlorobiphenyl injestion by humans, it would seem to be advisable to prepare the foods sampled in the manner in which they are normally prepared for consumption. Although PCB's are quite stable thermally and have only slight water solubilities, there is undoubtedly some loss on cooking. When only trace quantities are present, these losses could be very significant. This problem does not appear to have been addressed in the literature.

4. Animal Tissues

Most sampling of animal life for polychlorobiphenyl determination has been on marine fauna and predatory birds (especially sea birds). There is no standard for collection of tissue specimens and little effort has been made to compere

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the same types of tissues in different species of animals.

Adipose tissue (fat) appears to be a repository for PCB's in animals, although high levels have also been found in liver of the white sharks (124). Some animals possess two types of adipose (brown and white) in which the rates of metabolism differ greatly. For an accurate assessment of PCB residues in animals, careful consideration must be given to the selection of tissue(s).

Methods of preservation of specimens between collection and analysis have varied from study to study. Some analyses have been performed on animals in rather advanced states of decay (57). Although PCB's are generally quite resistant to degradation, chemical and bacteria breakdown in unpreserved samples could result in losses. Other decay products may also interfere with PCB determinations. Tissue or whole specimens should, therefore, be frozen, preferably with Dry Ice, until analyzed. Under no circumstances should chemical preservatives such as formaldehyde be used. Care should also be given to selection of storage vessels. Contamination by PCB's or other interfering organics could result from storage in plastic containers (although polyethylene bags may be acceptable).

Preparation of samples for analysis also varies greatly. Samples may be extracted wet (with quantification of data based on wet weight) or lyophilized before analysis. It is desirable to determine residue levels in terms of dry weight;

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however, drying by lyophilization may result of losses from volatilization. In the analysis of fatty tissues, the fat can be extracted along with the PCB's, separated and weighed for quantification of the PCB's in terms of dry weight of adipose tissue.

Analytically, the same methodologies which apply to the determination of organochlorine residues in fatty foods should serve equally well for all animal tissues. In addition, the FDA Pesticide Analytical Manual offers a general method for determination of chlorinated organic residues in human or animal adipose tissue (Volume III, Section HE211). This method is discussed under Section III, 6 of this paper.

Duke et al. (125) analyzed fish, crabs, and oysters for PCB's using essentially the FDA procedure for foods except that extractions (with petroleum ether) were carried out in Soxhlet apparatus. These investigators reported the PCB's found in the first fraction from the Florisil cleanup as Aroclor 1254.

Koemen et al. (21) used nearly the same method in isolating and determining PCB's in fish, mussels and birds. In this case dimethyl-formamide was substituted for acetonitrile in the partitioning step. DeVos and Koeman also employed the same technique for chickens (126).

Armour and Burke (29), Synder and Reinert (106) and Zitko (127) used silicic acid chromatography, following conventional cleanup methodologies, to separate PCB's from chlorinated pesticides in the analysis of various species of

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fish. Zitko et al. (124) utilized the same methodology in the analysis of mussels, liver, fat and other tissues from fish and sea birds and their eggs.

Gel permeation chromatography has been employed and Stalling et al. (107,128) for preparation of fish samples for PCB analysis

Risebrough (56) removed DDT compounds as interferences in the determination of PCB's in birds and fish by nitration and saponification, then quantified the PCB's by comparison to a p,p'-DDE standard using electron capture detection and microcoulometry.

Grant et al. (54) analyzed blood, liver, kidney, testes, heart, brain, spleen and fat samples from rats dosed with Aroclor 1254. Tissues were blended with hexane and anhydrous sodium sulfate, and the extracts were treated with fuming sulfuric acid before analysis by GC-ECD. PCB concentrations were calculated on the basis of wet tissue weights.

Liver samples taken from sea otters were digested in a perchloric-acetic acid mixture and the fat extracted with hexane in work reported by Rote and Murphy (20). FDA cleanup procedures and silicic acid-Celite separation were used.

Destructive chemical treatments such as those employed in the previous three studies are risky in that some unwanted alteration of PCB's may be effected.

