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PCB Residues in Bivalves and Sediments of Raritan Bay

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PCBs are frequent contaminants in aquatic biota and sediments and have been reported in shellfish (McDERMOTT et al. 1975) and estuaries (WHARFE & VAN DEN BROEK 1978, WILSON & FORESTER 1978). PCBs may enter the estuarine environment by many routes (i.e., air pollution, sewage, rivers, industrial outfalls) and accumulate in the sediments.

The Hudson River has received large amounts of PCB mixtures. Identification and quantification of residues in the upper Hudson River were reported by NADEAU & DAVIS (1976) and HETLING et al. (1978). Various Aroclors have been found in the upper Hudson River in the vicinity of Hudson Falls - Fort Edward, N.Y. Little data however, have been reported of the occurence of PCBs at the mouth of the Hudson estuary.

Our study was therefore performed to survey PCB contamination in the Raritan Bay - Lower N.Y. Bay complex. Sediments and bivalve populations were analyzed to determine quantities and types of PCB compounds present.

METHODS AND MATERIALS

Bivalves and sediments were sampled during June 1977. Sampling locations are illustrated in Figure 1. Sediments were sampled from 18 sites (Stations 1-14, OKWD, PB2, GK1 and GK2), and one intertidal site (OB1) on Staten Island. This site (OB1) was impacted earlier by several oil spills and is downstream from effluent discharged in the Arthur Kill. The site OKWD was near the outfall of the Oakwood Sewage Treatment Plant. Benthic sediments were sampled with a Peterson Grab ($0.1 m^3$). Several grabs per station were composited and sampled. Samples were then refrigerated at $4^{\circ}C$ until analyzed. All materials, before and after contact with the sediments were washed with hexane. Bivalves were sampled from 16 locations. Table 1 details the sampling locations and species sampled. Bivalves were returned to the laboratory, shucked, composited in jars (5 clams/jar) with tin-lined caps and frozen until analysis.

Glassware was prewashed 3X with hexane, and Na_2SO_4 used in analyses was baked at $450^{\circ}C$ for 3 h to remove impurities. Procedural blanks for analyses were performed concomittantly. Sediments were extracted for PCB content by a procedure in the EPA publication "Manual of Analytical Methods for the Analysis of Pesticide Residues in Human and Environmental Samples". Sulfur interference was removed by using a copper column procedure (STAINKEN 1978). Sample extracts were concentrated to 2 ml under nitrogen for analysis by

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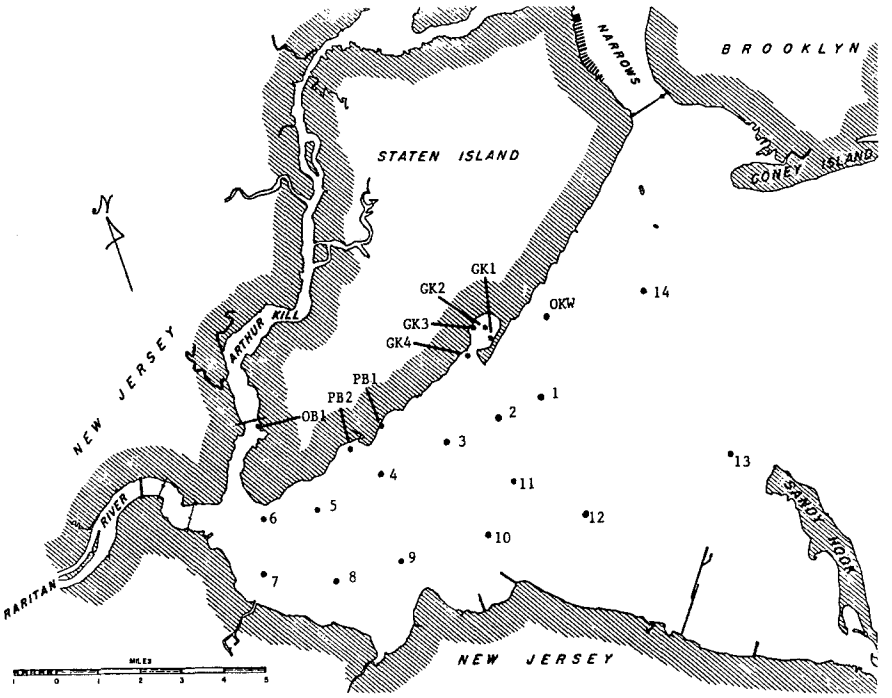

Figure 1. Sampling Stations in Raritan Bay - Lower New York Bay

gas chromatography (GC). To confirm the presence of PCB residues, duplicate samples were also treated by KOH digestion. In addition, samples with poor resolution were eluted through a Florisil column (REYNOLDS & COOPER 1975).

