Bull. Environm. Contam. Toxicol. 22,413-419 (1979)

Polychlorinated Biphenyls in Baltimore Harbor Sediments[1]

Raymond P. Morgan II[2,4] and Sheldon E. Sommer[3]
[2]Chesapeake Biological Laboratory, University of Maryland Center for Environmental and Estuarine Studies, Solomons, Md. 20688 and [3]Departments of Chemistry and Geology, University of Maryland, College Park, Md. 20742

Polychlorinated biphenyls (PCBs) are toxic aromatic organochloride compounds used in industry primarily in the manufacture of electrical products. The physical and chemical properties (low vapor pressure, low water solubility, inertness, stability at high temperatures, resistance to acids, bases and microbial activity, and fat solubility) making PCBs attractive to industrial use are also properties making PCBs persistent contaminants in the environment.

After JENSEN's (1966) initial confirmation of PCBs in wildlife, more reports of PCB contamination followed as reviewed in WALSH (1972), REYNOLDS (1971), DUSTMAN et al. (1971), and WALKER (1976). Generally, these reports continued to cover fish and raptors although some attention was beginning to center on other species, on soil, and on sediment.

After observing high levels of PCBs in many animals, concern was expressed over the possible toxicity of PCBs especially after MCLAUGHLIN et al. (1963) reported that Aroclor 1242 was toxic and teratogenic. Some of these early studies are reviewed in WALSH (1972), REYNOLDS (1971), and WALKER (1976) concerning toxicity and mode of action for PCBs.

WALKER (1976) points out that high concentrations of PCBs occur concomitently with heavy industrial activity. In this study, an analysis is made of sediments from Baltimore Harbor for the presence of two PCBs-Aroclor 1248 and Aroclor 1260.

METHODS

A total of 20 stations (Fig. 1) within Baltimore Harbor were sampled by piston corer equipped with a 4.6 m polycarbonate liner. Two cores were taken per station. Completion of coring took 6 days during 9 June to 15 June 1976.

---

[1] Contribution No. 843 from Chesapeake Biological Laboratory, University of Maryland Center for Environmental and Estuarine Studies, Solomons, Maryland 20688. This work was supported by the U.S. Environmental Protection Agency, Contract No. 68-01-1965.

[4] Present Address: William F. Clapp Laboratories, Inc. Battelle Columbus Laboratories, Duxbury, Massachusetts 02332