Widely different results may be obtained with different methods of quantification. For example, Risebrough and de Loppe (129) quantitated PCB's in two eggs of the Common Term

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using two different methods. When the areas of PCB peaks emerging after p,p'-DDE on the gas chromatogram (ECD) were compared with an Aroclor 1254 standard, concentrations of 308 and 214 ppm were calculated for the egg lipids. Comparison of the areas to the total area of the same peaks in an Aroclor 1260 standard, the values obtained were less than one-half of those calculated by the first method. Various quantitation techniques can lead, therefore, to widely differing results between laboratories.

PCB concentrations in Atlantic zooplankton were also reported by the above investigators (129). Levels ranging from 2 to 260 ppm were measured in lipids extracted with 2:1 hexane:acetone in a Soxhlet apparatus.

5. Plant Tissues

Most reports of PCB determinations in plant tissues have been on raw agricultural food products. Very little examination of non-agricultural flora has been undertaken.

Suitable analytical methodologies would be those designed for non-fatty foods discussed in Section III, 2 and III, 3 of this paper. Collection procedures would depend on the nature of the study. If environmental transport via food chains is of principal concern, plant life which serve as primary food sources for animal wildlife would be sampled. Edible portions would be taken, preserved and prepared for analysis. Preservation of plant samples is generally less troublesome than that of animal specimens,

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since decay is less rapid in the former. However, samples should be kept cool or preferably frozen until ready for analysis.

Perhaps the most important plant life for PCB accumulation and distribution along the food chain is marine flora. The common marine phytoplankton Cylindrotheca closterium has been found to concentrate PCB's present in water by a thousand-fold or more. Fish feeding on this diatom receive far more PCB's than they would otherwise extract from water and pass them along to man and other fish-eating animals. Keil et al. (52) determined the uptake of Aroclor 1242 by C. closterium by lyophilizing the sample, extracting with acetone and analyzing by gas chromatography. Identification was achieved by comparison of the relative retention times of the five major peaks. As previously mentioned, lyophilization could have resulted in losses of some PCB's from the sample and should be avoided. Centrifugation or filtration followed by air drying would have been preferable. It should be mentioned here that there is some evidence (52) that PCB's may inhibit photosynthesis in marine phytoplankton, which represent an important contribution to the world oxygen reserve. Varying sampling techniques for ocean plankton can lead to poor reproducibility and other problems (130). Samples are usually collected in nets. Mesh sizes vary and often no attempt is made to exclude sea-surface debris. Paint, oil and tar particles may be collected in the process.

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6. Human Tissues and Fluids

Analytical methodologies suitable for PCB assay in human tissues are described in Section III, 2 and III, 4 of this paper. In addition, Volume III of the FDA Pesticide Analytical Manual (131) is concerned with methods for organochlorine residues in human media. The U. S. Environmental Protection Agency has also conducted a nationwide human monitoring program for pesticides and PCB's (132). Analytical methods for that program have also been published (133).

The most commonly used method for isolation and cleanup of PCB's for human tissue is a modification of one devised by Mills (134) for pesticides in adipose tissue. The procedure is detailed in the Pesticide Analytical Manual (131). Adipose is ground with anhydrous sodium sulfate and sand, extracted with petroleum ether, filtered and weighed. The lipid extract is redissolved in petroleum ether and the organochlorine compounds are extracted into acetonitrile by liquid-liquid partitioning. Further cleanup and fractionation is accomplished by conventional Florisil chromatography. Polychlorobiphenyls and nonpolar organochlorine pesticides are eluted from the Florisil column with a mixture of 6% diethyl ether in petroleum ether. The chlorinated pesticides are removed by chromatography on silicic acid. The same or similar methodologies are applicable to liver, kidney, bone marrow, adrenal, gonads, brain and blood.

