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Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment*

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Abstract—Polychlorinated biphenyls (PCBs) were measured in interstitial waters and sediments at a site in New Bedford Harbor, Massachusetts, to study partitioning processes of hydrophobic organic compounds in marine sediments. Pore water concentrations of total PCBs, expressed as Aroclor 1254, increased with depth in the sediments with a maximum concentration of 17.1 μg/L at 9–11 cm. Apparent distribution coefficients of individual chlorobiphenyls decreased with depth and were related to dissolved organic carbon levels. Results from this site suggest that most of the PCBs in interstitial waters are sorbed to organic colloids. A simple three-phase equilibrium sorption model can explain many features of the data. Changes in the composition of individual chlorobiphenyls in the sediments were also apparent. Microbial degradation appears to be responsible for large relative depletions of several chlorobiphenyls with depth in the core.

INTRODUCTION

ESTUARINE AND COASTAL marine sediments act as short or long term reservoirs for many hydrophobic organic compounds (LEE *et al.*, 1979; WAKEHAM and FARRINGTON, 1980; HITES *et al.*, 1980; PRAHL and CARPENTER, 1983). Sorption reactions involving interstitial waters and sediment particles control the rates and mechanisms of transport of organic compounds within and out of sediments, and also affect the bioavailability of these compounds. Other diagenetic processes such as biological and chemical transformation reactions, diffusion, advection, and mixing and resuspension of the sediment bed, will also affect the distribution of hydrophobic organic compounds in sediments and pore waters (BERNER, 1980). The relative importance of each of these processes depends on the molecular structure, biological activity and physical-chemical properties of the individual organic compounds, as well as properties of the sedimentary environment.

We are studying PCBs (polychlorinated biphenyls) as model compounds to probe many of these processes. In addition, there are continuing environmental concerns with PCBs which require a better understanding of the fate of PCBs which have accumulated in surface sediments (NAS, 1979). PCBs are a mixture of 209 possible congeners which exhibit a wide range of physical and chemical properties. Their reported solubilities (MACKAY *et al.*, 1980) and octanol-water partition coefficients (RAPAPORT and EISENREICH, 1984; WOODBURN *et al.*, 1984) are representative of many hydrophobic organic compounds present in the marine environment. PCBs were widely used as industrial chemicals in the United States because of their thermal and chemical stability. The production and regulatory histories of PCBs, and estimates of their sources and transport pathways in the environment have been reviewed (NISBET and SAROFIM, 1972; NAS, 1979). PCBs are characterized by slow rates of chemical and biological degradation in the aquatic environment (NAS, 1979). PCB measurements in the field have been used in the study of particle-seawater partitioning (DEXTER and PAVLOU, 1978a), sediment transport in the Hudson River (BOPP, 1979, BOPP *et al.*, 1981), and the associations and transport of PCBs with particles in the Great Lakes (EISENREICH *et al.*, 1983, EADIE *et al.*, 1983).

Several chlorobiphenyls along with many other hydrophobic organic compounds have been utilized in laboratory sorption experiments with various sediments and soils (KARICKHOFF *et al.*, 1979; MEANS *et al.*, 1980; SCHWARZENBACH and WESTALL, 1981; CHIOU *et al.*, 1983). Laboratory studies have also quantitatively shown the importance of the partitioning of hydrophobic organic compounds with estuarine colloidal organic matter (MEANS and WIJAYARATNE, 1982, WIJAYARATNE and MEANS, 1984a). LANDRUM *et al.* (1984) measured partition coefficients for two polychlorobiphenyls with natural dissolved organic matter, and HASSETT and ANDERSON (1982) showed a reduction in the sorption of 2,2′-5,5′-tetrachlorobiphenyl to particles on addition of colloidal organic matter.

Predictions of partitioning of hydrophobic organic compounds based on experimental data are largely untested in the field. We report here an investigation of the partitioning of PCBs between the sediments and interstitial waters at a coastal marine site. This site is located in New Bedford Harbor (the Acushnet River Estuary) in southeastern Massachusetts. New Bedford Harbor has been heavily impacted by PCB pollution. The nature of this contamination has been recently reviewed (WEAVER, 1984; FARRINGTON *et al.*, 1985).

SAMPLING SITE AND METHODS

The sediments and interstitial waters were obtained from a large volume box core taken from the R/V Asterias at Station 67 of SUMMERHAYES *et al.* (1977) in the outer harbor of New

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Attachment XIX-13A

Bedford on September 1, 1983. This site, in 8 to 9 meters of water, has sediments which are characterized as organic rich (4–6% organic carbon), silty mud with occasional shell fragments. This location borders Butler's Flat and the navigation channel of the outer harbor. The sediment accumulation rate at this site is not known. SUMMERHAYES *et al.*, (1977) report that the sedimentation in this general area probably averages 2–3 mm/yr, but that the rate of sediment accumulation of the dredged navigation channel appears to be about 4 cm/yr. These workers report that the sediment accumulation in all of New Bedford Inner Harbor appears to have increased 5 to 10 fold since the construction of a hurricane barrier, which was completed in 1966, separating the inner and outer harbor. A minimum estimate of 1.0 cm/yr for a sediment accumulation rate at this site can be set from the presence of PCBs at the bottom of this 41 cm core, provided that the PCBs have not penetrated the sediment by some other mixing or migrational process. PCBs were first used in New Bedford in 1941 (WEAVER, 1984).

Sampling methods for the sectioning of muds and subsequent extraction and filtration of pore water employ inert atmosphere techniques. These methods, summarized here, are described by SHOLKOVITZ and MANN (1984) and are only slightly modified for trace organic analysis. A Sandia-Hessler Type MK3 sediment corer with a 0.25 m^2 by 70 cm box was used. The water overlying the sediment was siphoned off immediately after the core was brought on board. The sediment-water interface was undisturbed and a plexiglass sheet was placed over the surface of the mud. The small amount of headspace was purged with freon (Genetron 22) to minimize air penetration. Within two hours the box core was removed from its frame at the dock and transported for sectioning and pore water extraction. Sectioning was performed by replacing one side of the coring box with 18 interlocking, 2 cm wide plexiglass plates which allowed sectioning of 2 cm sediment horizons with a teflon coated, metal sliding sled. Each horizon was immediately transferred to a N_2 filled glove box and loaded into acid and acetone cleaned, 1 liter polypropylene centrifuge bottles. Four to six bottles were filled and centrifuged at about 3500 rpm (~3500 g's) for 20 minutes in a IEC model 6000 model centrifuge. The temperature was controlled at 20°C. The temperature of the mud was 20.5°C at sampling and did not change appreciably during sectioning. Centrifugation resulted in the extraction of 0.80 to 1.7 liters of pore water per 2 cm horizon, representing 38 to 56% of the water content in these sediments. The pore water was subsequently filtered under vacuum while continuously bubbling with N_2. Precombusted, 142 mm Gelman Type AE glass fiber filters, which have a nominal pore size of 1 μm, were used. The loss of PCBs from interstitial waters as a result of volatilization during vacuum filtration and a N_2 purge is expected to be minimal. The fraction of dissolved chlorobiphenyls lost from N_2 purging can be calculated as follows:

$$\text{fraction chlorobiphenyl lost} = 1 - C/C_0 = 1 - e^{-(H' \times b \times t/V)}$$

where H' (mL/cm^3) is the Henry's law constant for individual chlorobiphenyl in seawater, b is the flow rate of N_2 (cm^3/min.), t is the time and V is the volume of pore water filtered. A maximum of 0.2 to 2.0% loss is calculated from a Henry's law constant of 0.01 mL/cm^3 (MURPHY *et al.*, 1983) and the experimental conditions used, and would be reduced by lower activities of PCBs in solution due to associations with dissolved organic matter.