0007-4861/79/0022-0413 $01.40

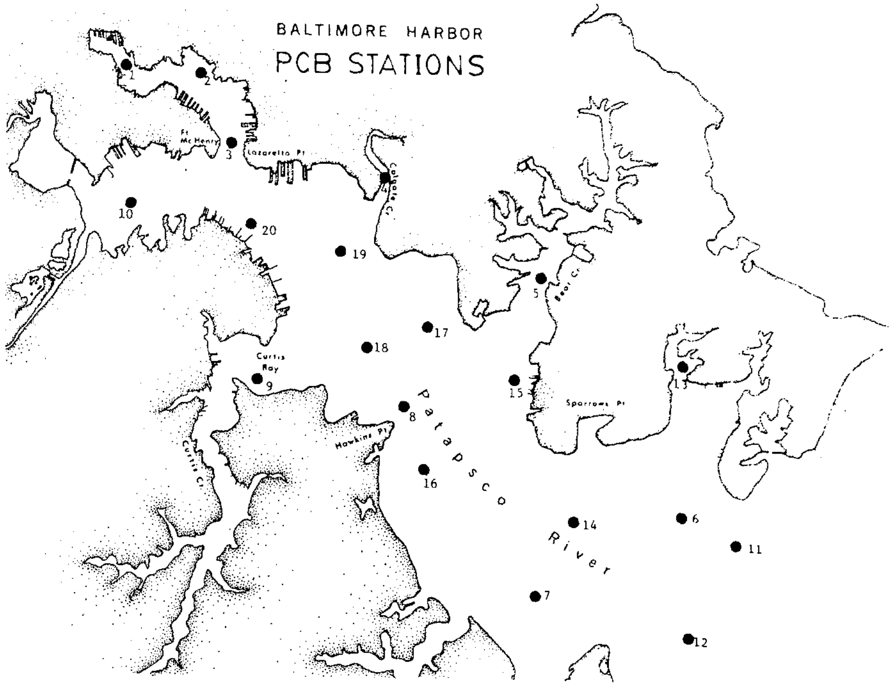

Fig. 1
Sampling (Coring) Stations for PCB
Analyses within Baltimore Harbor

Samples for PCB analyses were taken from the cores at four depths - 5 cm, 15 cm, 30 cm, and 61 cm. Core material was removed with wooden applicator sticks and immediately transferred to clean glass vials. Vials were sealed by first capping with aluminum foil (acetone-washed) and then capping with plastic lids.

All samples were shipped to Analytical Bio Chemistry Laboratories, Inc., Columbia, MO for PCB analyses. A weighed portion of the air-dried sample was adjusted to approximately 20% moisture. Each sample was extracted with methanol/chloroform (1:1) by blending in a Sorval Omni mixer. Following filtration, the extract was diluted with water and the PCBs partitioned into the chloroform. A series of repeated extractions and backwashings removed the methanol from the chloroform phase. The chloroform was evaporated and the residue subjected to Florisil column chromatography (20 g, 22 mm i.d.) in which the PCBs were eluted with 200 ml of hexane. The eluant was evaporated and transferred to a final volume of 5 ml. Microliter injections into a gas-liquid chromatograph equipped with Ni_{63} electron capture detectors were used for identification and quantification.

The GLC-EC parameters were: injector temperature - 255 C; column -1.83 cm x 4 mm, 2% OV-210, 1.5% OV-17 on Chrom W 100/120, temperature 205 C; and detector temperature - 300 C. Calculations were based on the middle five peaks of Aroclor 1248 and the last nine peaks of Aroclor 1260 and reported as ppm (w/w) air-dried basis. A peak ratio judgement was made to determine the species or peaks to be considered for identification and quantification.

A total of 80 samples were analyzed for Aroclor 1260 and 76 for Aroclor 1248. A 5 cm sample was not run for station 7 (Fig. 1). Duplicates were run on station 8 - 5 cm depth. Statistical procedures were from SOKAL AND ROHLF (1969). Computer analyses were run on a CDC computer using SPSS programs (NIE et al., 1975).

RESULTS

PCB concentrations by depth for the 20 stations (Fig. 1) sampled are presented in Table 1. High concentrations, greater than 1.0 ppm total PCBs at any one depth, are present at stations 1, 2, 3, 4, 5, 10, 15, and 18. Gross contamination of the upper sediments occurs at station 1 where PCB concentrations approach 84.2 ppm and remain high throughout the sediment column. Generally, stations 1, 2, 3, 4, 5, and 15 contain extremely high PCB levels, especially in the top 30 cm of the core.

Stations 8, 9, 13, 17, 19, and 20 are classified as being intermediately contaminated since their PCB concentrations at any one depth are less than 1.0 ppm and greater than 0.30 ppm total PCBs. The lower criteria of 0.30 ppm is based on the results from MUNSON et al. (1972) for average PCB concentrations in relatively clean Chesapeake Bay sediments. Station 20 did not have detectable PCBs in the upper 5 cm of the sediment column, but intermediate concentrations of PCBs are present below 15 cm. There is a possibility that recent scouring and dredging or a discontinuation of PCB input may have occurred at this station. Generally, there is a decrease in PCB concentration with sediment depth. Besides station 20, stations 9, 14, and 19 did not follow the pattern of lower PCB concentrations with depth. For four stations (4, 7, 11, and 12) no apparent pattern (within statistical limits) for PCBs exist. Twelve of the remaining stations, within statistical range, show decreasing PCB levels with sediment depth.

