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PARTITIONING OF PCBs IN MARINE SEDIMENTS

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ABSTRACT

Polychlorinated biphenyls (PCBs) are useful model compounds to study the physical-chemical processes which affect the biogeochemistry of hydrophobic organic compounds. In this study two box cores from New Bedford Harbor, Massachusetts, were analyzed for PCBs. Measurements are reported for total PCBs and several individual chlorobiphenyls for both the sediments and interstitial waters. Concentrations of total PCBs were highly elevated in the pore waters and reached a maximum of 20.1 $\mu\text{g/L}$ at the Outer Harbor site. Results from these two cores combined with predictions from laboratory experiments indicate that most of the PCBs measured in interstitial waters are actually sorbed to organic colloids. The partitioning of chlorobiphenyls between water column particulates and filtrate shows a greater importance of dissolved compounds due to lower concentrations of organic colloids. A simple three-phase equilibrium model involving colloids, dissolved phase, and chlorobiphenyls sorbed to particulate organic matter is presented to explain the observed partitioning.

INTRODUCTION

Polychlorinated biphenyls (PCBs) have a wide range physical-chemical properties [1,2] which are representative of many hydrophobic organic compounds present in the marine environment. Because of their slow rates of chemical and biological degradation [3], PCBs provide excellent model compounds to study the physical-chemical processes important in the biogeochemistry of organic compounds in sediments. Contemporary sediments are repositories for PCBs and many other hydrophobic, recalcitrant pollutants released to the environment. Many depositional environments are biologically and physically active, and sediment-interstitial water partitioning processes will control the rates at which organic pollutants are released back to the water column or taken up by the biota. In the water column, the transport and fate of hydrophobic organic compounds will also be affected by associations with suspended particles and colloidal substances. The extent of these partitioning reactions influence rates of particulate removal, dispersion, volatilization, and biological uptake.

The sorption reactions of PCBs and other nonpolar organic compounds with freshwater sediments and soils have been well studied with laboratory experiments [4,5,6,7,8,9]. These and other studies have documented the importance of the organic fraction of sediments in controlling aqueous sorption of these compounds. Linear partition coefficients, K_p (L/Kg), can be predicted for a range of sediments by a single organic carbon normalized partition constant, K_{oc} :

$$K_p = f_{oc} K_{oc} \quad (1)$$

where f_{oc} is the fraction organic carbon of the sorbent. K_{oc} increases with decreasing solubility and increasing hydrophobicity of the compound. K_{oc} has been shown to be related to the octanol-water (K_{ow}) coefficient of the sorbate:

$$\log K_{oc} = a \log K_{ow} + b \quad (2)$$

where the slope (a) ranges from 0.72 to 1.0 in studies by different workers using different compound classes [4,6,7,8].

Organic colloids and dissolved humic substances have also been shown in the laboratory to have high sorption affinities for hydrophobic compounds [10,11,12]. Estuarine and marine colloids have been operationally defined as those substances which pass a 0.4 to 1 μ m filter but are retained by a variety of ultrafiltration membranes which exclude most materials having dimensions greater than 1-4 nm. Colloidal substances include both submicron particles and macromolecular organic matter. The presence of colloidal organic matter has been shown to decrease the apparent sorption of 2,2',5,5'-tetrachlorobiphenyl and cholesterol onto riverine particles [13] and that of fatty acids with marine sediments [14]. Gschwend and Wu [9] have also demonstrated the effect of non-settling particles in decreasing partition coefficients of PCBs in laboratory sediment sorption experiments. Estuarine organic colloids appear to behave as sorbents for hydrophobic organic compounds in a manner similar to particulate organic matter [10,12]. Thus, there are experimental and field observation data establishing that associations of PCBs with colloidal substances will affect their rates and modes of transport in aquatic environments.

To study the partitioning of PCBs, we have investigated the distribution of PCBs in sediments from New Bedford Harbor, Massachusetts. Interstitial waters from these organic-rich, coastal sediments provide an environment with high concentrations of colloidal organic matter, and the observed distribution of individual chlorobiphenyls yields insights into the roles of sedimentary and colloidal organic matter in partitioning. Measured distribution coefficients or ratios, K'_d , are calculated as:

$$K'_d = \frac{S}{PW} \quad (L/Kg) \quad (3)$$

where S and PW are the sediment and pore water concentrations of individual chlorobiphenyls. The pore water concentration includes both dissolved and any colloid associated components. Comparison of measured K'_d s of PCBs in sediments provide a good test of predictive sorption models based on laboratory results.

In this chapter, we present results of PCB analysis from two box cores taken in New Bedford's inner and outer harbors. A more complete discussion of the biogeochemistry of PCBs in the outer harbor core is reported elsewhere [15], but we have incorporated examples of the partitioning data to better illustrate the role of organic colloids in sediment interstitial waters. To provide a useful comparison to the sediment investigations, we also report results from a water column partitioning study where two stations in New Bedford Harbor were occupied and sampled over a tidal cycle. Within the limitations of data sets available, the partitioning results from these studies are compared to a simple three-phase equilibrium partitioning model based on predictions from laboratory experiments.

SAMPLING SITES AND METHODS

The sampling sites of the sediment cores (Stations 67 and 84) and water samples (Stations 74 and 81) are shown in Figure 1. New Bedford Harbor is severely polluted by PCB contamination [16,17]. Concentrations of PCBs in surface sediments are highest in the upper part of the estuary, north of our Station 81, and generally decrease moving south through the outer harbor and out into Buzzards Bay.

Station 84 was sampled with a Soutar box corer, 0.04 m² x 1 m, off the RV Asterias on October 29, 1981. This site was in 3 meters of water and bottom water temperature was 13.1°C. Sediment samples of one to three cm depth were sectioned into glass quart jars shipboard. The upper three cm was heavily populated by a small (about one cm diameter) unidentified bivalve. Sediments were stored overnight at room temperature and pore water samples were extracted the following two days using a hydraulically powered, stainless-steel squeezer at 2000-2500 psi as discussed by Henrichs [18]. Interstitial water was filtered through two internal Reeve Angel glass fiber filters and an external Gelman Type AE glass fiber filter of a nominal pore size of 1.0 μ m. 75 to 240 ml pore water samples were obtained for each sediment depth and were stored in glass with 25 ml of CH₂Cl₂ for later PCB analysis.

