Polychlorinated Biphenyls in Fish and Shellfish of the Chesapeake Bay

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ABSTRACT—Polychlorinated biphenyls (PCB's) are a class of persistent, highly stable, almost universally distributed toxic industrial chemicals with an affinity for fatty tissues of terrestrial and aquatic animals. Their use other than in closed-system electrical applications, such as transformers and capacitors, is banned in the United States. In 1976, a survey of approximately 300 samples of mollusks and finfishes from 100 stations in the Maryland portion of the Chesapeake Bay and its tributaries revealed no instances of PCB levels exceeding or approaching generally accepted safe levels.

Introduction

Polychlorinated biphenyls (PCB's) were first synthesized in 1881 and prepared commercially in 1930 when physical characteristics and potential industrial applications were described (Standen, 1964). Since then they have been universally employed and highly regarded for their wide spectrum of useful chemical and physical properties, including low vapor pressure at ambient temperatures, resistance to combustion, remarkable chemical stability, high dielectric constant, high specific electrical resistivity, low water solubility, and high lipid solubility.

PCB's are synthesized commercially by controlled chlorination of biphenyls with anhydrous Cl_2 in the presence of iron filings or $FeCl_3$ as a catalyst, yielding a mixture of PCB's and HCl. The PCB's are identified by a four digit numbering code, the first two digits representing the molecular type, while the last two digits give the weight percent of chlorine (Fig. 1). Thus Aroclor 1254 (Monsanto)[1], is a 1-2 chlorinated biphenyl containing 54 percent chlorine. The line of biphenyls available from Monsanto, for example, ranged from 21 to 68 percent chlorine. Two hundred nine possible chlorobiphenyl isomers exist (Mieure et al., 1976).

Highly chlorinated PCB's are white crystalline solids, while the lower chlorinated compounds are clear, viscous liquids, the viscosity increasing with increased chlorine content. Practically, PCB's seldom appear as pure compounds, but rather as mixed isomers. The characteristics of PCB's which make them particularly suitable for industrial use are their thermal and chemical stability. Ironically, it is exactly these properties, plus the fact that PCB's are readily absorbed and concentrated as they proceed up the trophic levels of the food web, which makes them so environmentally hazardous.

As universal contaminants, PCB's have essentially the same distribution pattern as DDT. The ubiquitous presence of PCB's is partly explained by the range and diversity of their utility, which has been so extensive that scarcely anyone can or has escaped their contact.

Since 1971, the employment of PCB's has been closely restricted and at present they are principally used in "closed-system" transformers and capacitors. But prior to 1971, approximately 40 percent of U.S. PCB production went into such "open" applications as plasticizers, hydraulic fluids, lubricants, sealants, and adhesives; as laminates in the fabrication of safety glass, ceramics, and metals; and as additives in paints, varnishes, putties, and

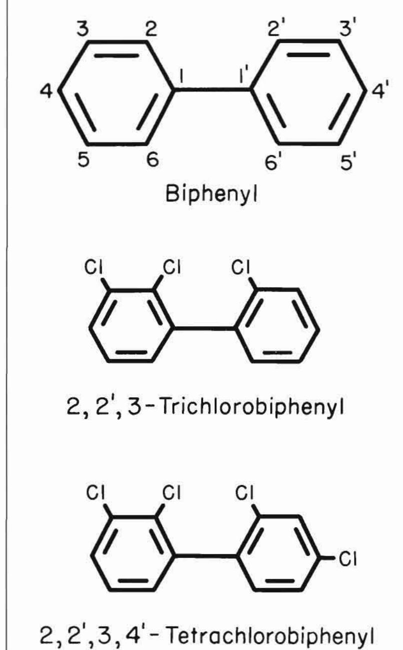

Figure 1.—Numbering system for biphenyl structure (from Mieure et al., 1976).

