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Session III:

ENVIRONMENTAL FATE AND OCCURRENCE

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MONS 064830

INTRODUCTORY REMARKS

Ian C. T. Nisbet, Ph.D.

This is Session III on Environmental Fate and Occurrence of PCB's. We have eight papers on residue levels of PCB's in the environment, followed by four papers on transport and transformation in the environment.

We are very short of time to present 12 papers in 4 hours, so I am going to be pressing on the speakers to cut down the time they spend as much as possible. I hope you will forgive them if they omit supporting details of some of what they say. We will not be able to entertain any questions or discussion until the end of the session.

I have been asked to introduce this session by explaining what we knew about PCB's in 1971 when Monsanto first made its voluntary restrictions on sales, so that we can see what has been learned in the last 4 years. At the end of 1971, Adel Sarofim and I reviewed the data that were available on the occurrence of PCB's in the environment and tried to construct a transport model.

We wrote two papers; a preliminary version was published in *Environmental Health Perspectives* (1:21-38, 1972), and a considerably fuller version came out a few months later in the journal *Environmental Research* (5:249-362, 1972), incorporating additional data, corrections, and a comparison of our transport model with observations of residue levels in the environment. It seems that almost no one has read this second paper in *Environmental Research*, the main reason probably being that it cost $8. The moral of the story for us scientists is that if we want our work to be read and quoted, we have to release large quantities of reprints into the environment, and direct them down environmental gradients into compartments where they will have maximum biological impact.

In these papers we did four things. The first was to review the data on production of PCB's in the United States and their uses. We reviewed what data were available on releases of PCB's into the environment, both deliberate releases and accidental ones. We filled in this information with what was essentially guesswork about the remaining releases into the environment, based on our knowledge of the lifetimes of products containing PCB's, disposal practices, and the likely behavior of PCB's in the environment, including their behavior during incineration. Our conclusion was there were three major routes of release of PCB's into the environment as of 1971. The most important, amounting to about three quarters of the total, we believed would be deliberate discarding of PCB's and products containing them, mostly into dumps and landfills. Much of this discarded material would be incorporated in sealed containers and plastic. We had no knowledge whatsoever whether the material put into dumps was leaching out or not.

The second most important route, accounting for two-thirds to three-quarters of the remaining disposal, we believed was into water. This was primarily attributable to losses of industrial fluids, including hydraulic fluids, dielectrics, heat exchange fluids, fluids in compressors, and disposal of scrap fluids from manufacturing operations.

The third route of release, which we thought accounted for the balance of the total, was into the air. We thought that there were several substantial contributions to release to the atmosphere, the major one being evaporation from plasticized products. We thought there were probably also substantial releases from incomplete burning in dumps and poorly operating incinerators, together with some releases from burning of scrap products. There was also known to be some release into the environment from dedusting agents containing PCB's used on roads and parking lots.

The second thing we did was to review what was known about transport of PCB's in the environment. This appeared to fall into two major categories, transport in air and transport in water. We guessed that most aerial transport was due to passive movement of PCB's trapped on airborne particulates, eventually returning to earth in rain and dustfall. We reviewed transport in water with particular respect to transport downstream into the Great Lakes and the sea. We thought there were a number of different methods of transport, all of which were significant. These included transport in solution, movement of sediment containing PCB's, dredging of contaminated sediment followed by dumping at sea, deliberate dumping at sea of industrial waste, dumping at sea of sewage sludge, transport in sewage to ocean outfalls, leaks directly into estuaries from coastal industries, and finally disposal from ships.

The third thing that we did was to compare our estimates of releases and transport to levels that had been reported in the environment. We found five major discrepancies.

1. Surveying the environment, we could not account for more than a very small fraction of PCB's that were being released or had been released in the past.

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We concluded that most of the PCB's that had been discarded in the past were still in dumps and landfills.

2. The amount that we estimated as being released into freshwater was very much larger than anything we could estimate as being transported to the sea. We concluded that PCB's were accumulating in sediments in rivers and lakes. We also thought that they were accumulating in sediments at sea on the continental shelf.
3. Most environmental residues were of pentachlorobiphenyls and higher chlorinated species, although about half of the releases into the environment at that time and in the past had been of tetrachlorobiphenyls and lower chlorinated species. Our conclusion was that the tetrochlorobiphenyls and lower chlorinated species were being rapidly degraded in the environment. This conclusion was based on the fact that we could not find any evidence for differential transport and dispersion of the lower isomers away from points of release.
4. PCB levels in the ocean and in marine organisms—plankton, fish, and birds—were much higher than could be accounted for by aerial transport. We suggested speculatively that the major source of PCB's in the ocean might be marine hydraulic fluids.
5. There were higher residues in terrestrial birds than could be accounted for by considering known dispersive uses.

Accordingly we posed in 1972 six major questions about PCB's in the environment:

1. What happens to chlorinated dibenzofurans in the environment? Are they released, are they persistent, and are they bioaccumulative?
2. Are the PCB's being discarded into dumps going to stay there or are they going to leak out in the future? This is perhaps one of the biggest environmental questions to be solved, because our estimate was that over the past few decades something of the order of 300,000 tons of PCB's had gone into dumps and landfills.
3. Are the PCB's that are now in sediments in freshwaters and the shallow sea going to be covered up and sequestered away from us, or are they going to be continually recycled back into the environment in future years?
4. Is it correct that the tetrachlorobiphenyls and the lower chlorinated species really are rapidly degraded, and is there significant human exposure to these lower chlorinated species?
5. What is the extent of human exposure, both the average and the extremes? We suggested some numbers in our papers, but we concluded that they were very ill-defined and that the extent of human exposure was very variable.
6. Finally, what would be the effect of Monsanto's curtailment of dispersive uses in 1971? We conjectured that this action would cut out only part of the influx into the environment, and that it would be a long time before some compartments in the environment show decreases in environmental levels.

These are the questions which I think will be addressed in part by our 12 speakers this morning. In my summary statement, I will come back and see how far we have come in answering those questions in the last 4 years.

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RESIDUES OF POLYCHLORINATED BIPHENYLS IN THE GENERAL POPULATION OF THE UNITED STATES

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Abstract

Residues of polychlorinated biphenyls have been found in human adipose tissue and in milk collected from the general population of the United States. In a national survey of human adipose tissue during fiscal years 1973 and 1974, 35.1 and 40.3 percent, respectively, of the tissue collected contained levels of 1 ppm or more of polychlorinated biphenyls on a wet-weight basis. Electron capture-gas chromatographic analysis of this tissue revealed that the compounds found in adipose tissue were most comparable to those prevalent in Aroclor 1254 and Aroclor 1260. Additionally, semi-quantitative estimation of these residues was accomplished by thin-layer chromatography. Evidence from gas-liquid chromatography-mass spectrometry indicated that the most frequently encountered polychlorinated biphenyl residues were penta-, hexa-, and heptachlorobiphenyl compounds.

Human milk samples collected in selected counties of Arkansas and Mississippi were found to contain trace quantities (<1 ppm) of polychlorinated biphenyls on a wet-weight basis.

Human exposure to polychlorinated biphenyls may come from direct contact with industrial products containing these compounds, from association with contaminated environmental components or from many combinations of the two. Intake of these compounds may occur by three routes: (1) ingestion, (2) respiration, and (3) absorption through the skin and mucous membranes. Most probably, all contribute to the total body burden of these chemicals; none of these routes of exposure can now be identified as the most important.

Polychlorinated biphenyls have been found in human adipose tissue collected for the National Human Monitoring Program as reported by Yobs (ref. 1). This program is a continuing ambient monitoring activity which functions to determine, on a national scale, the exposure of the general population to pesticides and to assess changes in these parameters when they occur. Polychlorinated biphenyls, in addition to certain organochlorine pesticides, are detected in human adipose tissue following a multiresidue analytical procedure stipulated by the National Human Monitoring Program for Pesticides.

The objective of this peper is to report the findings of polychlorinated biphenyls during the human monitoring surveys conducted in fiscal years 1973 and 1974. These results are compared to those obtained in the 1971 survey. Additionally, the results of the analysis of human milk for polychlorinated biphenyls are presented. Data from gas-liquid chromatography-mass spectrometric analysis of the polychlorinated biphenyls in human adipose tissue and milk are also reported.

Early confirmation of polychlorinated biphenyls in human depot fat was accomplished in 1967 by Widmark (ref. 2) using combined gas chromatography mass spectrometry. An article by Biros et al. (ref. 3) reported that two human adipose tissues examined by combined gas chromatography mass spectrometry were shown to contain substantial quantities of polychlorinated biphenyls ranging from pentachlorobiphenyl to decachlorobiphenyl and included at least 14 isomers and chlorine homologs. These samples, supplied by the National Human Monitoring Program for Pesticides, were selected because of indications of unusually high levels of these chemicals.

One of the laboratories routinely engaged in human tissue analysis, under contract to the National Human Monitoring Program for Pesticides, published data regarding the polychlorinated biphenyl content of human adipose tissue (ref. 4). According to this study, 41 to 46 percent of the general population had levels of 1 ppm or more of polychlorinated biphenyls with isomers contained in Aroclors 1254, 1260, 1262, and 1268. The presence of these compounds, ranging from pentachlorobiphenyl to decachlorobiphenyl, was confirmed in three samples by combined gas chromatography mass spectrometry.

Polychlorinated biphenyls were found in measurable amounts in 31.1 percent of 637 samples of human adipose tissue collected from the general population as part of the Human Monitoring Survey during 1971 (ref. 1). Sample collection involved 18 states and the District of Columbia. Positive samples were obtained from each political jurisdiction sampled.

Residues of these compounds have also been detected in other human tissues and milk. In a study of human milk collected in Colorado, 8 of 40 samples contained residues of polychlorinated biphenyls ranging from 40 to 100 ppb (ref. 5).

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METHODS AND MATERIALS

Samples of adipose tissue from individuals of the general population were obtained through the cooperation of pathologists and medical examiners in 75 selected collecting sites throughout the contiguous 48 States.

Sampling: A stratified random design, with sampling proportioned to populations, was followed for selecting cities in which tissue samples were collected. The strata were the nine census divisions as designated in the 1970 Census; the sampling units in each census region were cities with populations in excess of 25,000 people. The number of cities designated within each census division was based on population. The cities which served as collecting sites are shown in figure 1.

This design provided samples which are statistically representative of the general population. For each collection site, an annual sample quota was established to reflect the demographic distribution in that census division. The sample quota in each of these groups was allocated proportionally according to the age, sex, and race distribution, as determined by the 1970 Census.

Adipose tissue was collected by cooperating pathologists and medical examiners from postmortem examinations and from specimens which had been removed during therapeutic surgery. Thus, tissues were received from patients having pathological conditions as well as those dying from sudden acute illness or from trauma. Information recorded for each tissue sample included age, sex, race, and pathological diagnosis. Geographic residence was assumed to be in the general location of the hospital. Since the objective of the program was to reflect the pesticide and other pollutant burden in the general population, samples were not collected from cases in which a diagnosis of pesticide poisoning was suspected or known, from cachectic patients, or from patients who had been institutionalized for extended periods. Further details of the program were presented by Yobs (ref. 6).

Chemical Analysis: Samples were analyzed chemically by contract laboratories using only methodologies specified by the program. All laboratories were required to maintain acceptable performance levels in an interlaboratory quality assurance program established and moderated by the EPA Pesticides and Toxic Substances Effects Laboratory, Research Triangle Park, N.C. 27711. This laboratory also provided technical assistance for the analytical portion of the program.

Samples were analyzed for selected chlorinated hydrocarbon insecticides (table 1), and polychlorinated

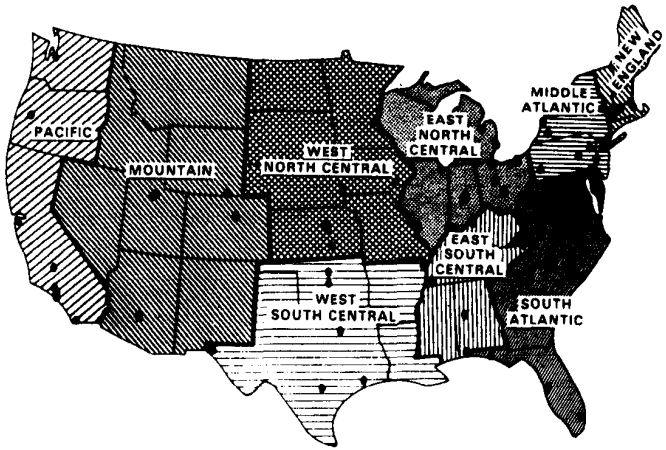


Figure 1. Map of the United States showing census divisions and collection sites for the National Human Monitoring Program for Pesticides.

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Table 1. List of chemicals detectable in human adipose tissue

o,p'-DDT	aldrin
p,p'-DDT	dieldrin
o,p'-DDE	heptachlor
p,p'-DDE	heptachlor epoxide
o,p'-DDD	endrin
p,p'-DDD	mirex
α-BHC	oxychlordane
β-BHC	trans-nonachlor
lindane	polychlorinated biphenyls
δ-BHC	hexachlorobenzene

biphenyls, using a modified Mills-Olney-Gaither procedure (ref. 6). Gas-liquid chromatography with electron capture detection was employed for basic compound identification and quantification. The analytical determinative procedure for polychlorinated biphenyls in tissue involved: (a) extraction, partitioning, and Florisil column chromatographic purification of the residues together with the chlorinated hydrocarbon pesticides present in the tissue sample, and (b), thin layer chromatographic (TLC) semiquantitative estimation of residues in the purified extract following elimination of interferences from o,p'- and p,p'-DDE, DDD, and DDT residues by chemical conversion to the respective isomer of dichlorobenzophenone. The details of the TLC procedure included treatment of the extract with ethanolic potassium hydroxide to effect dehydrochlorination of DDT and its analogs to DDE. This was followed by oxidation with chromium trioxide in acetic acid to convert DDE residues to dichlorobenzophenone, which may be conveniently separated from the polychlorinated biphenyl residues by the TLC procedure. The plates were coated with silver nitrate-impregnated aluminum oxide G and developed with 5 percent benzene in hexane. Ultraviolet visualization of the eluted polychlorinated biphenyl residues and semiquantitative comparison of sample spot intensity with those observed for standard materials completed the polychlorinated biphenyl determination.

A total of 140 human adipose tissue sample extracts from the general population have been subjected to analysis by combined gas chromatography-mass spectrometry (GC-MS) to confirm and identify polychlorinated biphenyl components stored in human tissue. Levels of total polychlorinated biphenyls in the samples based on TLC determination ranged from 0.4 to 3.5 ppm. The adipose tissue samples had been extracted and subjected to the purification procedures described earlier. Conversion of the DDT-type residues to dichlorobenzophenone was effected by the combined dehydrochlorination, oxidation, chemical procedures. A final Florisil column chromatographic step was included to further purify the polychlorinated biphenyl residues and remove the dichlorobenzophenones present at relatively high levels in the extract.

RESULTS AND DISCUSSION

The levels of polychlorinated biphenyls found in general population samples of adipose tissue during fiscal years 1973 and 1974 are presented in table 2. Results presented by Yobs (ref. 1) are included for comparative purposes. During fiscal years 1973 and 1974, 35.1 and 40.3 percent, respectively, of the tissues collected contained levels of 1 ppm or more of polychlorinated biphenyls on a wet-weight basis. These frequencies are slightly higher than the 32.5 percent figure reported by Yobs (ref. 1) and are slightly lower than those (41-45 percent) reported by Price and Welch (ref. 4). The percentage of tissues which contained quantifiable amounts of polychlorinated biphenyls appears to be remaining relatively constant. However, there does seem to be an increase in the percentage of tissues which contained trace levels of this chemical although the limit of detection (1 ppm) remained constant. It should be interesting to determine whether these trace values will be converted to quantifiable amounts as the exposure of the general population continues over time.

National frequencies for fiscal years 1973 and 1974 were compared to frequencies for each census division and are presented in figure 2. The New England, Middle Atlantic, South Atlantic, and East North Central Census Divisions had frequencies of quantifiable levels exceeding the national frequencies for both survey years. The Mountain and East South Central Census Divisions had levels higher than the national levels for one survey year and lower for the other survey year. The Pacific, West North Central, and West South Central had levels lower than the national levels for both survey years.

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Table 2. Levels of polychlorinated biphenyls in human adipose tissue

Data source	Sample size	Percent nondetected	Percent < 1 ppm	Percent 1-2 ppm	Percent > 2 ppm
Yobs, 1972	688	34.2	33.3	27.3	5.2
FY 1973 Survey	1277	24.5	40.2	29.6	5.5
FY 1974 Survey	1047	9.1	50.6	35.4	4.9

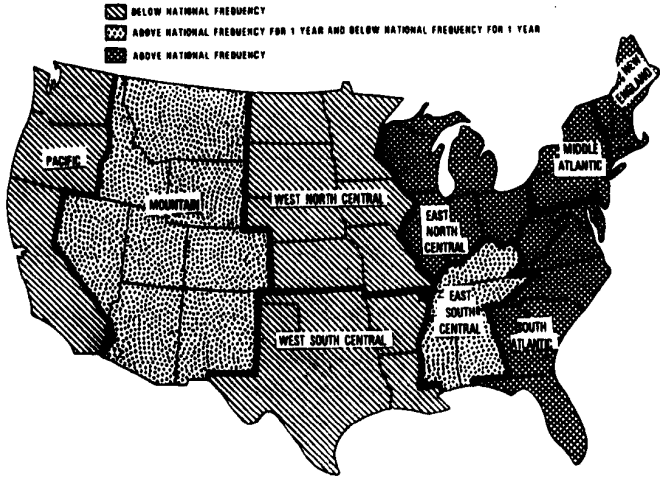


Figure 2. Map of the United States depicting census divisional frequencies of polychlorinated biphenyls.

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The most frequently encountered polychlorinated biphenyl residues in the human adipose tissue extracts examined by combined gas chromatography-mass spectrometry were the penta-, hexa- and heptachlorobiphenyl compounds.

As polychlorinated biphenyls enter a biological system, the less chlorinated isomers are apparently either metabolized or excreted. These biochemical reactions alter the original Aroclors, so that electron capture chromatograms of these compounds from biological systems do not exactly match available laboratory reference standards. However, it can be noted that results do indicate that the polychlorinated biphenyls found in human adipose tissue most closely resemble Aroclor 1254 and Aroclor 1260.

The National Human Monitoring Program also collected and analyzed 57 samples of human milk from selected areas of Arkansas and Mississippi. The survey design was related to rice culture areas in which the herbicide 2,4,5-T was used. All of these samples contained trace amounts of polychlorinated biphenyls, the presence of which were confirmed by combined gas chromatography-mass spectrometry in a composite sample.

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MONS 064837

PCB RESIDUES IN HUMAN ADIPOSE TISSUE AND MILK

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Abstract

Surveys of PCB residues in human adipose tissue suggest that females have lower residues than males, that residents of Central Canada (Manitoba and Saskatchewan) have lower levels than the rest of Canada, and that the majority of Canadians have an adipose tissue residue of 1 to 2 mg/kg. PCB residue in human milk of Ontario residents was found to be approximately 1 mg/kg fat.

Data on PCB residues in adipose tissue obtained in a national survey by Health and Welfare Canada and data obtained in a survey of residents of Ontario will be presented. Human milk PCB residue data obtained in Ontario will also be presented. The Ontario surveys were carried out by the Ontario Ministries of Health and of Agriculture and Food.

The adipose tissue samples were collected at autopsy. In all surveys, organochlorine pesticides as well as PCB residues were determined. The PCB and organochlorine pesticide residues were separated by column chromatography prior to gas-liquid chromatography and quantitation with an electron capture detector.

PCB residue data for human adipose tissues obtained in the Health and Welfare Canada survey are presented in tables 1 and 2.

All adipose tissues had detectable levels of PCB's and 30 percent of the samples had PCB residues greater than 1 mg/kg. The range of residues present was 0.11 to 6.60 mg/kg. There are some regional differences; 49 percent of the adipose tissues samples collected in Ontario had PCB residues greater than 1 mg/kg, while only 9 percent of the samples collected in Manitoba and Saskatchewan (Central Region) had PCB residues greater than 1 mg/kg. The other three regions were very similar with approximately 25 percent of the samples having residues greater than 1 mg/kg.

The mean PCB residue for all adipose tissues collected was 0.907 mg/kg (table 2). The residue present in adipose tissue from males was greater than that present in adipose tissue from females. Residues present were highest in samples collected in Ontario, with means of 1.165 and 0.859 mg/kg for males and females, respectively, and lowest in samples collected in Central Canada (Manitoba and Saskatchewan), with means of 0.621 and 0.377 mg/kg for males and females, respectively. Although differences were noted when the data were broken down (0 to 25 years, 26 to 50 years, 50+ years) to study the effect of age, these differences were not statistically significant.

The results of the surveys carried out by the Ontario government during the years 1969-1974 (table 3) suggest that the mean PCB residue in human adipose tissues collected in Ontario is higher than that reported in the survey by Health and Welfare Canada. However, the Ontario survey results are expressed on a fat basis, while the Health and Welfare Canada surveys are presented on a whole wet tissue basis. The adipose tissue contained approximately 80 percent extractable fat. Although the 1969-70 mean residue value is half that reported for the years 1971-72 and 1973-74, the authors believe this is due more to method refinement than to an actual doubling of PCB residue.

The PCB residue data obtained for the years 1971-72 and 1973-74 are broken down so that an age comparison for PCB residues can be made (table 4). Although the results have not been statistically analyzed, the 21- to 40-year age group did show somewhat lower residues than the 41- to 60- and 61- to 80-year groups.

Residue surveys were also carried out during the period (1969-1974) on human milk. The residue results suggest no change in PCB residue concentration during the years 1969-74 (table 5).

In summary, surveys of PCB residues in human adipose tissue suggest that females have lower residues than males, that residents of Central Canada (Manitoba and Saskatchewan) have lower levels than the rest of Canada and that the majority of Canadians have an adipose tissue residue of 1 to 2 mg/kg. PCB residue in human milk of Ontario residents was found to be approximately 1 mg/kg fat.

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Table 1. PCB residues in human adipose tissue

Region	Samples with PCB ≥ 1 mg/kg	Total No. samples	Percent samples with PCB ≥ 1 mg/kg
Ontario	28	57	49
Quebec	11	50	22
Atlantic	4	16	25
Central	2	22	9
Western	6	27	22
Canada	51	172	30

Table 2. PCB residues (mg/kg) in human adipose tissue

Sex	Atlantic	Quebec	Ontario	Central[a]	Western[b]	Canada
M	0.758(13)	1.125(30)	1.165(38)	0.621(11)	0.977(19)	1.020(111)
F	0.593(3)	0.723(19)	0.859(17)	0.377(11)	0.684(7)	0.685(57)
M&F	0.727(16)	0.969(49)	1.070(55)	0.499(22)	0.898(26)	0.907(168)

[a]Central = Saskatchewan and Manitoba.

[b]Western = Alberta and B. C.

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Table 3. PCB residues (mg/kg)[a] in human[b] adipose tissue

Year	Samples	Range	Mean
69-70	20	1.0-2.0	1.2
71-72	282	ND-18	2.5
73-74	129	0.6-11.0	2.3

[a]Fat basis.

[b]Ontario residents, Holdrient, et al. (ref. 1).

Table 4. PCB residues (mg/kg)[a] in human[b] adipose tissue

	Age		
Year	21-40	41-60	61-80
1971-72	0.5-6.0	ND-8.0	0.5-10.0
Mean	2.2	2.6	2.6
Samples	40	96	119
1973-74	0.6-6.0	0.7-7.0	0.6-11
Mean	2.1	2.2	2.5
Samples	13	47	54

[a]Fat basis.

[b]Ontario residents, Holdrient et al.

Table 5. PCB residues (mg/kg)[a] in human[b] milk

Year	Samples	Range	Mean
1969-70	43	0.7-1.2	1.0
1971-72	34	0.2-3.0	1.2
1973-74	19	0.1-2.5	1.2

[a]Fat basis.

[b]Ontario residents, Holdrient et al.

MONS 064840

LEVELS OF PCB's IN THE U.S. FOOD SUPPLY

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Abstract

The Food and Drug Administration has taken regulatory action since late 1969 to protect the consumer from foods found to contain hazardous levels of PCB's. It has monitored for PCB's in (1) specific products such as milk, (2) raw agricultural products, (3) commercial fish at the wholesale levels, and (4) the total diet. The foods examined were commercial products, essentially all in interstate commerce. Data will be presented on the concentration of PCB's obtained in different food commodities from 1969 through mid-1975. These data show that there has been a significant decrease in PCB levels in all foods with the exception of fish, where no particular trend has been noted. In the case of fish, almost all lots containing more than the FDA tolerance level of 5 ppm in the edible portion originated from the Great Lakes area. It is concluded that the procedures instituted to exclude the use of PCB's in the "open" applications have been effective, but that more needs to be done to prevent their entry into the aquatic environment.

The Food and Drug Administration (FDA) has taken regulatory actions since late 1969 against foods or feeds containing hazardous amounts of PCB's. The purpose of this paper is to summarize the data FDA has obtained on PCB levels in the different types of foods, and to cite the trends which have taken place since our first actions.

Table 1 summarizes the highlights from FDA's analysis of approximately 15,000 samples from November, 1969, through June, 1971. It will be noted that fish, cheese, milk, eggs, and byproducts used in animal feeds were the main commodities contaminated by PCB's. Such foods of animal origin were frequently found to contain significantly high levels of PCB's.

This table does not include data developed by the United States Department of Agriculture (USDA) in its surveillance of meat and poultry during this period. In addition, the data do not reflect the food contamination that occurred later as a result of the leakage of PCB-containing heat exchange fluid into a pasteurized fish meal, which in turn was fed to poultry and catfish. This was by far the most serious incident of PCB contamination of our food supply and led to very extensive regulatory actions by FDA and USDA, such as seizures and recalls of poultry, eggs, fish, and feeds.

During the surveillance period summarized in table 1, PCB's were not found in cereal grain and fresh fruits and vegetables. In late 1971, FDA established the fact that food packaging made from recycled paper which contained PCB's caused contamination of the contents, such as infant foods and cereals.

As a result of the above findings, FDA proposed certain regulations for PCB's in 1972. Table 2 shows our current regulations pertaining to PCB's in foods, animal feeds, and food packaging (ref. 1).

The first category of regulations covers the temporary tolerances for PCB's in products selected as a result of our monitoring activities, namely, milk, dairy products, poultry, eggs, animal feeds and their components, infant foods, and paper food packaging. Of these, fish are the only products which the PCB's contaminate primarily through the environment, in this case the waterways. The sources of the PCB's in the other foods and in food-packaging material were mainly industrial and agricultural uses which enabled PCB's to enter into food or animal feeds.

The second category of regulations is the prohibition of use of PCB's in such applications as heat transfer fluids, hydraulic fluids, paint components, adhesive components, etc., in plants that produce food, animal feed, or food-packaging materials.

These regulations were proposed in 1972 and are now officially established, with the exception of the maximum permissible level of PCB's in paper food-packaging material, which is an administrative guideline, pending the results of a hearing which has been granted.

Turning to the more recent period since 1972, the results obtained in FDA and USDA monitoring programs in fiscal years 1973, 1974, and 1975 are summarized in table 3. It can be seen that PCB's now contaminate far fewer types of foods than they did formerly. Although PCB's were reported in fish, milk, eggs, cheese, feed components, and poultry in fiscal years 1974 and/or 1975, the rates and levels of occurrence have declined drastically in all categories except fish.

The samples of fish FDA has analyzed were obtained through several different activities in the field. In fiscal years 1973 and 1974 we carried out Comprehensive Fish Surveys in which we analyzed freshwater and saltwater fish obtained at the wholesale level for

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Table 1. PCB findings, Nov. 1969--June 1971[a]

Food commodity	Positive findings	Avg. of positives (ppm)	Max. level (ppm)
Finfish	317	2.1	35.3
Oysters	12	Trace	Trace
Fish byproducts	6	1.8	5.0
Cheese	44	0.3[b]	1.0[b]
Milk	60	2.5[b]	22.8[b]
Eggs	17	Trace	0.5
Potato byproducts	12	1.1	4.2
Miscellaneous	11	1.9	6.5

[a]Approximately 15,000 samples examined.

[b]Fat basis.

Table 2. FDA regulations, PCB's

I. Temporary tolerances Commodity	PCB conc. (ppm)
Milk (fat basis)	2.5
Dairy products (fat basis)	2.5
Poultry (fat basis)	5.0
Eggs	0.5
Finished animal feed	0.2
Animal feed components	2.0
Fish (edible portion)	5.0
Infant and junior foods	0.2
Paper food-packaging material without PCB-impermeable barrier	10.0[a]
II. Use prohibited in food, feed, food packaging plants	

[a]Administrative guideline, pending hearing.

MONS 064842

Table 3. Summary of PCB's in foods, FY '73, '74, and '75

Food Commodity	FY '73 Percent positive	FY '73 Max. (ppm)[a]	FY '74 Percent positive	FY '74 Max. (ppm)[a]	FY '75 Percent positive	FY '75 Max (ppm)[a]
Fish	60.4	123.0	44.0	16.8	17.8	9.0
Milk	2.2	1.6	2.6	2.3	0.7	1.9
Eggs	1.1	Trace	4.2	11.0	0.0	N.D.
Cheese	0.9	0.5	2.6	2.8	0.0	N.D
Feed components	12.7	9.0	0.0	N.D.	0.3	0.9
Animal feeds	7.2	199.5	0.0	N.D.	0.0	N.D.
Processed fruits	4.5	19.2	0.0	N.D.	0.0	N.D.
Infant & jr. foods	1.1	Trace	0.0	N.D.	0.0	N.D.
	Percent positive	Percent above 5 ppm[a]	Percent positive	Percent above 5 ppm[a]	Percent positive	Percent above 5 ppm[a]
Meats & poultry (USDA)	1.9	0.19	1.2	0.07	0.3	0.06

[a]Milk, cheese, meats and poultry reported as ppm, fat basis.

PCB's, pesticides, and certain heavy metals. In addition, we analyzed fish obtained from our regular surveillance program for pesticides and PCB's, primarily in the raw products. Finally, we collected samples as a compliance followup after high levels of PCB's had been found in a particular species or area. The data obtained from these activities are valuable in showing which species and which areas are apt to be of concern, but it is difficult to determine whether there have been any significant trends because of the diversity of the sources of the fish samples and of the reasons for collecting them.

Figure 1 depicts the results obtained in the Comprehensive Fish Survey conducted in fiscal year 1973. It should be stressed that almost all the samples collected were commercial species intended for interstate commerce, and thus would not ordinarily include sports fish. No PCB's could be detected in over 70 percent of the samples collected. Only about 3 percent contained over 1 ppm, and 0.5 percent had over 5 ppm PCB's. It is interesting to note that the various species containing over 1 ppm were generally freshwater fish, or those which were apt to be near the shore. The only fish in this particular survey that contained more than the 5 ppm tolerance for PCB's were carp, with a maximum level of 20.5 ppm.

The results obtained in the Comprehensive Fish Survey for fiscal year 1974 are shown in figure 2. Over 80 percent of the samples analyzed in this survey did not contain PCB's, and no samples contained more than 2 ppm PCB's. However, it cannot be concluded that there was a down-trend, since it was necessary to stop this survey before it was half finished because of the necessity to divert manpower to the canned mushroom crisis. Nevertheless, freshwater fish again were most likely to contain the highest levels of PCB's.

Figure 3 depicts the results obtained with all samples of domestic finfish analyzed in fiscal years 1973, 1974, and 1975, from all FDA programs. The percentage of fish samples containing PCB's decreased in 1974 and 1975, but on the other hand, the percentage of PCB-containing samples which were above 5 ppm increased. Significantly, all these samples were from the districts in the Great Lakes area, and included such species as chubs, carp, and coho salmon.

MONS 064843

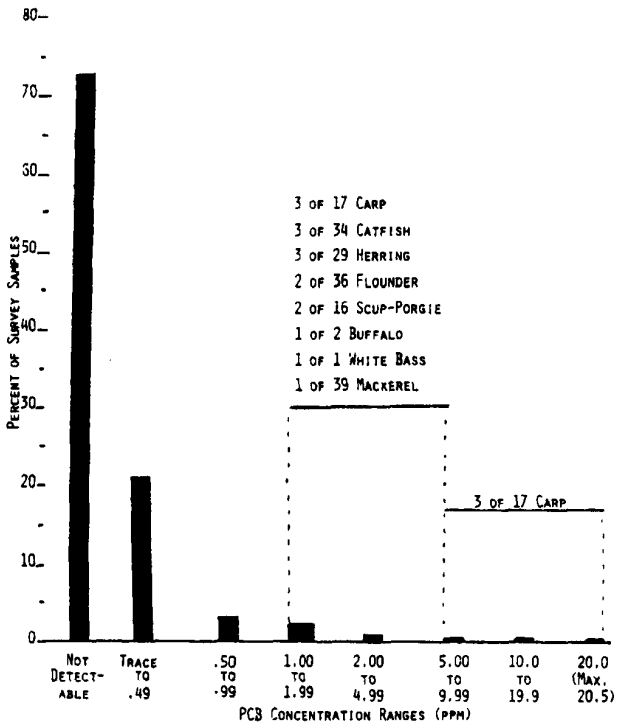


Figure 1. FY 1973 Comprehensive Fish Survey (41 species, 600 sample total).