A large volume box core was obtained at Station 67 with a Sandia-Hessler type MK3 sediment corer on September 1, 1983. The temperature of the sediment was 20.5°C and inert atmosphere techniques were used in the sectioning of the core and subsequent extraction and filtration of pore water. These procedures are explained in detail elsewhere [19,15] and resulted in the isolation of about 1.5 liters of pore water per two cm depth

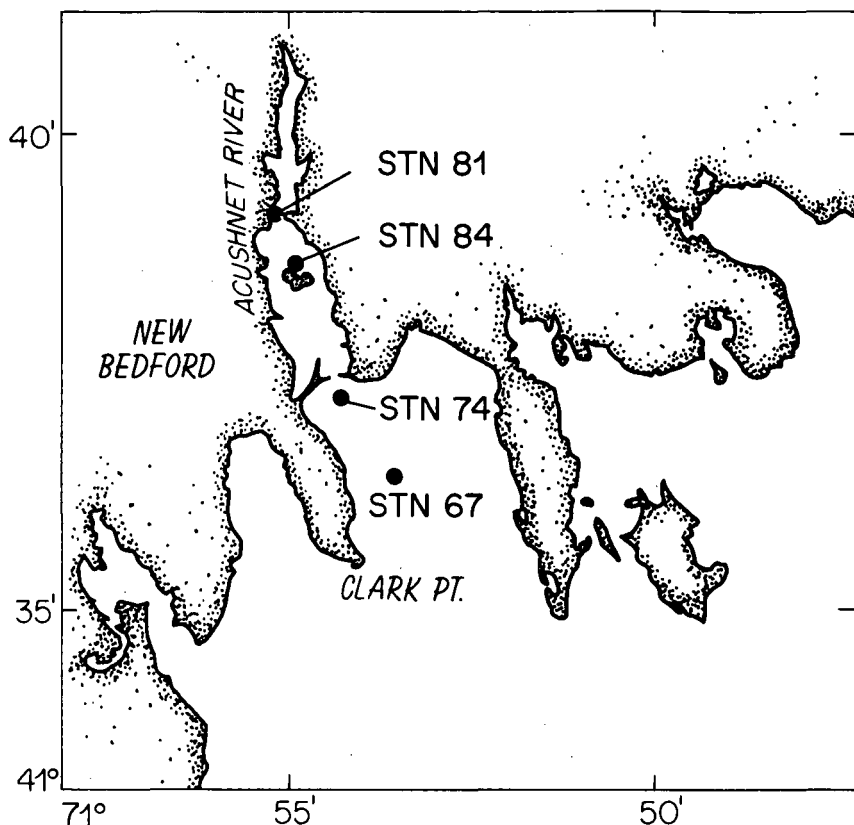


Figure 1. Map of New Bedford Harbor on the United States east coast.

horizon. Samples of pore water were stored and analyzed for PCBs, dissolved organic carbon (DOC), salinity, sulfate, and Fe and Mn. Frozen sediment samples were later analyzed for PCBs and CHN.

Water column samples were taken at Stations 81 and 74 throughout a complete tidal cycle on September 22, 1982. Samples were collected hourly in stoppered two liter flasks at both subsurface and near-bottom depths at both sites. CTD casts were also made at each site every hour. These samples, covering incoming and outgoing tides, were combined into 14-17 L composite samples. The eight combined samples were pressure-filtered through Gelman Type A/E glass fiber filters within ten hours of sampling, and filters were frozen until analysis. CH_2Cl_2 was added to the filtered samples and stirred vigorously in glass carboys.

Analysis of PCBs in all three sets of samples was similar with slight procedural modifications in chromatography and

quantification of total PCBs. Filtered water and pore water samples were extracted three times with CH_2Cl_2 in separatory funnels. Particulate material, filtered from each water sample, and wet sediments were Soxhlet extracted for 24 hrs. with 1:1 hexane:acetone (water particulates were extracted for an additional day with fresh hexane:acetone). Extracts are combined when necessary, dried over sodium sulfate, evaporated to near dryness, and chromatographed on silica gel columns. Chromatographic columns for sediment and interstitial water extracts employ a layer of activated copper to remove reduced and elemental sulfur. PCB fractions were eluted from the silica gel with either hexane or toluene in hexane and then analyzed by capillary column gas chromatography and electron capture detection on a HP5840 gas chromatograph equipped with a 30 meter DB5 fused silica column (J&W Scientific) using H_2 carrier gas. 2.0 μl syringe injections were made using the following conditions: 2 minutes at 40°C followed by rapid heating to 120°C (hold until 5 minutes; temperature programming at $2^\circ\text{C}/\text{min}$ to 230°C and then $4^\circ\text{C}/\text{min}$ to 270°C ; with a makeup gas of 5% methane/95% argon at 30 ml/min.

The apparent distribution coefficients, K'_d (equation 3), of 51 chlorobiphenyl peaks are calculated as the ratio of the peak areas of sediment and pore water samples multiplied times appropriate sample factors. The chlorobiphenyl identification of these peaks is given in Table I and is based on identifications by other workers [20,21,22,23,24,25], retention times of over 70 pure chlorobiphenyl standards (from Analabs and UltraScientific), and GCMS spectra of Aroclor PCB standards. Table I also lists the reported values of $\log K_{ow}$ determined by reverse phase HPLC [2] for many of these compounds.

Concentrations of total PCBs have been estimated as mixtures of Aroclor 1242 and Aroclor 1254 which are industrial mixtures of PCBs consisting primarily of di- through tetrachloro-, and tetra- through hexachlorobiphenyls, respectively. Total PCB estimates of sediments and pore waters were calculated by capillary gas chromatography described above and in [15]. Estimations of total PCBs in water column samples were determined by comparison to Aroclor standards on a Perkin-Elmer 900 gas chromatograph run isothermally at 190°C on a two meter column packed with 1.5% OV-17/1.95% QF-1 on Chromosorb W HP (100/120 mesh). Chlorobiphenyls 29 and 143 were used as internal standards in Station 67 samples and in the sediment and particulate samples in the other studies. Average recoveries of these internal standards were 80-95% in the various studies. Results from Station 67 incorporate internal standards as quantification standards, while the other samples do not. Concentrations and K'_d calculations for the latter samples do not correct for recoveries and have higher estimated errors (+15% in concentrations and +22% in K'_d) compared to those reported for Station 67 results [15].

Table I. PCB identification and associated values of $\log K_{OW}$ from Rapaport and Eisenreich [2].