When tissue quantity is limited or when levels of chlorinated organic residues are very low, a micro method is

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available (131). As little as 50 mg of tissue may be available from autopsy and biopsy samples. With the micro procedure 10 ppb of a given organochlorine compound can be detected on this size sample. The main difference between the micro and full-scale methods is a revisal of the extraction and partitioning schemes. In the micro method, acetonitrile is used for extraction, which in turn is diluted with water, and the pesticides and PCB's are then partitioned into hexane. Chromatography on a micro Florisil column calls for elution with hexane, followed by 1% methanol in hexane. For brain tissue, the concentrated hexane extract is treated with acetic anhydride and pyridine at 60-65°C, probably to release phospholipids.

Biros et al. (70) utilized the modified Mills procedure (131,134) to isolate PCB's from human adipose tissue. The presence of PCB's was determined by electron capture and microcoulometric gas chromatography and mass spectroscopy was used for identification and quantitation. These workers used a stainless steel capillary column coated with OV-1 in their GC-MS studies. It should be pointed out that organochlorine compounds can decompose on hot stainless steel surfaces so that caution should be exercised in using this method.

In a Japanese study (135) PCB's were determined in the skin of a still-born infant poisoned by Kaneclor 400 (a mixture of di-, tri-, tetra- and pentachlorobiphenyl with an average chlorine content of 48%). The tissue was chopped

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into small pieces and extracted separately with ethanol, ether and hexane. Partitioning into acetonitrile and Florisil cleanup were then carried out according to FDA procedures (131).

Collection of tissue samples from human beings is somewhat more complicated than in the case of wildlife. Sufficient quantities of tissues are rarely available from living subjects. Hair and body fluids are readily available but do represent ideal media for assessing PCB uptake and accumulation by humans. Autopsy materials, therefore, offer the best source for such studies.

The question then arises as to what tissues to sample and from what portion of the organ they should be taken. On this question, there seems to be considerable disagreement among biochemists, pathologists and others.

A recent protocol for the collection of autopsy tissue sets has been established by the U. S. Environmental Protection Agency for the Community Health and Environmental Surveillance System (136). This protocol calls for the 19 different tissues, including hair, fat, muscle, bone and vital organs, from autopsies. Stillborns, victims of homocides, suicides, accidental poisonings and embalmed bodies are excluded. Tissues are placed into Ziploke plastic bags (polyethylene) and frozen as soon as possible after removal from the body. (Comments regarding sample preservation and preparation for analysis are presented in Section III, 4 of this paper). Clean, rust-free instruments are to be used for the autopsy.

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Since it is often not possible or desirable to collect and/or analyze an entire organ, consideration was given as to what portion of that organ should be sampled in order to provide a representative specimen. On this there is little agreement apparent among workers in the field (137). For pollutant accumulation and storage studies, however, agreement that subcutaneous fat from the peritoneum is most valuable.

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6. Source Sampling and Measurements

According to Nisbet and Sarofim[138] possible routes of PCB entrance into the environment include leaks and spills from sealed equipment, losses in manufacture, vaporization or leaking from PCB formulations and waste disposal of PCB and PCB containing products. Incineration of waste is probably the only route which presents a configuration convenient for making direct, in-stack source emission measurements. For diffuse sources such as open dump burning, accurate emission data are virtually impossible to obtain. The usual practice is to use ambient sampling and analytical procedures in the vicinity of the source and to apply estimates of thermal and turbulent diffusion, deposition, etc. to derive an approximate emission rate.

No data are available on the amount of PCB that escapes into the atmosphere with combustion products from municipal and commercial incinerators. Monsanto reports that PCB may be completely destroyed when incinerated at 800°C for 10 seconds and it has been postulated that municipal incinerators would not be a major source. Nevertheless, no data are currently available to confirm this and it is possible that poorly operated industrial and municipal incinerator may be significant sources of emission. Often hearth incinerators do not provide the preferred form of incineration due to possible vaporization of PCB on the drying grate and by-passing the flame zone in units where adequate mixing is not provided.