TABLE 1
PCB Concentrations (ppm w/w) for Baltimore Harbor Stations

Level	No. of Stations	Depth(cm)	$\bar{x}$	SD	Range
High[1]	8	5	2.29	1.50	84.2-1.12[2]
		15	1.59	0.81	2.70-0.45
		30	0.74	0.49	1.65-0.29
		61	0.84	1.05	3.11-0.05
		All	1.48	1.31	84.2-0.05
Intermediate[1]	6	5	0.40	0.28	0.78-0.05
		15	0.44	0.27	0.76-0.12
		30	0.37	0.33	0.96-0.06
		61	0.21	0.18	0.53-0.05
		All	0.36	0.27	0.96-0.05

TABLE 1
(continued)

Level	No. of Stations	Depth(cm)	$\bar{x}$	SD	Range
Low[1]	6	5	0.13	0.07	0.21-0.05
		15	0.07	0.03	0.13-0.05
		30	0.05	0.00	
		61	0.09	0.07	0.19-0.05
		All	0.09	0.00	0.21-0.05

[1] High levels were defined as any PCB concentration at any sediment depth exceeding 1.0 ppm, intermediate as exceeding 0.30 ppm but not 1.0 ppm, and low as being below 0.30 ppm. A level of 0.05 ppm PCB was defined as a background concentration, although many of the values were calculated as being less than 0.05 ppm PCB.

[2] The high value of 84.2 was not used in calculating mean; Aroclor 1260 was masking 1248 values so that total values may be higher for the sample set at station 1.

There is a significant (at $p<0.001$, $r = 0.749$) correlation between Aroclor 1248 and 1260 values in the sediments. This relationship is expressed by the equation $Y = 0.183 + 0.692X$ where Y is Aroclor 1260 in ppm and X is Aroclor 1248 in ppm; the ratio of Aroclor 1248 to 1260 in Baltimore Harbor sediments is 0.86:1.

Three significant outliers (deleted from correlation analysis as are values of 0.05 ppm and lower PCBs) occur. At station 3 - 5 cm depth, the level of 1260 is over three times greater than the 1248 value. At station 15 for the 15 cm depth, the 1248 concentration is almost 2.5 times greater than the 1260 concentration. At station 10, the 1248 value is almost 2.5 times greater than the 1260 value at the 5 cm depth. These variations in the ratio of PCBs to each other may be a result of industrial usage patterns in the immediate area.

For all 20 stations, the correlation of PCB levels (Table 2) with depth indicate significant correlations of PCB levels for all depths except for the non-significant value (Table 2) of sediment depth 5 cm with sediment depth 30 cm. Inspection of Table 1 for this depth at all stations reveals a great deal of variation in PCB levels. The variation at the 30 cm profile may be due to weathering, sediment - PCB interaction, or variation in PCB usage throughout Baltimore Harbor in the recent past.

TABLE 2
Correlation of PCB Levels Among Sediment Depths

	Depth			
Depth	5 cm	15 cm	30 cm	61 cm
5 cm	1.00			
15 cm	0.80**	1.00		

TABLE 2
(continued)

	Depth			
Depth	5 cm	15 cm	30 cm	61 cm
30 cm	0.29	0.62**	1.00	
61 cm	0.96**	0.86**	0.51*	1.00

*Significant at $p \leq 0.05$, **Significant at $p \leq 0.01$

Factor analysis (Fig. 2) for total PCB concentration by station at all four depths indicates four significant clusters. Cluster A includes those stations (Fig. 1) with heavy to moderate PCB contamination throughout the sediment column, but with decreasing concentrations of total PCBs with depth. Cluster B contains two stations with essentially no PCB contamination. Cluster C contains three stations where fairly low values of PCBs occur, but for a sediment profile, the values may be high. Stations 4 and 20 are similar in 5 cm values of PCBs being low, but higher values of PCBs are present at the 15 cm level followed by a decrease in PCB concentrations at the 30 and 61 cm levels. Station 19 is not related to any cluster since the 5 cm PCB value is intermediate, followed by increased PCB levels at 15 cm, decreased levels at 30 cm and highest concentrations at 61 cm.