Peak no.	#Cl	PCB Isomer no. ^a	Identification	Relative Retention Time	$\log K_{OW}$ ^b	($\log K_{OW}$) ^c
1	2	4(d) +	2,2'	0.2776	4.89	4.89
	2	10	2,6		5.31	
2	2	7(d) +	2,4	0.3103	5.30	5.30
	2	9	2,5			
3	2	6	2,3'	0.3245	5.02	5.02
4	2	8(d) +	2,4'	0.3323	5.10	5.10
	2	5	2,3			
5	3	19	2,2',6	0.3594	5.48	5.48
6	3	18	2,2',5	0.3940	5.55	5.55
7	3 +	17(e) +	2,2',4	0.3964	5.76	
	2	15	4,4'		4.82	
8	3	24	2,3,6	0.4093	5.67	5.67
9	3	16 +	2,2',3	0.4215	5.31	5.53
		32	2,4',6		5.75	
10	3	26	2,3',5	0.4518	5.76	5.76
11	3	28(d) +	2,4,4'	0.4650	5.69	5.69
		31	2,4',5			
12	3	33 +	2',3,4	0.4800		
		21 +	2,3,4			
	4	53	2,2',5,6'			
13	3	22	2,3,4'	0.4916	5.42	5.42
14	4	UK (45)	2,2',3,6	0.4987		
15	4	52	2,2',5,5'	0.5226	6.09	6.09
16	4	49	2,2',4,5'	0.5288	6.22	6.22
17	4	47 +	2,2',4,4'	0.5331	6.29	6.29
		75	2,4,4',6			
18	4	44	2,2',3,5'	0.5536	5.81	5.81
19	3 +	37(e) +	3,4,4'	0.5581	4.94	
	4	42	2,2',3,4'			
20	4	41 +	2,2',3,4	0.5725	6.11	6.11
		64	2,3,4',6			
21	4	40	2,2',3,3'	0.5845	5.56	5.56
22	4	74 +	2,4,4',5	0.6112	6.67	6.67
		61	2,3,4,5			
23	4	70	2,3',4',5	0.6181	6.23	6.23
24	4 +	66(e) +	2,3',4,4'	0.6241	6.31	6.43
	5	95	2,2',3,5',6		6.55	
25	4	60	2,3,4,4'	0.6490	5.84	5.84
26	5	92 +	2,2',3,5,5'	0.6563	6.97	6.97
		84	2,2',3,3',6			
27	5	101	2,2',4,5,5'	0.6636	7.07	7.07
28	5	99	2,2',4,4',5	0.6714	7.21	7.21
29	5	83	2,2',3,3',5	0.6880		
30	5	97 +	2,2',3',4,5	0.6964	6.67	6.67
		86	2,2',3,4,5			
31	5	87	2,2',3,4,5'	0.7049	6.37	6.37
32	5	85	2,2',3,4,4'	0.7110	6.61	6.61
33	6 +	136 +	2,2',3,3',6,6'	0.7144	6.51	6.51
	4	UK				
34	5 +	110(d) +	2,3,3',4',6	0.7207		
	4	77	3,3',4,4'		5.62	
35	5	82	2,2',3,3',4	0.7370		
36	6	151	2,2',3,5,5',6	0.7415		
37	6	135 +	2,2',3,3',5,6'	0.7486	7.15	7.15
		144	2,2',3,4,5',6			

Table I continued.

Peak no.	#Cl	PCB Isomer no. ^a	Identification	Relative Retention Time	log K _{ow} ^b	(log K _{ow}) ^c
38	6	149	2,2',3,4',5',6	0.7611	7.28	7.28
39	5	118	2,3',4,4',5	0.7643	7.12	7.12
40	6 +	153	2,2',4,4',5,5'	0.8028	7.75	7.75
	6	132	2,2',3,3',4,6'			
	5	105	2,3,3',4,4'			
41	6	141	2,2',3,4,5,5'	0.8217		
42	6	137	2,2',3,4,4',5	0.8326	7.71	7.71
43	6	138	2,2',3,4,4',5'	0.8450	7.44	7.44
44	6 +	129(d) +	2,2',3,3',4,5	0.8564	7.32	7.32
	7	UK				
45	6	128	2,2',3,3',4,4'	0.8867	6.96	6.96
46	7	174	2,2',3,3',4,5,6'	0.9092		
47	7	177	2,2',3,3',4',5,6	0.9174		
48	6	156	2,3,3',4,4',5	0.9269		
49	8 +	200 +	2,2',3,3',4,5',6,6'	0.9359		
	6	157	2,3,3',4,4',5'			
50	7	180	2,2',3,4,4',5,5'	0.9555		
51	7	170	2,2',3,3',4,4',5	1.000		

(a) From Ballschmiter and Zell (22). (b) PCB isomer K_{ows} from (2). (c) Log K_{ows} used in log K_d vs log K_{ow} relationships. Log K_{ow} for the peak is assumed to equal that of the major isomer when the isomers are not fully resolved, and in some cases an average K_{ow} of two isomers is used when their contributions are similar and log K_{ows} are similar. (d) Reported to represent 70% or more of the mass of the peak (20,22,24,25) in Aroclor mixtures or as determined By GCMS. (e) Similar Contributions of isomers in peak (20,22,24,25 or GCMS).

RESULTS AND DISCUSSION

Sediment-Interstitial Water Studies

Station 84 sediments were organic rich and sulfate reducing. Organic carbon contents were determined at three depths, 0-1, 1-3, and 27-30 cm, and had corresponding per cent organic carbon contents of 6.83, 7.00 and 5.16 respectively. The profiles of total PCB concentration, expressed as the sum of Aroclor 1242 and 1254, in both the pore waters and sediments are illustrated in Figure 2. The pore water concentration of total PCBs in the 0-1 cm section is 1570 ng/L and can be compared to a overlying water "dissolved" PCB concentration of 170 ng/L. Interstitial water PCBs decrease rapidly below three cm and remain low with depth in the core. The blank for some of these samples cannot be neglected and would represent a pore water concentration of 50 ng/L for a 150 mL pore water sample. It is not certain to what extent contamination contributes to some of the deeper pore water results.

The sediment concentration of PCBs contrasts the pore water results in that the level of PCBs remains fairly constant

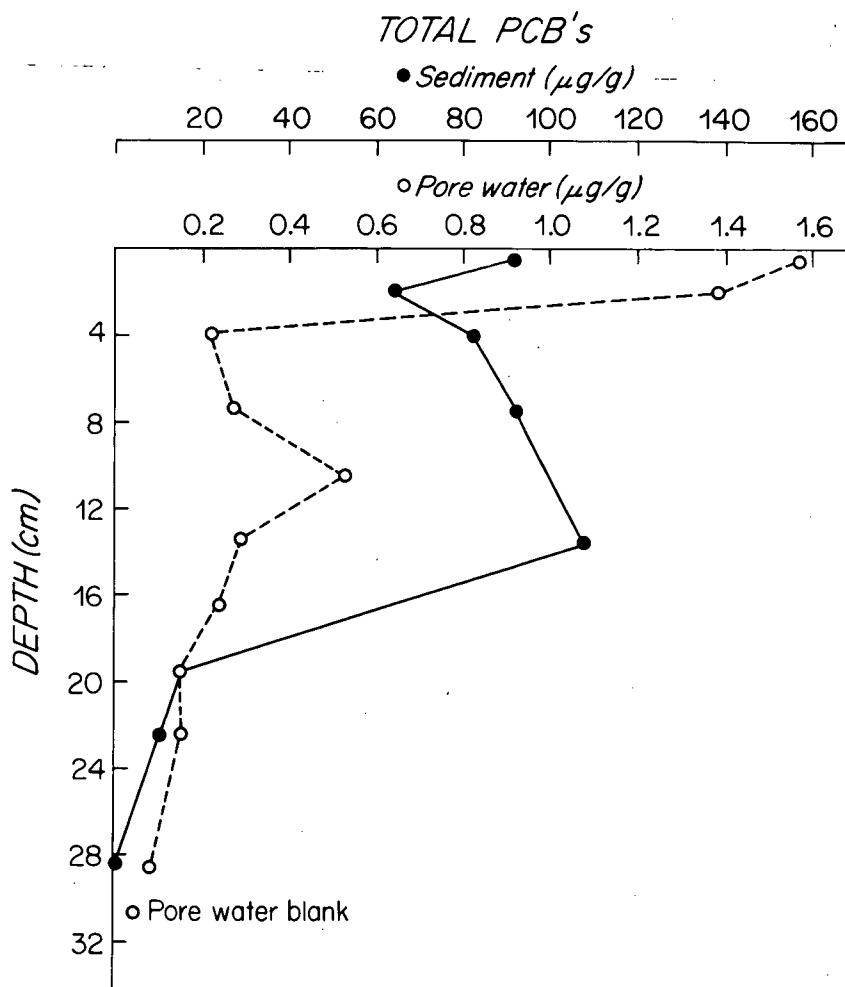


Figure 2. Total PCBs (Aroclors 1242 + 1254) in sediments and pore waters at Station 84.