Bivalves were then extracted for PCB content. Each composited sample was thawed, minced and 50 g (OB1, RB 13 & RB 6) or 25 g (all other samples) of tissue was homogenized in a Teflon pestle tissue grinder. The homogenate was mixed with 3X its weight of Na_2SO_4, occasionally stirred for 1.0 h and then remixed in a Waring blender for 30 s. The EPA Manual procedures for sediments cited above were then followed. The extracts were cleaned on florisil columns (REYNOLDS & COOPER 1975) and concentrated to 2 ml for GC analysis.

GC analyses were performed using a ^{63}Ni detector and a column packed with 1.5% OV-17 and 1.95% QF-1 on 100/120 mesh Gas Chrom Q. Inlet, column and detector temperatures were 225, 200, and 250°C, respectively; injection sample 0.5-2.0 ml; carrier gas 95% argon-methane at 29 ml/min.

Aroclors 1016, 1242, 1254 and 1260 were chromatographed as standards and matched with samples. A mixture of 1.5 uL containing Aroclor 1016 (406 pg/uL), Aroclor 1242 (398 pg/uL), Aroclor 1254 (400 pg/uL) and Aroclor 1260 (442 pg/uL) was also chromatographed for use as a quantitative standard. The area of three well resolved peaks within the standard mixture chromatogram was used to quantitate sample chromatograms. Relative retention times (RRT) of these peaks to p,p'-DDE were 37, 47 and 71. Matching of the RRTs of sample

peaks with standard RRTs was within $\leq$4% difference in RRTs.

RESULTS

Quantification of PCB residues in tissues and sediments is presented in Table 1. The range of residues in all bivalve tissues was found to be 12-360 ng/g tissue. The mean values found per species sampled were C. virginica 81 $\pm$ 32 ng/g tissue, M. arenaria 149 $\pm$ 67 ng/g tissue and M. mercenaria 131 $\pm$ 27 ng/g tissue. In contrast, the range of residues in sediments was 3.4-2035 ng/g.

Relationship of (1) sediment silt-clay content to sediment PCB content, (2) of sediment silt-clay content to tissue PCB content, and (3) of tissue PCB values to sediment PCB values were analyzed for linear regression. The low correlation coefficients indicated that these were not valid relationships. It appears that the silt-clay content of the sediments did not reflect the tissues or sediments PCB contents. However, the tissues at all sites generally contained greater residue values than the sediments. Areas which were considered mixed sands and muds (Station 3) or medium sands (Station OKWD) contained relatively high values of PCBs for sediments and tissues.

Matching of standard Aroclors to sediment residues was achieved by determining the percent of retention times of the standards matching the sediment sample retention times. Very few sediment retention times matched more than 70% with the standard mix of Aroclors. However, many sediments matched more than 50% with the individual Aroclors. The sediments appear to contain mixtures of various homologs of the Aroclors. Mixtures of Aroclors 1016 and 1242 appeared to occur in all sediments, Aroclor 1260 occurred frequently and 1254 less frequently.

Gas chromatograms of the PCB standards (Figure 2) compared to those of sediments (Figure 3) illustrate the complex mixtures of the sediment chromatograms. Peaks matching the retention times of DDE were found in some chromatograms and it is probable that other organohalogen substances occurred.

Qualitative matching of standard Aroclors to tissue residues indicated that the tissues also contained mixtures of Aroclors. The Aroclor mixture of 1016 and 1242 appeared to be the most prevalent, and 1260 more frequent than 1254. Gas chromatograms of tissue extracts are illustrated in Figure 4.