Small subsamples of pore water were saved for analysis of dissolved organic carbon (DOC), $SO_4^{=}$, Fe and Mn, and salinity. The remainder of the sample was then stored in glass along with 75 ml of CH_2Cl_2 for later analysis of PCBs. Subsamples of sediment were recovered from the centrifuge bottles, combined, and stored frozen in glass for later PCB and CHN analyses. A total of 41 cm of sediment depth were analyzed as 17 sections. Sectioning, extractions and filtrations were completed in approximately 12 hours.

ANALYTICAL METHODS AND CALCULATIONS

Standard techniques were used to determine pore water constituents. DOC was analyzed by a wet persulfate oxidation method adapted from STAINTON (1973). Sulfate was determined by barium sulfate precipitation, Fe and Mn by atomic absorption spectrometry, and chlorinity by $AgNO_3$ titration. Approximate precisions of these methods were 3, 2, 2, 4, and 0.7% respectively. Water content was determined after heating wet sediments to a constant weight at 110°C. CHNs of dry sediments, which had been treated with 10% HCl to remove small amounts of carbonate, were measured on a Perkin-Elmer CHN Analyzer.

The isolation and quantification of PCBs were as follows. Immediately prior to solvent extraction, both sediments and pore waters were spiked with an internal standard consisting of 2,4,5-trichlorobiphenyl and 2,2′,3,4,5,6′-hexachlorobiphenyl. The corresponding IUPAC numbers for these compounds are *29* and *143* respectively (BALLSCHMITER and ZELL, 1980). These two chlorobiphenyls do not occur in appreciable amounts in the industrial mixtures of PCBs and are used to monitor procedural recoveries and as quantification standards. Wet sediments were Soxhlet extracted for 24 hours with 350 ml of 1:1 hexane:acetone. An additional 24 hour extraction of sediments with fresh hexane:acetone gave 8.2 ± 3.0% of the individual chlorobiphenyls determined the previous day, and no additional recovery of spiked compounds. Pore waters were extracted in separatory funnels, shaking for 1.5 minutes, three times with 75 ml of CH_2Cl_2 and about 100 mg of sodium lauryl sulfate added to control emulsions. A fourth 5 minute pore water extraction yielded another 0.61 ± 0.10% of individual PCBs. These additional yields do not affect the results and biogeochemical interpretation presented here. Extracts were separated from aqueous phases in separatory funnels, dried with anhydrous Na_2SO_4, and concentrated with Kuderna Danish concentrators. A hexane fraction containing PCBs was collected from silica gel (1% deactivated) using a layer of activated copper under the silica gel to remove reduced sulfur.

PCBs were analyzed from concentrated hexane extracts by high resolution capillary gas chromatography with electron capture detection on a Hewlett-Packard 5840 gas chromatograph with a 30 meter DB5 fused silica column (J&W Scientific) operated with H_2 carrier gas using the following chromatographic conditions: a 2.0 μl splitless syringe injection; 2 minutes at 40°C followed by rapid heating to 120°C (hold until 5 minutes); temperature programming at 2°C/min to 230°C (60 min) and then 4°C/min to 270°C; makeup gas, 5% methane:95% argon at 30 ml/min.

All reagents were either solvent extracted or combusted, and solvents were distilled in glass. Procedural blanks were insignificant at the PCB levels of these samples except for a contamination problem in the 0–3 cm pore water sample where many of the higher molecular weight PCBs are not reported.

Several complementary methods were used to identify individual chlorobiphenyls in the industrial mixtures Aroclor 1242 and 1254, which are the source of PCBs in these samples (Aroclor 1242 and 1254 standards are Monsanto lot numbers AK-344 and AA-1 respectively). A significant portion of the PCBs used by the manufacturing plants in the area were actually Aroclor 1016 which is very similar in composition to Aroclor 1242 (NAS, 1979). Retention times of nearly 70 pure PCB standards (from Ultra Scientific and Analabs) were compared to those in the mixtures. GCMS spectra obtained with a Finnegan 4500 quadropole mass spectrometer coupled with a Carlo Erba 4160 glass capillary gas chromatograph confirmed the degree of chlorination of the various peaks. GC and GCMS identifications reported by other workers, using SE-54 and similarly coated columns, were consulted to obtain a consistent set of peak identifications (DUINKER and HILLEBRAND, 1983; MULLIN *et al.*, 1984; EISENREICH *et al.*, 1983; ALBRO and PARKER, 1979; ALBRO *et al.*, 1981; and BALLSCHMITER and ZELL, 1980). The relative amounts of contributing isomers in some unresolved peaks are still tentative, but this does not affect the identification of the chlorobiphenyls reported here.

Recoveries of internal standards *29* and *143* were 93.3 ± 13.3 and 98.9 ± 17.0% respectively for 16 sediment samples and, and 83.9 ± 12.9 and 92.8 ± 20.8% for 11 pore water samples. Five pore water samples from the 23-35 cm core sections were underspiked and no recoveries are reported. The error in recoveries is associated with variation in absolute detector response. However, except for the five underspiked pore water samples, relative responses of peaks to that of internal standard *143* were used. This resulted in precisions of better than 5%. Estimates of total PCBs as Aroclor 1254 were obtained by comparing the relative response of the 10 peaks of greatest area, A_i to that in a standard where the amounts of Aroclor 1254 (m_{1254}) and *143* (m_{143}) are known:

Aroclor 1254 (μg/g sample)

$$= \sum_{i=1}^{10} \frac{((A_i/A_{143})_S \cdot (A_{143}/A_i)_{STD} \cdot (m_{1254}/m_{143})_{STD} \cdot (m_{143}\text{spike}))}{10 \times \text{wt. sample (g)}}$$

where m_{143}spike is the amount of *143* spiked as an internal standard to the sample, *S* refers to sample, and STD refers to a standard mixture of Aroclor 1254 with isomer *143* added. To estimate Aroclor 1242, the 6 largest peaks in the mixture which do not appear in Aroclor 1254 were used, and standard *29* was used as the internal standard. Representative chromatograms of Aroclor standards, and samples are illustrated in a later section (Fig. 2) along with the chlorobiphenyl identifications used in Aroclor quantifications (Fig. 2 and Table 2).

A total of 46 separate PCB peaks were quantified. In addition, only qualitative information for 5 dichlorobiphenyls is presented because peak areas were too small for quantification. It is estimated that the precisions of the Aroclor calculations and other peak ratios are approximately 5% and that of apparent distribution coefficients, K'_d, are therefore about 7%. K'_d is calculated as the sediment concentration of individual chlorobiphenyls in the sediments divided by that measured in the interstitial waters, and is in units of L/Kg. The concentrations and distribution coefficients of PCBs from the pore water sections between 23 and 35 cm are uncorrected for average recoveries and represent a lower limit in concentrations.