(64 to 108 $\mu\text{g/g}$ total PCB) over the upper 15 cm before decreasing to levels nearly an order of magnitude lower in the region between 18 and 24 cm. The concentration of PCBs in the sediments at 27-30 cm decreases another two orders of magnitude to 0.10 $\mu\text{g/g}$. It is interesting to point out that a sediment accumulation rate of 1.7 cm/yr was calculated for a core at a nearby site using ^{210}Pb geochronology [26]. That sediment accumulation rate was for sediment which had presumably accumulated after 1966 when the hurricane barrier separating the inner and outer harbors was completed. Applying this rate to our core

gives a sediment accumulation of about 26 cm in the time since the construction of the hurricane barrier when the sedimentation rate in this area appears to have increased [26]. The marked drop in PCB concentration between 21-24 and 27-30 cm may either correspond to the changes in deposition corresponding to the construction of the hurricane barrier, or to an uncharacterized change in the source of PCB to the harbor.

The composition of individual chlorobiphenyls in the sediments is very similar to a mixture of Aroclor 1242 and Aroclor 1254. These two Aroclor mixtures were primarily used by the manufacturing plants in New Bedford along with Aroclor 1016 (Aroclors 1016 and 1242 are very similar in composition). This mixture of PCBs does not change appreciably with depth in the sediments which may indicate that the source of PCBs has remained fairly constant in composition over this time, and that there are not isomer specific diagenetic processes affecting the solid phase distribution of PCBs at this site.

The distribution of chlorobiphenyls in the interstitial waters are nearly identical to that in the sediments at the same depth. In other words, the apparent distribution coefficients, K'_d (equation 3), for all the individual compounds considered, generally vary by less than a factor of two. This constancy of K'_d over the wide range of K_{ow} s (Table I) exhibited by the different compounds is not expected if the observed distribution of PCBs represents equilibrium partitioning between the sediments and a dissolved phase in the pore water. In two-phase partitioning K'_d is equivalent to $foc K_{oc}$ (equation 1). Combining this relationship with equation 2, a predicted slope (a) of 0.72 to 1.0, and $\log K_{ow}$ values given in Table I, it is seen that K'_d should increase by two or more orders of magnitude from the dichlorobiphenyls to the less soluble hexa- and heptachlorobiphenyls. This is not the case, thereby suggesting that PCBs in the pore waters are not dissolved but associated with a filterable colloidal phase.

The profiles of K'_d with depth in the sediment for three chlorobiphenyls are given in Figure 3. The range of profiles indicates the similarity of compositions in the pore waters and sediments noted above. The values of K'_d for 153 increase from 4.8×10^4 at 1-3 cm to a high of 6.5×10^5 at 12-15 cm and then decrease with depth in the sediment. It is difficult to ascribe an explanation for these increases in K'_d with depth without further characterization of the interstitial water. A decrease in colloid concentration with depth would result in increased apparent distribution coefficients. The sediment hydrology (i.e. possible groundwater advection), and effect benthonic biota on the observed pore water concentrations are not known. A quantitative comparison of K'_d values for this core with predictions from two- and three-phase partitioning models is presented in more detail later in this chapter.

The results from the core at Station 67 provide a study which much more clearly illustrate the role of organic colloids in the partitioning of PCBs in coastal marine sediments [15]. Profiles of total PCBs, TOC, DOC, and K'_d s of selected iso-

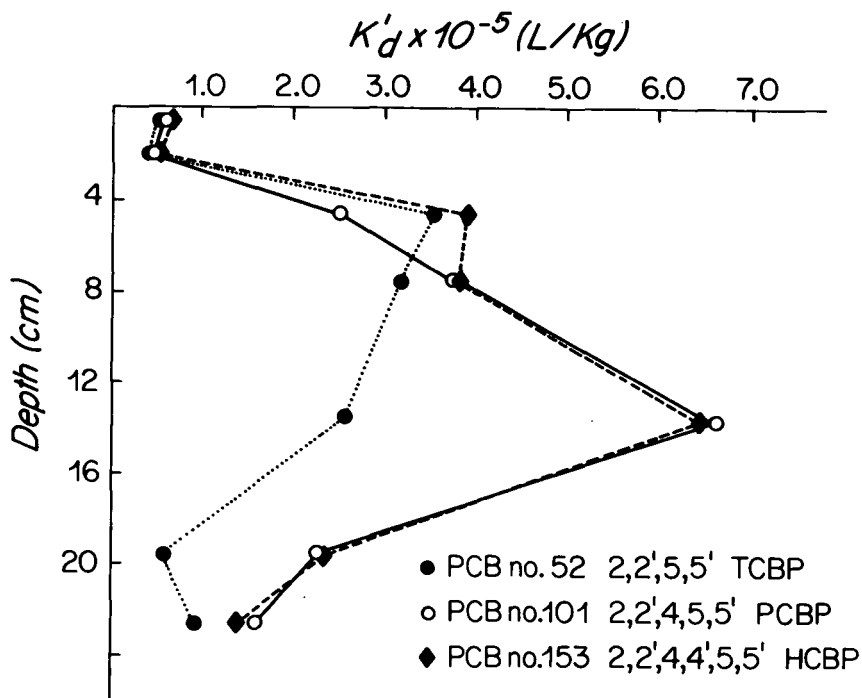


Figure 3. Depth profiles of K'_d for three chlorobiphenyls at Station 84.

mers are given in Table II. Pore water PCB concentrations are higher at this site, 1.31 to 20.1 $\mu\text{g/L}$, than at Station 84 although sediment concentrations are lower. The concentrations of PCBs in pore solution increase with depth over the upper 11 cm and remain high deeper in the core. Again, the composition of pore water PCBs is similar to the solid phase distribution. We have reported elsewhere [15] that the higher chlorinated, more hydrophobic chlorobiphenyls are slightly enriched in the pore waters and that K'_d actually tends to decrease with increasing K_{ow} . The profiles of K'_d for individual chlorobiphenyls decrease with depth over the upper 11 cm. These profiles of K'_d correlate well with the inverse of the DOC and pore water PCB profiles. It has been shown in other studies [27,28,29] that organic colloids can represent a high fraction of the DOC in interstitial waters of reducing sediments. Together, these observations suggest an important association of PCBs with organic colloids in the pore waters.

