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**Joint Program
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DOCTORAL DISSERTATION

**The Role of Colloidal Organic Matter
in the Marine Geochemistry of PCBs**

by

Bruce J. Brownawell

June 1986

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**Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543**

and

**The Massachusetts Institute of Technology
Cambridge, Massachusetts 02139**

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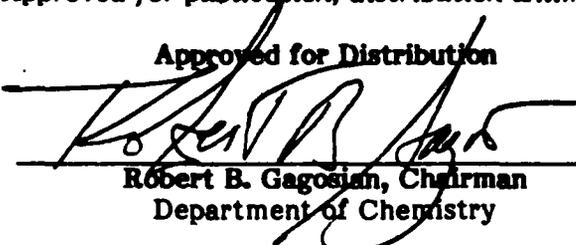
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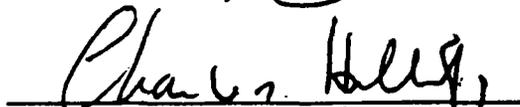
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**Robert B. Gagosian, Chairman
Department of Chemistry**


**Charles D. Hollister
Dean of Graduate Studies**

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THE ROLE OF COLLOIDAL ORGANIC MATTER
IN THE MARINE GEOCHEMISTRY OF PCBs

by

BRUCE J. BROWNAWELL

B.S., DePaul University, 1980

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
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at the

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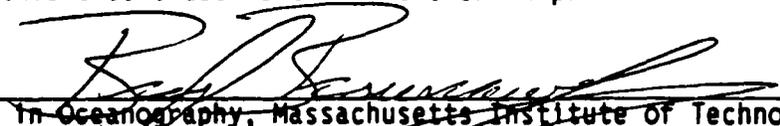
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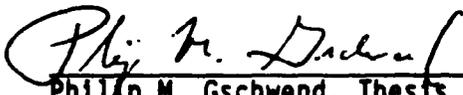
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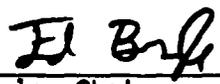

Joint Program in Oceanography, Massachusetts Institute of Technology
and Woods Hole Oceanographic Institution, and the Department of
Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute
of Technology

Certified by


John W. Farrington, Thesis Supervisor, and


Philip M. Gschwend, Thesis Supervisor

Accepted by


Edward Boyle, Chairman, Joint Committee for Chemical Oceanography,
Massachusetts Institute of Technology/Woods Hole Oceanographic
Institution.

ABSTRACT

Polychlorinated biphenyls (PCBs) were used as model hydrophobic organic compounds (HOC) to study physical-chemical processes which affect the speciation and fate of HOC in coastal environments. The focus of this study is on the sorption of PCBs with colloidal organic matter in seawater, and the influence of this process on the distribution of PCBs in coastal sediments. Laboratory and field experiments were used to make quantitative estimates of PCB-organic matter sorption, and to test predictions of three-phase equilibrium models.

A static headspace partitioning method was developed to measure the sorption of several individual chlorobiphenyls with colloidal organic matter enriched from coastal seawater by hollow fiber ultrafiltration. This technique directly measured the dissolved phase fugacity of PCBs in experimental bottles, and avoided uncertain separation techniques often used in isolating various chemical phases. Colloidal organic carbon normalized partition coefficients (K_{oc}) were determined from linear sorption isotherms, and increased from 1.9×10^4 (L/Kg) for 2,4'-dichlorobiphenyl to 3.5×10^5 for 2,2',3,4,5'-pentachlorobiphenyl. Sorption tended to increase with increasing octanol-water partition coefficients (K_{ow}) of the sorbate, and values of K_{oc} were within a range of those reported in other experimental sorption studies with sediments and dissolved humic substances. Experimental partitioning results support the hypothesis that HOC-organic colloid sorption is similar to HOC sorption by sediment organic matter.

PCBs were measured in the interstitial waters and sediments of three box cores obtained from New Bedford Harbor and Buzzards Bay, Massachusetts. The three sites studied had a wide range of sediment PCB concentrations, and reducing conditions provided environments containing high concentrations of colloidal organic matter. Dissolved organic carbon (DOC) and total sediment organic carbon (TOC) were measured in two cores to test the role of organic matter on the observed partitioning of PCBs. PCB concentrations, particularly those of less soluble chlorobiphenyls, were highly elevated in interstitial waters compared to water column concentrations at all three sites. The measured apparent distribution coefficients (K'_d) of individual chlorobiphenyls did not increase with hydrophobicity (K_{ow}) and indicate that a large fraction of PCBs in interstitial waters must be sorbed to organic colloids. A three-phase equilibrium sorption model, in which dissolved PCBs are in a dynamic equilibrium with colloidal and sediment organic matter, accounts for many aspects of the field data. There is good agreement of observed partitioning at New Bedford Station 67 and Buzzards Bay Station M with model calculations based on predictions derived from laboratory experiments of HOC sorption with sediments and organic colloids, but model calculations underpredict K'_d at Station 84 in New Bedford Harbor.

The sediment-interstitial water results were contrasted with a study of PCB partitioning in the water column at two stations in New Bedford Harbor. Measured K'_{ow} s of PCBs in the water column increased with K_{ow} and approached predictions based on two-phase, water-suspended particulate partitioning when the effect of organic colloids on high K_{ow} -PCBs was considered.

The effect of a mobile colloid-sorbed PCB phase on a general sediment transport model was evaluated. Enhanced migration of highly sorbed PCBs can be included in an apparent diffusivity term when steady-state conditions exist. Model calculations showed that diffusive migration of PCBs in typical coastal sediments is minor over 20 yr timescales. Comparisons with the ^{210}Pb profile provided additional evidence that the solid phase depth profiles of PCBs at Station M were controlled by biological mixing of the sediments and not pore water migration. Predictions based on results from Station M indicate that sediment diffusion and bioturbation of colloid-sorbed PCBs in surface sediments could provide a potentially important flux of PCBs across the sediment-water interface to the water column in Buzzards Bay.

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In memory of my father, and all the quiet mornings we shared
watching the fish jump next to our lines.

CHAPTER 1

GENERAL INTRODUCTION

INTRODUCTION

There are many reactions and transport processes which control the distribution and biogeochemical cycling of organic compounds in marine and freshwater environments (Duursma and Dawson, 1981; Schwarzenbach and Imboden, 1983/1984). The physical and physical-chemical associations of an organic compound in various biotic and abiotic phases, and the partitioning between those phases will strongly influence the types and rates of processes affecting it. The partitioning of organic compounds between dissolved and many possible abiotic phases can be considered analogous to chemical speciation of inorganic ions. The speciation of a biogenic or pollutant organic compound will depend on its source, time history, and properties of the compound, ecosystem, and abiotic phases present.

The isolation of various phases is often fraught with difficulties. Traditionally, filtration of natural waters with 0.2-0.45 μm membrane filters or nominal 1.0 μm glass fiber filters has been used to operationally separate dissolved and particulate phases. In many instances standard filtration methods are not adequate to determine truly dissolved phases for many organic compounds. For example, measured free amino acids in filtered, interstitial waters of marine sediments may be from the intracellular pools of filter-

able bacteria or may be released from bacteria as cells are disrupted during pore water extraction or filtration (Henrichs, 1980; Henrichs et al., 1984).

Sorption of hydrophobic organic compounds (HOC) to dissolved organic matter (DOM) may significantly affect their speciation (Means and Wijayarathne, 1982; Carter and Suffet, 1982). HOC encompass a broad range of compounds which have low solubilities in water but are relatively soluble in several nonpolar organic solvents. They tend to accumulate at aqueous-nonaqueous interfaces and are favorably partitioned into organic phases (Tanford, 1979). Molecular structures of HOC may contain both hydrophobic and hydrophilic portions. HOC which have highly polar functional groups (particularly those which are potentially ionized in natural waters) can interact with particulate material or dissolved organic matter by multiple mechanisms, including hydrogen-bonding, chemisorption, and ion-exchange (Means et al., 1982; Karickhoff, 1984; Westall and Schwarzenbach, 1985). Except where noted otherwise, this study is primarily concerned with the aqueous sorption of nonpolar HOC, such as PCBs, whose sorption is controlled by a set of non-specific interactions in both aqueous and sorbent phases.

It is the macromolecular organic matter or sometimes microparticulate fraction of DOM which acts as a sorbent for HOC (Hassett and Anderson, 1979, 1982; Means and Wijayarathne, 1982; Carter and Suffet, 1983; Wijayarathne and Means, 1984a; Chiou et al., 1986). The macromolecular organic matter in natural waters has been studied by a variety of techniques. Unfortunately, the composition and fraction of the total DOM collected is dependent on the isolation procedure used (Thurman, 1985; Carlson et al., 1985). High molecular weight DOM has been typically isolated as "humic-type" substances

(Thurman 1985), by ultrafiltration (Carlson et al., 1985) or by gel permeation chromatography (Hassett and Anderson, 1979). The extraction procedures and terminology defining aquatic humic substances have been borrowed from the soil science literature and are not entirely satisfactory for describing marine macromolecular organic matter because of differences in source, composition, and function (Pocklington, 1977). Nonetheless, the use of humic-substance terminology is retained when referring to some of the other studies cited in this report. The DOM isolated by all these procedures are of size between 0.001 and 1.0 μm in size, which are the dimensions which have been defined as colloidal (Vold and Vold, 1966).

Effects of colloidal organic matter on the speciation of HOC has been well documented. Sorption of a wide range of HOC with colloidal organic matter has been shown to decrease the apparent sorption of fatty acids to bentonite (Meyers and Quinn, 1973) in seawater, and to similarly decrease the sorption of dieldrin to aquifer sands (Boucher and Lee, 1972) and 2,2',5,5'-tetrachlorobiphenyl and cholesterol to suspended particulate matter (Hassett and Anderson, 1982) in freshwaters. DOM has been shown to influence the biological availability of hydrocarbons and polycyclic aromatic hydrocarbons (PAH) (Boehm and Quinn, 1976; Laversee et al., 1983; McCarthy et al., 1985), the base hydrolysis rate of the octyl ester of 2,4-D (Perdue and Wolf, 1982), and the volatilization rate of 2,2',5,5'-tetrachlorobiphenyl (Hassett and Milicic, 1985). Gschwend and Wu (1985) have modelled the partitioning of PCBs with freshwater sediments in batch sorption experiments in terms of three-phase equilibrium sorption where PCBs are sorbed to non-settling organic "colloids" in the supernatant. The effect of colloids in batch sorption

experiments had also been hypothesized by Voice et al. (1983) and Chiou et al. (1984). Using results presented here, Brownawell and Farrington (1985,1986) have interpreted an important influence of colloidal organic matter on the distribution of PCBs in coastal marine sediments. It is apparent from these and other studies that a quantitative estimate of HOC-organic colloid partitioning is essential in understanding the biogeochemical cycling and speciation of many HOC.

The aqueous sorption of HOC with natural sediments and soils has received a great deal of study and has resulted in quantitative treatments of sorption in the case of relatively nonpolar HOC (Karickhoff et al., 1979; Chiou et al., 1979, 1983; Means et al., 1980 and references therein; Schwarzenbach and Westall, 1981). These studies relate properties of both the solutes and sorbents to sorption and have been interpreted by these workers within the conceptual model of organic phase partitioning controlling the sorption of HOC to natural sediments (Chiou et al., 1979, 1983). It is expected on the basis of existing studies that the mechanism of HOC-organic colloid sorption is similar to that of sediment organic matter. However, a corresponding understanding of the important factors controlling HOC-colloid sorption is still lacking. Quantitative estimates of sorption of HOC to colloids are complicated in part by the difficulty and uncertainties involved in accurately determining HOC speciation experimentally.

In this dissertation, polychlorinated biphenyls have been used as model HOC to study the role of organic colloids in the geochemistry of HOC in a coastal environment. PCBs are useful field tracers and experimental probes to study these processes for the following reasons:

1.) Individual chlorobiphenyls exhibit a wide range of aqueous solubilities (Mackay et al., 1980a; Bruggeman et al., 1982) and octanol-water partition coefficients (K_{ow}) (Woodburn et al., 1984; Rapaport and Eisenreich., 1984) which bracket the properties of many anthropogenic and biogenic organic compounds of environmental and biogeochemical interest. It was expected, from the basis of previous work (Means and Wijayarathne, 1982; Hassett and Anderson, 1982) that compounds of this range of solubilities would be significantly influenced by organic colloids in environments having high concentrations of organic matter such as interstitial waters of reducing marine sediments.

2.) PCBs are relatively resistant to chemical and biological breakdown (NAS, 1979) which simplifies many aspects of field interpretation and experimental design.

3.) Low detection limits and high analytical resolution afforded by capillary gas chromatography with electron capture detection make possible the determination of low concentrations of individual chlorobiphenyls in environmental samples.

Numerous PCB measurements have also been made in the aquatic environment because of concern for their environmental effects and distributions (Risebrough et al., 1976; NAS, 1979). PCBs and other stable chlorinated hydrocarbons may potentially provide valuable tracers for the study of deep ocean biogeochemical processes (Farrington and Westall, 1986) and have been actively used as model HOC in the study of partitioning and transport processes in coastal (Dexter and Pavlou, 1978a), riverine (Bopp, 1979; Bopp et al., 1981), and lacustrine environments (Eisenreich et al., 1983; Eadie et al., 1983; Baker et al., 1985).

Both laboratory experiments and field measurements were performed in this study to quantitatively assess the role of colloidal organic matter on the marine geochemistry of PCBs. Experimental techniques were developed to measure partition coefficients of individual chlorobiphenyls with coastal marine organic colloids. The role of colloidal organic matter was further studied by analyzing sediment/pore water distributions of PCBs in three box cores from New Bedford Harbor and Buzzards Bay, Massachusetts. This is an area heavily impacted by PCB contamination (Weaver, 1984; Farrington et al., 1985) and sediment/pore water and particle/seawater partitioning of PCBs yields insights into the role of organic colloids on the speciation and transport of HOC in the marine environment. Field measurements of PCB partitioning also provide valuable tests of models of organic matter sorption or partitioning models derived from experimental studies.

The following review provides some basis for understanding sorption of nonpolar HOC with both sediments and colloidal organic matter, and the properties of solutes, sorbents, and the environment which are important. These review sections are intended to establish a framework from which models of HOC-organic matter sorption can be evaluated and field and experimental results can be interpreted.

SORPTION OF HOC WITH SEDIMENTS AND SOILS

It is useful to begin with a review of sediment or soil sorption of HOC because some results from organic colloid-HOC sorption studies suggest that

there are similarities in the mechanisms of sorption with colloidal organic matter and with sediment organic matter (Wijayarathne and Means, 1984b; Carter and Suffet, 1983; Garbarini and Lion, 1985). An understanding of sediment sorption is essential in studying the sediment biogeochemistry of PCBs and interpreting the role of colloidal organic matter on the observed distributions of PCBs in this study.

Sorption of HOC with natural sediments and soils has been widely studied, due to its recognized importance in removal, transport, and biogeochemical cycling of HOC in waste waters, groundwaters, and natural surface waters. The vast majority of work in this area have been laboratory studies of equilibrium sorption with freshwater sediments and soils. Outside the scope of this discussion is a review of an expansive soil science literature concerning pesticide and herbicide binding to soils (Stevenson 1972; Pionke and Chesters, 1973; Farmer, 1976). Some important early contributions of soil scientists to understanding the aqueous sorption of HOC are recognized by Karickhoff (1981). Furthermore, many herbicides and pesticides used in those studies are highly functionalized, and mechanisms involved in their sorption may differ from nonpolar HOC considered in this study (Hassett et al., 1981; Means et al., 1982; Mingelgrin and Gerstl, 1983; Karickhoff, 1984).

Equilibrium sorption studies have typically used batch sorption experiments, but a soil/sediment column chromatography approach has also been used (Schwarzenbach and Westall, 1981). Adsorption isotherms of nonpolar HOC on a wide range of soils and sediments exhibit linear sorption extending to equilibrium solute concentrations 0.30 - 0.95 of their solubilities (Chiou et

al., 1979; 1983; Karickhoff, 1981). This linear sorption behavior can be expressed as:

$$C_s = K_p C_d \quad (\text{eqn. 1-1})$$

where C_s and C_d are sorbed (typically $\mu\text{g/g}$) and dissolved concentrations ($\mu\text{g/ml}$), and K_p is the linear partition coefficient. Sorption isotherm data have often been fit or interpreted in terms of Freundlich or Langmuir adsorption isotherms. The Freundlich equations correspond to linear sorption when $1/n \approx 1$:

$$C_s = K_d C_d^{1/n} \quad (\text{eqn. 1-2})$$

where K_d equals the sorption constant and $1/n$ is an empirical constant. If data fit this equation ($n > 1$), it is likely but unproven that there are multiple mechanisms involved in sorption or that specific sorption sites are heterogeneous (Adamson, 1976). Many polar HOC, particularly those which can significantly hydrogen bond, exhibit non-linear sorption which can be described by the Freundlich equation (Hassett et al., 1981; Mingelgrin and Gerstl, 1983).

The Langmuir adsorption isotherm can be described as:

$$C_s = a C_d / (1 + b C_d) \quad (\text{eqn. 1-3})$$

or

$$\theta = b C_d / (1 + b C_d)$$

where a and b are constants and θ is the fraction of adsorption capacity occupied by adsorbate (Adamson, 1976; Mingelgrin and Gerstl, 1983). This model assumes that there are specific adsorption sites, and adsorption is limited to a monolayer. At $b C_d \ll 1$, eqn. 1-3 reduces to linear sorption. However, the isotherm curvature predicted from Langmuir type adsorption is not generally observed for nonpolar HOC even at near saturation levels of adsorbate (Chiou et al., 1979, 1984).

Linear partition coefficients have been determined for a wide range of nonpolar HOC on many sediments and soils. In some studies a large suite of well characterized soils and sediments of widely varying properties were used to study sorbent properties affecting sorption (Karickhoff et al., 1979; Means et al., 1980 and references therein; Schwarzenbach and Westall, 1981). These and other studies have demonstrated that K_p is well correlated with the organic carbon content of the sorbent and that normalizing K_p to the fraction organic matter (f_{oc}) of the sorbent provides a good predictor of sorption, K_{oc} , such that:

$$C_s = f_{oc} K_{oc} C_w \quad (\text{eqn. 1-4})$$

where $K_{oc} = K_p/f_{oc}$. K_{oc} often reduces the variation in sorption, which may vary by two orders of magnitude in K_p , to $\pm 20-30\%$ when $f_{oc} > 0.001$ (Karickhoff, 1981; Schwarzenbach and Westall, 1981). At $f_{oc} < 0.001$ the clay or mineral content of the sorbent begins to dominate sorption although K_p remains relatively low (Schwarzenbach and Westall, 1981). At higher f_{oc} , organic matter seems to dominate sorption. This is due to the much larger sorption capacity of organic matter.

K_{oc} increases with the hydrophobicity of HOC. $\log K_{oc}$ correlates well with $\log S$ (solubility) (Karickhoff et al., 1979; Chiou, 1979; Means et al., 1980) when the solubilities of compounds which are solids at room temperature (such as all the PCBs at 25°C) are corrected to the super-cooled liquid reference state. This is because the heat of fusion contributes to the solubility but not the hydrophobicity of the solute (Karickhoff, 1981; Chiou et al., 1982, 1983). $\log K_{oc}$ is also well correlated with $\log K_{ow}$:

$$\log K_{oc} = a \log K_{ow} + b \quad (\text{eqn. 1-5}).$$

where a and b are constants (Karickhoff et al., 1979; Means et al., 1980). Log K_{ow} is also linearly correlated with the super-cooled liquid log S (Chiou et al., 1981; Miller et al., 1985). It is shown in these studies that K_{ow} is primarily influenced by the aqueous phase activity coefficient γ_w , where by a Raoult's Law convention $\gamma_w = 1/SV_w$ and S is the aqueous molar solute solubility and V_w is the molar volume of solution. These and other results strongly suggest that sediment organic matter sorption like octanol water partitioning of HOC is the result of weak solute/water interactions (compared to water/water interactions) and is not due to strong or specific sorbate/sorbent interaction. Octanol-water partitioning of HOC has also provided a valuable predictor and model organic phase for biological uptake (Mackay, 1982) and other biological structure activity relationships (Leo et al., 1971; Hansch, 1980). The relationship between log K_{oc} and log K_{ow} (eqn. 1-5) has been experimentally determined by several workers with different compound classes. Some of these calibrations are shown in Table 1-1. It has been argued by Shellenberg et al. (1984) that the variability in a and b is primarily determined by the compound classes considered and only slightly affected by the nature of the natural sorbents. Given this interpretation, these correlations should strictly be applied to compounds whose structures and log K_{ows} are similar to the compounds on which the correlation is based. Another problem is that most of these correlations are based on HOC with log K_{ow} ranging from about (1.5 - 2.5) to (5.0 - 6.5), while some HOC of interest have higher log K_{ow} . Reported log K_{ow} for chlorobiphenyls range from 4.5 to 9.6 (Bruggeman et al., 1982). In order to further evaluate estimation methods of K_{oc} or K_p for sediments, it is useful to discuss some aspects of mechanistic sorption models of HOC. 5 1282

Table 1-1. Some reported correlations of $\log K_{oc}$ and $\log K_{ow}$ for different compound classes. Linear regressions are of the form $\log K_{ow} = a \log K_{oc} + b$. The equation of Chiou et al. (1983) has been converted from an organic matter based partition coefficient (K_{om}) to K_{oc} by assuming that the ratio of organic matter to organic carbon in Woodburn soil is 1.70.

Reference	Compounds considered	a	b	r ²
Karickhoff et al. (1979)	8 PAH and 2 chlorinated hydrocarbons	1.00	-0.21	1.00
Means et al. (1980)	22 compounds of various PAH and substituted aromatic compounds	1.00	-0.317	0.980
Schwarzenbach and Westall (1981)	12 alkyl and chloro-benzenes	0.72	0.49	0.95
Chiou et al. (1983)	12 aromatic hydrocarbons mostly chlorobenzenes and PCBs	0.904	-0.549	0.996

Organic Matter Partitioning Model

In a series of papers Chiou and co-workers (1979, 1981, 1983, 1984, 1985) and Karickhoff (1981, 1984) have proposed and discussed the merits of an organic phase partitioning model to describe sediment organic matter sorption of HOC. In this model, the uptake of HOC by sediments is a process of dissolution into an amorphous organic geopolymer, rather than physical adsorption. This model of sorption assumes equilibrium partitioning and involves other assumptions which can be readily tested.

Equilibrium between dissolved and sorbed phases is established when the fugacities of HOC are equal in both phases. Fugacity can be related to concentration by a fugacity capacity constant Z (e.g.: $f_s = C_s/Z_s$, where f_s is the fugacity of sorbed HOC) (after Mackay, 1979). Z is a function of temperature, pressure, and the properties of both the HOC and the phase considered. The dissolved phase and the sorbed phase are then related by:

$$C_s = (Z_s/Z_w)C_w \quad (\text{eqn. 1-6})$$

When Raoult's Law convention for activity coefficients (γ) is used and the sorbing phase is an organic solvent, such as octanol, the following expression is derived

$$C_o = \frac{\gamma_w^* V_w^*}{\gamma_o^* V_o^*} C_w \quad (\text{eqn. 1-7})$$

γ_w^* and γ_o^* are the activity coefficient of solute in water saturated with the organic phase (octanol here) and in octanol saturated with water, respectively (γ_w corresponds to the solute activity coefficient in pure water). Similarly V_w^* and V_o^* are the respective molar volumes of mutually saturated solvents. It is important to note that activity

coefficients and fugacity capacity constants are, in general, concentration dependent. Equations (1-6) and (1-7) only predict linear sorption or partitioning if both γ_w^* and γ_o^* or γ_w^*/γ_o^* are constant.

Constant γ is a valid assumption in dilute solutions of nonpolar HOC (Leo et al., 1971). This assumes no significant solute-solute interactions and that solute-solvent (sorber) interactions are non-specific and weak. HOC with high solubility in either phase may change the solvent characteristics of that phase. HOC such as PCBs (with low solubilities) are expected to behave ideally and to exhibit linear partitioning in an organic phase partitioning model.

Using the above convention Chiou et al. (1982) and Miller et al. (1985) have examined the effects of solubility and γ_o^* on K_{ow} . From eqn. (1-7) and the definition of solubility the following equation is easily derived (Chiou et al., 1982):

$$\log K_{ow} = \log SV_o^* - \log \gamma_o^* + \log (\gamma_w^*/\gamma_w) \quad (\text{eqn. 1-8})$$

As mentioned earlier the variation in $\log K_{ow}$ is controlled by $\log S$ which for HOC tends to decrease as molecular size of the solute increases (Miller et al., 1985). Changes in $\log \gamma_o^*$ are of secondary importance and γ_o^* also tends to increase with molecular size. γ_o^* may increase from near ideality ($\gamma_o^* = 2$) for high solubility HOC, to values which could be 20 times or more greater for some polychlorinated biphenyls (Chiou et al., 1982; Miller et al., 1985). It is of interest to note that from consistent data sets of Bruggeman et al. (1982) and Miller et al. (1985), it appears that the average γ_o^* for chlorinated aromatic compounds and PCBs are two to five times higher than for aromatic hydrocarbons and PAH. This indicates that

chlorinated aromatic compounds are not as well accommodated in octanol as are alkyl or unsubstituted PAH, and that predictive $\log K_{oc} - \log S$ relationships should be used with caution when based on dissimilar compound classes.

The last term in eqn. (1-8) accounts for the effect of organic co-solutes on the solubility of HOC in the aqueous phase. The effect of dissolved octanol (4.5×10^{-3} M at saturation or about 430 mg Org C/L) on K_{ow} has been shown to be very small (Chiou et al., 1982; Miller et al., 1985), but may have measurable effects on the solubility of low solubility HOC. Chiou et al. (1982) provide evidence the $\gamma_w^*/\gamma_w = 2.6$ for DDT. This would correspond to a "log K_{oc} " octanol in the water phase of 3.78 which is about 20-100 times lower than K_{oc} s reported by Carter and Suffet (1983) for DDT with colloidal organic matter. This and other data suggest that low molecular weight DOC has a small effect on the speciation of HOC in natural waters.

The value of the octanol-water system as a model for natural sorbent-water partitioning is illustrated by the good correlations of $\log K_{oc}$ and K_{ow} given in Table 1-1. Linear free energy relationships of this type have poor correlations when the nonpolar phases are quite different (Leo et al., 1971). With a long hydrocarbon chain, a hydroxyl moiety, and a relatively high water content at saturation (2.3 M) octanol is evidently able to readily accommodate a wide range of HOC. These properties of octanol may make it similar to natural geopolymers which have even higher water contents at saturation. However, the Raoult's Law convention for equating activities on a mole fraction basis breaks down when considering natural organic geopolymers like sedimentary humic-kerogen or dissolved colloidal organic matter because

of the large size differences of solutes and polymers (Chiou et al., 1983, Chiou, 1985). Chiou and co-workers (1983, 1985) have applied Flory-Huggins Theory for the dissolution of HOC in an amorphous polymeric phase. The interpretation from application of this model again suggests that solute incompatibility in the organic phase (increasing γ_o^*) is of secondary importance to γ_w^* in affecting K_{oc} . Flory-Huggins Theory has the advantage of predicting γ_o^* from the water content of the saturated polymer, the size difference of solute and polymer, and properties of the solute and polymer which are combined in a Flory-Huggins interaction parameter χ , which can be given according to Chiou et al. (1983) as:

$$\chi = \chi_s + (V/RT)(\delta - \delta_p)^2 \quad (\text{eqn. 1-9})$$

χ_s is the excess entropic contribution of the solute polymer interaction and depends on the characteristics of the three-dimensional structure of the polymer. V is the solute molar volume and δ and δ_p are the solubility parameters of solute and polymer. Use of Flory-Huggins theory is presently of limited applicability in predictions of HOC-organic matter sorption and such treatments are considered preliminary. For example, it is undetermined to what extent properties of natural sediment or colloidal organic matter of widely varying sources or structures (size and solvent properties) can influence γ_o^* and K_{oc} for a given HOC. Uncertainties involving the characteristics of natural organic matter and the solubility parameters of many HOC presently limit the usefulness of Flory-Huggins theory for predicting K_{oc} . However, this treatment does yield semi-quantitative understanding of γ_o^* and the other factors which affect K_{oc} .

An organic matter partitioning model helps explain many aspects of HOC sediment sorption. These can be summarized as follows:

1) HOC-sediment sorption can be described by linear sorption, up to near saturation levels of HOC. This is expected for nonpolar HOC in dilute solutions where there are no strong specific solute-solvent interactions. Adsorption models predict isotherm curvature at high relative saturation levels (e.g., eqn. 1-3). Note that saturation in the aqueous phase implies saturation in the sorbed phase.

2) No competitive effects on sorption are apparent with binary HOC solutions (Chiou et al., 1983, 1985). Instead HOC behave as ideal solutes partitioning between water and an organic phase.

3) The one-to-one correspondence of K_p and f_{oc} is consistent with organic matter providing a sorptive phase where partitioning is volume dependent, rather than surface area dependent.

4) HOC-organic matter partitioning is closely predicted from linear free energy relationships, which is expected from partitioning in other solvent systems (Leo et al., 1971). The good correlations of $\log K_{oc} - \log K_{ow}$ relationships are reasonable considering the solvent properties of octanol and sediment organic matter (Freeman and Cheung., 1981; Chiou et al., 1983). However, these predictive equations should be more accurate when applied to similar compound classes.

5) There are small associated enthalpies of sorption involved in sediment HOC sorption as calculated from using the Clausius-Clapeyron equation (Chiou et al., 1979, 1985). Calculated ΔH_{ads} are less exothermic than those found for physical adsorption of HOC (Chiou and Manes, 1974). The difference in the

molar heats of solution in a partitioning process are expected to be more positive where ΔH can even be endothermic.

There appear to be small effects of both temperature and ionic strength on the partitioning of HOC with organic matter. Leo et al. (1971) have tabulated the temperature dependence of solvent-water partitioning for several solutes and solvents. They find an average $\Delta \log K/\text{deg.}$ of 9.0×10^{-3} and the temperature dependence can be positive or negative, which indicates that partitioning will vary by less than a factor of two over relevant environmental temperature ranges. Temperature may affect the kinetics of sorption by affecting diffusion into sediment aggregates and the stability of those aggregates. Wu and Gschwend (1986) found negligible temperature effects on sorption kinetics.

A more complicated problem is the effect of ionic strength or salinity on organic matter partitioning. Electrolytes in solution may effect the activity coefficient of HOC in both the aqueous and organic phase. The effect of salts on the aqueous activity coefficient on pure water solubility can be described by the empirical Setschenow equation:

$$\log (S^{\circ}/S) = K C \quad (\text{eqn. 1-10})$$

where S° and S denote solubilities of HOC in pure water and salt solution of molar concentration C , respectively. The constant K depends upon the electrolyte and the HOC involved. The salt effects of mixtures of salts in seawater were shown to be additive (Gordon and Thorne, 1967). Although the 'salting out' constant for NaCl is lower than that of the other major salts in seawater, its effect dominates the salting out of naphthalene because of its high mole fraction in seawater (Gordon and Thorne, 1967). The salting out coefficient is predicted to increase with molar volume of the solute in both

McDevit-Long (McDevit and Long, 1952) and scaled particle (Masterson and Lee, 1969) theories. The solubility of biphenyl is decreased by about 35% at seawater salinity (Paul, 1952). Salting out constants for larger HOC such as PAH are now becoming available and do not increase greatly with increasing solute molar volume (Whitehouse, 1984). The effect of salinity of the solubility of PCBs is further examined in Appendix 1.

The possible effect of ionic strength and major ion chemistry on the organic phase is uncertain. If increased ionic strength acts to reduce the water content of the organic phase, it might enhance the compatibility of larger HOC with the organic phase, resulting in greater partitioning. On the other hand, increased hydrophobic interactions within the sediment organic matter might result in impeded diffusion of HOC to hydrophobic sorption sites. The effect of salinity on organic matter is probably not great, but there are no published studies relating the effect of seawater on organic matter partitioning, or comparing marine and freshwater sediments. Karickhoff et al. (1979) found that 20 g/L NaCl produced a 15% increase in K_{oc} for pyrene on pond sediment.

Unsolved Problems with Organic Phase Partitioning

There are several open or unexplained problems concerning HOC-sediment sorption which have been raised in the literature. These problems concern: 1) the apparent sorbent mass dependent partitioning of HOC, 2) the variability of K_{oc} s and $\log K_{oc} - \log K_{ow}$ relationships reported by different workers, and 3) the non-reversibility of sorption reported in some studies. Many of these problems are probably related, and some may or may not have

arisen due to difficulties involving experimental techniques. However, they are discussed separately below.

Sorbent Mass Dependent Partitioning

Several groups of investigators have reported that K_p or K_{oc} decreases with suspended solids concentration in batch adsorption experiments (Lotse et al., 1968; O'Connor and Connolly, 1980; Di Toro et al., 1982). In some cases this effect on K_p is more than an order of magnitude. If this phenomenon is real, it implies that either increasing solids concentration changes the structure or solvency of water and affects γ_w negatively (which is presently thought unjustifiable), or that particles tend to "communicate" to a greater extent thus blocking potential adsorption sites. This communication could be the result of increased aggregation. This blockage of sorbent sites is contrary to the organic phase partitioning model of HOC sorption described above for equilibrium sorption. However, Wu and Gschwend (1986) have shown that sorption/desorption kinetics of HOC are slower as aggregate size increases. Hence, kinetics and the possible blockage of sorbent sites or volumes are possible explanations for observed effects.

Recent studies have shown that centrifugation after equilibration in typical batch sorption studies is inadequate to remove suspended solids or colloidal organic matter from the supernate (Gschwend and Wu, 1985; Voice and Weber, 1985). In this case an apparent K_p (K'_d) is observed:

$$K'_d = C_s / (C_d + C_c) \quad (\text{L/Kg}) \quad (\text{eqn. 1-11})$$

where C_s , C_d , and C_c are sediment-sorbed, dissolved, and colloid- (or non-settling particle) sorbed concentrations of HOC. The prime in K'_d

reflects the incorporation of multiple equilibrium constants in the observed distribution ratio by analogy to pseudo reaction rate constants in chemical kinetics. The affect of C_c on K_d is easily modelled if both sorbent phases are described by linear organic phase partitioning. Substituting eqn. (1-4) into eqn. (1-11) yields:

$$K'_d = \frac{f_{oc_s} K_{oc_s}}{1 + f_{oc_c} K_{oc_c}} \quad (\text{eqn. 1-12})$$

where the subscripts s and c denote sediment and colloid, and in this case f_{oc_c} is the fraction of organic carbon in the supernate (mg Org C/L). $K_{p,true}/K'_d$ is then equal to $1 + f_{oc_c} K_{oc_c}$. Therefore batch sorption experiments are expected to yield $K_{p,true}$ (after Gschwend and Wu, 1985) when K_{oc_c} is small or when sorbent organic matter is sufficiently removed from the supernate. Typically, batch sorption experiments are run at total suspended solids concentrations on the order of 10^3 mg/L. Gschwend and Wu (1985) found that the ratio of organic colloids (or non-settling particulate organic matter) was about 5% of the total organic matter concentration for their particular conditions. For a typical sediment f_{oc} of 0.02 this would correspond to an f_{oc_c} of 1 mg/L. It can be seen that for a very hydrophobic solute like 2,2',4,4',5,5'-hexachlorobiphenyl used in the studies of Di Toro et al. (1982, 1985) ($\log K_{oc,true}$ was recently estimated as 6.61 by Di Toro et al. (1985)) under the above conditions $K_{p,true}/K'_d$ could be on the order of 4, which is within a factor of two of effects observed. This calculation assumes $K_{oc_c} \approx K_{oc_s}$.