MONS 064844

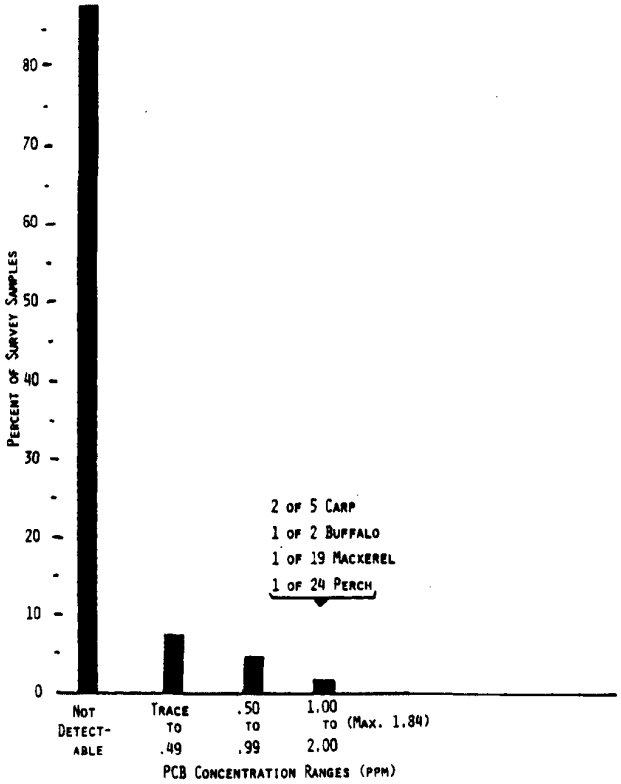


Figure 2. FY 1974 Comprehensive Fish Survey (38 species, 269 sample total).

MONS 064845

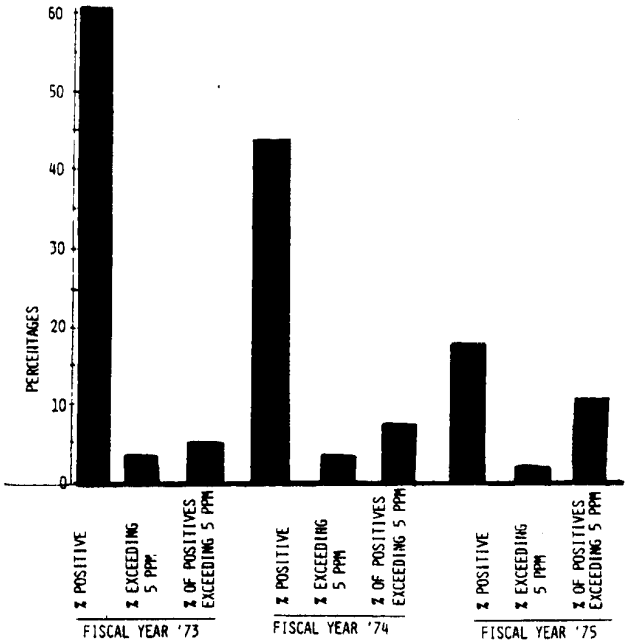


Figure 3. PCB's in fish, all programs.

As mentioned previously, it is difficult to draw any conclusions as to whether there is a significant trend, because of the changing sources and objectives from year to year. The percentage of samples examined which contained more than 5 ppm PCB's stayed in the same general range (2.2 to 3.5 percent).

These results from FDA's surveillance programs show that PCB's do not generally occur in significant levels in saltwater fish, and indeed that only a small percentage of freshwater fish in interstate commerce contain more than 5 ppm PCB's. Further, the waterways in which commercial fish are likely to contain high levels of PCB's are those which are contiguous with industrialized areas.

Thus far, we have reviewed the general levels of PCB's in individual food types. What do these findings mean in terms of average intake of PCB's from the entire diet? FDA conducts a continuing survey of the Total Diet, in which composites of 12 different food categories are analyzed. Table 4 presents the composites in which PCB's were found in the FDA Total Diet Surveys from fiscal years 1971 through the first half of fiscal year 1975. It can be seen that the meat-fish-poultry composites contained PCB's much more frequently than any other of the food groups. With regard to the findings of PCB's in the composites of fruits, vegetables, and cereals in fiscal years 1972 and 1973, it should be noted that these composites include processed and packaged

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Table 4. Total Diet Studies--American teenage male

	Percent of composites containing PCB's								
	Food class composites								
Fiscal Year	Dairy products	Meat, fish & poultry	Grain & cereal products	Potatoes	Legume vegetables	Root vegetables	Garden fruits	Oils, fats & shortening	Sugars and adjuncts
1971		47	13						
1972	6	46	6		6	3	3	17	6
1973	10	33	17	3				3	
1974		43							3
1975 (1st half)		40							

Table 5. Estimates of daily PCB intakes (Total Diet Study--teenage male)

	Average daily intake of PCB's[a]	
Fiscal year	Total diet (μg/day)	Meat-fish-poultry food class (μg/day)
1971	15.0	9.5
1972	12.6	9.1
1973	13.1	8.7
1974	8.8	8.8
1975 (1st half)	8.7	8.7

[a]Lower limit of quantitative reporting = 0.05 ppm with analytical method employed.

MONS 064847

foods as well as raw foods purchased in retail stores. Since we have hardly ever detected PCB's in the raw products, the PCB's probably contaminated these foods during processing or from the packaging. This hypothesis is borne out by the fact that no PCB's have been found in these composites in 1974 or 1975, after our regulations had a chance to take effect.

FDA chemists have found that the source of the PCB's in the meat-fish-poultry composite is almost always due to the fish component. It is interesting to note that the frequency of findings in this composite has remained quite constant since fiscal year 1971. Significantly, PCB's are now generally found only in this fish-containing composite of the Total Diet Survey. This reflects the beneficial results of FDA and USDA in their efforts to prevent the uses of PCB's that could lead to direct contamination of foods, and of the U.S. manufacturer in limiting the sales of PCB's to "closed" electrical uses.

In calculating the average daily intake from the Total Diet Survey, we must be aware of the shortcomings in the use of composites, where the level of occurrence of the contaminant in the composites may be at or just below the limits of detection. How we handle "Trace" and "Not Detected" can have a significant effect on our estimates of the daily intake. Table 5 gives the estimated average daily intakes of PCB's by a young male adult, for fiscal years 1971 through the first half of 1975, where we have ascribed a certain level to all "Trace" in all composites and to "Not Detected" in the meat-fish-poultry composites where PCB's are still commonly detected. It can be seen that there has been a marked decrease in the estimated total intake.

However, the estimated intake will tend to continue at the FY 1975 level, as long as (1) fish remain almost the sole source of detectable PCB's and (2) the entry of PCB's into the waterways is not decreased.

In summary, the breadth of occurrence of PCB's has narrowed to the point where freshwater fish are now the primary source of PCB's in our diet. Thus, the daily PCB intake for the average citizen is low, since his consumption of freshwater fish is low, and even here, most of the commercial freshwater fish contain less than 5 ppm PCB's.

However, the estimated intake of the average consumer is only a guidepost, and the Food and Drug Administration must consider the dietary consumption patterns of significant sectors of the population which are significantly different from the average. For example, PCB intake could be quite different for those people whose diets include substantial quantities of sports fish.

For the future, (1) we must continue to monitor for PCB's in foods and food-packaging materials to maintain the beneficial results already obtained, and (2) means must be employed by the responsible Federal and State agencies to effectively halt the entry of PCB's into the aquatic environment.

REFERENCE

1. Food and Drug Administration, "Polychlorinated Biphenyls (PCB's)," *Federal Register*, Vol. 38, No. 129 (July 6, 1973), pp. 18096-18104.

MONS 064848

LEVELS OF PCB's IN CANADIAN COMMERCIAL FISH SPECIES

John M. Graham*

Abstract

For purposes of examining PCB levels in various environments, Canada is divided into four study areas: area 1 is the Pacific sector; area 2 is Central Canada; area 3 covers the Great Lakes; and area 4 is the Atlantic sector. The tables included give detectable levels of PCB's in various species—ground fish, estuarial and pelagic fish, and crustaceans and mollusks—for the respective areas.

I will briefly summarize the work that the Inspection Branch has done in analyzing marine and freshwater species. And I am going to start by reporting on four areas in Canada (figure 1). Areas 1 and 4 involve marine species; area 2 is the central part of Canada excluding the Great Lakes; and area 3 contains the Great Lakes, which are of quite a bit of interest to us.

Table 1 is a brief summary of the PCB's that we have found in our marine species, subdivided as ground fish, pelagic, estuarial, mollusks and crustaceans, and miscellaneous. The landings are given in pounds, the levels are mean levels of PCB's, and the samples analyzed are in parentheses. One thing worth noticing is the high level in bluefin tuna, which is 2.65 ppm. We explain this by the fact that bluefin tune is usually landed at 600 to 700 pounds. It is a very large fish and at the top of the food chain.

Another point of interest that you might note is the fish oils with a mean level of 5.1 ppm. Finally, fish meal is at a level of about 0.16 ppm. This is because, during the manufacture of fish meal, most of the oil is extracted.

As shown in figure 1, area 2 is the central part of Canada, excluding the Great Lakes. Table 2 gives PCB levels for freshwater species in that area. The production amounts to some 70 million pounds of fish annually. There are detectable levels of PCB's, but usually very, very low. These are from large northern lakes, and usually no industry is close by. The median level is 0.10 ppm.

All our samples are based on the edible portion of the fish and that portion that would normally be consumed by the consumer. The samples are taken either by commercial fishermen or by our inspectors, so that we know the exact location at which the samples are collected. Sample size is usually 15 pounds of the fillet or edible portion and a minimum of five fish.

I have subdivided the Great Lakes–St. Lawrence River system into the lakes and the river. Table 3 shows our finding on Lake Superior, which amounts to close to 3.3 million pounds of fish per year. As you can see, the lake trout is the highest in this lake, based on our findings. We also find that it varies between the inshore lake trout or shallow-water lake trout and the deepwater, or fatty, lake trout.

Table 4 shows Lake Huron, Canadian side, amounting to some 2.1 million pounds. Chub at the 2-ppm level, and carp and suckers are relatively high. Coho salmon is not normally considered a commercial species in Canada. There is quite a volume available to sports fishermen and commercial fishermen. They sell it as part of an incidental catch.

Now we come to Lake Erie (table 5), which some people say is a dead lake, but it has an annual planting of some 31 million pounds of fish. Alewives, rock bass, and carp are slightly high. The highest is catfish and again coho salmon, which is 3.14 ppm.

Table 6 shows Lake Ontario, which, as you can see, has a little bit of a problem (or a lot of problems). Smelt is at 4.16, and eels are 17.14 ppm. Again the coho salmon is up there. The eels in Lake Ontario are quite high. The eels in the St. Lawrence river system (table 7) show about 8 ppm. I have broken the eels down into their size range and given the medians.

Note the last line. A 4½-pound eel ranges from 3 to 30 ppm, so that we really cannot manage this fishery on a size or weight basis. It is going to be extremely difficult. It looks as if we are going to have to terminate the licenses for this fishery.

These eel figures are in contrast to the figures that we had for eels in the Maritime Provinces. The eels in Maritime Provinces are 0.56 ppm. So it is apparent that we will be able to keep one section of this fishery open and must try to manage or close the other one.

We presently have a 2,500-sample survey for the Great Lakes. Health & Welfare, Canada, established a temporary guideline of 2 ppm in fish; this means that we are going to have to break some of our lakes down into areas, geographic areas, and put restrictions on them either by length or weight. I do not see the problem getting any better in the next year.

MONS 064849

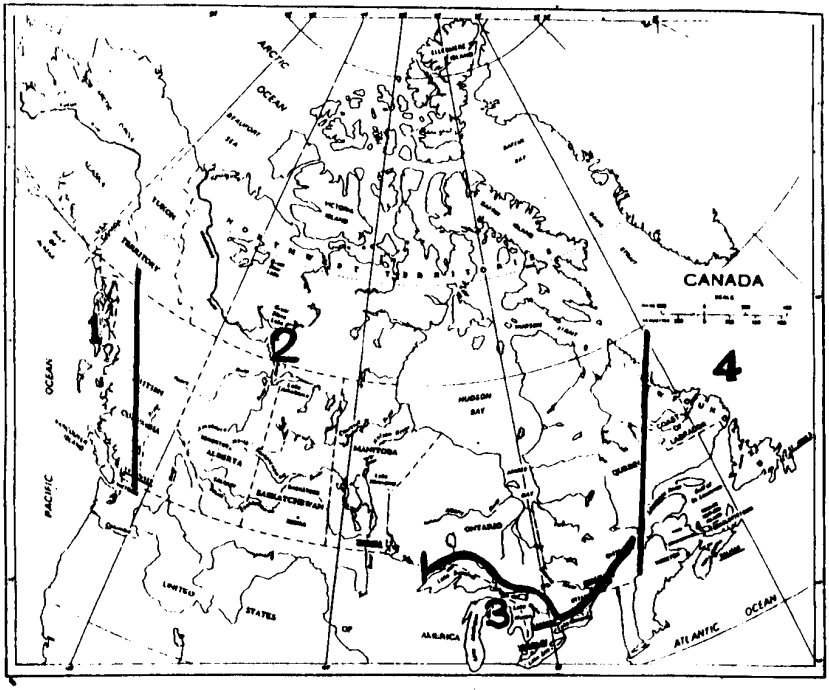


Figure 1. Four fish species areas in Canada.

MONS 064850

Table 1. Polychlorinated biphenyls in commercial fish and fishery products, areas 1 and 4 (marine)

	Description and species	Landings (pounds)	PCB's (mean ppm)
Groundfish	(catfish, cod, flounder, haddock, halibut, lingcod, pollock, redfish, red snapper, rockfish, sablefish, skate, sole, plaice, tomcod)	1,191,701,000	0.07 (141)
Pelagic-esturial	(Alewife; capelin; dogfish; herring; mackerel; salmon; smelt; swordfish; tuna: albacore-skipjack-yellowfin; whale)	1,131,868,000	0.39 (73)
	Bluefin	----	2.65
	Eel - Maritime Provinces	762,000	0.56 (19)
Mollusks & Crustaceans	Clams; crabs; (dungeness-queen-red-rock) lobster; mussels; oysters; scallops; shrimp	100,144,000	0.12 (56)
Miscellaneous	Fish oils	----	4.51 (12)
	Fishmeal		0.16 (71)

Table 2. Polychlorinated biphenyls in commercial fish and fishery products, area 2 (freshwater)

Species	Landings[a] (pounds)	PCB's (mean ppm)
Buffalo fish, carp, goldeye, mallet, perch, pike, pickerel, sauger, trout, whitefish	70,000,000	0.10 (113)

[a]Landings of less than 25,000 pounds per species are not included.

MONS 064851

Table 3. Polychlorinated biphenyls in commercial fish and fishery products, (area 3)

Location	Major species	Landings[a] (pounds)	PCB (mean ppm)
Lake Superior (A)	chub	306,000	0.96 (8)
	lake herring	1,611,000	1.17 (10)
	lake trout	195,000	2.02 (37)
	whitefish	328,000	0.68 (11)
	smelt	788,000	0.35 (6)
	yellow perch	67,000	0.31 (5)
		3,295,000	

[a]Landings of less than 25,000 pounds per species are not included.

Table 4. Polychlorinated biphenyls in commercial fish and fishery products, (area 3)

Location	Major species	Landings[a] (pounds)	PCB (mean ppm)
Lake Huron (B)	chub	671,000	2.09 (17)
	whitefish	950,000	0.95 (8)
	carp	56,000	1.55 (4)
	suckers	176,000	1.33 (12)
	yellow pickerel	269,000	0.61 (9)
	sheepshead (drum)	29,000	0.75 (2)
	coho salmon	noncommercial	5.11 (6)
		2,151,000	

[a]Landings of less than 25,000 pounds per species are not included.

MONS 064852

Table 5. Polychlorinated biphenyls in commercial fish and fishery products, (area 3)

Location	Major species	Landings[a] (pounds)	PCB (mean ppm)
Lake Erie	alewife	332,000	1.22 (14)
	rock bass	49,000	0.27 (2)
	carp	41,000	1.27 (7)
	yellow perch	12,190,000	0.19 (10)
	smelt	15,760,000	0.42 (21)
	yellow pickerel	234,000	1.16 (9)
	white bass	2,346,000	1.26 (28)
	catfish	88,000	2.04 (8)
	bullhead	109,000	0.26 (4)
	sheepshead (drum)	354,000	0.74 (15)
	coho salmon	noncommercial	3.14 (8)
		31,503,000	

[a]Landings of less than 25,000 pounds per species are not included.

Table 6. Polychlorinated biphenyls in commercial fish and fishery products, (area 3)

Location	Major species	Landings[a] (pounds)	PCB (mean ppm)
Lake Ontario (D)	bullhead	248,000	0.73 (12)
	yellow perch	699,000	1.23 (10)
	smelt	103,000	4.16 (17)
	white perch	290,000	1.84 (22)
	sunfish	203,000	0.74 (6)
	carp	395,000	1.69 (10)
	rock bass	42,000	1.76 (18)
	eel	222,000	17.14 (49)
	coho salmon	noncommercial	4.97 (3)
		2,205,000	

[a]Landings less than 25,000 pounds per species are not included.

MQNS 064853

Table 7. Polychlorinated biphenyls in commercial fish and fishery products, (area 3)

Location	Major species	Landings[a] (pounds)	PCB (mean ppm)
St. Lawrence River (E)	sturgeon	77,000	2.32 (5)
	eel	435,000	7.94 (216)

Species	Size	Range	Mean PCB
eel	<2½ pound	(0.11- 7.99)	2.95 (66)
	2½ pound-4½ pound	(1.68-22.8)	8.19 (72)
	>4½ pound	(2.82-29.7)	12.37 (43)

[a]Landings of less than 25,000 pounds per species are not included.

MONS 064854

THE OCCURRENCE OF PCB IN THE NATIONAL FISH AND WILDLIFE MONITORING PROGRAM

Charles R. Walker*

Abstract

The National Fish and Wildlife Monitoring Program has as its objective to ascertain, on a national scale, the amounts of pesticides and contaminants in some fish, birds, and mammals. Testing is done through repeated sampling over time. The species chosen to be monitored are freshwater fish, mallard and black duck, and starling.

PCB residues in freshwater fish were found to be highest in certain river systems that lie in industrial areas. For mallards and black ducks, concentrations were greatest in ducks in the Atlantic flyways. Starlings from all over the Nation showed PCB contamination; however, over the 1970-1974 period, there was an apparent decline in residue levels, except in certain specific areas such as Austin, Alabama. Related monitoring indicates that PCB may be especially threatening to endangered species, with serious effects on the survival of their young.

The National Fish and Wildlife Monitoring Program was initiated in 1967 as a cooperative Federal effort conducted jointly by the Bureau of Commercial Fisheries and the Bureau of Sport Fisheries and Wildlife in the U.S. Department of the Interior, and the Water Supply and Sea Resources Program of the National Center for Urban and Industrial Health, Public Health Service, U.S. Department of Health, Education, and Welfare (ref. 34). The current National Pesticide Monitoring Program is sponsored by the Monitoring Panel of the Federal Working Group on Pest Management that includes components drawn from the Environmental Protection Agency, the Tennessee Valley Authority, the National Science Foundation, and the Departments of Agriculture, Defense, Commerce, Interior, and Health.

The monitoring objective was to ascertain on a national scale the amount of pesticides and related materials in components of the environment and trends of these levels with time through repeated sampling and analysis of environmental components (refs. 34,37,38). The Fish and Wildlife Service program consists of three elements: (1) freshwater fish, (2) mallard and black duck, and (3) starlings.

The Freshwater Fish Program originally consisted of sampling fish from 50 stations in the continental United States as it was initiated in 1967 (refs. 24,25). In 1970 this was expanded to include 100 stations sampled on an annual basis and included the conterminous United States and Alaska (ref. 30). Criteria for selection of specific sampling station locations included the following, in the order of priority: (1) availability of desired species of fish; (2) relationship to station locations for other phases of the National Pesticide Monitoring Program (refs. 11,14,19,67,69), particularly those stations used for monitoring surface water samples; (3) existence of State-sponsored monitoring programs or cooperative participation by a State conservation agency; and (4) availability of suitable manpower and facilities to make field collections. In the late 1960's, the toxicological significance and the detection of polychlorinated biphenyl compounds in fish and wildlife along with the interferences with organochlorine pesticide analysis became apparent (refs. 31,32,33,43,45,50,54,66). This problem stimulated the development of analytical methods for the separation and identification of PCB in fish samples from the National Monitoring Program (refs. 26,28,52,53,57,58).

The cleanup of solvents (refs. 20,56), selective partition of PCB from pesticides (refs. 1,3,4,7,16,18,26,53,55,58,59), quantitative determination (refs. 2,9,46,54,57,62), and confirmation methods (refs. 2,6,8,29,51,52) utilizing gas chromatography-mass spectrometry became practical for Federal agencies to use in the National Pesticide Monitoring Program by 1970. In the Freshwater Fish Program, samples of three to five fish were taken of three species representing different tropic levels to comprise each composite sample. All composite samples of white fish were analyzed for the most common organochlorine insecticides, including DDT, DDE, TDE, dieldrin, aldrin, endrin, BHC, heptachlor epoxide, chlordane, toxaphene, and beginning with the 1970 collections, polychlorinated biphenyl compounds (PCB), as well as the percent lipid content of the fish (ref. 61). Whereas these analysis were contracted to private and other Federal laboratories, a cross-check quality assurance program was conducted on about 10 percent of the samples by our Fish-Pesticide Research Laboratory at Columbia, Missouri. The number of pesticides and related contaminates that were detected in the cross-check analyses grew from 19 compounds in 1970 to 33 parent compounds, homologs, or metabolites by 1973 (table 1).

The mallard and black duck monitoring program

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MONS 064855

Table 1. Organochlorine pollutants detected by initial and confirmatory laboratories from 1967-1974

Pollutant	1967	1968	1969	1970	1971	1972	1973
DDE	I[a]	I	I	I C[b]	I C	I C	I C
DDD o,p'isomers	I	I	I	I C	I C	I C	I C
DDT	I	I	I	I C	I C	I C	I C
DDE				C	C	C	C
DDD p,p'isomers				C	C	C	C
DDT				C	C	C	C
1232				C	O[c]	O	O
1242					C	O	O
1248 Aroclor®				C	C	C	O
1254			I	I C	I C	I C	I O
1260				C	C	C	I O
dieldrin	I	I	I	I C	I C	I C	I C
aldrin	I	I	O	I C	I C	O O	I C
endrin	I	I	O	I C	I C	I C	I C
BHC			I	I C	I C	I C	I C
lindane	I	I	O	O	O	O	O C
heptachlor	I	I	I	I C	O C	O C	O C
heptachlor expoide	I	I	I	I C	I C	I C	C
chlordane	I	I	I	O C	I C	I O	C
cis-chlordane					C	C	C
toxaphene	I	I	O	O C	I C	I C	I C
hexachlorbenzene (HCB)					C	C	C
heptachlor norborene							C
oxychlordane							C
hexachlor norbornadiene							C
2,4-D PGBE							C
pentachlorobenzene							C
hexachloro-1,3-butadiene							C
ethylhexylphthalate				C	O	O	O
dibutylphthalate					C	O	O
dioctylphthalate					C	O	O
DEHP						C	O

[a] I-indicates a pollutant was reported in the results from the initial analyses.

[b] C-indicates a pollutant was reported in the results from the confirmatory analyses.

[c] O-indicates a pollutant was found in previous years but not reported later.

MONS 064856

was conducted in cooperation with State agencies in conjunction with the fall migration of waterfowl and the hunting season in each of the conterminous States (refs. 17,21,22,23,64). Through a process of systematic subsampling, a series of wings, approximately 12,500 annually, are drawn from each State. These are composited for analysis into samples of 25 wings each representing a sample from each State in proportion to the harvest. Mallard duck wings are collected in the Pacific, Central, and Mississippi flyways whereas both the mallard and black duck were represented in those samples from the Atlantic flyway, depending on the availability of species. Pesticide analysis included chlorinated hydrocarbon pesticides and beginning with the 1969 sampling also included polychlorinated biphenyl compounds.

The National Monitoring Program for starlings, a widely distributed and abundant species, was especially designed to sample five degree latitude/longitude blocks covering the contiguous 48 States with up to four randomly selected collecting sites within each block (refs. 34,41,42,63). Ten birds were collected at each sample site and composited for analysis in the fall of even years at approximately 125-130 sites. Organochlorine pesticides were analyzed in the 1967-68 samples and beginning with the 1970 samples polychlorinated biphenyl compounds were analyzed in 1970-72 and 1974 samples.

Freshwater Fish Monitoring Program

Polychlorinated biphenyl compounds have been detected in certain rivers and areas in unusually high concentrations and confirmed in a quality control cross-check analysis among several laboratories (refs. 54,61).

PCB residues have been found in 40 to 60 percent of the samples in residue concentrations exceeding 0.5 mg/kg (figure 1). More than 98 percent of the samples during the period of 1969-71 contained residues in at least one composite sample exceeding these criteria. Geographically, the higher concentrations appear to be

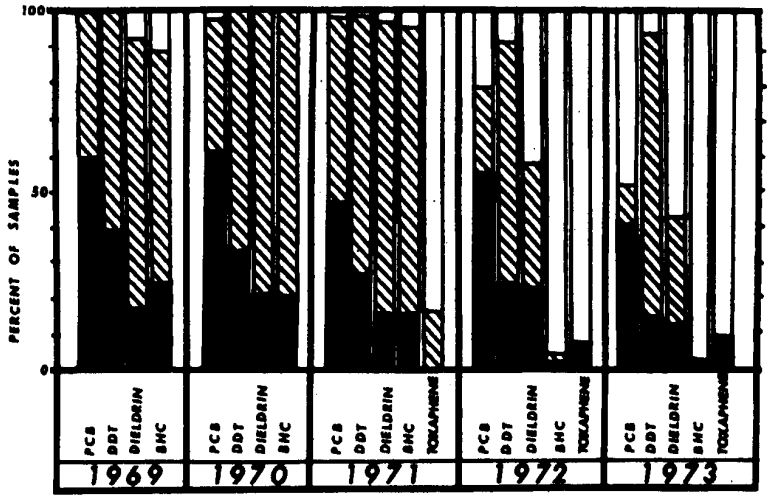


Figure 1. Percentage of fish sampled from 1969-1973 in the National Pesticide Monitoring Program that contained either no detectable residues (white), residues (cross-hatched), or levels exceeding the criteria established to be biologically significant (solid black: >0.5 mg/kg PCB: >1.0 mg/kg DDT; and >0.1 mg/kg dieldrin, BHC, or toxaphene) (ref. 69).

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associated with certain river systems having industrial activity (refs. 54,61) (tables 2 and 3). PCB residues expressed as Aroclor 1254 were found in five major river systems in the Atlantic coastal region, with residues exceeding 5 mg/kg. Four of these stations had residues exceeding 10 mg/kg during the last 5 years. Fish in four of the Great Lakes stations had PCB concentrations exceeding the 5 mg/kg level and all stations reported concentrations exceeding 0.5 mg/kg. In the Mississippi River system, the Allegheny and Ohio were the hot spots, with seven out of the eight stations reporting residue concentrations in excess of 5 mg/kg. Thirty-one of thirty-five stations in this river system reported residues in excess of 0.5 mg/kg in the 1970-73 sampling programs. The highest residues, often exceeding 10 mg/kg were found in the Allegheny, Kanesha, Cumberland, Tennessee, and Ohio Rivers along with stations on the Mississippi River at Memphis, Tennessee, and the Missouri River at Herman, Missouri. Other monitoring stations that were found to have residue levels exceeding 5 mg/kg during the sampling periods 1970-73 included: the Willamette River on the Columbia system; the Rouge River in the Pacific coastal drainage; the Sacramento River in California; the Chena River tributary of the Yukon in Alaska; and the Rio Grande, Alabama, and Mississippi Rivers in the Gulf States region. Only in two sample periods of 1972-73 and in the current monitoring samples, which are still yet to be fully analyzed, has there been a downward trend, but this occurs only in those samples where residues are not being detected. The stations where high residues have been noted in the past still remain relatively contaminated with PCB. Unlike the decline of DDT in Great Lakes fishes, PCB concentrations do not show significant changes and may trend upward in salmonids, as indicated in special investigations conducted by Willford (ref. 69), and Veith (ref. 60).

Just as it is exceedingly important to distinguish PCB from organochlorine pesticides, we must also make positive identifications of the different Aroclors so that they may be correctly expressed in stoichiometric calculation. For example, in table 4, let us examine some of those stations with high PCB concentrations. The composition of PCB residues in selected fish samples taken during the National Pesticide Residue Monitoring Program illustrates the difficulties in equating all residues to one type of Aroclor, such as 1254. In this illustration we can readily show that the expression of PCB from the Ohio, Mississippi, and Hudson drainage would certainly misrepresent the true distribution of PCB isomers if they were all stoichiometrically expressed as 1254. The best analogy I can offer to illustrate this is if we were to express all of the hardness or alkalinity of water as calcium carbonate, when indeed the actual chemical analysis indicated that most of the carbonates existed as magnesium carbonate.

This relationship has two dimensions. The first is that the lower Aroclor series are more highly biodegradable than are the higher series such as 1254 and 1260. A PCB residue in fish taken downstream following degradation would thus appear to be composed primarily of the 1254 or 1260 isomer. However, the toxicity and potential biological effect would be more serious with regard to the Aroclors 1232, 1242, and 1248, as noted in table 4. This was particularly evident in the 1970 cross-checks, in which we were finding that results of two other laboratories typically expressed PCB levels at concentrations of only 5 to 20 percent of that found in the sample by the more sophisticated procedures used by our Fish-Pesticide Research Laboratory (refs. 52,54,55,57,58).

Mallard and Black Duck Monitoring Program

White and Heath report that polychlorinated biphenyl residues were highest in the Atlantic flyways; the mean value of 1.36 ppm occurred in black duck in both 1969 and 1972 (ref. 64). Mallards from the same flyway averaged 1.24 and 1.29 ppm for samples taken in 1972 and 1969 respectively (figure 2 and table 5). These levels compared to mallard duck wings from the Mississippi flyway, where average values were found to be 0.66 and 0.44 ppm on a wet weight basis for the years 1972 and 1969. Both the Central and Pacific flyways had residues of approximately 0.1 ppm during 1972 and 0.2 ppm in 1969. The overall trend in the concentration of PCB would appear to be downward in the Central and Pacific flyways; however, this was significantly different at the $P < 0.05$ in the analysis of variance calculation. The increase in concentration observed in the Mississippi flyway and status quo for the Atlantic flyway have not been significantly changed over the same period of time (refs. 21,22,23,64). The recent studies by White and Kaiser (ref. 65) on the mortality of ruddy ducks in the Delaware system, however, did indicate the seriousness of PCB residues. They found Aroclor 1260 residues or the bioaccumulation of pentachloro and hexachloro biphenyl compounds that exceed the levels found in our National Monitoring Program by almost tenfold.

Starling Monitoring Program

PCB has been found in all of the starling samples taken in 1970, 1972, and 1974 (figure 3). The level of residues appears to be declining throughout this period; however, some areas continue to report exceedingly high concentrations—for example, in the Austin, Alabama,

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Table 2. Stations with residues in at least one composite exceeding 0.5 mg/kg total PCB's, from an estimate based on Aroclor 1254 (asterisk and double asterisks denote residues in excess of 5.0 and 10.0 mg/kg, respectively)

River (location)	1970	1971	1972	1973
Atlantic Coastal Streams				
Penobscot R. (Old Town, ME)			X	
(Stillwater R.)				
Kennebec R. (Hinckley, ME)				
L. Champlain (Burlington, VT)	X	X	X	X
Merrimac R. (Lowell, MA)	X*	X**	X**	X**
Connecticut R. (Windsor Locks, CT)	X*	X**	X**	X*
Hudson R. (Poughkeepsie, NY)	X**	X**	X**	X**
Raritan R. (Highland Park, NJ)	X*	X	X*	X
Delaware R. (Camden, NJ)	X	X	X**	X**
Susquehanna R. (Conowingo, MD)	X	X	X	X
Potomac R. (Little Falls, MD)	X	X	X	X
James R. (Richmond, VA)	X	X		X
Roanoke R. (Roanoke Rapids, NC)	X	X	X	X
Cape Fear R. (Elizabethtown, NC)	X	X	X	
Pee Dee R. (Dongola, SC)	X		X	X
Cooper R. (Summerton, SC)	X		X	X
Savannah R. (Savannah, GA)	X		X	X
Altamaha R. (Doctortown, GA)	X		X	
St. Johns R. (Welaka, FL)	X	X		X
St. Lucie Canal (Indiantown, FL)	X			
Gulf Coastal Streams				
Suwanee R. (Old Town, FL)	X		X	
Apalachicola R. (Jim Woodruff Dam, FL)	X	X	X	X
Alabama R. (Chrysler, AL)	X	X	X*	X
Tombigbee R. (McIntosh, AL)	X	X		
Mississippi R. (Luling, LA)	X	X	X*	X
Brazos R. (Richmond, TX)	X	X	X	X
Colorado R. (Wharton, TX)	X	X	X	X
Nueces R. (Mathis, TX)				

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Table 2. (con.)

River (location)	1970	1971	1972	1973
Rio Grande (Brownsville, TX)				X*
Rio Grande (Elephant Butte, NM)	X	X	X	
Rio Grande (Alamosa, CO)	X*			X
Pecos R. (Red Bluff Lake, TX)	X		X	
Great Lakes Drainage				
Gennessee R. (Scotsville, NY)	X	X	X	X
St. Lawrence R. (Massena, NY)	X*	X*	X**	X
L. Ontario (Port Ontario, NY)	X	X**	X*	X*
L. Erie (Erie, PA)	X	X	X	
L. Huron (Bay Port, MI)	X	X*	X	X*
L. Mighigan (Sheboygan, WI)	X	X**	X*	X*
L. Superior (Bayfield, WI)	X	X	X	X
Mississippi River System				
Allegheny R. (Natrona, PA)	X**	X**	X**	X*
Kanawha R. (Winfield, WV)	X**	X	X**	X*
Wabash R. (New Harmony, IN)	X	X	X	X
Ohio R. (Marietta, OH)	X**	X**	X**	X**
Ohio R. (Cincinnati, OH)	X**	X**	X**	X**
Ohio R. (Metropolis, IL)	X	X*	X*	X
Cumberland R. (Clarksville, TN)	X	X	X**	X*
Tennessee R. (Savannah, TN)	X	X	X**	X*
Wisconsin R. (Woodman, WI)	X	X	X	X
Des Moines R. (Keosauqua, IA)	X	X	X	X
Illinois R. (Beardstown, IL)	X	X	X	X
Mississippi R. (Little Falls, MN)	X			
Mississippi R. (Guttenburg, IA)	X	X	X	X
Mississippi R. (Cape Girardeau, MO)	X	X	X	X
Mississippi R. (Memphis, TN)	X	X	X**	X**
Arkansas R. (Pine Bluff AR)	X	X		
Arkansas R. (Keystone Reservoir, OK)	X	X	X	
Arkansas R. (John Martin Reservoir, CO)				
Verdigris R. (Oologah, OK)	X			
Canadian R. (Eufaula, OK)	X			

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Table 2. (con.)