DISCUSSION

Sediment residues appeared to contain mixtures of Aroclors which have been subjected to weathering and degradative effects (CAREY & HARVEY 1978). Previous studies (NADEAU & DAVIS 1976, SPAGNOLI & SKINNER 1977) indicated that Aroclors 1016, 1242, 1248 and 1254 were present in the upper Hudson River. Aroclors 1016 and 1242 were the ones most frequently detected in this study. Sediment PCB values reported for the Hudson have ranged from 7-6700 ppm (NADEAU & DAVIS 1976, HETLING et al. 1978). The types and amounts of PCBs found in

TABLE 1. Quantification of PCB residues in tissues and sediments. Bivalves sampled were Mercenaria mercenaria, Mya arenaria and Crassostrea virginica.

Sampling Station	Species	ng/g tissue	ng/g dry sediment
1.	M. mercenaria	12	3
2.	C. virginica	113	28
	M. mercenaria	143	
3.	M. mercenaria	41	2035
4.	M. mercenaria	281	37
5.	M. mercenaria	91	9
6.	M. mercenaria	65	16
7.	M. arenaria	151	9
8.	M. arenaria	31	6
9.			17
10.	M. mercenaria	135	670
11.	M. mercenaria	127	153
	C. virginica	48	
12.	M. mercenaria	91	299
13.	M. mercenaria	110	72
14.			13
OB1	M. arenaria	263	467
OKWD	M. mercenaria	360	7
GK1			17
GK2	M. mercenaria	73	117
PB2	M. mercenaria	170	59

this study may indicate downstream transport. The mean value of PCBs in the sediment was 110 ng/g dry sediment (excluding the outlier value from Station 3). Although a direct relationship between sediment type and PCB content was not evident, some sampling stations had higher values than others. The stations with higher values (3,10,11, 12,2,4) are towards the center of the bay and may represent concentrations and deposition from hydrographic conditions. The general flow in this area was described by PATTEN (1962).

The tissues extracted contained mixtures of Aroclors with homologs of 1016 and 1242 most prevalent, and 1260 more frequent than 1254. McDERMOTT et al. (1975) also found residues of 1242 widely distributed in a marine ecosystem. The variation in matching tissue contents with individual Aroclors may reflect selective uptake.