In two studies (Gschwend and Wu, 1985; Bowman and Sans, 1985) constant K_{oc_s} were observed when care was taken to minimize sorbing materials in the

supernate, and losses to wall adsorption were considered. The explanation given for apparent sorbent mass dependent partitioning given by eqn. (1-10) cannot easily explain adsorbent mass effects in experiments reported by Voice et al. (1983) and modelled by Voice and Weber (1985). These results show greater influence of solids concentrations for chlorobenzene ($\log K_{ow} = 2.84$) and naphthalene ($\log K_{ow} = 3.36$) than for more hydrophobic compounds. Furthermore, the results and model of Gschwend and Wu (1985) predict an asymptotic approach to K_p , true as solids concentration decreases. Because of the important implications of the model Voice and Weber (1985) use to explain these data, a simple calculation illustrates that the data may be due to an experimental artifact caused by incomplete phase separation. These authors report $\log K_{oc}$ on the order of 2.7 to 2.9 for chlorobenzene, and 3.2 to 3.6 for naphthalene at their highest solids concentration. These values are on the order of $\log K_{ow}$ and are compared to $\log K_{oc}$ of 1.68 reported for chlorobenzene (Chiou et al., 1983) and 2.94 for naphthalene (Karickhoff, 1981). Thus their lowest $\log K_{oc}$ values are on the high end. A calculation of the fraction HOC sorbed (f_s) at a solids concentration of 20 mg/L (where the dependence of K_p on decreasing solids is quite steep) and the high solids concentration K_p s given above can be made:

$$f_s = \frac{1}{1 + 1/(K_p \text{ SS} \times 10^{-6})} \quad (\text{eqn. 1-13})$$

where SS is suspended solids concentration (mg/L), f_s is then on the order of 4.0×10^{-4} for chlorobenzene and 1.6×10^{-3} for naphthalene. These estimates of f_s are high if literature values of K_{oc} reported above are used instead. Such low values of f_s make analytical measurement of the

sorbed concentration (C_s) nearly impossible, and good mass balances are misleading. In this case, C_s can not be determined by difference because f_s is so small. When C_s is determined by filtration (Voice and Weber, 1985) relatively small amounts of water and associated solutes which sorb to a glass fiber filter can provide a large error when K_p and the total solids concentration are small. For example, in the experiments described above, K_p is about 20 for chlorobenzene and the total amount of suspended solids in the low solids case is 0.5-1.0 mg. If 50 to 100 mg of water (with solutes) are sorbed to the filter, then C_s (and K_p) is overestimated by 3.5 to 11 times. It is also likely that even low K_{ow} HOC will significantly sorb to glass fiber filters when compared to the amount sorbed to 0.5 to 1 mg of suspended sediment. Both of these effects will be effectively masked as K_p and SS increase. This potential artifact, if unrecognized in experimental design, will lead to adsorbent mass effects similar to those observed in this case, and might also explain anomalous mass dependent partitioning reported by Oliver (1985).

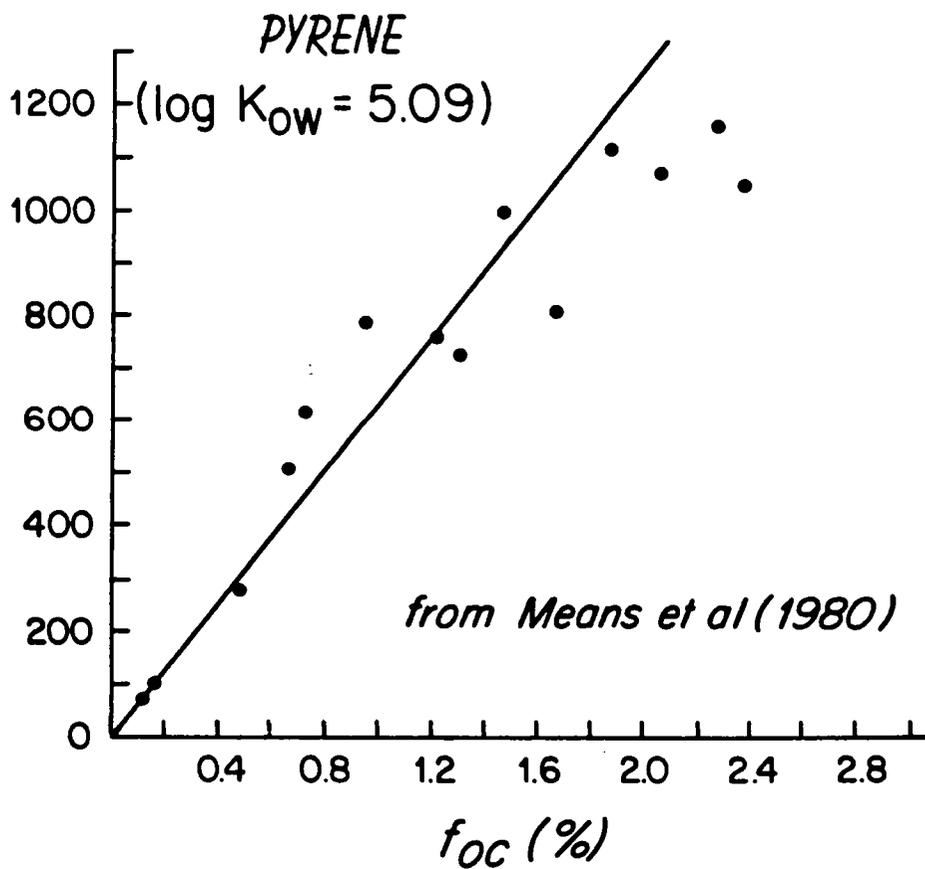
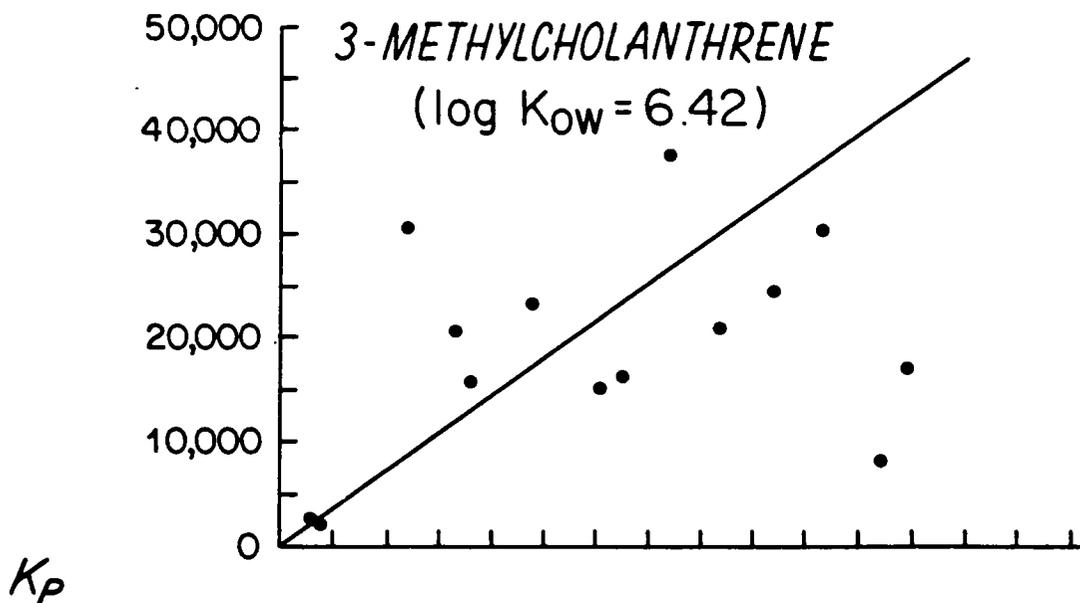
In summary, adsorbent mass dependent partitioning could be the result of aggregation which could kinetically hinder sorption or block surface sorption sites. It is more likely that incomplete separation of phases, and poor experimental design are responsible for many instances of observed solids effects. The work of Garbarini and Lion (1985) shows no effect of solids concentration on the sorption of toluene with soil organic matter and dissolved humic acid. This study directly measured the dissolved phase fugacity and avoided potential artifacts described above.

The Constancy of K_{oc}

Understanding the variability of K_{oc} for HOC on different substrates is of obvious importance in predicting their speciation in aquatic environments. Values of K_{oc} reported in the literature often vary by more than a factor of ten. Careful review of the literature suggests that the variability in K_{oc} is generally low for nonpolar HOC which have $\log K_{ow} < 5.0-5.5$. An example of this variability is shown in Figure 1-1, which are sorption data replotted from Means et al. (1980). Linear partition coefficients were determined on a wide range of sediments and soils, in which f_{oc} varied by a factor of about 20. The slope of K_p vs. f_{oc} provides an average K_{oc} . A single K_{oc} predicts the partitioning well for pyrene with a relative standard deviation of 19%. Partitioning of 3-methylcholanthrene is less well predicted by a constant K_{oc} and ranges by a factor of 17. This is a worst case scenario as other very hydrophobic PAH used in this study have somewhat lower ranges of K_{oc} but still have high relative standard deviations. Karickhoff (1981) and Schwarzenbach and Westall (1981) also report that partitioning of low K_{ow} -HOC can be well described by a constant K_{oc} .

There are at least three reasons for increased scatter in K_{oc} for larger, more hydrophobic compounds. The first is that the potential artifacts of incomplete phase separation becomes significant as $\log K_{oc}c$ increases above 5 for typical experimental conditions. Secondly, batch sorption experiments are typically equilibrated for 24 hours, which may not be sufficient to attain equilibria with less accessible organic matter. Sorptive uptake and release is thought to be a diffusion controlled process into porous sediment aggregate (Karickhoff, 1980, 1984; Wu and Gschwend, 1986) or a

Figure 1-1. Plot of K_p vs f_{oc} for pyrene and 3-methylcholanthrene with 14 sediments and soils. Data replotted from Means et al. (1980). Solid lines indicate the average K_{oc} for all sorbents.



polymeric organic gel (Freeman and Cheung, 1981). This diffusion is impeded by sorption and path length. Characteristic times for sorptive equilibria are inversely related to K_{oc} and increase as aggregate size increases (Karickhoff, 1980; Karickhoff and Morris, 1985; Wu and Gschwend, 1986). Karickhoff (1980) has reported that 35 to 60% of sorptive uptake of two to four ring PAH occurred in minutes, but that a slower component of sorbed chemical could take days to weeks for complete equilibration. The studies above indicate that for HOC with $\log K_{ow} > 5$ sorption may be kinetically retarded such that characteristic sorption times on some sediments can be on the order of weeks to months. Because continued sorptive uptake is slow after several hours, equilibrium conditions may easily be assumed falsely. This effect would be expected to give low K_{oc} values for sediments with high f_{oc} and long diffusive paths (large aggregate sizes).

Finally, a third explanation for K_{oc} variability relates to the structure and polarity of sediment organic matter. Freeman and Cheung (1981) have related the partitioning and desorption of HOC in sediment organic matter to the solution of solutes in a gel, where partitioning can be described as:

$$\ln K_{oc} = A - BL + (V/RT)f(\delta) \quad (\text{eqn. 1-14})$$

where A and B depend on pore structure within the "humic-kerogen" gel, L is the size of the solute, V is the solute molar volume, and $f(\delta)$ is a solubility parameter function which predicts the solute partitioning between solvent (water in this case) and organic matter phases. This model suggests that the size of the solute and the polymeric network of the sediment organic matrix could exclude solutes from sorption sites (or volumes) into which smaller solutes may have access. This effect would be similar to gel

permeation or size exclusion chromatography. Size exclusion from sorption sites, or alternatively steric constraints on inward diffusion of HOC in sediment organic matter aggregates could explain some K_{oc} variability for large solutes. The magnitude of this possible effect is uncertain, but might explain why the order of K_{oc} is reversed for some solutes when compared on different sorbents (Means et al., 1980; Landrum et al., 1984).

The problems associated with measurements and correlative estimation of K_{oc} for HOC with high K_{ow} is well illustrated in Table 1-2, which summarizes literature values of $\log K_{oc}$ for individual polychlorobiphenyls and also their reported $\log K_{ow}$ s. Figure 1-2 graphically illustrates $\log K_{oc}$ vs. $\log K_{ow}$ and compares them to predicted values based on three correlations given in Table 1-1. The data tend to fall into two populations. Points 1-7 are determinations made in two laboratories and are well described by line number 2 which is a correlation partially based on four of these values. The other values of K_{oc} are primarily the unpublished determinations by Shian-chee Wu and Philip M. Gschwend (personal communication). In these latter experiments, care was taken to reduce the effect of supernatant colloids. The higher K_{oc} values of these points could be the result of a reduced colloid effect. However, the variability of K_{oc} for PCBs on different sediments and soils has not been determined. There is evidence of curvature in the $\log K_{oc}$ at high $\log K_{ow}$. Even though colloid concentrations can be reduced, they are not eliminated in the studies of Gschwend and Wu (1985). Low concentrations of colloids in batch sorption experiments could explain the observed effects. It is not known whether the dependence of $\log K_{oc}$ on $\log K_{ow}$ can be expected to remain linear at

Table 1-2

PCB K_{oc} s with Sediments and Soils

Pt. No.	Chlorine Substitution	(PCB No.) ^a	Study	$\log K_{ow}$ (Refs.) ^b	$\log K_{oc}$
1	2-	(1)	Chiou et al. (1983)	4.50 ± 0.09 n=4 (2,3,5,8) ^c	3.46
2	2,2'-	(4)	"	4.90 ± 0.10 n=3 (2,3,5) ^c	3.91
3	2,4'-	(8)	"	5.11 ± 0.02 n=3 (1,2,5)	4.12
4	2,4,4'-	(28)	"	5.68 ± 0.06 n=3 (1,3,5)	4.61
5	2,4'-	(8)	Hague and Schmedding (1975)	4.50 ± 0.09	4.13
6	2,2',5,5'-	(52)	"	6.05 ± 0.23 n=3 (1,3,7)	4.90
7	2,2',4,4',5,5'-	(153)	"	7.36 ± 0.43 n=3 (1,2,3)	5.57
8	2,2',4,4',6,6'-	(155)	Karickhoff et al. (1979)	7.00 ± 0.61 n=3 (3,6,8)	6.08
9	2',3,4-	(33)	Gschwend and Wu (1985 and unpublished data)	5.57 (1)	5.25
10	2,2',5,5'-	(52)	"	6.05 ± 0.23	5.69
11	2,2',4,5,5'-	(101)	"	6.49 ± 0.48 n=5 (1,2,3,4,8)	5.79, 5.93 ^d
12	2,2',4,4',5,5'-	(153)	"	7.20 ± 0.48 (1,2,3,4)	6.16
13	2,2',3,4,5,5',6	(185)	"	7.93 (3)	6.18, 6.28 ^d

^aIUPAC numbers for chlorobiphenyl identification.

^bThe reported error is one std. deviation for $n > 3$ b-References are the following: 1) Rapaport and Eisenreich (1984), 2) Woodburn et al. (1984), 3) Bruggeman et al. (1982), 4) Chiou et al. (1977), 5) Chiou et al. (1983), 6) Karickhoff et al. (1979), 7) Chiou et al. (1985), 8) Miller et al. (1985).

^cValue of reference 1) rejected for being $> 4 \sigma$ from the mean

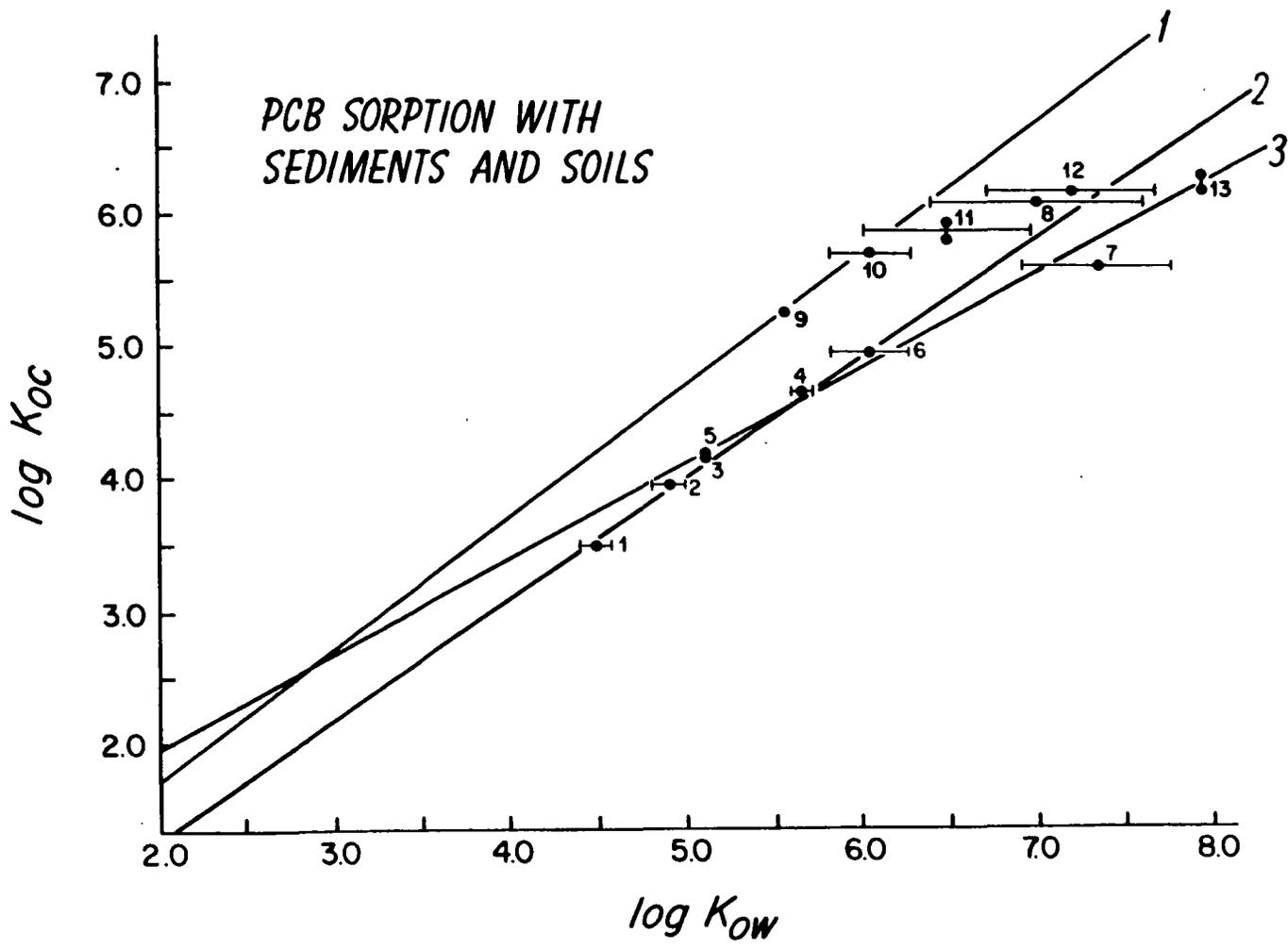
^d K_{oc} s reported on 2 different sediments.

$\log K_{ow} > 6$. Chiou (1985) reports curvature in the log of the trioleon-water partition coefficient at $\log K_{ow} > 5.5$. A decreased effect of K_{ow} on K_{oc} might be the result of increased solute incompatibility in the organic matter (greater than that found in octanol) or steric constraints on the sorption of HOC in polymeric organic matter.

Figure 1-2 and Table 1-2 illustrate another critical problem in understanding and predicting sorption of HOC. There is a large error in comparing literature reports of $\log K_{ow}$ for HOC having $\log K_{ow} > 6.0$. Experimental measurements of K_{ow} for these compounds are very difficult (Leo et al., 1971) and careful examination of the data in Table 1-2 does not yield insight into any determinant errors associated with any of the laboratories or techniques used. The use of K_{ow} in predicting K_{oc} for very hydrophobic compounds is probably still better than using aqueous solubilities. Water solubilities of PCBs have larger reported variability (Mackay et al., 1980a). The measurements of solubility are often complicated by very small aggregates or crystals of undissolved compound. Solubilities determined by the coupled column liquid chromatographic technique of May et al. (1978) yield results which are consistent with batch solubility measurements and may overcome aggregate problems.

In summary, there are several possible sources for variability found in K_{oc} . Inaccurate determinations of K_{oc} can be caused by incomplete phase separations, insufficient equilibration times, or faulty experimental design. Real variability in K_{oc} caused by differences in sorbent phases is difficult to ascertain because of the aforementioned experimental problems. Errors both in K_{oc} and K_{ow} do not permit a good evaluation of estimation methods based on $\log K_{oc} - \log K_{ow}$ relationships. Despite these limitations, it appears

Figure 1-2. Literature values of $\log K_{oc}$ for PCBs with sediments and soils vs $\log K_{ow}$. Data points and errors associated with $\log K_{ow}$ are numbered and correspond to those given in Table 1-2. Three solid lines refer to predicted $\log K_{oc}$ - $\log K_{ow}$ relationships based on three of the correlations given in Table 1-1: line 1 (Means et al., 1980); line 2 (Chiou et al., 1983); line 3 (Schwarzenbach and Westall, 1981).



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from Figure 1-2 that K_{oc} can be estimated within a factor of ten or so. For HOC with $\log K_{ow} > 6$, further understanding of sorption with natural sediments will require experimental methods which do not involve phase separations as well as more accurate estimates of HOC physical properties such as K_{ow} .

Sorption Reversibility

A partitioning model for HOC-organic matter sorption implies that sorption is reversible. Several studies have reported non-reversible sorption or hysteresis of "adsorption"-desorption isotherms (Di Toro et al., 1982; Wildish et al., 1980; Pierce et al., 1974). Isotherm hysteresis could easily be the result of incomplete equilibration during either the forward or reverse sorption process. If the forward reaction is not complete, sorbate will tend to diffuse both back to solution and into the sediment-organic matter aggregate during the desorption process. Such an effect would produce non-reversible sorption isotherms when desorption is not complete. Several studies have now shown that adsorbed HOC can be completely recovered by gas purging or column leaching experiments (Karickhoff, 1980; Schwarzenbach and Nestal, 1981; Karickhoff and Morris, 1985; Oliver, 1985; Wu and Gschwend, 1986). Gschwend and Wu (1985) have discussed how incomplete phase separation can lead to non-singular sorption isotherms and might explain the careful experiments of Di Toro et al. (1982).

The studies cited above have shown that HOC which are sorbed to sediments after laboratory equilibration can be completely desorbed if sufficient time is allowed. The situation with HOC sorbed to sediments which have subsequently "aged" or have been diagenetically transformed in the environment

might be much different. The possibility that chemical or biochemical transformations of sediment organic matter, or even mineral precipitation might effectively "lock" HOC into sorbed phases for indefinite timescales is untested. Oliver (1985) measured desorption of chlorinated HOC from contaminated lake sediments and found that 39 to 65% of sorbed chemical (determined by solvent extraction) was released after 40 days. No general conclusions can be made from this study in terms of sorbate or sorbent effects on desorption.

The gel partition model for HOC sorption discussed above (Freeman and Cheung, 1981) predicts that desorption from the gel will depend on the interactions of solvent with the gel. Solvents which are soluble in the gel and cause swelling act to promote desorption. Alternatively, it might be expected that increasing ionic strength or salinity could lead to a partial collapse of the gel, thereby impeding the desorption of sorbate. Wildish et al. (1980) report increased hysteresis of desorption isotherms when PCBs "adsorbed" in distilled waters were then desorbed in water of increasing salinity. Further study of the extent and kinetics of desorptive processes are necessary to predict HOC speciation and fate.

SORPTION OF HOC WITH COLLOIDAL ORGANIC MATTER

The study of HOC sorption with colloidal organic matter has received relatively little attention until quite recently. Early studies showed natural marine DOM could apparently increase the solubility of n-alkanes and isoprenoid hydrocarbons in seawater (Boehm and Quinn, 1973), and that

dissolved humic substances solubilized phthalate esters and DDT (Matsuda and Schnitzer, 1971; Wershaw et al., 1969). It has been only in the last few years that quantitative experimental studies of HOC-organic colloid sorption have been reported (Means and Wijayarathne, 1982; Carter and Suffet, 1982). However, from a number of studies conducted in the last few years several generalizations can be made regarding HOC-organic colloid sorption.

1) The high molecular weight or colloidal fraction of DOC is primarily responsible for changes in the speciation of HOC. Very high concentrations of octanol and phenoxyacetic acid have been shown to increase the solubility of DDT to a small extent (Chiou et al., 1983, 1986), but low molecular weight co-solutes do not have a measurable effect on γ_w for more soluble HOC (Miller et al., 1985; Chiou et al., 1986). Measured effects are many times higher for high molecular weight (colloidal) organic matter. Gel permeation chromatography has shown that HOC can elute with high molecular weight DOC (Hassett and Anderson, 1979; Landrum et al., 1983; Wijayarathne and Means, 1984a), providing strong evidence that HOC are physically sorbed to hydrophobic sites of colloidal organic matter.

2) Sorption isotherms of HOC with colloidal organic matter indicate linear partitioning (Carter and Suffet, 1982; Wijayarathne and Means, 1984b) and solute competition for sorption was not observed (Chiou et al., 1986). This suggests that the mechanism involved is probably similar to sorption of HOC with sediment organic matter. The results of Landrum et al. (1984) suggest that desorption rates of HOC from organic colloids must be very rapid. Fluorescent quenching techniques suggest that sorption of PAH with dissolved humic acids is complete in 5-10 minutes (McCarthy and Jimenez, 1985). These

results are supported by the work of Hassett and Milicic (1985) and are reasonable considering the high surface to volume ratio of colloidal material.

3) Some studies suggest that there is a great deal of variability in K_{oc} depending on the type and source of colloidal organic matter. Carter and Suffet (1983) report a tremendous range of K_{oc} for DDT determined on humic and fulvic acids which were collected from different sources. Means and Wijayarathne (1982) report a factor of 8 range in the K_{oc} of atrazine with estuarine colloidal organic matter collected from different stations in the Patuxent and Choptank Rivers. Carter and Suffet (1983) and Chiou et al. (1986) found large differences in the sorption of DDT and other HOC with humic and fulvic acids from different sources. In both studies it was found that humic substances extracted from soils had greater sorption capacities than dissolved humic substances isolated from ponds and rivers. It was also observed that humic acids had correspondingly higher sorption capacities than fulvic acids. These studies suggest that molecular weight and polarity are important in determining the sorption capacity of colloidal organic matter. Chiou et al. (1986) found that sorption decreased as the oxygen content and presumably the polarity of humic substances increased. Aquatic humic acids have higher average molecular weights ranging from 1,000 to much greater than 10,000 compared to fulvic acids which have reported molecular weights ranging from 500 to 5,000 (Thurman et al., 1982; Thurman, 1985; Stuermer and Harvey (1974). It is not known what the dependence of sorption is on the size of the colloidal organic matter. The sorbent macromolecule probably has to at least partially accommodate (dehydrate) a solute to produce an apparent partitioning process. Thus, a fulvic acid of molecular weight of 500-2,000 may not be able

to accommodate large HOC such as PCBs (M.W. = 189-488) to the same extent as higher molecular weight organic matter. Gabarini and Lion (1985) found that humic acid which was coated to alumina particles was a less effective sorbent than when it was dissolved in solution, possibly indicating that sorbed humic acid has less freedom to accommodate HOC. Leo et al. (1971) noted that the sorption of drugs to various proteins consistently showed a weaker dependence on hydrophobicity than partitioning in other solvents (i.e., $a = 0.55$ in equation 1-5) and speculated that this was due to incomplete accommodation or desolvation of water around the small organic molecules when they are sorbed to proteins. In other words there may be a greater amount of surface "adsorption" versus partitioning into an organic phase. Chiou et al. (1986) found that polarity of the sorbent was very important in affecting partitioning. Polyacrylic acid polymer of 90,000 M.W. was an ineffective sorbent for HOC, due to its high polarity and lack of intramolecular hydrophobic regions.

4. Many studies have shown that the effect of organic colloids on the speciation of HOC increases with hydrophobicity of the solute (Matsuda and Schnitzer, 1971; Boucher and Lee, 1972; Boehm and Quinn, 1976; Carter and Suffet, 1983; Wijayarathne and Means, 1984b). In partitioning experiments performed with the same technique and source of colloidal organic matter, $\log K_{oc}$ is correlated with $\log K_{ow}$ (Carter et al., 1983; Landrum et al., 1984; Wijayarathne and Means, 1984b; McCarthy and Jimenez, 1985).

HOC sorption with colloidal organic matter has often been studied using soil humic acid as a model sorbent. The results of six studies using a wide range of experimental techniques is given in Table 1-3 and are plotted along with correlations based on sediment organic matter sorption in Figure 1-3. It

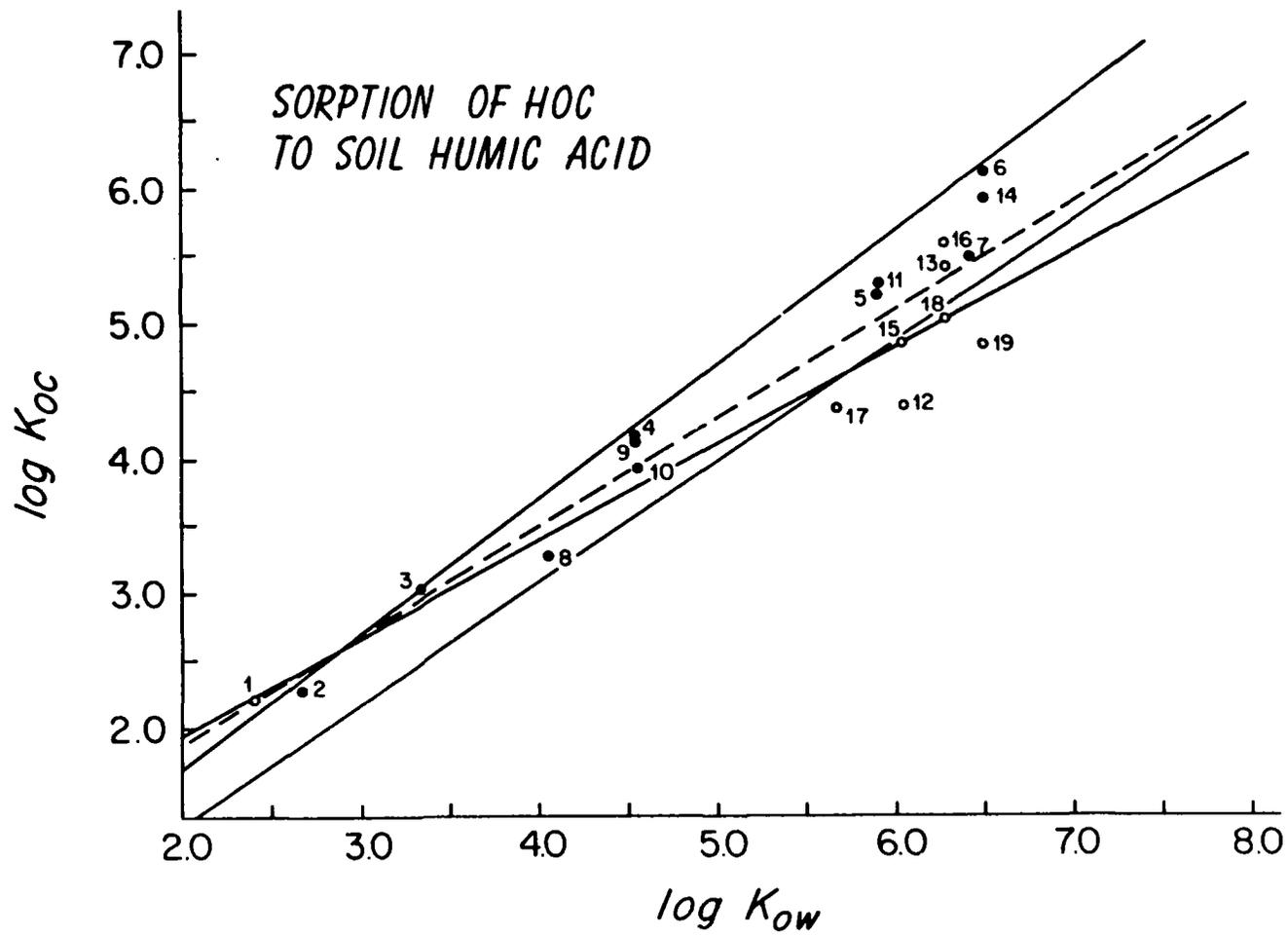
Table 1-3

Literature Values of K_{oc} for HOC-Sediment Humic Acid Sorption

Pt. No.	Compound	Study	$\log K_{ow}$ (Refs.)*	$\log K_{oc}$
1	Trichloroethylene	Garbarini and Lion (1985)	2.41 \pm 0.12 n=2 (7,8)	2.20
2	Toluene	"	2.67 \pm 0.02 n=2 (1,7)	2.27
3	Naphthalene	McCarthy and Jimenez (1985)	3.33 \pm 0.03 n=3 (1,7,9)	3.02
4	Anthracene	"	4.54 \pm 0.09 n=3 (1,2,9)	4.16
5	Benzantracene	"	5.91 (1)	5.23
6	Benzo(a)pyrene	"	6.50 n=2 (1,2)	6.15
7	3-Methylcholanthrene	"	6.42 ()	5.51
8	Biphenyl	Landrum et al. (1984)	4.05 \pm 0.08 n=3 (1,2,7)	3.27
9	Anthracene	"	4.54 \pm 0.09	4.15
10	Phenanthrene	"	4.55 \pm 0.09 n=3 (1,2,9)	3.92
11	Benzantracene	"	5.91	5.30
12	2,2',5,5'-Tetrachlorobiphenyl	"	6.05 \pm 0.23 n=3 (2,3,11)	4.40
13	p,p' DDT	"	6.28 \pm 0.08 n=2 (10,13)	5.44
14	Benzo(a)pyrene	"	6.50 n=2	5.95
15	2,2',5,5'-Tetrachlorobiphenyl	Hassett and Millicic (1985)	6.05 \pm 0.23	4.87
16	p,p' DDT	Carter and Suffet (1982)	6.28 \pm 0.08	5.61
17	2,4,4'-Trichlorobiphenyl	Chiou et al. (1986)	5.68 \pm 0.06 n=3 (2,3,6)	4.40
18	p,p' DDT	"	6.28 \pm 0.08	5.06
19	2,2',4,5,5'-Pentachlorobiphenyl	"	6.49 \pm 0.48 n=5 (2,3,4,5,7)	4.87

*Error refers to 1 std. deviation for $n \geq 3$. Numbered references refer to: 1) Mackay et al. (1980b), 2) Bruggeman et al. (1982), 3) Rapaport and Eisenreich (1984), 4) Woodburn et al. (1984), 5) Chiou et al. (1977), 6) Chiou et al. (1983), 7) Miller et al. (1985), 8) from Garbarini and Lion (1985), 9) Karickhoff et al. (1979), 10) Chiou et al. (1982), 11) Chiou (1985), 12) from Carter and Suffet (1983), 13) from Landrum et al. (1984).

Figure 1-3. Literature values of $\log K_{oc}$ for HOC with dissolved sediment humic acids. Filled circles are PAH data and open circles are for chlorinated hydrocarbons. Data points are numbered as given in Table 1-3. The three solid lines are the same as in Figure 1-2. The dashed line describes the linear regression of all data points: $\log K_{oc} = 0.818 \log K_{ow} + 0.193$ ($r^2 = 0.905$).



5
1
2
1
1

is seen that the sorption of HOC with soil humic acid is well within the predictions which are based on sediment/soil organic matter partitioning. This would suggest that the mechanisms involved in the two processes are probably very similar. It is of interest to note that the K_{oc} s reported for PCBs and DDT tend to fall below those of PAH. The PAH data is well described by the correlation of Means et al. (1980) which is largely based on PAH. However, because of uncertainties involved in different experimental methods for determining sorption it is not possible to conclude whether there are real differences in sorption of PAH and PCBs.