River (location)	1970	1971	1972	1973
White R. (DeValls Bluff, AR)	X	X	X	
Yazoo R. (Redwood, MS)	X	X		
Red R. (Alexandria, LA)	X	X		X
Red R. (Lake Texoma, OK)				
Missouri R. (Hermann, MO)	X	X**	X*	X*
Missouri R. (Nebraska City, NE)	X	X	X	X
Missouri R. (Garrison Dam, ND)				
Missouri R. (Great Falls, MT)	X	X	X	X
Big Horn R. (Hardin, MT)	X		X	
Yellowstone R. (Sidney, MT)				
James R. (Olivet, SD)	X	X	X*	X
N. Platte R. (Lake McConaughy, NE)				
S. Platte R. (Brule, NE)		X	X	X
Platte R. (Louisville, NE)	X		X	X
Kansas R. (Bonner Springs, KS)	X	X	X	X
Hudson Bay Drainage				
Red R. (North) (Noyes, MN)	X	X	X	X
Colorado River System				
Green R. (Vernal, UT)				
Colorado R. (Imperial Reservoir, AZ)				
Colorado R. (Lake Havasu, AZ)				
Colorado R. (Lake Mead, NV)		X	X	
Colorado R. (Lake Powell, AZ)				
Gila R. (San Carlos Reservoir AZ)				
Interior Basins				
Truckee R. (Fernley, NV)	X	X	X	X
Utah L. (Provo, UT)		X		
Bear R. (Preston, ID)	X	X	X	X

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Table 2. (con.)

River (location)	1970	1971	1972	1973
California Streams				
Sacramento R. (Sacramento, CA)	X	X	X*	X
San Joaquin R. (Los Banos, CA)	X		X	
Columbia River System				
Salmon R. (Riggins, ID)	X	X		
Snake R. (Hagermann, ID)	X	X	X	X
Snake R. (Lewiston, ID)	X	X	X	
Sanke R. (Ice Harbor, WA)	X	X	X	X
Yakima R. (Granger, WA)	X		X	
Williamette R. (Oregon City, OR)	X	X	X*	X
Columbia R. (Bonneville, OR)	X		X	X
Columbia R. (Pasco, WA)	X	X	X	X
Columbia R. (Grand Coulee, WA)	X	X	X	X
Pacific Coastal Streams				
Klamath R. (Hornbrook CA)				
Rogue R. (Gold Ray Dam, OR)	X	X	X	X*
Alaskan Streams				
Chena R. (Fairbanks, AK)	X	X	X*	X
Kenai R. (Soldatna, AK)				
Hawaiian Streams				
Waikele Stream (Waipahu, HI)	X	X	X	X
Manoa Stream (Honolulu, HI)			X	

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Table 3. Environmental contaminants in fish (refs. 52, 53, 54, 55)

	Residue (μg/g whole body)[a]			
	1970	1971	1972	1973
Hudson, R., Poughkeepsie, N.Y.	213	93 76	61 118	104 69
Ohio R. Marietta, Ohio	122 38	77 -	16	7.5 6.0
Cincinnati, Ohio	133 66	156 -	20 43	45
Metropolis, Ill.				8.6
Lake Michigan Sheboygan, Wis.	7.8	53	2.6 4.9	11 4.4
Merrimac R. Lowell, Maine	98	45	8.8	8.5

[a]Each value represents analysis of single fish.

Table 4. Composition of PCB residues in selected fish samples from the 1970 National Pesticide Residue Monitoring Program (ref. 54)

River	Location	Species	PCB residue as Aroclor type (μg/g whole body)				
			1232	1248	1254	1260	total
Ohio	Cincinnati, O.	Carp	10.2	75	42	6.0	133
Ohio	Cincinnati, O.	White crappie	15.9	17	27	5.6	66
Ohio	Marietta, O.	Channel catfish	38	23	11	4.9	77
Ohio	Marietta, O.	Channel catfish	15.6	5.2	12.6	4.6	38
Yazoo	Redwood, Miss.	Smallmouth buffalo	72	—	1.4	—	73
Hudson	Poughkeepsie, N.Y.	Goldfish	8.6	173	32	—	213
Allegheny	Natrona, Pa.	Walleye	—	5.2	26	4.6	35
Delaware	Camden, N.J.	White perch	—	8.0	6.8	3.9	19
Cape Fear	Elizabeth Town, N.C.	Gizzard shad	18.9	—	2.6	1.1	23
Lake Ontario	Port Ontario, N.Y.	White perch	12.9	—	4.8	1.2	19
Mississippi	Memphis, Tenn.	Drum	11.2	—	4.5	3.4	19
Merrimac	Lowell, Mass.	Yellow perch	13.8	75	6.1	3.2	98

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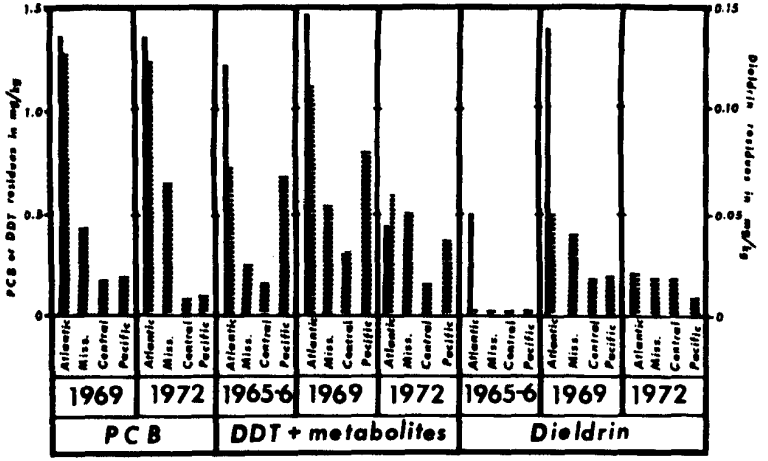


Figure 2. Trends of PCB and organochlorine pesticide residues measured in samples of duckwings from each flyway in the National Pesticide Monitoring Program: black duck (solid bar); mallard (broken bar).

station, the 1970 analysis showed 24.3 ppm in 1972 and 19.9 ppm and a 1.8 ppm concentration in 1974 (table 6). PCB's appear to be ubiquitous throughout the Nation and occur generally in a concentration of less than 5 ppm, with an arithmetic mean for 1970 of 0.85 ppm, for 1972 of 0.43 ppm, and for 1974 of 0.12 ppm on the wet weight basis (figure 4).

Related Investigative Monitoring Programs for Wildlife

The widespread occurence of PCB in ecosystems may be most serious to fish-eating species (refs. 5,10,13) and to the rates of bioaccumulation up the food chain (refs. 38,43,49). Special investigative monitoring activities of the U.S. Fish and Wildlife Service laboratories at Patuxent, Maryland, have been reported on the bald eagle relative to pesticides and PCB levels vs. autopsy and analysis (refs. 15,40,44). In endangered or threatened species, PCB residues may have serious effects on survival of young since some effects have been documented on certain behavioral patterns (refs. 35,36). Residues observed in the National Monitoring Program may pose a hazard to animals that have demonstrated particular sensitivity to PCB concentrations affecting organ function, behavior, growth, and/or reproduction (refs. 27,36,48,50,52).

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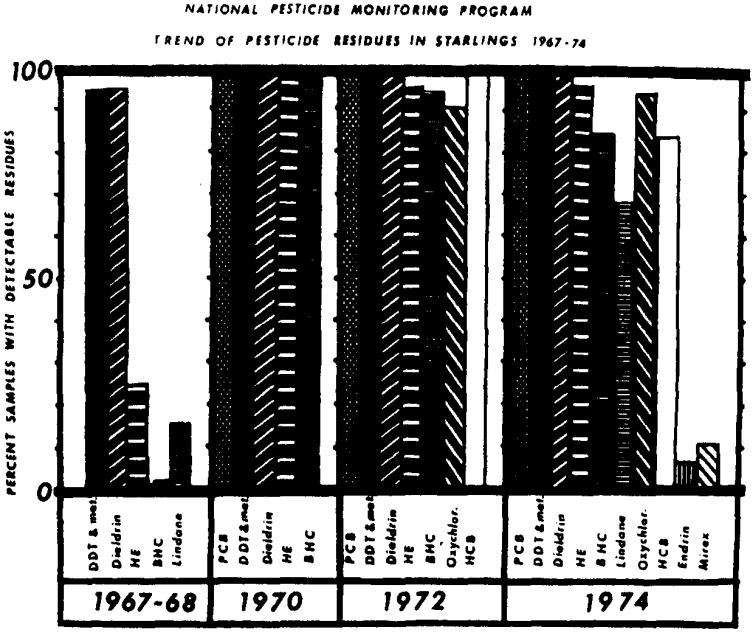


Figure 3. Percentage of starling samples containing PCB and organochlorine pesticides in the National Pesticide Monitoring Program.

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Table 5. Mean residues of PCB in wing-pools by major flyway, 1972 and 1969

Species	Flyway	Year	No. of Pools	Residues (ppm wet weight) Mean	Std. Error
Black Duck	Atlantic	1972	44	1.36	0.149
		1969	42	1.37	0.161
Mallard	Atlantic	1972	21	1.24	0.230
		1969	19	1.29	0.457
Mallard	Mississippi	1972	61	0.66	0.303
		1969	51	0.44	0.061
Mallard	Central	1972	56	0.10[a]	0.013
		1969	49	0.20	0.039
Mallard	Pacific	1972	55	0.11[a]	0.009
		1969	51	0.20	0.014

[a] $P < 0.05$ (Analysis of variance).

Table 6. Means, ranges, and geometric mean PCB in starlings from each collecting period, 1967-68 through 1974

Year	No. of Pools	PCB[b] (ppm wet weight) $\bar{x} \pm$ S.E.	Range	Geom. $\bar{x}$
1967-68	360	-	-	-
1970	125	0.663 ± 0.196	0.09 - 24.30	0.358
1972	130	0.425 ± 0.153	0.037 - 19.90	0.215
1974***[a]	126	0.112 ± 0.016	0.006 - 1.88	0.068

[a] Mean residues for 1974 were significantly lower than for 1972:

*** = $P<0.001$.

[b] PCB were not analyzed in 1967-68.

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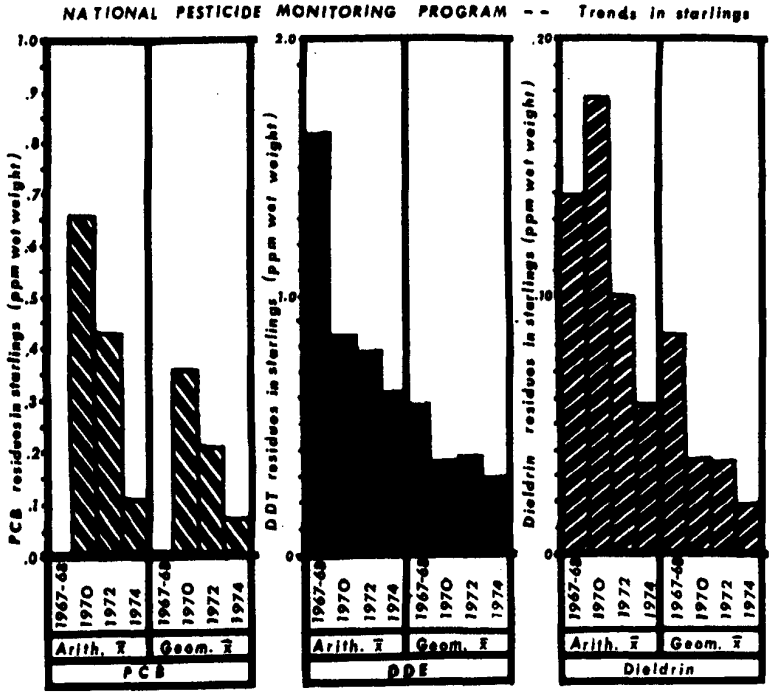


Figure 4. Trends of PCB and organochlorine pesticide residues measured in pooled samples of starlings taken in the National Pesticide Monitoring Program.

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TRENDS OF POLYCHLORINATED BIPHENYLS IN THREE LAKE MICHIGAN FISHES

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Abstract

*Concentrations of polychlorinated biphenyls (PCB's) were determined from 1972 through 1974 in three species of fish collected in the fall from eastern Lake Michigan. Mean concentrations in whole fish ranged in different years from 5.24 to 5.66 ppm in bloaters (*Coregonus hoyi*), 10.4 to 12.2 ppm in coho salmon (*Oncorhynchus kisutch*), and 12.9 to 22.9 ppm in lake trout (*Salvelinus namaycush*). There was no evidence of a decline in average PCB residues in the fish sampled after the introduction in 1970-71 of voluntary controls on the sale of PCB's in the United States.*

INTRODUCTION

Past investigations have shown that substantial levels of polychlorinated biphenyls (PCB's) were present in fish from the open waters of Lake Michigan during the late 1960's. Veith and Lee (ref. 1) reported residues of Aroclor 1254 ranging from 14 to 25 ppm in three coho salmon (*Oncorhynchus kisutch*) and 6 to 25 ppm in eight rainbow trout (*Salmo gairdneri*) collected from western Lake Michigan during the spring of 1969. Stalling and Mayer (ref. 2) reported a PCB concentration (sum of Aroclors 1248 and 1254) of 13 ppm in a single coho salmon collected from eastern Lake Michigan during the fall of 1969. Extensive collections and analyses of fish from Lake Michigan in 1971 confirmed the approximate levels of PCB contamination found in 1969, and further demonstrated that residues in excess of 5.0 ppm were common in several species of fish (refs. 3,4).

Because of the potential effects of PCB's on fish and consumers of fish, the Great Lakes Fishery Laboratory in 1972 incorporated analysis of PCB's with its routine program of pesticide analysis in Lake Michigan fishes. The program is designed to permit the accurate determination and statistical evaluation of contaminant levels and trends with time in fish from Lake Michigan. Particular emphasis is placed on the yearly evaluation of contaminants in samples of bloaters (*Coregonus hoyi*) that are similar in terms of fish size, location of catch, and time of year sampled. Bloaters are particularly useful for contaminant evaluation for several reasons: they represent an important commercial species that concentrates pesticides and PCB's; they reflect local conditions because they are essentially nonmigratory; and they are generally easy to catch in adequate numbers. Lake trout (*Salvelinus namaycush*) and coho salmon are also sampled annually because of their current importance as sport fishes and their role in salmonid restoration programs. In addition, the analysis of lake trout provides an estimate of contaminant levels in a long-lived predatory species from the same geographic location as the bloaters; and coho salmon serve as potential indicators of lakewide contaminant trends because of their extensive migrations.

This report presents the trends of average PCB concentrations in Lake Michigan bloaters, lake trout, and coho salmon in 1972-74. The data provide a basis for determining the effectiveness of past efforts to reduce the contribution of PCB's to the Lake Michigan environment, as evidenced by the level of contamination in the fisheries. Voluntary restrictions on PCB sales in the United States were introduced in 1970-71.

FISH SAMPLING PROCEDURES

Bloaters (240-280 mm total length) and lake trout (500-700 mm) were collected by gill net each fall (September-October) in southeastern Lake Michigan, off Saugatuck, Michigan. Coho salmon (600-750 mm) were collected in east-central Lake Michigan near Ludington, Michigan, in 1972, near the entry to Portage Lake in 1973, and from the lower weir on the Platte River in 1974.

All fish were placed in plastic bags previously determined to be free of pesticides and PCB's. The packaged fish were frozen whole or packed in ice, transported to the Great Lakes Fishery Laboratory, and stored at approximately -30° C. Before analysis, the bloaters were measured and weighed, sorted according to sex and length, grouped into 10-fish composite samples, and homogenized (whole fish) by repeatedly passing them through a meat grinder. A portion of the sample was then further homogenized in a food blender. Individual lake trout and coho salmon were measured, weighed, sexed, and the whole fish similarly homogenized.

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ANALYTICAL PROCEDURES

Ten grams of homogenized fish were mixed with anhydrous sodium sulfate and extracted by the method of Hesselberg and Johnson (ref. 5). Lipids were removed from the extract by gel permeation chromatography in an automated system similar to that described by Stalling et al. (ref. 6), after which the pesticides and PCB's were separated on either silicic acid without Celite 545 (ref. 7) or on silica gel (ref. 8). The PCB's were quantitated on a gas chromatograph equipped with electron-capture detectors (^{63}Ni, 8μc) and a 5-ft x 1/8-in. ID glass column packed with 1.5 percent OV-101 on 80-100 mesh glass beads or Chromosorb W. Recoveries of PCB's from fortified samples of fish tissue average 88 percent by the described method. We performed confirmatory analyses on each sample using a second, 10-g portion of tissue saponified in alcoholic potassium hydroxide (ref. 9).

Results were calculated by summing the heights of all peaks on the chromatogram attributable to PCB's, and comparing them with the sum of peak heights obtained from analytical standards composed of Aroclors 1248, 1254, and 1260 (1:1:1). No corrections were made for losses incurred during analysis or the presence of PCB's in blanks. All results are reported as total PCB's in wet weight of tissue.

TRENDS OF PCB's

Mean concentrations of total PCB's during 1972-74 ranged from 5.24 to 6.66 ppm in bloaters, 10.4 to 12.2 ppm in coho salmon, and 12.9 to 22.9 ppm in lake trout (table 1). A plot of mean PCB concentrations in bloaters versus year of collection (figure 1) suggests no change in PCB's during the 3 years of sampling. Statistical analysis involving Student's *t* test (ref. 10) and the annual samples representing 110 to 160 fish showed that minor differences between mean PCB concentrations for the three sample dates were not significant. We therefore conclude that mean PCB concentrations have remained essentially unchanged since 1972 in large, adult bloaters off Saugatuck, Michigan.

A plot of mean PCB concentrations in coho salmon from 1972 to 1974 also fails to show any definite change pattern (figure 2). The mean concentrations of PCB's in these fish appear to have varied randomly between 10.4 and 12.2 ppm. Statistical analyses show that the decline between 1973 and 1974 is highly significant ($P > 0.01$) but that the 1972 samples do not differ significantly from either the 1973 or 1974 samples. Thus despite the evidence of significant variation among the three sample groups, there is no statistical evidence of a

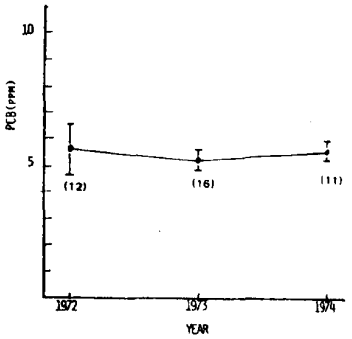


Figure 1. Trends of PCB's in Lake Michigan bloaters off Saugatuck, Michigan. Mean concentrations in whole fish (wet weight) with 95 percent confidence intervals (vertical lines). Number of 10-fish composites shown in parentheses.

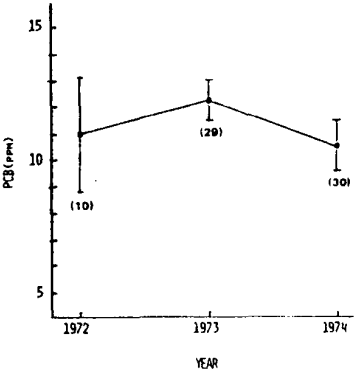


Figure 2. Trends of PCB's in coho salmon from eastern Lake Michigan. Mean concentrations in whole fish (wet weight) with 95 percent confidence in intervals (vertical lines). Number of fish in parentheses.

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Table 1. Concentrations of PCB's in fall collections of Lake Michigan bloaters and lake trout taken off Saugatuck, Michigan, and coho salmon from between Ludington, Michigan, and the Platte River

Species and Year	Date collected	Number of fish	Mean length (mm)	Mean weight (g)	Mean lipid (percent)	Range of total PCB's (ppm)	Mean total PCB's (ppm)[a]
Bloater							
1972	10/19	120(12)[b]	255	177	21.6	3.12-8.17	5.66(0.95)
1973	9/27	160(16)[b]	250	165	20.0	4.20-6.33	5.24(0.37)
1974	10/9	110(11)[b]	257	175	21.6	4.83-6.22	5.57(0.31)
Coho salmon							
1972	9/19	10	693	4,156	7.3	4.93-15.4	10.9(2.1)
1973	9/21	29	620	2,967	6.0	8.24-16.6	12.2(0.8)
1974	10/1	30	665	3,148	5.4	6.99-16.3	10.4(0.9)
Lake trout							
1972	9/28	9	648	2,576	18.5	3.53-25.3	12.9(4.8)
1973	9/19	30	602	2,353	16.0	9.36-30.6	18.9(2.1)
1974	10/9	30	616	2,514	16.5	7.05-47.4	22.9(3.7)

[a]Concentrations in whole fish, wet weight, with 95 percent confidence interval in parentheses.

[b]Number of composite samples, 10 fish/sample, given in parentheses.

general increase or decrease during 1972-74 in mean PCB concentrations in coho salmon from eastern Lake Michigan.

Mean concentrations of PCB's in lake trout collected off Saugatuck, Michigan, appear to have increased from 1972 to 1974 (figure 3). Although statistical analyses show no significant differences between consecutive years, the increase between 1972 and 1974 is highly significant ($P > 0.006$). Because of the comparatively small number of lake trout collected in 1972 (9 fish) and the high variability in PCB residues generally encountered between individual lake trout (table 1), the level of confidence in the results is low and interpretation of the apparent trend must be approached with considerable caution. Although PCB's appear to have increased in lake trout, there is no evidence of an upward trend of residues in bloaters (which represent the most reliable indicator of trends) or coho salmon; consequently additional sampling will be required to determine if the apparent upward trend of PCB's in lake trout is real. We can safely conclude, however, that mean PCB concentrations have not declined in lake trout taken off Saugatuck, Michigan.

TRENDS OF OTHER CHLORINATED HYDROCARBONS

Mean concentrations of DDT and its metabolites (total DDT) in the same samples of Lake Michigan fishes employed for the PCB study declined 69, 48, and 26 percent respectively in bloaters, coho salmon, and in lake trout during the period 1972-74 (ref. 11). Total DDT residues in fish decreased significantly within 1 year after the ban (1969-70) on the use of DDT in the

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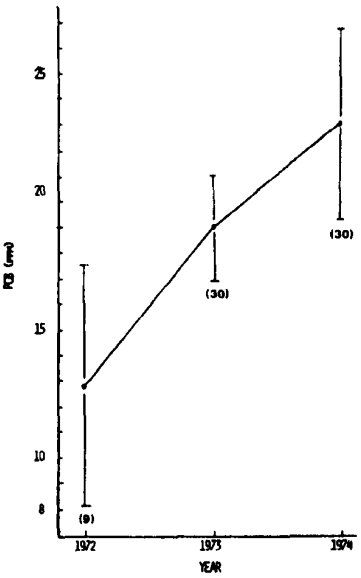


Figure 3. Trends of PCB's in Lake Michigan Lake trout off Saugatuck, Michigan. Mean concentrations in whole fish (wet weight) with 95 percent confidence intervals (vertical lines). Number of fish in parentheses.

States bordering Lake Michigan. During 1970-74, mean concentrations of total DDT dropped 87, 73, and 56 percent in bloaters, coho salmon, and lake trout respectively.

Mean concentrations of dieldrin in the same fish samples showed no definite trend from 1970 to 74 (ref. 11). The lack of change is probably due to the common use of dieldrin during the early 1970's. The rapid reduction of DDT residues in Lake Michigan fishes and the lower bioaccumulation characteristics of dieldrin lead us to believe that the recent ban (1974) on the manufacture and use of aldrin and dieldrin will result in a rapid decline of dieldrin residues in Lake Michigan fishes.

SUMMARY AND CONCLUSIONS

Mean concentrations of PCB's in Lake Michigan bloaters collected off Saugatuck, Michigan, have remained essentially unchanged since yearly analyses were initiated in 1972. Similarly, PCB residues in coho salmon from eastern Lake Michigan show no definite pattern of change. Residues of PCB's in lake trout collected off Saugatuck, Michigan, are highly variable and indicate a possible, but unconfirmed, upward trend in mean PCB concentrations. Thus, voluntary restrictions in 1970-71 on the sale of PCB's ithe United States have not led to a decrease in PCB concentrations in the Lake Michigan fishes sampled.

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MONS 064875

A NOTE ON POLYCHLORINATED BIPHENYLS IN AIR

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Abstract

Samples of ambient air were collected using an ethylene-glycol impinger sampler, and analyzed for selected pesticides and polychlorinated biphenyls in suburban locations in Florida, Mississippi, and Colorado. Preliminary results for samples taken in April, May, and June of 1975 show that PCB's were present at all locations.

Samples of ambient air were collected and analyzed for selected pesticides and polychlorinated biphenyls. Suburban locations in Miami, Florida, Jackson, Mississippi, and Fort Collins, Colorado, were sampled using an ethylene-glycol impinger sampler essentially the same as reported by Enos et al. (ref. 1) except that an improvement of air flow rate was made. The air flow rate was maximized and calibrated at ca. 30 l/min. Each sampler was operated for a 24-hour period to collect one sample. The analyses of samples were done by extraction with hexane followed by cleanup with fluorsil column chromatography, using a mixture of diethyl ether and petroleum ether for elution; the fraction containing the polychlorinated biphenyls and some organochlorine pesticides underwent further separation by silicic acid column chromatography. Quantitation of the polychlorinated biphenyls was done by summation of major peaks employing the dual-column gas chromatography with electron capture detector.

Preliminary results for samples taken in April, May, and June of 1975 show that PCB's were present at all locations. Although the data varied, the average concentration at each of the three locations was approximately 100 nanograms per cubic meter. The presence of polychlorinated biphenyls in ambient air samples taken in Miami and Jackson has been confirmed by combined gas chromatography-mass spectrometry. Initial identification of the polychlorinated biphenyls indicates that they were most comparable to the Aroclor 1254 standard.

In July the number of sampling sites was expanded to five with the addition of Lafayette, Indiana, and Harrisburg, Pennsylvania. Results from all sites should be available in the near future.

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POLYCHLORINATED BIPHENYLS IN THE SURFACE WATERS AND BOTTOM SEDIMENTS OF THE MAJOR DRAINAGE BASINS OF THE UNITED STATES

D. Steve Dennis, Ph.D*

Abstract

Data gathered from monitoring activities indicate the widespread occurrence of PCB's in surface waters and bottom sediments of the major drainage basins of the United States. A preliminary assessment of PCB levels shows median residue levels of the positive detections for the years 1971 to 1974 ranging between 0.1 to 3.0 µg/l for unfiltered water samples and from 1.2 to 160.0 µg/kg for bottom sediments. The highest levels were found in basins east of the Mississippi and bottom sediments may contain concentrations of PCB's many times higher than those in the overlying water.

INTRODUCTION

Within the past few years, particularly in the past year, polychlorinated biphenyls (PCB's) have been identified as a major contaminant of natural waters. PCB's in the hydrologic environment can originate from several sources including: (1) runoff from sewage sludges disposed of on land, (2) discharge of industrial and municipal wastes (this includes treated as well as untreated wastes), (3) accidental spills or improper waste disposal practices, and (4) formerly as ingredients of pesticides or as carriers for pesticides. Probably the largest amount of PCB's in the environment results from industrial and municipal discharges to inland and coastal waters (refs. 1–5).

Although much attention has been focused on estimating levels of PCB's in aquatic organisms, and the potential hazards involved, few data are available on the occurrence of PCB's in water and bottom sediments. The U.S. Department of Interior's Geological Survey and the U.S. Environmental Protection Agency's (EPA) Office of Pesticide Programs, Technical Services Division, through their National Water Monitoring Program for Pesticide Residues and various water-resource-assessment projects, are accumulating data which permit a preliminary assessment of PCB contamination of the Nation's drainage basins. The data presented here were gathered by the Geological Survey. They show the occurrence of PCB's (PCB mixtures predominately resemble Aroclor 1254) in whole water samples (i.e., water samples which are unfiltered) and in bottom sediments in the 17 major drainage basins of the United States and Puerto Rico (figure 1) for the years 1971 to 1974. All data were obtained from STORET, which is EPA's computerized information system that draws on both State and Federal agencies for parametric data relating to water quality.

Although there is not a nationwide program specifically designed to assess PCB levels in the aquatic environment, the present Geological Survey and EPA water monitoring programs are expanding and gradually increasing to more adequately determine PCB levels in the surface waters of the United States. These programs are also being designed to determine both national and regional trends in the concentration of PCB's.

METHODS AND PROCEDURES

Water samples were collected either by depth integration at the center of flow or by the equal-transit-rate method. In the latter method a standard suspended-sediment sampler, such as the US D-49 suspended-sediment sampler, was used to collect a velocity- and discharge-weighted sample. Samples were taken at a number of equally spaced verticals across a stream, depending on stream width (usually three sites were sampled across a stream). The transit rate of movement of the sampler from the water surface to the stream bed and back to the surface was the same at all verticals. Samples collected at each vertical were composited into a single sample intended to represent the entire flow across the stream.

Bottom sediments were sampled by collecting a series of cores across the stream bed using piston type or US BMH-60 or US BM-54 bed material samplers or a commercial core sampler. When a core sampler was used, cores were composited to form a representative sample of the stream bed (see refs. 5,6 for a description of sampling procedures).

Once the samples were collected, PCB residues were analyzed by the multiple-pesticide-residue methods for water, suspended sediment, and bottom sediment described by Goerlitz and Brown (ref. 7).

Basic identification of PCB residues was made by dual-column electron capture/gas-liquid chromatography and confirmed by gas-liquid chromatography or mass spectrometry. The amount of PCB's was determined by matching the peaks on the chromatogram with the nearest commercial formulation. The reported values are subject to some error because of the complexity of multiple peaks resulting from mixtures of PCB's in environmental samples.

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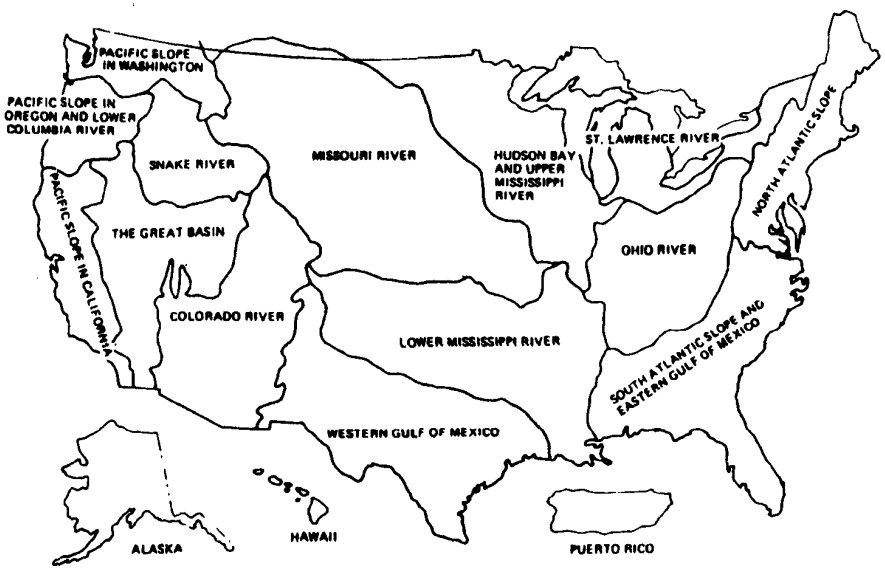


Figure 1. Map showing the major drainage basins in the United States and Puerto Rico.

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Table 1 PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1971

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	12	58.3	0.2	0.1 - 2.1
2. South Atlantic Slope and Eastern Gulf of Mexico	12	0	ND	ND
3. Ohio River	-	-	-	-
4. St. Lawrence River	15	26.7	0.3	0.1 - 0.5
5. Hudson Bay and Upper Mississippi River	-	-	-	-
6. Missouri River	1	0	ND	ND
7. Lower Mississippi	1	100.0	3.0	3.0
8. Western Gulf of Mexico	9	44.4	0.3	0.1 - 0.7
9. Colorado River	-	-	-	-
10. Great Basin	-	-	-	-
11. Pacific Slope Basins in California	-	-	-	-
12. Pacific Slope Basins in Washington	-	-	-	-
13. Snake River	-	-	-	-
14. Pacific Slope Basins in Oregon and Lower Columbia River	-	-	-	-
15. Alaska	-	-	-	-
16. Hawaii	-	-	-	-
17. Puerto Rico	-	-	-	-

Note: - = no samples; ND = not detected.

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Table 2. PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1972

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	112	17.0	0.1	0.1 - 0.3
2. South Atlantic Slope and Eastern Gulf of Mexico	122	0.8	ND	ND
3. Ohio River	10	20.0	0.2	0.1 - 0.2
4. St. Lawrence River	29	13.8	0.1	0.1 - 0.2
5. Hudson Bay and Upper Mississippi River	12	16.7	0.3	0.2 - 0.3
6. Missouri River	34	0	ND	ND
7. Lower Mississippi	39	2.6	0.1	0.1
8. Western Gulf of Mexico	93	8.6	0.3	0.1 - 2.6
9. Colorado River	24	0	ND	ND
10. Great Basin	9	0	ND	ND
11. Pacific Slope Basins in California	20	0	ND	ND
12. Pacific Slope Basins in Washington	14	0	ND	ND
13. Snake River	-	-	-	-
14. Pacific Slope Basins in Oregon and Lower Columbia River	3	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	3	0	ND	ND

Note: - = no samples; ND = not detected.