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[1]Reference to trade names or commercial firms does not imply endorsement by the National Marine Fisheries Service, NOAA.

caulking compounds. They were incorporated into washable wall coverings and upholstery materials, and were widely used for flame- and waterproofing canvas and synthetic yarns.

After serving such expendible uses, such PCB's became (and continue to become) "lost" into the environment whsre they infiltrate the biosphere and continue to resist degradation. Since PCB's were used extensively in printing inks and dye microencapsulation for carbonless duplicating papers, these persistent agents thereby still find a ready entry into recycled paper and paper products.

As chemical toxicants, PCB's are unique since, unlike most other persistent contaminants (i.e., pesticides), they were never consciously distributed into the environment.

Effects on Humans

The deleterious effects of PCB's on human health became evident in 1968 when a Japanese rice oil became massively contaminated with PCB leaking through a defective heat exchanger (Kuratsume, 1976). Over 1,000 clinical cases of the new disease called "kanemi yusho" (literally "oil disease") occurred with an estimated subclinical exposure of up to 15,000 subjects. In this episode involving Kanechlor 400, a Japanese manufactured PCB, the average clinical case ingested about 2,000 mg of PCB. It was estimated that the minimum dose for breeching the clinical horizon was 500 mg ingested over 50 days—approximately 200 μg/kg body weight per day (Higuchi, 1976; Kuratsume, 1976).

Four stages of the disease were identified: latent, visceral, manifest, and delayed. The latent stage was asymptomatic in the adult, but PCB entered the tissues and, in lactating mothers, was transferred to nursing infants via the milk. Dark pigmentation of the infants' nail beds and mucus membranes of the eyes were signs of latent contamination.

In the visceral stage, victims experienced nausea, vomiting, and weak to mild jaundice with coughing and bronchitis. The manifest stage was characterized by dermatological signs with dark pigmentation of skin and nails, runny eyes, hair loss, numbness of extremities, dizziness, and some long-range chronic effects.

In the delayed or tardy stage, the pathologic signs and symptoms remained latent for up to 3 years following the rice oil incident.

As awareness of the Japanese episode spread through the medical and scientific community, PCB's were identified as cosmopolitan contaminants in air, water, animal, and human tissues, where they show an affinity for and accumulate in fats.

PCB Control

During the intervening years, Federal and State legislation has increasingly restricted the use of PCB's with the objective being ultimate elimination. Their use in other than limited closed systems (capacitors and transformers) is presently banned and disposal of existing PCB stocks is closely regulated by Federal and State laws. PCB levels in terrestrial, aquatic, and marine ecosystems and their biota are being monitored routinely by State and Federal agencies.

Maryland's Department of Health and Mental Hygiene includes PCB analyses among an array of parameters assayed in finfish and shellfish from the Chesapeake Bay, the Nation's largest and most productive estuary. The State of New York has a comparable program for monitoring PCB's in the Hudson River watershed and estuary (Hetling et al., 1978).

Filter-feeding bivalve mollusks are efficient concentrators of most particulate and some dissolved pollutants and heavy metals and they are sometimes employed as indicator species. Monitoring shellfish serves both to determine their safety and wholesomeness as food and to evaluate the condition of their aquatic environment.

Materials and Methods

The Maryland Department of Health and Mental Hygiene continually monitors the edible fishes of the Chesapeake Bay and its tributaries for heavy metals, chlorinated hydrocarbons, and other physical and biological parameters (Fig. 2). During 1976 approximately 300 samples of finfish and shellfish collected from 100 stations in Maryland's portion of the Chesapeake Bay and its tributaries were analyzed for PCB's. Shellfish were collected by tongs or dredges while finfish were taken by trawls, gill nets, or hook-and-line. Occasionally, samples were obtained on station from commercial fishermen. Mollusks were sampled on a year-round basis, and finfish were sampled as they were seasonally available.