It is not known how good a model soil humic acid is for colloidal organic matter found in different natural waters. The amount and nature of colloidal organic matter found in natural waters is dependent on the isolation methods used (Thurman, 1984; Carlson, 1985). It is not yet possible to determine whether large differences (Means and Wijayarathne, 1982; Carter and Suffet, 1983; Wijayarathne and Means, 1984b; Chiou et al., 1986) in reported K_{oc} for HOC-organic colloid sorption are due to differences in organic matter or the methods used. Landrum et al. (1984) found highly variable K_{oc} measured on samples taken in the Great Lakes and were lower than those determined for Aldrich humic acid. However, those K_{oc} s were normalized to total DOC, which significantly underestimates the sorption to colloidal organic matter.

The development of experimental methods for accurately measuring HOC-organic colloid sorption have been a major limitation in this area of study. Many methods have been tried and it is apparent that none of them are generally applicable to all HOC of interest. Because some methods may suffer from severe limitations, it is useful to briefly review some of them.

Like sediment sorption studies, methods which involve active phase separations to determine dissolved HOC concentration are subject to possible artifacts. Some methods which have used phase separation to measure sorption include centrifugation (Poirier et al., 1972), gel permeation chromatography (Hassett and Anderson, 1979), reverse-phase liquid chromatography (Landrum et al., 1984), ultrafiltration (Means and Wijayarathne, 1982) and volatilization kinetics (Hassett and Millicic, 1985).

Centrifugation will obviously overestimate the dissolved concentration of HOC (C_d). The other methods are complicated by the fact that both solute and sorbent can be highly surface active. Gel permeation chromatography and liquid chromatographic methods are limited because they depend on sorbed HOC being eluted with the macromolecular organic matter. However, the concentration of bound HOC has been shown to increase with flow rate, which suggests that desorption kinetics may be too rapid to accurately measure equilibrium distributions (Landrum et al., 1984). Significant breakthrough of dissolved HOC occurred at the high flow rates used in the study of Landrum et al. (1984).

The use of ultrafiltration to separate dissolved and colloid-sorbed HOC is limited in application to HOC which do not significantly interact with the ultrafilter. Solute polarization of colloidal organic matter at the membrane interface can also be expected to impede the passage of free solute into the ultrafiltrate. The high shear and large surface area provided by hollow fiber ultrafiltration should minimize any effect of solute polarization. However, the use of this technique has been limited to two studies (Means and Wijayarathne, 1982; Wijayarathne and Means, 1984b). Their results for K_{oc} of

linuron, atrazine, and three PAH are several times those reported for sediments and soils (Karickhoff, 1981; Means et al., 1980) or those reported for soil humic acid (Table 1-3). These results for HOC sorption with estuarine colloidal organic matter should be compared to another method to test the assumptions involved.

Volatilization kinetics experiments (Hassett and Millicic, 1985) provide a promising method for measuring C_a . However, there are a few problems and assumptions which must be satisfied. The effect of container walls must be known. HOC like PCBs can significantly sorb to glass and the desorption kinetics of HOC from walls must be known during the purging process. Organic colloids may also sorb to the container. The effect of added colloidal organic matter on the sorption and desorption of HOC from container walls, also has to be evaluated. Finally, it is not well established that the mechanism of HOC exchange into the vapor phase are not affected by the presence of colloidal organic matter, although the volatilization kinetics of oxygen are unaffected (Hassett and Millicic, 1985).

Non-separation, equilibrium methods for measurement of HOC-organic colloid partitioning are preferable. Several techniques have been used. Fluorescence quenching techniques (McCarthy and Jimenez, 1985) are limited to compounds which are significantly fluorescent, and sorbent fluorescence may interfere with interpretation of results. Equilibrium dialysis has been used (Guy et al., 1980; Carter and Suffet, 1982, 1983; McCarthy and Jimenez, 1985) and is limited to HOC which can easily pass through dialysis bags. Landrum et al. (1984) report difficulty in obtaining equilibrium in dialysis bags, measured over several days, and dialysis gave higher K_{oc} than those found using

reverse-phase liquid chromatography. Carter and Suffet (1983) report some large discrepancies in reported K_{oc} , when dialysis was compared to solubility and sorption methods. In spite of the uncertainties, equilibrium dialysis is an attractive method which yields results which are consistent with other methods (see Figure 1-3).

Two methods have been reported which measure the effect of colloidal organic matter on the apparent solubility of HOC. K_{oc} is calculated from the increase in solution HOC concentration and the organic colloid concentration. Solubility enhancement can be measured by isopiestic methods (equilibration with HOC saturated vapor) (Haas and Kaplan, 1985) or by standard solubility measurements (Boehm and Quinn, 1973; Carter and Suffet, 1983; Chiou et al., 1986). The latter technique should be interpreted with caution. Solubility measurements of very hydrophobic compounds like PCBs are often complicated by the presence of suspended microscopic crystals or aggregates of undissolved compound (see Mackay et al., 1980a). It is expected that the presence of surfactant-like organic colloids could significantly enhance the kinetic stability of an undissolved phase in solution. This could explain the decrease in solubilization by marine DOM of n-alkanes and isoprenoid hydrocarbons with increasing standing time. "Solubilization" methods are limited in general because they can only give partitioning data in the case of saturation in both the organic and dissolved phases. γ_o^* may not be constant as saturation is approached. Therefore, these studies do not necessarily give information regarding "low loading" of sorbate which is of more general interest.

Equilibrium headspace partitioning can be used to determine the effect of colloidal organic matter on the fugacity of dissolved HOC. In dilute solution

the vapor concentration is directly proportioned to the dissolved activity by Henry's Law. Headspace partitioning has been used to measure the solubility of hydrocarbons (McAuliffe, 1966), the Henry's Law constants for PCBs (Murphy et al., 1983), the partitioning of HOC between miscible solvents (Leo et al., 1971), the thermodynamics of alcohol-micelle partitioning (Spink and Colgan, 1983), and the sorption of toluene and trichloroethylene with soil and humic acid (Garbarini and Lion, 1985). This method is limited to HOC with significant vapor pressures or Henry's Law constants. The method of Garbarini and Lion (1985), which only measures the vapor phase, can be applied to HOC that do not sorb to container walls.

In summary, the partitioning of HOC with colloidal organic matter appears to be quite similar to that with sedimentary organic matter. Despite uncertainties regarding experimental methods, it appears that sorption of HOC with dissolved soil humic acids is well predicted by correlations based on sediment organic matter. More work needs to be done to examine the variability and properties of natural colloidal organic matter which influence partitioning. Finally, with the exception of estuarine studies by Means and Wijayarathne (1982) and Wijayarathne and Means (1984b) there are no quantitative studies of HOC-marine organic colloid sorption.

MARINE COLLOIDAL ORGANIC MATTER

There have been several studies of macromolecular organic matter in seawater. It must be cautioned that any generalizations or comparisons of

results from these studies is necessarily complicated by the different isolation methods used in the various studies. There have been many techniques used to concentrate and isolate colloidal organic matter and are reviewed by Aiken (1985). Most often, macromolecular organic matter has been studied as operationally defined humic substances (Stuermer and Harvey, 1977; Harvey et al., 1983) or by retention by various size ultrafilters (Sharp, 1973; Ogura, 1977; Carlson, 1985).

Marine humic substances are usually defined by their extraction from acidified seawater using hydrophobic XAD-2 resins (Stuermer and Harvey, 1974; 1977; Mantoura and Riley, 1975; Harvey et al., 1983). They have also been extracted by other adsorbents including activated charcoal (Kerr and Quinn, 1975) and nylon (Sieburth and Jenson, 1968). Marine humic substances are base soluble, polyelectrolyte, organic acids which account for most of UV-visible absorption in seawater. Because of their yellow color, marine humic substances have been termed Gelbstoffe (Kalle, 1966). Marine humic substances do not include DOM which is too hydrophilic at pH 2.0 to sorb to XAD-2 resin (Thurman and Malcolm, 1978; Ram and Morris, 1982) or compounds which interact so strongly with XAD-2 that they are not eluted with base from XAD-2. Both of these fractions may contain colloidal organic matter of unknown properties. The amount of unrecovered DOC is not great, but can be 30% of the humic substances (Stuermer, 1975; Kerr and Quinn, 1975; Thurman, 1985). Unrecovered material may have low carboxyl and hydroxyl functionality and hydrophobic interactions with XAD-2 prevent elution even at high pH (Thurman, 1985).

Humic substances are further divided into fulvic (acid and base soluble) and humic acid (base but not acid soluble) fractions. Fulvic acids generally

make up 65-95% of marine humic substances (Stuermer and Harvey, 1974; Harvey et al., 1983). Several studies, including those above, indicate that humic substances make up about 5-30% of DOC in seawater (reviewed by Thurman, 1984), and depends upon the location and depth of sampling. Marine fulvic and humic acids have many properties similar to freshwater and soil humic substances even though they are defined differently by extraction methods (Thurman, 1985). Careful characterization techniques have shown that there are important differences in marine and freshwater/terrestrial humic substances (Stuermer and Payne, 1976; Gagosian and Stuermer, 1977, Kerr and Quinn, 1980; Harvey et al., 1983). Marine humic substances are found to have more aliphatic character, less aromatic and phenolic content, and lower oxygen functionality than freshwater humic substances. These and other studies indicate that marine humic substances are relatively stable products of autochthonous (phytoplankton based) organic matter decomposition. Carlson and Carlson (1984) have presented evidence suggesting that exudates from macroalgae can be an important source of humic-type DOM in certain coastal environments. Proposed structures and formation pathways of marine humic substances are discussed by Gagosian and Stuermer (1977) and Harvey et al. (1983).

The molecular weight distributions of marine humic substances may be similar to their freshwater counterparts. Stuermer and Harvey (1974) found that 55 to 73% of seawater fulvic acids were of molecular weight less than 700 determined by gel permeation chromatography and the remainder was less than 5,000. The molecular weight of marine humic acid has not been determined by this approach. Thurman et al. (1982) report that the average molecular

weight of freshwater fulvic acids determined by small angle x-ray diffraction is 500-2000 and that humic acid fractions range from 1,000 to greater than 10,000 molecular weight. Many techniques have been employed to estimate the molecular weight or size of macromolecular organic matter. Methods include gel permeation chromatography, ultrafiltration, small angle x-ray scattering, ultracentrifugation, viscometry, and colligative property measurements. The application and limitations of each of these methods is reviewed by Thurman et al. (1982) and Wershaw and Aiken (1985).

Ultrafiltration studies separate DOM on the basis of size and also on the basis of physical-chemical interactions with the membranes used and do not result in strict molecular weight cutoffs. For instance dissolved soil fulvic acids of about 1,000 molecular weight are highly retained by an ultrafiltration membrane of reported 50,000 M.W. cutoff and a hollow fiber filter of 10,000 M.W. cutoff (Kwak and Nelson, 1977). The use and limitations of ultrafiltration to fractionate size fractions of organic matter are discussed by Buffle et al. (1978). They found that results of ultrafiltration studies can depend greatly of interactions of dissolved or colloidal organic matter in the retentate (aggregation), and interactions of DOM with the membrane, changing the properties of the filter and modifying filtration.

Several investigators have studied the distribution and molecular weight range of colloidal organic matter using ultrafiltration. The ranges of reported molecular weights are generally complex and extend to greater than 100,000 M.W. in some studies (Ogura, 1974, 1977; Wheeler, 1976). However, comparisons of ultrafiltration procedures for seawater have not been made with other methods of molecular weight determination. Carlson et al. (1985) have

recently reported that an average of 34% of the DOM in North Atlantic waters is of molecular weight greater than 1,000 and 6% had molecular weight greater than 30,000. These workers report no trends with proximity to the coast or depth in the water column. This report also provides a detailed review of other marine ultrafiltration studies and interprets those results in light of procedural artifacts found in their own studies.

Characterization of estuarine and coastal organic colloids shows them to be distinct from freshwater colloidal substances (Maurer, 1976; Zsolnay, 1979; Sigleo et al., 1982; Means and Wijayarathne, 1984). These studies show that marine colloidal organic matter has a high amino acid and carbohydrate content, which in the case of estuarine colloidal material resembles the composition of phytoplankton (Sigleo et al., 1983; Means and Wijayarathne, 1984). Zsolnay (1979) used pyrolysis gas chromatography to illustrate the different chemical structures of coastal and riverine colloidal organic matter. In contrast to organic colloids defined by ultrafiltration, aquatic humic substances have very small relative amounts of carbohydrates and amino acids and are lower in nitrogen content (Gagosian and Stuermer, 1977; Harvey and Boran, 1985; Thurman, 1985). It is clear that these two types of procedures yield organic matter with different composition. Both types of studies indicate that marine colloidal organic matter is autochthonous in origin, but is in lower concentration and constitutes a lower percentage of DOC than in most freshwater environments (see Thurman, 1985). Studies of the decomposition of marine colloids have shown them to be quite resistant to degradation (Ogura, 1972; Skopintsev, 1981).

Future research should be aimed at understanding what the actual differences are in isolation procedures, both in terms of chemical characterization and the properties or function of isolated material. Ultrafiltration enrichment minimizes structural changes in colloidal organic matter which could be caused by extreme pH changes, desiccation, and precipitation. This is particularly true for hollow fiber ultrafiltration methods. Although changes in chemical structure and molecular configuration might be expected to affect the sorptive properties of colloidal organic matter, the possible effects of isolation and preparation methods are undetermined.

COLLOIDAL ORGANIC MATTER IN INTERSTITIAL WATERS

Dissolved organic matter exists in elevated concentrations in the interstitial waters of marine sediments (Starikova, 1970; Krom and Sholkovitz, 1977; Henrichs, 1980). These and other studies suggest that the levels of DOC in interstitial waters are closely related to the organic carbon content of the sediments, the redox chemistry of interstitial waters, and the remineralization rate observed. In the interstitial waters of reducing sediments with high remineralization rates, DOC is highly elevated and often increases with depth (Starikova, 1970; Nissenbaum et al., 1972; Krom and Sholkovitz, 1977; Elderfield, 1981; Henrichs, 1980; Orem and Gaudette, 1984). Fifty to ninety percent of DOM in reducing pore waters is defined as colloidal by ultrafiltration (Krom and Sholkovitz, 1977; Orem and Gaudette, 1984; Orem

et al., 1986). The DOC concentrations are lower in oxic sediments studied, which usually also have lower sediment organic carbon levels (Starikova, 1970; Krom and Sholkovitz, 1977; Henrichs et al., 1980).

The properties, cycling, and transport of the colloidal organic matter in sediment interstitial waters are important in controlling the distribution and transport of sorbed HOC. Some studies have applied UV and infrared absorption, and elemental analysis to study the colloidal organic matter, and have found it to be similar to marine humic substances (Nissenbaum et al., 1972; Krom and Sholkovitz, 1973; Elderfield, 1981). Nissenbaum et al. (1972) postulated that condensation reactions of simple sugars and carbohydrates and other free monomers produced marine humic substances or melanoiden type polymers in interstitial waters, and that interstitial water humic substances might be the precursors to sediment fulvic and humic acids. An alternative hypothesis is that of Orem et al. (1986) who propose that interstitial water DOM, represents the partially degraded "labile" fraction of sedimentary organic matter and that interstitial waters provide a conduit for further degradation and transport from the sediment. The processes which are important in the production of interstitial water colloidal organic matter are untested, but it is fairly clear that there is a strong involvement of microbially mediated diagenetic reactions.

One property of colloidal organic matter which controls its distribution and transport in interstitial waters is its tendency to sorb onto sediment particles. The dynamics of dissolved-particulate organic matter interactions are poorly understood in sediments or seawater. Various types of particle surfaces are rapidly covered with a film of surface-active organic matter when

placed in seawater (Niehoff and Loeb, 1974; Hunter, 1980). Davis and Gloor (1981) found that the high molecular weight fraction (> 1,000 M.W.) of Lake Greifensee DOM preferentially complexed with colloidal alumina. Hedges (1978) measured the reactions of synthesized melanoiden compounds as model humic substances with kaolinite and montmorillonite clays. He found that the Freundlich constant for adsorption (eqn. 1-2) was 100-1,500. These studies suggest that colloidal organic matter in 'sediment-rich' interstitial waters might be highly "sorbed" to the sediments and that transport of colloidal materials would be impeded by this process.

The importance of colloid-particle interactions of marine colloids with natural sediments, which are already coated with organic matter is unknown. The mechanisms and reversibility of these types of reactions are important unanswered questions.

POLYCHLORINATED BIPHENYLS AS MODEL HOC

There are 209 possible chlorobiphenyl congeners, and nearly half of them have been identified in commercial mixtures and environmental samples (Ballschmiter and Zell, 1980; Duinker and Hillebrand, 1983; Capel et al., 1985). PCBs were commercially produced in this country by Monsanto Corporation and sold as complex mixtures which are viscous liquids under the trade name Aroclor. Aroclor mixtures were most commonly named with a numbering system whose last two digits represent the average percentage chlorine in the mixture (e.g., Aroclor 1254 is 54% chlorine by weight). PCBs were first

produced commercially in 1929 and found wide application because of their high thermal stability and dielectric properties. They were primarily used in transformers and capacitors, but were used in a wide variety of products including paints, papers, and as fire-retardants. They were first recognized as being a significant environmental contaminant in 1966 (Jenson, 1966).

Following reports of human health and environmental effects of PCBs, Monsanto limited sales of PCBs to closed electrical systems in 1970 and U.S. production of PCBs ceased in 1978. Of the 1.4 billion lbs of PCBs produced in the U.S., an estimated 750 million lbs were still in use in 1982 (Miller, 1982). Because of the large quantities of PCBs still in use and the fact that PCBs may be recycled in the environment many times (Murphy et al., 1985), they will probably continue to be introduced into the marine environment for many years to come.

A large number of measurements of PCBs in various compartments of the environment have been reported. Some scientific studies have been motivated by the concern over the distribution, transport, and environmental effects of PCBs. More generic studies in the laboratory and the field have related the properties of individual chlorobiphenyls or unresolved (by gas chromatography) isomer groups to various processes involved in the biogeochemical cycling of all HOC. As previously discussed in this chapter, PCBs are good models for surface active nonpolar HOC in the marine environment.

The understanding of the biogeochemical cycling of PCBs has been hindered by the common practice of treating PCB mixtures as a single chemical entity. The solubilities and vapor pressures of individual chlorobiphenyls span approximately five orders of magnitude (Bruggeman et al., 1982; Bidleman,

1984). Relating distributions of total PCBs in the environment (or in laboratory experiments) to physical or chemical processes is analogous to measuring total bomb-fallout radionuclides.

Comparisons and generalizations regarding total PCB measurements can be useful, but it is generally misleading to use such data to model the biogeochemical processes affecting PCBs (i.e., calculation of atmospheric or surface water residence times). Recent studies have emphasized this fact and have made important progress in the use of PCBs as model HOC (Bopp, 1979; Bopp et al., 1981; Tanabe et al., 1982; Gschwend and Wu, 1985). Progress has also been made in obtaining chlorobiphenyl identifications (Duinker and Hillebrand, 1983; Mullin et al., 1984) and physical chemical property data (Bruggeman et al., 1982; Rapaport and Eisenreich., 1984; Bidleman, 1984; Burkhard et al., 1985).

Field measurements of unresolved isomer groups of chlorobiphenyls have provided tests for equilibrium partitioning between seawater and suspended particulates (Dexter and Pavlou, 1978a) and between water and suspended sediments in the Hudson River (Bopp, 1979; Bopp et al., 1981). The studies of Bopp and co-workers demonstrated the value of PCBs as tracers in sediment transport, and found sediment compositions of PCBs could be related to water-sediment partitioning in the overlying water. Studies of PCBs in the Great Lakes have shown that sediment resuspension is responsible for large inputs of PCBs back into the water column (Eadie et al., 1983; Baker et al., 1985). Eadie et al. (1983) and Eisenreich (1984) have measured highly elevated concentrations of PCBs in interstitial waters of sediments from Lake Michigan and Lake Superior. Baker et al. (1983) have interpreted the seasonal

increase of Aroclor 1242 type PCBs in the hypolimnion of Lake Superior to be the result of a flux of these compounds from sediment interstitial waters.

There have been few studies concerning the marine geochemistry of PCBs in the last ten years. The importance of long range atmospheric transport of PCBs to the open ocean has been recognized (Harvey and Steinhauer, 1974; Bidleman and Olney, 1974; Atlas and Giam, 1981; Tanabe et al., 1982). Measurements of PCBs in seawater are very difficult due to very low concentrations and possible contamination problems (Risebrough et al., 1976; Farrington and Westall, 1986). In a series of papers Harvey and co-workers (1973, 1974, 1976) measured PCB distributions in the surface waters of the North and South Atlantic Ocean. From the results of several cruises they reported a sharp decline in surface water PCB concentrations from an average of 35 ng/L in 1971-1972 cruises in the North Atlantic to levels averaging 0.8 - 2.0 ng/L in 1973-1974. Their data from 1973-1975 is internally self consistent but have been criticized as being too high on the basis of mass balance consideration (Risebrough et al., 1976; NAS, 1979).

Later measurements have been made in the north and west Pacific, the eastern Indian Ocean, and in the Antarctic Ocean by Tanabe and co-workers (1980, 1982, 1983). They have measured a relatively small range of PCB concentrations in surface waters over this broad geographical area: 0.25 - 0.56 ng/L for 1975 cruises, 0.29 - 1.11 ng/L in 1976, 0.23 - 0.59 ng/L in 1978, 0.27 - 0.38 ng/L in 1979, and 0.039 - 0.25 ng/L in 1981- 1982 cruises. More volatile, lower chlorinated biphenyls are relatively enriched in both the atmosphere and surface waters with increasing distance from land (Tanabe et al., 1982). The amount of PCBs sorbed to particles increased with

decreasing solubility of individual chlorobiphenyls and increased from oligotrophic to eutrophic waters as particle concentrations increased (Tanabe and Tatsukawa, 1983). These authors calculated a residence time of total PCBs to be on the order of a month in eutrophic waters and about six months in oligotrophic waters. As mentioned before, this calculation is very much dependent on the individual chlorobiphenyls present.

There have also been relatively few published data for PCBs in coastal waters, but reported measurements are typically higher than open ocean measurements. For example, de Lappe and co-workers (1980) report total PCB measurements of 0.39 to greater than 90 ng/L of total PCBs in Massachusetts coastal waters (the high values are for New Bedford Harbor), and total PCB concentrations were reported to range from 2.6 - 8.7 ng/L in various bays and coastal waters on the west coast of the United States (Pavlou and Dexter, 1979).

In summary, it is not yet clear whether measured PCB values in the marine environment have decreased or that the lower concentrations merely reflect improved analytical methods. Well preserved sediment, ice core, or coral records could answer many questions. Improved methods of in-situ sampling for PCBs in the deep sea, combined with greater understanding of controls on PCB (HOC) speciation, would make these compounds a valuable tracer for the study of the cycling of not only other HOC, but also the transport and cycling of particulate organic matter in the sea.

The following study was performed to evaluate the role of colloidal organic matter in affecting the speciation of HOC in a coastal marine environment. New Bedford Harbor and surrounding Buzzards Bay provided an

environment heavily impacted by PCBs (Weaver, 1984; Farrington et al., 1985) where field measurements of PCB could be used to test models of organic matter partitioning.

ORGANIZATION OF THIS DISSERTATION

Chapter 1 has been an introduction to the problem of sorption of HOC to sedimentary and particularly colloidal organic matter. In it is also a review illustrating the strengths and weaknesses of organic matter partitioning models applied to the speciation of PCB-like compounds in natural waters. Chapter 2 describes a passive headspace partitioning method for measuring the sorption of several individual chlorobiphenyls with colloidal organic matter isolated from samples taken off Chemotaxis Dock on Nantucket Sound, Massachusetts. Results are discussed in terms of equilibrium partitioning and other results in the literature. These results are also related to the speciation of PCBs in seawater and unsolved questions in the literature concerning HOC sorption processes.

Chapter 3 presents results from three box cores obtained in New Bedford Harbor and Buzzards Bay, Massachusetts. These cores provided detailed profiles of PCBs in interstitial waters and sediments. The observed distributions of a large number of individual chlorobiphenyls are interpreted in terms of a three-phase equilibrium partitioning model. The quantitative role of colloidal organic matter on the interstitial water speciation of these compounds is evaluated. Compositional changes of individual chlorobiphenyls

are observed in one of the sediment cores from New Bedford Harbor. A discussion of possible processes affecting PCB composition in sediments is important in interpreting observed pore-water/sediment partitioning and in understanding the mobility of PCBs in sediments. Finally, the results from water column PCB partitioning studies are presented as a useful comparison to sediment/pore water environments because of much lower concentrations of colloidal organic matter.

Chapter 4 addresses the important issue of PCB transport within and out of sediments. The effect of a mobile colloid-sorbed phase on a general diagenetic transport model is considered. Model calculations illustrate the role of colloidal organic matter on the migration of PCB-like compounds within sediments. Sediment concentrations of PCBs and ^{210}Pb from a sediment core in Buzzards Bay are used to calculate the fluxes across the sediment-water interface at that site and to test models of sediment mixing.

Some of the important conclusions from this dissertation are summarized along with a general discussion of important problems in Chapter 5. There are also three appendices. Appendix 1 discusses the Henry's Law constants measured in experiments and compares them to measurements and predictions reported in the literature. Appendix 2 summarizes some important aspects and problems encountered in earlier headspace partitioning experiments. Appendix 3 lists some complete data sets from which figures and smaller data tables in Chapter 3 were derived.

CHAPTER II

SORPTION OF PCBs BY COASTAL MARINE ORGANIC COLLOIDS
DETERMINED BY STATIC HEADSPACE PARTITIONING

INTRODUCTION

The speciation of hydrophobic organic compounds (HOC) in natural waters is often influenced by sorption reactions involving sediments and suspended particulate material. Similarly, it is now recognized that sorption of many HOC with colloidal organic matter (operationally defined as passing 0.2 to 1.0 μm filters and being retained by ultrafilters of 1 to 5 nm pore diameters) and dissolved humic substances may significantly affect the transport, fate and biogeochemical cycling of HOC's in both marine and fresh waters. Due to the uncertainty involved in what fractions of dissolved organic matter (DOM) are isolated by different methods of studying high molecular weight DOM, the term colloidal organic matter is used loosely to include macromolecular organic matter operationally defined by other isolation procedures in the literature. Sorption of HOC with organic colloids has been shown to decrease the apparent sorption of several HOC to clays, sediments, and suspended particles (Boucher and Lee, 1972; Meyers and Quinn, 1973; Hassett and Anderson, 1982), to affect the rate of volatilization of 2,2',5,5'-tetrachlorobiphenyl (Hassett and Millicic, 1985), to affect biological uptake of HOC by aquatic organisms (Boehm and Quinn, 1976; Laversee et al., 1983; McCarthy and

Jimenez, 1985), and to decrease the hydrolysis rate of the 1-octyl ester of 2,4-D (Perdue and Wolf, 1982). Brownawell and Farrington (1985, 1986) have interpreted sediment/pore water and water column distributions of PCBs in terms of simple three-phase equilibrium partitioning involving dissolved, particulate, and colloidal organic phases. Gschwend and Wu (1985) have similarly modelled PCB partitioning in batch sorption studies by including an observable, non-settling ("colloidal") organic phase in sorptive equilibria with the dissolved phase.

The understanding and prediction of biogeochemical processes affecting the transport and fate of HOC's in natural waters requires accurate estimations of their speciation. There has been considerable progress in elucidating mechanistic and predictive aspects of aqueous sorption of neutral HOCs to sediments and soils (Chiou et al., 1979, 1983; Karickhoff et al., 1979; Karickhoff, 1980; Schwarzenbach and Westall, 1981; Means et al., 1982; Wu and Gschwend, 1986). From these and other studies has evolved a sediment organic matter partitioning model where HOC are dissolved into a bulk organic phase coating sediment particles. In this process, sorption is primarily controlled by the solute's incompatibility in the aqueous phase and a set of very nonspecific interactions in the organic phase. It has been shown in the above studies that sorption can be well predicted with a knowledge of sediment properties and sorbate hydrophobicity through linear free energy relationships (see Chapter I).

It is expected from studies of HOC-organic matter partitioning and some recent HOC-organic colloid sorption studies that the mechanisms of sorption of relatively non-polar HOC, such as PCBs, with colloidal organic matter will be

similar to that with sediment organic matter. As yet a corresponding state of knowledge concerning the controlling factors and predictability of HOC-organic colloid sorption does not exist. This is in part due to the difficulty of experimentally distinguishing dissolved and colloid sorbed phases in solution. Quantitative measurements have been reported for the sorption of atrazine, linuron, and several PAH's with estuarine colloidal organic matter (Means and Wijayarathne, 1982; Wijayarathne and Means, 1984) and for several HOC with fresh water humic substances or dissolved organic matter (Carter and Suffett, 1982; 1983; Landrum et al., 1984; Hassett and Millicic, 1985; McCarthy and Jimenez, 1985; Garbarini and Lion, 1985).

An examination of the literature reveals several methods have been used to study HOC-colloid sorption in dilute solutions. These include centrifugation (Poirrier et al., 1972), gel permeation (Hassett and Anderson, 1979; Wijayarathne and Means, 1984a), reversed phase liquid chromatography (Landrum et al., 1984), ultrafiltration (Means and Wijayarathne, 1982; Wijayarathne and Means, 1984b), volatilization kinetics (Hassett and Millicic, 1985), equilibrium dialysis (Carter and Suffett, 1982, 1983; Landrum et al., 1984; McCarthy and Jimenez, 1985b), and recently equilibrium headspace partitioning (Garbarini and Lion, 1985). With the exception of dialysis and headspace partitioning, these techniques potentially suffer from uncertainties derived from incomplete phase separations, disequilibria caused during phase separations, or sorptive exchange of HOC with container walls and other surfaces during phase separation. It will be shown here that the passive headspace partitioning method similar to that recently reported by Garbarini and Lion (1985) can be extended to less soluble HOC if the solution phase is

also measured. This additional measurement is necessary when HOC are appreciably sorbed to container walls.

A study of the sorption of several polychlorobiphenyls with colloidal organic matter isolated from nearby Nantucket Sound, Massachusetts, USA by a static headspace partitioning method is reported in this chapter. This method is adapted from that used by Murphy et al. (1983) for direct measurement of Henry's Law constants for individual chlorobiphenyls. Headspace partitioning has been used in studying alcohol binding to deoxycholate micelles (Spink and Colgan, 1983), and recently in the study of sorption of toluene and trichloroethylene (Garbarini and Lion, 1985). This method measures the fugacity of dissolved HOC directly and largely overcomes experimental problems involved in phase separations mentioned above. PCBs were chosen as model compounds for this study because of the range in their solubilities (which are representative of many other HOCs), their expected sorption behavior, and low detection limits and relatively high vapor pressures (which enable measurement of a mixture of chlorobiphenyls in the vapor phase by capillary gas chromatography and electron capture detection). Extrapolation of these results to field distributions of PCBs will allow tests of sorption models of HOCs in the marine environment (Brownawell and Farrington, 1985, 1986). Finally insights to PCB speciation in natural waters will contribute to our knowledge of the fate of these and other xenobiotic organic compounds.

EXPERIMENTAL METHODS

Colloidal organic matter was enriched from coastal seawater sampled off of Chemotaxis Dock, Woods Hole Oceanographic Institution (see Figure 3-1A) on Nantucket Sound, Massachusetts. Twenty-liter water samples were collected at about 1 meter depth by direct lowering of a prerinsed 20 L stainless steel filtration bomb from the end of the pier which has a water depth of about 3 meters. The water sample collected on July 23, 1985, for the partitioning experiment reported here, was collected by repeated lowerings of a stoppered 5.0 L glass flask to the same depth to avoid any surface microlayer contamination. Water was then immediately pressure-filtered through 142 mm diameter Nuclepore 0.4 μm membrane filters with Gelman Type AE glass fiber filters serving as prefilters in stainless steel filter holders. Glass fiber filters were precombusted at 500°C overnight and 5 liters of distilled water were filtered through each of the filters used to reduce DOC contamination which apparently derives from the Nuclepore filters. Filtrations took 3 to 6 hours to complete and generally necessitated the use of three changes of filters to process the entire 20 L sample. Filtrates were collected in 5 gallon glass carboys which had been previously rinsed with acetone, hexane, CH_2Cl_2 , and 10% HCl. At the beginning of filtration, 2.0 mL of 1% NaN_3 was added to the filtrate to minimize microbial transformations or degradation of dissolved organic matter during subsequent ultrafiltration or partitioning experiments.

Ultrafiltrations of filtered seawater were performed within 24 hr of filtrations using recirculating Amicon H₁P₅ hollow fiber ultrafiltration cartridges having a nominal molecular weight cutoff of 5000 MW. The

ultrafiltration apparatus was also rinsed with two changes of distilled water and about 500 mL of filtered seawater prior to each use. The cartridge was stored in 0.1% NaN₃ in the refrigerator between uses. Ultrafiltration rates for seawater are about 60 mL/min and the ultrafiltration of 20 L takes 5 to 7 hours. Final retentate volumes were 205 to 500 mL corresponding to enrichments in the retentate of 31.7 to 75.2 times.

Duplicate samples of filtered seawater, ultrafiltrate, and retentate were taken for DOC analysis. DOC was analyzed by wet persulfate oxidation using an adaptation of the method described by Stainton (1973). One aspect of DOC determinations is worth noting. Before sealing the samples with H₂SO₄ and persulfate they are bubbled for 10 minutes with oxygen. In every case, retentate samples containing enriched organic colloids foamed during bubbling while filtered seawater and ultrafiltrate samples did not. Foaming was also observed in DOC samples collected from interstitial waters reported in Chapter 3. This indicates that colloidal organic matter in coastal seawater and sediment interstitial waters acts to reduce the surface tension of those waters (see Barger and Means, 1985).

Colloidal organic carbon concentrations were calculated by subtracting the ultrafiltrate DOC and dividing by the enrichment factor. The estimated precision of the DOC determinations was 5%. For four water samples analyzed before July 1985, the sum of ultrafiltrate and colloid organic carbon concentration was 0.26 ± 0.15 mg/L greater than the original filtered water samples. Pyrolysis gas chromatography and pyrolysis gas chromatography/mass spectrometry on enriched colloid samples obtained on April 12, 1985 and June 13, 1985 indicated that there was organic silicone contamination in dialyzed

retentate samples. The source of this contamination was probably the silicone tubing used in pumping the retentate through the ultrafiltration cartridge using a peristaltic pump. After June 13, 1985 a stainless steel/Teflon gear pump was used with stainless steel and glass tubing to minimize DOC contamination. There was a deficit of ultrafiltrate plus retentate DOC relative to the original sample of 0.17 ± 0.12 mg/L in the sample taken on July 23, 1985 which was used in the experiment discussed here. It is not certain to what extent silicone contamination may have affected the DOC results measured in the earlier samples. Filtration and ultrafiltration of an interstitial water sample was performed using inert atmosphere techniques (Brownawell and Farrington, 1986) on a composite (2-15 cm) sediment grab sample obtained from Station M (Chapter 3) in Buzzards Bay. Sampling and centrifugation of sediments and filtration of interstitial water were performed within 8 hours using procedures described in elsewhere (Brownawell and Farrington, 1986). Filtration and ultrafiltration of interstitial waters were performed in a nitrogen purged glove bag.