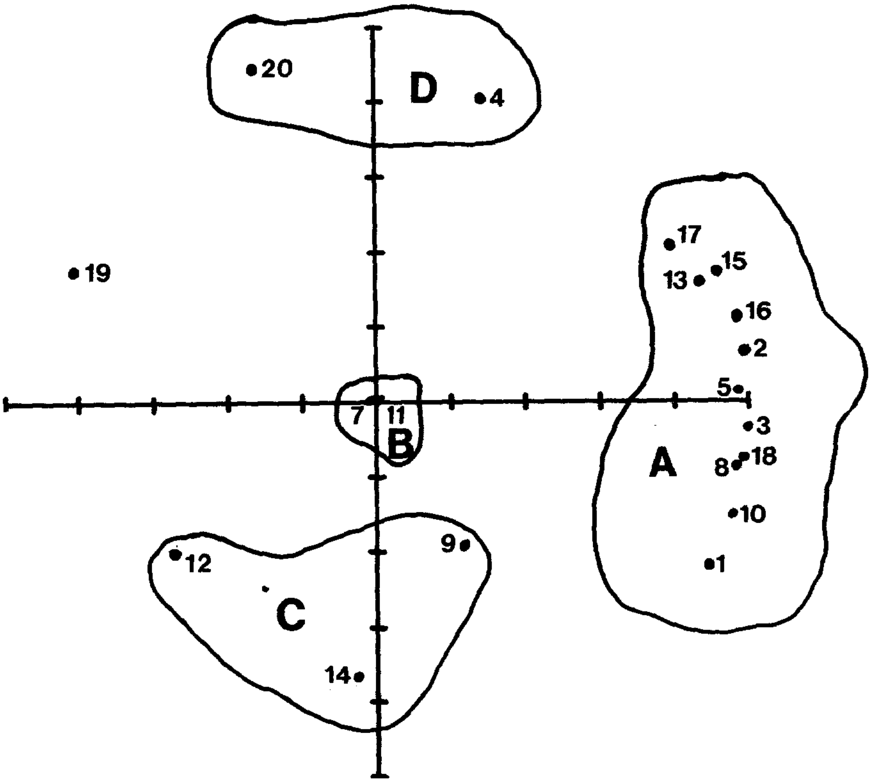

Fig. 2
Factor Analysis for Baltimore Harbor Stations

DISCUSSION

Sediment concentrations of PCBs except for special cases at station 20 (low level) and stations 15 and 18 (high levels) tend to be elevated from station 19 to station 1 - the inner seven kilometers from approximately Colgate Creek through the Northwest Branch. From station 9 (Curtis Bay) to station 6 (Old Road Bay), PCB concentrations are greater than 0.05 ppm, but less than 1.00 ppm of total PCBs. Outside of the entrance to the harbor, PCB concentrations drop to levels below 0.05 ppm. Two factors may account for the accumulation of increased levels of PCBs in Baltimore Harbor. Obviously, PCBs have been released into the water in the past. First there is the possibility of present releases still being made into the harbor with PCBs being entrapped into the sediment column. Second, current patterns in Baltimore Harbor may tend to contain pollutants within the harbor confines. A unique three-layered circulation system (PRITCHARD 1968) in Baltimore Harbor may minimize transport of material out of the area.

The predominance of Aroclor 1260 over 1248 is also of interest. Either more 1260 is in use in Baltimore Harbor or some of the 1248 is being slowly lost since the lower Aroclors are highly biodegradable (WALKER 1976). WALKER (1976) points out that for systems where a variety of Aroclors are present, it is more important to measure PCBs as a sum of the chlorohomologs (mono, di, etc.) rather than as 1242, 1248, 1260, etc.

Of 80 possible station-depth combinations, 19 have PCB concentrations greater than 1.00 ppm, 22 have concentrations greater than 0.30 ppm but less than 0.99 ppm total PCBs, and 39 have concentrations less than 0.30 ppm total PCBs. DENNIS (1976) summarizes PCB levels in sediments from the North Atlantic and South Atlantic drainage basins; he finds for 99 samples (North Atlantic) a median value of 31.0 ppb with a range of 2.8-800.0 ppb and for 171 samples (South Atlantic) a median value of 11.0 ppb with a range of 2.0-430.0 ppb. Obviously, the majority of samples from Baltimore Harbor are considerably higher than the values reported by DENNIS (1976).