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Table 3. PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1973

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	109	3.7	0.1	0.1
2. South Atlantic Slope and Eastern Gulf of Mexico	114	4.4	0.1	0.1 - 20.0
3. Ohio River	6	0	ND	ND
4. St. Lawrence River	31	3.2	0.1	0.1
5. Hudson Bay and Upper Mississippi River	30	10.0	0.2	0.1 - 0.4
6. Missouri River	95	0	ND	ND
7. Lower Mississippi	291	0.7	1.6	0.2 - 2.9
8. Western Gulf of Mexico	362	1.7	0.3	0.1 - 0.6
9. Colorado River	64	0	ND	ND
10. Great Basin	12	0	ND	ND
11. Pacific Slope Basins in California	73	0	ND	ND
12. Pacific Slope Basins in Washington	33	0	ND	ND
13. Snake River	2	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	9	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	37	0	ND	ND

Note: - = no samples; ND = not detected.

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Table 4. PCB's in whole water samples in the major drainage basins of the United States and Puerto Rico for 1974

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/l	Range of positive detections in µg/l
1. North Atlantic Slope	51	2.0	0.1	0.1
2. South Atlantic Slope and Eastern Gulf of Mexico	151	0	ND	ND
3. Ohio River	24	0	ND	ND
4. St. Lawrence River	38	0	ND	ND
5. Hudson Bay and Upper Mississippi River	33	0	ND	ND
6. Missouri River	28	0	ND	ND
7. Lower Mississippi	269	2.6	0.1	0.1 - 0.2
8. Western Gulf of Mexico	325	1.2	0.3	0.2 - 0.7
9. Colorado River	52	0	ND	ND
10. Great Basin	12	0	ND	ND
11. Pacific Slope Basins in California	74	2.7	0.1	0.1
12. Pacific Slope Basins in Washington	13	7.7	0.1	0.1
13. Snake River	11	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	8	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	68	1.5	0.8	0.8

Note: - = no samples; ND = not detected.

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Table 5. PCB's in bottom sediments in the major drainage basin of the United States and Puerto Rico for 1971

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	3	100.0	50.0	10.0 - 100.0
2. South Atlantic Slope and Eastern Gulf of Mexico	19	63.2	64.5	10.0 - 200.0
3. Ohio River	1	100.0	8.8	8.8
4. St. Lawrence River	1	100.0	10.0	10.0
5. Hudson Bay and Upper Mississippi River	-	-	-	-
6. Missouri River	2	100.0	1.2	0.3 - 2.0
7. Lower Mississippi	4	100.0	30.0	10.0 - 80.0
8. Western Gulf of Mexico	20	100.0	10.0	2.0 - 290.0
9. Colorado River	-	-	-	-
10. Great Basin	-	-	-	-
11. Pacific Slope Basins in California	-	-	-	-
12. Pacific Slope Basins in Washington	-	-	-	-
13. Snake River	-	-	-	-
14. Pacific Slope Basins in Oregon and Lower Columbia River	-	-	-	-
15. Alaska	-	-	-	-
16. Hawaii	-	-	-	-
17. Puerto Rico	-	-	-	-

Note: - = no samples; ND = not detected.

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Table 6. PCB's in bottom sediments in the major drainage basins of the United States and Puerto Rico for 1972

Drainage basin	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	56	57.1	10.0	5.0 - 800.00
2. South Atlantic Slope and Eastern Gulf of Mexico	101	32.7	30.0	5.0 - 500.00
3. Ohio River	-	-	-	-
4. St. Lawrence River	10	90.0	20.0	2.0 - 800.0
5. Hudson Bay and Upper Mississippi River	3	0	ND	ND
6. Missouri River	22	81.8	2.0	2.0
7. Lower Mississippi	25	48.0	2.0	2.0 - 2400.0
8. Western Gulf of Mexico	66	43.9	4.0	2.0 - 250.0
9. Colorado River	7	71.4	2.0	2.0
10. Great Basin	9	66.7	2.0	2.0
11. Pacific Slope Basins in California	6	83.3	20.0	2.0 - 190.0
12. Pacific Slope Basins in Washington	9	44.4	2.0	2.0
13. Snake River	1	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	1	100.0	2.0	2.0
15. Alaska	-	-	-	-
16. Hawaii	1	0	ND	ND
17. Puerto Rico	-	-	-	-

Note: - = no samples; ND = not detected.

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Table 7. PCB's in bottom sediments in the major drainage basins of the United States and Puerto Rico for 1973

Drainage Basin	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	58	70.7	10.0	4.0 - 4000.0
2. South Atlantic Slope and Eastern Gulf of Mexico	123	48.8	10.0	5.0 - 600.0
3. Ohio River	4	25.0	20.0	20.0
4. St. Lawrence River	24	91.7	20.0	5.0 -13000.0
5. Hudson Bay and Upper Mississippi River	14	0	ND	ND
6. Missouri River	17	0	ND	ND
7. Lower Mississippi	57	1.8	20.0	20.0
8. Western Gulf of Mexico	188	3.7	50.0	14.0 - 180.0
9. Colorado River	4	0	ND	ND
10. Great Basin	7	0	ND	ND
11. Pacific Slope Basins in California	14	0	ND	ND
12. Pacific Slope Basins in Washington	12	0	ND	ND
13. Snake River	1	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	-	-	-	-
15. Alaska	2	0	ND	ND
16. Hawaii	1	0	ND	ND
17. Puerto Rico	6	16.7	5.0	5.0

Note: - = no samples; ND = not detected.

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Table 8. PCB's in bottom sediments in the major drainage basins of the United States and Puerto Rico for 1974

Drainage basins	Sample size	% of positive detections	Median of positive detections in µg/kg	Range of positive detections in µg/kg
1. North Atlantic Slope	99	56.6	31.0	2.0 - 800.0
2. South Atlantic Slope and Eastern Gulf of Mexico	171	25.7	11.0	2.0 - 530.0
3. Ohio River	6	33.3	35.0	9.0 - 61.0
4. St. Lawrence River	40	60.0	20.0	3.0 - 700.0
5. Hudson Bay and Upper Mississippi River	26	0	ND	ND
6. Missouri River	5	0	ND	ND
7. Lower Mississippi	81	9.9	10.5	1.0 - 39.0
8. Western Gulf of Mexico	157	21.7	27.0	2.0 - 330.0
9. Colorado River	3	0	ND	ND
10. Great Basin	4	0	ND	ND
11. Pacific Slope Basins in California	26	11.5	2.0	2.0 - 65.0
12. Pacific Slope Basins in Washington	5	0	ND	ND
13. Snake River	4	0	ND	ND
14. Pacific Slope Basins in Oregon and Lower Columbia River	1	0	ND	ND
15. Alaska	-	-	-	-
16. Hawaii	-	-	-	-
17. Puerto Rico	18	27.2	160.0	10.0 - 640.0

Note: - = no samples; ND = not detected.

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RESULTS

Tables 1 through 8 present the PCB residue data by year for water and bottom sediments. For each year the following is given: number of samples, percent of positive detections, median of positive detections, and maximum of positive detections in µg/l for water and µg/kg for bottom sediments (one µg/l and one µg/kg are roughly equivalent to one ppb).

Not all drainage basins had detectable levels of PCB's in both water and bottom sediments. However, it should be noted that this may be in part due to the location of sampling stations within drainage basins and/or the small number of samples within drainage basins.

Median residue levels of the positive detections in whole water samples ranged from 0.2 to 3.0 µg/l, 0.1 to 0.3 µg/l, 0.1 to 1.6 µg/l, and 0.1 to 0.8 for all drainage basins for 1971, 1972, 1973, and 1974, respectively (tables 1 to 4). For both these data and the data for each basin there is no indication of an increase in PCB levels and in many instances the levels decreased. The highest PCB level was found in the South Atlantic Slope and Eastern Gulf of Mexico basin and in general, the highest levels were found in basins east of the Mississippi. One might speculate that this is due to the presence of certain industries in the eastern United States.

Bottom sediments showed a pattern similar to that of water with the highest PCB residue levels occurring in the eastern United States (table 5 to 8). Median residue levels of the positive detections for all basins ranged from 1.2 to 64.5 µg/kg, 2.0 to 30.0 µ/kg, 5.0 to 50.0 µg/kg, and 2.0 to 160.0 µg/kg for 1971, 1972, 1973, and 1974, respectively. The data indicate that, as with the whole water samples, the levels decreased in some basins. However, it appears as if PCB's are more persistent in bottom sediments.

DISCUSSION

The data which I have presented here indicate that PCB's are widespread in the surface waters and bottom sediments of the Nation. Crump-Wiesner et al. (ref. 9) also found PCB's to have a ubiquitous occurrence and distribution in surface water, ground water, and bottom sediments. According to Veith and Lee (ref. 8) ". . . the chlorinated biphenyls may be one of the more widespread. . ." environmental contaminants.

It is well documented that bottom sediments may contain concentrations of pesticide residues many times higher then the overlying water (refs. 10-13). The data presented here and previously published data (refs. 1,4,9,14) indicate that a similar relationship holds true for PCB's. Even in drainage basins, where PCB's were not detected in water samples such as the Missouri River, they were present in bottom sediments. It is assumed that this is due to the low water solubility and high specific gravity of PCB's (ref. 14). According to Nisbet and Sarofim (ref. 14), ". . . it is expected that most of the PCBs discharged into the environment will be resting as sludges or adsorbed in the sediment at the bottom of rivers or lakes near their point of discharge, and that transport in streams will be primarily by means of waterborne particles."

Finally, it is important to note that although PCB's are found in water and bottom sediments, this information must be related to the entire aquatic environment before the data can be adequately evaluated. This is because (1) PCB's in solution and sorbed on organic and inorganic particles are available for introduction into food chains, (2) PCB's are accumulated in the tissues of animals which are exposed to water and bottom sediments containing PCB's, (3) biological magnification may occur in food chains, and (4) all components in an aquatic ecosystem are interrelated.

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PCB's IN AGRICULTURAL AND URBAN SOIL

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Abstract

Polychlorinated biphenyls in soil have been monitored since 1972 as part of the National Soils Monitoring Program, originally established to measure pesticide residue levels in agricultural soils, raw agricultural commodities, and urban soils across the Nation. The PCB's are monitored as part of this program because of their chemical similarity to certain chlorinated pesticides.

The PCB's have rarely been detected in agricultural soils of the United States. Only 0.1 percent of the soil samples collected in the National Soils Monitoring Program for 1972 contained detectable PCB levels. However, detectable levels of PCB's occur more frequently in urban soils. Of the 19 metropolitan areas sampled since 1971, 12 of the cities, or 63 percent showed detectable PCB levels. The most commonly encountered PCB was Aroclor 1254, which was identified in approximately 40 percent of the positive samples, while Aroclor 1260 was prevalent in about 20 percent of the positive samples. In the remaining 40 percent of the positive samples, no identification was made of the specific Aroclor. The occurrence of these compounds appears to be more prevalent in the "urban" portion (within the city limits) than in the "suburban" portion (remainder) of these metropolitan areas.

INTRODUCTION

The occurrence of polychlorinated biphenyls (PCB's) in environmental media has been known and well-documented for several years; it is only recently that the magnitude of the contamination has created widespread concern.

These compounds have been monitored in agricultural and urban soils since 1972 as part of the National Soils Monitoring Program. This program was established to measure pesticide residue levels in agricultural soils, raw agricultural commodities, and urban soils across the Nation. It was initiated by the U.S. Department of Agriculture and is now operated by the U.S. Environmental Protection Agency. The PCB's are monitored as part of this program because of their chemical similarity to certain chlorinated pesticides.

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SAMPLING PROCEDURES

For cropland sampling, 50 cores 5.1 x 7.6 cm in size were collected over an evenly spaced 5 x 10 grid on each 4-hectare site (ref. 1). In urban sampling, this procedure was modified to collect 16 cores on a 4 x 4 grid over a 225-m^2 plot (15 x 15 m) (ref. 2). Field processing was similar for both types of samples; the cores were composited, thoroughly mixed, and sieved through a 6.3-mm mesh, and a 2-l subsample was sent to the EPA Technical Services Division's Pesticide Monitoring Laboratory in Bay St. Louis, Mississippi, for chemical analysis.

ANALYTICAL PROCEDURES

Sample Preparation

A 300-g subsample was dampened with water and extracted with 800 ml of 3:1 hexane:isopropanol solvent. The isopropanol was removed by three distilled water washes and the hexane extract was dried through anhydrous sodium sulfate and stored at low temperature for subsequent gas-liquid chromatographic analysis.

Gas-Liquid Chromatography

Analyses were performed on gas chromatographs equipped with tritium foil electron affinity detectors. A multiple system of polar and nonpolar columns was utilized for identification and confirmation. Instrument parameters were as follows:

Columns:

Glass, 6 mm o.d. x 4 mm i.d., 183-cm long, packed with one of the following: 9% QF-1 on 100/120-mesh Gas-Chrom Q; 3% DC-200 on 100/120-mesh Gas-Chrom Q; or 1.5% OV-17/1.95% QF-1 on 100/120-mesh Supelcoport.

Carrier Gases:

5% methane-argon at a flow rate of 80 ml/min; prepurified nitrogen at a flow rate of 80 ml/min.

Temperatures:

Detector	200°C
Injection port	250°C
Column QF-1	166°C
Column DC-200	170°–175°C
Mixed column	185°–190°C.

Sensitivity or minimum detection levels were 0.05 to 0.1 ppm. The average recovery rate in soil was 90 to 110 percent.

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DISCUSSION

Agricultural Soils

PCB's have rarely been detected in the Nation's agricultural soils. Of the 1,856 soil samples collected in 1972 as part of the National Soils Monitoring Program, only 2 samples or 0.1 percent contained detectable levels of PCB's.

Urban Soils

Detectable levels of PCB's occur more frequently in urban soils than in agricultural soils. Of the 19 metropolitan areas sampled since 1971, 12 of the cities, or 63 percent showed detectable levels of PCB's. Corresponding data are presented in tables 1-4. The most commonly encountered PCB was Aroclor 1254, which was identified in 39 percent of the positive samples, while Aroclor 1260 was prevalent in 21 percent of the positive samples. Although no attempt was made to identify the specific Aroclor in 39 percent of the positive samples, it is likely that a majority contained Aroclor 1254.

All sites sampled within a metropolitan area were classified into two of four categories. First, sites were identified as either "lawn" or "waste," to indicate whether or not they seemed likely to receive regular maintenance. Secondly, each site was classified as urban if it was within the city limits, and suburban if it was located in the remainder of the metropolitan area.

When the positive sites in the 12 cities were categorized in this manner, 42 percent were lawn sites (maintained), while 58 percent were waste sites (not maintained). This difference was not considered significant. However, the second categorization showed that 70 percent of the PCB-positive sites were urban, or within the city limits, whereas only 30 percent were classified as suburban sites. In comparison, the ratio of urban to suburban sites for these 19 cities was 37 percent to 63 percent.

In summery, PCB occurrence in agricultural soils is extremely rare and is not considered a problem. However, the occurrence of these compounds is more prevalent in metropolitan areas, particularly within city limits, and monitoring should be continued to determine trends over time.

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Table 1. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1971. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified
Baltimore, Md.	156	6	3.9	0.09	0.74	0.02	0.001	1260
Gadsden, Ala.	55	1	1.8	11.94		0.21	*[b]	not identified
Hartford, Conn.	48	ND[a]	-					
Macon, Ga.	43	ND	-					
Newport News, Va.	78	1	1.3	3.30		0.04	*	1254

[a] ND = Not detected.

[b] * = Geometric mean estimate not calculated when less than two positive values present.

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Table 2. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1972. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified
Des Moines, Iowa	82	3	3.7	0.34	0.94	0.03	0.002	not identified
Fitchburg, Mass.	35	ND[a]	-					
Lake Charles, La.	70	1	1.4	1.31		0.02	*[b]	1254
Pittsburgh, Pa.	189	1	0.5	1.01		0.01	*	not identified
Reading, Pa.	49	ND	-					

[a] ND = Not detected.

[b] * = Geometric mean estimate not calculated when less than two positive values present.

Table 3. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1973. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified
Evansville, Ind.	82	ND[a]	-					
Greenville, S.C.	86	3	3.5	0.13	1.59	0.02	0.001	1254
Pittsfield, Mass.	45	ND	-					
Tacoma, Wash.	95	6	6.3	0.18	0.63	0.03	0.003	1-1254 5-not identified
Washington, D.C.	116	2	1.7	0.32	0.80	<0.01	0.001	1-1254 1-not identified

[a] ND = Not detected.

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Table 4. Occurrence of polychlorinated biphenyls in soils of five U.S. cities sampled in 1974. U.S. Environmental Protection Agency Urban Monitoring Program

Location	Total No. of sites	No. of positive detections	Percent of positive detections	Detected values (ppm) Minimum	Maximum	Arithmetic mean (ppm)	Geometric mean estimate (ppm)	PCB type-if identified	Percent of Analyses Completed
Durham, N.C.	66	1	1.5	0.40		0.01	*[b]	1254	94
Gary, Ind.	89	5	5.6	0.50	3.33	<0.01	0.003	1-not identified 4-1254	100
San Francisco, Calif.	119	3	2.5	0.39	1.15	<0.01	0.001	1-not identified 1-1254 1-1260	71
Springfield, Ill.	72	ND[a]	-						100
Pine Bluff, Ark.	59	Analyses not completed							

[a] ND = Not detected.

[b] * = Geometric mean estimate not calculated when less than two positive values present.

MONS 064892

MARINE INPUTS OF POLYCHLORINATED BIPHENYLS OFF SOUTHERN CALIFORNIA

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Abstract

Rates of polychlorinated biphenyl (PCB) transport via potential input routes to the coastal waters off southern California have been quantified. Submarine discharge of municipal wastewater was found to be the single largest source, contributing 5,400 kg of these synthetic organics in 1974. However, inputs via this route appear to be decreasing, as the corresponding estimate for 1971 exceeded 19,000 kg. Bottom sediments around the largest outfalls contain up to 10 ppm PCB. Dry aerial fallout also appears to be an important source. The estimated deposition rate of 1254 PCB onto the coastal waters during 1973-74 was 1,800 kg/yr; highest inputs were measured off the Los Angeles Basin. This region also contributed the most PCB in surface runoff, although less than 900 kg were discharged annually during 1972-73 via storm and dry-weather flow. Direct industrial discharges to San Pedro and San Diego Harbors did not appear to be a significant PCB source, totaling less than 260 kg/yr. Although antifouling paints may have been a very significant source in the past, present inputs are negligible. Also, despite high contamination levels measured in three major harbors, we found no evidence of significant PCB transport from these harbors to the adjacent coastal waters.

INTRODUCTION

Polychlorinated biphenyls (PCB's) have been used for more than 4 decades in a wide variety of industrial products (refs. 1,2). Within the last 10 years, the problem of environmental contamination by these synthetic organic compounds has become a subject of increasing concern (refs. 3,4,5). Here we report the results obtained to date on the routes by which PCB's enter one coastal marine ecosystem, the Southern California Bight, and the rates at which inputs occur.

MUNICIPAL WASTEWATERS

Every day, over 1 billion gallons (approximately 4 x 10^9 l) of municipal wastewaters are discharged from submarine outfalls to the Southern California Bight. Almost 95 percent of these wastewaters are released by five major treatment plants.† By sampling these five plants, we have been able to obtain a reasonably representative picture of PCB inputs to the Bight via this route. Resultant effluent concentrations and estimated annual mass emission rates for 1972-75 are summarized in table 1; details of sampling and analytical procedures are presented elsewhere (ref. 6). These data indicate that in recent years there has been a significant decrease in the amount of PCB's discharged through these outfall systems.

The municipal wastewater discharges have resulted in obvious contamination of the bottom sediments around the larger outfall systems. Figure 1 illustrates concentrations of total PCB measured in surface sediments collected around the Hyperion outfalls in Santa Monica Bay. The maximum concentration measured near the longer Hyperion outfall (the sludge line) and the JWPCP outfalls were similar, on the order of 10 ppm (mg/dry kg). However, within a few kilometers of the Hyperion sludge discharge, the surface sediment concentrations of PCB had fallen to about 0.2 ppm. Near the JWPCP outfalls, large vertical gradients were observed, with values decreasing by one to two orders of magnitude over a 30-cm depth. We estimate that the load of 1254 PCB in these Palos Verdes Shelf sediments (50 sq km) is on the order of 6 metric tons (ref. 7). Surface sediments around the Orange County outfall did not exhibit large gradients of total PCB in 1975; the median value was 0.1 ppm, with values ranging from 0.04 to 0.3 ppm. Similar concentrations were measured 6 months after discharge commenced in 1971, indicating little buildup of PCB's in these sediments since then.

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†These treatment plants are located near the following stations indicated in figure 2: Oxnard-Port Hueneme; Hyperion-Santa Monica; JWPCP-Palos Verdes Peninsula; Orange Co.-Newport Beach; Point Loma-midway between La Jolla and the U.S.-Mexico border.

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Table 1. Representative PCB concentrations and mass emission rates[a] from major municipal wastewater discharges to the Southern California Bight, 1972-75

Discharger	Total Susp. Solids (mg/l)	Concentration (µg/l)	Mass Emission Rate (kg/yr)	Concentration (µg/l)	Mass Emission Rate (kg/yr)
1972					
JWPCP	290	24	11,600	ND	-
Hyperion					
Effluent	90	ND	-	0.3	140
Sludge	7,670	280	1,780	ND	-
Orange Co.	150	28	5,800	ND	-
Point Loma	140	ND	-	0.9	120
Oxnard	70	ND	-	0.2	3
Total			>19,180		>260
1973					
JWPCP	260	3.9	1,930	1.6	790
Hyperion					
Effluent	80	ND	-	0.38	180
Sludge	7,500	ND	-	26	170
Orange Co.	150	ND	-	1.4	290
Point Loma	160	ND	-	0.48	70
Oxnard	130	ND	-	0.35	6
Total			>1,930		1,510
1974					
JWPCP	280	1.9	910	0.76	360
Hyperion					
Effluent	80	0.11	50	0.24	110
Sludge	7,300	72	470	50	320
Orange Co.	110	6.0	1,890	0.89	210
Point Loma	140	6.6	950	0.74	110
Oxnard	170	0.1	1	0.24	3
Total			4,270		1,110
1975					
JWPCP		0.6	290	0.52	250
Hyperion					
Effluent		0.06	30	0.18	80
Sludge		34	220	28	180
Orange Co.		5.2	1,230	0.63	150
Point Loma		1.1	160	0.39	60
Oxnard		0.03	0.4	0.16	2
Total			1,930		720

[a]The following 1974 flow values (million gallons per day) were used for calculations of preliminary 1975 mass emission rates: JWPCP—350; Hyperion effluent—340; Hyperion sludge—4.7; Orange Co.—170; Point Loma—100; Oxnard—10.

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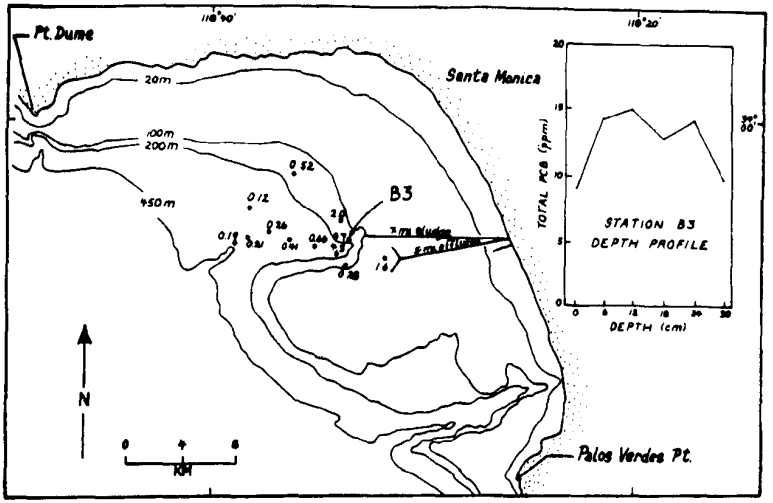


Figure 1. Concentrations of total PCB (mg/dry kg) measured in the top 2 cm of bottom sediments collected during July 1971 off the Hyperion submarine outfalls in Santa Monica Bay.

We have found that benthic organisms trawled from these regions are highly contaminated with PCB's. Crab and flatfish muscle tissue contain on the order of 1 ppm total PCB, approximately 100 times the levels measured in specimens from uncontaminated control stations. Details of these studies are presented elsewhere in these proceedings (ref. 8) and a background paper (ref. 9).

SURFACE RUNOFF

In water year 1971-72, we conducted a detailed survey of chlorinated hydrocarbon inputs to the Southern California Bight via storm runoff. During the major storms of the year, time series of depth-integrated samples were collected in an all-metal sampler near the mouths of four major drainage channels—the Santa Clara River, Ballona Creek, the Los Angeles River, and the Santa Ana River.* Analyses of the preserved samples were conducted by Dr. R. Risebrough and B. de Lappe at Bodega Marine Laboratory (University of California at Berkeley). The following year, we resurveyed one of these channels on a limited basis. Los Angeles River runoff was sampled during four storms and analyzed in our laboratory. Subsequently, two seasonal collections of dry-weather flow were made from channels located throughout the Bight (ref. 6).

Table 2 presents final flow-weighted mean PCB concentrations in 1971-72 storm runoff in the four channels samples. In table 3 we list flow-weighted mean PCB concentrations for the four Los Angeles River storm flows sampled in 1972-73, and compare the yearly averages for this channel with those for 1971-72. To aid in the comparison, we also list corresponding results for total DDT and dieldrin. In light of the variation measured in concentrations during any given storm, and the fact that two water years and two laboratories were involved, the agreement between the flow-weighted means is remarkably good. Because of this general agreement, we concluded that the data from the 1971-72 Bight-wide storm runoff survey could be extrapolated to the following year, on the basis of relative flow rates.

*These channels discharge surface runoff near the following stations indicated in figure 2: Santa Clara R.-Port Hueneme; Ballona Ck.-Santa Monica; Los Angeles R.-midway between Palos Verdes Peninsula and Newport Beach; Santa Ana R.-Newport Beach.

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Table 2. Flow-weighted mean concentrations (μg/l) of PCB in storm runoff via major channels in southern California, 1971-72

Channel	Volume[a] (10^6 cu m)	1242 PCB	1254 PCB	Total PCB
Santa Clara	9.0	0-0.13	0-0.16	0-0.29
Ballona	2.6	0-0.43	0.47	0.47-0.90
Los Angeles	9.0	1.2-1.9	0.9-1.1	2.1-3.0
Santa Ana	1.0	ND	0.11-0.23	0.11-0.23

[a]Accumulated storm flow from which samples were obtained for chlorinated hydrocarbon analysis.

Table 3. Flow-weighted mean concentrations (μg/l) of chlorinated hydrocarbons in Los Angeles River storm runoff, 1971-73

Date	Total DDT	Dieldrin	1242 PCB	1254 PCB	Total PCB
4-7 Dec 72	0.66	0.12	0-1.1	0.51	0.5-1.6
27 Feb to 1 Mar 73	1.5	0.16	0-3.2	1.0	1.0-4.2
6-9 Mar 73	0.78	0.16	0-1.0	0.83	0.8-1.8
11-12 Mar 73	0.60	0.08	0-2.6	0.71	0.7-3.3
Average blank	<0.004	<0.001	<0.002	<0.001	<0.003
Averages					
1972-73	0.92	0.14	0-1.9	0.77	0.8-2.7
1971-72	0.93	0.16	1.2-1.9	0.9-1.1	2.1-3.0

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The results indicate that the Los Angeles River carried an order of magnitude more PCB's via storm runoff than any other channel in the Bight. Further, the estimated input of 1254 PCB in storm runoff from the major channels in the Los Angeles Basin was 235 kg, constituting 86 to 98 percent of the estimated total storm runoff input of this contaminant to the Bight. These channels also carried more than 80 percent of the dry-weather input of 1254 PCB. A comparison of mass emission rates for all areas via the dry-weather and storm runoff for water year 1972-73 is presented in table 4. This summary illustrates that, although dry-weather flow constituted almost 20 percent of the total surface runoff volume during the year, it carried only about 5 percent of the measurable PCB's. Thus, it appears that storm runoff is the dominant mode for surface runoff inputs of PCB to the Bight, and that the Los Angeles Basin is the principal source region.

AERIAL FALLOUT

We conducted our aerial fallout surveys by exposing glass plates sprayed with mineral oil for about 1 week at 13 coastal and 5 island stations between Point Conception and the U.S./Mexico border. Two 13-week surveys were conducted in summer 1973 and spring 1974, and a 3-week survey was conducted during fall 1974. Although fallout rates of 1242 PCB were not obtainable, apparently because of poor retention of this relatively volatile mixture, the collection efficiency for 1254 PCB over 1-week exposure was determined to be about 50 percent (ref. 6).

During the first two surveys, net flux values for 1254 PCB generally ranged between 50 and 150 ng/sq m/day; values at certain coastal stations at the edge of the Los Angeles Basin were higher. During the third survey, however, values were higher by a factor of 2, on the average. The fall and winter seasons in southern California are characterized by desert (Santa Ana) winds, which occur periodically and transport the polluted air of the Basin out over the Bight. These data yielded seasonal fallout estimates for spring, summer, and fall of about 1,400, 1,430, and 2,700 kg/yr, respectively. Giving equal weight to each seasonal survey results in an estimated annual input of about 1,800 kg/yr 1254 PCB to the study area via dry aerial fallout. (Rainfall is so infrequent in this region that its overall effect is judged to be negligible.)

The estimated annual aerial inputs of 1254 PCB to the individual sectors of the study area are shown in

Table 4. Estimated 1972-73 mass emission rates of PCB via storm and dry-weather runoff to the Bight

Type	Volume (10^6 cu m)	PCB (kg/yr) 1242	1254	Total
Storm	574	0-520	240-270	240-790
Dry weather	127	0-30	7-8	7-40
Total	700	0-550	250-280	250-830
% dry weather	18	2	7	3-5

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figure 2. Highest values (each over 100 kg/yr) occurred in the five sectors off Los Angeles and Orange Counties (centering around the Palos Verdes Peninsula). This portion of the coastal plain of southern California is most affected by air pollution. The three sectors between Zuma Beach and Newport Beach (100 km by 50 km), which account for only about 10 percent of the 50,000-sq-km study area, received approximately 25 percent of the total measured PCB input. Thus, we find a pattern similar to that for surface runoff: The central basin area appears to be the single most important source of 1254 PCB transported via the atmosphere to the waters of the Bight.

DIRECT INDUSTRIAL DISCHARGE

Most of the industrial wastewaters released directly to marine waters off southern California occur in San Pedro and San Diego Harbors. These harbors also receive a wide variety of industrial discharges. Thus, we were able to study a number of different types of industrial effluents under similar conditions by surveying the two harbors (ref. 6). Estimates for overall industrial inputs of 1254 PCB to San Pedro Harbor were obtained by calculating flow-weighted concentrations in three types of effluents—power plant cooling water, fish cannery wastes, and "other industrial" discharges. The flow-weighted concentrations were then multiplied by the reported total flows of each of the three classes of industrial wastewaters into San Pedro Harbor to obtain estimates of annual mass emission rates. The values are presented in table 5. Corresponding data for San Diego Harbor are given in table 6.

These data provide no indication of significant release of PCB's to the harbors from the industrial effluents studied. However it should be noted that shipyard-related discharges into Los Angeles Harbor had the highest 1254 PCB concentrations of the industrial discharges surveyed; vessel cooling water, ballast effluent, and oil tanker clean-down water contained 0.6, 1.5, and 2.1

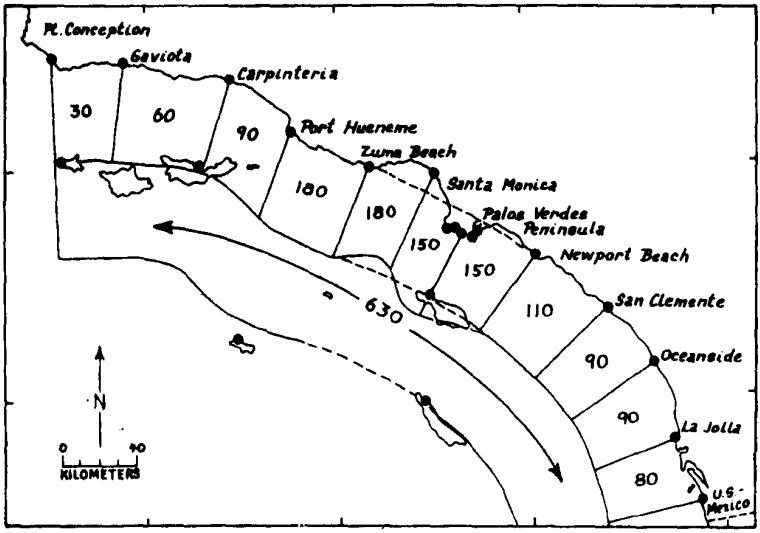


Figure 2. Estimated annual input of 1254 PCB (kg/yr) to sectors of the Southern California Bight via dry aerial fallout during 1973-74.

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Table 5. *Flow-weighted mean concentrations and estimated 1973* mass emission rates of 1254 PCB in industrial discharges to San Pedro Harbor

Discharge type	Total flow (mgd)	Concentration (µg/l)	Mass emission rate (kg/yr)
Power plant cooling water	1,020	0.01	14
Fish cannery wastes	15	0.09	2
Other industrial wastes	250	0.10	35
Total			50

Table 6. Flow-weighted mean concentrations and estimated 1974 *mass emission rates of PCB in industrial discharges to* San Diego Harbor

		1242 PCB		1254 PCB	
Discharge type	Total flow (mgd)	Concentration (µg/l)	Mass emission rate (kg/yr)	Concentration (µg/l)	Mass emission rate (kg/yr)
Cooling waters	757	<0.03	<30	0.01	10
Brine waters	0.5	<0.01	<0.01	0.05	0.03
Flume waters	2.8	<0.02	<0.07	0.01	0.05
Total			<30		10

µg/l 1254 PCB respectively. These relatively high levels are consistent with our observations that highest levels of this contaminant in harbor mussels occurred in regions of greatest vessel activity (ref. 8-11).