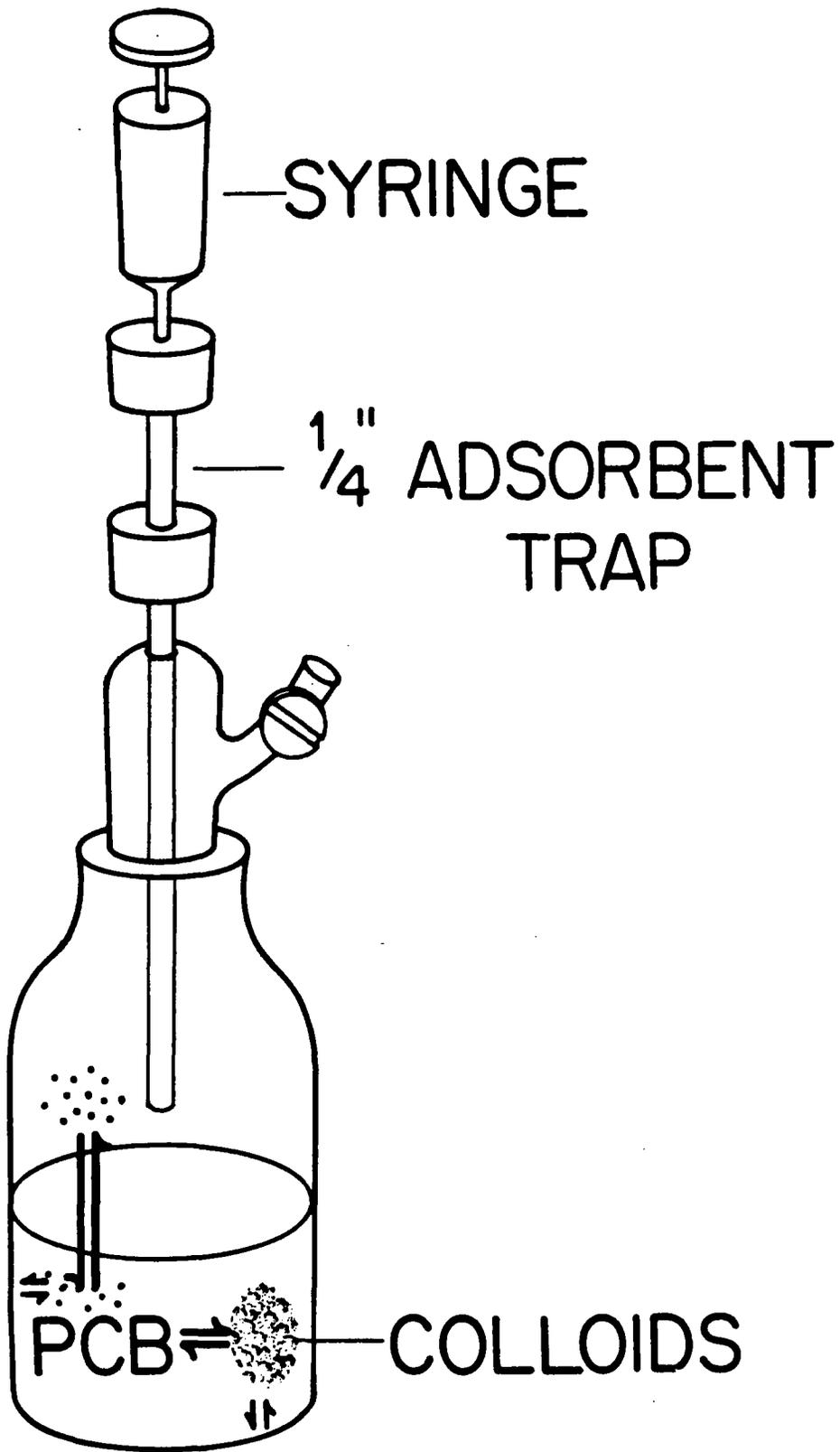
The pH and particulate organic carbon (POC) concentrations were measured on some of the samples. pH was determined with an Orion combination pH electrode, and POC was measured on a Perkin-Elmer CHN analyzer.

The sorption of five individual chlorobiphenyls with enriched colloidal organic matter from Chemotaxis Dock was studied by using a static equilibrium headspace partitioning approach. The following five chlorobiphenyls used were obtained from Ultra Scientific or Analabs and used as received: 2,4'-dichlorobiphenyl, 2,4,4'-trichlorobiphenyl, 2,3',4',5-tetrachlorobiphenyl, 2,2',3,4,5'-pentachlorobiphenyl, and 2,2',3,4,4',5'-hexachloro-

biphenyl. The respective IUPAC chlorobiphenyl numbers for these compounds is 8, 28, 70, 87, and 138. These chlorobiphenyls provided a wide range of physical chemical properties (Rapaport and Eisenreich, 1984) and expected sorption behavior. The results from three initial partitioning experiments were complicated either by uncertainty involving equilibrium conditions, DOC contamination or the possible effect of silicone contamination and are partially discussed in Appendices 1 and 2. The methods and results presented here are for an experiment performed with colloidal organic matter isolated from the sample obtained on 7-23-1985.

A stock solution of the five PCBs dissolved in ultrafiltered seawater was prepared by evaporating an isooctane standard solution of PCBs in the bottom of a 1-liter Pyrex brand low actinic glass reagent bottle (these bottles were also used in the partitioning experiments) and equilibrating with ultrafiltrate on an orbital shaker for 24 hours. A volume, ranging from 5.0 to 80 mL of stock solution was added to each of six control (ultrafiltrate only) bottles, and the same amounts to six bottles in which 20.0 mL of retentate had also been added. The final volume of each of the twelve experimental bottles was made up to 100 mL with clean ultrafiltrate. Four samples were taken for PCB concentrations in the stock solution during the course of experimental bottle preparation. The resulting concentrations of di- through hexachlorobiphenyl were 17.1 ± 1.5 , 20.3 ± 0.87 , 5.68 ± 0.25 , 2.64 ± 0.099 , and 0.806 ± 0.030 ng/mL, respectively. The experimental bottle design is illustrated in Figure 2-1. The total volume of the experimental vessels is 1100 ± 10 cm³, so that there was 1 liter of headspace in each bottle. The Drechsel stoppers were adapted with Teflon stopcocks and Swagelock

Figure 2-1. Illustration of the experimental bottles used in equilibrium headspace partitioning experiments.



fittings, with Teflon ferrules, to allow for gas sampling of the headspace at atmospheric pressure. The sealed bottles were then shaken for 24 hr on the orbital shaker. Two of the bottles were sampled for vapor phase PCBs after an additional 12 hours and all twelve bottles were then sampled three times at additional 24 hr intervals. At the end of the last vapor phase measurement, replicate samples were taken for solution phase PCBs, DOC determinations, and finally the bottles were emptied and analyzed for PCBs adsorbed to the container walls. All solution transfers and sampling were made with glass pipettes, beakers, and centrifuge tubes which had been rinsed with acetone, hexane, methylene chloride, 10% HCl, and distilled water to insure against PCB or organic carbon contamination. The experimental bottles were also soaked in chromic acid and combusted at 500°C overnight to eliminate DOC contamination which had been observed in earlier experiments. The experiments were performed at room temperature which was $22 \pm 1.5^\circ\text{C}$ during the course of the experiment.

Methods of PCB determination in various phases of experimental bottles required somewhat different techniques which are outlined below.

Vapor Phase PCB Measurements

The determination of vapor phase PCBs is the most difficult measurement to make in these experiments due to the relatively low Henry's Law constants and the low concentrations of chlorobiphenyls used here. With a ten times greater volume of vapor than seawater in this experiment, the measured fractions of total chlorobiphenyls in the vapor still ranged from less than 0.5 to 7.5% of

the total amounts in the bottles. Therefore the sampling of a fraction of the vapor phase does not significantly affect the amount of PCBs in the bottles. The vapor phase was collected with an adsorbent trap fitted to the top of the apparatus with a Swagelock-connection and to a 50 cm³ syringe with a specially adapted Swagelock-to-Luer tip connector. The desired volume of vapor is sampled by first opening the stopcock on the sidearm to the atmosphere and then slowly (about 10 seconds) pulling a volume of vapor through the trap. The concentrations of total PCBs in indoor air has been reported by MacLeod (1981) to be 0.044 to 0.24 pg/cm³ and would not interfere with the measurements of individual chlorobiphenyls measured in the headspace in these experiments. In this experiment the traps used were 5.7 cm lengths of 1/4" stainless steel tubing which were filled with 200 mg of Florisil and capped with plugs of precombusted glass wool. Florisil (60-100 mesh) was used which had been combusted at 500°C, methylene chloride extracted, and deactivated with 1% water. Some previous experiments using Tenax traps which were subsequently desorbed thermally proved less satisfactory (Appendix 2). Due to the low amount of chlorobiphenyls added to the bottles in this experiment, it was necessary to sample 100 cm³ of headspace to measure chlorobiphenyls in all of the bottles. If the mixing of incoming atmosphere in the bottles is instantaneous with respect to the sampling then analytically determined vapor concentrations will be greater than 0.955 times the actual equilibrium concentrations (i.e., dilution is small). If mixing between the top of the headspace and the bottom, where the vapor is sampled, is incomplete during sampling, then the measured concentrations will be somewhat more accurate. The PCB containing traps are fitted to a short

column and eluted with 10 mL of 20% methylene chloride in hexane into 15 mL glass centrifuge tubes. An internal standard of chlorobiphenyls 29 (2,4,5-tri-chlorobiphenyl) and 143 (2,2',3,4,5,6'-hexachlorobiphenyl) was added by 10-200 μ L injections from hexane standards. Micro-Snyder columns were fitted to the top of the tubes and samples were evaporated to 0.5 mL in a hot water bath and transferred by pipette to tared 4 mL glass vials with three rinses of hexane. The samples were further concentrated with a nitrogen stream and the vials weighed prior to gas chromatography. Final sample volumes were 20 μ L to 1.5 mL. PCBs were determined by high resolution capillary gas chromatography with electron capture detection for all of the samples in this experiment. A Hewlett-Packard 5840 gas chromatograph with a 30 m DB5 fused silica capillary column (J&W Scientific) operated with H₂ carrier gas was used under the following conditions: a 2.0 μ L splitless syringe injection at 40°C with an initial hold of 2 minutes; rapid heating to 120°C (5 minutes); temperature programming at 6°C/min to 270°C (30 minutes), and finally another hold at 270° for 10 minutes. ECD makeup gas was 5% methane:95% argon at 30 mL/min. The concentrations of individual chlorobiphenyls are determined from their relative response factors to internal internal standard 143.

The concentrations of chlorobiphenyls in the vapor phase of the experimental bottles were not observed to change greatly over the course of the experiments, although there is greater variability in the vapor phase concentrations than in the solution phase measurements. The average relative standard deviations in the vapor phase were 11.1, 8.9, 10.9, 9.9, and 15.2% for di- through hexachlorobiphenyl, respectively.

Solution Phase Measurements

Duplicate samples of the solution phase were obtained by first drawing 10.0 mL of water into a volumetric glass pipette, and subsequently discarding the first 10 mL in an effort to pre-equilibrate the inside walls of the pipette with the solution containing PCBs. The next two 10 mL samples were emptied into 15 mL centrifuge tubes containing 1 mL of hexane and PCB internal standards. The PCBs were extracted from solution by shaking the tubes for 90 sec and pipetting off the hexane directly into tared 4 mL vials. The extraction procedure was repeated two more times. The extraction of water samples containing the enriched organic colloid samples was complicated by tenacious emulsions which were not easily separated by centrifugation or standing. A few drops of sodium lauryl sulfate in acetone proved to be effective in breaking these emulsions. The determination of PCBs in hexane extracts was identical to that described above for vapor samples. However the precisions of the solution phase measurements, calculated as the average relative difference from the mean, were much better than the corresponding vapor phase analysis: 3.3, 1.9, 1.2, 0.80, and 0.98% respectively for di-through hexachlorobiphenyl. These small errors are slightly smaller than those determined previously, or that can be expected normally from syringe injections of internal standards.

Container Wall Measurements

The experimental bottles were emptied of solution after samples were taken for DOC and the bottles were first shaken for 1 minute with 25 mL of acetone. The acetone was emptied into 250 mL separatory funnels, and the bottles (with

tops) were similarly extracted twice with 25 mL of hexane. The extracts were combined and 100 mL of methylene chloride-extracted, distilled water and PCB internal standards were added. The aqueous phase (containing acetone) was twice back-extracted with 25 mL of hexane using another separatory funnel. The three hexane extracts were combined and concentrated in Kuderna Danish evaporators. PCB determinations of hexane extracts were the same as those reported above.

RESULTS AND DISCUSSION

Ultrafiltration Results

DOC concentrations, enriched colloidal organic carbon (COC) concentrations, and other properties of six Chemotaxis Dock water samples are reported in Table 2-1. The DOC concentrations range from 0.95 to 2.38 mg/L and are similar to DOC measurements of 1.98 and 2.77 mg/L on unfiltered samples previously reported at this site (Stuermer and Harvey, 1974). POC was 0.32 and 0.28 mg/L in the two samples investigated in this study for comparison. The POC concentrations are 23 to 34% of DOC and are slightly higher than the concentrations of colloidal organic carbon (COC) which were 0.12 to 0.29 mg/L and averaged 18% of the total DOC. It is not known whether some of these results are biased by organic silicone contamination, although the July 23rd, 1985 sample obtained after removing the silicone tubing from the ultrafiltration system, is not significantly different. Stuermer and Harvey (1974) reported that 3.7 and 4.7% of the DOC in two samples at Chemotaxis Dock

Table 2-1. Results from filtration and ultrafiltration of seawater sampled at Chemotaxis Dock on Nantucket Sound, Massachusetts.

Date mon-day-yr	Temp. (°C)	pH	DOC (mg/L)	COC (mg/L)	f _{coc}	POC (mg/L)
3-21-1984	3.3	7.91	1.15	0.29	0.25	
8-29-1984	22.8	8.11	2.38	0.27	0.11	
4-11-1985	6.3	8.05	1.18	0.14	0.12	
6-13-1985	13.5		0.95	0.27	0.28	0.318
7-09-1985	21.8	8.21	1.45	0.12	0.084	
7-23-1985	23.2	7.98	1.20	0.27	0.23	0.28
Average Chemotaxis Dock DOC			1.38	0.23	0.18	
pore water	21.6	7.88	10.3	8.03	0.78	18,000*
2-15 cm from Stn. M						

* estimated from sediment properties at Station M given in Chapters 3 and 4.

were isolated as dissolved humic substance. The DOC and organic colloid concentrations measured in the interstitial water sample from Station M are higher than levels found in the water column. 78% of the DOC was enriched as a colloidal fraction by ultrafiltration. These results are consistent with other studies where ultrafiltration was performed on interstitial waters from reducing marine sediments (Krom and Sholkovitz, 1977; Orem and Gaudette, 1984).

Partitioning Experiment

The individual chlorobiphenyls were distributed in the experimental bottles according to their different Henry's Law constants and tendencies to sorb both to colloidal organic matter in solution and to the container walls. The fractions of added chlorobiphenyls which were measured in the vapor, solution, and sorbed to the walls are reported in Table 2-2. It is clear that the fractions of chlorobiphenyls found in the vapor were reduced in the experimental bottles to which colloids were added and also decreased with increasing chlorine substitution. The fraction of PCBs found on the container walls is quite large and increases with hydrophobicity of the PCBs. It is important to note that for the tri- through pentachlorobiphenyls the ratio of wall sorbed to solution phase PCBs is about double in the colloid-added bottles compared to the controls. The amount of wall adsorbed hexachlorobiphenyl is about 160% of that extracted from solution in both cases. It is also observed that the total recovery of chlorobiphenyls in the experimental bottles is good with the exception of the low and variable recoveries reported for 2,4'-dichlorobiphenyl. The recoveries for this compound and the effects on the interpretation of partitioning results are discussed later in the next section.

Table 2-2. The distribution of five chlorobiphenyls in the experimental bottles where Fr_v , Fr_T (the total PCB found in solution), and Fr_w are the fractions of individual chlorobiphenyls accounted for in the three analytically determined phases. The standard deviations of these values are included in parenthesis.

Chlorobiphenyl	ultrafiltrate bottles				colloid-added bottles			
	Fr_v	Fr_T	Fr_w	Total Rec. (%)	Fr_v	Fr_T	Fr_w	Total Rec. (%)
2,4'-di CBP	0.058 (.015)	0.737 (.142)	0.073 (.026)	86.9 (18.0)	0.022 (.018)	0.468 (.223)	0.042 (.023)	50.8 (26.6)
2,4,4'-tri CBP	0.0613 (.0067)	0.771 (.023)	0.121 (.018)	95.7 (3.9)	0.044 (.045)	0.658 (.020)	0.205 (.068)	90.7 (6.9)
2,3',4',5-tetra CBP	0.037 (.0080)	0.732 (.015)	0.214 (.089)	98.4 (9.5)	0.019 (0.0030)	0.555 (.033)	0.308 (.090)	88.4 (8.3)
2,2',3,4,5'-penta CBP	0.030 (.010)	0.612 (.034)	0.286 (.060)	92.1 (9.5)	0.0095 (.0027)	0.439 (.039)	0.412 (.154)	86.6 (13.8)
2,2',3,4,4',5-hexa CBP	0.013 (.0024)	0.354 (.062)	0.577 (.128)	95.5 (13.4)	0.0076 (.0021)	0.333 (.045)	0.550 (.156)	89.1 (13.2)

The distribution of PCBs between various phases in the experimental bottles can be best interpreted in terms of the concept of fugacity. Fugacity (in units of pressure) can be considered as the escaping capacity that a chemical exerts in a given phase (Mackay, 1979; Mackay and Patterson, 1981). The fugacity of an individual chlorobiphenyl is equal in all phases at equilibrium. In this experiment the phases include the dissolved (aqueous) phase, the vapor phase, chlorobiphenyl sorbed to colloids, and also PCB sorbed to the walls; i.e.: $f_d = f_v = f_c = f_w = \dots = f$, where f is the fugacity and the subscripts d , v , c , and w correspond to dissolved, vapor, colloid sorbed, and wall sorbed phases, respectively throughout this chapter.

The fugacity is related to concentration, C , through a fugacity capacity constant Z (after Mackay, 1979), where Z is generally a function of temperature, pressure, phase composition, and the nature of the chemical.

$$C_d = Z_d f_d \quad (\text{eqn. 2-1})$$

For an ideal gas, $Z_d = 1/H$ where H is the Henry's Law constant of an individual chlorobiphenyl and $Z_v = 1/RT$ (Mackay and Patterson, 1981). At equilibrium then:

$$C_d H = C_v RT \quad (\text{eqn. 2-2})$$

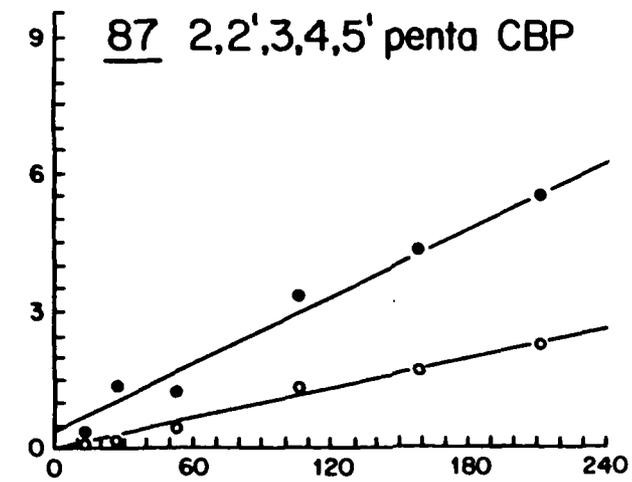
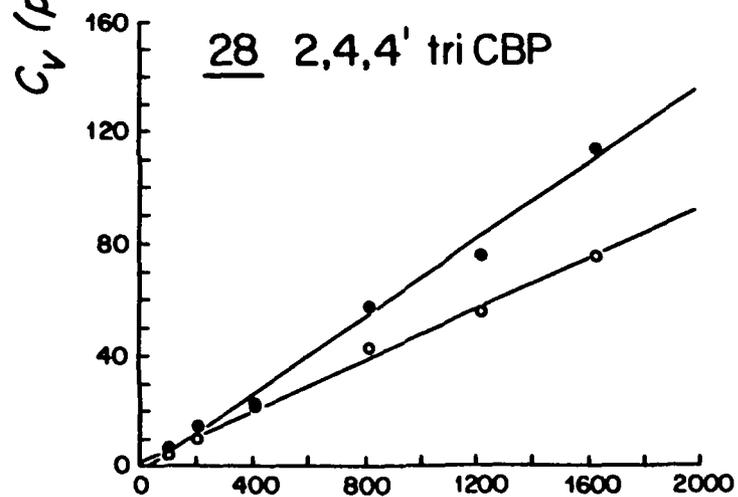
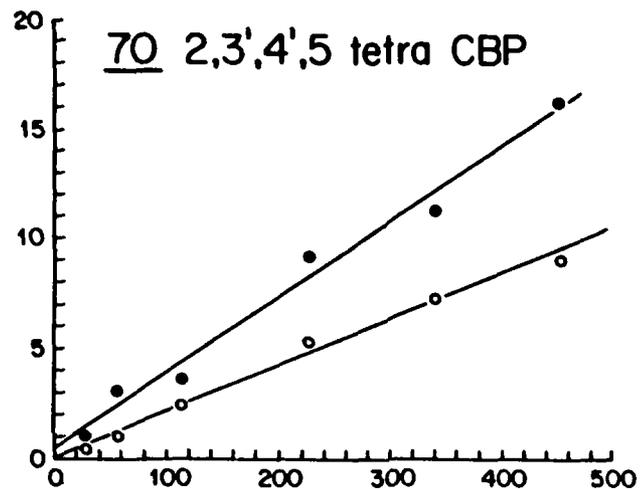
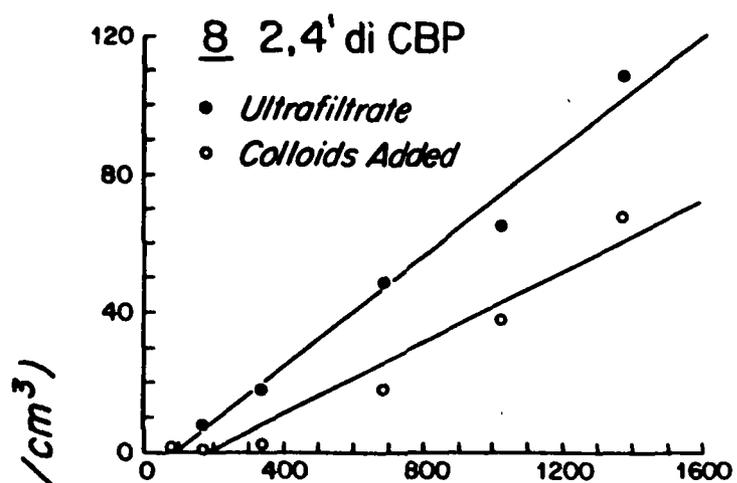
$C_v RT/H$ provides a direct measure of C_d as long as H is constant over the dilute range of concentrations provided by PCBs (or most non-polar HOCs) in seawater. Constant H is a valid assumption if there are no significant

solute-solute interactions in either phase, and that increasing C_a does not affect the "solvent" of the aqueous phase (Leo et al., 1971; Mackay and Patterson, 1981). Results from this and other experiments (Appendix 1) indicate that C_v is linearly related to C_a determined both in distilled and ultrafiltered seawater over a wide range of C_a .

Figure 2-2 shows that, for the di- through pentachlorobiphenyls, the vapor concentration, C_v , was consistently less in the bottles in which enriched colloidal organic matter had been added than in the control (ultrafiltrate only) bottles. C_v was also decreased for the hexachlorobiphenyl 138 in the only two colloid-added bottles in which it was detected. The concentrations of 138 were too small in the vapor of the colloid-added bottles to permit accurate determination. A small sample students t test for parallelism (Kleinbaum and Kupper, 1978) showed that the slopes of the linear regressions of C_v vs. the amount of chlorobiphenyl added to the bottles were significantly lower in colloid-added experiments than in the controls at $P < 0.0005$ for tetra- and pentachlorobiphenyl and at $P < 0.025$ for di- and trichlorobiphenyl. These results indicate that colloidal organic matter had a significant effect on the solution phase fugacity of chlorobiphenyls investigated in this study.

The lowered C_v of chlorobiphenyls in the colloid-added bottles is largely due to sorption of PCBs to colloidal organic matter in solution. As shown above (Table 2-2), C_w was also consistently higher in bottles in which colloidal organic matter was added. This suggests that organic colloids changed the sorbent properties of the walls, probably by adsorbing onto the walls themselves. Several clean inorganic surfaces, including silica, have

Figure 2-2. Plots of the vapor phase concentrations of four chlorobiphenyls vs. the amount of chlorobiphenyl added to each bottle. Filled and open circles indicate data for bottles equilibrated with ultrafiltrate only and with enriched colloidal organic matter (4.07 mgC/L), respectively.



Amount Added (ng)

been observed to be rapidly coated by marine DOM when added to seawater (Niehof and Loeb, 1974; Hunter, 1980). Davis and Gloor (1981) found that the colloidal organic matter fraction (> 1000 MW) preferentially adsorbed to colloidal alumina. Therefore, it is likely that a fraction of the added colloids adsorbed to the container walls, and enhanced PCB sorption onto the walls. This is consistent with the fact that a DOC of 4.17 ± 0.24 mg/L was found in the colloid-added bottles compared to an estimated 4.82 ± 0.18 mg/L which was added. It is not known whether the small percentage of colloidal organic matter which sorbed to the walls had a similar sorption capacity for HOC as that remaining in solution.

The sorption of PCBs and other nonpolar HOC to colloidal organic matter has been reviewed in Chapter I. Previous studies have suggested that sorption of HOC with colloidal organic matter is quite similar to sorption with natural sediments and that a model of sorption where HOC partition into an amorphous polymeric organic phase can explain many aspects of observed sorption behavior. Sorption isotherms have indicated linear partitioning (Carter and Suffet, 1982; Wijayarathne and Means, 1984b) and sorption could be described by:

$$C_e = K_{oc} C_a \quad (\text{eqn. 2-3})$$

where C_e is normalized to organic carbon (e.g., in units of ng/g org C) and K_{oc} is the organic carbon normalized partition coefficient. K_{oc} has proven to be a valuable predictor of sorption for HOC with natural sediments and depends primarily on the hydrophobicity of the solute (Karickhoff et al., 1979; Means et al., 1980; Schwarzenbach and Westall, 1981). K_{oc} for sediments can be reasonably well predicted from the aqueous activity coefficient or octanol-water partition coefficient (K_{ow}) of HOC using experimentally

derived linear free energy relationships. The use and limitations of K_{oc} for predicting and understanding organic matter partitioning were discussed in Chapter I.

The sorption of PCBs to the colloidal organic matter in solution for these experiments can be determined by using the measured C_v and the total concentration of chlorobiphenyl in the solution (C_T). C_T is the sum of dissolved and colloid sorbed concentrations of an individual chlorobiphenyl:

$$C_T = C_d + C_e \quad (\text{eqn. 2-4})$$

C_d can be calculated from the vapor concentration by eqn. 2-2. In this experiment, H/RT ((ng/cm³ air)/(ng/cm³ water)) is estimated from the slope of C_v vs. C_T in the six bottles in which PCBs were equilibrated with only ultrafiltrate. This assumes $C_T = C_d$ in those bottles. The linear dependence of C_v for all chlorobiphenyls with increasing C_T in ultrafiltrate bottles indicates that PCBs in solution are either dissolved or that a constant fraction of C_T is dissolved. Combining equations 2-2 and 2-4 gives C_e (in ng/g of organic carbon):

$$C_e = (C_T - C_v / (H/RT)) (10^6 / \text{DOC}) \quad (\text{eqn. 2-5})$$

The sorption isotherms of C_e vs. C_d for each chlorobiphenyl can then be generated from the data for C_T and C_v and DOC for each of the bottles in which enriched colloidal organic matter was added. DOC in this case is the amount of DOC determined at the end of the experiment minus that in the ultrafiltrate bottles. If some fraction of the low molecular weight ultrafiltrate DOC acts as a sorbent for PCBs, H/RT and thus C_e will be underestimated. However, this can only account for a small effect because the amount of operationally defined colloidal organic carbon is about 4.5 times

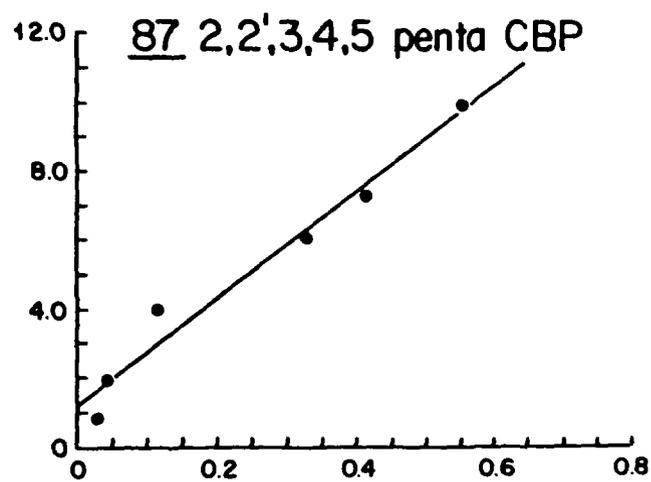
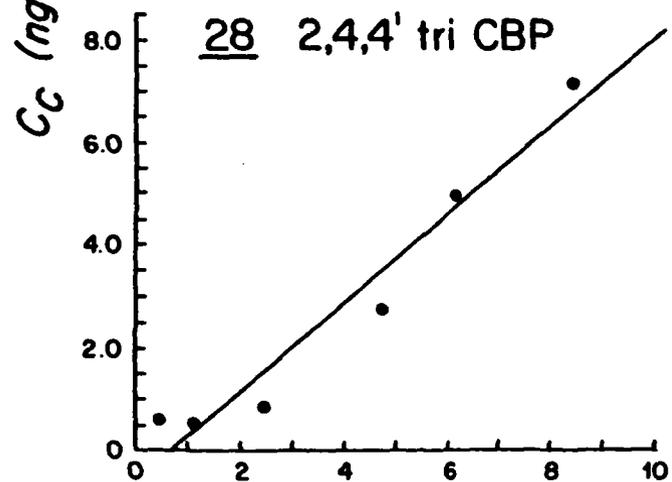
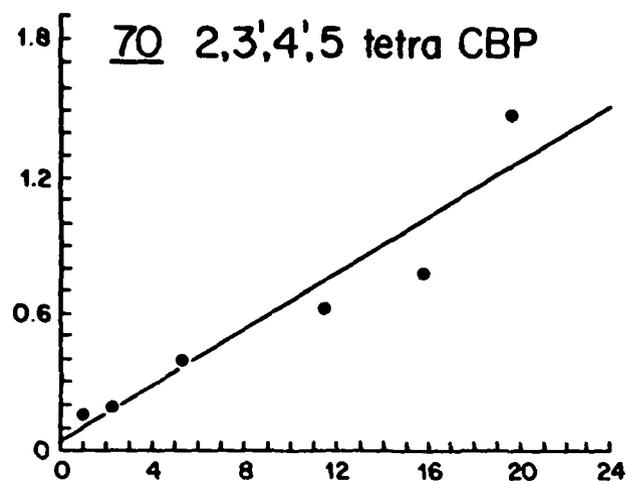
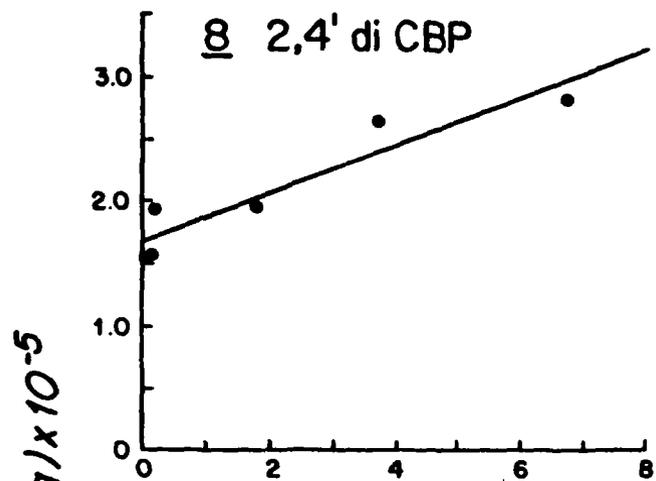
greater than ultrafiltrate DOC in this experiment, and low molecular weight dissolved organic matter is known to have a much smaller effect on the speciation of HOC (see Chapter I, Chlou et al., 1983, 1986; Miller et al., 1985; Burris and MacIntyre, submitted). The resulting sorption isotherms for di- through pentachlorobiphenyl are shown in Figure 2-3. The isotherms for tri- through pentachlorobiphenyl are consistent with linear sorption or partitioning of HOC with colloidal organic matter described by eqn. 2-3 which was found in other studies (Means and Wijayarathne, 1982; Carter and Suffett, 1982; Wijayarathne and Means, 1984b). The large non-zero y-intercept for dichlorobiphenyl is in part due to errors involved in estimating H/RT and the small effect colloidal organic matter has on the speciation of dichlorobiphenyl under the experimental conditions used. The slope of C_e vs. C_a for this chlorobiphenyl still increases linearly and is not significantly affected by using other values of H/RT in eqn. 2-4. Further problems involved in the interpretation of results for dichlorobiphenyl are discussed later.

The slopes of the sorption isotherms determined by linear regression directly give K_{oc} (eqn. 2-3). The slopes are significantly greater than zero at $P < 0.01$ using a student t test (Kleinbaum and Kupper, 1978) for all four chlorobiphenyls, and the resulting values of K_{oc} are shown in Table 2-3. The value for dichlorobiphenyl is also included even though the data plotted in Figure 2-2 does not conform to eqn. 2-3. Log K_{ow} s for these four compounds are also compared to log K_{oc} in Table 2-3. K_{oc} is 6.6 to 26 times lower than K_{ow} for the 4 chlorobiphenyls studied, and log K_{oc} shows a general increase with log K_{ow} . It is not certain whether the K_{oc} of tetrachlorobiphenyl is actually lower than that of trichlorobiphenyl due to

Table 2-3. The K_{oc} 's of four chlorobiphenyls calculated from the slopes of the sorption isotherms shown in Figure 2-3. The errors are one standard deviation and the source of the K_{ow} 's are found in Table 2-4.

Chlorobiphenyl	K_{ow}	K_{oc}
2,4'-di CBP	1.29×10^5	$1.91 (\pm 0.35) \times 10^4$
2,4,4'-tri CBP	4.79×10^5	$8.50 (\pm 1.17) \times 10^4$
2,3',4',5-tetra CBP	1.55×10^6	$6.12 (\pm 1.04) \times 10^4$
2,2',3,4,5'-penta CBP	4.07×10^6	$1.54 (\pm 0.141) \times 10^5$

Figure 2-3. Sorption isotherms for four chlorobiphenyls. C_e and C_d are calculated from C_v and C_T by eqns. 2-2 and 2-5.



C_d (ng/cm³)

the experimental uncertainties involved.

The calculation of sorption isotherms from the data for C_v and C_r by equations 2-2 and 2-5 does not account for the effect that organic colloids adsorbed to container walls may have on the speciation or distribution of PCBs in the experimental bottles. This approach is justified as the results are a function of the enriched colloidal organic matter left in the solution at the end of the experiment. It is not known how representative the remaining colloidal organic matter is compared to that lost or originally present in the seawater sample. However, 84% of the amount of enriched colloidal organic matter added to the bottles is accounted for in solution at the experiment's conclusion. It is possible to calculate a whole bottle effect of colloidal organic matter on the fugacity of chlorobiphenyls using the data shown in Figure 2-1. A K_{oc} normalized to the total amount of enriched colloidal organic matter added to the bottles can be calculated from the differences in the slopes of C_v versus the amount of PCB added in the colloid added bottles (B_c) and ultrafiltrate only (B_u) experiments in the following way:

$$K_{oc} = \frac{(B_u - B_c) 10^6}{B_c \cdot \text{DOC}} \quad (\text{eqn. 2-6})$$

where DOC is the amount of enriched colloidal organic matter added to the bottles (4.07 mg C/L). This approach is essentially that used in the headspace experiments of Garbarini and Lion (1985) and Spink and Colgan (1983) to measure the speciation of organic compounds which are more soluble and do not sorb to container walls. The results for $\log K_{oc}$ calculated by eqn. 2-6 are given in Table 2-4 and are compared to $\log K_{oc}$ calculated from the

Table 2-4. Summary of chlorobiphenyl/organic colloid sorption results.