The possible formation of highly toxic chlorinated dibenzofurans (CBDF) and dibenzo-dioxines in the burning of waste containing chlorinated phenols and PCB should be investigated. Vos, et. al[6] suggest that the

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purification of PCB by a procedure involving blowing oxygen through the heated product may be the source of the extremely toxic CBDF found in some of the manufactured products. Current chemical techniques are not sufficiently sensitive to detect quantities that might be environmentally significant (sub nanogram or even sub picogram). Attempts should be made to determine if detectable amounts of the chlorinated dibenzofurans or dibenzodioxines are present at burning sources where there is a potential for incomplete pyrolysis and there are relatively rich levels of PCB or chlorinated phenyl in the refuse.

Although source sampling measurements on PCB have not been reported, sampling systems for detecting pesticides have been used. Stanley, et. al. (139) used a sampling train composed of a glass filter, a Greenburg-Smith impinger containing hexglene glycol and an adsorbent tube filled with alumina to detect various pesticides. The distribution of the pesticide through the three components was determined. At higher concentrations (417 ng/m^3), the per cent on the filter was highest. At lower concentrations the distribution was spread more evenly throughout the train. Caution should be exercised before reaching conclusions regarding the form of the pesticide based on the component on which it is collected. Collection efficiency studies by Miles et. al.[140] revealed that large retention percentages were found when vaporous pesticides were passed through glass, paper or membrane filters.

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V. CONTROL TECHNOLOGY

A. Background

1. Production and Uses of PCB's

PCB production in the United States during 1972 was about 15 million kg (compared to the peak of about 39 million kg in 1970). The Monsanto Company estimates that about 62% of 1972 production will be used for capacitors, and the other 38% for transformers (1). Capacitors will use mainly Aroclor 1016, but also some Aroclor 1221, while transformers will use Aroclor 1242 and 1254. Monsanto sells only to customers who handle and use the material responsibly, thereby controlling at least the primary distribution of PCB's (2). Previously common uses in plasticizers, hydraulic fluids, etc. have presumably been negligible since 1970, but disposal of pre-1970 PCB-containing products will continue for many years.

2. Sources of PCB losses to the environment

Sources of PCB losses to the environment include:

a. manufacture of PCB's

b. shipment and transfer of PCB's

c. manufacture and use of PCB-containing products

d. incineration of waste PCB's

e. sewage and sewage treatment

f. solid waste disposal in open dumps

g. solid waste disposal by landfill

h. solid waste disposal by incineration

Substantial data on discharges of PCB's from these sources are non-existent. One estimate (3) is that about 30,000 tons have been discharged into the atmosphere and about 300,000 tons to dumps over the last 40 years (out of a total accumulated loss to the environment of approximately

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390,000 tons). Of these totals, the current residual inventories were estimated to be about 20,000 tons in the atmosphere and 250,000 tons in dumps.

While there is reason to believe that the restriction of PCB's to electrical uses in recent years has reduced the rate of loss to the environment, possible alternatives for further control of losses will be considered below, on a source-by-source basis.

B. Emissions Control Alternatives

1. Manufacture of PCB's

The manufacturing of PCB's is described in early patents by Jenkins (4) and more recently by Hubbard (5) of the Monsanto Co. The process consists of two basic steps conducted in closed equipment: (a) chlorination of biphenyl (or mixtures of biphenyls and terphenyls) with anhydrous chlorine in the presence of iron turnings (as a catalyst) at a temperature of about 150°C and near atmospheric pressure and (b) distillation, either batch or fractional, under reduced (~50 mm Hg) pressure. The distilled products as liquid PCB's are generally blended and may be treated further with activated clay to improve their properties for electrical application. Following this treatment, a filtration step is required.

Recovery of PCB's from process off-gas and vent streams is typically done with demisters (for droplet deentrainment), air-cooled condensers, or shell-and-tube heat exchangers. Water absorbers are used to trap the HCl released during the chlorination step. At Monsanto plants the entire vent system is reportedly interconnected, and both water and steam (vacuum) jets are used to achieve directed flow of the vented gas. We have no data on the volumetric flowrates or PCB concentrations in off-gas or vent streams. Monsanto reports that PCB, if present in the combined vent gas, is below

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10 ppb (6). For comparison, the industrial hygiene threshold limit values in air for PCB's with 42% and 54% chlorine are about 80 ppb and 40 ppb, respectively (14).