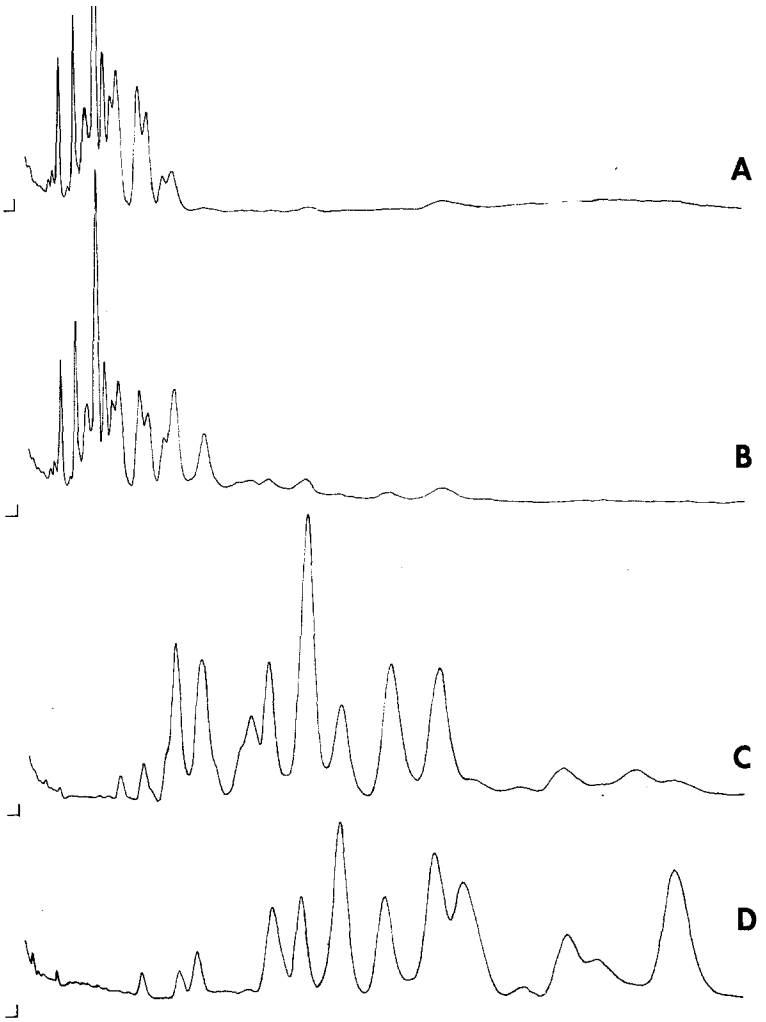

Figure 2. Gas chromatograms of PCB standards, Aroclor 1016 (A), Aroclor 1242 (B), Aroclor 1254 (C), and Aroclor 1260 (D).

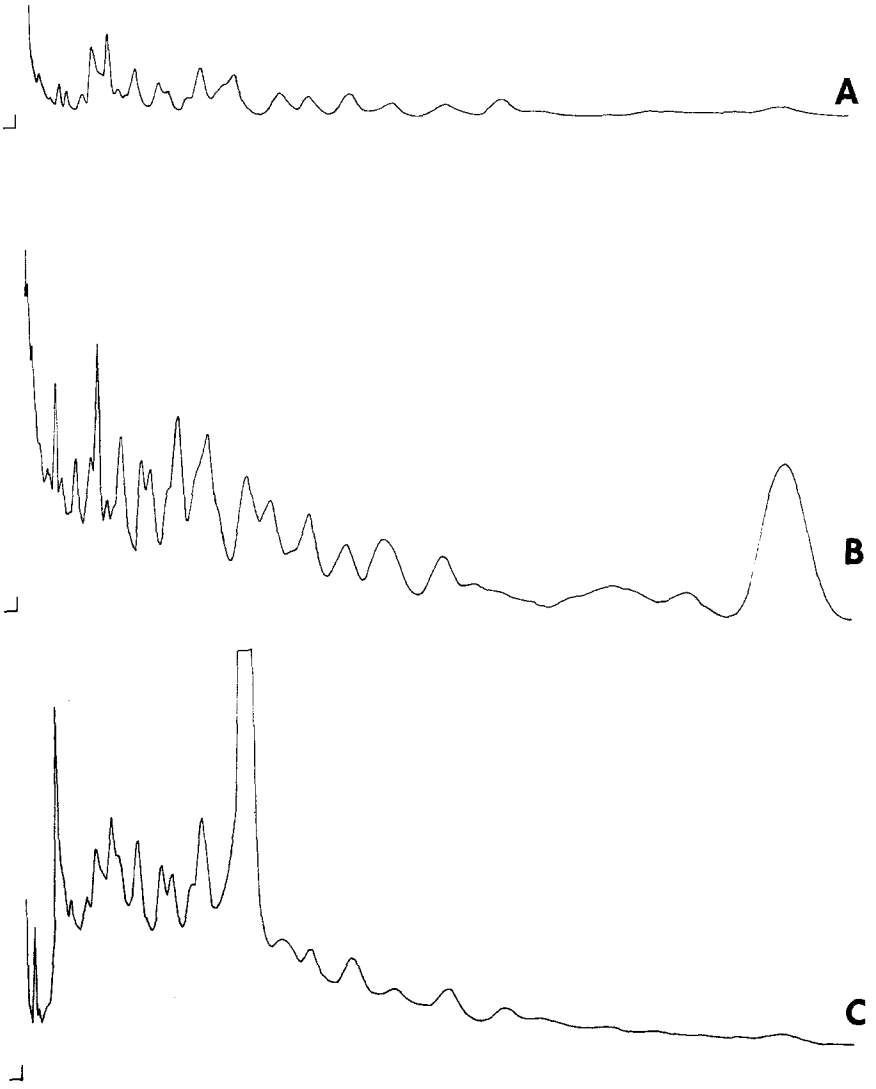

Figure 3. Gas chromatograms of sediments from sampling stations 2 (A), 3 (B), and OB1 (C).