RESULTS AND DISCUSSION

Interstitial water and sediment characterization

Pore water profiles of Mn, Fe and $SO_4^=$ (Fig. 1A) reflect suboxic diagenesis in this core. The reaction sequence in the oxidation of organic matter in marine sediments has been well studied (FROELICH *et al.*, 1979; ALLER, 1980a). The maxima of reduced Fe and Mn in the 0-3 cm section indicate oxygen depletion in this upper layer. The profile of sulfate suggests that sulfate reduction occurs near the surface and the smoothness of the profile indicates that oxygen is depleted throughout the core. The removal reactions of Fe with depth in this core do not appear to be as efficient as those for Mn. It is expected that the sulfide would be an effective sink for reduced Fe (ALLER, 1980b). A

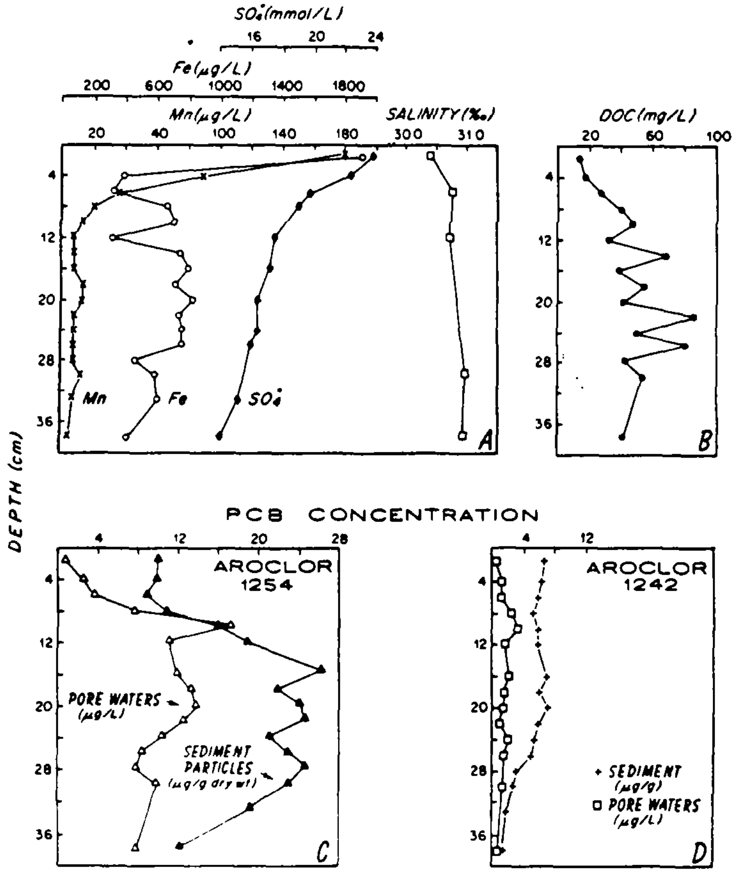

FIG. 1. (A-B) Interstitial water profiles of Fe, Mn, $SO_4^=$, salinity, and DOC. (C-D) Profiles of total PCBs as Aroclor 1254 and Aroclor 1242 in sediments and pore waters.

Table 1. Profiles of bulk sediment properties and Aroclor concentrations in sediments and pore waters.

Depth (cm)	% H_2O	TOC (%)	TON (%)	C/N	DOC (mg/L)	Aroclor 1242 Sed.* (μg/g)	Aroclor 1242 P.W.* (μg/L)	Aroclor 1254 Sed. (μg/g)	Aroclor 1254 P.W. (μg/L)
0-3	55.85	6.06	0.63	9.6	14.4	6.45	0.421	10.1	0.893
3-5	55.87	5.23	0.51	10	17.4	6.14	1.00	9.88	2.61
5-7	54.97	3.74	0.36	10	27.7	5.72	1.04	8.86	3.68
7-9	50.60	4.98	0.48	10	40.3	5.10	2.27	10.9	7.70
9-11	51.26	4.40	0.40	11	47.9	5.62	3.03	16.0	17.1
11-13	47.69	4.14	0.34	12	32.6	5.65	1.57	18.9	11.1
13-15	50.98	3.85	0.31	12	68.7				
15-17	52.58	4.02	0.32	13	39.2	6.77	1.98	26.2	11.8
17-19	53.22	4.74	0.39	12	55.1	5.89	1.40	21.9	13.4
19-21	53.42	4.98	0.40	12	42.0	6.84	1.20	23.9	13.7
21-23	55.71	5.96	0.53	11	87.0	5.76	0.953	24.5	12.6
23-25	59.48	5.68	0.51	11	50.9	5.09	1.88	21.0	10.4
25-27	57.98	4.78	0.41	12	81.4	4.62	1.33	22.8	8.35
27-29	54.98	4.86	0.42	12	43.7	2.81	0.522	24.5	7.85
29-31	46.95	5.33	0.43	12	54.2	2.40	1.17	22.8	9.86
31-35	45.67	5.45	0.35	16		1.66		19.1	
35-41	39.92	4.76	0.34	14	41.4	1.27	0.532	12.1	7.65

* Sed. = sediment, P.W. = pore water.

subsample of pore water from the 35–41 cm section also was filtered through a 0.40 μm Nuclepore filter. This resulted in a 79% reduction of Fe in the filtrate, so that we infer an association of Fe with a colloidal phase. Near constant measurements of chlorinity (Fig. 1A) in this core indicate that groundwater advection is not measurable at this site.

The concentrations of DOC in the interstitial waters (Table 1) are consistent with the range of concentrations and depth profiles reported for other reducing nearshore marine sediments (NISSENBAUM *et al.*, 1972; KROM and SHOLKOVITZ, 1977; HENRICHS, 1980; ELDERFIELD, 1981; HENRICHS and FARRINGTON, 1984; and SHOLKOVITZ and MANN, 1984). Krom and Sholkovitz showed that the increase in DOC with depth was due to an increase in colloidal organic matter. Several of these workers did UV and infrared spectroscopic studies of the colloidal organic matter, and found it to appear similar to melanoiden or marine humic substances (NISSENBAUM *et al.*, 1972; KROM and SHOLKOVITZ, 1977; and ELDERFIELD, 1981).

The sediments at this site are enriched in total organic carbon (Table 1). The changes in organic carbon and water contents with depth indicate either changes in the source of organic carbon, non constant sedimentation or non steady-state diagenesis of organic carbon. It can also be seen that the C/N ratio increases steadily downcore with a local minima in the profile from 21–25 cm. This trend may represent preferential nitrogen metabolism or changes in the quality and quantity of natural organic matter supply.