VESSEL ANTIFOULING PAINT

In 1973, we surveyed numerous drydock or haulout facilities in southern California harbors and marinas (ref. 12). Our objective was to obtain a representative picture of antifouling paint usage in southern California. In only 7 of the 28 wet paint samples analyzed, 1242 PCB or 1254 PCB were detected; levels were generally on the order of 1 mg/l or below. Although two samples had total PCB concentrations of approximately 40 mg/l, median values for 1242 and 1254 PCB were 0.3 mg/l and 0.7 mg/l, respectively. Combination of these median values with the estimated 300,000 liters of antifouling paint applied annually to recreational, commercial, and naval vessels in marinas and harbors of the Bight

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indicates that marine inputs of PCB from this source now are completely negligible.

However, four samples of old paint scraped from vessel bottoms yielded total PCB concentrations of 270, 3,300, 56,000, and 150,000 ppm, respectively. Furthermore, the two highest concentrations (approximately 5 and 15 percent on a dry weight basis) correspond with an observation by Dr. V. McClure,* who found that a paint chip collected in a zooplankton trawl in 1970 contained approximately 10 percent PCB. Polychlorinated biphenyls are reported to have been used extensively as a plasticizer in paints before such use was banned in this country in 1971. Our survey revealed that, on the average, the density of antifouling paints used in southern California is about 1.5 dry kg/l. Therefore, if such paints did contain 10 percent PCB in the past, an application rate of 300,000 l/yr would correspond to a PCB usage of 45,000 kg/yr. Antifouling paints are designed to slough off with time, and an estimated 5 to 10 percent of the old paint removed from vessel bottoms is believed to be carried back to the harbor waters (ref. 13). Thus these observations point to the possible importance of antifouling paints in the past as a source of PCB's to the coastal marine environment.

*National Marine Fisheries Service, La Jolla, personal communication.

HARBOR FLUSHING

In view of the relatively high levels of PCB contamination found in southern California harbors (refs. 8-11), we attempted to determine if any significant levels of PCB's could be detected in the waters moving from such harbors into the open ocean during periods of peak tidal flow (ref. 6). Figure 3 illustrates the results obtained from the San Diego Harbor survey; net concentrations of 1254 PCB for the replicate samples of each collection period are plotted against tidal flow. Although there is some evidence of increased PCB concentrations near the time of tide reversal, when the greatest influence of "back harbor" water would occur near the harbor mouth, the measured concentrations were extremely low; flow-weighted mean concentrations for San Pedro† and San Diego Harbors were 1.5 and 1.8 ng/l, respectively.

By combining the measured concentrations with tidal flow values obtained from the current meter measurements and channel geometrics, we obtained estimates for maximum net transport of 1254 PCB from the harbors to the adjacent coastal ecosystem. Because of the extremely low concentrations observed, none of the

†Located just east of Palos Verdes Peninsula (figure 2).

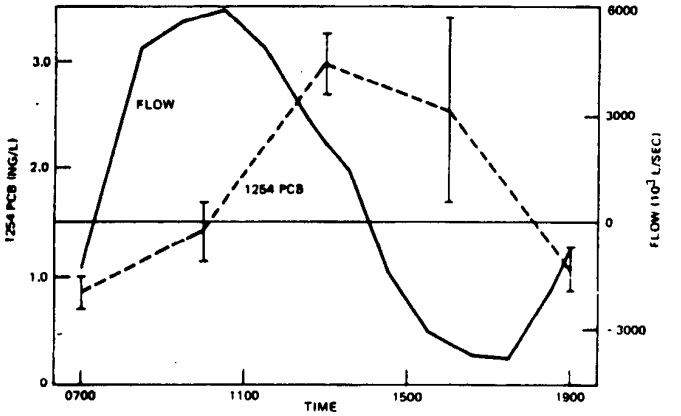


Figure 3. Concentrations of 1254 PCB in surface seawater collected over a semidiurnal tidal cycle at the mouth of San Diego Harbor, November 12, 1974. Positive flow represents outflowing water; negative, inflowing. Vertical bars indicate individual replicate values.

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values exceeded 50 kg/yr when extrapolated to an annual basis. Thus, these pilot seawater surveys have provided no indication that any of the three harbors is now a significant source of polychlorinated biphenyls to the coastal marine ecosystem.

OCEAN CURRENT ADVECTION

As a part of this inputs study, we attempted to estimate the quantities of measurable chlorinated hydrocarbons in surface seawater annually flowing through the Southern California Bight. In October 1973, we sampled surface seawater at seven stations along a north/south transect (120°35'W) at the northwestern edge of the Bight (ref. 8). The transect began off Point Conception and ended approximately 300 km west of Oceanside. Circulation patterns (ref. 14) indicated that the transect chosen should have intersected California Current water flowing into the Bight.

Replicate 40-liter samples were collected in a stainless steel bucket, which was lowered from the bow of a research vessel that was slowly underway. Immediately upon collection, the replicate samples were passed through polyurethane foam columns and taken to Bodega Marine Laboratory for analysis. The results indicated average concentrations for total DDT and 1254 PCB of 0.7 and 0.4 ng/l, respectively.

These data may be used to obtain rough estimates of the quantity of these synthetic organics carried into the Bight via ocean current advection. Taking the length of the Bight as 500 km and the width influenced by the coast as 100 km, the effective study area is 5×10^{10} sq m. Assuming the mixed surface layer to be 50 m, the volume of the mixed layer is 2.5×10^{12} cu m. It has been shown that the mean residence time of water in this mixed layer is on the order of 3 months (ref. 14). Thus, the estimated advective flow rate of California Current water through the Southern California Bight is 10^{13} cu m/yr, equal to 10^{16} l/yr. Corresponding estimates for advective flux rates of measurable DDT and 1254 PCB compounds are 7,000 and 4,000 kg/yr, respectively.

CONCLUSIONS

Table 7 summarizes input rates of polychlorinated

Table 7. Inputs of PCB's to the Southern California Bight

Route	Year	PCB's (kg/yr) 1242	1254	Total
Municipal wastewater	1974	4,300	1,100	5,400
Surface runoff	1972-73	≤ 550	250	≤ 800
Aerial fallout	1973-74	-	1,800	-
Industrial discharges	1973-74	< 180[a]	60	< 250
Antifouling paint	1973	< 1	< 1	< 1
Harbor flushing[b]	1974	-	< 150	-
Ocean currents	1973	-	4,000	-

[a] Assuming that the maximum 1242/1254 PCB ratio (3:1) found in San Diego Harbor also applies to San Pedro Harbor industrial discharges.

[b] San Pedro, Newport, and San Diego Harbors.

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biphenyls to the marine waters off southern California. These data indicate that, in recent years, municipal wastewaters have been the dominant source of PCB's to this coastal marine ecosystem. In 1974, more than 5 metric tons of this synthetic organic material were discharged via the five major treatment plants in the Bight; the fact that the 1254 PCB values for municipal wastewaters and ocean current transport were of the same order of magnitude testify to the importance of the wastewater input route.

Aerial fallout is the other important route by which PCB's enter the waters of the Bight. The 1973-74 estimate of 1,800 kg for 1254 PCB exceeded the 1974 input from municipal wastewaters (1,100 kg), and the fact that PCB levels in municipal wastewater are continuing to decrease suggests that aerial transport of these contaminants may become the dominant input mode in the future.

Finally, these studies have demonstrated that, in southern California, surface runoff is only a secondary PCB source, while contributions from industrial discharges and antifouling paint use in the major harbors appear to be insignificant. Although intertidal mussels in these harbors had an order of magnitude more PCB in their soft tissues than did nearby coastal specimens, we found no evidence that harbor flushing constitutes a significant source of polychlorinated biphenyls to the coastal marine ecosystem.

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MONS 064902

PCB CONTAMINATION OF SOUTHERN CALIFORNIA MARINE ORGANISMS

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Abstract

In the past, the submarine discharge of municipal wastewater has been the dominant source of PCB to the marine environment off southern California. However, the level of input from this source has steadily decreased during the period 1972 (> 19,000 kg/yr) to 1975 (2,600 kg/yr). Despite the significant decrease in this input, no significant decrease was observed over the 3-year period 1971-72 to 1974-75 in the level of PCB in muscle tissue of Dover sole, Microstomus pacificus, *collected from the major municipal wastewater discharge sites. In contrast, similar surveys of the intertidal mussel,* Mytilus californianus, *indicated that the PCB levels in this marine organism had significantly decreased over the same time period.*

Bight-wide surveys of M. californianus *and the yellow rock crab,* Cancer anthonyi, *indicate that PCB contamination of these marine animals is low but widespread. Levels of PCB in the harbor mussel,* M. edulis, *were highest in specimens collected from areas of intense vessel activity. A convenient and effective system for continuously monitoring PCB levels in the marine environment is described.*

INTRODUCTION

Over the last 4 years, the Southern California Coastal Water Research Project has been studying the inputs of PCB's to the Southern California Bight. A number of sources of PCB's (most closely resembling Aroclors 1242 and 1254) to the marine environment off southern California have been identified and their inputs quantified. The submarine discharge of municipal wastewater has been the dominant source of PCB to the marine environment off southern California. However, the level of input from this source has steadily decreased during the period 1972 (> 19,000 kg/yr) to 1975 (2,600 kg/yr). Dry aerial fallout also appears to be an important source, and if wastewater inputs continue to decrease, fallout may become the dominant input mode of the future. PCB inputs from surface runoff are of secondary importance, and those from direct industrial discharges and vessel antifouling paints are relatively insignificant. Detailed results of our inputs studies are presented elsewhere in these proceedings (ref. 1) and in a background paper (ref. 2).

Other workers have studied PCB contamination off California and elsewhere in the United States in the past decade. During the summer of 1975, several reports of high PCB levels in fish collected from Lake Michigan and the Hudson River caused public concern about PCB residues in commercial fish and sport fish (refs. 3-6). Munson's work in California (ref. 7) indicated that, in 1972, concentrations of these chlorinated hydrocarbons were low but widespread in the southern California marine community.

The work of Allen and his colleagues (ref. 8) with rhesus monkeys attests to the toxic effects of short-term, low-level (25 ppm) exposures to PCB's on non-human primates. Later results of their experiments on the monkeys showed that exposure to PCB's at the 2.5- and 5-ppm levels was related to spontaneous abortions and the birth of undersized infants (ref. 9). Also, de Long et al. (ref. 10) found PCB's to be associated with premature births in the California sea lion.

In conjunction with our studies of PCB sources, we undertook research into the fates and effects of PCB's in marine animals. Our research involved several organisms common locally (the Dover sole, *Microstomus pacificus*, a benthic flatfish; the yellow rock crab, *Cancer anthonyi*; and an open coast and a harbor mussel, *Mytilus californianus* and *M. edulis*, respectively), and three distinct programs:

- Regional surveys of PCB levels in the flatfish, the crab, and the mussels. Specimens from stations throughout the Southern California Bight (fig. 1) were analyzed to determine the levels of PCB's present in their tissues and plot the distribution of the substances in the Bight. Changes over time were noted, as were relationships between the concentration levels and man's centers of activity along the coast (wastewater discharge, major harbors). We also sought to identify the dominant PCB

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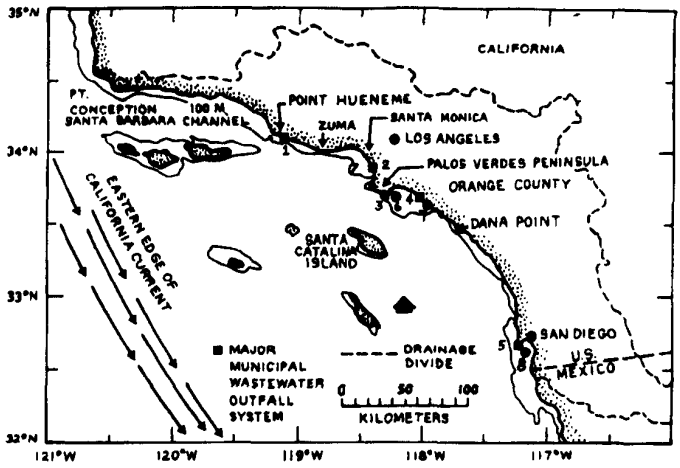


Figure 1. The Southern California Bight. Outfall systems are (1) Oxnard City, (2) Hyperion, Los Angeles City, (3) Whites Point, Los Angeles County, (4) Orange County, and (5) San Diego City. Major harbors are (6) San Pedro, (7) Newport, and (8) San Diego.

present by determining if the PCB's found most closely resembled Aroclor 1242 or Aroclor 1254.* Finally, we investigated the PCB levels in specimens of the flatfish afflicted with a fin erosion disease prevalent around several southern California wastewater outfalls.

- A study of the relative amounts of PCB's in the various tissues of the flatfish and the crab.
- The design of a convenient and effective system for continuously monitoring PCB levels in the marine environment.

This paper presents a brief summary of the results of these studies.

SAMPLING PROCEDURES AND CHEMICAL ANALYSIS

McDermott et al. (ref. 11) report in detail the procedures used for the collection and preparation of biological samples as well as the subsequent PCB analyses by electron-capture gas chromatography for all research programs discussed in this paper.

RESULTS AND DISCUSSION

Regional Surveys of PCB's in Marine Animals

Two Bight-wide surveys of PCB contamination in the benthic flatfish, Dover sole, were conducted during 1971-72 and 1974-75 (ref. 11). The results of these regional surveys (table 1) revealed that PCB levels in specimens collected near the three largest municipal wastewater discharge sites off Palos Verdes, Santa Monica, and Orange County were significantly higher than levels found in specimens from regions with little or no wastewater discharge. Despite the high levels of PCB in the fish from the outfall areas, less than 2 percent of all Dover sole taken in the two surveys had muscle tissue PCB concentrations that exceeded the Federal Food and Drug Administration's tolerance of 5 mg/wet kg in the edible portion of fish intended for interstate commerce.

Over the 3-year study period, municipal wastewater

*Throughout the text, 1242 PCB and 1254 PCB have been used to distinguish between substances most closely resembling Aroclor 1242 and Aroclor 1254, respectively.

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Table 1. Total PCB concentrations (mg/wet kg) in muscle tissue of Dover sole *Microstomus pacificus*.[a]

Region	1971-72 (n^b = 110)		1974-75 (n^c = 165)	
	Region median	Station range	Region median	Station range
Point Hueneme	0.1	0.1	0.06	0.05-0.07
Santa Monica	1.5	0.4-2.8	2.0	1.0 -2.3
Palos Verdes	1.9	1.1-6.3	1.3	0.06-2.5
Orange County	0.7	0.1-1.2	0.6	0.3 -2.8
Dana Point	0.06	0.03-0.09	0.7	0.03-0.14
San Diego	-	-	0.2	0.09-0.6
Santa Catalina Island	0.04	0.03-0.04	0.05	0.03-0.07

[a]After ref.11. There is no statistically significant difference between the 1971-72 and the 1974-75 levels.

[b]Composite samples of Dover sole muscle tissue.

[c]Individual samples of Dover sole muscle tissue.

emissions of total PCB decreased (ref. 1). Yet we observed no statistically significant decrease in the levels of total PCB in the Dover sole. This finding indicates that other factors or inputs of these chlorinated hydrocarbons are involved in maintaining the total PCB levels in this fish.

During 1971 and 1974, Bight-wide surveys of the open coast mussel were also conducted (refs. 11,12). The results are shown in table 2. A regional survey of the yellow rock crab was also conducted during 1971 (ref. 11). Table 3 presents the median concentration of total PCB in the muscle tissue of the crabs collected in each region. These surveys indicate that the PCB contamination levels in these animals are low but widespread. Levels of total PCB in specimens near the major outfall systems were generally 10 to 100 times higher than levels in specimens collected from coastal or island control sites; however, the Federal tolerance level for PCB compounds was not exceeded in the edible portion of any specimens of these two species. The two surveys of *M. californianus* indicate that the level of PCB contamination in these mussels had decreased significantly over the 3-year interval, 1971-74, with a median percent decrease of 54 percent.

The dominant PCB observed in the three species surveyed was 1254 PCB; the other PCB identified was 1242 PCB. The percent composition of total PCB in the muscle tissue samples from the crab and mussel specimens was similar to that in the Dover sole muscle samples. The median 1974-75 composition of total PCB in muscle tissue of Dover sole taken near the five major discharge sites was 67 percent 1254 PCB and 33 percent 1242 PCB. This contrasted with the median 1974 composition of municipal wastewater emission of PCB: 29 percent 1254 PCB and 71 percent 1242 PCB. These data, along with a comparison of total PCB levels in Dover sole muscle tissue, surface sediments, and municipal wastewater emissions (table 4), indicate that the PCB levels in Dover sole are not dependent only upon the level of PCB discharged in wastewaters and that other factors, such as the solubility, volatility, the sediment load, or the relative biological uptake and

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Table 2. Concentrations (mg/wet kg) of the PCB most closely resembling Aroclor 1254 in the whole soft tissues of *Mytilus californianus*.[a]

Station	1971	1974
Coastal		
Gaviota	0.05	0.01
Santa Barbara	0.03	0.02
Port Hueneme	0.12	0.37
Point Dume	0.08	0.04
Palos Verdes Peninsula		
Point Vicente	0.38	0.10
Royal Palm	0.52	0.14
San Clemente	0.05	0.02
Point Loma	0.12	0.06
Island		
Anacapa	0.01	0.01
Santa Barbara	0.07	0.02
Santa Catalina	0.02	0.01
San Nicolas	0.02	0.01
San Clemente	0.02	0.02

[a]After refs. 11, 12.

Table 3. Regional survey of total PCB concentrations (mg/wet kg) in the muscle tissue of individual yellow rock crabs, *Cancer anthonyi*, 1971-72.[a]

Region	No. of samples	Region median	Station range
Santa Monica	12	0.68	0.13 -2.2
Palos Verdes	16	0.82	0.30 -1.8
Outside San Pedro Harbor	5	0.49	0.32 -0.83
Orange County	9	0.32	0.23 -0.54
Ensenada[b]	3	0.014	0.012-0.018

[a]After ref. 11.

[b]Three chelae (*Cancer* species) purchased in fish market.

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Table 4. Comparison of total PCB levels in muscle tissue of Dover sole, *Microstomus pacificus*, and bottom surface sediments and PCB mass emission rates in municipal wastewater.[a]

Region	1971-72 Dover sole (mg/wet kg)	1971-72 Sediments (mg/dry kg)	1971-72 Municipal waste (kg/yr)	1974-75 Dover sole (mg/wet kg)	1974-75 Municipal waste (kg/yr)
Palos Verdes	1.9	3.6	11,600	1.3	1,270
Santa Monica	1.5	0.53	1,920	2.0	956
Orange County	0.7	0.02	5,800	0.6	2,100
San Diego	-	0.01	118	0.2	1,050
Point Hueneme	0.1	0.004	3	0.1	5

[a]After refs. 1,2,11.

retention rate of a given PCB are involved in the resulting levels of PCB's in this marine animal.

Distribution of PCB's in Tissues of a Benthic Flatfish and Crab

In February 1975, special collections of Dover sole were made off Palos Verdes and Orange County for the analysis of PCB's in the muscle, liver, gonad, heart, and kidney tissues (ref. 11). The results are presented in table 5. The level of PCB in the liver tissue was 10 to 20 times higher than the levels observed in the other tissues analyzed. To determine the liver and muscle tissue burdens of the two sets of fish, the median concentrations of PCB in the specific tissue was applied to the average wet weight of that tissue:

	Liver burden	Muscle burden	Ratio, liver to muscle
Palos Verdes	0.04 mg	0.02 mg	2
Orange County	0.02 mg	0.03 mg	0.7

The liver-to-muscle tissue burden ratio for PCB in Palos Verdes Dover sole was 2; for Orange County specimens, the ratio was 0.7. There are two possible explanations for the high liver-to-muscle tissue burden ratio in the Palos Verdes fish. A review of the literature indicates that (1) in metabolic disturbances, the lipid (fat) content in liver tissue may significantly increase, and (2) chlorinated hydrocarbons, which are hepatic poisons, induce fatty livers. As chlorinated hydrocarbons are associated with lipids, if either one or both of these situations had occurred in the Palos Verdes Dover sole, it would have resulted in an increase in the total PCB levels in the liver and a higher liver-to-muscle tissue burden ratio. The lipid content of these tissues is being studied, and further work on the physiological and ecological implications of these tissue burdens is underway.

Analysis of the PCB concentrations in the reproductive organs of *C. anthonyi* indicate that the gonadal tissues generally contain PCB levels five to ten times higher than the muscle tissue levels (ref. 11). Also, in females, the gonad had an absolute tissue burden of PCB that was 25 percent higher than the muscle tissue burden (see table 6).

As the reproductive organs of this crustacean are exposed to considerably higher levels of this synthetic organic than is the muscle, spawning may represent a significant distribution mechanism of these contaminants in the marine environment, and a significant factor in the elimination of a large percentage of the body burden of these materials from the crab. The long-term effects of PCB concentrations on reproduction or other biological processes in this crustacean are unknown.

Fin Erosion and PCB Levels in a Benthic Flatfish

The Dover sole collected off Palos Verdes are frequently affected by fin erosion; the disease has recently also become prevalent off Orange County. Data on specimens with eroded fins and those with healthy fins taken in 1974 in single trawls were paired. Utilizing the

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Table 5. Total PCB concentrations (mg/wet kg) in composite samples of tissues of Dover sole, *Microstomus pacificus*, 1975[a]

Tissue	Palos Verdes		Orange County	
	Median	Range	Median	Range
Muscle	0.7	0.1-1.1	1.1	0.6-1.4
Liver	15	11-18	8.3	4.8-13
Gonads	1.4	0.8-5.2	0.8	0.7-4.6
Heart	1.8	1.5-3.2	0.5	0.4-0.8
Kidney	0.8	0.6-1.1	0.6	0.6-0.8

[a]After ref. 11.

Table 6. Analysis of PCB concentrations in the reproductive organs of *Cancer anthonyi*

	Male	Female
Percent of combined gonad/muscle tissue weight		
Gonad	7	27
Muscle	93	73
Tissue burden (mg)		
Gonad	0.009	0.031
Muscle	0.025	0.025

Wilcoxon signed-rank test, the levels of PCB in the muscle tissue of the unaffected fish and the diseased fish were found to be different at the 90 percent confidence level ($p = 0.10$). Although this level is not considered to be statistically significant, it shows a strong tendency for the total PCB levels to be higher in the diseased fish. The median values for the diseased and unaffected groups were 2 and 1 mg/wet kg, respectively (refs. 11,13).

If this association was dependent upon the input level of PCB, one would expect fin erosion to be dominant off Orange County where the input level of PCB is the greatest. One would also expect to find it off Santa Monica and San Diego where the level of input is similar to Palos Verdes. However, this is not the case. There are several possible reasons for the association between high PCB levels and fin erosion. The disease is predominantly found in the Palos Verdes region: Palos Verdes sediments have the highest levels of PCB in the Bight, thus contaminated sediments could be the dominant factor. Also, PCB—in combination with other constituents present in this region (DDT, hydrogen sulfide, trace metals)—could be involved in the development of the disease. It is also possible that PCB uptake is enhanced in diseased fish; hence the higher levels could be the result of the disease rather than a cause. These relationships are being studied further.

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Surveys of PCB's in Harbor Mussel

Composite samples of the whole soft tissues of *Mytilus edulis* collected from three major southern California harbors (San Pedro, Newport, and San Diego) were analyzed for PCB's (ref. 11).

The survey showed that the harbor mussels had contamination levels up to 20 times those found in specimens of the same species collected from nearby coastal sites. Highest levels were found in mussels taken near regions of heavy vessel activity. Figure 2 shows the data for San Diego Bay, where the range of total PCB values near the commercial docks and navy moorings (0.80 to 1.3 mg/wet kg) is three to four times higher than the values observed at other inner harbor sites, and ten times greater than levels in nearby coastal mussels.

The levels of 1254 PCB in seawater at the mouths of the harbors were generally on the order of 1 part per trillion (ref. 1,2). The values of 1254 PCB in the whole soft tissues of the harbor mussels were 100,000 times these seawater levels.

Although most antifouling paints presently applied to vessel bottoms in southern California contain PCB concentrations of less than 1 mg/dry kg, a few samples of pre-1970 paint chips averaged about 10 percent PCB or 100,000 mg/dry kg (ref. 14). Thus it is possible that thousands of kilograms of this synthetic material could have been released annually to the harbor and coastal marine ecosystems, before the widespread use of non-recoverable PCB's was discontinued in the United States in the early 1970's.

Bouy Mussels: An Offshore Biomonitoring System

In June 1974, 4- to 6-cm long specimens of *M. californianus* were collected from Point Sal, an area known to be relatively free of PCB contamination. Within 1 day of collection, these mussels were transported to a taut-line bouy anchored off Whites Point, where wastewaters from Los Angeles County's Joint Water Pollution Control Plant discharged (ref. 11). The mussels were placed in net bags fastened at five levels between the sea surface (0.5 m) and the bottom sediments (35 m), which are highly contaminated with trace metals and chlorinated hydrocarbons at this site (refs. 15-17).

The mussels transported to the bouy system off Palos Verdes appeared to survive well under the test conditions: Less than 10 percent mortality was observed at any of the five levels (0.5 to 35 m) at which the mussels were suspended during the 3-month study.

On the average, mussels living at Royal Palm Beach, inshore of the buoy, contained 17 times as much PCB as the control specimens at the time of their transfer to the buoy northwest of the outfalls. Thus, exposure of these mussels to PCB was greatly increased upon their transfer to the discharge region.

The results indicated that there was a direct relationship between uptake of PCB and proximity of the bioindicator to the contaminated bottom sediments and to the wastewater plume, which is trapped beneath the thermocline. The bottom specimens became approximately 10 times as contaminated as did the surface specimens.

At the end of the 13-week period, the 1254 PCB concentrations in the whole soft tissues of specimens collected from Level 5 (closest to the bottom sediments) were approaching 0.4 mg/wet kg; those specimens from Level 1 (at the surface) were at 0.04 mg/wet kg. To date, the highest 1254 PCB concentration measured in the water above the outfalls is 4 ng/l (ref. 12). This suggests a concentration factor on the order of 100,000 for 1254 PCB in the whole soft tissues of *M. californianus*, a number in good agreement with the estimate for *M. edulis* in the harbors.

SUMMARY

1. No statistically significant decrease in the Bight-wide levels of PCB in the muscle tissue of Dover sole was observed over the 3-year period 1971-72 to 1974-75.

2. The level of PCB contamination of the open coast mussel decreased significantly over the 3-year interval, 1971-74, with a median percent decrease of 54 percent.

3. Regional surveys of the yellow rock crab and open coast mussel indicate that PCB contamination levels in these animals are low but widespread.

4. For all three species surveyed, PCB levels in specimens collected near major outfall systems were generally 10 to 100 times higher than levels in specimens collected from coastal or island control sites.

5. The dominant PCB observed in the three species surveyed most closely resembled Aroclor 1254; the other PCB identified most closely resembled Aroclor 1242. In contrast, the dominant PCB discharged via municipal wastewaters most closely resembled Aroclor 1242.

6. The liver tissue of Dover sole generally had concentrations of PCB's 10 to 20 times greater than the levels found in the muscle, gonad, heart, and kidney tissues.

7. The liver-to-muscle tissue burden ratio for total PCB in Palos Verdes Dover sole was three times higher than the ratio for Orange County specimens.

8. The reproductive organs of the yellow rock crab generally contain PCB levels five to ten times higher than the muscle tissue levels.

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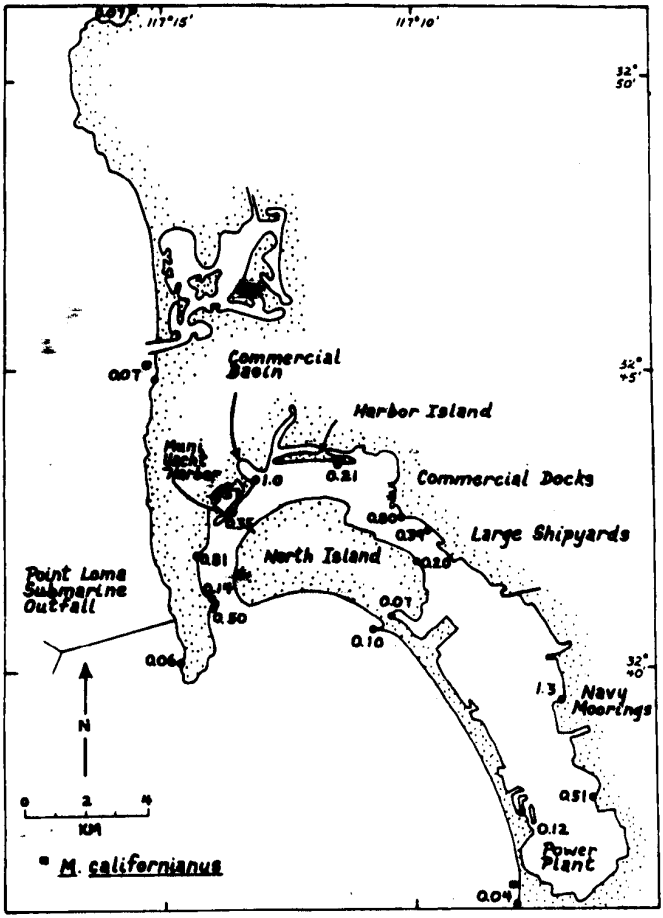


Figure 2. Total PCB concentrations (mg/wet kg) in whole soft tissues of *Mytilus edulis* in San Diego Bay, January 1974. (After ref. 11).

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9. PCB's were found to be associated with the fin erosion disease prevalent in Dover sole collected around major municipal wastewater discharge sites at the 90 percent confidence level ($p = 0.10$).

10. Harbor mussels had PCB contamination levels up to 20 times those found in specimens of the same species collected from nearby coastal sites. Highest levels were found in mussels taken near regions of heavy vessel activity.

11. Although the mussel used in the buoy system was an intertidal organism, less than 10 percent mortality was observed at depths to 35 m. This mussel's hardiness, its ubiquitous distribution along many coastlines around the world, its very high ability for concentrating chlorinated hydrocarbons above seawater values, and its apparent ability to rapidly respond to changes in environmental levels of such contaminants make it a very useful bioindicator, both in natural intertidal communities and on offshore substrates.

The widespread use of nonrecoverable PCB's was curtailed in the United States during the early 1970's. However, the inputs of these persistent substances are still diffuse and difficult to control. There is a need for more knowledge of the effects of these materials in the marine environment; in particular, uptake rates, persistence, and biological effects should be studied.

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MONS 064911

TRANSPORT OF CHLORINATED HYDROCARBONS IN THE UPPER CHESAPEAKE BAY

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Abstract

Under contract to the Maryland State Department of Natural Resources, the staff of the Westinghouse Ocean Research laboratory (together with subcontractors at Johns Hopkins University and the University of Maryland) recently completed the Upper Bay Survey—a program having as the central task the study of the routes, rates, sources, sinks, and reservoirs of chlorinated hydrocarbons (CHC's) in the upper Chesapeake Bay. Data from the field portion of this program will be presented; in particular, the levels of PCB's, chlordane, and DDTR found in bottom sediments, suspended particulates, zooplankton, and shellfish will be summarized. The discussion will include the role of sediment deposits as traps for CHC's; suspended particulates as transport vehicles for CHC's; movement of CHC's from the suspended particulate reservoir into the biological system, particularly shellfish and zooplankton; and the sources of CHC's in the upper Chesapeake Bay.

INTRODUCTION

The concept of the Upper Bay Survey grew directly from the Chester River Study (ref. 1), a program of more limited scope, which was completed in the fall of 1972. An objective of that program was to provide the Maryland Department of Natural Resources with environmental and resource management information essential to the local shellfish industry. These studies were directed toward determining the source and fate of chlorinated hydrocarbons and selected trace metals in the waters and sediments of this estuary. The approach was multidisciplinary. The project as a whole was considered experimental, since it was to encompass many aspects of an estuarine ecosystem with the declared purpose of supporting the practical needs of natural resource managers. Thus, the Chester River Study was a program of focused, applied research rather than a more basic program to extend knowledge in estuarine sciences.

As a result of this program, it became clear that the upper Chesapeake Bay was the most likely source of sediment-borne materials considered potentially harmful to the living resources of the Chester River. An extension of the Chester River project encompassing the bay between the Severn and Susquehanna Rivers became the next logical step in assessing the impacts of man-made substances in the bay ecosystem. The Upper Bay Survey (funded by the Mayland Department of Natural Resources) was begun in December 1973—once again multidisciplinary, but also multiinstitutional with the participation of scientists from the University of Maryland and The Johns Hopkins University. A 12-month research program was implemented with the following five definitive objectives:

1. To determine concentrations, distributions, and sources for chlorinated hydrocarbons (CHC's) including pesticides and polychlorinated biphenyls (PCB'S), and to determine the nature of transport paths, mechanisms, and rates in the Chesapeake Bay's waters, sediments, and organisms.
2. To determine immediate and longer-tarm biological consequences of chlorinated hydrocarbons and PCB'S on commercially important species.
3. To determine the distribution of bacteria on sediments and suspended particles of the upper bay, and to perform toxicological studies of the combined effects of pesticides and bacteria on oysters.
4. To institute numerical models for projecting contaminant distribution relative to the sources and to develop interrelations to biological impacts resulting from changes in the upper Chesapeake Bay's input stresses.
5. To report results in a format conveniant for resource management and in a format for computer storage, retrieval, and augmentation.

In this paper, the data resulting from the chlorinated hydrocarbon analyses of bottom sediments, suspended sediments, zooplankton, and shellfish will be presented and discussed.

METHODS

Sample Collection. The bottom sediments were collected as grab samples using either a Wildoo-Eckman Bottom Sampler or a Ponar Grab Sampler. In the laboratory, a portion of the sample was retained for sediment grain-size and clay mineralogy analyses, and the remainder air-dried for about 1 week. The shellfish samples were collected with a modified bottom trawl or a Ponar Grab Sampler and frozen for later analysis.