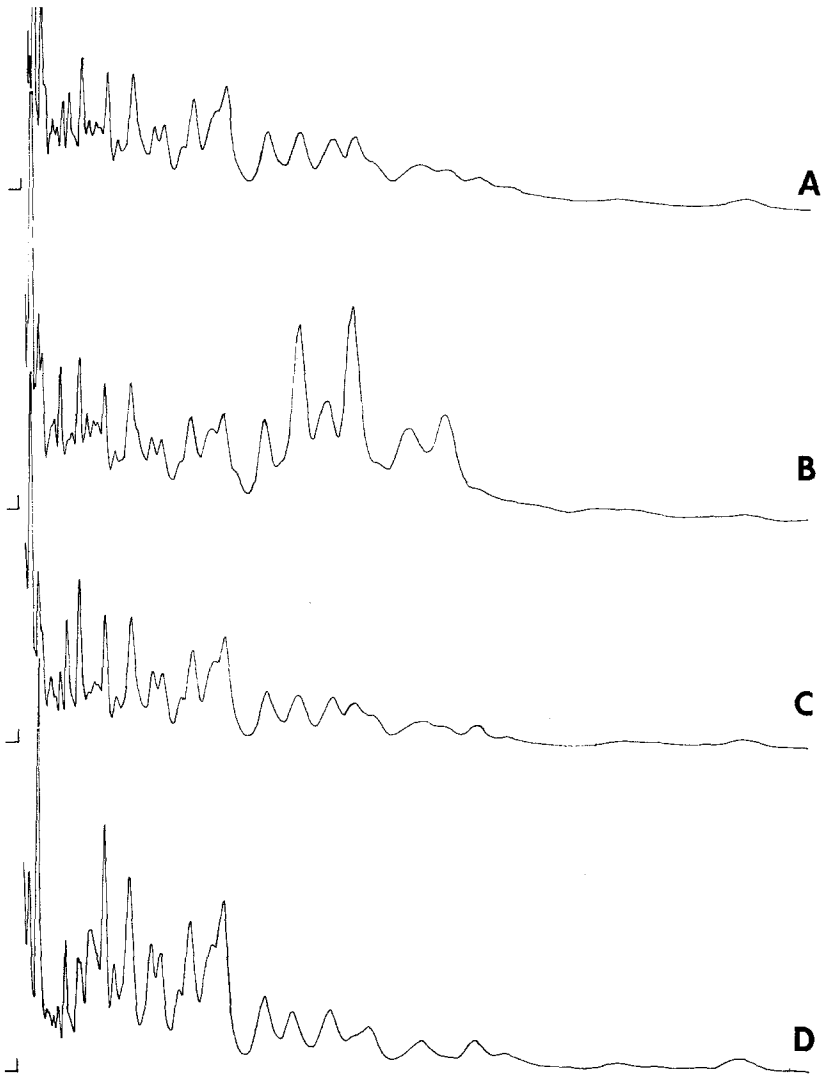

Figure 4. Gas chromatograms of bivalve tissues from sampling stations 6 (A), 7 (B), 10 (C), and 13 (D).

COURTNEY & DENTON (1976) and LANGSTON (1978) reported selective uptake of Aroclor homologs by bivalves. The lower chlorinated isomers tended to accumulate in tissues more frequently.

Tissue values of PCBs in this study ranged from 12-360 ng/g of tissue with a mean of 128 ng/g tissue for all bivalves sampled. WHARFE & VAN DEN BROEK (1978) reported a range of 44-268 ng/g wet weight in M. edulis from an estuarine environment and ranges of 0.2-200 ppm PCB concentrations in macroinverebrates from the lower Hudson estuary have been described (HETLING et al.1978). Therefore, the values found in this study are similar to other areas receiving pollutants. The differential uptake by the biota may reflect the bay hydrography. Higher tissue values tend to occur in the center and lower portions of Raritan Bay (Stations 2,4,10,11,13).

The study suggests that PCBs are entering the Bay and accumulating. The mechanism by which PCBs are sedimented, or accumulated by bivalves is unclear. The hydrography of the bay may contribute via current gyres acting as concentrating mechanisms.

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