PCB composition and concentrations

The composition of individual PCBs in the sediments is similar to a mixture of Aroclor 1242 and Aroclor 1254; Aroclor 1242 consisting primarily of di-, tri-, and tetrachloro biphenyls and Aroclor 1254 consisting of tetra-, penta-, hexa-, and heptachloro biphenyls. Differences in composition of PCBs between sediment samples at different depths, and between sediment and pore water at the same depth, are seen in Fig. 2. Surface sediments have a composition of

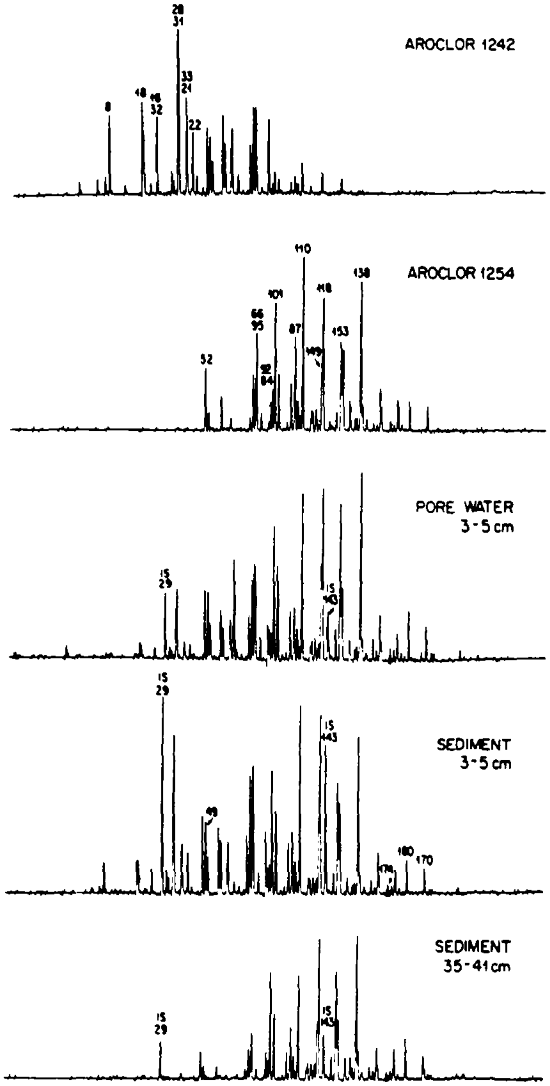

FIG. 2. Capillary gas chromatograms of PCB Aroclor standards, pore water and sediment samples from 3–5 cm depth, and the 35–41 cm sediment sample. Retention times increase along the x-axis. Chlorobiphenyl numbers indicate identification of peaks used in total Aroclor calculations and other chlorobiphenyls reported here (see Table 2).

Table 2. PCB IUPAC numbers and structures.

IUPAC no.	Stucture
8	2,4'-dichlorobiphenyl
18	2,2',5-trichlorobiphenyl
16)*	2,2',3-trichlorobiphenyl
32	2,4',6-trichlorobiphenyl
28)	2,4,4'-trichlorobiphenyl
31	2,4',5-trichlorobiphenyl
33)	2',3,4-trichlorobiphenyl
21	2,3,4-trichlorobiphenyl
22	2,3,4'-trichlorobiphenyl
49	2,2',4,5'-tetrachlorobiphenyl
52	2,2',5,5'-tetrachlorobiphenyl
66)	2,3',4,4'-tetrachlorobiphenyl
95	2,2',3,5',6-pentachlorobiphenyl
92)	2,2',3,5,5'-pentachlorobiphenyl
84	2,2',3,3',6-pentachlorobiphenyl
101	2,2',4,5,5'-pentachlorobiphenyl
87	2,2',3,4,5'-pentachlorobiphenyl
110	2,3,3',4',6-pentachlorobiphenyl
149	2,2',3,4',5',6-hexachlorobiphenyl
118	2,3',4,4',5-pentachlorobiphenyl
138	2,2',3,4,4',5'-hexachlorobiphenyl
153	2,2',4,4',5,5'-hexachlorobiphenyl
170	2,2',3,3',4,4',5-heptachlorobiphenyl
174	2,2',3,3',4,5,6'-heptachlorobiphenyl
180	2,2',3,4,4',5,5'-heptachlorobiphenyl

* these chlorobiphenyls are not resolved by our GC analysis.

PCBs which is very similar to a mixture of the Aroclor 1242 and Aroclor 1254 standards shown, with somewhat lower concentrations of some of the more soluble di- and trichlorobiphenyls relative to Aroclor 1242. This could be the result of increased solubilization or degradation of those compounds either in the sediments or in the water column during transport to the sediment. There are smooth changes in the composition of PCBs in the sediments. The di-, tri-, and tetrachlorobiphenyls are depleted with increasing depth in the core, while the penta-, hexa-, and heptachlorobiphenyls maintain a nearly constant composition. The resulting compositions of PCBs are seen to resemble Aroclor 1254 quite closely with varying amounts and compositions of the lower chlorinated compounds which have little resemblance to Aroclor 1242 deeper in the core.

The profiles of Aroclors 1254 and 1242 in sediments and interstitial waters (Figs. 1C and 1D; Table 1) illustrate the increase in pore water concentrations of PCBs with increasing depth in the core. The concentrations of Aroclor 1254 in interstitial waters are highly elevated, 0.893 to 17.1 μg/L, and exhibit a maxima in the profile at a depth of 9–11 cm. These concentrations can be compared to water column concentrations of 11 to 20 ng/L at a nearby station in the outer harbor (BROWNAWELL and FARRINGTON, 1985). They can also be compared to reported solubilities of Aroclor 1254 in seawater of 4.36 μg/L (DEXTER and PAVLOU, 1978b) and 24.7 μg/L (WIESE and GRIFFIN, 1978). The concentrations of many of the higher chlorinated, less soluble, compounds exceed the reported solubilities of chlorobiphenyl isomer groups in a mixture of Aroclor 1254 in seawater (DEXTER and PAVLOU, 1978b). EADIE *et al.* (1983) have reported elevated concentrations of pore water PCBs in 3 Lake Michigan surface sediments. Total PCB concentrations of 0.159–0.342 μg/L were reported in interstitial waters of sediments of much lower total PCB concentration (63.5 to 160 ng total PCB/g sediment). Unlike these sediments, the Lake Michigan pore waters were greatly enriched in Aroclor 1242. DUINKER and HILLEBRAND (1979) have measured PCB concentrations of 10–40 ng/L in the interstitial waters of sediments from the Rhine-Meuse Estuary.

The sediment concentrations of Aroclor 1254 also increase between the 7–9 and 15–17 cm sections, but this increase is not nearly as dramatic as that in the pore waters. Aroclor 1242 (Fig. 1D) makes a substantial contribution to the total PCBs in the surface sections and gradually diminishes in importance with depth. The PCBs in pore waters at this site are enriched in the more highly chlorinated isomers and Aroclor 1242 type compounds occur in lower amounts. However, concentrations of Aroclor 1242 in interstitial waters are also elevated above water column values of 17 to 32 ng/L (BROWNAWELL and FARRINGTON, 1985.)

The profile of DOC (Fig. 1B) can be compared to either the profile of Aroclor 1254 or total pore water PCBs (Aroclors 1242 + 1254). The similarity of these profiles, especially over the upper 13 cm, is suggestive of an association of PCBs with dissolved organic matter. The apparent supersaturation of many chlorobiphenyls in pore waters is consistent with this hypothesis.