One hundred thirty-one samples of mollusks (principally American oyster, *Crassostrea virginica*) and 146 samples of finfish—principally bluefish, *Pomatomus saltatrix*; striped bass, *Morone saxatilis*; white perch, *Morone americana*; and weakfish, *Cynoscion regalis*—were included in the study. All samples were analyzed for pesticides and heavy metals. Several miscellaneous shellfish and finfish were also analyzed, including roe samples of gravid striped bass, white perch, and yellow perch, *Perca flavescens*, and the meat of three blue crabs, *Callinectes sapidus*.

For pesticide and PCB analyses, finfish were gutted and filleted and the fillets used for extraction. Mollusks were scrubbed clean, shucked and drained, and the shell liquor discarded. In both cases approximately 200 g of meat were homogenized. For finfish 50-g and for shellfish 100-g portions of homogenate were utilized. Analytical procedures were in accordance with the U.S. Food and Drug Administration (FDA) procedures (McMahon and Sawyer, 1977). Homogenates were extracted with acetonitril. The acetonitrile extracts were diluted with water, the residues transferred to petroleum ether, and the ether put through a Florisil column[2] to separate the residues from the other extracted substances. Hexane was used as the first eluant to separate the PCB's from most of the other chlorinated hydrocarbons. The eluate

[2]10 percent DC 200 on Chromosorb WHP, 80/100 mesh; column temperature 190°C.