Suspended particulate samples were collected from surface, midwater, and 0.5 m from the bottom at the sampling stations illustrated in figure 1. The suspended

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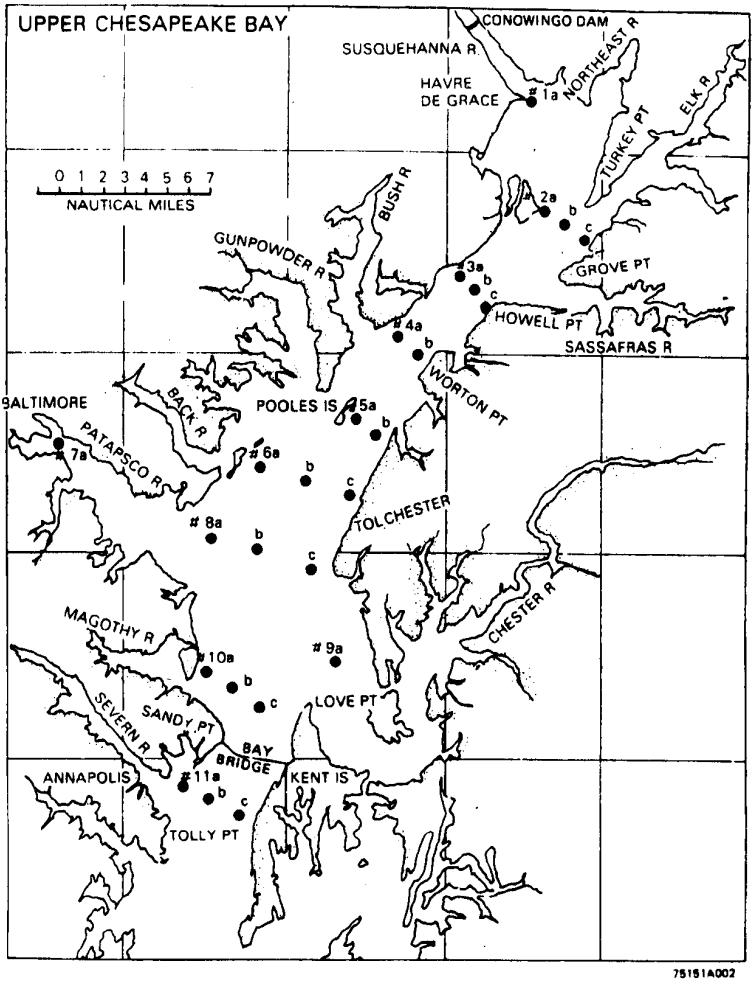


Figure 1. The principal stations at which samples and measurements were taken in the Upper Bay Survey.

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particulates were collected by filtration through Gelman type-A glass-fiber filters having nominal pore diameters of 5-8 μ (the functional pore size appeared much smaller because our tests with Chesapeake Bay water showed that nothing which passed through this filter could be retained on a 0.45 μ Millipore filter). In order to get sufficient sample for chlorinated hydrocarbon analysis (in excess of 0.3 g dry weight) as much as 100 l of water was filtered depending upon the concentration of suspended particulates in the water (usually in the range, 3 to 30 mg/l).

Figure 2 shows the filter apparatus and a filter loaded with suspended particulates. It was determined empirically that filtering until two filters 14.5 cm in diameter became clogged provided the minimum amount of sample required. The bay water entered a ¾ inch garden hose suspended at the appropriate depth, passed through the filter, through the pump, and into a calibrated vessel for volume estimation. The wet filters were folded, wrapped in aluminum foil and transported to the laboratory. In the laboratory the samples were air-dried (about 2 days) and stored wrapped in foil until analysis. The weight of sample collected (and subsequently extracted) was determined by a calculation using the volume of water filtered and the concentration of suspended particulates in the water.

Two procedural restrictions prevented direct determination of the suspended particulate sample weights: first, the filters had to be preextracted with solvents to remove interfering substances and sealed in foil until use, which made preweighing undesirable; and second, had preweighing been done, the subsequent weights would have been dubious because these filters tend to shed and flake. At each point in time and space where a suspended particulate sample was collected for chlorianted hydrocarbon analysis, two suspended particulate samples were collected on 4.7 cm diameter Millipore or Nucleopore membrane filters (pore size 0.46 and 0.6 μ respectively)—one for determing the suspended particulate concentration and one for determining the suspended particulate grain-size diameters (ref. 2).

Zooplankton samples were collected as oblique tows with paired half-meter standard oceanographic nets using hexane rinsed 202-μ Nitex netting. A calibrated T.S.K.-type mechanical flowmeter was placed in the mouth of each of the two nets to record the volume of water passing through. Upon completion of each tow, the nets were carefully washed to concentrate the plankton in the cod end. After removal of the larger, gelatinous material by passage through a 4-mm sieve, the samples were concentrated with a 202-μ sieve. From each pair of net samples, one net collection was preserved for taxonomic and biomass enumerations, and the other sample was passed through a hexane-extracted Gelman glass-fiber filter to collect the zooplankton. The resultant pad of zooplankton (including the filter) was frozen and retained for later analysis.

Sample Preparation. All of the samples were extracted using Soxhlet extraction with 2:1 hexane-acetone (the biological samples were first dried by being ground with anhydrous sodium sulfate). All of the extracts were subjected to fuming sulfuric acid cleanup procedures (refs. 3,4) prior to gas chromatographic analysis. Before the acid treatment procedure, the bottom sediment extracts were treated wtih activated alumina. Most of the bottom sediment extracts, some of the suspended sediment extracts, and several of the zooplankton extracts contained sulfur, which was removed by treatment with elemental mercury (ref. 5).

Chlorinated Hydrocarbon Analysis. The chlorinated hydrocarbons were identified and quantitated by multicolumn, electron-capture, gas-liquid chromatography. Peak relative retention times and peak heights (or areas) were compared to those of standard compounds. The amounts of PCB's and chlorinated pesticides were estimated by a manual subtraction procedure correcting for the overlapping peaks.

RESULTS AND DISCUSSION

Table 1 summarizes the chlorinated hydrocarbon levels found in the various types of samples collected in the upper Chesapeake Bay.

The standard deviation values given in table 1 emphasize the fact that the range of CHC values observed within any particular sample type was very broad. The values for CHC's on suspended sediment and zooplankton varied greatly from one station to the next during the same collection period or at the same station from one collection period to the next. Apparently these values fluctuate rapidly enough (temporally and spatially) that only the unusually large events in terms of time and/or space will be observed at enough points to describe a trend when the sampling is limited to a fairly small number of samples, as in this program. The multidisciplinary approach of this program, however, circumvents this problem somewhat by providing many different types of data that are comparable in space and time. As will be seen below, these data then can be examined for interrelationships relevant to the understanding of the dynamics of chlorinated hydrocarbon movements in the upper Chesapeake Bay.

For the purposes of this discussion, the PCB's will be discussed as total PCB (the sum of the values reported as Aroclor 1242, 1248,1254, and 1262), and in some

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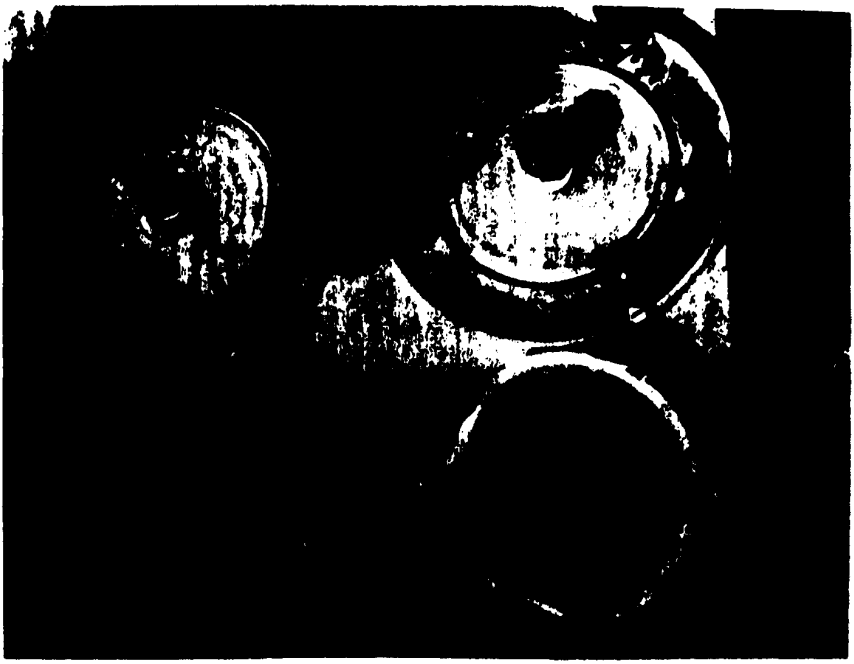


Figure 2. Filtering apparatus for collecting suspended sediment samples and a Gelman filter containing suspended sediments.

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Table 1. Average chlorinated hydrocarbons found in the upper Chesapeake Bay (Standard deviations are in parentheses)

Sample type	Number of samples	Total PCB	Total chlordane	Total DDT
Shellfish (wet, ppm)[a]	26	0.052(0.037)	0.016(0.017)	0.035(0.041)
Plankton (wet, ppm)	70	0.50(1.4)	0.041(0.032)	0.16(0.68)
Suspended sediment (dry, ppm)[b]	66	0.92(0.87)	0.061(0.086)	0.057(0.066)
Bottom sediment (dry, ppm)	54	0.28(0.57)	0.0052(0.014)	0.051(0.067)
Plankton (H_2O, ppt)[c]	69	0.042(0.164)	0.0038(0.0083)	0.010(0.035)
Suspended sediment (H_2O, ppt)	68	12(14)	0.53(0.88)	0.78(1.5)

[a]The values are expressed as µg CHC found per g wet weight of material extracted.

[b]The values are expressed as µg CHC found per g dry weight of material extracted.

[c]The values are expressed as ng of CHC found per l of water filtered to collect the material extracted.

cases, all of the CHC's found will be summed and discussed as total CHC. The PCB residue pattern observed most often matched Aroclor 1254 or a mixture of Aroclors 1254 and 1262. (Aroclor 1242 or 1248 was found in many of the samples.)

By comparing the bottom sediment data with the suspended sediment (dry) data, one can see that the PCB and chlordane concentration are 4 to 10 times higher in the suspended sediments. The higher values in the suspended sediment probably occur for one, or most likely, both of the following reasons: the average grain-size of the suspended sediments is much smaller than that of the bottom sediments, resulting in a greater surface area for adsorption per unit weight; and although the suspended sediments are primarily inorganic materials, the phytoplankton, which were included in these samples, probably bioconcentrated chlorinated hydrocarbons to some extent.

If one accepts the above discussion, one is left with the dilemma that the DDTR does not appear higher in the suspended sediments as do the PCB and chlordane. But all uses of DDT were banned in the United States at the end of 1972. If this ban had the effect of decreasing the DDT levels flowing into the Chesapeake Bay, the concentrations of DDT residues in the suspended sediments would be less relative to those in the bottom sediments because the bottom sediment samples consist of materials deposited during the sampling year and previous years as well, while the suspended sediment samples consist primarily of materials that entered the bay during the sampling year. While this explanation is plausible, it seems somewhat suspicious that samples

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were taken fortuitously at just the right time to yield exactly the same DDT residue levels in both the suspended sediments and the bottom sediments.

The data in table 1 also show that the CHC's are bioconcentrated in passing from the suspended sediment into the zooplankton. To evaluate the magnification, one must first convert the plankton (wet) values to plankton (dry) to allow comparison with the suspended sediment (dry) values. If one conservatively uses 0.10 as the plankton dry weight to wet weight ratio (ref. 6), one then multiplies all of the plankton (wet) values by 10 to convert to plankton (dry) and then calculates the following bioconcentrations as the CHC's pass from the suspended sediments to the zooplankton: PCB, 5.4; chlordane, 6.7; and DDTR, 28. The DDTR value seems unreasonably high, and it probably is. If two anomalously high DDTR values are excluded from the total and the average is computed from the other 88 values, the average DDTR in plankton (wet) become 0.045, leading to a magnification of 7.9—a value more compatible with the others.

The CHC data for suspended sediments and zooplankton are expressed in two ways, as mentioned earlier, but further amplification should be made. Environmental residues of chlorinated hydrocarbons (chlorinated pesticides and polychlorinated biphenyls) usually are reported as parts per million (ppm) dry weight (or wet weight) based upon the dry weight (or wet weight) of sample which was extracted for the analysis. If the levels are very low, parts per billion (ppb) or parts per trillion (ppt) also are used. The data then represent the concentration of CHC's present in that sample. In the consideration of transport of CHC's (rates, routes, etc.) the amount of CHC being transported by a water movement frequently is of more interest than the concentration of the CHC's on the suspended sediments in the water.

Therefore, in addition to the date being presented in the usual fashion, the zooplankton and suspended sediment CHC data are presented as nanograms (10^{-9}g) of CHC on zooplankton or suspended sediment per liter of water (by definition, ppt). These values represent the amount of CHC associated with the suspended sediments or the zooplankton contained in a 1 liter sample of bay water. In a sense, the numbers can be compared directly because they have been normalized to a unit volume of water. For instance, referring to table 1, one finds the average PCB values in the bay water on suspended sediment and zooplankton to be 12 ppt and 0.042 ppt, respectively. On the average, a given volume of bay water will have about 300 times as much PCB in the suspended sediment fraction as in the zooplankton fraction.

Using these values, one also could calculate approximate biomagnification values from the shellfish data. The concentrating ability of shellfish usually is expressed as the level accumulated in the shellfish tissue (wet weight) divided by the exposure concentration in the water. Using the values for CHC in the water column on suspended sediment, the shellfish concentration factors are approximately: PCB, 4,000; chlordane, 30,000; and DDTR, 45,000. These values should be considered rough estimates, because the average values used for CHC's in the water column probably do not represent accurately the values at the water-bottom sediment interface inhabited by these shellfish.

Figure 3 is a log-log plot of total CHC concentration in the water column on suspended sediment (ppt) versus the concentration of suspended sediment in the water (mg/l). Although the data points are widely scattered, the data could best be enclosed in an oblong field with an upward tilt to its long axis. This indicates a positive relationship between the parameters plotted (if the parameters were unrelated—that is, varied independently—the long axis of the oblong would be either vertical or horizontal). The correlation obviously is not followed closely by all of the data, but in general, it indicates that the bay water samples which had high suspended sediment concentrations also had high levels of CHC's in the water on suspended sediments. If all suspended sediments in the water contained the same amounts of CHC's (ppm, dry weight), a perfect correlation would have been observed in figure 3. The variations in the concentrations of CHC's on suspended sediments are responsible for the scattering of the data.

Figure 4 is a log-log plot of total CHC's in the water on zooplankton (ppt) versus the zooplankton biomass in the water (mg/m^3). Although the data are somewhat scattered, there is an obvious positive relationship—as the zooplankton population in the water increases (increasing biomass), the amount of CHC's in the water on zooplankton increases. The existence of this relationship establishes that there is movement of CHC's into the aquatic food chains which include the zooplankton community. The fact that the zooplankton population contains only a small fraction of the CHC's present in the water column, considered with the relationship observed in figure 3, suggests that the movement of CHC's into the biological system (via zooplankton) from the nonbiological system (suspended sediments) is not influenced by changes in the concentration of suspended sediment but is regulated by whatever regulates the zooplankton population. One could visualize the suspended sediments in the water column as being a reservoir of CHC's, which flow into the biological system when zooplankton blooms occur.

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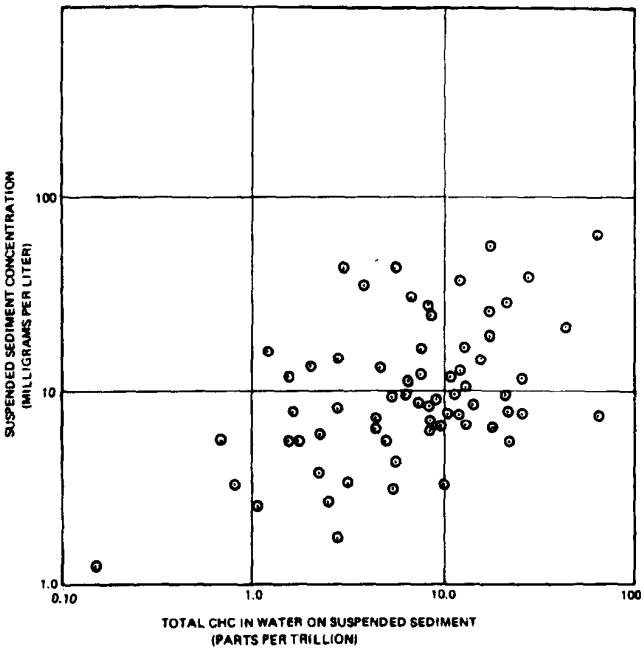


Figure 3. A plot of the log of the suspended sediment concentration in the water (milligrams per liter) versus the log of the total CHC concentration in the water associated with the suspended sediment (parts per trillion).

Obviously, this concept is an over simplification of a very complex system. More likely, the phytoplankton are important in the transport of CHC's from the non-biological reservoir into the zooplankton food-chain. Unfortunately, the sampling procedure for gathering suspended sediments involved pumping the water through a filter, so the phytoplankton were included in the fraction called suspended sediments. To overcome this limitation, it had been hoped to estimate the influence of changes in the phytoplankton population through the use of measurements of the chlorophyll level in the water column. Figure 5 presents a log-log plot of the zooplankton biomass versus the chlorophyll-a concentration in the water column. These parameters appear to be independent variables. A similar plot (not shown) of the chlorophyll-a concentration versus the concentration of CHC's in the water column on zooplankton yielded a very similar result. If the phytoplankton have a direct role in the pathway of CHC's into the zooplankton community, the chlorophyll-a data shown here do not indicate it.

Whatever the details of the pathway for CHC's from the suspended sediment reservoir into the zooplankton, it seems that only a very small percentage of the CHC's in the water column are associated with the zooplankton (average of 12 ppt PCB in the water column on suspend-

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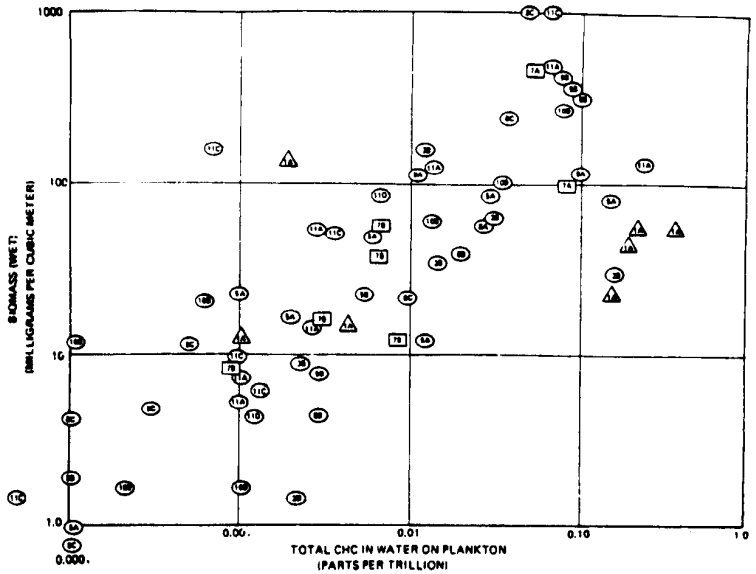


Figure 4. A plot of the log of zooplankton biomass (milligrams weight per cubic meter) versus the log of the total CHC in the water associated with the zooplankton (parts per trillion).

ed sediment versus 0.042 on zooplankton). However, to quantify the rate of movement of the CHC's via this pathway one would need information about turnover rates in the plankton community. Regarding resource management, one should consider that a change in bay conditions that would increase the zooplankton population would probably have the effect of increasing the flow of CHC's from the suspended sediment reservoir into the biological system. This could create adverse consequences as all aquatic species of commercial interest at some time in their lifecycle make up a part of the zooplankton community.

By far, the largest route for the transport of CHC's from the suspended sediment reservoir probably is a result of sediment deposition. The areas of deposition of fine-grain sediments can be visualized as sinks where the CHC's attached to suspended sediments collect. As in the Chester River Study (ref. 1), the chlorinated hydrocarbons in the bottom sediments were found highest where the median grain-size diameters were the lowest. Baltimore harbor is a trap for fine-grain sediments in the upper Chesapeake Bay and, as such, functions as a sink for CHC's from the suspended sediment reservoir. Figure 6 shows that PCB, for instance, was much higher in the sediments of Baltimore harbor than elsewhere in the bay. It would be necessary to analyze core slices and establish the three-dimentional concentration gradient in order to estimate the mass of CHC's contained in the bottom sediment sinks. (A core from the Chester River was found to contain layers of widely varying levels of CHC's to a depth of 50 centimeters—reference 1.)

A number of mechanisms exist for movement of

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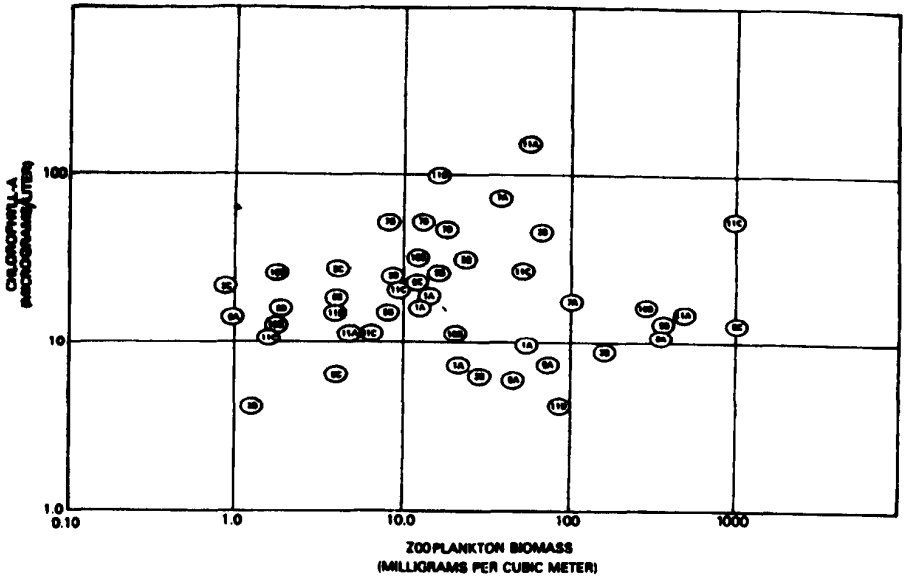


Figure 5. A plot of the log of the chlorophyll–a concentration in the water (micrograms per liter) versus the log of the zooplankton biomass in the water (milligrams per cubic meter).

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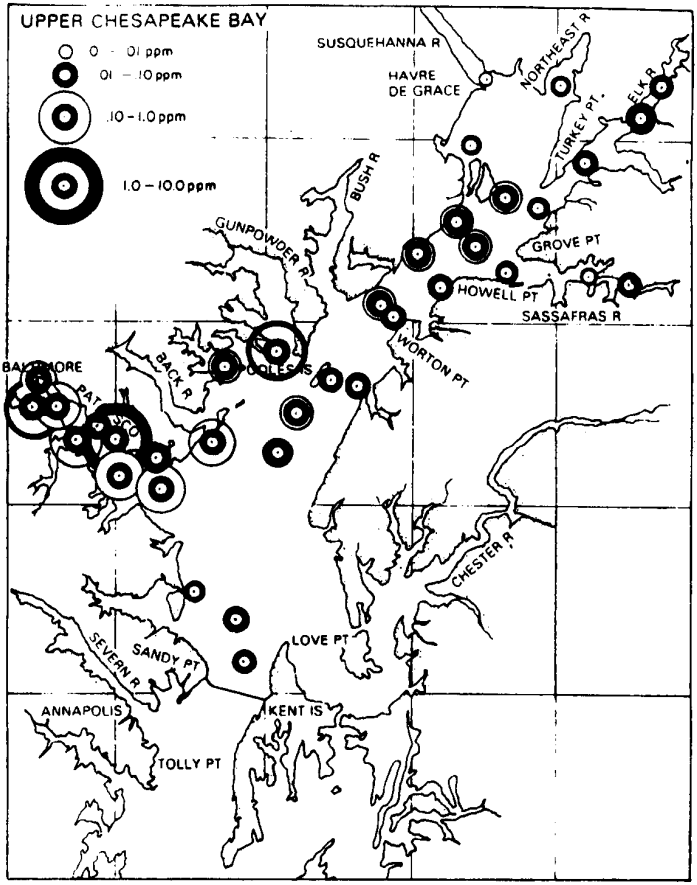


Figure 6. A representation of the concentration of PCB's in bottom sediments samples from the upper Chesapeake Bay.

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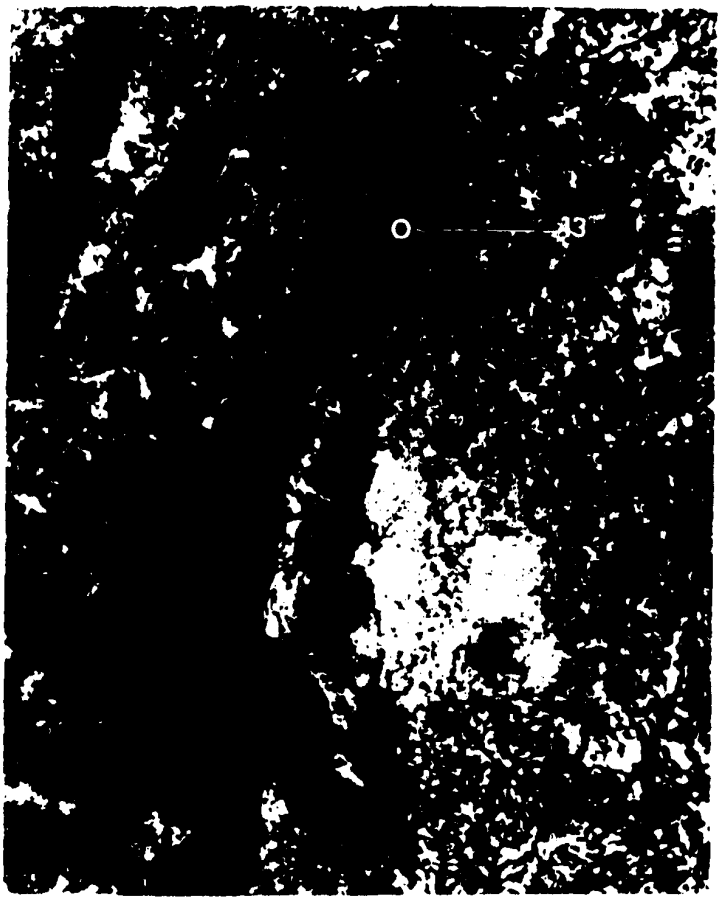


Figure 7. A portion of an Earth Resources Technology Satellite–1 photograph taken April 3, 1974, showing suspended sediment influx into the upper Chesapeake Bay from the Susquehana River. Samples were taken at station "13".

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CHC's out of the bottom sediment sinks. When one considers the fine-grain fractions in the upper Chesapeake Bay as a whole, resuspension of this material by tidal scour probably is the major reentry route from the sinks to the suspended sediment reservoir (ref. 7). In the Baltimore harbor area, however, maintenance dredging of navigational channels is a major mechanism for removal of sediments containing chlorinated hydrocarbons from the bottom sediment sink. Although the subsequent fate of this dredged material is a subject clouded by great controversy, during the dredging and subsequent overboard discharge of this material, undoubtedly, a substantial quantity returns to the suspended sediment reservoir.

The Susquehenna River appears to be the major source of chlorinated hydrocarbons to the upper Chesapeake Bay. Nearly all of the suspended sediment in the upper bay originates from the Susquehanna River—entering primarily during the few brief periods of high flow (ref. 7). Figure 7 is an ERTS-1 (Earth Resource Technology Satelite-1) photograph showing the sediment influx at the beginning of a freshet period in April 1974. During this freshet period, suspended sediment samples were collected at the location designed "13" in figure 7. Analysis of these samples (together with other samples collected during the study) indicated that, when they enter the bay, the suspended sediments appear to carry sufficient burden of PCB's and DDT residues to account for levels observed at the lower stations without postulating additional sources. The chlordane values appear low, however, suggesting substantial inputs from other sources. As is discussed in greater detail elsewhere (ref. 4), the urban-industrial activities concentrated in and around Baltimore harbor appear to generate locally high concentrations of PCB and DDT residues, but seem not to contribute a major portion of the total budget of these materials in the upper bay. It seems likely, however, that the harbor area does contribute a large portion of the chlordane found in the upper bay.

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RECENT STUDIES OF TRANSPORT OF PCB'S TO MARINE ENVIRONMENTS

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Abstract

The deep ocean waters and sediments are a potential sink for chlorinated biphenyl compounds, removing them from food webs which provide input to man. Data on PCB levels in seawater are as yet unsatisfactory or too few to permit a reliable estimate of the amounts of PCB that have so far entered the oceans. Formulation of a global mass balance equation for the major kinds of PCB compounds would be useful in predicting future contamination levels.

Chlorinated biphenyl compounds have been reported in many marine environments, including those of the Arctic (ref. 1) and the Antarctic (ref. 2); with the DDT compounds they have become contaminants throughout the global ecosystem. Concentrations reported are occasionally high, including those in seawater of the North Atlantic (ref. 3), in marine birds of coastal areas (refs. 4,5,6), in birds feeding on the eggs of other sea birds (ref. 7) and in peregrine falcons (*Falco peregrinus*) of Amchitka Island in the Aleutians (ref. 8).

The high levels which have been reported from both coastal and marine environments raise two questions. Do these levels represent a threat to local ecosystems and to human consumers? And do the high levels indicate that the oceans, particularly the deep waters and marine sediments, can be considered an ultimate sink in which polychlorinated biphenyls are unlikely to enter food webs that provide nourishment to man? Deposition in marine sediments might then be a significant pathway of removal of these pollutants from the biosphere. Attempts to answer the latter question would require formulation of a global mass balance equation of the chlorobiphenyls, which would express the present burden of PCB's in the oceans in terms of global production figures and use patterns. A preliminary formulation of such a global mass balance equation based on North American production and use of PCB has been presented by Nisbet and Sarofim (ref. 9). The present paper reviews some of the work relating to the transport of polychlorobiphenyl compounds to marine environments that has been carried out since Nisbet and Sarofim presented their preliminary model.

Just as it has become misleading to speak of "DDT" in the environment without reference to the individual compounds, so has it become misleading to speak of "PCB" in the environment without reference to the kind of PCB. Thus, the majority of the chlorinated biphenyls used in the United States has consisted of the trichlorinated preparations (ref. 10), whereas PCB reported in marine environments usually consists of penta- or hexachlorobiphenyls. It is therefore meaningless to discuss PCB concentrations in seawater in reference to input from rivers if the former consist predominately of pentachlorobiphenyls and the latter of trichlorobiphenyls.

Nature of PCB Compounds in Marine Environments

The higher vapor pressures of the lower chlorinated PCB compounds (ref. 11) and the production end use figures (refs. 9, 10) suggest that larger quantities of these have entered the marine environment than have the penta- and hexachlorobiphenyls. Thus Bidleman and Olney (ref. 12) found that the majority of the PCB residues in air over the Sargasso Sea consisted of tri- and tetrachlorobiphenyls. Similarly, PCB entering the sea as a component of the wastewaters of Southern California has consisted predominately of trichlorobiphenyls (D. R. Young, R. W. Risebrough, B. W. de Lappe, T. C. Heesen, and D. J. McDermott, unpublished data). Trichlorobiphenyls have occasionally been detected in seawater of the Southern California Bight (ref. 13), but PCB usually reported in seawater has consisted of pentachlorobiphenyls (refs. 3, 14, 15, 16). Bidleman and Olney (ref. 12) have reported that the chlorobiphenyls in their seawater extracts from the Sargasso Sea were predominately hexachlorobiphenyls. Tri- and tetrachlorobiphenyls have been detected in marine fish from the Aleutians and in ptarmigan (*Lagopus mutus*), an arctic grouse that feeds on the tundra (ref. 8). Many extracts of marine species, however, do not contain tri- or tetrachlorobiphenyls in concentrations equivalent or approaching those of the penta- and hexachlorobiphenyls. Bacterial degradation of the lower chlorinated compounds (ref. 17) is a possible pathway of breakdown but the low concentrations of PCB in seawater might not prompt bacteria to synthesize the necessary enzymes for their metabolism, unlike the bacterial response in artificial environments where PCB compounds are the only carbon source. A major difficulty in recording the lower chlorinated compounds in seawater has been the presence in the majority of extracts of high concentrations of other compounds which interfere with the analysis. The higher vapor pressures of the lower chlorinated compounds and their

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longer residence time in the atmosphere might result in higher rates of breakdown by ultraviolet light, but evidence to support this hypothesis is apparently lacking. In higher vertebrates, metabolism to hydroxylated derivatives of unknown significance in the marine environment accounts for the disappearance of some of the tri- and tetrachlorobiphenyls. Formulation of a global mass balance equation of "PCB" therefore makes little sense unless it is done with reference to individual compounds or at least to the major classes of chlorobiphenyls.

Chlorinated Dibenzofurans in the Environment

Other papers presented at this symposium have expressed the current concern over the possible exposure of man to chlorinated dibenzofurans. Preparations of PCB have been shown to produce birth defects in birds (refs. 18, 19, 20), similar to those which have occasionally been observed in populations of terns, *Sterna hirundo*, and *S. dougallii*, breeding in Long Island Sound and feeding on small fish (ref. 21). The observed defects are comparable to those produced by the chlorinated dibenzodioxins (ref. 22). The presence of the chemically related chlorinated dibenzofurans in PCB preparations (refs. 23, 24, 25) suggests that the defects may be caused by these contaminants rather than by chlorobiphenyls.