Chlorobiphenyl (PCB no.)	log K_{ow}	log K_{oc}		
		$C_v/Amt.$ ¹	Isotherm ²	prediction ³
2,4'-di CBP (8)	5.11	5.11 (4.43) ⁴	4.29	4.37
2,4,4'-tri CBP (28)	5.68	5.07	4.93	4.84
2,3',4',5-tetra CBP (70)	6.19	5.20	4.79	5.26
2,2',3,4,5'-penta CBP (87)	6.61	5.54	5.19	5.60

1. K_{oc} calculated from eqn. 2-6
2. From Table 2-3
3. Prediction from correlation based on dissolved soil humic acid sorption derived from Figure 1-3: $\log K_{oc} = 0.818 \log K_{ow} + 0.193$.
4. Value in parenthesis is calculated from data shown in Figure 2-4 where C_v is plotted vs. the amount of dichlorobiphenyl recovered.

sorption isotherms of C_e versus C_o given earlier in Table 1-3 and the predictions of $\log K_{oc}$ based on studies of dissolved soil humic acids given in Table 1-3 and Figure 1-3. The K_{oc} 's estimated from this approach are higher than those calculated from the isotherm analysis of PCBs and organic colloids left in solution and, with the exception of dichlorobiphenyl, are in reasonable agreement with the predictions based on soil humic acid results for HOC sorption. If the whole bottle effect calculation of K_{oc} is indicative of the true sorptive properties of colloids had they remained in solution, it is implied that, at least for tri- through pentachlorobiphenyl, the colloids which adsorbed to the walls had a greater sorption affinity than the bulk of the colloidal organic matter which remained in solution.

The results for chlorobiphenyl 8 are complicated by the low and variable recovery of this compound in the experimental bottles noted above and seen in Table 2-2. Figure 2-4 shows the results for dichlobiphenyl when C_e is plotted against the amount recovered. This plot when contrasted with Figure 2-2 would suggest a much smaller difference in the colloid-added and control experiments for this compound. These results combined with the low recoveries of 8 in colloid-added bottles may be due to at least three possible reasons:

- 1) 8 was lost or degraded in some of the experimental bottles before or during the course of the experiments, and that Figure 2-2 illustrates the small effect colloids had on the distribution of 2,4'-dichlorobiphenyl in this experiment. This compound is the most volatile used in the experiments. It is not known whether this compound might be more sensitive to photochemical degradation than the other chlorobiphenyls studied. However, photochemical

reactions should have been minimized by the experimental protocol.

2) 8 was inefficiently extracted from some phase(s) in the bottles containing colloids. This most likely would be a colloid-sorbed phase since most of the recovered dichlorobiphenyl is in the analytically determined solution phase (C_T). However wall-sorbed phases might also be important. It is not evident why the extraction efficiency of dichlorobiphenyl would be less than that of the other chlorobiphenyls. Chlorobiphenyls with less chlorine substitution (and particularly less ortho-chlorine substitution) are retained to a greater extent by activated charcoal (Stallings et al., 1980) and silica gel (observations from this study) when eluted with hexane or other non-polar solvents. This is either due to steric hindrance to adsorption sites or greater aromaticity of more planar, less chlorinated biphenyls.

3) 2,4'-dichlorobiphenyl may have been lost in some samples during analytical extraction and evaporation steps and an evaporative loss of 8 occurred without a concomitant loss of internal standard 29 or chlorobiphenyl 28. From the work of Bidleman (1984) it is expected that 8 has a vapor pressure about five times that of either of the trichlorobiphenyls so that unaccounted for loss may occur during evaporation.

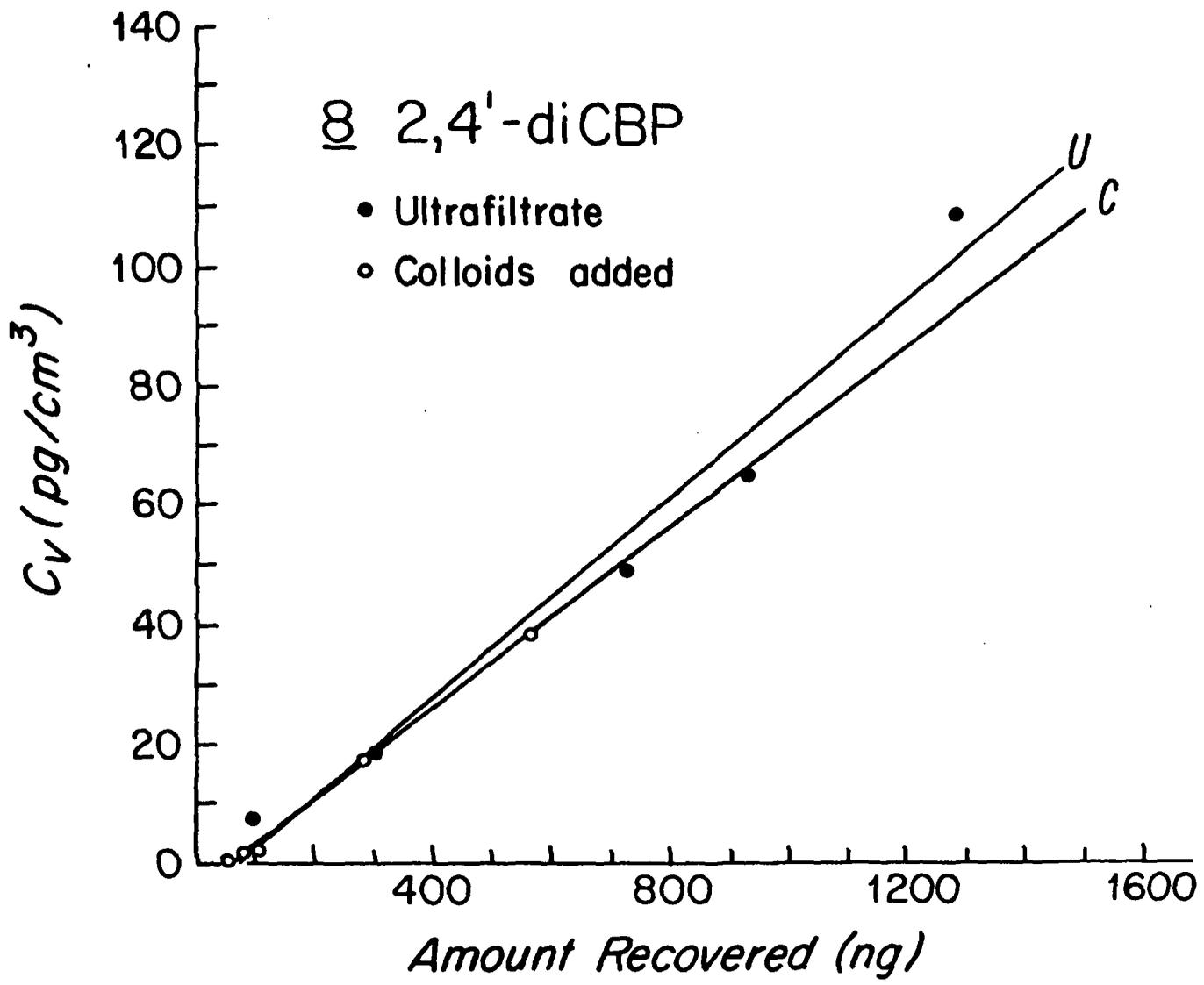
Further work is necessary to distinguish between reasons for the inconsistent recoveries of dichlorobiphenyl and to be sure of the interpretation of the partitioning results presented here for this compound.

As mentioned above, and reviewed in Chapter I, $\log K_{oc}$ increases with $\log K_{ow}$ in a linear relationship for the sorption of HOC with soil and sediment organic matter:

$$\log K_{oc} = a \log K_{ow} + b \quad (\text{eqn. 2-7})$$

Figure 2-4. Plot of C_v vs. the amount of 2,4'-dichlorobiphenyl recovered from each experimental bottle. Again the filled and open circles represent data from equilibrations with ultrafiltrate only and enriched colloidal organic matter, respectively.

5 1363



where a and b are empirical constants. It was shown in Chapter I that the combined results of several determinations of K_{oc} for HOC with dissolved soil humic acids were well predicted by correlations of eqn. 2-7 derived from soil and sediment studies (see Figure 1-3 and Table 1-2) within the uncertainties involved in experimental measurements of K_{oc} and K_{ow} . This suggests that the mechanisms of sorption are similar for sediment-bound and dissolved humic acids from similar origin. It is not known how good a model soil humic acid is for marine or freshwater colloidal organic matter. Several studies have shown that the sorption of HOC to natural colloidal organic matter or total dissolved organic matter also tends to increase with K_{ow} (Carter and Suffet, 1983; Landrum et al., 1984; Wijayarathne and Means, 1984b; Chiou et al., 1986) and that the role of colloidal organic matter on the speciation of HOC increases with hydrophobicity (Matsuda and Schnitzer, 1971; Boucher and Lee, 1972; Boehm and Quinn, 1976).

The results from this study have been compared to the other results for sorption of HOC to natural colloidal organic matter from freshwaters and estuaries in Table 2-5 and Figure 2-5. These combined results reveal a few insights. First the values of K_{oc} determined in this study for PCBs with marine colloidal organic matter are within the range of those predicted by correlations of $\log K_{oc}$ and $\log K_{ow}$ found in soil-sediment sorption studies. $\log K_{oc}$ for the PCBs are similar to those found for PCBs with soil and sediment organic matter but are lower than those found by Wu and Gschwend for freshwater sediments (see Figure 1-2). $\log K_{oc}$ s determined for di- and trichlorobiphenyl are closely predicted by the equation for the sorption of HOC with dissolved soil humic acids given in Figure 1-3. K_{oc} s for

Table 2-5

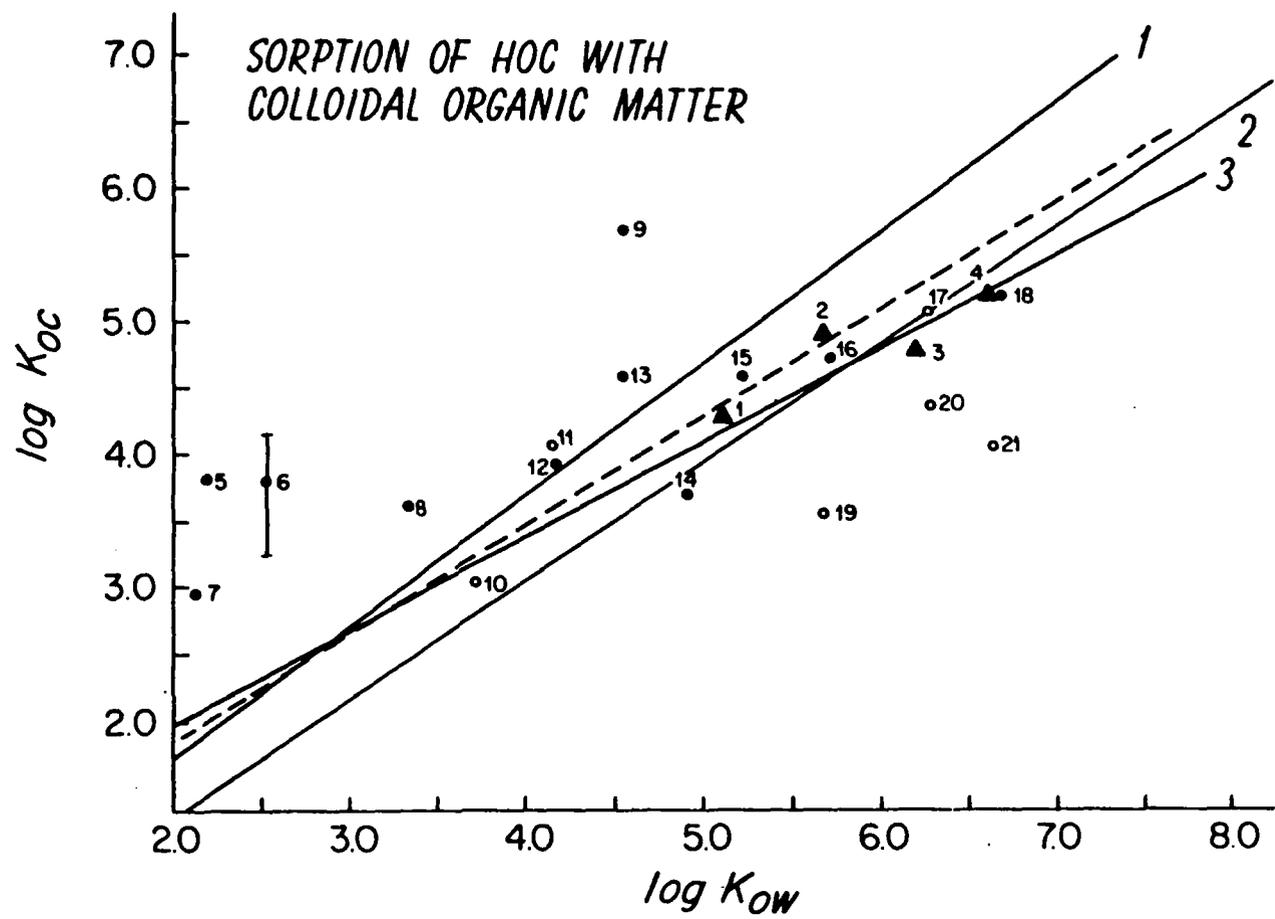
A survey of literature reports of HOC sorption with colloidal organic matter isolated from natural waters.

Pt. No.	Compound	Study ¹	log K _{ow} (Refs.) ²	log K _{oc}
1	2,4'-di-CBP	This study	5.11 ± 0.02 n=3 (3,4,6)	4.29
2	2,4,4'-tri-CBP	" "	5.68 ± 0.06 n=3 (2,3,6)	4.93
3	2,3',4',5'-tetra-CBP	" "	6.19 ± 0.22 n=3 (2,3,9)	4.79
4	2,,',3,4,5'-penta-CBP	" "	6.61 ± 0.24 n=2 (2,3)	5.19
5	linuron	Means and Wijayarathne	2.19 (12)	3.81 (3.79-3.83)
6	atrazine	(1982)	2.52 (12)	3.80 (3.23-4.13)
7	benzene	Wijayarathne and Means	2.13 n=2 (1,7)	2.96
8	naphthalene	(1984b)	3.33 ± 0.03 n=3 (1,7,8)	3.61
9	anthracene	" "	4.54 ± 0.09 n=3 (1,2,8)	5.71
10	lindane	Carter and Suffet	3.71 ± 0.01 n=2 (11,12)	3.04
11	1,2,4-triCB	(1983)	4.14 ± 0.13 n=2 (2,11)	4.06
12	fluorene	" "	4.16 ± 0.12 n=4 (1,2,7,11)	3.95
13	anthracene	" "	4.54 ± 0.09	4.60
14	dibutylphthalate	" "	4.19 (11)	3.70
15	fluoranthrene	" "	5.22 n=2 (1,2)	4.59
16	dicyclohexylphthalate	" "	5.71 (11)	4.72
17	p,p' DDT	" "	6.28 ± 0.08 n=2 (9,13)	5.09
18	di-2-ethyl-hexylphthalate	" "	6.69 (11)	5.15
19	2,4,4'-tri-CBP	Chiou et al. (1986)	5.68 ± 0.06	3.56
20	p,p' DDT	" "	6.28 ± 0.08	4.40
21	2,2',4,5,5'-penta-CBP	" "	6.49 ± 0.48 n=5 (2,3,4,5,7)	4.08

1. Points 5-9 used estuarine colloidal organic matter, 10-18 used Pakim Pond humic acid, and 19-21 used Suwanee River humic substances.

2. Error refers to 1 std. deviation when n > 3. Numbered references for log K_{ow}'s refer to: 1) Mackay et al. (1980b), 2) Bruggeman et al. (1982), 3) Rapaport and Eisenreich (1984), 4) Woodburn et al. (1984), 5) Chiou et al. (1977), 6) Chiou et al. (1983), 7) Miller et al. (1985), 8) Karickhoff et al. (1979), 9) McDuffie (1980), 10) Chiou et al. (1982), 11) from Carter and Suffet (1983), 12) from Karickhoff (1981), 13) from Landrum et al. (1984)

Figure 2-5. The combined results of literature values of $\log K_{oc}$ vs $\log K_{ow}$ for HOC with colloidal organic from natural waters. The numbered points correspond to the data found in Table 2-4. Triangles represent the chlorobiphenyl results calculated from Figure 2-3 and open circles are other data for chlorinated hydrocarbons. The three solid lines refer to predictive $\log K_{oc} - \log K_{ow}$ relationships based on soil and sediment sorption studies given in Table 1-1 and Figure 1-2. The dashed line represents the correlation found for HOC with dissolved soil humic acids in Chapter I (See Figure 1-3).



tetra- and pentachlorobiphenyl fall below the prediction based on dissolved humic acid, but are close to predictive lines 2 and 3 in Figure 2-4 which were both mainly based on results for chlorinated aromatic hydrocarbons.

It is apparent from Figure 2-4 that there is considerable scatter in the K_{oc} 's reported by different workers for HOC sorption with different samples of colloidal organic matter. When grouped together, these data suggest that K_{ow} alone is a poor predictor of HOC/organic colloid sorption. As discussed in Chapter 1, differences in $\log K_{oc}$'s determined in various studies and also from predictions may be due to differences in the isolated colloidal organic matter studied, differences in the interactions of different HOC or classes of HOC with colloidal organic matter, and differences or problems associated with the experimental methods used for measuring HOC/colloid sorption.

Colloidal organic matter collected from different environments by various isolation procedures have been shown to have highly variable sorptive properties with respect to HOC. Table 2-5 shows that K_{oc} for atrazine ranged by a factor of eight for different samples obtained from the Patuxent and Choptank Rivers (Means and Wijayarathne, 1982). Atrazine and linuron are nitrogen containing chloro-s-triazine and phenyl urea herbicides, respectively, and may sorb to organic matter or mineral surfaces via hydrogen bonding or other binding mechanisms which are more site specific than that of nonpolar HOC such as PCBs considered in this study. $\log K_{oc}$ for sorption of some aromatic amines with sediments and soils were enhanced over those predicted from $\log K_{oc}$ and more variable than nonpolar HOC (Means et al., 1982). Highly polar or ionic HOC can be sorbed by multiple mechanisms (Karickhoff, 1984) and therefore should not be strictly compared to sorption

of nonpolar HOC. However, the range in K_{oc} reported for atrazine is not easily explained by small differences in salinity, and reflects changes in the colloidal organic matter sampled at different locations at different times.

Carter and Suffet (1983) measured large differences in the K_{oc} of DDT with soil and freshwater humic substances from different sources. They found that soil humic acids had a higher binding capacity for DDT than freshwater humic acids which in turn were higher than corresponding aquatic fulvic acids. This trend is consistent with the findings of Chiou et al. (1986) who hypothesized that it was primarily the polarity of isolated humic substances, as reflected by their oxygen contents, which influenced the relative binding affinity of dissolved humic substances. It is likely that the size and three-dimensional configuration of colloidal organic matter are important properties determining the sorptive characteristics of isolated material. It is of interest to note that the sorption results of Chiou et al. (1986) shown in Table 2-5 and Figure 2-5 are for Suwanee River humic and fulvic acids, and are much lower than the $\log K_{oc}$'s reported for DDT (Carter and Suffet, 1983), PCBs (this study), or predictions based on correlations of $\log K_{oc}$ and $\log K_{oc}$ derived from laboratory studies of sediments or dissolved soil humic acid (see Figure 2-5 and Chapter 1). Carter and Suffet (1983) found that the sorption of DDT with Suwanee River fulvic acid was negligible and much lower than that determined for other humic substances studied. Landrum et al. (1984) have also reported variable $\log K_{oc}$'s for a range of nonpolar HOC with several samples from the Great Lakes. Those workers normalized K_{oc} to the total DOC measured and therefore the results are not easily comparable to each other or the other results in Figure 2-4.

It is undetermined how the procedures used in the isolation of colloidal organic matter may influence its chemical or the three-dimensional structure. Garbarini and Lion (1985) found that the binding of dissolved humic acid to alumina decreased its sorption capacity. It is anticipated that isolation procedures which result in flocculation, aggregation, or configurational changes in organic colloids could have a significant effect on their sorptive properties. Aggregate size and disaggregation have been shown to influence the sorption kinetics of HOC with sediment particles (Karickhoff and Morris, 1985; Wu and Gschwend, 1986). The hollow fiber ultrafiltration technique used by Means and Wijayarathne (1982) and in this study avoids high concentrations, dessication, and pH and salinity changes which could cause structural changes in isolated colloids.

Variability in observed sorption of HOC which arise from molecular properties other than their hydrophobicities (i.e., their aqueous phase activity coefficients) are difficult to ascertain, and will depend on the mechanism or type of interaction with the organic phase. In an organic phase partitioning model, sorption will depend on how well the sorbate is accommodated in the organic phase. It is suggested from solubility and octanol-water partitioning studies (Bruggeman et al., 1982; Miller et al., 1985) that PCBs are less well accommodated in octanol than are PAHs and have organic phase activity coefficients that are 2-5 times higher. Differences in $\log K_{oc} - \log K_{ow}$ correlations reported for different compound classes with soils and sediments (see Table 1-1) imply that the ratio of the organic phase activity coefficient of the sorbate in octanol and sediment organic matter are dependent on the class of HOC considered (i.e., that octanol is a better model

phase for some HOC than others). It is interesting that the sorption data for PCBs and chlorinated hydrocarbons tends to fall below those of PAH in the results for dissolved humic substances (Figure 1-3) and for natural colloidal organic matter (Figure 2-4). However no conclusions are yet possible because of uncertainties involved in methods used in various sorption studies (see Chapter 1) and in the variability of sediment and colloidal organic matter studied.

If the sorption of HOC with colloidal organic matter involves interactions with specific hydrophobic regions or sites on or within macromolecular organic matter, then it could be expected that molecular size and shape of HOC would influence the observed partitioning. Mingelgrin and Gerstl (1983) discuss some evidence supporting an effect of molecular shape on sorption of HOC with soil organic matter. Similarly the gel partitioning model of Freeman and Cheung (1981) for the sorption of HOC with sediment organic matter, suggests that steric constraints on the diffusion of HOC into sediment organic matter may be important and would depend on the size of the sorbate and the three-dimensional structure and cross-linking of the polymeric organic matter.

The ability of colloidal matter to accommodate HOC in a partitioning mechanism will depend on the relative size and properties of the sorbate and sorbent. The colloidal organic matter in seawater is poorly characterized and many of its properties depend on the isolation procedure used (Thurman, 1985; Carlson et al., 1985; see Chapter 1). Carlson et al. (1985) report that an average of 28% of the DOC in North Atlantic surface waters was retained by ultrafilters of 1,000 MW nominal pore size and that an additional 6% was enriched by 10,000 MW filters. Wijayarathne and Means (1984a) found most

estuarine colloidal organic matter was of an approximate molecular weight of 10,000 as determined by gel permeation chromatography. Finally, Stuermer and Harvey (1974) found most marine humic substances are isolated as fulvic acid type material with molecular weight ranges from less than 700 to 5,000 MW. It has been shown that fulvic acids are efficiently retained by various hollow fiber and membrane ultrafilters having reported molecular weight cutoffs of up to 10,000-50,000 MW (Kwak and Nelson., 1977). Therefore the macromolecular or colloidal organic matter in seawater (defined by ultrafiltration or other procedures) may have a range of molecular weights, which on the low end may only be a two or three times larger than those of many HOC of interest. The ability of marine colloidal organic matter to accomodate a hydrophobic organic sorbate must depend on the size requirement of the sorbate and some properties, including size, of the colloid. Studies of sorption with dissolved polymers of well characterized molecular weights and composition (Chiou et al., 1986) would aid in the understanding of HOC/organic colloid partitioning.

The apparently small dependence of the observed $\log K_{oc}$'s on $\log K_{ow}$ for the four chlorobiphenyls in this study could be due to the increasing size requirements of chlorobiphenyls with increasing chlorine substitution. Leo et al. (1971) summarized the results of several studies of drug binding (primarily barbiturates) to proteins and found a consistently weaker dependence of binding on $\log K_{ow}$ than that found in other organic solvent partitioning systems (i.e., $a = 0.55$ in eqn 2.6). They proposed that it was unlikely that the sorbate molecules were fully accomodated into the organic protein phase and that partially dehydrated, surface-bound mechanisms of sorption were involved. Landrum et al. (1984) observed reversals in the order

of sorption of a range of HOC and DOC from different locations. In other words, K_{oc} did not always exactly follow increases with K_{ow} in waters sampled and was probably related to different properties of the dissolved organic matter present. It is not yet possible to draw conclusions regarding relative effects of PCB size and their hydrophobicities from this limited data set.

The difficulty of experimentally determining dissolved HOC concentrations in laboratory organic colloid sorption studies further complicates the comparison of K_{oc} 's reported by different workers. Problems and limitations involved in different methods for determining HOC speciation were discussed in Chapter 1. However Figure 1-3 illustrates that several different methods do yield results for HOC-dissolved soil humic acid sorption which are consistent with each other and agree with predictions based on sediment and soil organic matter sorption studies. Several observations regarding the data in Table 2-5 and Figure 2-5 can be made to shed some light on the apparent variability of K_{oc} . Points 5-9 in Table 2-5 are the only data available using a hollow fiber ultrafiltration technique for distinguishing dissolved and colloid-sorbed concentrations of HOC. Relatively high K_{oc} 's for atrazine and linuron have been reported with soils and sediments (Karickhoff, 1981), which is not unusual for polar, nitrogen containing HOC (Karickhoff, 1984). However the K_{oc} 's reported by Wijayarathne and Means (1984b) for benzene, naphthalene, and anthracene are several times higher than their reported K_{ow} 's or measurements of K_{oc} for other PAH on Pakim Pond humic acid (Carter and Suffet, 1983). It can be argued that K_{ow} could provide an approximate upper limit for K_{oc} if sorption is described as a bulk organic

phase partitioning process. However it is not clear whether HOC/organic colloid sorption involves partitioning into an organic phase or simply partial accomodation with an adsorbed or surface bound phase. Normalization of sorption to organic carbon may be misleading due to the high surface to volume ratio of colloidal material. Highly elevated K_{ow} 's have been reported for DDT sorbed to surface films of octanol (Platford, 1982). So, that while these determinations of K_{oc} by ultrafiltration should not be discounted, the assumptions involved in the method should be further verified and results checked by other experimental methods.

The results of Chiou et al. (1986) illustrated by points 19-21 in Figure 2-4 were obtained using a solubilization technique. These data were for Suwanee River humic and fulvic acids which were found to have an anomalously low sorption capacity in the work of Carter and Suffet (1983). Also solubilization techniques only yield sorption results in the limiting case of saturation of HOC in both aqueous and organic phases. It is not yet determined whether partitioning of HOC with organic colloids remains linear at near saturation levels. If saturation effects are apparent, then measured K_{oc} values will be less than those expected in the more general low-loading case. Again it is not possible to ascertain whether these latter values of $\log K_{oc}$ are lower than the others because of the source of colloidal organic matter or are due to the experimental methods employed.

In summary, the results from this headspace partitioning experiment are within the range of values measured by Carter and Suffet (1983) for other HOC using primarily equilibrium dialysis methods, and are also within the range of those predicted from correlations with $\log K_{ow}$ based on soil, sediment, and

dissolved soil humic acid studies. When viewed together in Figure 2-5, reported literature values of $\log K_{oc}$ for HOC with natural organic colloids illustrate: (1) the sparsity of information presently available on the properties of colloidal organic matter which are important in controlling the variability in observed sorption behavior, (2) the second-order mechanisms of HOC-colloid interactions, and (3) the questions concerning the general applicability of experimental methods used.

GENERAL DISCUSSION

The results from this experiment provide direct evidence for the sorption of chlorobiphenyls to colloidal organic matter by determining the decrease in fugacity of dissolved PCBs in experimental bottles. Sorption isotherms are consistent with linear partitioning, and K_{oc} generally increases with K_{ow} and are within a range of K_{oc} 's determined by soil, sediment, and dissolved humic acid sorption studies. Together these results support the model that HOC-organic colloid sorption is controlled by partitioning into a colloidal organic phase. However, because of the small size disparity between PCBs and some fraction of the enriched colloidal organic matter, and variability of K_{oc} 's reported with dissolved organic matter from different sources (Means and Wijayarathne, 1982; Carter and Suffet, 1983; Landrum et al., 1984; Chiou et al., 1986), more work is needed to understand the properties of colloidal organic matter which may be important. Ultrafiltration is likely an artificial separation of dissolved organic matter into fractions which sorb

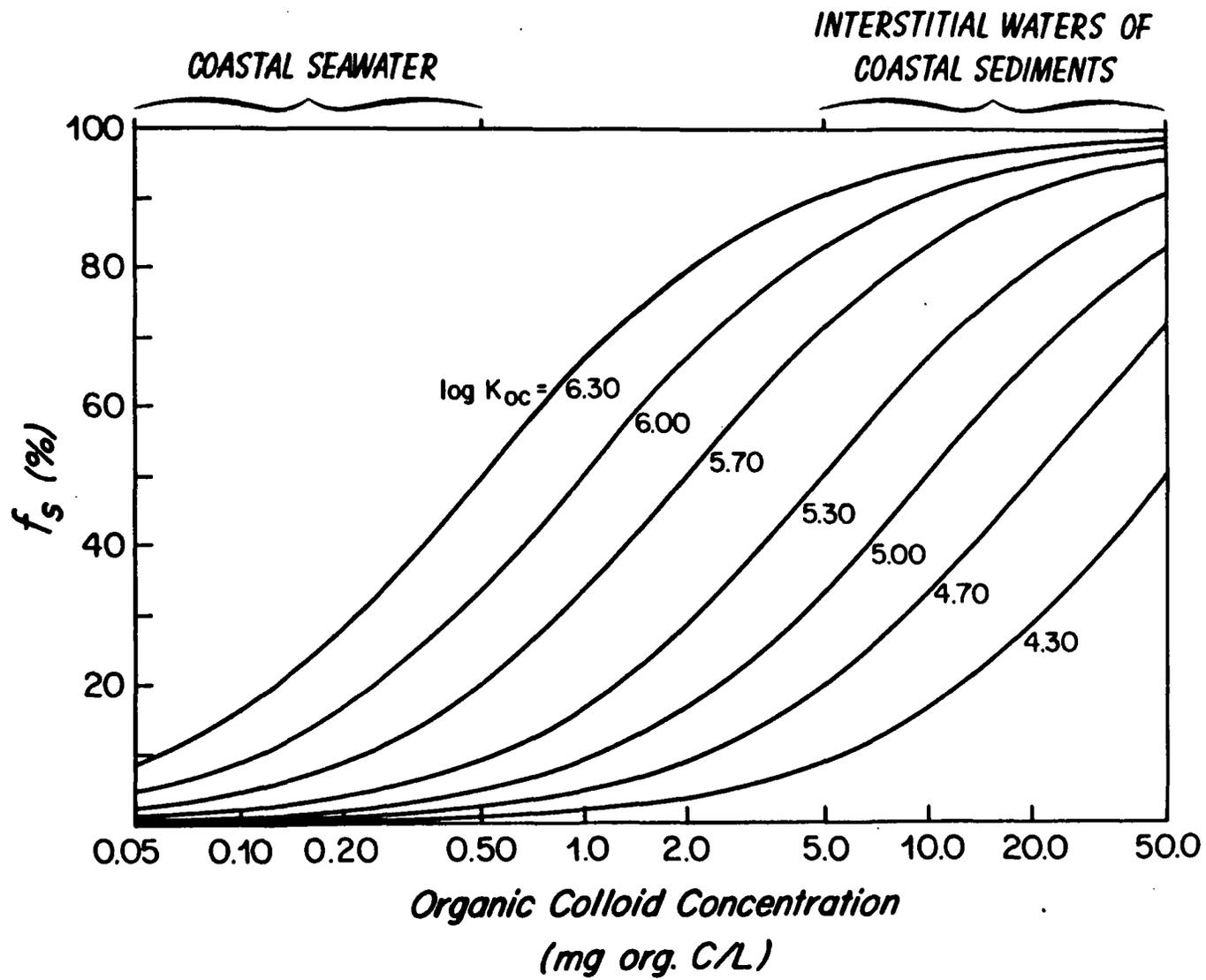
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and do not sorb HOC. Future studies should determine whether separation by ultrafiltration or some other property of dissolved organic matter in natural waters provides a good predictor of HOC speciation. Other properties of dissolved organic matter which do not involve uncertain isolation procedures may be useful. Surface tension or interfacial surface tension at a hydrophobic surface are examples of natural water properties which might offer predictive tools for estimating HOC sorption in various water samples just as f_{oc} is used to estimate K_p in the case of sediment sorption.

The results of PCB partitioning with marine organic colloids have important implications for understanding both distributions of HOC in the aquatic environment and in laboratory experiments where colloidal organic matter may be present. Figure 2-6 illustrates the importance of colloidal organic matter on the speciation of HOC as a function of K_{oc} and the concentration of colloidal organic carbon. f_s is the fraction of HOC in a filtered water sample which is sorbed to organic colloids. It is seen that only 0.4% of an HOC with $\log K_{ow}$ of 4.30, such as 2,4'-dichlorobiphenyl in this study, will be sorbed at organic colloid concentrations of 0.20 mg C/L. This concentration of colloidal organic carbon is within the range reported in this and other studies in oligotrophic coastal and open ocean waters (Sharp, 1973; Maurer, 1976; Zsolnay, 1979; Carlson et al., 1985). Penta- and hexachlorobiphenyls having $\log K_{oc}$'s of 5.7 and 6.0 will be 9.1 and 17% sorbed at the same colloid concentrations. The fraction HOC sorbed to colloids is expected to increase in many lakes, rivers, and more productive estuaries and coastal waters where the concentrations of colloidal organic matter and their proportion of the total DOM can be considerably greater

Figure 2-6. The fraction of HOC in solution which is sorbed to colloidal organic matter as a function of the concentration of colloidal organic matter and the K_{oc} of the compound. The range of constant K_{oc} 's plotted here is probably representative of most di- to hexachlorobiphenyls sorbed with natural colloidal organic matter.



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(Wheeler, 1976; Zsionay, 1979; Sigleo et al, 1980; Thurman, 1985). It is seen from Figure 2-6 and the data in Table 2-5 that colloidal organic matter in the interstitial waters of reducing marine sediments is expected to exert a significant influence on the speciation of PCBs. Interstitial water colloidal organic carbon concentrations of 8.0 to greater than 50 mg/L have been reported in suboxic marine sediments (Nissenbaum et al., 1973; Krom and Sholkovitz, 1977; Orem and Gaudette, 1984; Orem et al., 1986). Brownawell and Farrington (1985, 1986) concluded that most PCBs in interstitial waters of New Bedford Harbor sediments must be associated with colloidal organic matter. It is not yet known how similar the sorption capacities of interstitial water colloids are to those enriched from the water column in this study.

An estimation of the dissolved phase concentration of HOC in surface waters is necessary to predict the diffusive flux between the atmosphere and water. Some evidence has been presented that the Great Lakes may at times be a source of PCBs to the atmosphere (Murphy et al., 1983; Eisenreich and Looney, 1983). Baker et al. (1985) report a surface water DOC of 2.52 mg/L in Lake Superior. If colloidal organic carbon concentrations are 1.0 mg/L and have a binding capacity similar to those measured in this study, then approximately 2.0 to 30% of the chlorobiphenyls measured here would be in a colloid sorbed phase. This indicates that any large apparent supersaturations of HOC in the Great Lakes or open ocean surface waters are probably not due to sorption of HOC with colloidal organic matter. This may not be the case for HOC which are more hydrophobic than pentachlorobiphenyl or in surface waters with higher organic colloid concentrations.