Partitioning of PCBs between sediments and interstitial waters

The composition of PCBs in the pore waters is similar to that of the sediments at each depth interval although the more highly chlorinated congeners generally are enriched in the interstitial waters when compared with the sediment phase. The partitioning of PCBs between the sediments and interstitial waters is certainly important in evaluating the diagenetic processes and remobilization of PCBs in sediments. The measured distribution coefficients of individual chlorobiphenyls can also be used to study sorption processes of hydrophobic organic compounds in natural marine sediments and to evaluate the role of dissolved and particulate organic matter on the observed partitioning. Sorption reactions of these compounds with fresh water sediments and soils have been extensively studied using laboratory experiments. It has been demonstrated that sorption of neutral, relatively non-polar compounds correlates well to the organic carbon content of the sorbent (KARICKHOFF *et al.*, 1979; MEANS *et al.*, 1980; and SCHWARZENBACH and WESTALL, 1981). These workers found that an organic carbon normalized partition coefficient, K_{oc}, is a good predictor of partitioning for a given hydrophobic organic compound onto a wide range of sediments and soils, at $f_{oc} > 0.001$:

$$K_{oc} = K_p/f_{oc}$$

where K_p is the partition coefficient determined from the linear sorption isotherm determined experimentally and f_{oc} is the fraction organic carbon. The organic carbon fraction has also been shown to control the sorption of DDT with marine sediments (PIERCE *et al.*,

1974) and to influence the partitioning of PCB Aroclor 1254 onto a variety of marine derived substrates (HIRAIZUMI *et al.*, 1979). Several investigators have shown that log K_{oc} varies inversely with the logs of water solubilities and directly with log octanol-water partition coefficients of a wide range of solutes, encompassing greater than seven orders of magnitude in aqueous solubilities (CHIOU *et al.*, 1979; KARICKHOFF *et al.*, 1979; SCHWARZENBACH and WESTALL, 1981; and MEANS *et al.*, 1980). These relationships have been shown to hold for compounds having solubilities as low as many of the hexachlorobiphenyls. A solvent-water partitioning model has been presented to describe sorption behavior of nonionic organic compounds with soils and sediments (CHIOU *et al.*, 1979; CHIOU *et al.*, 1983).

The presence of natural DOC has been shown to decrease the apparent sorption of fatty acids onto bentonite in seawater (MEYERS and QUINN, 1973) and to decrease the adsorption of dieldrin onto aquifer sand (BOUCHER and LEE, 1972), and cholesterol and tetrachlorobiphenyl onto suspended particles (HASSETT and ANDERSON, 1982). POIRRIER *et al.* (1972) and CARTER and SUFFETT (1982) both demonstrated high partitioning or binding affinity of colloids and humic acids with DDT. HASSETT and ANDERSON (1979, 1982), MEANS and WIJAYARATNE (1982) and WIJAYARATNE and MEANS (1984b) suggest that it is the operationally defined high molecular weight or colloidal fraction of DOC which is important in partitioning. Finally, estuarine colloidal organic matter has been shown to have relatively high partition coefficients with two herbicides and three polycyclic aromatic hydrocarbons (PAH) (MEANS and WIJAYARATNE, 1982; WIJAYARATNE and MEANS, 1984a). These studies suggest that the partitioning of hydrophobic organic compounds with natural organic colloids may be similar to that of sedimentary organic matter.

On the basis of results from the above studies and the high DOC levels in this core, we propose that a significant fraction of all the chlorobiphenyls present in pore water solution are associated with organic colloids. For the purposes of discussion, we have assumed that the concentration of organic colloids is reflected by the DOC profile, which is a reasonable assumption based on the work of KROM and SHOLKOVITZ (1977). Thus, measured distribution coefficients of PCB isomers or components are treated as apparent distribution coefficients

$$K'_d\ (\text{L/kg}) = \frac{S\ (\mu\text{g/kg})}{D + C\ (\mu\text{g/L})} \qquad (1)$$

where S, D, and C are the concentrations of PCB components in the sediment or solid phase, dissolved and colloidal phases, respectively.

Profiles of K'_d for 51 resolved and unresolved chlorobiphenyls have been generated and all show a decrease over the upper 11 cm and remain low deeper in the core. Examples of K'_d are given in Table 3, and selected profiles are illustrated in Fig. 2. K'_d values of individual chlorobiphenyls range from about 5×10^2 to 2×10^4 and are considerably lower than water column K'_d measurements of PCBs in Puget Sound (DEXTER and PAVLOU, 1978a, PAVLOU and DEXTER, 1979), the Hudson River (BOPP, 1979), Lake Superior (EISENREICH *et al.*, 1983) and several other environments where the role of colloids may not be as great, due to lower concentrations of DOC and correspondingly lower concentrations of colloids. K'_d values ranged from 10^4 to 10^7 in those studies. EADIE *et al.*, (1983) also report similarly low K'_d values, 248 to 7000, for PCBs in the interstitial waters of Lake Michigan. The elevated concentrations of PCBs, low K'_ds, and correlation of these properties with DOC (Fig. 3 compared to Figs. 1B, C and D) strongly implicate a considerable colloidally associated PCB phase in this sediment, even for the more soluble trichlorobiphenyls.

The role of both colloidal and sedimentary organic matter can be further evaluated by comparing a simple three-phase equilibrium sorption model, in which both colloidal and sediment bound phases exist in a dynamic

Table 3. Apparent distribution coefficients (K'_d) of ten polychlorinated biphenyls with decreasing depth in the sediment. Stuctures corresponding to the IUPAC chlorobiphenyl numbers are found in Table 2. A complete data set of the K'_ds of all 46 resolved and unresolved chlorobiphenyls can be obtained from the authors.

Depth (cm)	$K'_d \times 10^{-3}$ (L/Kg)									
	18	28+31	49	52	101	110	138	153	170	180
0–3	14.3	24.7	11.3	12.3	11.6	13.2	*	*	*	*
3–5	5.32	8.00	3.66	4.11	3.63	4.46	3.14	3.42	2.62	2.35
5–7	3.12	5.60	2.77	2.84	2.17	2.62	2.08	2.00	2.20	1.97
7–9	1.48	2.97	1.48	1.68	1.34	1.74	1.08	1.25	0.896	0.770
9–11	1.11	2.88	1.22	1.32	0.950	1.17	0.668	0.746	0.515	0.487
11–13	2.84	3.22	2.18	2.36	1.68	2.23	1.19	1.48	0.792	0.749
15–17	2.67	7.04	2.43	3.08	2.31	2.83	1.70	1.90	0.894	1.02
17–19	3.57	8.79	2.43	2.45	1.59	2.10	1.20	1.48	0.905	0.837
19–21	4.33	10.2	2.36	2.04	1.72	2.15	1.52	1.62	0.839	1.06
21–23	5.74	11.6		1.73	1.78	2.79	1.54	1.92	0.871	1.01
23–25	1.53	6.25	2.65	2.68	2.03	2.50	1.38	1.74	0.950	0.900
25–27	1.80	7.43	3.18	3.31	2.63	3.39	2.12	2.51	1.73	1.54
27–29	2.89	10.1	5.05	4.88	3.33	3.78	2.30	2.73	1.67	1.55
29–31	1.12	2.91	3.38	3.51	2.66	3.18	1.91	2.29	1.37	1.28
35–41	2.17	1.86	1.41	1.67	1.93	1.41	1.40	1.53	1.27	1.56

* Interference from contamination.