Sediments appear to be a pool for PCBs in estuarine and marine systems (DUCE et al. 1974) with concentrations of sediment PCBs inversely proportionate to water depth. HARVEY (unpublished data, DUCE et al., 1974) found PCB concentrations ranging from 400 ng/g sediment (ppb) in inshore Massachusetts to 0.3 ng/g sediment in the Hatteras Plain. For San Francisco Harbor, PCBs range from 0.026 to 0.833 ppm (PACIFIC NORTHWEST LABORATORIES 1974). DUKE et al. (1970), investigating an industrial spill of Aroclor 1254, found sediment containing up to 486 ppm of PCBs.

PCB contamination tends to be associated with industrialization or with accidents. WALKER (1976) points out that PCB residues in fish are high in heavily industrialized riverine systems. KOO (1975) points out that over 170 potential sources of industrial wastewaters are present in Baltimore Harbor with two major sewage treatment plants (a possible source of PCBs since chlorination is a standard operating procedure) discharging 76,000 m^3/day of treated sewage into Baltimore Harbor.

The input of PCBs into estuarine waters is the result of a variety of processes (WALSH 1972) (1) agricultural runoff, (2) industrial/municipal discharge, (3) drift and rainfall and (4) accidental/careless discharge. Although PCBs are relatively insoluble in water, they may be made soluble by humic acids as occurs with pesticides (WERSHAW et al. 1969). PCB transport may come not only from water movement, but also from the involved process of sediment flocculation and resuspension - a phenomena in the estuarine system. In addition, differential solubilities of PCBs may result in precipitation (WALSH 1972). No matter what the level of PCB input may be to a system, the possibility exists that biomagnification and bioaccumulation could occur to an extent which could be damaging to a population or to the entire aquatic community.

ACKNOWLEDGEMENTS

We appreciate the assistance of Dr. L.E. Cronin and R.H. Wagner. Ron Copp assisted in statistical analysis.

REFERENCES

DENNIS, D.S.: National Conference on Polychlorinated Biphenyls. p. 183 (1976)

DUCE, R.A., P.L. PARKER and C.S. GIAM: Pollutant Transfer to the Marine Environment. NSF/IDOE Pollutant Transfer Workshop, Port Aransas, Texas. (Published in Rhode Island) 55 pp (1974)

DUKE, T.W., J.I. LOWE and A.J. WILSON, JR.: Bull. Environ. Contam. Toxicol. 5, 171 (1970)

DUSTMAN, E.H., L.F. STICKEL,L.J. BLUS, W.L. REICHEL and S.N. WIEMEYER: Trans. 36th N.A. Wildl. Natur. Res. p 118 (1971)

JENSEN, S.: New Scientist 32, 612 (1966)

KOO, T.S.Y.: In: A Biological Study of Baltimore Harbor. CEES Spec. Rep. No. 6. Solomons, Md. (1975)

MCLAUGHLIN, J., J.P. MARLIAC, M.J. VERRETT, M.K. MUTCHLER and O.G. FITZHUGH: Toxicol. Appl. Pharmacol. 5, 760 (1963)

MUNSON, T.O.: In: Chester River Study, Volume II. (Ed. by W.D. CLARKE, H.P. PALMER and L.C. MURDOCK). Westinghouse Electric Co. (1972)

NIE, N.H., C.H. HULL, J.G. JENKINS, K. STEINBRENNER and D.H. BENT: Statistical Package for the Social Sciences. McGraw Hill, Inc. (1975)

PACIFIC NORTHWEST LABORATORIES, BATTELLE MEMORIAL INSTITUTE: Characterization of Pollutant Availability for San Francisco Bay Dredge Sediments. Crystalline Matrix Study - Phase I. Final Report to U.S. Army Corps of Engineers, Contract DACW07-73-C-0080. 102 pp (1974)

PRITCHARD, D.W.: In: Proc. Governor's Conf. Chesapeake Bay, Annapolis, Maryland (1968)

REYNOLDS, L.M.: Residue Rev. 34, 27 (1971)

SOKAL, R.R. AND F.J. ROHLF: Biometry, W.H. Freeman and Co. San Francisco, 776 pp (1969)

WALKER, C.R.,: Fisheries 1, 19 (1976)

WALSH, G.E.: J. Wash. Acad. Sci. 62, 122 (1972)

WERSHAW, R.L., P.J. BURCAR, and M.C. GOLDBERG: Environ. Sci. Technol. 3, 271 (1969)