The presence of colloidal organic or noncentrifugable organic matter (supernatant organic matter is termed colloidal here although they are generally not determined by filtration) can affect the separation of dissolved and sediment-bound HOC in common batch sorption studies (Voice et al., 1983; Chiou et al., 1984; Gschwend and Wu, 1985; Voice and Weber, 1985). Gschwend and Wu (1985) and Voice and Weber (1985) have used different approaches to model how the sorption of HOC to organic matter in the supernatant can explain the sorbent mass dependent partitioning reported in several studies (O'Connor and Connolly, 1980; DiToro et al., 1982; Voice et al., 1983). Gschwend and Wu (1985) have assumed a three-phase equilibrium where dissolved HOC are in equilibrium with both sediment-bound and organic colloid-bound phases. Their model fits the measured data if it is assumed that the K_{oc} 's of organic colloids are about the same as those of sediments for PCBs. The data in Table 2-5 and Table 1-2 show that the K_{oc} 's of PCBs measured by Gschwend and Wu (1985) are about three to five times higher than PCBs with similar K_{ow} 's measured in this study. It is likely that the organic matter measured as DOC in their experiment was associated with small, non-settling particles, which might have different sorption characteristics. In any case, the K_{oc} 's of PCBs with organic colloids are within the range of those measured for soils, sediments, and dissolved soil humic substances and could then be expected to have an effect on laboratory sediment sorption experiments where suspended solids concentrations or K_{oc} are great (see Chapter I).

Observations of apparent sediment mass dependent sorption have been interpreted by an alternative model by Voice and Weber (1985). In this model, HOC are first irreversibly sorbed to dissolved organic matter in solution and

then both dissolved and DOM-bound HOC subsequently sorb to the sediment phase. This model has some weaknesses. First, there is no present justification for irreversible binding between HOC and dissolved organic matter. Several studies indicate that both forward and reverse rates of sorption must be rapid (Landrum et al., 1984; Hassett and Milicic, 1985; McCarthy and Jimenez, 1985). Second, in order to fit the model to observed results, these authors find that the K_{oc} for binding of HOC to dissolved organic matter must be many times higher than K_{ow} and actually increase with decreasing K_{ow} . The results from this study show that this cannot be true for PCBs in coastal seawater. By directly measuring the dissolved phase fugacity of PCBs, the existence of an unknown bound-phase can be discounted. It has also been shown that the sorption of trichloroethylene and toluene does not depend on the concentration of suspended solids by using headspace partitioning (Garbarini and Lion, 1985). It is shown in Chapter I how insufficient phase separations for both high and low K_{oc} solutes can result in incorrect determinations of sorption.

CONCLUSIONS

1) A static headspace partitioning method can be used to directly measure the speciation of PCBs in experimental equilibration experiments without the need for operational phase separations. The fugacity of individual chlorobiphenyls was significantly decreased in experimental bottles to which enriched colloidal organic matter from coastal seawater was added. The

calculation of sorption isotherms from this data showed that the sorption was dependent on the properties of the solutes.

2) The general increase in K_{oc} with K_{ow} and shape of sorption isotherms are consistent with a mechanistic model of HOC organic phase partitioning which has successfully described many aspect of HOC sediment sorption. The K_{oc} 's reported for PCBs in this study are in the range of those reported in other experimental sorption studies with soils, sediments, and dissolved soil humic substances. This provides further evidence that sorption of HOC with colloidal organic matter is similar to sorption with other organic phases.

3) PCBs were adsorbed to container walls, and the adsorption of a small fraction of colloidal organic matter apparently enhanced sorption of PCBs onto the walls. Results from this experiment suggest that the sorption capacity of wall-adsorbed colloids may have been different compared to those remaining in solution.

4) Review of other studies of the sorption of HOC with natural colloidal organic matter indicates that there may be significant variability in the sorption capacities of different samples of colloidal organic matter. Dissolved organic matter is probably represented by a continuum of sizes and polarities, and ultrafiltration provides an operational separation of colloidal organic matter. Future studies should evaluate the ability of ultrafiltration and perhaps other properties of natural waters to adequately serve as predictors of HOC speciation in natural waters. Sorption studies with well-described model sorbents should be used to understand second order features of the mechanisms of sorption of HOC with macromolecular organic matter.

5) Comparisons of headspace partitioning should be made with other experimental methods for determining HOC/organic colloid sorption to further evaluate the method and to see whether variability of reported K_{oc} 's between studies are due to the methods used or colloid variability.

CHAPTER III

BIOGEOCHEMISTRY OF PCBs IN COASTAL MARINE SEDIMENTS AND INTERSTITIAL WATERS

INTRODUCTION

Estuarine and coastal marine sediments act as short or long-term sinks for many hydrophobic organic compounds (HOC) (Lee et al., 1979; Wakeham and Farrington, 1980; Hites et al., 1980; Prahl and Carpenter, 1983). Sorption reactions involving interstitial waters, sediment particles, and organic colloids control rates and mechanisms of transport of organic compounds within and out of sediments. Other diagenetic processes such as biological and chemical transformations, diffusion, advection, and mixing and resuspension of the sediment bed, will influence the distribution of HOC in sediments and interstitial waters (Berner, 1980). The relative importance of each of these processes will depend on the source, molecular structure, biological activity, and physical-chemical properties of the individual organic compounds, as well as properties of the sedimentary environment.

Polychlorinated biphenyls (PCBs) were studied as model HOC to probe many of these processes in coastal sediments. The wide range of solubilities of individual chlorobiphenyls (Mackay et al., 1980; Bruggeman et al., 1982) and their slow rates of chemical or biological degradation (NAS, 1979) make PCBs especially valuable tracers for studying sorption processes under natural field conditions. PCB measurements in the field have been used to study

particle-seawater partitioning of HOC (Dexter and Pavlow, 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; Baker et al., 1985) and the Pacific Ocean (Tanabe and Tatsukawa, 1983). The production and regulatory histories of PCBs, and estimates of their sources and transport pathways have been reviewed (Nisbet and Sarofim, 1972; NAS, 1979).

The sorption of PCBs and other nonpolar HOC with freshwater sediments and soil has been well studied with laboratory experiments (Karickhoff et al., 1979; Chiou et al., 1979; 1983; Means et al., 1980; Schwarzenbach and Westall, 1981; Gschwend and Wu, 1985). These and other studies have demonstrated the importance of the organic matter fraction of sediments in controlling the aqueous sorption of HOC. Sorption can be described by a solvent/solvent partitioning process where HOC dissolve into the polymeric organic matter which coats sediment particles (see Chapter 1). Sorption is observed to be reversible, and linear partition coefficients, K_p (L/Kg), can be estimated for a given compound by a single organic carbon normalized partition coefficient, K_{oc} :

$$K_p = f_{oc} K_{oc} \quad (\text{eqn. 3-1})$$

where f_{oc} is the fraction organic carbon of the sorbent. Sorption is driven by the incompatibility of the solute in water and therefore K_{oc} increases with decreasing solubility of the compound. K_{oc} has been related to the octanol-water partition coefficient (K_{ow}) of the sorbate (Table 1-1):

$$\log K_{oc} = a \log K_{ow} + b \quad (\text{eqn. 3-2})$$

where a and b are empirical constants determined from experimental results. It is not certain how much of the variability in a and b reported by different workers in Table 1-1 is due to the different compound classes considered or to experimental methods used (Chapter 1).

Colloidal organic matter has also been shown to have high sorption affinities for HOC in laboratory experiments (Means and Wijayarathne, 1982; Carter and Suffet, 1982; Chapter 2). Estuarine and marine colloids have been operationally defined as those substances which pass a 0.4 to 1 μm filter but are enriched in a retentate by a variety of ultrafiltration membranes which retain materials larger than 1 to 4 nm. Colloidal substances include both submicron particles and macromolecular organic matter. The results from Chapter 2, and other studies summarized in Chapters 1 and 2, indicate that the sorption of HOC with organic colloids is probably similar to sorption with sedimentary or particulate organic matter. Organic carbon normalized partition coefficients determined for HOC-organic colloid sorption are within a range of values predicted from sediment and soil sorption studies using equation 3-2 (Chapter 2).

Predictions of HOC speciation based on organic matter sorption models are largely untested in the field. In this study, the distribution of PCBs in sediments and interstitial waters was investigated in sediments obtained from New Bedford Harbor and Buzzards Bay, Massachusetts. Interstitial waters from these organic-rich, coastal sediments contain high concentrations of colloidal organic matter, and it is expected that significant fractions of

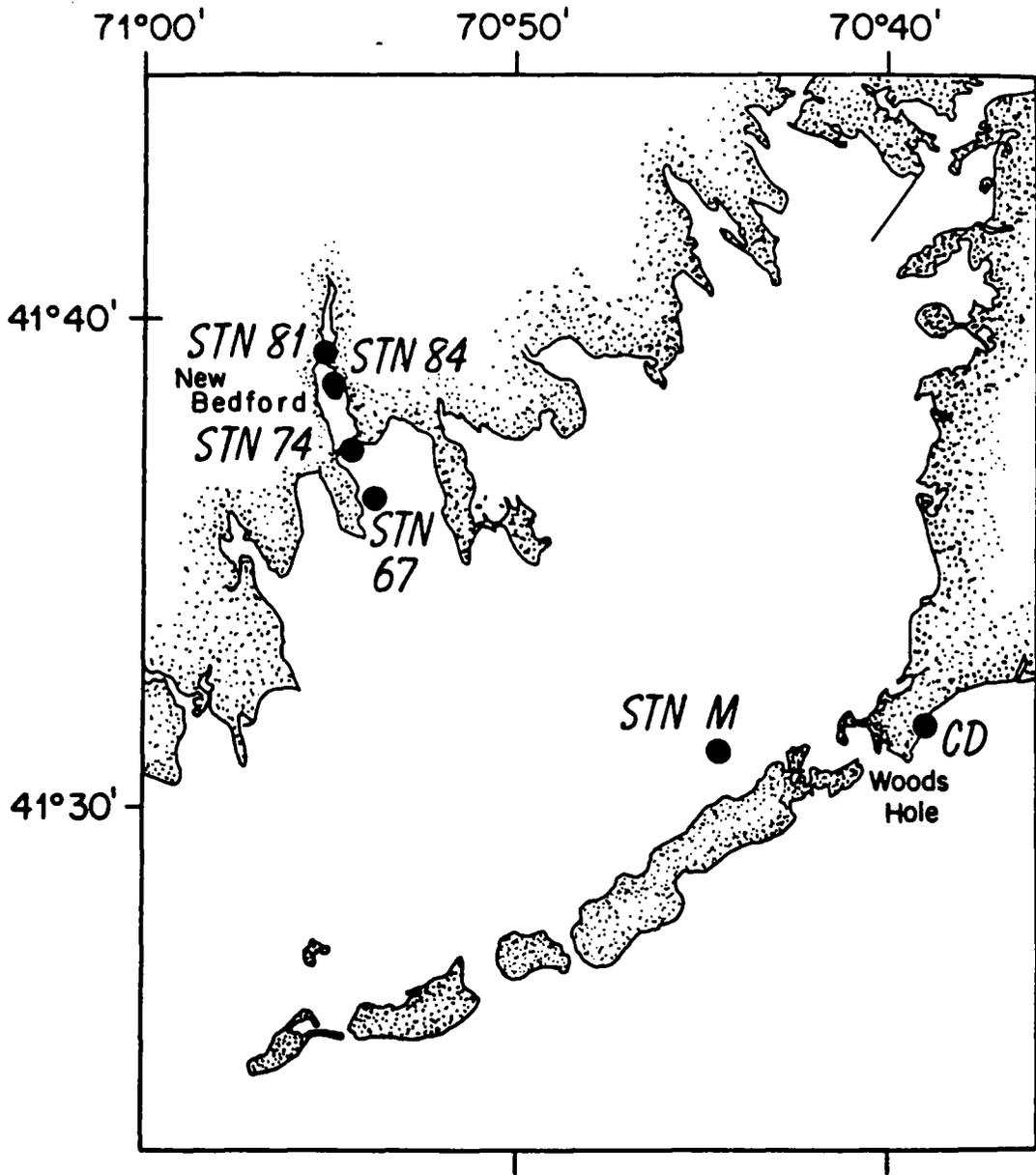
chlorobiphenyls in pore waters are sorbed to organic colloids (Figure 2-6). The observed distributions of individual chlorobiphenyls between sediments and interstitial waters yield insights into the roles of sedimentary and colloidal organic matter in the speciation of HOC in sediments and provide tests of predictive sorption models based on laboratory experiments.

An investigation of the partitioning of PCBs in two box cores obtained in New Bedford Harbor (the Acushnet River Estuary) and one box core from a station in eastern Buzzards Bay is reported in this chapter. New Bedford Harbor is heavily impacted by PCB contamination from the activities of two large capacitor manufacturers. The nature, distribution, and history of this contamination have been recently reviewed (Weaver, 1984; Farrington et al., 1985). Concentrations of PCBs in the sediments of these three sites ranged over nearly five orders of magnitude. The results are reported from a water column partitioning study where two stations in New Bedford were occupied and sampled over a tidal cycle, to provide a useful comparison to the sediment investigations. The partitioning results from sediment and water column studies are compared to three-phase equilibrium sorption models to test predictions of partitioning based on laboratory experiments.

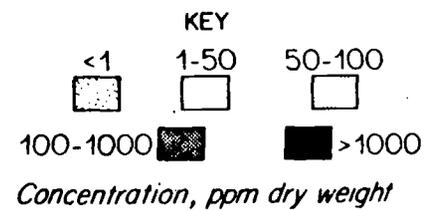
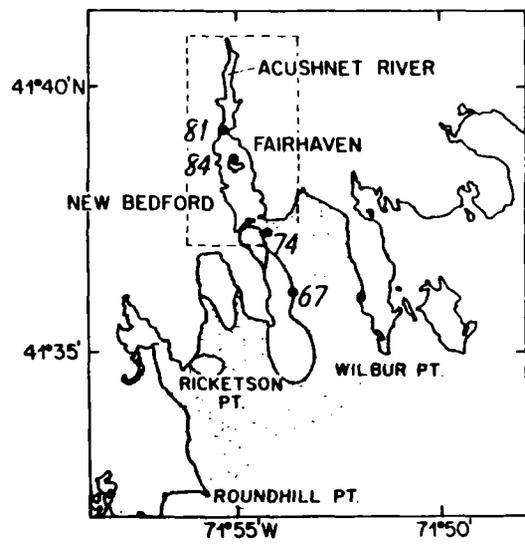
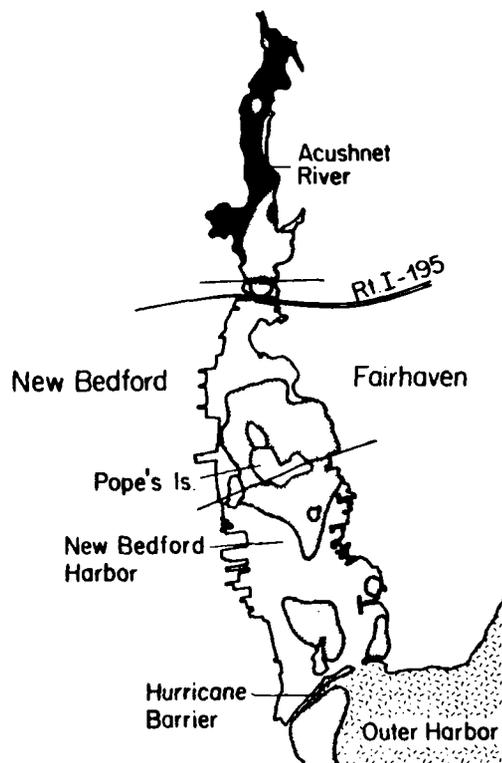
SAMPLING SITES AND METHODS

The sampling sites of the sediment cores (Stations 67 and 84 in New Bedford Harbor and Station M in Buzzards Bay) and water samples (Stations 74 and 81) are shown in Figures 3-1A and 3-1B. Concentrations of PCBs in surface sediments are highest in the upper part of the estuary, north of Station 81,

Figure 3-1A. Map of Buzzards Bay, Massachusetts, including the Chemotaxis Dock (CD) water sampling site in Nantucket Sound. The sediment coring and water column sampling stations in New Bedford Harbor are shown in Figure 3-1B, which also depicts the distribution of PCBs in New Bedford Harbor (from Farrington et al., 1986).



PCB's In Surface Sediments (as Aroclor 1254) In Acushnet River Estuary and New Bedford Harbor



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and generally decrease moving south through the outer harbor and out into Buzzards Bay (see Figure 3-1B).

Station 84 was sampled with a Soutar box corer, 0.04 m² x 1 m, deployed off the R/V Asterias on October 29, 1981. This site was in 3 meters of water and bottom water temperature was 13.1°C. Sediment samples of 1 to 3 cm were sectioned into glass jars aboard Asterias. The upper 3 cm were heavily populated by a small unidentified bivalve. Sediments were stored overnight at room temperature and pore water samples were extracted the following 2 days using a hydraulically powered, stainless steel squeezer at 2000-2500 psi as discussed by Henrichs (1980). Interstitial waters were filtered through two internal Reeve Angel glass fiber filters and an external Gelman Type A/E glass filter of a nominal pore size of 1.0 µm. Seventy-five to 240 mL of pore water were obtained for each sediment depth and were stored in glass with 25 mL of CH₂Cl₂ for later PCB analysis. The remaining sediment samples were stored frozen.

A more detailed characterization of the sediment interstitial water biogeochemistry of PCBs was performed at the other two sites. A large volume box core was obtained at Station 67 of Summerhayes et al. (1977) in the outer harbor of New Bedford on September 1, 1983. Sampling methods for the sectioning of muds and subsequent extraction and filtration of pore water employed inert atmosphere techniques. These methods 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 m² 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 2 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 N₂-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) for 20 minutes in an IEC model 6000 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 N₂. Precombusted, 142 μm 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 N₂ purge is expected to be minimal. The fraction of dissolved chlorobiphenyls lost from N₂ purging can be calculated as follows:

$$\text{fraction chlorobiphenyl lost} = 1 - C/C_0 = 1 - e^{-KH \times b \times t/V}$$

where H (mL/cm³) is the Henry's law constant for individual chlorobiphenyl in seawater, b is the flow rate of N₂ (cm³/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/cm³ (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), SO₄²⁻, Fe, Mn, and salinity. The remainder of the sample was then stored in glass along with 75 mL of CH₂Cl₂ 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.

A large-volume box core was also obtained at Station M, using the Sandia-Hessler Type MK3 sediment corer, on September 19, 1984. The sediment temperature was 21.2°C. This site is in 15 m of water and is the same location described by Martin (1985) and McNichol (1986). The sediments are characterized as fine-grain muds with organic carbon levels of 1.6 to 3.8%. The sediments are 17% clay and 93% silt/clay (from Martin, 1985). The interstitial water chemistry, trace metal geochemistry and transport, remineralization of organic matter, and sediment mixing processes have been studied at this site over seasonal cycles in the works of Martin (1985) and McNichol (1986).

The procedures used for sampling, sectioning, pore water extraction and filtration were the same as those described for Station 67 with a few exceptions. Freon was not used to purge oxygen from the core top. However, the Plexiglass sheet contacted the sediment interface and impeded any oxygen

penetration. The sectioning of the core was begun within two hours of sampling and the lack of a grey-brown oxidized interface on the black sediment surface indicated that significant oxygen penetration did not occur. The core was sectioned into 16 sections of the upper 43 cm of sediment, and resulted in pore water volumes of 0.882 to 2.00 L/section. Pore water filtration was performed with N_2 purging of the filtration vessel instead of bubbling to minimize the possibility of any evaporation or flocculation problems noted above. Samples for sediment and pore water determinations were taken and stored as described above for Station 67. One mL samples were also taken for alkalinities at this site.

Water column samples were collected at Stations 81 and 74 throughout a complete tidal cycle on September 22, 1982. Samples were collected hourly in stoppered 2-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 10 hours of sampling, and filters were frozen until analysis. CH_2Cl_2 was added to the filtered samples and stirred vigorously in glass carboys.

ANALYTICAL METHODS AND CALCULATIONS

Standard techniques were used to determine pore water constituents at Station 67 and Station M. DOC was analyzed by a wet persulfate oxidation method adapted from Stainton (1973). It should be noted that persulfate

oxidation of organic matter in seawater may be incomplete and this procedure has been reported to give results which are 85-90% of those determined by dry combustion (MacKinnon, 1981). However, it is not expected that the results and interpretations reported here are significantly biased by this potential problem. Sulfate was determined by barium sulfate precipitation, Fe and Mn by atomic absorption spectrometry, chlorinity by AgNO_3 titration, and alkalinity by Gran titration. Approximate precisions of these methods were 3, 2, 2, 4, 0.7, and 1%, respectively. Water content of sediments was determined by difference, after heating to a constant weight at 110°C . CHN of dry sediments, which had been adjusted to a pH of 2 with HCl to remove small amounts of carbonate, were measured on a Perkin-Elmer CHN analyzer. Unsupported ^{210}Pb on 15 ground sediment samples from Station M were determined by measuring ^{210}Pb and ^{226}Ra by non-destructive low energy gamma counting (Yakoyma and Nguyen, 1977; Cutshall et al., 1983).

The isolation and quantification of PCBs in all sample sets were similar with slight procedural modifications in chromatography and quantification. Immediately prior to solvent extraction, all sediments and most pore water samples 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. Wet sediments and filtered particulate samples were Soxhlet extracted for 24 hours with 350 mL of 1:1 hexane:acetone. An additional 24 hours extraction of sediments with fresh hexane:acetone gave $8.2 \pm 3.0\%$ of the

individual chlorobiphenyls determined the previous day and no additional recovery of spiked compounds. Sediment samples from Station M and filtered particulate samples were all extracted for a second 24 hours with fresh solvent. Pore waters from Stations M and 67 were extracted in 2-liter 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. Station 84 pore waters and filtered seawater samples were also extracted three times with CH_2Cl_2 in 0.5 and 5 L separatory funnels, respectively. A fourth 5-minute pore water extraction yielded another $0.61 \pm 0.10\%$ of individual chlorobiphenyls. These additional yields do not affect the results and biogeochemical interpretations presented here. Extracts were separated from aqueous phases in separatory funnels, dried with anhydrous Na_2SO_4 , and concentrated in 500 mL Kuderna-Danish concentrators to about 1 mL volumes.

Concentrated extracts in 1 mL of hexane were chromatographed on silica gel columns containing a layer of activated copper to remove elemental sulfur. The grade, mesh size, and amount of deactivation with water of the silica gel differed for each set of samples. In each case a PCB fraction was eluted from silica gel with either hexane or toluene in hexane (for water column samples) and again concentrated in 125 mL Kuderna-Danish concentrators. Hexane extracts were transferred to tared 4 mL vials and then concentrated with a stream of nitrogen just prior to gas chromatography. Evaporation of extracts was not allowed to go to total dryness for any samples.

Pentachlorobenzene was added as another internal standard just prior to GC injection of the sediment and pore water samples from Station M and was used as a quantitation standard (QS) in those samples.

Individual chlorobiphenyls were isolated and analyzed from concentrated extracts by high resolution capillary gas chromatography (GC) with electron capture detection on a Hewlett-Packard 5840 gas chromatograph with a 30 m DB5 fused silica column (J & W Scientific) operated with H₂ 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 cm³/min.

All reagents and glassware were either solvent extracted with acetone, hexane, and CH₂Cl₂ or combusted overnight at 500°C. All solvents were distilled in glass (Burdick and Jackson). Procedural blanks were insignificant at the PCB levels of all sediment and most pore water samples in this study. Procedural blanks are significant for the pore water samples from the deeper sections at Station 84. Blank levels were improved in later analysis and only contribute substantial interference to some of the later eluting chlorobiphenyls in pore waters from the bottom two Station M sections. There was also evidently an isolated contamination problem in the 0-3 cm pore water sample at Station 67 and as a result many of the higher molecular weight PCBs are not reported.

Several complimentary methods were used to identify individual chlorobiphenyls in the industrial mixtures, Aroclor 1242 and Aroclor 1254, which are the primary 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 was 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) and mixtures of 51 chlorobiphenyl congeners obtained from the National Research Council, Canada, were compared to those in mixtures. Gas chromatography/mass spectrometry (GCMS) spectra obtained with a Finnigan 4500 quadrupole 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 (Albro and Parker, 1979; Ballschmiter and Zell, 1980; Albro et al., 1981; Eisenreich et al., 1983; Duinker and Hillebrand, 1983; Mullin et al., 1984; Capel et al., 1985). The relative amounts of contributing congeners in some unresolved peaks is still tentative, but does not affect the identifications of major peaks or interpretation of results given here. The identification and relative retention times of 51 chlorobiphenyls which appeared in most samples from New Bedford Harbor are given in Table 3-1. In the samples from Station M several octa-, nona-, and decachlorobiphenyl were also tentatively identified by their retention times. These congeners do not occur in Aroclor 1254 or New Bedford Harbor sediments. In addition, chlorobiphenyl 105 (peak 40 in Table 3-1) is resolved from 153 on the column used to analyze Station M samples. Table 3-1 also lists a consistent set of log K_{ow} s for many of these chlorobiphenyls reported by Rapaport and Eisenreich (1984).

Recoveries of internal standards 29 and 143 were consistently high. At Station 84 they were 94.8 ± 17.1 and $85.4 \pm 14.4\%$, respectively, for eight sediment samples. For Station 67 the respective recoveries of 29 and 143 were

93.3 ± 13.3 and 98.9 ± 17.0% for sixteen sediment samples and 83.9 ± 12.9 and 92.8 ± 20.8% for eleven pore water samples. Five pore water samples from the 23-35 core sections at Station 67 were not properly spiked and no recoveries are reported. The error in absolute recoveries is associated with variation in absolute detector response, and where possible relative responses of peaks to that of internal standard 143 were used. This resulted in precisions of better than 5%. Most of the samples from Station M showed recoveries of greater than 100% for 143 due either to a higher abundance of 143 in these samples than in Aroclor 1254 or New Bedford samples, or to another interfering peak. The average recoveries of 29 and 143 for these samples were 100 ± 11.2% and 134 ± 39.6%, respectively, for sixteen sediment samples and 105.3 ± 15.3% and 123.5 ± 23.0% for fourteen pore water samples.

The apparent distribution coefficients (K'_d) of all identified chlorobiphenyls were calculated for sediment/pore water samples in units of L/Kg in the following manner:

$$K'_d = \frac{(A_i/A_{is})_{sed} m_{is} m_{pw}}{(A_i/A_{is})_{pw} m_{is} m_{sed}} \quad (\text{L/Kg}) \quad (\text{eqn. 3-3})$$

where A_i and A_{is} are the peak areas of chlorobiphenyl and internal standard, m_{is} is the mass of internal standard spiked in the sample, and m_{pw} and m_{sed} are the weights of pore water and dry sediments extracted. Internal standards used in calculations are 143 in Station 67 samples and QS

Table 3-1. PCB retention times and identification using capillary gas chromatography conditions given in the text. K_{ow} s are from Rapaport and Eisenrich (1984).

Peak no.	#Cl	PCB 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			

Peak no.	%Cl	PCB 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 (1980). (b) PCB K_{ow}s from Rapaport and Eisenreich (1984). (c) Log K_{ow}s 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_{ow}s are similar. (d) Reported to represent 70% or more of the mass of the peak (Albro and Parker, 1979; Albro et al., 1981; Duinker and Hillebrand, 1983; Eisenreich et al., 1983) in Aroclor mixtures or as determined by GCMS. (e) Similar Contributions of isomers in peak (as reported in above references or by GCMS).

in Station M samples. For Station 84 and particulate water determinations K'_d was calculated as:

$$K'_d(i) = \frac{(A_i \times SF)_{sed} \cdot m_{pw}}{(A_i \times SF)_{pw} \cdot m_{sed}} \quad (\text{eqn. 3-4})$$

where SF is the total volume of extract divided by the volume injected (2 μ L). The K'_d s calculated by equation 3-4 assume the same recoveries of samples and constant absolute response factors and have higher associated errors than those determined at Stations 67 and M.

Absolute concentrations (C_i) are reported for individual chlorobiphenyls in Station M samples. These were calculated for 33 chlorobiphenyls:

$$C_i = \frac{(A_i / A_{QS}) \cdot m_{QS}}{RRF_i \cdot m_{sample}} \quad (\text{eqn. 3-5})$$

where RRF_i is the relative response factor of an individual chlorobiphenyl to internal standard QS. Relative response factors were calculated from the response curves of six dilutions of 51 chlorobiphenyls obtained from National Research Council, Canada. Relative response factors were found to be nearly constant over two orders of magnitude for almost all congeners and calculated RRF s agreed well with 24 quantitative laboratory standards with the exception of PCB 105 which had an RRF 87% greater than the laboratory standard.

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 tetrachlorobiphenyls and tetra- through hexachlorobiphenyls, respectively. Estimates of total PCBs as Aroclor 1254

were obtained by comparing the relative response of the ten peaks of greatest peak area, A_i , to that in a standard where the amounts of Aroclor 1254 (m_{1254}) and internal standard (m_{is}) are known:

Aroclor 1254 ($\mu\text{g/g}$ sample)

$$= \frac{\sum_{i=1}^{10} (A_i/A_{is})_s \cdot (A_{is}/A_i)_{STD} \cdot (m_{1254}/m_{is})_{STD} \cdot (m_{is} \text{ spike})}{10 \times \text{wt. sample (g)}} \quad (\text{eqn. 3-6})$$

where m_{is} is the amount of internal standard spiked in the sample. To estimate Aroclor 1242, the 6 largest peaks in the mixture which do not appear in Aroclor 1254 were used. For Station 67 samples internal standard 143 was used to calculate Aroclor 1254 and 29 was used to calculate Aroclor 1242. For Station M samples the QS internal standard was used to calculate both Aroclor mixtures because of the uncertainties in using internal standard 143 in those samples. These later calculations assume 100% recovery of samples which is justified by the consistently high recoveries of 29 in all samples. The calculation of Aroclor mixtures for Station 84 and other underspiked pore water samples were performed in an analogous manner, but were referenced to external standards and therefore have higher associated errors. 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 (100/200 mesh). Representative chromatograms of Aroclor standards, and samples are illustrated in a later section (Figure 3.5).

It is estimated that the precisions of all peak ratios reported here are approximately 5%, as are the Aroclor calculations for Station 67 samples. The precision of K'_d determinations in Station 67 samples is therefore about 7%. The concentrations for Station 84 and water column samples are not corrected for recoveries and small injection to injection changes in absolute detector response and have higher estimated errors ($\pm 15\%$ in concentration and $\pm 22\%$ in K'_d). Estimated errors for Station M are intermediate ($\pm 10\%$ in concentration and $\pm 14\%$ in K'_d).

RESULTS AND DISCUSSION

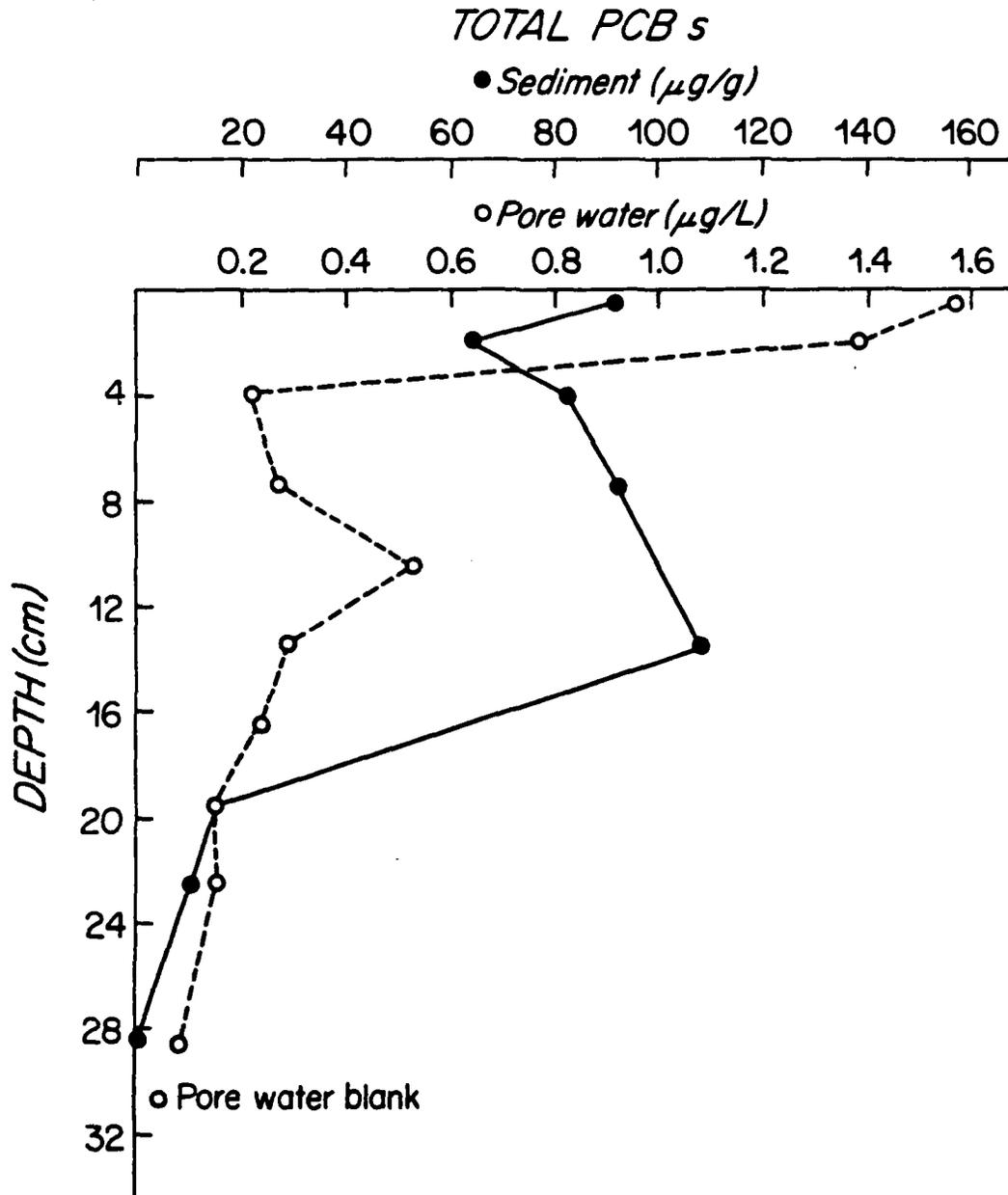
A discussion of the sediment biogeochemistry and partitioning of PCBs at each of the three sites is given separately below. These sections are followed by a more general treatment of a three-phase equilibrium sorption model to describe the distributions of chlorobiphenyls in sediments at these sites. The results from sediment-pore water partitioning are then contrasted with those from water column partitioning studies.

Station 84

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 percent 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 3-2. The pore water concentration of total PCBs in the

Figure 3-2. Total PCBs (Aroclors 1242 + 1254) in sediments and pore waters at Station 84.

5 1406



5 1407

0-1 cm section is 1570 ng/L and can be compared to a overlying water filtered water PCB concentration of 170 ng/L. Interstitial water PCB concentrations decrease rapidly below 3 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.

The sediment concentration of PCBs contrasts with the pore water results in that the level of PCBs remains fairly constant (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 (Summerhayes et al., 1977). 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 sediment accumulation rate in this area appears to have increased. 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. 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 no marked congener-specific diagenetic processes affecting the solid phase distribution of PCBs at this site.