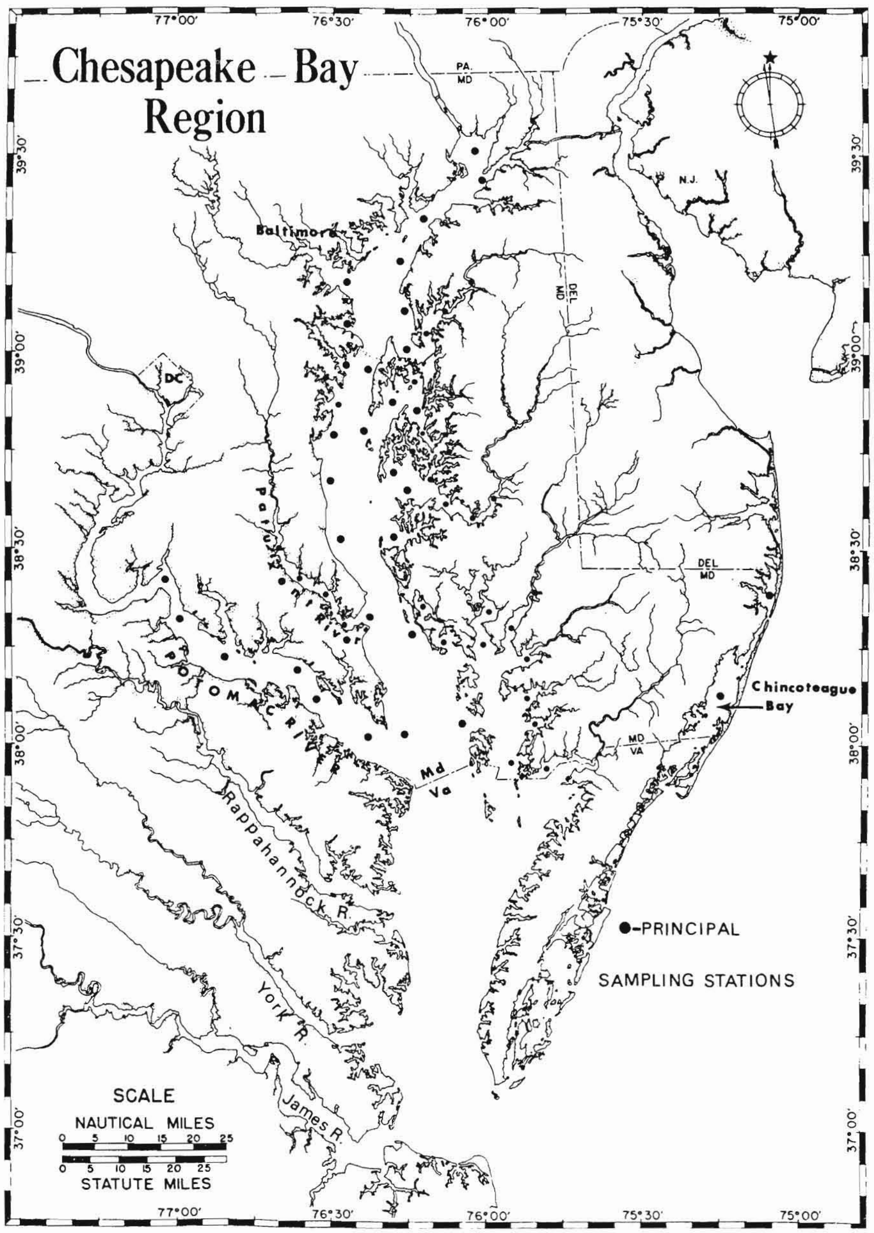

Figure 2.—Chesapeake Bay showing principal sampling stations.

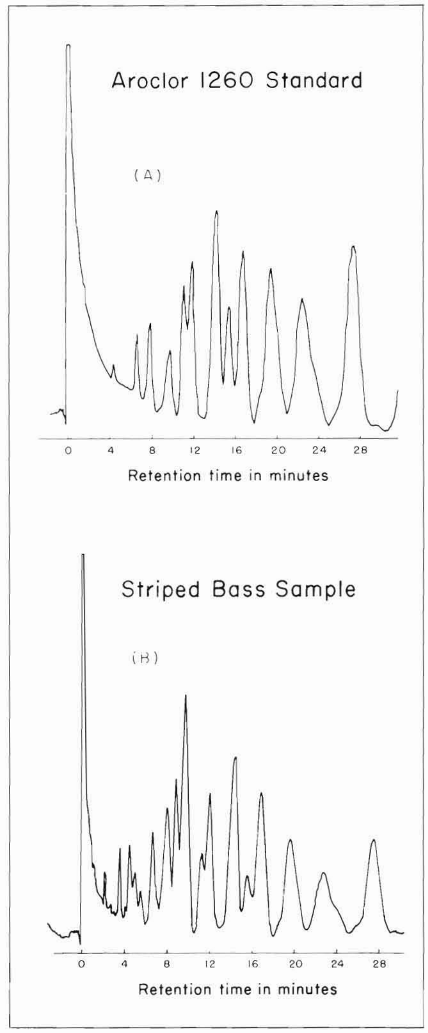

Figure 3.—Gas chromatograms of standard Aroclor 1260 (A), and of striped bass sample (B). Gas chromatography was performed on a Barber Coleman 5360 chromatograph with 10 percent DC on Chromosorb WHP (80/100 mesh) and electron capture detector (^{63}Ni). The injection temperature was 250°C and the column temperature was 230°C.

was concentrated and the residues identified and quantitated on Perkin Elmer Models 900 and 3920 and Barber Colman Model 5360 gas chromatographs equipped with ^{63}Ni detectors. Retention time of peaks in the standard were matched against peaks in the sample (Fig. 3) and concentrations were calculated from height of matching peaks.

Results

Finfish results for both PCB 1254 and 1260 are summarized in Table 1 and for shellfish in Table 2[3]. Combined results are listed in Table 3. In 80 finfish samples the level of PCB 1254 averaged 0.20 ppm while in 66 samples PCB 1260 showed an average concentration of 0.34 ppm. The weighted PCB's average for 146 samples tested was slightly less than 0.27 ppm, with a range of 0 to 0.98 ppm. Striped bass averaged 0.23 ppm, bluefish about 0.35

[3]Detection limits are valid to parts per billion (ppb).

Table 1.—Maryland PCB survey of finfish, 1976.