Accidental release of PCB vapor could occur, of course, through equipment failure. However, process conditions are relatively modest, so one would expect the failure rate to be low. Wherever spills can occur (for example, in loading tank cars), concrete drainage pads with curbs are used that drain to a special sump collection system. This design is also used for process operating floors. Short-term evaporation from spills is expected to be small because of low vapor pressure at ambient temperatures (see Table VI-1). Liquid spills can be controlled with the help of various sorbents, sawdust, sand, or synthetic materials such as those developed for oil spills. Maintaining temperatures below 55°C in storage and handling of PCB's is recommended (7).

Table VI-1

Approximate Equilibrium Partial Pressures of
Various Aroclors (PCB's) at Selected Temperatures

	Equilibrium Partial Pressure (ppm by volume)		
Aroclor No.	25°C	55°C	100°C
1016	8	50	530
1242	0.13	10	530
1254	0.003	1.2	105

PCB-containing solid waste and PCB wastage from the production process is disposed on-site by Monsanto in special incinerators (8). Because of the above factors and since the manufacture of PCB's in the U.S. is entirely

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by one experienced firm, the manufacturing process presumably emits small quantitites of PCB's to the environment. Without more complete data than are presently available, however, this remains a presumption.

2. Shipment and Transfer of PCB's

Liquid chlorinated biphenyls are packed and shipped in galvanized steel drums or in tank cars constructed of nonrusting metals such as aluminum or tin-coated metal; filling is through closed pipe systems (5). Emission of PCB's to the environment during shipment and transfer would occur mainly by spillage and accidental release. Special curbed, concrete pads are used at the manufacturer's fill stations. These drain to a completely separate sump system so control is maintained over waste PCB. Secondary manufacturers, such as capacitor manufacturers, also use separate sewer/sump systems.

Spilled liquid can be absorbed on sawdust-like materials, sand, or synthetic materials such as used for oil spills. For large spills, the absorbent could be processed to recover the PCB (for example, by solvent extraction); for smaller spills, the most appropriate disposal methods would be incineration in a special PCB waste incinerator, or burial at a landfill site.

To our knowledge, no measurements of PCB losses from shipment and transfer operations have been made.

3. Manufacture and Use of PCB-containing Products

Current (1973) PCB production is being directed almost solely for capacitors and transformers. Earlier uses, in addition to the electrical industry included uses in heat exchangers, lubricants and hydraulic fluids, PCB-plasticized products, pesticides, and inks and paints, where the potential for emission of PCB's to the atmosphere was relatively high, as was the problem of waste disposal from these uses.

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The electrical industry has published a proposal for standards in handling and disposal of PCB's (7). Proposed specifications for handling PCB's in plants where capacitors and transformers are manufactured recommend keeping the temperature of PCB oils below 55°C to limit volatilization, and give guidelines for handling spills and keeping contaminated materials in closed containers.

Sampling of ventilation stacks in one capacitor assembly plant (6) where Aroclor 1016 has been used for the past year showed PCB levels of about 0.06 ppm by volume (range of analyses 0.03 to 0.09 ppm). Five stacks were sampled, using a 10-min sampling time per hour for a 25-hr period. A detailed description of the total ventilation system was not reported. Samples of air taken 2-3 miles from the plant showed no detectable PCB levels. Sampling was done by methods suggested in the NEMA proposal (7).

The ventilation exhaust rate at this plant is not known; at the concentrations reported, however, PCB losses would be slightly less than one kg per million cubic meters of ventilation air. Unless ventilation rates are very high, one would not expect from these data that capacitor and transformer assembly plants would be environmentally significant sources of PCB losses. More emissions data are needed to confirm this, however.

4. Incineration of Waste PCB's

Present knowledge indicates that proper incineration of waste PCB's must involve a suitable balance between dwell time and temperature in the incinerator, plus oxygen availability. Also, a suitable scrubber must be provided downstream of the incinerator to remove the HCl that is formed. Typical requirements are: (1) 2-second dwell time at 1100°C and 3% excess oxygen in the stack gas; or (2) 1-1/2-second dwell time at 1500°C and 2% excess oxygen in the stack gas (7).