In the following section we further evaluate the partitioning results from these cores in terms of a three-phase partitioning model. Comparison of the data with model calculations based on predictions from laboratory experiments illus-

Table II. Profiles of TOC, DOC, Total PCBs, and K'_d s
of Selected Isomers at Station 67.

Depth	TOC	DOC	Total PCBs		$K'_d \times 10^{-3}$ (L/Kg)		
cm	%Org C	mg/L	Sediments ($\mu\text{g/g}$)	Pore Waters ($\mu\text{g/L}$)	Chlorobiphenyl no.:		
					<u>52</u>	<u>101</u>	<u>153</u>
0-3	6.06	14.4	16.6	1.31	12.3	11.6	—
3-5	5.23	17.4	16.0	3.61	4.11	3.63	3.42
5-7	3.74	27.7	14.6	4.72	2.84	2.17	2.00
7-9	4.98	40.3	16.0	9.97	1.68	1.34	1.25
9-11	4.40	47.9	21.6	20.1	1.32	0.950	0.746
11-13	4.14	32.6	24.6	12.7	2.36	1.68	1.48
15-17	4.02	39.2	33.0	13.8	3.08	2.31	1.90
17-19	4.74	55.1	27.8	14.8	2.45	1.59	1.48
19-21	4.98	42.0	30.7	14.9	2.04	1.72	1.62
21-23	5.96	87.0	30.3	13.6	1.73	1.78	1.92
23-25	5.68	50.9	26.1	12.3	2.68	2.03	1.74
25-27	4.78	81.4	27.4	9.68	3.31	2.63	2.51
27-29	4.86	43.7	27.3	8.37	4.88	3.33	2.73
29-31	5.33	54.2	25.2	11.0	3.51	2.66	2.29
35-41	4.75	41.4	13.4	8.18	1.67	1.93	1.53

trates the quantitative importance of organic colloids and serves as a basis for evaluating the assumptions in the model.

Partitioning Model for PCBs in Sediments

The aqueous sorption of neutral, hydrophobic organic compounds with sediments and soils involves nonspecific, noncompetitive interactions with the organic fraction of the sorbent [4,5,6,8]. The driving force of sorption is largely entropic having relatively low enthalpic contributions [5,8,30]. The solvent partitioning model proposed by Chiou and co-workers [5] incorporates these and other observations, and appears to explain laboratory studies of sorption quite well. Among the assumptions implicit in this model are that sorption is: 1) independent of both solute and sorbent concentration, 2) reversible, and 3) that all of the sorptive "volume" of the organic matter is accessible to solutes for sorption. Assumptions one and two are somewhat controversial [9,31,32,33,34] but are supported by some laboratory experiments [9,35]. The discrepancies may be largely attributable to an experimental artifact in centrifugation [9,30,34]. The third assumption is supported by the constancy of K_{oc} over a large range of f_{oc} [4,6].

Partitioning of hydrophobic organic compounds with sediment organic matter or octanol depends primarily on solute solubility in water [4,6,7,8] and to a lesser extent on solute incompatibility with water-saturated organic phases [8,36]. The ability of octanol-water partitioning to mimic sorption by sediment organic matter is demonstrated by the good correlations of $\log K_{oc}$ and $\log K_{ow}$ (equation 2) [4,6,7,8] and is presumably due to similar polarities of the water-saturated organic phases.

Although not studied to the same extent, organic colloids appear to behave as sorbents in a manner similar to sediment organic matter [10,11,12]. Wijayarathne and Means [12] have shown a dependence of $\log K_{oc}$ and $\log K_{ow}$ of polycyclic aromatic hydrocarbons (PAH) with estuarine colloidal organic matter which corresponds well with one previously observed for freshwater sediment organic matter. It was suggested that K_{oc} of colloids (K_{occ}) was several times that of sediments (K_{ocs}) but salinity differences in the two studies limit this comparison.

In natural waters dissolved PCBs will tend to approach equilibrium with both sediment and colloidal organic phases. At equilibrium, equations 1 and 3 can be combined to yield:

$$K'_d = \frac{f_{oc}^s K_{oc}^s D}{D + f_{oc}^c K_{oc}^c D} \quad (4)$$

where D is the dissolved concentration and f_{ocs} and f_{occ} are the fraction organic carbons of sediment and colloidal phases respectively. f_{occ} is some fraction, α , of the total measured

DOC, and it is further assumed for this model that $K_{ocs} = K_{occ}$. Equation 4 then becomes:

$$K'_d = \frac{f_{oc} s K_{oc} s}{1 + \alpha \text{DOC} K_{oc} s} \quad (5)$$

Comparisons of our sediment-interstitial water K'_d data and model predictions of K'_d from two-phase (equation 1) and three-phase (equation 5) partitioning models are presented in Figures 4 and 5. The three solid lines are two-phase predictions of $\log K'_d$ vs $\log K_{ow}$ and are based on measured f_{ocs} and experimentally determined $\log K_{oc}$ vs $\log K_{ow}$ relationships published by three workers [6,7,8]. Line 1 from Means et al. [6] is for a wide range of hydrophobic organic compounds including PAH and is nearly identical to a relationship reported by Karickhoff et al. [4]. Lines 2 [8] and 3 [7] are for chlorinated aromatic hydrocarbons and result in predictions of K'_d of PCBs which are significantly lower than line 1. Differences in the three correlations may be due to the different compound classes considered [7] or possibly to differences in experimental protocol.

Two other points need to be made in comparing these predictions to the data reported here. First, for the most part, these relationships are based on solutes with $\log K_{ow} < 6.0$ while the PCBs considered here have $\log K_{ows}$ ranging from 4.89 to 7.75. The validity of the extrapolations has not been adequately tested. Secondly, the effect of seawater ionic strength and major ion composition on sediment sorption has not been well studied. Seawater electrolytes may have effects on the activity of PCBs in both the aqueous and sediment organic matter phases. Salting-out of non-electrolytes has been well studied for smaller molecules [37,38] but good data for large chlorinated hydrocarbons are lacking. It can be assumed that increases in aqueous phase activity coefficients of PCBs will increase sorption (K_{oc}) by 0.1 to 0.4 log units, probably increasing with degree of chlorination. In the sediment organic matter phase, salinity increases could possibly change sorbate activity coefficients by affecting the conformation, charge density, or water content of the organic matter.