Species and PCB	Number of samples	PCB levels (ppm) Mean	Median	Range
Finfish (1254)				
Rockfish	44	0.23	0.18	0 to 0.58
Bluefish	2	0.32	0.32	0.31 to 0.33
Seatrout (weakfish)	12	0.05	0.05	0.02 to 0.13
White perch	13	0.21	0.24	0 to 0.42
Yellow perch	3	0.20	0.18	0.13 to 0.29
Pumpkinseed	1	0.35	0.35	
Mehaden	1	0.49	0.49	
Channel catfish	1	0.43	0.43	
Carp	1	0.12	0.12	
Spot	1	0.07	0.07	
Flounder	1	0	0	
(1254) Averages and range	80	0.20	0.16	0 to 0.58
Finfish (1260)				
Rockfish	4	0.24	0.25	0.22 to 0.26
Bluefish	62	0.35	0.32	0.04 to 0.98
(1260) Averages and range	66	0.34	0.31	0.04 to 0.98
(Both PCB's) Averages and range		0.27	0.23	0 to 0.98

Table 2.—Maryland PCB survey of shellfish, 1976.

Species and PCB	Number of samples	PCB levels (ppm) Mean	Median	Range
Shellfish (1254)				
Oysters	115	0.02	0.03	0 to 0.07
Hard Clams	3	0.02	0.02	0 to 0.03
Softshell clams	13	0.02	0.03	0 to 0.06
Averages and range	131	0.02	0.03	0 to 0.07
Shellfish (1260)				
Blue crabs	3	0.05	0.05	0.04 to 0.05

Table 3.—Maryland PCB survey of shellfish and finfish, 1976.

Species and PCB	Number of samples	PCB levels (ppm) Mean	Median	Range
Shellfish (1254)				
Oysters	115	0.02	0.03	0 to 0.07
Hard clams	3	0.02	0.02	0 to 0.03
Softshell clams	13	0.02	0.03	0 to 0.06
Shellfish (1260)				
Blue crabs	3	0.05	0.05	0.04 to 0.05
Shellfish (1254 & 1260) average & range	134	0.02	0.03	0.00 to 0.07
Finfish (1254)				
Rockfish	44	0.23	0.18	0 to 0.58
Bluefish	2	0.32	0.32	0.31 to 0.32
Seatrout (weakfish)	12	0.05	0.05	0.02 to 0.13
White perch	13	0.21	0.24	0 to 0.42
Yellow perch	3	0.20	0.18	0.13 to 0.29
Pumpkinseed	1	0.35	0.35	0.35
Mehaden	1	0.49	0.49	0.48
Channel catfish	1	0.43	0.43	0.43
Carp	1	0.07	0.07	0.07
Spot	1	0.07	0.07	0.07
Flounder	1	0.00	0.00	0.00
Finfish (1254) average & range	80	0.02	0.16	0.00 to 0.58
Finfish (1260)				
Rockfish	4	0.24	0.25	0.22 to 0.26
Bluefish	62	0.35	0.32	0.04 to 0.98
Finfish (1260) average & range	66	0.34	0.31	0.04 to 0.98
Finfish (1254 & 1260) average & range	146	0.26	0.26	0.00 to 0.98
Finfish roe (1260)				
Rockfish	1	2.20	2.20	
White perch	1	0.33	0.33	
Yellow perch	2	2.55	2.55	1.77 to 3.33
Finfish roe (1260) average & range	4	1.90	1.98	0.33 to 3.33

ppm, weakfish (sea trout) 0.50 ppm, and white perch 0.21 ppm.

Bivalve mollusks had almost negligible PCB burdens, showing a mean level of 0.02 ppm in 131 samples. Oysters, the most important food resource in the Chesapeake Bay, ranged from 0 to 0.07, with an average 0.02 ppm of PCB 1254. Softshell clams, *Mya arenaria*, showed mean and median levels identical to oysters. Three blue crab, *C. sapidus*, samples tested for PCB 1260 also gave low readings with mean and median levels of 0.05 ppm. With both finfish and shellfish, no area tested in Maryland waters showed marked PCB increases above the mean or median.