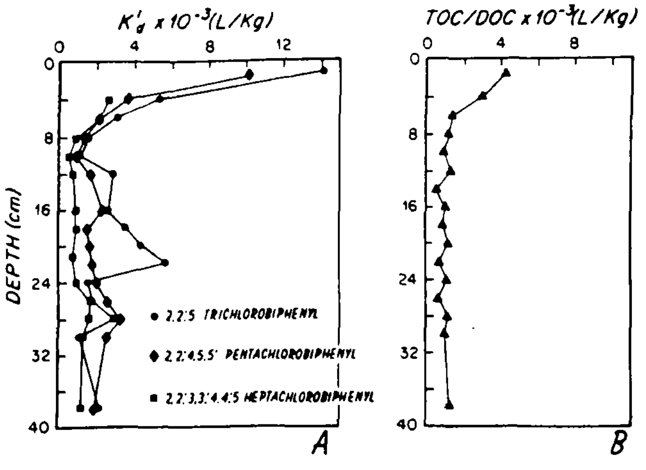

FIG. 3. (A) K'_d profiles of three chlorobiphenyls. (B) TOC/DOC profile.

equilibrium with a truly dissolved phase. The concentrations of these two sorbed phases can be estimated by a knowledge of the appropriate $K_{oc}s$. We substitute for Eqn. (1) the following:

$$K'_d = \frac{f_{oc}sK_{oc}sD}{D + f_{oc}cK_{oc}cD} \qquad (2)$$

where $f_{oc}s$ and $f_{oc}c$ are the mg of total organic carbon in a Kg of dry sediment and mg of colloidal organic carbon per liter of pore water, respectively, and $K_{oc}s$ and $K_{oc}c$ are the sediment and colloidal carbon normalized partition coefficients. In the case where D is small compared to $f_{oc}c\ K_{oc}c\ D$, the expression reduces to:

$$K'_d = \frac{f_{oc}sK_{oc}s}{f_{oc}cK_{oc}c} \qquad (3)$$

Since $K_{oc}s$ and $K_{oc}c$ are not known for the compounds of interest, it is further assumed that colloidal organic matter has a sorption affinity similar to sedimentary organic matter for hydrophobic organic compounds. Studies with natural estuarine colloids indicate $K_{oc}c$ may be several times that of $K_{oc}s$ although the slopes of the solubility dependence on K_{oc} are identical (WIJAYARATNE and MEANS, 1984a; MEANS and WIJAYARATNE, 1982). Unpublished, experimental studies in our own laboratory indicate that carbon normalized partition coefficients of PCBs with marine colloids are similar to those reported for freshwater sediments. Therefore, in the limit where most of the amount of PCB in pore solution is colloid-bound, an estimate of K'_d is simply the concentration ratio of organic carbon between sediment and colloidal organic phases: $K'_d \simeq f_{oc}s/f_{oc}c$. In Fig. 3 we have compared the profile of TOC/DOC to that of K'_d for a few PCB isomers. We assume that $f_{oc}c$ is reflected by the total DOC concentration. The similarity of the model K'_d with those actually measured is surprisingly good, especially for the more highly chlorinated isomers.

The other major assumption in this model is that of equilibria between all three phases. There is controversy in the literature involving hysterisis and reported "nonreversibility" of adsorption and desorption of hydrophobic organic compounds with sediments (DI TORO and HORZEMPA, 1982; GSCHWEND and WU, 1985). KARICKHOFF (1980) has shown that several sorbed PAH could be completely desorbed from sediments, but that the kinetics of desorption were slower than adsorption and that this rate could be modelled as a two step process. The rate of the slow, rate controlling, process decreased with increasing ring size and K_{oc}. The desorption rate constant for pyrene was as slow as 0.031 hr^{-1}. It is expected that the desorption rate for many PCBs could be considerably slower than pyrene and decrease as the degree of chlorination increases. It is not well understood how the organic content of the sediment and salinity of solution might affect adsorption-desorption kinetics. It is also not known how biological and chemical transformation and alteration of the sedimentary organic matter during diagenesis may affect the desorbability of sediment bound compounds. One further complicating factor is that there are dynamic interactions between sedimentary, colloidal and non-colloidal dissolved organic carbon. The nature and kinetics of these reactions are largely unknown. However, sediments, below the sediment-water interface and in the absence of bioturbation, provide an environment where long time scale (years) equilibria can be approached and the extent of disequilibria minimized. In comparison, the overlying water column can be considered a much more dynamic and open system, where significant departures from equilibrium may occur.

The K'_d's measured are chlorobiphenyl specific and tend to decrease with increasing degree of chlorination and decreasing solubility. Figure 4 shows the range and average K'_d as a function of the chlorine substitution (nCl) for three representative sediment sections. This trend is opposite of what is expected on the basis of solubility considerations. A strong inverse dependence of solubility on partitioning of PCBs is expected from laboratory results (KARICKHOFF *et al.*, 1979;

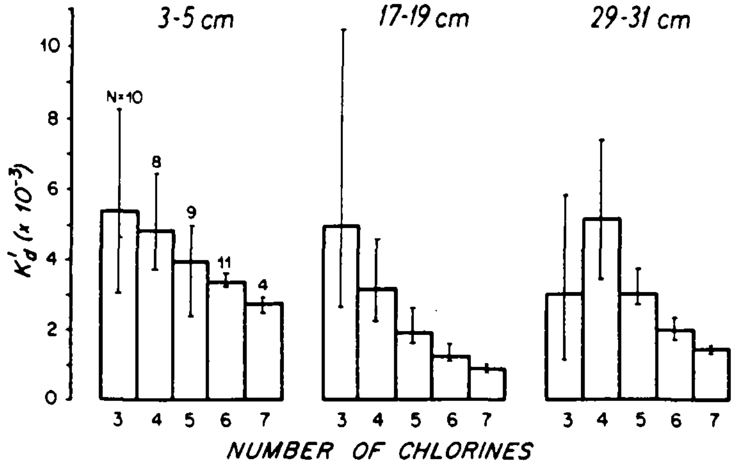

FIG. 4. Bar graphs of the mean K'_d as a function chlorine number for three representative depths. N equals the number of isomers or pairs of unresolved isomers considered and the bars represent the range of K'_d values determined.

SCHWARZENBACH and WESTALL, 1981; CHIOU *et al.*, 1983) and has been observed in the water column measurements in the field (BOPP, 1979; PAVLOU and DEXTER, 1979). In contrast, it should be noted that EISENREICH *et al.* (1983) report no clear trend of K'_d with increased degree of chlorination for PCBs in the water-column of Lake Superior. The lack of solubility dependence on K'_d in our data is even more compelling evidence that the observed distribution is not simply two-phase sediment-water partitioning.