The distribution of chlorobiphenyls in the interstitial waters is nearly identical to that in the sediments at the same depth. In other words, the apparent distribution coefficients, K'_d , for all the individual compounds considered, generally vary by less than a factor of two within a particular interval (Table 3-2). This constancy of K'_d over the wide range of K_{ow} s (Table 3-1) 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 $f_{oc} K_{oc}$ (equation 3-1). 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 representative chlorobiphenyls are given in Figure 3-3. The range of observed distribution coefficients 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

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

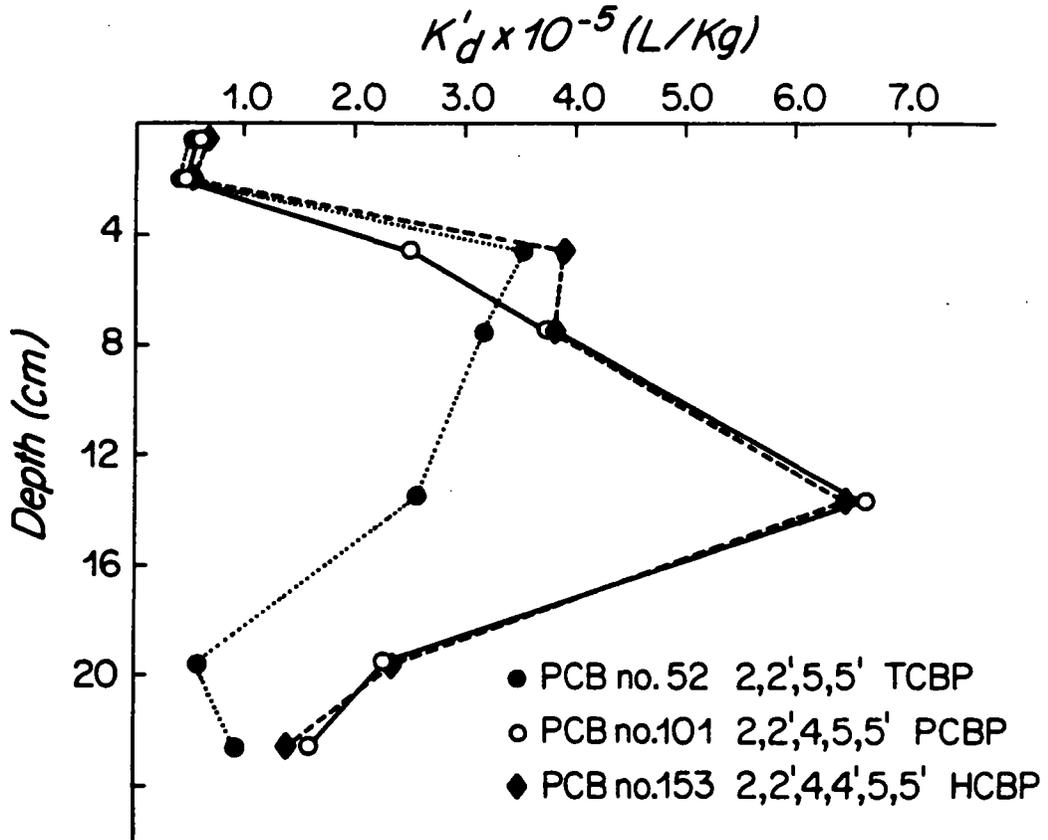


Table 3-2. Total PCBs (as Aroclors 1242 and 1254) and selected K'_d s for three chlorobiphenyls at Station 84. PCB #'s and structures are given in Table 3-1.

Depth (cm)	Total PCBs				$K'_d \times 10^{-5}$ (L/kg)		
	Sediments (mg/g)		Pore waters (ng/L)		Chlorobiphenyl #		
	Aroclor 1242	Aroclor 1254	Aroclor 1242	Aroclor 1254	54	101	153
0-1	42	49	780	790	0.528	0.589	0.664
1-3	30	34	690	690	0.411	0.455	0.479
3-6	40	42	96	120	3.55	2.50	3.90
6-9	48	44	180	93	3.17	3.75	3.82
9-12			370	160			
12-15	46	62	180	109	2.56	6.58	6.48
15-18			150	88			
18-21	6.2	8.8	100	50	0.599	2.28	2.36
	5.3	5.0	126	36	0.934	1.61	1.40
27-30	0.055	0.045	77	13			
blank	7.2×10^{-4}	7.8×10^{-4}	24	26			

5 1412

increased apparent distribution coefficients. The sediment hydrology (i.e., possible groundwater advection), and the effect of benthic 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.

Station 67 - Interstitial Water and Sediment Characterization

Pore water profiles of Mn, Fe, and SO_4^{2-} (Figure 3-4A) reflect suboxic diagenesis of organic matter in this core. The reaction sequence of electron acceptors in the oxidation of organic matter in marine sediments has been well studied (Froelich et al., 1979; Aller, 1980a). The maxima of reduced iron and Mn in the 0-3 cm section indicate oxygen depletion in this upper layer. The profile of sulfate and black mud observed at the sediment-water interface of this core when collected suggest 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 the core do not appear to be as efficient as for Mn. It is expected that the sulfide would be an effective sink for reduced Fe (Aller, 1980b). A 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, suggesting an association of Fe with a colloidal or micro-particulate phase. Near constant measurements of chlorinity (Figure 3-4A) in this core indicate that groundwater advection is not measurable by this method at this site.

The concentrations of DOC in the interstitial waters (Table 3-3) are consistent with the range of concentrations and depth profiles reported for

Figure 3-4. (A-B) Interstitial water profiles of Fe, Mn, SO₄, salinity, and DOC. (C-D) Profiles of total PCBs as Aroclor 1254 and Aroclor 1242 in sediments and pore water.

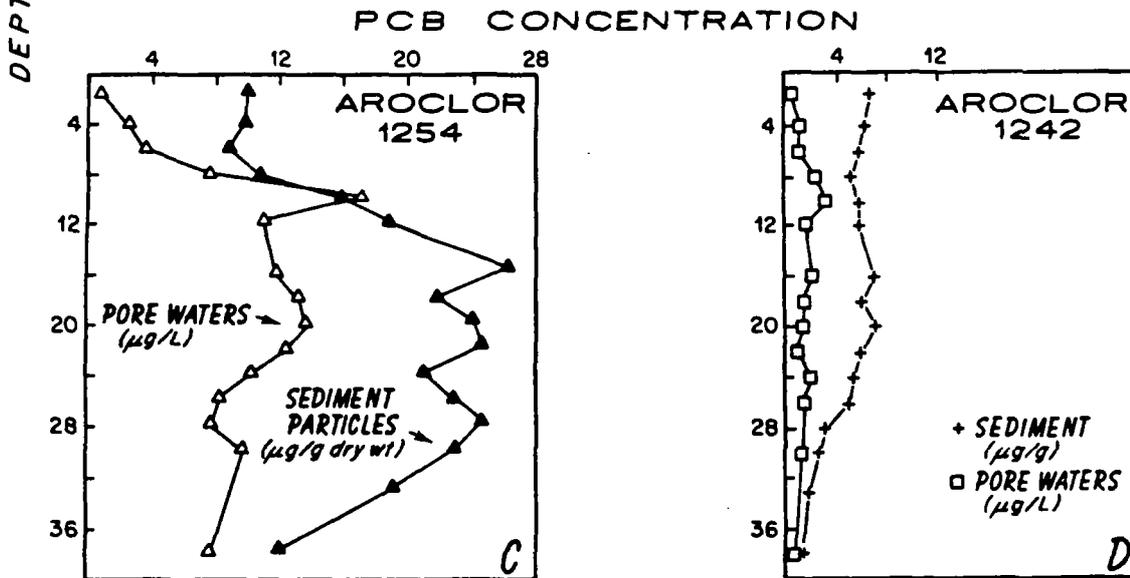
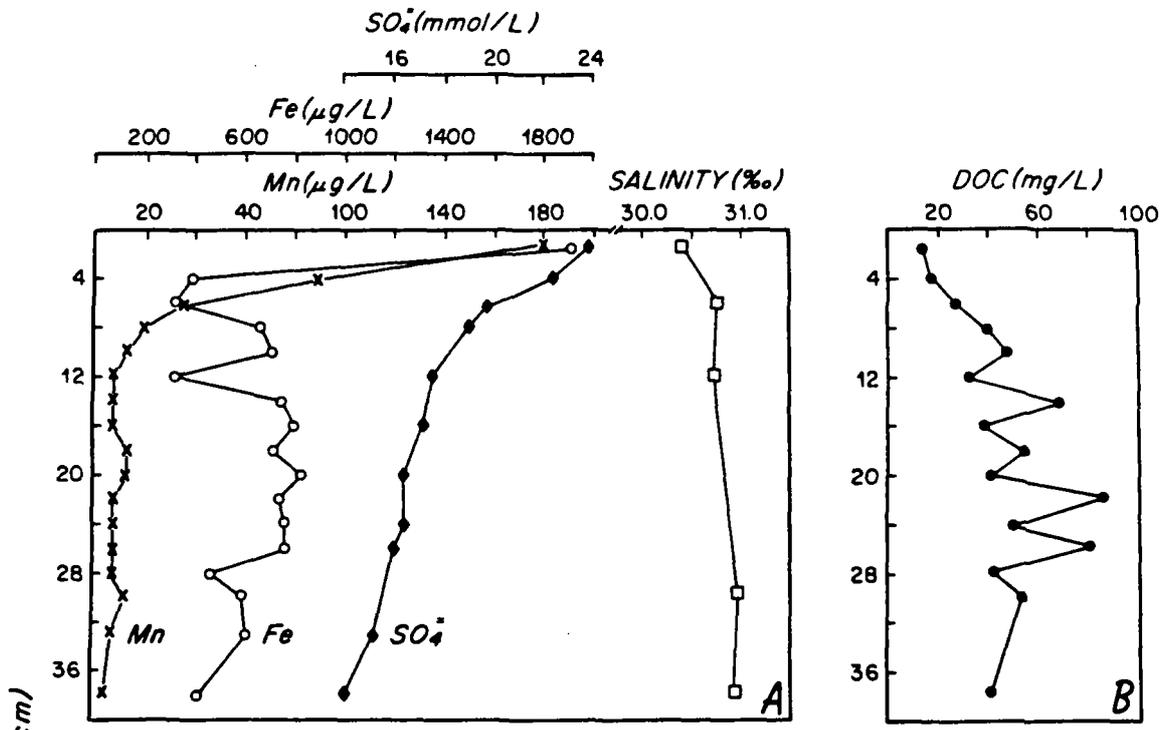


Table 3-3. Profiles of bulk sediment properties and Aroclor concentrations in sediments and pore waters.

Depth (cm)	% H ₂ O	TOC (%)	TON (%)	C/N	DOC (mg/L)	Aroclor 1242		Aroclor 1254	
						Sed.* (ug/g)	P.W.* (ug/L)	Sed. (ug/g)	P.W. (ug/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	xx	xx	xx	xx
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.

xx not analyzed.

** pore water sample spilled and recovery unknown.

other reducing nearshore sediments (Nissenbaum et al., 1972; Krom and Sholkovitz, 1977; Henrichs, 1980; Elderfield, 1981; Henrichs and Farrington, 1984; Orem and Gaudette, 1984). Results from some of these studies (Nissenbaum et al., 1972; Krom and Sholkovitz, 1977; Orem and Gaudette, 1984) and ultrafiltration of Buzzards Bay interstitial water (Chapter 2) suggest that most of the DOC in these sediments is colloidal. Krom and Sholkovitz (1977) showed that the increase in DOC with depth was due to an increase in the colloidal fraction. The depth profiles of DOC in coastal sediments are probably the result of a balance between production and consumption of DOC by microorganisms and benthic infauna, diffusion, and both reversible and irreversible reactions with sedimentary organic matter and mineral phases. The source and biogeochemical cycling of interstitial DOC are not well known (see Chapter 1), but spectroscopic studies of colloidal organic matter have shown it to be similar to melanoiden or marine humic substances (Nissenbaum et al., 1972; Krom and Sholkovitz, 1977; Elderfield, 1981).

The sediments at this site are also enriched in total organic carbon (Table 3-3). 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 minimum in the profile at from 21-25 cm. This trend may represent preferential nitrogen metabolism or changes in the quality and quantity of natural organic matter supply to the sediments.

PCB Results at Station 67

A mixture of PCBs which appear in Aroclors 1242 and 1254 are again present in sediments and interstitial waters at Station 67. The composition of individual chlorobiphenyls in the surface sediments are very similar to those found at Station 84 in the inner harbor. Capillary gas chromatograms of PCBs in sediment samples at different depths, and in sediment and pore water samples at the same depth are compared with Aroclor 1242 and Aroclor 1254 standards in Figure 3-5.

There are smooth changes in the relative amounts 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 (see Figure 3-8). 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.

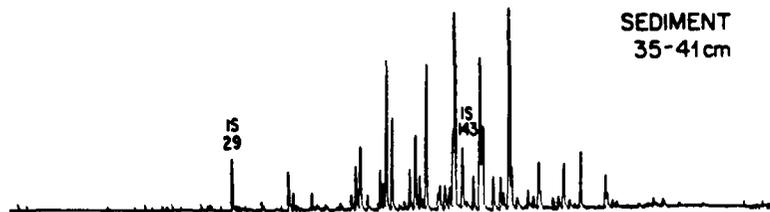
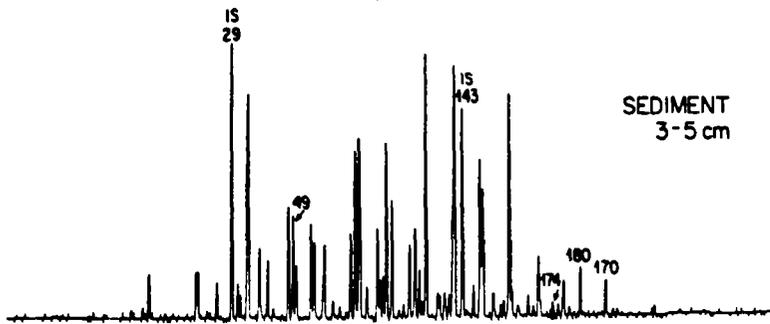
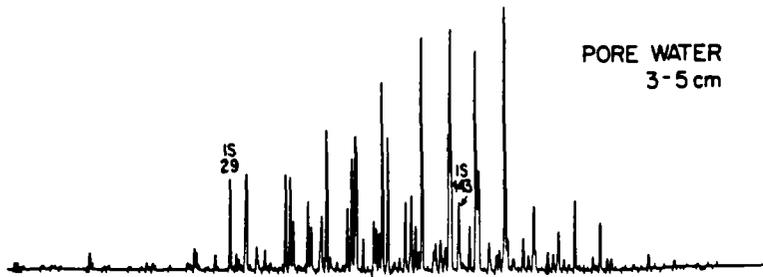
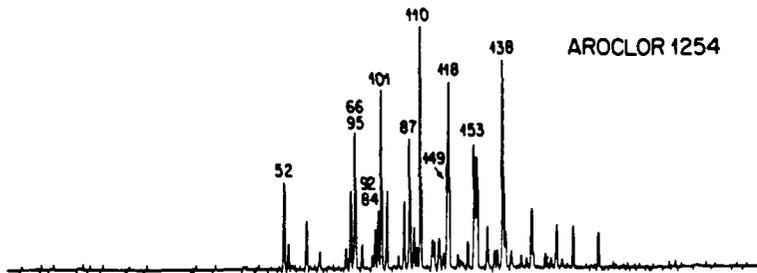
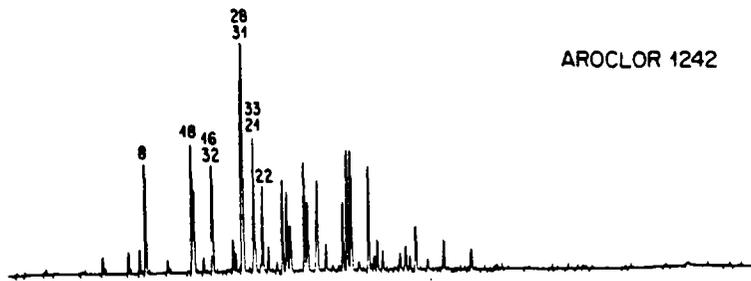
The profiles of Aroclors 1254 and 1242 in sediments and interstitial waters (Figure 3-4C and D and Table 3-3) illustrate the increase in pore water concentrations of PCBs with increasing depth in the core. The concentrations of Aroclor 1254 in interstitial waters are highly elevated, 0.893 to 17.1 $\mu\text{g/L}$, and exhibit a maximum 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 Station 74 in the outer harbor. These concentrations are similar to reported solubilities of Aroclor 1254 in seawater of 4.36 $\mu\text{g/L}$ (Dexter and Pavlou, 1978b) and 24.7 $\mu\text{g/L}$ (Wiese and Griffin, 1978). The concentrations of many of the higher chlorinated, less soluble, compounds exceed the

reported solubilities of chlorobiphenyl congener 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 three Lake Michigan surface sediments. Total PCB concentrations of 0.159-0.342 $\mu\text{g/L}$ were reported in interstitial waters of sediments of much lower total PCB concentration (63.5 to 160 ng total PCB/g sediment). Unlike the sediments in this study, the Lake Michigan pore waters were greatly enriched in Aroclor 1242 type compounds. 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 (Table 3-3 and Figure 3-4D) makes a substantial contribution to the total PCBs in the surface sections at Station 67 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 at Station 74.

The profile of DOC (Figure 3-4B) 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.

Figure 3-5. Capillary gas chromatograms of PCB Aroclor standards, pore water and sediment samples from 3-5 cm depth, and the 35-41 cm sediment sample at Station 67. Retention times increase along the x-axis. Chlorobiphenyl numbers indicate identifications of peaks used in Aroclor calculations and some other chlorobiphenyls reported at this site. See Table 3-1 for complete list of PCB identifications, structures and relative retention times.



Profiles of K'_d for the 51 resolved and unresolved (by GC) chlorobiphenyls given in Table 3-1 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 3-4, and selected profiles are illustrated in Table 3-4 and Figure 3-6. K'_d values 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 Pavlow, 1978a; Pavlow and Dexter, 1979), the Hudson River (Bopp, 1979), Lake Superior (Eisenreich et al., 1983), the Pacific Ocean (Tanabe and Tatsukawa, 1983) and several other environments where the role of colloids may not be as great. K'_d values ranged from 10^4 to 10^7 in those studies. Eadie et al. (1983) also report low K'_d values, 298 to 7000, for PCBs in the interstitial waters of Lake Michigan surface sediments. The elevated concentrations of PCBs, low K'_d s, and correlation of these properties with DOC (Figure 3-6 compared with Figures 3-4B, C and D) strongly implicate a considerable colloiddally associated PCB phase in the interstitial waters at this site, even for the more soluble trichlorobiphenyls.

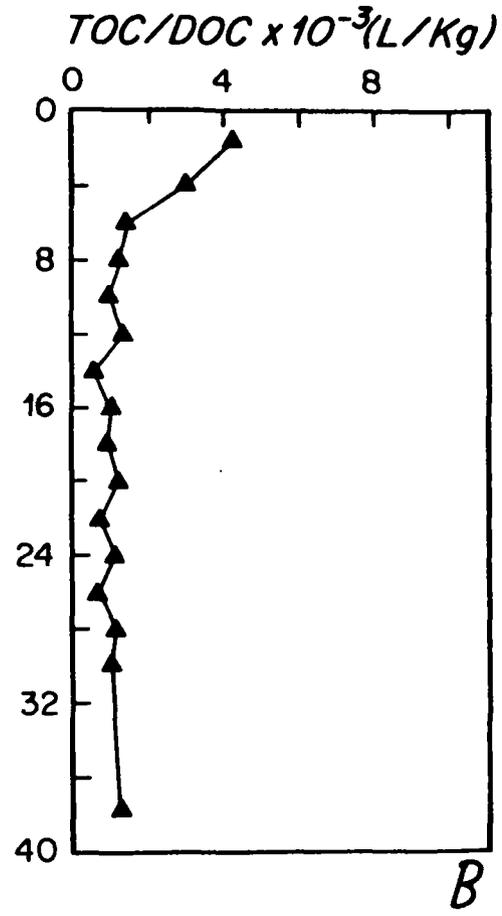
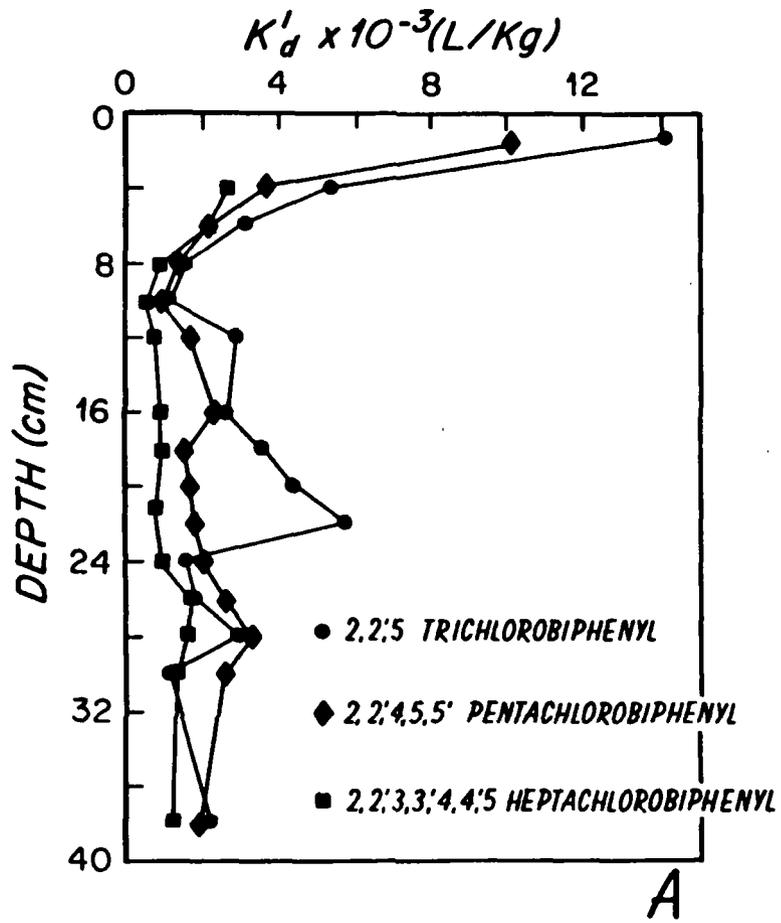
Other colloidal phases which may exist in interstitial waters (e.g., colloidal iron or sulfur phases) can probably be discounted as important sorbent phases for PCBs, because of the higher concentrations and sorption capacity of colloidal organic matter in interstitial waters. Maximum interstitial water Fe levels were 1.9 mg/L at Station 67 and colloidal elemental (plus polysulfide) sulfur concentrations in interstitial waters of reducing sediments are not observed to exceed 0.90 to 10.8 mg S/L (Luther et al., 1985). It was noted above that colloidal organic carbon levels in pore waters of reducing sediments range from 8 to greater than 50 mg/L.

Table 3-4. Apparent distribution coefficients (K'_d) of ten polychlorinated biphenyls with depth in the sediment. Structures corresponding to the IUPAC chlorobiphenyl numbers are found in Table 3-1. A complete data set of the K'_d 's of all 46 resolved and unresolved chlorobiphenyls can be found in Appendix 3.

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.

Figure 3-6. (A) K'_d profiles of three chlorobiphenyls at Station 67. (B)
The corresponding TOC/DOC profile



Furthermore, the organic matter fraction dominates sorption when $f_{oc} > 0.001$ in the case of sediments (Schwarzenbach and Westall, 1981), and the organic fraction of colloidal phases in interstitial waters will always be high.

The role of both colloidal and sedimentary organic matter can be more effectively interpreted by comparing the apparent distribution coefficients to a three-phase equilibrium sorption model. In this view, both colloidal and sediment-bound phases exist in a dynamic equilibrium with a truly dissolved phase. The analytical or apparent distribution coefficients of individual chlorobiphenyls include both a dissolved concentration, C_d , and colloid-sorbed concentration, C_c (e.g., units of ng/L), in the denominator:

$$K'_d \text{ (L/Kg)} = \frac{C_s}{C_d + C_c} \quad \text{(eqn. 3-7)}$$

where C_s is the sediment sorbed PCB concentration. C_s and C_c can be substituted for by equation 3-1 and the definition of K_p (eqn. 1-1)

$$K'_d = \frac{f_{ocS} K_{ocS} C_d}{C_d + f_{ocC} K_{ocC} C_d} \quad \text{(eqn. 3-8)}$$

where f_{ocS} and f_{ocC} are the Kg of total organic carbon in a Kg of dry sediment and Kg of colloidal organic carbon per liter of pore water, respectively, and K_{ocS} and K_{ocC} are the sediment and colloidal carbon normalized partition coefficients. C_c is predicted to dominate C_d for PCBs in sediment interstitial waters which have high organic colloid concentrations (see Chapter 2). In the case where C_d is small compared to $f_{ocC} K_{ocC} C_d$, the expression reduces to:

$$K'_d = \frac{f_{ocS} K_{ocS}}{f_{ocC} K_{ocC}} \quad (\text{eqn. 3-9})$$

The values of K_{ocS} and K_{ocC} are not accurately known for PCBs with the sediments and interstitial water colloids at these sites. However, the results from laboratory experiments in this work (Chapter 2) and other studies in the literature (reviewed in Chapters 1 and 2) suggest that carbon normalized partition coefficients of PCBs and other nonpolar HOC with marine and freshwater organic colloids are similar to those reported for freshwater sediments. It is assumed in this discussion that $K_{ocS} = K_{ocC}$.

Furthermore, it is assumed that the concentration of colloidal organic carbon f_{ocC} is reflected by the total DOC as was discussed earlier. It is then seen that, in the limit where C_o is much greater than C_d , an estimate of K'_d is simply the concentration ratio of organic carbon in sediment and interstitial waters:

$$K'_d = \text{TOC/DOC} \quad (\text{eqn. 3-10})$$

In Figure 3-6 the profile of TOC/DOC is compared to the K'_d of a few chlorobiphenyls. The similarity of the model K'_d with those actually measured is quite good, especially for the more highly chlorinated congeners. Some of the assumptions made in this simple model are further evaluated in later sections.

One major assumption in this model is that of equilibria between all three phases. There is some controversy in the literature involving the reversibility of sorption and desorption processes for PCBs with sediments (DiToro and Horzempa, 1982; Wu and Gschwend, 1986; see Chapter 1). However, several studies have demonstrated that HOC can be completely desorbed from

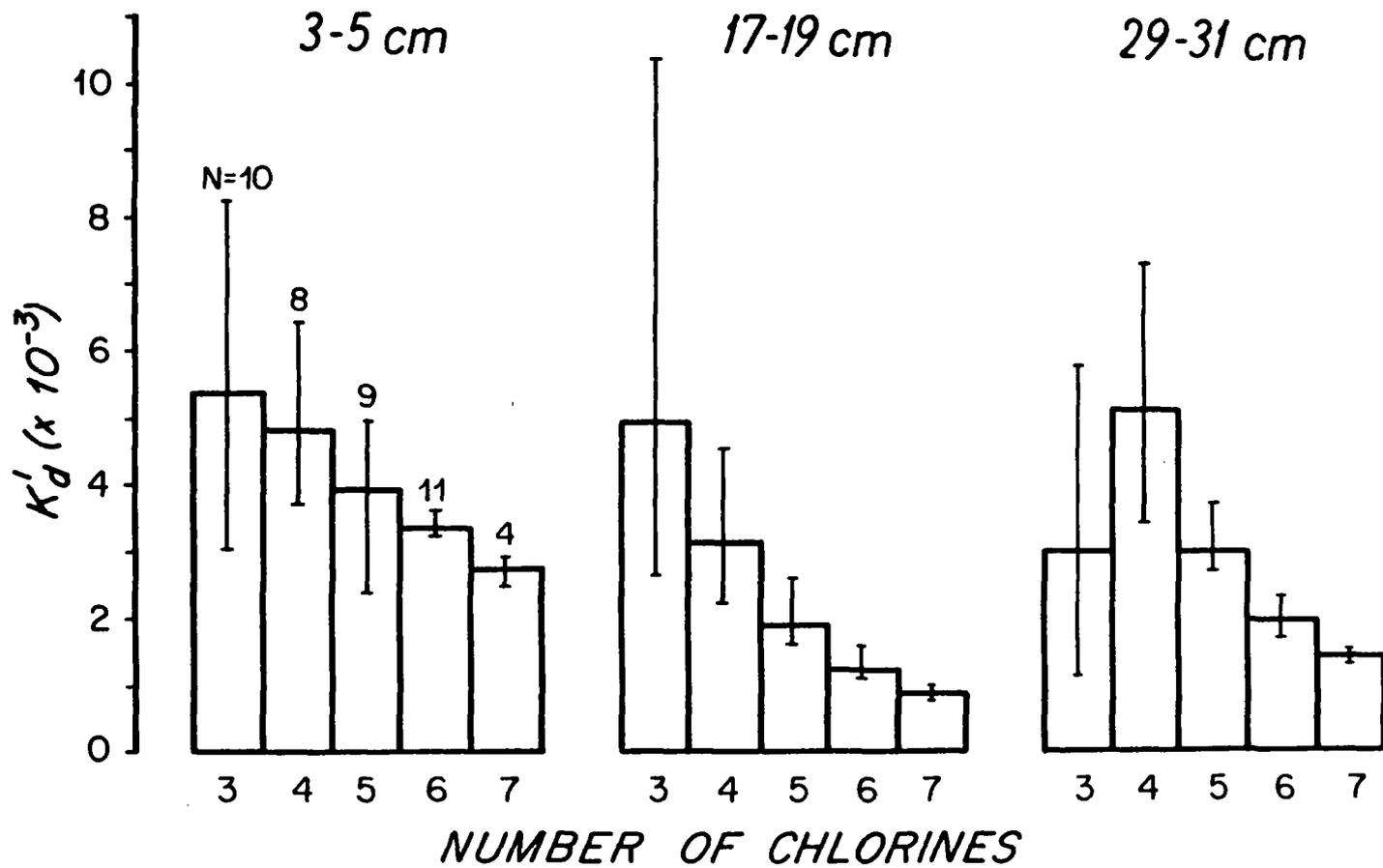
sediments, but that desorption is apparently diffusion limited for some fraction of the sorbed compound (Karickhoff, 1980; Karickhoff and Morris, 1985; Wu and Gschwend, 1986).

Sorption kinetics are well described by an intraparticle radial diffusion model where sorption is impeded by the partitioning of the compound (K_{oc}), the pathlength of diffusion (particle radius), and influenced by the nature of the sediment aggregates considered (Wu and Gschwend, 1986). The results from the above studies with less highly sorbed HOC can be extrapolated with the radial diffusion model of Wu and Gschwend to predict the sorptive timescales of PCBs in sediments (Wu and Gschwend, 1986). The time for 50% of chlorobiphenyls with K_{ps} of 10^3 - 10^5 to desorb from 50 μ m diameter silty clay sediments into pore water, in which PCBs are continuously removed, ranges from less than 2 hours to more than 70 days. This assumes sediment aggregate properties similar to those determined by Wu and Gschwend and an average aqueous diffusivity of PCBs of 4×10^{-6} cm^2/sec . However, in bulk sediment (sediment plus pore water) there is generally less than 0.1% of the total PCBs in the interstitial waters, and desorptive release and equilibration of surface bound PCBs with interstitial waters are expected to be very fast (Karickhoff, 1980; Wu and Gschwend, 1986). In the absence of processes which remove or mix PCBs in interstitial waters on timescales rapid compared to sorption, it is concluded that assuming sorptive equilibria between sediments and interstitial waters should be appropriate. One further complicating factor is that there are dynamic interactions between sedimentary, colloidal, and non-colloidal dissolved organic matter. The nature and kinetics of these reactions are largely unknown. However, sediments below the sediment-water interface and in

the absence of extensive bioturbation provide an environment where long time scale 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 equilibria may occur. This is particularly true in situations where compounds exist substantially in the dissolved phase at equilibrium.

The K'_d 's measured are chlorobiphenyl-specific and tend to decrease with increasing degree of chlorination and decreasing solubility. Figure 3-7 shows the range and average K'_d as a function of the chlorine substitution (nCl) for three representative core sections. The observed trend is opposite to that which is expected on the basis of solubility considerations. As discussed for Station 84 results, a strong inverse dependence of partitioning of PCBs with sediments on the aqueous activity coefficient is expected from laboratory results (Karickhoff et al., 1979; Chiou et al., 1983; Gschwend and Wu, 1985) and has been observed in water column measurements reported here and in other environments (Bopp, 1979, Pavlou and Dexter, 1979; Tanabe and Tatsukawa, 1983). In contrast, it should be noted that Eisenreich et al. (1983) report no clear trend of K'_d with increasing degree of chlorination for PCBs in the water column of Lake Superior. The lack of K'_d dependence on K_{ow} in the sediments in this study is even more compelling evidence that the observed distributions are not simply the result of two-phase, sediment-water partitioning.

Figure 3-7. Bar graphs of the mean K'_d as a function of chlorine number for three representative depths at Station 67. N equals the number of isomers or unresolved isomers considered and the bars represent the range of K'_d values determined.



Compositional changes of PCBs in Station 67 sediments

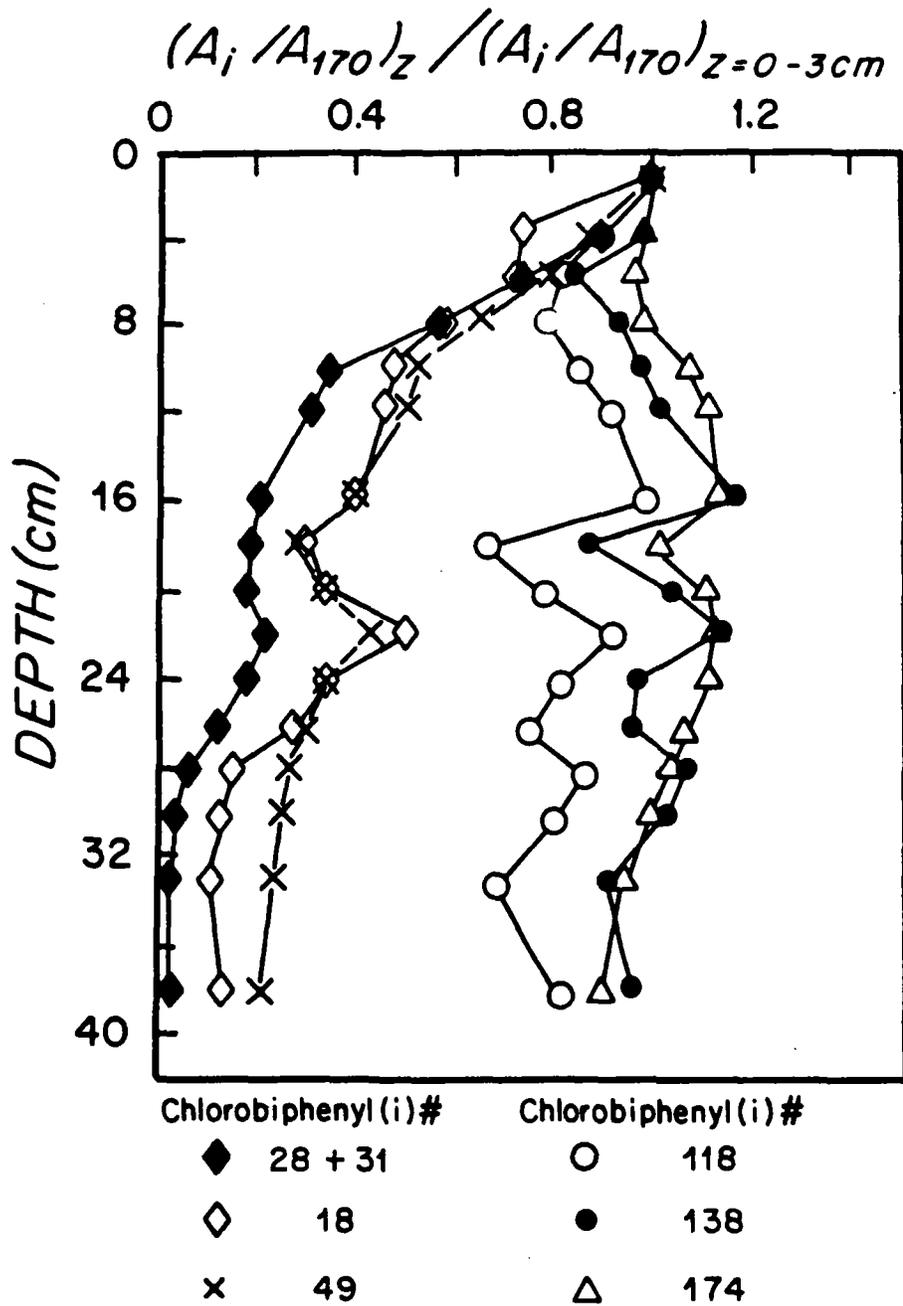
There are marked changes in the composition of PCBs with increasing depth in this core at Station 67. These changes in the sediment PCBs have been evaluated by looking at changes in peak area ratios with depth. PCB no. 170 (2,2',3,3',4,4',5- heptachlorobiphenyl) was chosen as the reference compound, because it did not show apparent depletion relative to other chlorobiphenyls, and is not expected to be readily biodegradeable, or be appreciably mobile in a dissolved form. The area ratio of each individual 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 Figure 3-8. The relative amounts of the di- and trichlorobiphenyls decrease faster than the tetrachlorobiphenyls and the relative amounts of the penta-, hexa- and heptachlorobiphenyls remain essentially constant with depth. 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 ratio of this peak to 170 is depleted at 35-41 cm to 2.2% of that in the 0-3 cm section (Figure 3-8). 2,3,4'-trichlorobiphenyl (chlorobiphenyl no. 22) is similarly depleted to 1.4% of its surface ratio. Variations in the area ratios of penta- through heptachlorobiphenyls are small.