A model of three-phase partitioning (equation 5) is represented in Figure 4 by line 4. This curve assumes $f_{occ} = 10$ mg/L in the pore water at Station 84 at 1-3 cm. The major assumption is that both K_{ocs} and K_{occ} can be predicted by the regression defining line 1 ($\log K_{oc} = 1.0 \log K_{ow} - 0.32$). This assumption is somewhat arbitrary for the reasons stated above, but fits the data better than the other lines and does illustrate the effect of colloidal organic matter on the observed distribution of PCBs. The three-phase model adequately describes the constancy of $\log K'_d$ with increasing $\log K_{ow}$ for this range of compounds but underpredicts the magnitude of K'_d by about 0.8 log units. Two-phase partitioning predicted by line 1 overpredicts $\log K'_d$ for $\log K_{ow} > 6.0$, but under-

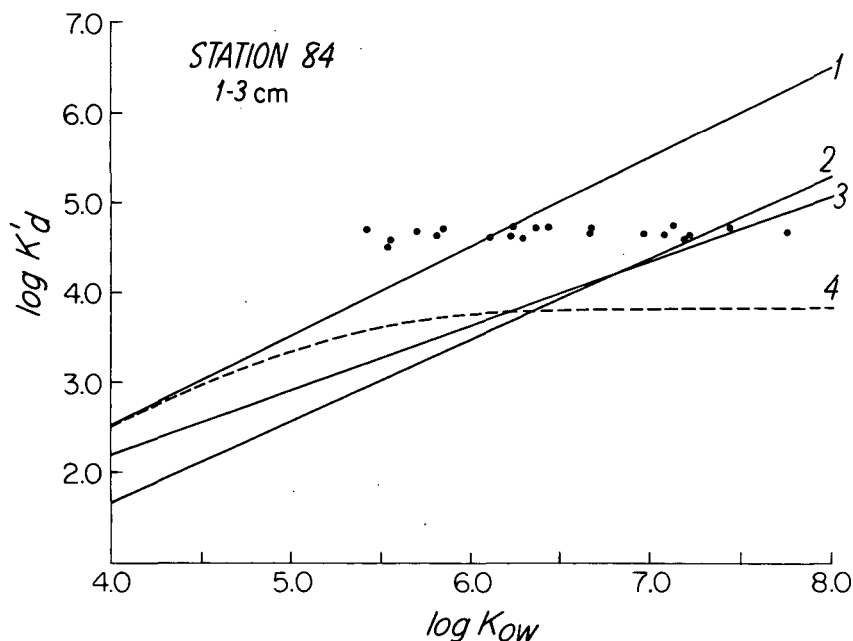


Figure 4. $\log K'_d$ vs $\log K_{ow}$ of individual chlorobiphenyls from 1-3 cm section at Station 84. Solid lines 1.(6), 2.(8), and 3.(7) are predictions of two-phase partitioning of PCBs based on laboratory experiments. Line 4. represents the three-phase partitioning model (Equation 5.) predicted using assumptions given in the text.

predicts K'_d in lines 2 and 3. Prediction of K'_d by all four lines becomes worse as K'_d increases with depth in the core (Figure 3). These high K'_d values cannot presently be explained. It is possible that processes such as diagenetic alteration of sediment organic matter and mineral precipitation in some aged sediments could "trap" sorbed PCBs and make them less accessible for aqueous desorption. There have been few desorption studies of sediments contaminated in the field.

Measured K'_d s of individual chlorobiphenyls at Station 67 are plotted for two representative depths in a similar manner (Figures 5a and b). The three-phase model curves incorporate measured values of DOC and assume $\alpha = 1$ in equation 5. These results demonstrate a surprisingly good fit of the data to the simple three-phase model, and clearly illustrate the effective lowering of K'_d from predictions based on two-phase partitioning. Results from 17-19 cm show the small decrease of $\log K'_d$ with increasing $\log K_{ow}$, which is apparent in all sediment depths at this site [15]. This trend of K'_d being higher for the lower chlorinated biphenyls may be the result of the smaller

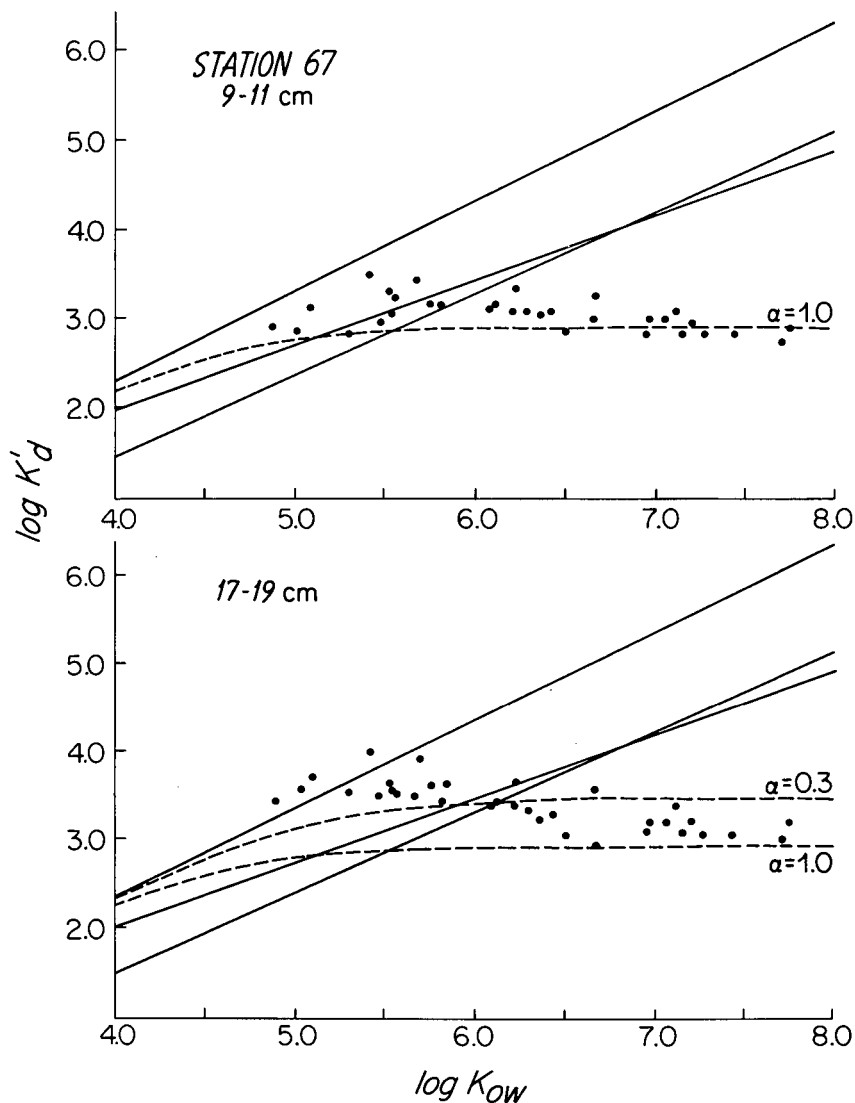


Figure 5. $\log K'_d$ vs $\log K_{ow}$ for two representative sediment intervals at Station 67. Model lines are the same as in Fig. 4. Figure b. illustrates the effect of assuming a lower α (0.3) in Equation 5.

compounds being able to access more of the sorptive volume of the sediment organic matrix. However there is little evidence of steric hindrance to sorption in other sediment sorption

studies, although sorption kinetics have been shown to be slower for larger more hydrophobic compounds [35]. There is evidence at Station 67 of microbial degradation of di- through tetra-chlorobiphenyls [15]. If this process occurs in pore waters at a rate comparable to sediment desorption, then measured K'_d may represent disequilibria and be higher than predicted.