The enrichment in pore water of more highly chlorinated congeners relative to lesser chlorinated congeners is not easily explained. A diagenetic removal of tri- and tetrachlorobiphenyls occurring in pore water solution could explain their apparent depletion in pore waters if the desorption kinetics from the sediments are of similar time scales. Such processes still cannot explain the trends that occur with the penta- through heptachlorobiphenyls, which show no evidence of any removal. KARICKHOFF (1980) also found that the slow step in the adsorption rate decreased with molecular weight of the solute, and FREEMAN and CHEUNG (1981) have proposed a gel partition model for sorption in which the kinetics of sorption are diffusion controlled. Very slow adsorptive/absorptive approaches to equilibrium might explain the lower K'_ds for the less soluble compounds. However, an examination of the K'_ds for the range of chlorobiphenyls and for increasing depth in the core does not support the hypothesis of slow approach to equilibrium in this case. The K'_d of the trichlorobiphenyls does drop below that of the average tetrachlorobiphenyl in the bottom two sections. An explanation which is consistent with the results is that not all of the sorptive volume in the sedimentary organic matter is accessible to large hydrophobic organic compounds. If there is a steric hindrance to sorption sites, it might be expected that as molecular size increases with increasing nCl the effective volume of accessible sorbent organic matter decreases. This could explain why colloidal organic matter, with its greater surface to volume ratio, apparently competes more effectively for larger chlorobiphenyls. Such a proposed mechanism needs to be tested, and may be specific for sediment type, type of organic matter in sediment, and appreciably influenced by interstitial water salinity and major ion chemistry.

Compositional changes of PCBs in the sediments

Compositions of PCB in many sediment profiles from the Hudson River estuary have been measured (BOPP, 1979; BOPP *et al.*, 1981). There were only slight changes in peak ratios with depth, and those were directly attributable to changes in the up-river PCB source which was well documented. In contrast, there are marked changes in the composition of PCBs with increasing depth in our core. These changes in the sediments have been evaluated by looking at changes in in peak area ratios with depth. PCB no. *170* (2,2',3,3',4,4',5-heptachlorobiphenyl) was chosen as the reference compound, because it did not show apparent depletion relative to other PCBs, and is not expected to be readily biodegradeable, or be appreciably mobile in a dissolved form. The area ratio of each PCB to *170*, A_i/A_{170}, has been calculated and profiles of this ratio normalized to that in the surface section have been generated. Examples of these profiles are seen in Fig. 5. The relative concentrations of the di- and trichlorobiphenyls decrease faster than the tetrachlorobiphenyls and the relative concentrations of the penta-, hexa- and heptachlorobiphenyls remain essentially constant. The extent of the depletion is isomer specific within the di-, tri- and tetrachlorobiphenyls. The relative depletions of some of the chlorobiphenyls are striking. The major peak in Aroclor 1242 is an unresolved mixture of isomers *28* and *31*. The relative concentration of this peak is depleted at 35–41 cm to 2.2% of that in the 0-3 cm section (Fig. 5). 2,3,4'-trichloro-

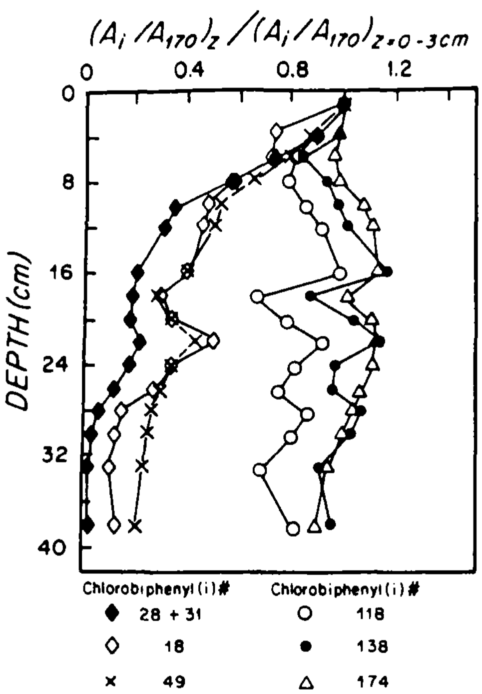

FIG. 5. Profiles of the area ratios of individual chlorobiphenyls (i) in the sediments to *170* normalized to the ratio measured in the surface sediment (Z = 0–3 cm). The structures of the chlorobiphenyl #'s are given in Table 2.

biphenyl (chlorobiphenyl no. *22*) is similarly depleted to 1.4% of its surface ratio. Variations in the relative concentrations of penta- through heptachlorobiphenyls are small.

The relative concentrations of most of the di-, tri-, and tetrachlorobiphenyls decrease as smooth profiles with local maxima at 21–23 cm. Note that these maxima in relative concentration of many chlorobiphenyls correspond to a minima in the C/N ratio and to local maxima in organic matter and water contents. These changes may be a function of either a change in the source or type of sediment or past injection of relatively fresh sediment from above into these depth horizons by the activities of large burrowing organisms. Visual observations and interstitial water sulfate does not indicate evidence of recent large scale burrowing.

Processes which need to be considered in evaluating compositional changes are: 1) changes in the source of PCBs to the sediment bed over time, 2) migration, *via* diffusion or advection of PCBs in the interstitial water, 3) chemical transformations, and 4) biological degradation of PCBs. BOPP *et al.* (1981) have suggested that changes in suspended particle concentration with time and subsequent deposition can result in changes in PCB composition with depth, with the less soluble chlorobiphenyls being enriched in times of high suspended loads. However, source changes of PCBs are unlikely to explain the major features of our profiles. Aroclor 1242 type mixtures are changed dramatically as the major chlorobiphenyls are nearly completely depleted in the bottom sections of the core. The composition of Aroclor 1254 remains relatively unchanged except for the tetrachlorobiphenyls. The smooth, chlorobiphenyl specific nature of the depletion profiles within both formulations, and near constant ratios of penta- through heptachlorobiphenyls argues against abrupt changes in the source of PCBs to the sediment. Other sediment samples and a core from the inner harbor show compositions similar to those in the surface sediment here, and compositional changes with depth have not been observed (BROWNAWELL and FARRINGTON, 1985).

Migration of hydrophobic organic compounds in sediments has not been satisfactorily studied. Diffusion of sediment bound PCBs is impeded by sorption and their high K'_ds. The mean distance that a particle tracer will migrate in the sediment can be estimated by $\sqrt{D't}$ (BERNER, 1976) where D' in this case can be estimated by $D_s/1 + K'_d$, where D_s is the sediment diffusion coefficient of solute in seawater corrected for sediment tortuosity. Assuming a D_s of 10^{-6} cm^2/sec for a dissolved PCB, a K'_d of 10^3, and that the sediment profile represents about 20 years, then the mean distance that a PCB particle tracer will migrate is 0.79 cm. Pore water advection could be a more effective way to mobilize PCB in sediments, but the salinity shows no evidence of appreciable groundwater advection at this site. However, seawater can advect without salinity changes. If advection or diffusion were controlling the solid phase concentrations to any extent, it would not be expected that the composition of the higher molecular weight isomers would remain so constant, as these isomers are enriched in pore water solution in ratios unlike that of the sediment. The migrational properties of colloidal organic matter and associated sorbates will be different than that of dissolved solutes. Diffusion of hydrophilic organic colloids may be much less impeded by sorption than that of dissolved PCBs. The role and migrational properties of organic colloids in sediments need to be better understood to critically evaluate remobilization of hydrophobic organic compounds in sediments.