Four incidental samples of fish roe were included in the study. This was insufficient to constitute a representative sample, but possibly adequate to indicate a trend (Table 4). As expected, the gametes showed appreciably elevated PCB (1260) levels as compared with somatic tissues, averaging 1.9 ppm with a range of 0.33 to 3.33. White perch roe averaged 0.33 ppm while striped bass and yellow perch averaged 2.20 and 2.55 ppm, respectively.

Table 4.—PCB (1260) content of finfish roe.

Species	Number of samples	PCB levels (ppm) Mean	Median	Range
Rockfish (striped bass)	1	2.20	2.20	2.20
White perch	1	0.33	0.33	0.33
Yellow perch	2	2.55	2.55	1.77-3.33
Average and range	4	1.90	1.98	0.33-3.33

Discussion

The PCB values of finfish in our study averaged approximately 0.26 ppm, well below the present FDA limit of 5 ppm and an order of magnitude below the proposed 2 ppm standard. In 1976, Westinghouse Electric Corporation conducted a study of PCB's in the Chesapeake Bay for the Environmental Protection Agency (Munson et al., 1976). In 27 samples of striped bass from the Maryland portion of the Chesapeake Bay, the Westinghouse study showed an average PCB burden of 0.26 ppm, an almost identical value to our findings with approximately 140 samples of mixed species.

PCB levels in Chesapeake Bay fishes determined by the Annapolis Laboratory of the Environmental Protection Agency were also in general agreement with ours (Forns[4,5]). Conversely, findings by New York State's ongoing PCB monitoring program indicated levels in New York's freshwater and estuarine finfishes substantially higher

[4]Forns, J. M. 1975. Marine biology. *In* T. O. Munson, D. K. Fla, and C. Rutledge (editors), Upper bay survey, final report to the Maryland Department of Natural Resources, II, p. 1-35. Westinghouse Ocean Research Laboratory, Annapolis, Md.

[5]Forns, J. M. 1976. PCB concentrations in striped bass and eggs. Final report to EPA, No. WD6-99-0673B, 10 p. Westinghouse Ocean Research Laboratory, Annapolis, Md.

Table 5.—PCB levels in selected New York finfish, 1977.[1]

Location	Species	No. of samples	Average PCB levels (ppm)
Lake Ontario	Smallmouth bass	297	4.02
	Trout	20	5.30
	White perch	81	4.11
St. Lawrence River	Smallmouth bass	46	2.20
	White perch	14	5.00
Hudson River	Striped bass	116	13.85

[1]Derived from: New York State Department of Environmental Conservation, 1977. Monthly report on toxic substances impacting on fish. Division of Fish and Wildlife Report I, April 20, 1977, 14 p.

than some we have found (Hetling et al., 1978; Table 5). Munson et al. (1976) found that Virginia samples were generally higher than those from the Maryland portion of Chesapeake Bay.

The PCB in bivalve mollusks was predominantly compound 1254 and in the decapod crustacean blue crabs it was mainly formula 1260. In the finfish 1254 was also predominant, except for bluefish, where 1260 again prevailed (Tables 1-3). Munson et al. (1976) found PCB 1254 predominant in Maryland fishes while 1260 predominated in the Virginia portion of the Bay. However, regardless of geographic origin, the predominant PCB in finfish roe was 1260, again in accordance with our findings (Table 4).

The current FDA tolerance or "action level" for PCB's in foodfish is 5 ppm. Barring drastic, unanticipated increases in concentrations, PCB's in edible fishes from the Chesapeake Bay should remain far below existing or proposed maximum permissible levels. Preliminary findings from our 1978 Chesapeake Bay Survey show no significant variations for the results reported here.

Acknowledgments

The authors are grateful to personnel in the Environmental Health Administration and the Laboratories Administration of the Maryland Department of Health and Mental Hygiene for sample collection and analysis. We thank Hardy J. Chou of the Laboratories Administration for editorial review.

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