Figure 5b shows the effect of assuming a lower colloid concentration ($\alpha = 0.3$) on model calculations. The calculation of α from equation 5 and the observed K'_d s of 101 for all sediment depths yield values of 0.223 to 0.967 and average 0.573. These estimates of organic colloid concentrations in pore waters are consistent with those operationally defined by ultrafiltration in other studies [27,28,29].

Water Column Partitioning Studies

The concentrations of total PCBs in the water column were five to ten times higher in the inner harbor samples at Station 81 than at Station 74 in the outer harbor (Table III). Large differences in concentration over the tidal cycle were not observed, nor was there a large gradient between surface and bottom water samples. CTD casts at both stations indicated that the water column was fairly well mixed at the time of sampling.

The concentrations of total PCBs are nearly evenly distributed between particulates and the filtrate or "dissolved" phases. However, the composition of PCBs in these two phases is very different. The more soluble chlorobiphenyls are enriched in the filtrate. This difference in composition is illustrated by the gas chromatograms of particulate and dissolved fractions of one sample (Figure 6). Not all of the peaks in

Table III. Tidal Cycle Concentrations of Total PCBs.

Sample	Particulates	Filtrate ng/L	Total
Incoming Tide			
Station 81, Surface	183	329	512
Station 81, Bottom	134	152	286
Station 74, Surface	28	52	80
Station 74, Bottom	22	28	50
Outgoing Tide			
Station 81, Surface	386	289	675
Station 81, Bottom	232	244	476
Station 74, Surface	27	36	63
Station 74, Bottom	30	41	71

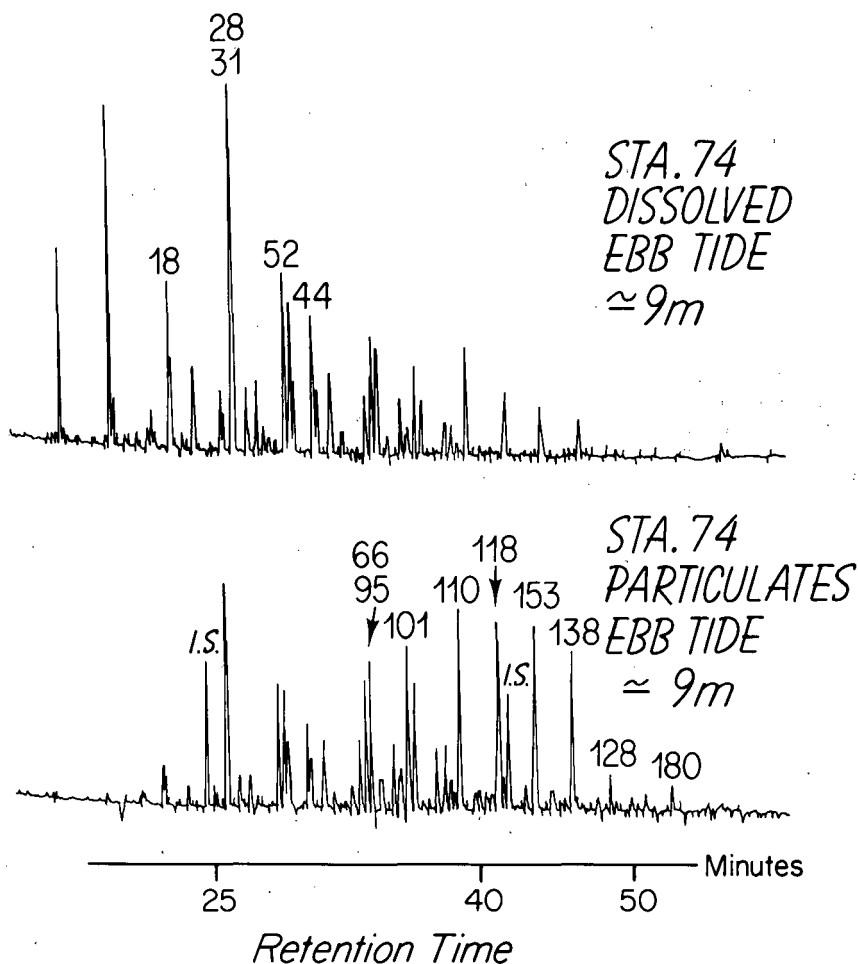


Figure 6. Capillary gas chromatograms of "dissolved" and particulate PCBs from New Bedford Harbor Station 74. Numbers are PCB numbers given in Table I. I.S.: internal standard.

the gas chromatograms are PCBs, some of which have been labeled with IUPAC chlorobiphenyl numbers (Table I). The trend of K'_d increasing with degree of chlorination or K_{ow} agrees with observed partitioning of PCBs in the Hudson River [39], Puget Sound [40], and Pacific Ocean [41], and is predicted by the models of two-phase partitioning described earlier.

Plots of $\log K'_d$ vs $\log K_{ow}$ for these eight water column samples provide a good comparison to the results from

sediment-interstitial water studies. Because measurements of suspended-solids concentrations and f_{ocs} were not made on the water samples, we have had to assume values in the range of those measured in an extensive survey of these properties in New Bedford Harbor [26], which covered tidal and seasonal cycles. Assumed values for suspended solids concentrations and f_{ocs} are 3.0 mg/L and 0.20 for surface samples, and 5.0 mg/L and 0.15 for bottom samples. These assumptions are probably valid within a factor of three and do not affect calculated slopes of $\log K'_d$ vs $\log K_{ow}$ presented later.

Figure 7 shows the increase of $\log K'_d$ with $\log K_{ow}$ for the surface sample at Station 81 during the incoming tide. K'_d increases from 1.8×10^4 for chlorobiphenyl 4 to 1.6×10^6 for 137. $\log K'_d$ parallels $\log K'_d$ predicted by line 1 for $\log K_{ow} \leq 6.1$ and then increases less rapidly for greater $\log K_{ows}$. The three-phase model depicted by line 4 assumes an f_{occ} of 0.25 mg/L, which is consistent with reported measurements made in coastal waters [42] and unpublished results from our own lab. The three-phase model calculations do show that reasonable assumptions of f_{ocs} and f_{occ} can explain the observed partitioning of PCBs and that, under these conditions, the quantitative role of organic colloids on observed K'_ds is minimal until $\log K_{ows}$ exceed 6.0. This is not the case in pore