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Commercial facilities exist for high-temperature incineration of waste PCB liquids at Monsanto Co. (St. Louis, Missouri), Chem-Trol Pollution Services, Inc. (Blasdell, New York), and Rollins-Purle, Inc. (Bridgeport, New Jersey, Scotlandville, Louisiana, and Deer Park, Texas). Software (e.g., PCB-soaked materials) and hardware (metal items containing PCB residues) are treated for recovery of the PCB's (for example, by solvent washing), and the solvent is then incinerated.

The Monsanto Co. system employs a steam-injector system for feeding the liquids into the incinerator with temperatures being maintained at 1100-1400°C with auxiliary natural gas. Exit gases are quenched to about 80°C by contact with water. Gas is then passed through a high-energy venturi scrubber for removal of particulates. Before exhausting to air at about 40°C, gases are passed through a packed column scrubber to remove residual HCl. Other systems appear to be similar and also use HCl scrubbers and particulate removal equipment (6).

Although these commercial incincerators are presumably highly efficient in destroying PCB's, we know of no emissions data that confirm their performance. Considering the amounts that may be fed to these units (the Monsanto incinerator has a capacity of 4500 tons per year), small inefficiencies in combustion could lead to relatively large emissions. If significant emissions do exist, one would not expect the HCl and particulate scrubbers to remove PCB vapor or PCB condensation aerosol less that about 2 microns diameter. On the other hand, PCB's condensed or adsorbed onto particles larger than 2 micorns would be mostly removed by high-energy venturi scrubbers. Discussion of possible emissions and their control from PCB waste incinerators must necessarily be qualitative, due to lack of data.

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5. Sewage and Sewage Treatment

PCB residues have been found in municipal and industrial waste waters, and in effluents and sludges from sewage treatment plants (8) (9) (10.). The majority of the PCB's end up in the sewage sludge, which is either used as landfill (or soil conditioner) or incinerated. Because they are relatively non-volatile and easily adsorbed onto surfaces, one would not expect the polychlorinated biphenyls to be very mobile (to either water or air) once they were spread on the land in sewage sludge. Sludge incinerators could be expected to release PCB's to the atmosphere. No emissions data are known to exist, however, so there is no way to quantify atmospheric losses or determine whether a significant fraction of PCB emissions are captured by the scrubbers that are typically used for particulate control.

With the trend toward limiting the uses of polychlorinated biphenyls to electrical uses, one would expect PCB concentration in sewage and sewage sludge to be decreasing. Such a trend has been apparent for the last 2 or 3 years (11), so efforts to improve control technology for these sources may not be warranted.

6. Solid Waste Disposal in Open Dumps

One estimate has been made that 400 tons of PCB's were released to the atmosphere in the U.S. in 1970 from open burning in dumps (3). One would expect that there would be relatively little loss by ambient evaporation, because of low volatilities and the fact that much of the PCB in dumps is presumably in sealed capacitors. There are no known data to firm this supposition, however.

The importance of open dumps as a source of PCB losses should be decreasing as a result of controls on open burning and restricted uses

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of polychlorinated biphenyls. If emissions data were obtained that indicated further controls were needed, the two most practicable alternatives would probably be to regulate against disposal of transformers and large capacitors in dumps, and to cover open dumps to reduce ambient evaporative losses.

7. Solid Waste Disposal by Landfill

Landfill sites should present much less of a PCB environmental problem than open dumps. Evaporative losses should be less, and although leaching could conceivably lead to some losses to surrounding water systems, two references in the literature (12,75) suggest that little or no leaching was occurring from the two landfill sites tested.

The two general groups of PCB-containing solid wastes that are disposed at landfills are (a) plastics, papers, and other products made prior to 1970, plus small capacitors (containing less than about 1 kg of PCB) that are used in fluorescent fixtures and residential air conditioning equipment, and (b) waste materials and equipment from major electrical uses of PCB's, including manufacture and disposal of transformers and large industrial-type capacitors (containing more than 1 kg of PCB).