Extracts of mallards (*Anas platyrhynchos*) that had been fed PCB of known dibenzofuran content were examined for the presence of chlorinated dibenzofurans. The chlorinated dibenzofurans originally present in the Aroclor 1254 were found to be metabolized or otherwise excreted at a much faster rate than the pentachlorobiphenyls and were not found in the extracts (ref. 26). It would therefore appear unlikely that these compounds would be accumulated in marine food webs. In the light of other results that have been presented at this symposium, it might be worthwhile to look in the environment for those individual PCB compounds from which dibenzofurans might be formed in vivo, and to examine tissues of species exposed to these compounds for the presence of the furans.

Comparative PCB Levels in Marine Environments

Relative contamination levels of different oceanic areas by PCB compounds have recently been reviewed by Ohlendorf et al. (ref. 27) and by Risebrough et al. (ref. 13); marine birds were used as indicator organisms. In the North Atlantic, PCB contamination appears to increase from west to east; contamination levels in the vicinity of Iceland appear comparable to those in the Aleutians in the North Pacific. In the southern hemisphere, levels in biocoenetic equivalents of northern species are approximately one order of magnitude lower. The difference between the two hemispheres reflects therefore the relative industrialization of the two areas. Data that would permit a more detailed comparison between the Atlantic and the Pacific are as yet insufficient.

PCB in Seawater

Determinations of the PCB levels in seawater have been reported from both the Pacific and the Atlantic. Williams and Robertson (ref. 15) have reported PCB, p,p'-DDT, and p,p'-DDE values in subsurface water from the outer California Current and at two stations in the North Central Pacific Gyre, both in the vicinity of 31° N.155° W. Water was collected in 2.5- liter glass bottles, 10-15 cm below the surface. Reported PCB values in the subsurface water, including filtrate and filtered fractions, were 2.5×10^{-12} g/g in the California Current and 4.5×10^{-12} g/g at one of the North Central Pacific Gyre stations.

Scura and McClure (ref. 16) utilized a column containing 5% activated carbon powder, 10% MgO, and 85% refined diatomaceous earth for the determination of chlorinated hydrocarbons in 1-liter samples of seawater collected off the Southern California coast. Reported PCB concentrations at five stations in the Southern California Bight ranged from 3 ppt to 9.6 ppt (10^{-12} g/g) at the surface; concentrations reported in five samples obtained at depths from 500 to 1,500 meters ranged from 2.3 to 10.3 ppt. In the majority of samples, p,p'-DDE and p,p'-DDT were detected; DDE concentrations ranged from <0.1 ppt to 1.0 ppt at the surface and from 0.3 to 1.2 ppt at depths from 500 to 1,500 meters. Concentrations of p,p'-DDT were somewhat lower.

Bidleman and Olney (ref. 12) have reported PCB and DDT concentrations at eight stations in the Sargasso Sea in 1973. PCB concentrations in subsurface water were lower than detectability (<0.9×10^{-12} g/g) at four of the stations and ranged from 1.0 to 3.8×10^{-12} g/g at the others. Concentrations of p,p'-DDT were 0.5×10^{-12} g/g at one station but were below detectability (<0.15×10^{-12} g/g) at the others. Samples were collected in 3.8-liter glass jugs at depths approximately 30 cm below the surface. Substantially higher concentrations were measured in the surface microlayer. These concentrations were calculated by reference to Aroclor 1260. Concentrations calculated by reference to Aroclor 1254 may have been up to two times higher (ref. 28).

Because of the difficulties in extracting large volumes of seawater with organic solvents, Harvey et al. (ref. 3) developed a column extraction system using Amberlite XAD-2 resin. Seawater samples in volumes ranging between 19 and 80 liters were obtained in a large volume sampler and passed through the resin on board

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ship. Also, the extracts were analyzed on board ship. Reported PCB concentrations, calculated by reference to Aroclor 1254, averaged 35 x 10^{-12} g/g at the surface and 10 ppt at 200 meters. At depths of 100, 1,500, and 3,000 meters reported concentrations were >1 ppt. Samples were obtained in the summer of 1972 (ref. 3).

In 1973 and 1974, substantially lower values were recorded and it was concluded that PCB concentrations in North Atlantic surface waters had declined 40-fold over the 2-year period as a result of restrictions on PCB use (ref. 14). At two stations sampled in 1973 (09° N. 40° W. and 32° N. 70° W.) samples were obtained through the water column. PCB concentrations ranged from 4.3 ppt at 10 meters to 1 ppt at 3,000 meters at the former site and from 0.4 to 1.9 ppt at depths between 10 meters and 5,100 meters at the latter.

Harvey et al. (ref. 14) estimated that the decline of PCB concentrations would require removal of 2 x 10^4 tons of PCB from the upper 200 meters over the 2-year period, assuming a mean concentration in 1972 of 20 x 10^{-12} g/g in the upper 200 meters of the North Atlantic between 26° N. and 63° N.; the volume was assumed to be 10^{16} liters. The estimate of the volume over this area at a depth of 200 meters appears, however, to be low, perhaps by an order of magnitude since the corresponding area would be 5 x 10^6 km^2. The area of the Atlantic, including the North and South Atlantic, is 82 x 10^6 km^2 (ref. 29). Thus, since the PCB reported consisted predominantly of pentachlorobiphenyls, in the order of 10^5 metric tons of pentachlorobiphenyls would have to be removed from the upper 200 meters. From 1957 through 1974, a total of only 124 million pounds, equivalent to 5.6 x 10^4 metric tons of pentachlorobiphenyls (Aroclor 1254), was sold in the United States (ref. 10). Sales in 1970, the peak year of U.S. production, amounted to 5.6 x 10^3 tons. Since the mean depth of the Atlantic is 3,926 meters (ref. 29) and since PCB was recorded at depths to 3,000 meters, the estimated pentachlorobiphenyl content of the North Atlantic would be correspondingly higher. If the average concentration throughout the water column were assumed to be 1 ppt, the average depth assumed to be 3,900 meters and the area of the North Atlantic between the equator and 65° N. were assumed to be in the order of 47 x 10^6 km^2, the pentachlorobiphenyl content would be in the order of 180,000 metric tons, higher than the total U.S. domestic use.

Similarly, the PCB concentrations reported from the Pacific by Scura and McClure (ref. 16) and by Williams and Robertson (ref. 15) appear to be too high. If a mean value of 1 ppt were assumed for the upper 200 meters of the North Pacific and the area from the equator to 65° N. is 82 x 10^6 km^2, 16,000 tons of pentachlorobiphenyls would be present in this volume. This represents three times the U.S. use in 1970.

Nisbet and Sarofim (ref. 9) and the Panel on Hazardous Trace Substances (ref. 30) estimated that 1.5-2.5 x 10^3 tons per year of PCB had been discharged into the atmosphere from North America. A large fraction of this amount can be expected to consist of lower chlorinated PCB compounds such as the tri- and tetrachlorobiphenyls.

To eliminate the very significant problems of contamination during collection and extraction, and the difficulties of working with low volumes of seawater, we have worked towards the development of an in situ sampling system, such that all materials in contact with seawater that is sampled can be cleaned in the laboratory to a desired background level and wrapped in clean containers, to be unwrapped only immediately prior to use. The system would extract water at a desired depth and could be rewrapped immediately upon retrieval and stored under appropriate conditions until analysis.

Our own values obtained with this system have been substantially lower than those recorded by other investigators. Thus 23 extracts of seawater obtained off Western Mexico in 1975 contained no detectable chlorobiphenyls; volumes extracted were in the order of 100 liters. In 22 of these samples, concentrations of pentachlorobiphenyls were less than 100 parts per quadrillion (10^{-15} g/g); in 11 samples, concentrations were less than 50 x 10^{-15} g/g (ref. 13). We believe these values to be more consistent with the requirements of a global mass balance equation, yet intercalibration of all methodologies used to determine organochlorines in seawater is urgently required.

River Transport of Chlorobiphenyls to the Marine Environment

Nisbet and Sarofim (ref. 9) estimated that 4 to 5 x 10^3 tons/year of PCB were discharged into fresh and coastal waters in the peak year of PCB use. This estimate was based upon use figures and industrial end disposal practices in effect at that time. Of the total PCB, about 1,000 tons may be assumed to have consisted of pentachlorobiphenyls. Analysis of wastewaters and of surface runoff entering the Southern California Bight since 1971 has shown that trichlorobiphenyls have constituted the majority of the total PCB residues. In this area, PCB input into the sea from wastewaters is considerably higher than the input from surface runoff. Estimated total PCB input into the Bight from these sources in 1972 was 20 tons; in 1974 total input was estimated to be 6.5 tons (Young et al., op. cit.).

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Atmospheric Transport of PCB's to Marine Environments

Peel (ref. 31) was unable to detect PCB compounds in samples of Antarctic snow obtained in December 1969 inland from the British Antarctic Station at Halley Bay (75°31'S. 26°42'W.). The samples represented the previous 5 to 10 years' accumulation. Total concentrations of p,p'-DDT and p,p'-DDE ranged from 0.1 to 2.0 x 10^{-12} g/g. On this basis, the argument was advanced that on a global scale the atmosphere is not the predominant mode of transport of PCB. These results, therefore, appear inconsistant with those of Bidleman and Olney (ref. 12) and Harvey and Steinhauer (ref. 32), who were able to detect PCB in samples of marine air at concentrations considerably in excess of those of the DDT compounds.

In 1975 we extracted Antarctic snow in situ on Doumer Island in the Antarctic Peninsula (63°36.5'W. 64°51.3'S.); eggs of three species of antarctic penguins (*Pygoscelis adeliae, P. papua, P. antarctica*) were obtained to look for PCB in the food webs and to compare residues with those obtained 5 years previously (ref. 2). Eleven 99-liter samples of snow were extracted by techniques described elsewhere (R. W. Risebrough, W. Walker II, B. W. de Lappe, unpublished manuscript). PCB concentrations, as pentachlorobiphenyls, ranged from 30 to 1,200 x 10^{-15} g/g; median concentration was 300 x 10^{-15} g/g. The median total DDT:PCB ratio in these samples was 8.

Pentachlorobiphenyls were detected in all of 27 penguin eggs of the three species obtained in 1975. In addition, 15 eggs of the Adelie penguin obtained in Arthur Harbor on Anvers Island, near Palmer Station, on 26 December 1973 also contained pentachlorobiphenyls. The median DDE:PCB ratio was 3.0. Concentrations of p,p'-DDT were low compared to those of p,p'-DDE. Furthermore, reexamination of extracts of 14 Adelie penguin eggs obtained at the same site in Arthur Harbor in 1970 showed the presence of PCB compounds in all extracts. A variety of unknown compounds had previously interfered with the detection of pentachlorobiphenyls. These however, could be destroyed by rigorous saponification (R. W. Risebrough and T. T. Schmidt, unpublished data).

Total DDT:PCB ratios recorded in several of the subantarctic samples from the Auckland Islands ranged between 2 and 4 (ref. 33), comparable to those recorded in the Antarctic penguin eggs. Moreover, concentrations of DDE and PCB were equivalent north and south of the Convergence. Thus, fallout patterns of chlorinated hydrocarbons appear to be equivalent north and south of the Antarctic Convergence, which separates waters derived both from the melting of the Antarctic Icecap and from upwelling from waters of the southern Atlantic, Pacific, and Indian Oceans. Residues in the Antarctic have therefore derived from atmospheric transport rather than from oceanic circulation. The possibility that the residues of organochlorine pollutants in Antarctica have resulted from human activities at the scientific bases has been examined and discounted (ref. 34).

Changes in PCB Contamination Levels in the Marine Environment

PCB levels in mussels, *Mytilus*, at several sites in the Southern California Bight, have declined between 1971 and 1974 (B. W. de Lappe, R. W. Risebrough, P. Millikin, and D. R. Young, unpublished data). As discussed above, the reported decline of PCB values in the North Atlantic mixed layer (ref. 14) appears unlikely. The seabird data (refs. 35, 7, 27) do not indicate a decline in the North Atlantic between 1971 and 1973.

Most meetings, particularly international meetings discussing pollution problems of the marine environment, have recommended monitoring programs that would follow with time changes in the levels of particular pollutant classes. These recommendations have yet to be implemented; indeed, we might be reluctant to support such recommendations without assurance that the numbers obtained would be meaningful. A "Mussel Watch" (ref. 36) will shortly be underway in the United States which will examine mussels, principally *M. edulis* and *M. californianus*, from coastal sites for PCB and other chlorinated hydrocarbons, as well as for plutonium isotopes, petroleum compounds, and selected metals. Many variables, including salinity, temperature, particulate content of the water, gonadal condition, time of year, size of the organism, microhabitat, etc., can be expected to affect the variance of the determinations obtained in such monitoring programs. Nevertheless, the program does provide a beginning, which hopefully will determine how levels of chlorobiphenyls change in a marine environment in response to changes in production and use practices.

Summary

The deep ocean waters and sediments are a potential sink for chlorinated biphenyl compounds, removing them from food webs which provide input to man. Data on PCB levels in seawater are as yet unsatisfactory or too few to permit a reliable estimate of the amounts of PCB that have so far entered the oceans. Formulation of a global mass balance equation for the major kinds of PCB

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compounds would be useful in predicting future contamination levels.

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UPTAKE OF THREE POLYCHLORINATED BIPHENYLS, DDT AND DDE BY THE GREEN SUNFISH, *Lepomis Cyanellus* Raf

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Abstract

The ubiquitous occurrence of polychlorinated biphenyls (PCB's) in aquatic organisms demonstrates the extreme persistence of these materials and their resistance to being metabolized in fish to water-soluble products (refs. 1,2,3,4,5). The complex mixtures of chlorinated biphenyls in commercial PCB's makes quantitative research on the physiological effects of these compounds and their susceptibility to metabolism very difficult. However, the availability of three ^{14}C biphenyls—2,2',5-trichlorobiphenyl, 2,5,2',5'-tetrachlorobiphenyl, and 2,4,5,2',5'-pentachlorobiphenyl—provides a partial solution to this problem as these three pure isomers are major components of three important commercial PCB's, namely, 1242, 1248, and 1254 (ref. 6). Recently the fate of these pure chlorinated biphenyl isomers has been examined in a model ecosystem. The substantial accumulation of both the tetra- and pentachlorobiphenyl isomers by the mosquito fish, Gambusia affinis *Baird and Girard, 15.6 and 119.7 ppm (parts per million), respectively, clearly demonstrated the necessity for the examination of the uptake of these materials from water by fish (ref. 7). This communication reports the uptake of three pure ^{14}C PCB's, DDT, and DDE by the green sunfish,* Lepomis cyanellus *Raf.*

MATERIALS AND METHODS

The three pure (> 99 percent by tlc, thin-layer chromatography, and radioautography) chlorinated biphenyls were obtained from Mallinckrodt and had the following specific activities in mCi/mM: 2,2',5-trichlorobiphenyl 9.83; 2,2',5,5'-tetrachlorobiphenyl 9.78; and 2,4,5,2',5'-pentachlorobiphenyl 9.78. The ring-labeled ^{14}C DDT and DDE were available from previous work and had specific activities of 0.264 and 5.59 mCi/mM, respectively (ref. 8). Fifteen green sunfish weighing 50-150 mg were placed in 2 liters of aged tap water for a 24-hour acclimation period, then two concentrations, approximately 1 and 3 ppb, of the five compounds in acetone were added to the jars. Each concentration was run at 22 ° C in triplicate and the fish were fed *Daphnia magna* Straus twice a week during the experiment. The experimental design as described in table 1 is taken in part from the study on the uptake of DDT and methoxychlor by several species of fish (ref. 9). This type of experiment models the pulsed introduction of pesticides or industrial chemicals into the aquatic environment. Each point on the graphs represents the average of three fish and when the standard deviation for each point was divided by the average for each point, an average of 22 percent was obtained for all of the experiments.

Analysis of concentrations of the various compounds in the fish was accomplished by solubilizing the fish individually in scintillation vials with one ml Protosol® (New England Nuclear) at 60° C for 4 to 6 hours and then adding Aquasol® (New England Nuclear) for scintillation counting. This method assumes that all the radioactivity is parent compound, which, except for the trichlorobiphenyl which undergoes substantial metabolism, (see table 3) was an excellent assumption. At the end of the experiment the remaining fish were ground in acetone and the extracts were spotted on tlc plates (silica gel GF-254, Brinkmann, 0.25 mm) and developed in Skellysolve B for metabolite distribution by radioautography (Blue Brand X-ray film, Eastman Kodak) and liquid scintillation counting. The fluid used for counting contained PPO (7 g), POPOP (0.05 g), and napthalene (120 g) in 1 liter dioxane. Quenching for both the fish and tlc analysis was corrected using an external standard.

RESULTS AND DISCUSSION

Tables 1 and 2 show the experimental design of the uptake study and the amounts of ^{14}C compounds added to the environment of the fish. The data in table 3 describe the metabolite distribution of the compounds at the end of this uptake investigation. Table 4 contains data showing the bioconcentration of the three ^{14}C PCB's, DDT, and DDE. Figures 1 through 5 show the time-dependent uptake of the five compounds by *Lepomis cyanellus* Raf. Figure 6 shows the relationship for the three PCB's and DDE between the unextractable radioactivity in *Gambusia affinis* Baird and Girard in the

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Table 1. Timetable for experiment on uptake of three PCB's, DDT, and DDE by *Lepomis cyanellus* Raf

Day	Treatment
0	Add ^{14}C in acetone
2	Take out one fish, weigh and count ^{14}C
3	Take out one fish, weigh and count ^{14}C
9	Change water and add ^{14}C in acetone
10	Take one fish, weigh and count ^{14}C
13	Take one fish, weigh and count ^{14}C
16	Take one fish out, weigh and count ^{14}C, grind remaining fish up in acetone, spot acetone extracts on tlc for metabolite distribution

Table 2. Amounts of three PCB's, DDT, and DDE added to environment of *Lepomis cyanellus* Raf

	First	Second		First	Second
Trichlorobiphenyl	ppb	ppb	DDT	ppb	ppb
Low	0.94	2.80	Low	0.11	0.11
High	2.80	5.61	High	0.33	0.33
Tetrachlorobiphenyl			DDE		
Low	2.50	1.57	Low	1.13	2.25
High	7.50	5.00	High	3.40	6.75
Pentachlorobiphenyl					
Low	1.77	1.77			
High	5.31	5.31			

Table 3. Percent distribution of ^{14}C-labeled PCB's, DDT, and DDE at end of experiment in *Lepomis cyanellus* Raf

	Parent	Polar*
Trichlorobiphenyl	18.39	81.61
Tetrachlorobiphenyl	98.84	1.16
Pentachlorobiphenyl	99.41	0.69
DDE	99.00	1.00
DDT	97.23	2.27

*Rf = 0 Skellysolve B

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Table 4. Bioconcentration of ^{14}C-labeled PCB's, DDT, and DDE in *Lepomis cyanellus* Raf. after 15 days

Trichlorobiphenyl	54
Tetrachlorobiphenyl	460
Pentachlorobiphenyl	1,510
DDE	890
DDT	17,500

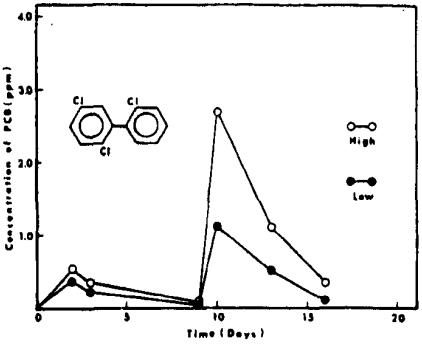


Figure 1. Time-dependent uptake of trichlorobiphency by *Lepomis cyanellus* Raf

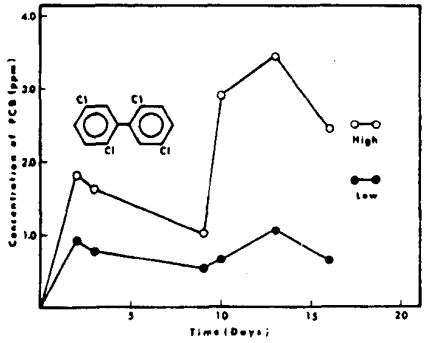


Figure 2. Time-dependent uptake of tetrachlorobiphenyl by *Lepomis cyanellus* Raf

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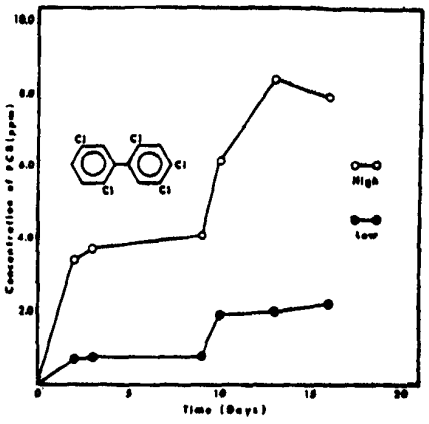


Figure 3. Time-dependent uptake of pentachlorobiphenyl by *Lepomis cyanellus* Raf

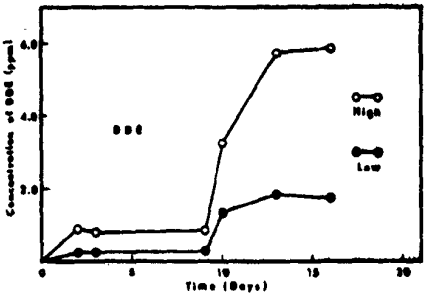


Figure 4. Time-dependent uptake of DDE by *Lepomis cyanellus* Raf

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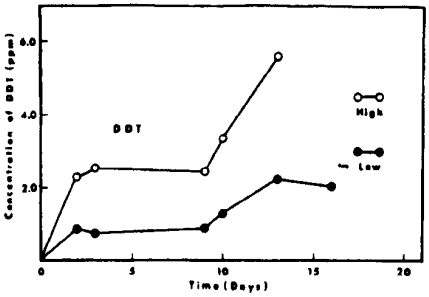


Figure 5. Time-dependent uptake of DDT by *Lepomis cyanellus* Raf

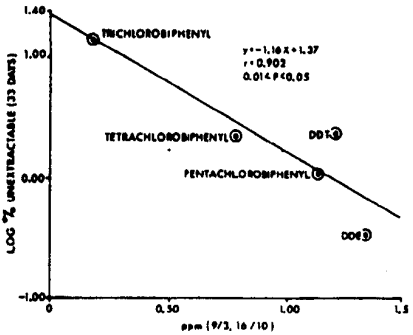


Figure 6. The relationship for the three PCB's and DDE between the unextractable radioactivity in Gambusia affinis Baird and Girard in the 33-day ecosystem and the average change in concentration of radioactivity from day 3 to day 9 and day 10 over day 16.

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33-day ecosystem (ref. 7) and the average change in concentration of radioactivity from day 3 to day 9 (ppm day 9/ppm day 3) and day 10 over day 16 (ppm day 16/ppm day 10). Each point on figure 6 on the abscissa is an average of four values.

It is quite clear from examination of figures 1 through 5 that three of the compounds—namely the pentachlorobiphenyl, DDT, and DDE—have similar uptake curves in that the fish retain the radiolabeled compound after it is added to the environment of the fish. The point for the last day for DDT is not shown, as the fish died before final value could be measured. The tetrachlorobiphenyl is retained somewhat less than pentachlorobiphenyl, DDT, and DDE, in that a few days after a peak concentration is reached after addition of labeled biphenyl the curve begins to drop. The trichlorobiphenyl differs dramatically from the preceding four compounds, in that after the peak concentration the curve drops off sharply.

This type of metabolic susceptibility for chlorinated biphenyls, namely that the lower chlorinated biphenyls undergo metabolism more readily than the higher chlorinated PCB's, has been shown for the complex commercial mixtures using rats (ref. 10) and Japanese quail (ref. 11). However, the literature appears to be lacking in metabolism studies on pure isomers of the PCB's except for some work on 4-chlorobiphenyl in the rabbit (refs. 12, 13). A comparative metabolism study with pigeons, rats, and trout and 4-chlorobiphenyl, 4,4'-dichlorobiphenyl, 2,5,2',5'-tetrachlorobiphenyl, and 2,4,5,2',4',5'-hexachlorobiphenyl has been reported (ref. 13). These authors found that the trout could not hydroxylate any of these compounds while the pigeon and rat were able to hydroxylate all but the hexachlorobiphenyl. Recently an elimination study with the rhesus monkey and two pure ^{14}C biphenyls—2,4'-dichlorobiphenyl and 2,5,2'-trichlorobiphenyl—has been reported but no metabolite structure or distribution was reported (ref. 14). The first hydroxylated metabolite from a higher chlorinated biphenyl has been reported in a study of the excretion products of 2,4,3',4'-tetrachlorobiphenyl in rats (ref. 15). These authors identified two hydroxylated species as the 2- and 5-hydroxy derivatives of the tetrachlorobiphenyl. Further, the 5-hydroxy biphenyl was determined to be about four times more toxic to the rat than the tetrachlorobiphenyl.

The data reported in this paper corroborate quite well the information already available, except for the trout, on the metabolism of PCB's by organisms. In the present work the data indicate rather convincingly that the green sunfish is able to transform the trichlorobiphenyl into polar species as only 18 percent (table 3) of the radioactivity in the fish was parent material at the end of the experiment. Perhaps species differences and temperature optimum of detoxifying enzymes account for the discrepancy between the relative abilities of the trout and green sunfish to metabolize chlorinated biphenyls. Further, previous investigations have shown that trout liver microsomes as compared to mouse liver microsomes are very inefficient at introducing a hydroxyl group into an aromatic nucleus such as biphenyl (ref. 16) and therefore the reported inability of trout to hydroxylate any chlorinated biphenyl is not surprising.

Finally, figure 6 clearly demonstrates an interesting relationship between the dynamics of uptake in the present study, that is, the change in concentration of the biphenyls in the fish after labeled compounds are added to the water of the fish, and the percent unextractable radioactivity in *Gambusia affinis* Baird and Girard in the 33-day model ecosystem experiment. This is a logical relationship, as it would be expected. The greater the metabolic susceptibility, the larger the amount of incorporation of ^{14}C radioactivity into unextractable polar compounds.

This study emphasizes the need for further research and information on uptake and metabolism of polychlorinated biphenyls by aquatic organisms. It has been established that 2,5,2'-trichlorobiphenyl is quite susceptible to metabolism by the green sunfish, and 2,5,2',5'-tetrachlorobiphenyl and 2,4,5,2',5'-pentachlorobiphenyl are much less susceptible. These latter two chlorinated biphenyls, especially the pentachloro isomer, resemble the relatively metabolic inert chlorinated hydrocarbons DDT and DDE. Much of the previous work, and this paper, deal with the qualitative assessment of metabolic susceptibility as a function of number of chloro substituents. This type of information is useful as it provides the background data for work that desperately needs to be done on the effect of chlorine isomer distribution on metabolic susceptibility, and, even more important, the further structural elucidation of the hydroxylated chlorinated biphenyls.

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LABORATORY MODEL ECOSYSTEM STUDIES OF THE DEGRADATION AND FATE OF RADIOLABELED TRI-, TETRA-, AND PENTACHLOROBIPHENYL COMPARED WITH DDE

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Abstract

Radiolabeled tri-, tetra-, and pentachlorobiphenyls (PCB) and DDE were studied in a laboratory model ecosystem for degradation pathways, and biomagnification in alga, snail, mosquito, and fish. Trichlorobiphenyl was degraded in all the organisms of the model ecosystem much more rapidly than tetrachlor- and pentachlorobiphenyl. Pentachlorobiphenyl was approximately as persistent as DDE. There was a linear relationship between lipid/water partition and ecological magnification and between water solubility and ecological magnification. No evidence of conversion of DDE to PCB was detected.

The laboratory model ecosystem previously described (ref. 1) has been employed for the estimation of the environmental fate of DDT and a number of its analogues (refs. 2,3,4) and for study of aldrin, dieldrin, endrin, mirex, lindane, and hexachlorobenzene (ref. 5). The methodology developed has yielded useful information about (1) the degradation pathways of the various xenobiotics, (2) the toxic effects of the compounds and their degradation products, (3) their comparative biomagnification and food chain concentration, and (4) their comparative biodegradability; all in organisms of five phyla linked in several food chains. This information has proved of value in characterizing the potential environmental pollutant effects of candidate insecticides (refs. 4,6) and of plasticizers (ref. 7). In this paper we report the application of these techniques to a better understanding of the comparative environmental properties of trichloro-, tetrachloro-, and pentachlorobiphenyl (PCB's), and of dichlorodiphenyl-dichloroethylene (DDE) the persistent DDT degradation product.

Methods and materials

The laboratory model ecosystem evaluation was carried out in a small glass aquarium with a sloping terrestrial-aquatic interface of pure white sand exactly as previously described (ref. 1). The ^{14}C-radiolabeled compounds were applied quantitatively from acetone solution at 5.0 mg (or ca. 1 kg per ha) to *Sorghum vulgare* seedlings grown in the terrestrial portion. The treated leaves were consumed by fourth instar salt marsh caterpillar larvae *Estigmene acrea*, whose activities and fecal products contaminated the aquatic portion of the system.

The radiolabeled products were transferred through several food chains, e.g., alga (*Oedogonium cardiacum*) → snail (*Physa*); plankton → water flea (*Daphnia magna*) → mosquito (*Culex pipiens quinquefasciatus*) → fish (*Gambusia affinis*). After 33 days in an environmental chamber at 26° C and a 12-hr photoperiod at 5,000 foot candles simulated daylight, the organisms were extracted with acetonitrile and the ^{14}C-radiolabeled compounds evaluated by TLC on silica gel containing fluorescent marker (E. Merck GF-254) and radioautography on no-screen X-ray film. Liquid scintillation counting of the individual components was done in cocktail D (5 g PPO and 100 g naphthalene in dioxane to make 1 liter) and counts were corrected to dpm by using channels ratio quenching correction. The residues, after extraction, were counted by total combustion to $^{14}CO_2$ by the Schoniger oxygen flask technique (ref. 8) to determine the unextractable radioactivity. Whenever possible, the identity of individual components on the TLC plates was determined by cochromatography with known standards and by extraction and mass spectrometry.

Radiolabeled Compounds. The individual ^{14}C-labeled PCB's were obtained from Mallinkrodt, St. Louis, Missouri. They were: 2, 5,2'-trichlorobiphenyl (2,5-dichlorophenyl-ring-UL-^{14}C), 9.91 mCi per mmole with >98 percent radiopurity and 41.5 percent Cl, and a principal constituent of Aroclor 1242 (ref. 9); 2,5,2',5'-tetrachlorobiphenyl (ring-UL-^{14}C), 9.87 mCi per mmole with >98 percent radiopurity and 48.7 percent Cl, and a principal constituent of Aroclor 1248 (ref.9); and 2,4,5,2',5'-pentachlorobiphenyl (2',5'-dichlorophenyl- ring-UL-^{14}C), 9.87 mCi per mmole with >98 percent radiopurity and 54.4 percent Cl, a principal constituent of Aroclor 1254 (ref. 9).

^{14}C-labeled 2,2-bis-(p-chlorophenyl)-1,1-dichloroethylene (DDE) was prepared from ^{14}C-ring-UL p,p'-DDT obtained from the Radiochemical Centre, Amersham, England, 5.48 mCi per mmole, by dehydrochlorinating with 1.0 M alcoholic KOH, and purifying on

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a silicic acid column with hexane elution to 99 percent radiopurity.

Results

PCB's. The movement of ^{14}C radioactivity from *Sorghum* plants into the water phase of the model ecosystem is shown in figure 1. All three chlorinated biphenyls reached a maximum concentration in water at about 7 days after treatment and the levels of contamination declined as the PCB's were taken up by the organisms of the system. The levels of the chlorinated biphenyls in the water phase (table 1) were in the ppb range, below the water solubility of the compounds as determined by radiotracer technique (table 2).

Radioautographs of the extracts from the components of the model system after TLC are shown in figure 2. The data in table 1 represent the quantitative distribution of the ^{14}C in the spots on the TLC plates. The results for the three PCB's are also expressed in table 2 in terms of ecological magnification (E.M.) (ppm in organism/ppm in water) and of biodegradability index (B.I.) (ppm polar degradation products/ppm nonpolar products). The E.M. values for the parent compounds increased substantially with the number of chlorine atoms, from trichlorobiphenyl (41.5 percent Cl) to tetrachlorobiphenyl (48.7 percent Cl) to pentachlorobiphenyl (54.4 percent Cl). Conversely, the B.I. values decreased with increasing degree of chlorine. This consistent and regular behavior gives added confidence that these parameters are ecologically significant (ref. 4) and must be a function of the number of C-H bonds available for hydroxylation by microsomal oxidations in the various organisms. The spots of low R_f value (0.02-0.06), figure 2, are presumably hydroxylated PCB compounds and the polar radioactivity (R_f 0.0) is thought to consist of conjugates of these compounds. Wellnofer et al. (ref. 10) have found 4-chloro-4'-hydroxybiphenyl as a metabolite of 4-chlorobiphenyl from soil fungus, *Rhizopus japonicus*. Yoshimura and Yammamoto (ref. 11) have reported the 5-hydroxylated derivative as the major and the 3-hydroxylated derivative as the minor excretion product of 2,4,3',4'-tetrachlorobiphenyl in the rat. Hutzinger et al. (ref. 12) have shown that rat and pigeon could hydroxylate 2,5,2',5'-tetrachlorobiphenyl but they could not detect hydroxylated metabolites in brook trout. However, the

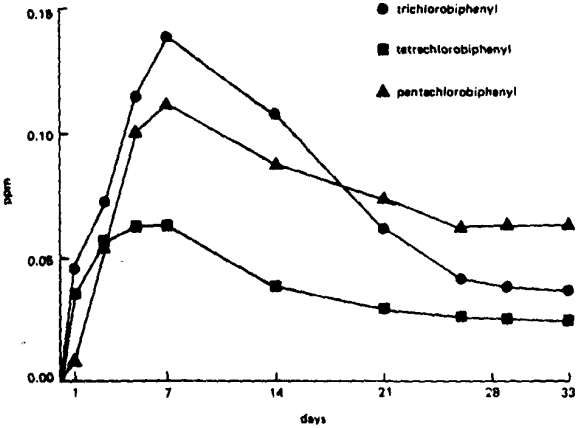


Figure 1. Movement of total ^{14}C radioactivity from plants into the water phase of the model ecosystem and uptake by organisms.