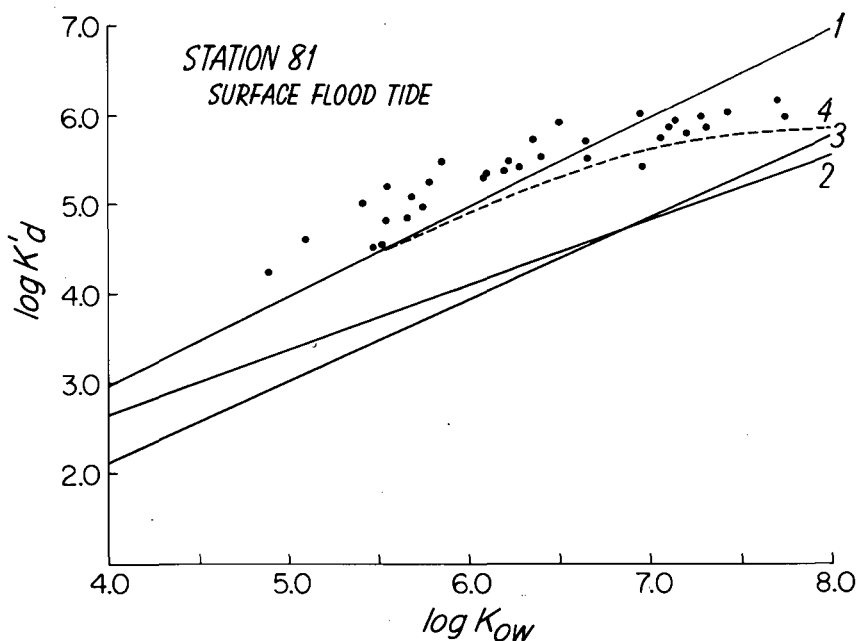


Figure 7. $\log K'_d$ vs $\log K_{ow}$ for Station 74 water column sample. Lines are as given in preceding figures with assumptions of f_{ocs} and f_{occ} given in the text.

Table IV. Regression Parameters of $\log K_{OC} = a \log K_{OW} + b$
for Tidal Cycle Stations 81 and 74.

Sample	a	b	r
Incoming Tide			
Station 81, Surface	0.589	2.39	0.912
Station 81, Bottom	0.498	3.07	0.870
Station 74, Surface	0.514	2.87	0.874
Station 74, Bottom	0.556	2.23	0.855
Outgoing Tide			
Station 81, Surface	0.534	2.95	0.916
Station 81, Bottom	0.526	2.88	0.916
Station 74, Surface	0.562	2.53	0.886
Station 74, Bottom	0.558	2.52	0.914
Including only $\log K_{OWs} \leq 6.11$			
Incoming Tide			
Station 81, Surface	0.879	0.75	0.853
Station 81, Bottom	0.579	2.58	0.690
Station 74, Surface	0.309	3.98	0.475
Station 74, Bottom	0.527	2.35	0.448
Outgoing Tide			
Station 81, Surface	0.860	1.12	0.863
Station 81, Bottom	0.640	2.21	0.740
Station 74, Surface	0.832	0.97	0.731
Station 74, Bottom	0.756	1.38	0.729
Predictions from Laboratory Experiments (6,7,8)			
Line 1. Means et al. (6)	1.00	-0.32	0.990
Line 2. Chiou et al. (8)	0.904	-0.78	0.994
Line 3. Schwarzenbach and Westall (7)	0.72	0.49	0.975

waters or in other organic rich waters where organic colloid concentrations can be many times higher.

The linear regression parameters, a and b, from equation 2 have been calculated. In Table IV, we first list these parameters derived from considering all data points, and compare them to those from the three model lines. It is seen that the slopes do not differ much between samples, 0.50 to 0.59, and are lower than the laboratory derived slopes of 0.72 to 1.0. The $\log K_{OC}$ intercepts are quite high and their absolute values are dependent on the assumptions of POC that we have made. However, we interpret both of these observations to be consistent with the expected curvilinearity of this relationship when considering chlorobiphenyls with high K_{OW} . The linear regressions have

also been calculated by only considering data for isomers with $\log K_{ow} \leq 6.11$ where two-phase partitioning is expected to be more nearly approximated. There are increased errors associated with the correlations derived from the smaller data sets. In the six samples which exhibit the least scatter in data, the slopes are increased closer to those predicted from two-phase partitioning. There are also corresponding decreases in b for those samples.

Departure from equilibrium partitioning can be expected to be greater in the water column than in sediment pore waters, where the latter can be considered a much less open and dynamic environment. The main source of PCBs to the water column in New Bedford Harbor is probably resuspension of contaminated sediments. A desorptive approach to equilibrium in the water column would result in higher $\log K'_d$ and the observed slope of $\log K'_d$ vs $\log K_{ow}$ would be increased if desorption kinetics are slower for the more hydrophobic chlorobiphenyls [35]. Disequilibria caused by volatilization will also tend to increase observed partitioning and the effect on the slope would depend on the relative rates of vapor exchange and desorption kinetics of the individual isomers. Within the limitations of both the data here and models of seawater partitioning, it is not possible to distinguish whether equilibrium partitioning of PCBs is established in the water column. We suggest that the results do show that dissolved PCB phases are more important in observed water column distributions as is predicted by our simple three-phase partitioning model.

CONCLUSIONS

It is proposed that the observed partitioning of individual chlorobiphenyls between particulates and filtered water samples is controlled not only by solution-sediment sorption but also by partitioning between solution and organic colloids which can represent a high fraction of DOC in interstitial waters. We have presented the following evidence that most PCBs measured in the interstitial waters at these two sites are bound to organic colloids:

- 1) The compositions of PCBs in the pore water at both stations are very similar to those in the sediments. If sediment-solution partitioning were the only processes involved, the more soluble, lower chlorinated PCBs would have lower observed K'_d s and thus would be enriched in the pore solution. We have found this to be the case in the water column where colloids may be present in much lower concentrations. At Station 67, K'_d actually decreases with increasing degree of chlorine substitution. This trend is the opposite of what solubility considerations predict for a two phase system.
- 2) Pore water concentrations in surface sediments are elevated at both stations. At Station 67 the concentrations of all PCBs increase with depth and K'_d s decrease over the upper

11 cm. DOC concentrations increase over this same interval.. We believe these trends are due to sorption of PCBs onto organic colloids whose concentrations are reflected by the DOC. The high values of K'_d at Station 84 and increase of K'_d with depth at this site are not easily explained.

- 3) A simple three-phase equilibrium partitioning model can describe the observed partitioning of PCBs at Station 67 and does predict the constancy of $\log K'_d$ vs $\log K_{ow}$ at Station 84.

The high concentrations of PCBs in pore waters provide a relatively large and potentially mobile pool of PCBs. Pore water PCBs may be taken up by benthic organisms in contact with the sediments or be transported back into the water column by diffusion or mixing of the sediments. There is little knowledge concerning the role of PCB-colloid associations in the bioavailability of PCBs or in the mobility of PCBs in sediments, which in light of these results are important considerations for understanding the biogeochemical cycling and long term fate of PCBs in coastal sediments.

A three-phase partitioning model for PCBs in the water column predicts a greater importance of dissolved PCBs due to much lower concentrations of organic colloids. The observed partitioning approaches predictions based purely on sediment-solution sorption when the effect of organic colloids on high K_{ow} compounds is considered. A more critical evaluation of organic matter-seawater partitioning and also of the kinetics of processes which may affect disequilibria, are necessary to further evaluate these sorption models.

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