The first group covers such a diverse range of products that control of their disposal would be virtually impossible. The National Electrical Manufacturers Association (NEMA) has proposed disposal regulations for the second group (7). The regulations would specify disposal of non-combustible materials such as used containers and transformer parts (after the PCB oils had been drained and washed out with solvents). Compliance with such regulations (e.g., by electric utilities and large industrial users) would be voluntary.

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The rate of biological degradation of PCB's in landfills is unknown. If build-up in the soil should be found to be a problem, the most reasonable control alternative would appear to be to regulate against disposal of large sources (transformers and large capacitors) at landfill sites.

β. Solid Waste Disposal by Incineration

Municipal, commercial, and industrial incinerators do not, in general, operate with the combination of temperature, dwell time, and excess oxygen that are designed into the special PCB waste incinerators. Considering the poor operation and maintenance that are common with municipal and commercial incinerators, it is reasonable to expect that PCB's (mostly in wastes from previously acceptable, non-electrical uses) will be volatized or partly combusted.

Recent qualitative data show that polychlorinated biphenyls can be present in particulates emitted from municipal incinerators, and that some of the PCB's are removed from the stack gas by particulate removal devices. Fly ash samples from municipal incinerators in Media, Pa., and New Orleans, La., contained PCB's (15). The Media sample was taken from the bottoms of a clarifier in the scrubbing water system for a baffle-type scrubber; the New Orleans sample was obtained from the hopper of a multiple cyclone-type collector (16).

These data indicate that from these two municipal incinerators (a) PCB's were being emitted; (b) some of the PCB's were present as (or on) particulates; (c) some of the PCB's were being removed along with other particulates by existing control devices. No testing was done for gaseous PCB's or particulate PCB's at the outlet of the control devices.

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and unfortunately, no follow-up quantitative measurements were planned (17). Until such data are obtained, discussion of the effect of particulate control devices on PCB removal from incinerators must continue to be qualitative.

Some incinerators have electrostatic precipitators for particulate emission control, but most have either low-energy scrubbing devices or no controls at all. Low-energy aqueous scrubbers would only remove PCB's associated with relatively large particulate (say larger than about 5 microns in diameter). Electrostatic precipitators could be expected to remove PCB's adsorbed on particles as small as about 2 microns quite well. For the size range about 0.1 micron to 2 microns, precipitators are notably less effective for removal than for other sizes (13). PCB mists (i.e., condensation aerosols) less than about 0.1 micron diameter, if present, should be removed to a considerable (but unpredictable) extent by precipitators. Although their resistivity is quite high (greater than 5x10" ohm-cm; ref. 5), PCB's would be present in very low concentrations compared to other particulates, so their deposition on the collecting plates could not be expected to adversely affect electrostatic precipitator performance.

C. Summary

Control of polychlorinated biphenyl losses to the environment has been greatly improved in recent years (since 1970) by three factors: (1) restriction of sales nearly exclusively to electrical uses, where the PCB's are relatively nondispersed and wastes are relatively controllable; (2) commercial availability of special incinerators for destruction of PCB wastes; and (3) restriction of burning in open dumps.

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Future losses will come mainly from PCB manufacture; waste PCB incinerators; transformer and capacitor manufacturing; spills during transportation; incineration of municipal, sewage, and commercial wastes (sources that should decline in importance as inventories of PCB-containing products manufactured before 1970 are depleted); and possibly ambient evaporation and leaching from dumps that contain large accumulations of PCB-containing wastes. Official standard guidelines for handling and disposal of capacitor and transformer materials containing PCBs have been published by the National Electrical Manufacturers Association (18).

Because of the potential importance of aerial transport of PCB's, emissions data (both before and after any existing emissions control devices) from PCB manufacturing plants, PCB waste incinerators, capacitor and transformer manufacturing plants, sewage sludge incinerators, and municipal incinerators should be obtained. These data would better define these processes as sources of PCB losses to the environment, and clarify whether further control of emissions is needed.

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