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Table 1. Distribution of chlorinated biphenyls and their degradation products in the model ecosystem

	Chlorinated biphenyl equivalents (ppm)				
	H_2O	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
I. 2,5,2′-trichloro-biphenyl total ^{14}C	0.03845	23.2155	31.2015	2.7030	3.2055
Unknown I (R_f 0.66[a])	0.00015	15.9575	18.9720	1.1995	0.2085
trichlorobiphenyl (R_f 0.56)	0.00020	1.4630	1.1590	0.1630	1.2800
Unknown II (R_f 0.23)	0.00005	0.0520	0.6480	+	0.1595
Unknown III (R_f 0.10)	–	–	0.9735	–	–
Unknown IV (R_f 0.06)	0.00055	–	0.5460	–	–
Unknown V (R_f 0.04)	0.00040	–	0.2205	–	–
Unknown VI (R_f 0.03)	0.00040	0.0685	0.4410	–	–
Polar (R_f 0.0)	0.02265	0.5185	3.9315	0.4795	0.9985
Unextractable	0.01405	5.1560	3.3100	0.8610	0.5590
II. 2,5,2′,5′-tetrachloro biphenyl total ^{14}C	0.02065	23.6845	53.7465	14.5335	15.5685
tetrachlorobiphenyl (R_f 0.[illegible])	0.00120	21.5975	47.3275	12.6745	14.2360
Unknown I (R_f 0.23)	0.00005	0.3220	0.7560	0.1070	0.0890
Unknown II (R_f 0.04)	0.00155	0.1030	0.4360	–	–
Polar (R_f 0.0)	0.01225	0.3275	3.9850	0.9670	0.8545
Unextractable	0.00560	1.3345	1.2420	0.7850	0.3900
III. 2,5,2′,4′,5′-penta-chlorobiphenyl total ^{14}C	0.04340	62.4660	633.0165	181.4565	127.6945
pentachloro-biphenyl (R_f 0.55[a])	0.00985	53.8440	587.3545	170.8480	119.7060
Unknown I (R_f 0.46)	–	0.6850	8.6210	2.4070	2.5380
Unknown II (R_f 0.39)	0.00020	0.5080	2.2490	1.3195	0.5810
Unknown III (R_f 0.21)	0.00015	0.1425	1.9365	1.0520	0.3285
Unknown IV (R_f 0.04)	0.00030	–	0.5000	–	–
Unknown V (R_f 0.02)	0.00385	0.2570	7.4965	–	0.7450
Polar (R_f 0.0)	0.02055	1.6265	16.5550	2.6745	2.3610
Unextractable	0.00850	5.4330	8.3040	3.1555	1.4350

[a]TLC with hexane (Skellysolve B, bp 60-68°C).

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Table 2. Ecological magnification (E.M.) and biodegradability index (B.I.) of PCB's and DDE compared with water solubility and partition coefficient

Chemical	H_2O solubility (ppb)	Partition coefficient	Ecological magnification (E.M.)				Biodegradability index (B.I.)			
			Alga	Snail	Mosquito	Fish	Alga	Snail	Mosquito	Fish
tri-Cl-PCB	16	7,803	7,315	5,795	815	6,400	0.30	0.17	0.35	0.60
tetra-Cl-PCB	16	8,126	17,997	39,439	10,562	11,863	0.015	0.082	0.076	0.060
penta-Cl-PCB	19	16,037	5,464	59,629	17,345	12,152	0.029	0.027	0.0134	0.019
DDE	1.3	18,893	11,251	36,342	59,390	12,037	0.069	0.049	0.033	0.050

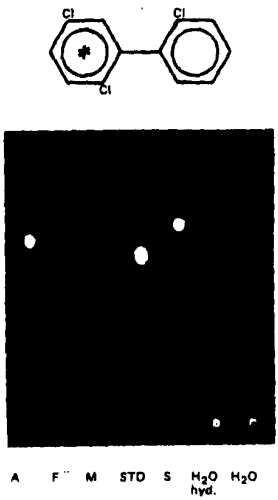


Figure 2A. Radioautogram of TLC plate containing extracts of water and organisms treated with 2,5,2'-trichlorobiphenyl. A (alga), F (fish), M (mosquito larva), S (snail) and STD (^{14}C-radiolabeled compound).

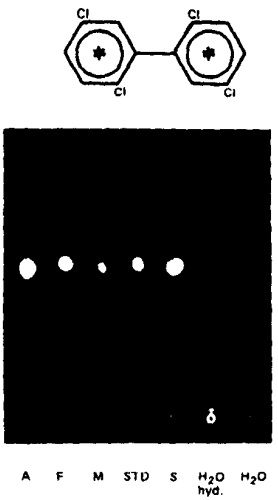
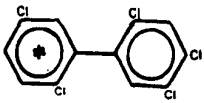


Figure 2B. Radioautogram of TLC plate containing extracts of water and organisms treated with 2,5,2',5'-tetrachlorobiphenyl. A (alga), F (fish), M (mosquito larva), S (snail) and STD (^{14}C-radiolabeled compound).

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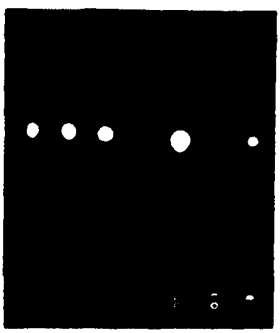
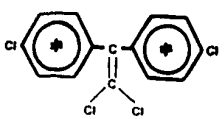


Figure 2C. Radioautogram of TLC plate containing extracts of water and organisms treated with 2,4,5,2',5'-pentachlorobiphenyl. A (alga), F (fish), M (mosquito larva), S (snail) and STD (^{14}C-radiolabeled compound).



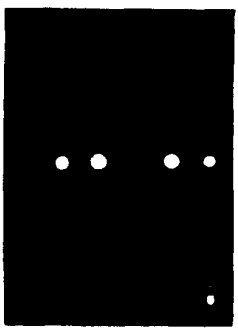


Figure 2D. Radioautogram of TLC plate containing extracts of water and organisms treated with DDE. A (alga), F (fish), M (mosquito larva), S (snail) and STD (^{14}C-radiolabeled compound).

amounts of polar material in *Gambusia* (figure 2, table 1) suggest that this fish is able to slowly hydroxylate this tetrachlorobiphenyl.

The pentachlorobiphenyl with B.I. values of 0.019 to 0.027 in fish and snail is very comparable in model ecosystem behavior to DDT, B.I. 0.015 and 0.044 (ref. 4) and this suggests that the two compounds should behave similarly in the environment (ref. 13). Properties of the tetrachlorobiphenyl were similar to those of the pentachlorobiphenyl (figure 2) but the trichlorobiphenyl was much more degradable. A prominent degradative product (R_f 0.66) is stored in alga, snail, and mosquito larva in much greater quantities than the parent compound. This compound is less polar (higher R_f) in the hexane solvent than any of the three PCB isomers. As shown in table 1, it is magnified to very high values, 106,382X in alga and 126,480X in snail, is stored in lipids, and is highly persistent. Its presence in high amounts in alga and in the snail and mosquito, which are alga feeders, suggests that it might be formed by photochemical processes during photosynthesis in the alga. This compound forms slowly and no traces of it were visible in 3-day uptake studies of trichlorobiphenyl by alga, snail, daphnia, mosquito, or fish (ref. 14) although it appeared in alga in 14-day studies. To date we have been unsuccessful in identifying the unknown by mass spectrometry.

DDE. This compound has been implicated as a possible environmental precursor of PCB isomers through photooxidation reactions involving radical rearrangements to 3,6-dichlorofluorenone intermediates (refs. 15,16,17). Although such rearrangements could logically produce 4,4'-dichlorobiphenyl, it is difficult to see how trichloro- and tetrachlorobiphenyls could be

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formed as suggested by Maugh (ref. 18). Moreover, Kamar et al. (ref. 19) could detect only bis-(p- chlorophenyl)-chloroethylene (DDMU) after ultraviolet irradiation of DDE. Because of the ecological importance of these possible rearrangements, we have reinvestigated the behavior of DDE in the model ecosystem (ref. 1) to determine if any PCB-like products could be formed under the simulated daylight of the model ecosystem (5,000 *foot candles) in an environmental chamber.* The radioautograph showing the fate of pure DDE is presented in figure 2. When the extracts of water and organisms were developed on TLC plates with Skellysolve B (hexane fraction) there was no trace of any ^{14}C-labeled compounds with R_f values between 0.05 and 0.47 (DDE) or of any less polar materials with higher R_f values. Under these conditions, as shown in figure 2, trichlorobiphenyl has R_f 0.43, tetrachlorobiphenyl R_f 0.50, and pentachlorobiphenyl R_f 0.53. Detection levels with the techniques used are approximately 0.1 ng (e.g., spot at alga origin in DDE, figure 2) or about 0.00002 percent of the total ^{14}C applied. Thus under the model ecosystem conditions, there is no evidence of formation of PCB isomers from DDE.

DDE is extremely stable in the tissues of the living organisms of the model ecosystem and is stored as approximately 92, 93, 95, and 97 percent of the total ^{14}C in snail, alga, fish, and mosquito larva. The percent of unextractable ^{14}C in these organisms ranged from 0.10 to 0.93 (table 3). The B.I. value for DDE in fish was 0.049 and the E.M. value 12,037 (compared with 0.032 and 27,358 found by Metcalf et al.) (ref. 1). From these values *it is apparent* that DDE is a more stable environmental pollutant than 2,4,5,2',5'-pentachlorobiphenyl (table 1), which was stored in the organisms at 86 to 94 percent of the total radioactivity, with from 1.12 to 8.67 percent of unextractable ^{14}C, and had a B.I. of 0.019 and an E.M. of 12,152 in fish.

It is of interest that Sodergren (ref. 20), using a model aquatic ecosystem, found no major metabolic changes in DDE occurring in passage through a food chain into fish, although similar experiments with a polychlorinated biphenyl mixture (Clophen A) showed that the lower fractions with low chlorine content were degraded when transported through the food chain, as was 2,5,2'-trichlorobiphenyl in our experiments. However, in our studies (figure 2, table 3), the water phase contained several polar radiolabeled degradation products. These were resolved on silica gel into at least 11 distinct compounds using a solvent of benzene:dioxane:acetic acid (90:30:1) and we are presently attempting to identify the pathway of DDE degradation in the environment.

Biomass Recovery. To determine the relative availability of the various organisms of the model ecosystem as reservoirs for the bioaccumulation of the micropol*lutants studied, the total amounts of* ^{14}C*-labeled products* recovered from the principal organisms of the model ecosystems treated with tri-, tetra-, and pentachloro-PCB's, and with DDE were evaluated, as shown in table 4. The evaluations were made on the basis of total recovery of the applied pollutant; of recovery of the maximum amount of pollutant in water (figure 1) for each of the four principal organisms, alga, snail, mosquito, and fish; and of biomass recovery (four organisms) of the total amount of pollutant lost from water (figure 1). The figures of table 4 are very revealing

Table 3. Distribution of DDE and degradation products in the model ecosystem

	DDE equivalents (ppm)				
	H_2O	*Oedogonium* (alga)	*Physa* (snail)	*Culex* (mosquito)	*Gambusia* (fish)
Total ^{14}C	0.00384	7.4720	38.1958	24.8588	7.8653
DDE (R_f 0.49*)	0.00062	6.9759	22.5325	36.8223	7.4632
Unknown I (R_f 0.05)	0.00009	–	0.8035	–	–
Polar (R_f 0.0)	0.00223	0.4881	1.1612	1.2448	0.3746
Unextractable	0.0009	0.0080	0.3616	0.1087	0.0275

*TLC with hexane (Skellysolve B, bp 60-68°C).

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Table 4. Biomass recovery of chlorinated biphenyls, and DDE from organisms of model ecosystem

% Recovery	Alga	Snail	Mosquito	Fish
		trichlorobiphenyl		
^{14}C in solution	0.18	0.015	0.0017	0.12
total ^{14}C	0.033	0.0028	0.00032	0.021
(biomass) of ^{14}C lost from solution ---	0.45			
		tetrachlorobiphenyl		
^{14}C in solution	3.33	1.04	0.23	1.91
total ^{14}C	0.28	0.088	0.019	0.16
(biomass) of ^{14}C lost from solution ---	8.7			
		pentachlorobiphenyl		
^{14}C in solution	4.57	19.0	2.32	11.8
total ^{14}C	0.74	3.06	0.37	1.90
(biomass) of ^{14}C lost from solution ---	57.2			
		DDE		
^{14}C in solution	22.4	4.03	2.25	20.2
total ^{14}C	0.24	0.044	0.055	0.22
(biomass) of ^{14}C lost from solution ---	65.8			

in terms of the biodegradability of the various compounds. The highest recoveries of the ^{14}C lost from solution were obtained from the organisms with DDE, 65.8 percent, and pentachlorobiphenyl, 57.2 percent. With tetrachlorobiphenyl, recoveries of 8.7 percent were still substantial, but with trichlorobiphenyl (recovery 0.45 percent), the compound was nearly completely degraded and excreted.

Degradation in Salt Marsh Caterpillar. This animal was chosen, after considerable study, as the dispersing agent for the model ecosystem because it was able to ingest a large variety of organic compounds without apparent injury (ref. 14). The effects of passage of the PCB isomers through the insect are of interest as representing the first stage in the biodegradation of these compounds. Figure 3 shows radioautographs of TLC plates of extracts of feces and body homogenates from larvae feeding on about 30 μg of ^{14}C PCB incorporated in a synthetic diet. Figure 3 and the quantitative evaluation of the radioactivity in the various spots shown in table 5 demonstrate conclusively the much greater degradability of the trichlorobiphenyl over the tetrachlorobiphenyl and pentachlorobiphenyl. With the trichloro compound, the caterpillar feces contained 91 percent of the recovered ^{14}C, with the remainder in the body homogenate, while with the tetrachloro- and pentachlorobiphenyls, the feces contained 21 percent and 24 percent of the radioactivity. The unknown (R_f 0.06) found in feces after trichlorobiphenyl is probably the principal hydroxylated degradation product leading to the very large amount of polar radioactivity. Whereas only low levels of trichlorobiphenyl were retained in the salt marsh caterpillar body, with tetrachloro- and pentachlorobiphenyl the major portion of ^{14}C was retained in the insect body.

DDE passed through the salt marsh caterpillar largely unchanged, with 81 percent of the total radioactivity recovered retained in the body homogenate and 19 percent in the fecal excreta (table 5).

Ecological Magnification. The uptake and concentration of organic compounds by living organisms either directly or through food chains appear to be a function of two important factors: (1) their high lipid solubility and low water solubility, e.g., a large lipid/water partition coefficient, and (2) their resistance to degradation by enzymatic processes, especially the multifunction

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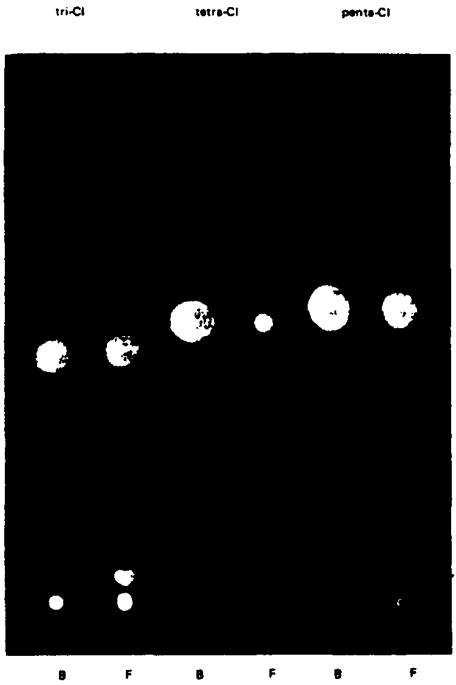


Figure 3. Radioautogram of TLC plate containing extracts of bodies and feces of salt marsh caterpillar larvae fed ^{14}C-labeled 2,5,2'-tri-, 2,5,2',5'-tetra-, and 2,4,5,2',5'-pentachlorobiphenyls. B (body homogenate), and F (fecal excreta).

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Table 5. Metabolism of ^{14}C-radiolabeled compounds by salt marsh caterpillar[a]

	Body	Feces
A. 2,5,2'-trichlorobiphenyl total ^{14}C (%)	8.66	91.34
Unknown I (R_f 0.53[a])	0.64	–
trichlorobiphenyl (R_f 0.43)	5.84	8.91
Unknown II (R_f 0.31)	0.27	0.37
Unknown III (R_f 0.13)	0.05	0.12
Unknown IV (R_f 0.05)	0.10	4.67
Unknown V (R_f 0.02)	0.11	0.92
Polar (R_f 0.0)	1.65	76.35
B. 2,5,2',5'-tetrachlorobiphenyl total ^{14}C (%)	78.68	21.32
tetrachlorobiphenyl (R_f 0.50[a])	75.60	15.08
Unknown I (R_f 0.41)	0.99	1.36
Unknown II (R_f 0.05)	0.13	–
Unknown III (R_f 0.03)	trace	0.20
Polar (R_f 0.0)	1.96	4.64
C. 2,5,2',4',5'-pentachlorobiphenyl total ^{14}C (%)	75.86	24.14
pentachlorobiphenyl (R_f 0.53[a])	74.00	20.70
Unknown I (R_f 0.46)	0.74	0.74
Unknown II (R_f 0.39)	0.62	0.56
Unknown III (R_f 0.03)	0.08	0.08
Polar (R_f 0.0)	0.42	2.06
D. 2,2-*bis*-(*p*-chlorophenyl)-1,1-dichloroethylene (DDE) total ^{14}C (%)	80.59	19.41
DDE (R_f 0.49[a])	76.88	19.37
Polar (R_f 0.0)	3.71	0.04

[a]TLC with hexane (Skellysolve B, bp 60-68°C).

oxidase enzymes (ref. 14). Hamelink et al. (ref. 21) have suggested that the water insolubility of highly lipid-soluble compounds provides the driving force in producing lipid storage, through a series of simple partitionings from water to lipids. We have correlated the E.M. values for the PCB's and DDE from the fish of the model ecosystems with both water solubility (table 2) in figure 4, and with the octanol/water partition value (table 2) in figure 5. Because the values for the PCB's and DDE fall closely together, the relationships have been extended using values for aniline, anisole, benzoic acid, chlorobenzene, and nitrobenzene taken from other model ecosystem studies (ref. 22). For the limited number of compounds included, the correlation between physical properties and biomagnification is excellent. The regression equation for log water solubility vs. log E.M. (figure 4) was:

$$y = 4.4806 - 0.4732X; \quad n = 9, \quad r = -0.9677.$$

The regression equation for log partition coefficient (Hansch's π) vs. log E.M. (figure 5) was:

$$y = -0.7504 + 1.1587X; \quad n = 9, \quad r = 0.9771.$$

Thus for the organic compounds studied, the properties of water solubility and octanol/water partition coefficient appear to provide a realistic estimate of the biological magnification found in living organisms.

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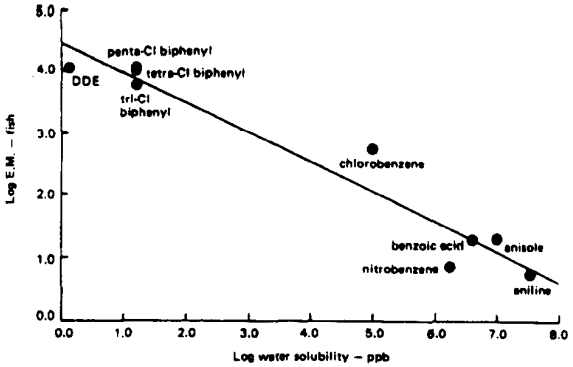


Figure 4. Plot of log E.M. (ecological magnification) for fish vs. log water solubility (ppb).

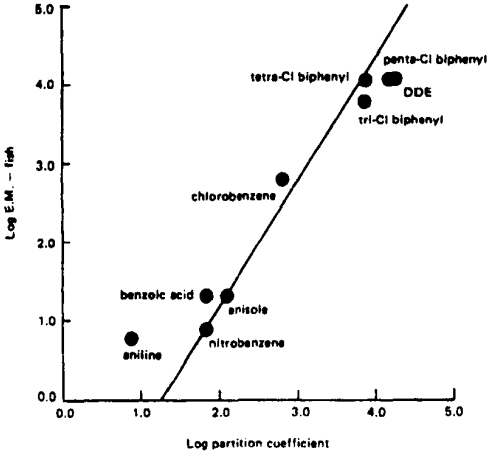


Figure 5. Plot of log E.M. (ecological magnification) for fish vs. log octanol/water partition coefficient.

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ENVIRONMENTAL TRANSPORT AND OCCURRENCE OF PCB's IN 1975

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Abstract

Despite curtailment of some dispersive uses, environmental levels and rates of transport of PCB's have not changed greatly since 1972. This is probably due in part to the continued release of materials in service prior to 1971 and in part to time lags in environmental transport and dissipation.

Surprisingly high concentrations of PCB's matching Aroclor 1254 are still being found in air, in precipitation, and in dry fallout.

As yet, there is little evidence that significant quantities of PCB's are being leached from dumps.

Human exposure to PCB's is highly variable. Some sport fishermen and breast-fed infants have especially high intakes.

Almost nothing is known about the environmental behavior of chlorinated dibenzofurans.

I think the organizers of the conference may have expected me to compose a global transport model while this session was going on. I have not attempted to do this, except to make some quick calculations on the back of an envelope.

My general conclusion from what I have heard today and yesterday about the release and concentrations of PCB's in the environment in 1975 is that most of what we have learned since 1972 is reasonably consistent with the very crude model that Serafim and I constructed in 1972. That is not to say that the model was right. All it says is that our ignorance about the exact rates and routes of transport of PCB's in the environment is nearly as profound in 1975 as it was in 1972.

I have found only one area where there does seem to be substantial quantitative discrepancy between our 1972 model and the data generated subsequently; that is, the numbers reported to us here and published in the interim,† on concentrations in air and air transport. We have heard some numbers of the order of 200 parts per trillion of PCB's in snowmelt, reports of numbers of the order of 100 nanograms per cubic meter for concentration of PCB's in air, and the number of the order of 70 – 200 and locally up to 2,000 nanograms per square meter per day for rates of dry deposition. These are all somewhat higher than we anticipated on the basis of our model.

If we extrapolate up on the back of an envelope basis from 200 nanograms per square meter per day over the whole continent, that comes out to be something of the order of 1,000 tons. Similarly, if you extrapolate up from 100 parts per trillion in rainfall over the entire continent, you get something of the order of 1,000 tons.

Now, it may be that the numbers we heard were biased toward urban areas, where the concentration of PCB's may be higher than they are in the United States as a whole. Even so, we are now being given numbers that suggest that at least 1,000 tons of PCB's per year are falling out onto the terrestrial environment of the United States in rain and particulate matter. That is about as large as numbers we had envisaged for total releases of PCB's into the air in 1971. What makes the problem worse is that nearly all the PCB's that are found in dry fallout, in the air, and in precipitation look like Aroclor 1254, whereas we had thought that only about half of the materials released into the environment even in 1971 would be Aroclor 1254, and a good deal of them would be Aroclor 1242.

So it seems to me that aerial releases and aerial transport are rather larger than anything we could account for according to our knowledge of the uses and releases that we surveyed in 1972. We need to find out where all this material in the air resembling Aroclor 1254 is actually coming from.

One possibility is that it may be coming from leaks from supposedly sealed uses. Perhaps we ought to be looking at transformers to see how much PCB's vaporize from them.

I would now like to go to the six questions which I posed at the beginning of this session and see what we have learned in the course of this conference toward solving these outstanding problems.

1. What happens to chlorinated dibenzofurans in the environment? I think the answer is that still we know almost nothing. We know they are being released into the environment, since they are present in small quantities in commercial PCB's. Dr. Kuratsune in his presentation yesterday indicated that they are actually formed in the environment during use, and Dr. McKinney's presentation suggested they might be formed by metabolism

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†Persson, B., *Ornis Scandinavica*, 2:127-138 (1971); Sodergren, A., *PCB-Conference II 1972*:15-18 (National Swedish Environment Protection Board, 1973); Bengtson, A. A. and A. Sodergren, *Ambio*, 3:84-86 (1974); Munson, T. O., Ch. 6 in *Upper Bay Survey* (Westinghouse Electric Corporation, Final Report to the Maryland Department of Natural Resources, in press).

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under certain circumstances. On the other hand, Dr. Risebrough's presentation suggested that they are not retained in the bodies of birds even when they are ingested; that conflicts with Dr. Kuratsune's information that they are retained extraordinarily efficiently in human tissue.

2. What happens to PCB's in dumps? Again, we know almost nothing. Some numbers were mentioned yesterday for water leaking out of dumps; I did some back-of-the-envelope calculations which suggested that the quantities of PCB's escaping are not yet very significant. One is talking about quantities of the order of hundreds of kilograms per year nationwide—certainly not more than a few tons.

3. Are PCB's in sediments going to be covered up or are they going to be continually recycled? There have been some hints in what has been said today that they are going to be recycled. The information from Ms. McDermott about PCB's in areas where there is shipping activity, and information from Dr. Munson about the movement of PCB's in suspended sediments around Chesapeake Bay suggests that these PCB's in shallow waters are not going to stay there and be covered up and disappear. They are going to be with us for a long time into the future.

4. Is it correct that tetrachloro-biphenyls and lower chlorinated species are rapidly degraded and is there significant human exposure to these lower species? I think that we have had very adequate evidence here that tetrachloro isomers are indeed degraded rather rapidly, but not as rapidly as we would like. Dr. Sanborn's presentation just now suggested that in fish the major difference in the efficiency of uptake, retention, and metabolism comes between trichlorobiphenyls and tetrachlorobiphenyls, and that fish do indeed retain tetrachlorobiphenyls fairly efficiently. That was supported by date from the National Fish Monitoring Program, which suggested that a substantial fraction of the PCB's in the fish look like Aroclor 1242 and 1248; that means that they include substantial quantities of tetrachlorobiphenyls. This in turn implies that humans are exposed to tetrachlorobiphenyls. Although the tetrachlorobiphenyls appear to be rare in human tissue, what that tells us is that humans do not retain tetrachlorobiphenyls. It does not tell us that they are not exposed to them.

This has some important implications from the regulatory point of view. We may have to consider, for example, whether Aroclor 1016 is environmentally "safe," in the sense that modest releases can be regarded as acceptable. These data indicate that releases of Aroclor 1016 into water will lead to human exposure, at least to tetrachlorobiphenyls.

5. What is the extent of human exposure? The date derive from two sides, monitoring of human tissue and monitoring of human food. Human tissue monitoring tells us that human exposure is very widespread. Human food monitoring tells us that most PCB's in human food are in fish.

Unfortunately, that makes it very difficult to estimate human exposure quantitatively, because we know from the fish monitoring program that the levels of PCB's in fish are extraordinarily variable in space. Despite the large number of samples that have been taken by the Canadian program and by the FDA, it is very difficult to define an average exposure. I would go so far as to say that an "average" exposure is a meaningless concept, because some individuals who live in areas where fish residues are high will get exposures 100 times greater than the average, whereas those persons who live in areas where there is little contamination, or who do not like fish, will get very little.

Nevertheless, we do have some numbers for human dietary exposure. The Total Diet Program in the United States gave a figure of the order of 9 micrograms per day for the intake of the average adult. I also did some calculations from Mr. Graham's figures on the Canadian commercial fish to see how many kilograms of PCB's were brought in in Canadian commercial fish and what fraction was eaten. That led me to a figure around 5 micrograms per day for the average intake of the average person in the Canadian population. We have to remember that the average adult does not eat much fish.

Unfortunately, these figures are quite misleading because it is very easy for an individual who is a sports fisherman and who catches salmon, or trout, or chub to take in very much more than that. One calculation in our 1972 paper indicated that it would be very easy for a fisherman or a member of his family to average 300 micrograms per day: this would represent about 4 micrograms per kilogram per day for an adult.

One important point is that exposure of breast-fed infants is likely to be very much greater than that of any adult, even an individual who likes fish. Although Dr. Kutz did not give numerical estimates of PCB levels in human milk in this session, earlier data suggest that a typical level would be around 30 parts per billion.* This leads to an estimate of 4–5 micrograms per kilogram per day intake for the average breast-fed infant. There would

*PCB levels reported in human milk have been in the range 10–100 ppb: Risebrough, R. W., and V. Brodine, *Environment* 12:16-27 (1969); Westöö, G., Norén, K., and M. Andersson, *Vår Föda*, 22:10-31 (1970); Acker, L., and E. Schulte, *Naturwissenschaften*, 57:497 (1970); Savage, E. P., Tessari, J. D., Malberg, J. W., Wheeler, H. W., and J. R. Bagby, *Pesticides Monitoring Journal*, 7:1-5 (1973). A concentration of about 30 ppb would correspond to the median level of about 1 ppm reported in human fat.

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be many above the average and many below.

Accordingly, when considering averages, we should remember that certain individuals are going to get 10 to 100 times the exposure of the average person, as calculated from an average diet.

6. The most complicated question posed in 1972: what would be the effect of Monsanto's curtailment of dispersive uses? A number of speakers yesterday and today have talked about decreases of PCB levels in certain areas or compartments of the environment. For example, there have been decreases in the total dietary intake estimated from the FDA Total Diet Program, in the frequency of findings of PCB's in milk and fish in the FDA's surveillance samples, and in runoff into the Southern California coastal waters. On the other hand, we have also heard about some levels that have not changed, particularly levels in fish in Lake Michigan.

There are three reasons why the curtailment of sales by Monsanto in 1971 should not have been expected to lead to an immediate reduction in environmental levels. One is that not all the closed system uses are actually closed. There are some losses that we heard about today, even from transformer and capacitor uses, which are systems as closed as we are likely to get. Secondly, and more important, there is still a large backlog of products containing PCB's, that were in service prior to 1971, which are still in service and are still being discarded and still leaching. Some of the users of hydraulic fluids, heat transfer fluids, compressors, and so on, are probably still using PCB's that they had several years ago. Certainly the scrapping of capacitors and any losses that may result from disposal of transformers are going to lead to releases for years into the future.

Finally, there is an environmental inertia: it takes a long time after the input into the environment is cut off for the levels in fish, for example, to go down. The time lags will depend on the part of the system under consideration; it is evidently quite short for mussels in Southern California, but is longer for the fish in the same area. Time lags have been quite short for the starlings, which reflect terrestrial uses, and for soil residues. The time lag is likely to be long for somewhere like Lake Michigan, which is a closed system, with a large reservoir of PCB's in the sediment. So I think we should not have hoped for a very rapid decline in PCB's since 1971.

On the other hand, it has been somewhat disappointing that it has been so difficult to find any change in the first 3 or 4 years.

One of the longest time lags of all is likely to be in human tissue, because there is evidence that PCB's are retained for an extremely long time in human tissue. We will probably have to wait for some considerable time after PCB levels have declined in fish before we see a significant decline in human tissue residues.

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GENERAL DISCUSSION OF SESSION III

DR. JOSEPH HIGHLAND (Environmental Defense Fund, Washington, D.C.): I want to ask Dr. Jelinek about the survey for fresh fish. Were there many differences in the last several years in the program which might lead to differences in the levels of the species. I was wondering if you could tell us a little bit more about that. I am not very clear on what differences you are talking about.

DR. CHARLES JELINEK (Food and Drug Administration, Washington, D.C.): First of all, one of the big differences is in the fact that all of our activities included compliance followups when we found any species or areas that had high levels. And we are going to dig in on that to find out just how much of a problem it is.

Obviously, from a statistical standpoint, that would throw things way out of whack. You are not getting representative sampling. That is one big difference, in the years where you have a higher proportion of that, you are apt to have a higher proportion of violative samples.

In our comprehensive fish survey program, which we carried out in 1973 and half of 1974, we included saltwater and freshwater fish. So again, you are probably going to have pretty low frequency of high findings, because we did pick up a lot of saltwater fish there. In our regular pesticide surveillance program, that is carried out more within the confines of the United States, although there are some coastal water fish that might be picked up, so that would sort of be in between these two activities. Where you try to combine all these together, it is just impossible to decide, at least with the data that we have, whether there have any changes.

DR. JAMES R. SANBORN (Illinois Natural History Survey, Urbana, Illinois): Our national monitoring program does look at three types of fishes, the predator, and one intervening. Locating the fish in each sampling does create a problem. So we get a cross section of the fish's species. We do notice that many species have a much higher fat content than others. And even if there is a variation within those species as to their body conditions, you would find a correct relationship in the amount of fat and the age of the fish. Consequently, when we look at those fish—lake trout can exist in those environments within a period of time and gather a rather substantial amount of adipose tissue. The goldfish, for example, is a very fat fish. You will find it loaded with PCB's and pesticides.

MR. DONALD TESLACK (EPA): I'd like to find out if there is any data—how does 99 percent average?

DR. JELINEK: I don't believe I have that figure here, and I would hate to speak from memory, sir. If you want to, you know, you can leave me your name and I can see—

DR. IAN C. NISBET (Massachusetts Audubon Society, Lincoln, Massachusetts): Speaking from memory, I believe it would be 95 percent.

DR. ROBERT GOLDEN (Environmental Protection Agency, Washington, D.C.): I understand that fishmeal is used to feed poultry extensively. Is there any information available possibly on secondary exposure to humans?

DR. JELINEK: Well, these levels that we are finding now in poultry, or rather USDA is the one who monitors poultry, are exceedingly low. In the one slide there, the 1 percent of poultry that the findings were on were down around 1 ppm or something like that.

Also, I would say this: our tolerance for PCB's in finished animal feed is two-tenths of a ppm, which is just above the limits of our analytical methods for accurate reproducible quantitative results of animal feed. So we set the tolerance there at almost what you would call the analytical nondetectable method for enforcement purposes.

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