Rapid rates of degradation of several chlorinated hydrocarbons have been observed in reducing environments. Reductive dehalogenation appears to be the main pathway and converts DDT to DDD (GLASS, 1972; ZORO *et al.*, 1974), DTE to DDE (BELAND *et al.*, 1974), and lindane to benzene (BELAND *et al.*, 1976) under reducing conditions. Anaerobic degradation to toxaphene mixtures has also been reported in anaerobic soils (PARR and SMITH, 1976) and in salt marsh sediments (WILLIAMS and BIDLEMAN, 1978). These and other papers dispute the role of biological processes in this mechanism. ZORO *et al.*, (1974) argue that the reduction is purely chemical and that reduced iron porphyrins may be important in catalyzing this reduction in nature. The reduction potentials of chlorinated hydrocarbons are an indicator of whether a compound can break down in this manner. BELAND *et al.* (1976) state that as a rule organochlorine compounds with a first reduction potential (E_{2d}) more positive than -1.521 V *versus* a saturated calomel electrode will reductively dehalogenate under strongly reducing conditions and those compounds with an E_{2d} less than -1.757 V will not. E_{2d} values ranging from -1.771 to -2.126 V have been reported for several chlorobiphenyls which can exist in industrial formulations of PCB (FARWELL *et al.*, 1973). The ease of reduction tends to increase with increasing number of chlorines, which is opposite of the trend reported in the chlorobiphenyl depletions noted here. BROWN *et al.* (1984) have noted decreases of highly chlorinated biphenyls in highly contaminated sediment cores from the upper Hudson River. Increases in mono- and dichlorobiphenyls not present in Aroclor mixtures were also observed. These workers suggest that PCBs were reductively dechlorinated by anaerobic bacteria, because chemical reductants are not known for PCBs at environmental levels. Recent results (SULFITA *et al.*, 1983) demonstrate microbial dehalogenation of haloaromatic substrates by strict methanogens in culture.

Aerobic microbial degradation of PCBs has been extensively studied with both mixed and pure cultures. Susceptibility to, and rates of degradation are seen to be chlorobiphenyl specific and depend on both the number and substitution of chlorines. SHIARIS and SAYLER (1982) and BAILEY *et al.* (1983) showed degradation of monochlorobiphenyls by natural assemblages of freshwater microorganisms but none for higher chlorinated congeners. CAREY and HARVEY (1978) found small amounts of degradation of 2,2′,5-trichlorobiphenyl and 2,2′,5,5′-tetrachlorobiphenyl in experiments with marine bacteria but not degradation in experiments which were performed anaerobically.

The primary mechanism of degradation in pure culture studies involves dioxygenase attack preferentially at the 2′,3′-positions (FURUKAWA *et al.*, 1979; MASSE *et al.*, 1984). The major pathway of degradation of many PCBs is postulated to proceed through formation of the 2′3′-dihydro-diol compounds, reduction to the corresponding 2′3′-diols, which are then cleaved by meta fission at the 1′2′ position to the 6-oxo-dienoic acids and finally to the chlorobenzaoic acids. FURUKAWA *et al.* (1978) report the rates of biodegradation for 31 chlorobiphenyls by species of *Alcaligenes* and *Acinetabactor*. Relative rates of degradation by both species generally decrease to very low rates for the tetra- and pentachlorobiphenyls. The relative rates of degradation within the trichlorobiphenyls reported is quite similar to the relative degrees of isomer depletion in the sediment profiles. The reported degradation rates for 2,4,4′- and 2,4′,5-trichlorobiphenyls are between 6 and 25 times faster than for 2,2′,5-trichlorobiphenyl. The same relationship in the depletion profiles of these isomers is seen in Fig. 5. Chlorine substitution factors which influence the rate of degradation are complicated and can be related to the number of active sites or vicinal hydrogens available, field effects which will stabilize electrophilic attack (particularly at the 2,3 vicinal hydrogen positions), and steric effects which can also effect the planarity of the biphenyl molecule.

The specificity and relative rates of chlorobiphenyl depletion in our core seem to be consistent with the pattern expected for microbial diagenesis. However, this site is very reducing and microorganisms would not be able to use the oxidative pathways outlined above. Sporadic introduction of oxygen by burrowing organisms is an unlikely explanation given the smooth profiles extending to 41 cm. Some type of microbially mediated electrophilic degradation would explain our observations. However, the nature of the populations, and the mechanisms of transformation are not understood.

GENERAL DISCUSSION

We suggest that the data for this core coupled with other data from the literature support our hypothesis that the biogeochemistries of PCBs in the interstitial waters of this core were largely affected by an association of PCBs with organic colloids. Interactions of PCBs and other hydrophobic organic compounds with organic colloids will influence remobilization rates of these compounds in sediments and are likely to affect rates of diagenetic transformations. The quantitative role of organic colloids will depend on the quantity and quality of organic matter in the sediments as well as physical chemical properties of the compound of interest. Profiles of interstitial water PCBs indicate a diffusional flux to the overlying water column. However, uncertainties concerning the migrational behaviour of colloids and the importance of mixing processes within the sediments prevent reasonable calculations of this flux. Consideration of these processes is necessary in calculating residence times of many organic compounds in sediments. Further studies should also be aimed at developing a better understanding of the role of organic colloids in the bioavailability of hydrophobic organic compounds that are known or potential xenobiotic compounds.

CONCLUSIONS

1) Highly elevated concentrations of PCBs are reported in the interstitial waters of an organic rich coastal sediment from New Bedford Harbor. Evidence has been presented to suggest an important role of organic colloids in the biogeochemistry of PCBs in this sediment. Several lines of evidence indicate an association of PCBs with colloids in interstitial waters:

a) PCB concentrations increase with depth to supersaturated levels for many chlorobiphenyls. This increase correlates with the DOC profile.

b) K'_d decreases with depth in the sediment for all of the chlorobiphenyls measured. The magnitude and shape of the K'_d profiles can be modelled reasonably well assuming three-phase equilibria where the dissolved phase is small compared to the colloidal phase.

c) The compositions of chlorobiphenyls in pore water solution and the reverse trend in the K'_d with nCl's are not that expected in a 2-phase, solid-solution partitioning situation. An important colloidal phase needs to be invoked to explain these distributions.

d) The results from relevant laboratory studies would indicate that a high percentage of PCBs that are in pore water solution will be sorbed to organic colloids at the level of colloids which probably exists here.

2) Isomer specific depletions of di-, tri- and tetra-chlorobiphenyls were observed with increasing depth in this core. This is probably the result of microbial degradation of PCBs at this site, although the lack of oxic conditions requires the presence of microbial degradation pathways yet to be characterized.

3) These results indicate that a greater understanding of partitioning of hydrophobic organic compounds with organic colloids is necessary in evaluating the mobility and bioavailability of these compounds in sediments.

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