The relative amounts 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 minimum 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. 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 were well documented. Bopp et al. (1981) have also 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 these 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. Sediment samples from Station 84 show a composition similar to those in surface sediments here, and large changes with depth were not apparent.

Figure 3-8. Profiles of the area ratios of individual chlorobiphenyls (i) in the sediments to 170 normalized to the same ratio measured in the surface sediment (Z = 0-3 cm). The structures of the chlorobiphenyl #'s are given in Table 3-1.



Migration of hydrophobic organic compounds in sediments has not been satisfactorily studied and is considered in Chapter 4. Diffusion of sediment-bound PCBs is impeded by sorption. The mean distance that a particle tracer will migrate in the sediment can be estimated by $(D_{app}t)^{1/2}$ (Berner, 1976) where D_{app} in this case can be estimated by $D_s / (1 + [(1-\phi)/\phi]\rho_s K_p)$. D_s is the sediment diffusion coefficient of solute in seawater corrected for sediment tortuosity, ϕ is sediment porosity, ρ_s is the dry sediment density, and K_p is the true partition coefficient for PCBs with sediments. Assuming a D_s of 3×10^{-6} cm²/sec for a dissolved PCB, a K_p of 10^3 , a density of solids in bulk sediment of 1.0 g/cm³, and that the sediment profile represents about 20 years, then the mean distance that a PCB particle tracer will migrate is 1.4 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 congeners would remain so constant, as these compounds 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 those of dissolved solutes. Diffusion of hydrophilic organic colloids may be 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 of 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 breakdown 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 no removal of 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 no 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 chlorobenzoic 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 by Furukawa et al. (1978) are 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 Figure 3-8. 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 degrees of chlorobiphenyl depletion in this core seem to be consistent with the pattern expected for microbial transformation. 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 these observations. However, the nature of the populations, and the mechanisms of transformation are not understood.

Station M - Sedimentary Geochemistry

The interstitial water chemistry has been studied at Station M over three seasonal cycles in the works of Martin (1985) and McNichol (1986). Suboxic diagenesis near the sediment water interface is indicated by maxima in dissolved Mn in the upper 0.5 cm throughout the seasonal cycle. Fe is reduced in the upper 0.5 cm in warm summer and fall samplings but shows a maximum closer to 2 cm in the winter when sulfate reduction rates are lower near the sediment water interface. The sediment from this core was black at the sediment-water interface and the upper cm of sediment was sulfidic indicating sulfate reduction and an absence of oxygen in the pore waters at this site.

The profile of DOC is given in Table 3-5 and Figure 3-9B and shows a large maximum of DOC in the 1-3 cm core section. This profile is consistent with other DOC profiles measured at this site (McNichol, 1986). In most of these profiles, a subsurface maxima of DOC corresponds to a sharp gradient in alkalinity (Figure 3-9B), suggesting that the production of DOC is favored in zones of rapid remineralization of organic matter and that there are chemical, biological, or physical-chemical removal processes for DOC with depth in the core. The levels of DOC below the 1-3 cm maxima are within a range of those measured in the other samplings at this site (McNichol, 1986). In that work, pore waters were extracted with a Reeburgh squeezer and filtered through 0.40 μm membrane filters. This suggests that the extraction techniques used do not strongly affect DOC separation and that the use of a glass fiber depth filter does not significantly bias the measurement of colloidal organic matter. In other words, the small amount of larger particles which might pass through a glass fiber depth filter, and do not pass a membrane filter of discrete pore diameter, do not bias the organic carbon measurement. The concentrations of DOC at this site are slightly lower than those measured at other stations in Buzzards Bay (Henrichs, 1980; Sholkovitz and Mann, 1984).

The profiles of water content, TOC, and TON are also given in Table 3-5. The water content and calculated porosities decrease smoothly and agree well with average values determined at this site by Martin (1985). The levels of TOC are enriched and variable in the upper 9 cm. The concentration profile below 9 cm decreases to concentrations consistent with those profiles determined by McNichol (1986). The concentration (2.87 - 3.79%) and depth of penetration of enriched organic carbon levels are greater than that determined

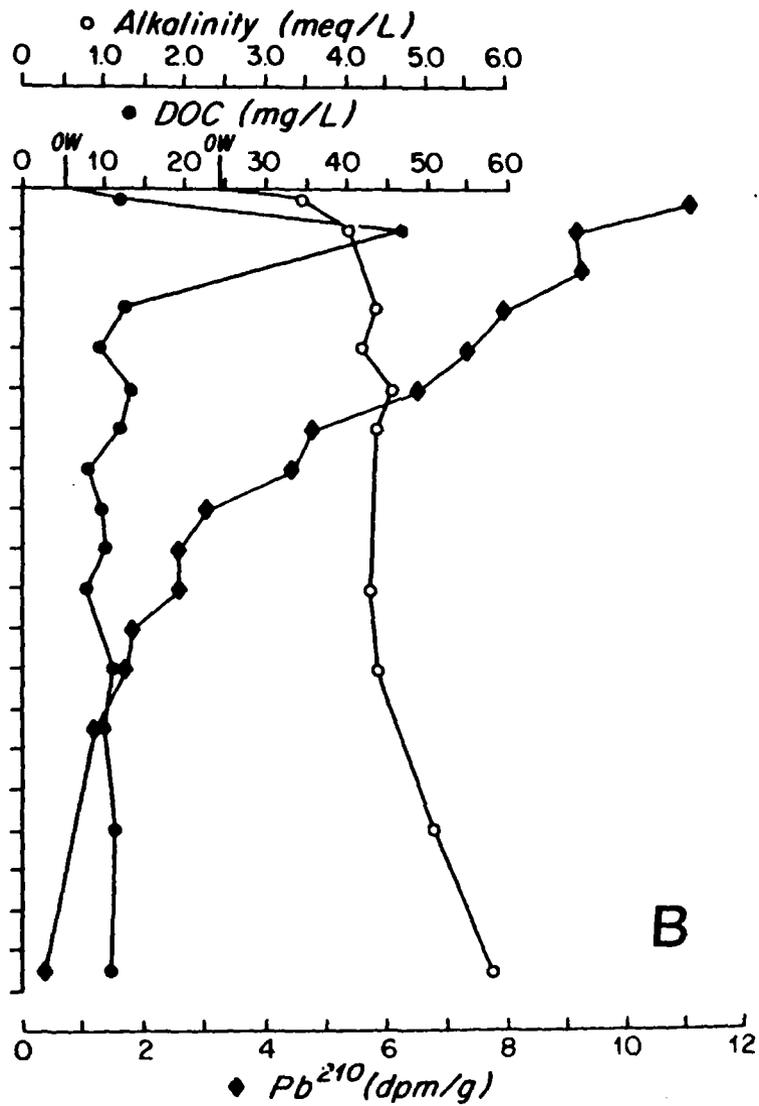
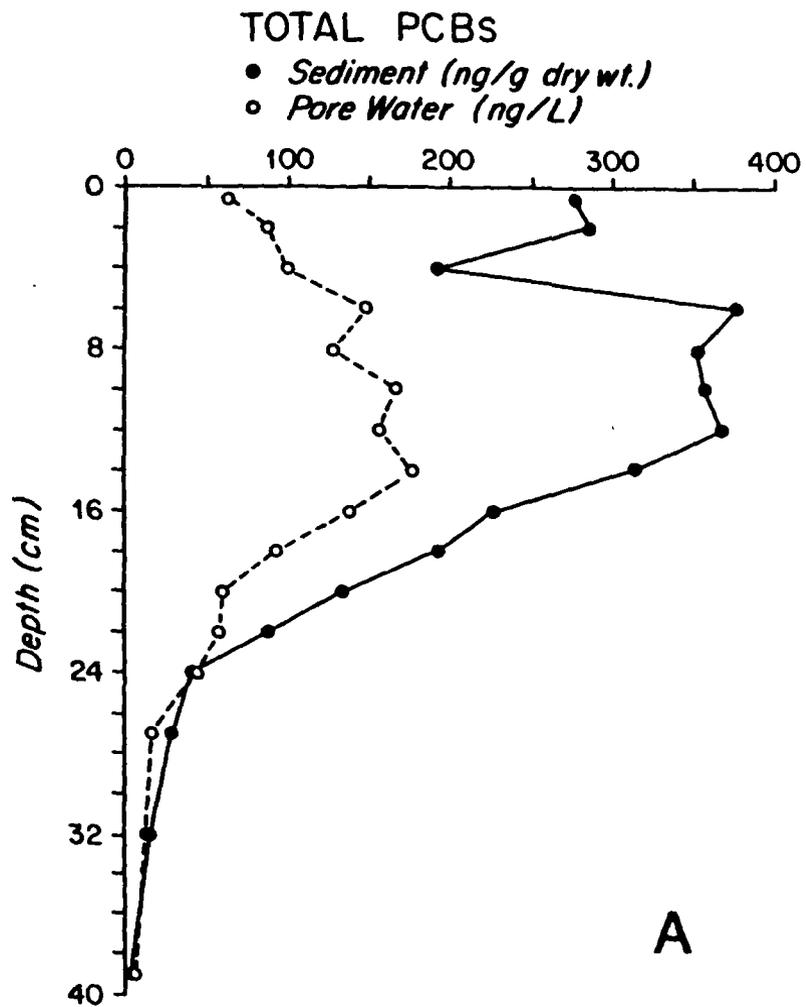
Table 3-5. Profiles of bulk sediment properties and Aroclor concentration profiles in sediments and pore waters at Station M.

Depth (cm)	% H ₂ O	TOC (%)	TON (%)	C/N	DOC (mg/L)	Aroclor 1242		Aroclor 1254		X's ²¹⁰ Pb (dpm g ⁻¹)
						Sed. (ng/g)	P.W. (ng/L)	Sed. (ng/g)	P.W. (ng/L)	
0-1	68.2	3.17	0.42	7.5	12.1	85.0	11.1	191	51.1	11.0±0.4
1-3	67.7	2.87	0.37	7.8	46.3	67.2	18.4	218	67.4	9.1±0.3
3-5	62.7	3.73	0.48	7.8		52.3	15.9	138	82.7	9.2±0.3
5-7	60.3	3.79	0.48	7.9	12.3	190	25.2	235	121	7.9±0.3
7-9	59.7	3.43	0.44	7.8	9.33	116	25.5	235	100	7.3±0.3
9-11	56.1	2.31	0.28	8.2	13.2	112	29.9	244	136	6.5±0.3
11-13	53.8	2.55	0.30	8.5	11.6	141	27.0	251	128	4.7±0.3
13-15	52.3	1.93	0.22	8.8	7.94	88.3	37.7	225	137	4.4±0.3
15-17	52.3	2.20	0.25	8.8	9.38	48.3	19.5	177	116	3.0±0.3
17-19	52.0	1.91	0.23	8.3	10.0	46.4	16.6	145	74.0	2.6±0.3
19-21	52.3	2.15	0.25	8.6	7.84	26.8	9.5	105	49.3	2.6±0.3
21-23		2.01	0.24	8.4		19.1	13.5	66.7	43.8	1.8±0.3
23-25	50.4	2.13	0.24	8.9	11.1	8.2	9.5	32.9	33.3	1.5±0.2
25-29		1.96	0.22	8.9	10.0	4.8	4.2	22.5	12.2	1.2±0.2
29-35	50.4	2.64	0.31	8.5	11.5	2.7	3.1	12.0	9.3	
35-43		1.67	0.19	8.8	10.9	N.D.	1.5	2.4	4.1	0.4±0.2

N.D.: not detected due to interference.

Figure 3-9. (A) Concentration profile of total PCBs (Aroclors 1242 + 1254) in sediments and pore waters at Station M. (B) The profile of unsupported ^{210}Pb ($^{226}\text{Ra} - ^{210}\text{Pb}$) in the sediments and the interstitial water profiles of alkalinity and DOC. The concentration of these properties in the overlying water of the box core (o.w.) are also given and indicate a small contamination from the pore waters during coring.

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by McNichol, who found maximum TOC concentrations of 2.45 - 3.29% during different samplings over a seasonal cycle. The C/N ratio in sediments also increased slightly with depth at this site, suggesting preferential nitrogen metabolism. The C/N ratios at this site are lower than those of Station 67 and might reflect a different source of organic matter to the sediments.

The unsupported ^{210}Pb depth profile is shown in Figure 3-9B and given in Table 3-5. The activity of ^{226}Ra was constant at 1.7 ± 0.1 dpm with the exception of the 3-5 cm section which had an activity of 1.2 dpm. The profile of unsupported ^{210}Pb decreased logarithmically with depth and is the result of sedimentation, sediment mixing, and radioactive decay. An apparent sedimentation rate can be calculated from the slope of $\ln A_z$ vs. depth (z):

$$\ln A_z = -\lambda/s \cdot z + \ln A_0 \quad (\text{eqn. 3-11})$$

where A_z is the unsupported ^{210}Pb activity at depth z, s is the sedimentation rate, and λ is the decay constant of ^{210}Pb (0.03108 yr^{-1}). The slope of $\ln A$ vs z below 10 cm (where there is a slight slope break) yields an apparent sedimentation rate of 0.329 cm/yr. This sedimentation rate can be compared to a rate of 2.95 cm/yr determined by a similar analysis of ^{210}Pb at Station P in Buzzards Bay (Farrington et al., 1977). However, this sedimentation rate yields an apparent age of 118 years at the center of the 35-43 cm sediment section. The penetration of PCBs to this sediment horizon (Figure 3-8A and Table 3-5) indicates that relatively deep sediment mixing must partially account for the distribution of ^{210}Pb and PCBs at this site. A lower sedimentation rate of 0.05 cm/yr has been estimated from ^{14}C analysis from three sections below 30 cm at this site (McNichol, 1986). The occurrence of deep biological mixing is supported by determinations of pore

water irrigation from ^{222}Rn deficits in pore waters below 20 cm (Martin, 1985), and visual observations of worm tubes below 20 cm (McNichol, personal communication). A further discussion of sediment mixing and sedimentation at this site is included in Chapter 4.

PCB Results at Station M

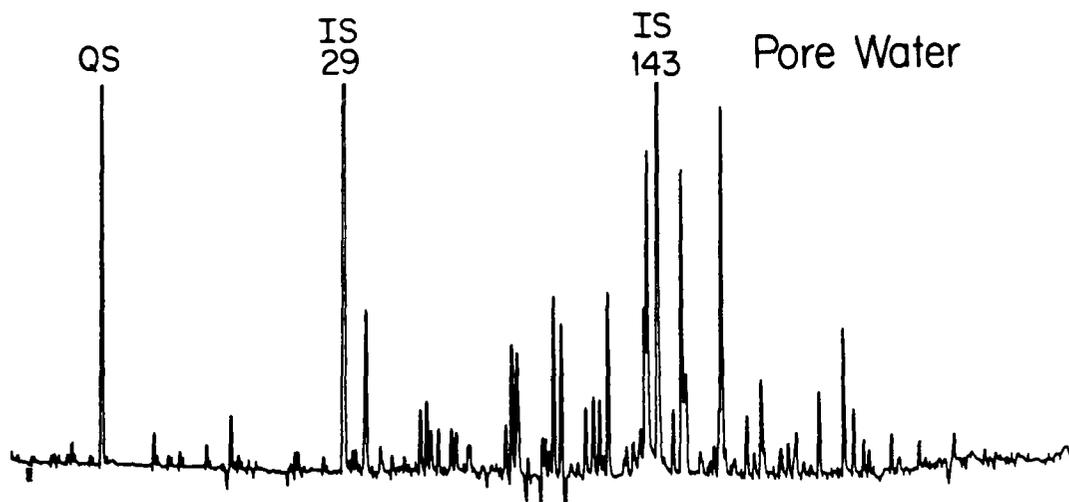
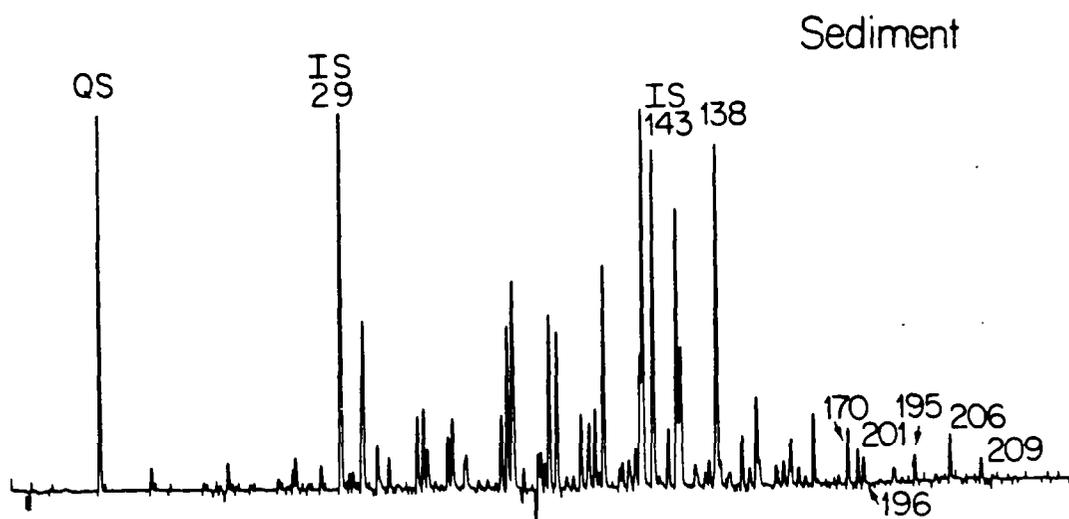
The concentrations of total PCBs in the sediments at Station M, calculated as the sum of Aroclor 1242 and 1254, are shown to be 25-500 lower than those found at the New Bedford Harbor stations (Table 3-5, Figure 3-9). The concentrations of total PCBs in the upper 17 cm are 190 to 390 ng/g and are higher than surface sediment concentrations of 39.2 ng/g in a Narragansett Bay core at a station 5-10 km down-estuary from a municipal sewage outfall and industrial complex (Wade and Quinn, 1979). The sediment concentrations are comparable to those in sediments from the upper Hudson Bay (130-200 ng/g) and New York Bight sewage sludge dumpsite (60 to 2200 ng/g) (Boehm et al., 1985). Sediment samples from Los Angeles Harbor decreased from 214 to 46 ng/g away from a sewer outfall (Choi and Chen, 1976). These comparisons with stations having similar sediment types and close proximity to direct PCB inputs indicate that PCBs at Station M are comparable to levels found in other coastal and urban harbor environments, which have large local sources of PCBs, and are higher than levels found in other coastal sediments more remote from concentrated inputs. Thus, the major source of PCBs to this site is likely resuspended sediments which have been transported away from New Bedford Harbor.

The composition of PCBs in sediments and interstitial waters are illustrated by the chromatograms shown in Figure 3-10. These compositions of

Figure 3-10. Capillary gas chromatograms of PCBs in sediments and pore waters at a 1-3 cm depth at Station M. IS refers to internal standards 29 and 143 and QS is the quantification standard (pentachlorobenzene). The chromatograms are labeled with the tentative identifications of several congeners not reported in New Bedford Harbor. The structures of these PCB #'s are as follows:

- 201 2,2',3,3',4',5,5',6-octachlorobiphenyl
- 196 2,2',3,3',4,4',5',6-octachlorobiphenyl
- 195 2,2',3,3',4,4',5,6-octachlorobiphenyl
- 194 2,2',3,3',4,4',5,5'-octachlorobiphenyl
- 206 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl
- 209 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

Station M, 1-3cm



chlorobiphenyls resemble the mixtures of Aroclor 1242 and 1254 found in New Bedford Harbor sediments (compare with the surface sediment sample in Figure 3-5), but are depleted in more soluble, less chlorinated biphenyls. The preferential loss of more soluble PCBs is expected during transport of sediments into cleaner waters because of faster desorption kinetics and a greater tendency to partition into the aqueous phase followed by dilution with cleaner waters and exchange to the atmosphere. In addition to chlorobiphenyls which appear in Aroclors 1242 and 1254, and New Bedford Harbor samples, decachlorobiphenyl and several octa- and nonochlorobiphenyls are tentatively identified in Station M samples. The presence of these congeners, and differences in the profiles of these compounds and other heptachlorobiphenyls from other congeners indicates a second, smaller source of PCBs to this site. Potential sources of PCBs include atmospheric transport and local marine operations (e.g., the composition of PCBs that may have been used in boat bottom paints (NAS, 1979) is not known).

The compositions of the major chlorobiphenyls in the sediments remains fairly constant with depth in the core. Figure 3-11B shows that the concentration ratios of representative penta- and hexachlorobiphenyls to hexachlorobiphenyl 138 are relatively constant with depth. 138 is used as a composition reference instead of 170 at this site because the relative concentration of 170 covaries with the higher chlorinated biphenyls which are enriched in the 1-3 cm section and in sediments below 20 cm (Figure 3-11C). The relative concentrations of di-, tri-, and tetrachlorobiphenyl are more variable (Figure 3-11A) and tend to covary with depth. The compositions of these more soluble congeners are more sensitive to changes in the time

histories and suspended solids concentrations of sediments during transport than are the penta- and hexachlorobiphenyls which are associated with particles to a greater extent during transport. It is not possible to determine whether the relative decrease in trichlorobiphenyls, such as 28 + 31, is due to microbial degradation or not. Unfortunately, interfering peaks in the chromatograms below 25 cm prohibited the quantitation of many di- and trichlorobiphenyls in those samples. Interstitial water concentrations of these congeners in deeper sections indicate that they are not substantially depleted as they are at Station 67.

The concentration profiles of total PCBs (Figure 3-9A) and several individual chlorobiphenyls (Table 3-6 and Figure 3-12) show broad subsurface maxima between 5 and 15 cm. The low PCB concentrations in the 3-5 cm section corresponds to the anomalously low ^{226}Ra activity at that depth and indicate a different sediment type or source. The fact that the PCB composition is not unusual for this sample indicates that the sediments may be diluted with material low in ^{226}Ra and PCBs.

A decrease in the supply of PCBs to the surface sediments in recent years is suggested from the PCB profiles and comparison with unsupported ^{210}Pb . If the distribution of PCBs with depth in the sediments is largely controlled by biological mixing (versus sedimentation) and the source of PCBs to the sediment interface has not changed (e.g., constant source for the last 40 years) then a profile concave downward from the interface is expected. This simple continuous source mixing model assumes a constant mixing rate with depth and an infinite spatial domain for mixing (see Chapter 4). The observed subsurface maxima in PCBs compared to a continuous source mixing model

Figure 3-11. The concentration ratios of several chlorobiphenyls to chlorobiphenyl 138 (C_i/C_{138}) with depth at Station M normalized to the same ratio in the 0-1 cm section. PCB numbers correspond to the structures given in Table 3-1 and Figure 3-10.

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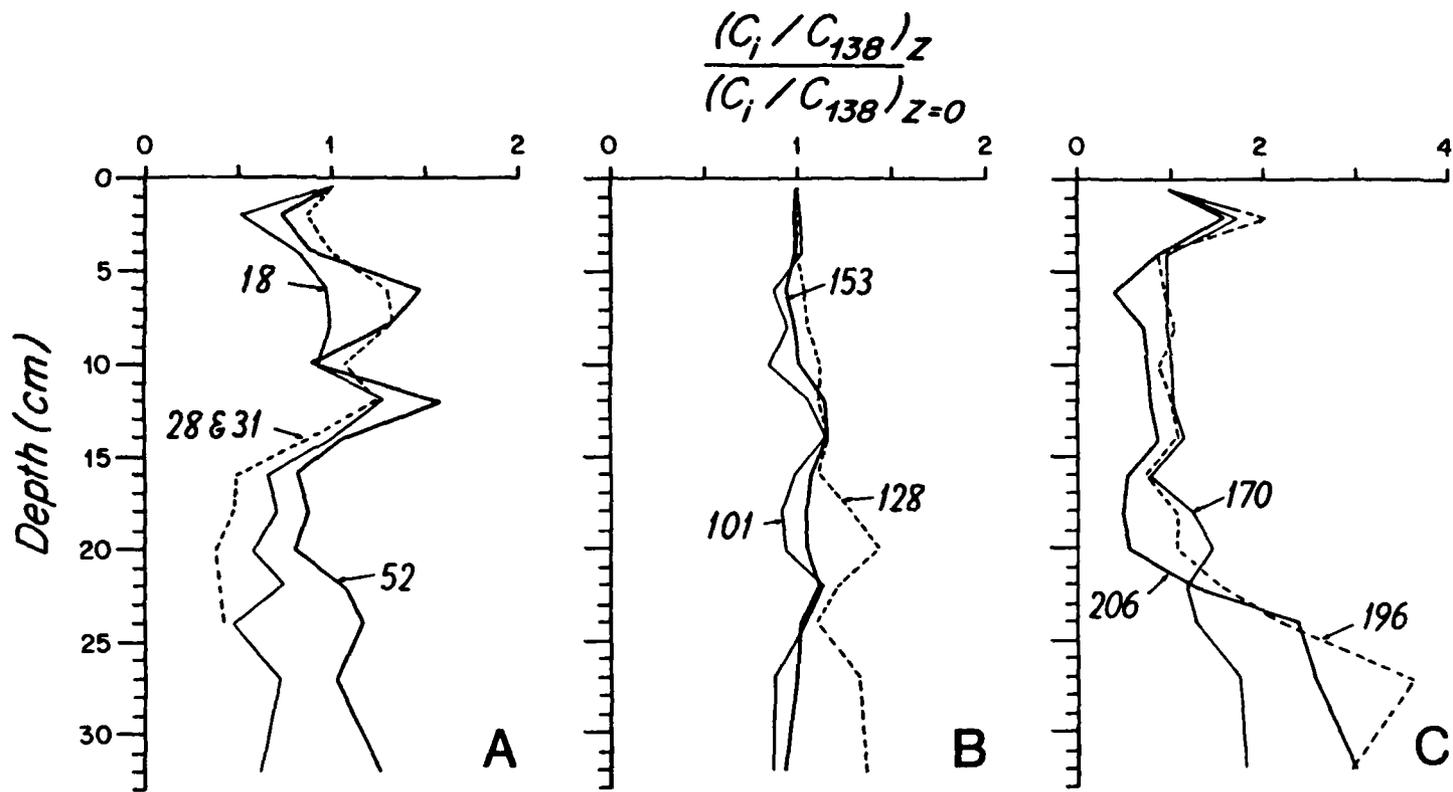
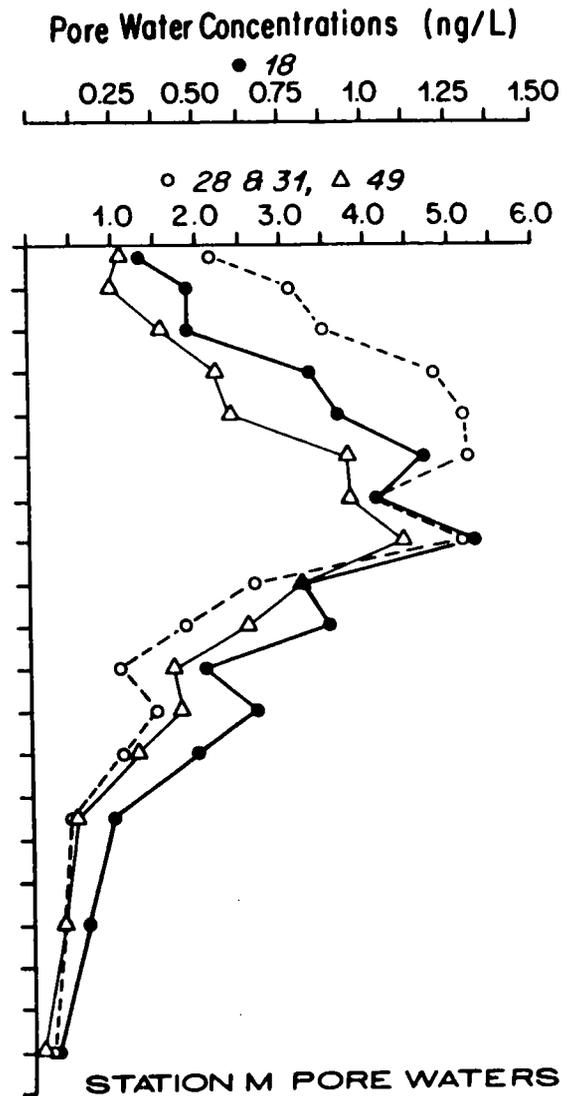
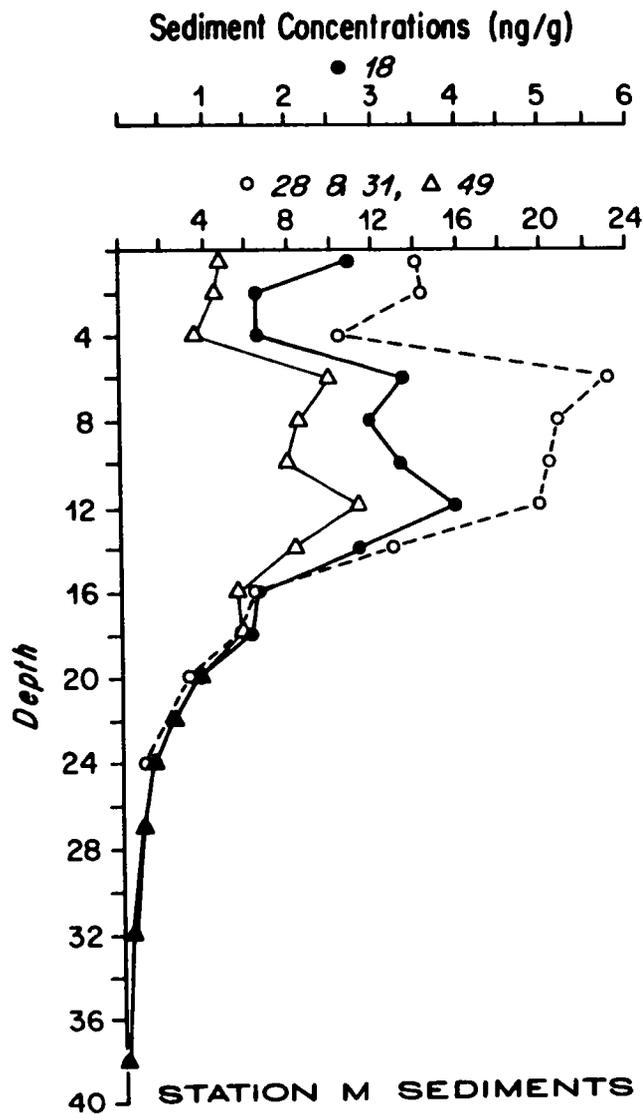


Table 3-6. Concentration profiles of individual chlorobiphenyls in sediments and pore waters at Station M. Structures of PCB #'s are given in Table 3-1 and Figure 3-10.

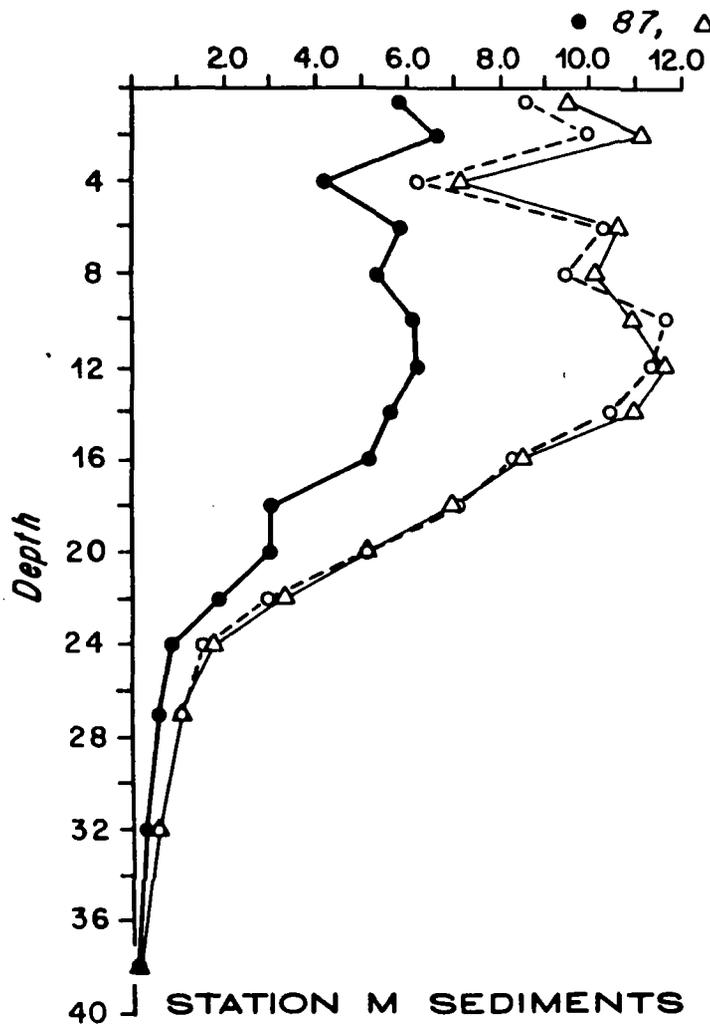
Depth (cm)	Sediments (ng/g dry wt.)								Pore waters (ng/L)							
	28 + 31	52	101	87	153	138	170	206	28 + 31	52	101	87	153	138	170	206
0-1	14.1	5.46	9.50	5.81	8.60	10.4	1.2	0.820	2.17	1.13	2.31	0.726	3.9	3.57	0.440	0.154
1-3	14.3	4.66	11.1	6.63	9.92	12.0	2.39	1.50	3.11	0.938	3.00	2.75	3.42	3.24	0.424	0.865
3-5	10.3	3.53	7.10	4.19	6.19	7.53	0.865	0.512	3.49	1.35	4.61	2.43	3.84	4.88	0.625	0.593
5-7	23.1	10.3	10.6	5.82	10.3	13.2	1.47	0.416	4.82	2.00	7.11	4.58	5.82	5.81	0.795	0.830
7-9	20.7	7.86	10.1	5.33	9.46	11.5	1.29	0.650	5.17	1.97	6.30	3.16	4.60	4.96	0.585	0.950
9-11	20.3	6.65	10.9	6.05	11.6	13.9	1.68	—	5.21	2.90	6.60	3.58	6.49	8.96	1.79	0.895
11-13	19.8	9.90	11.6	6.16	11.3	11.8	1.53	0.736	4.09	2.85	7.32	3.07	5.75	6.92	0.752	0.264
13-15	12.9	6.04	10.9	5.59	10.4	10.7	1.43	0.709	5.14	3.23	7.67	2.96	6.57	7.21	0.751	—
15-17	6.27	3.81	8.50	5.12	8.23	9.31	0.813	0.396	2.65	2.32	6.58	2.53	5.76	6.37	0.610	0.507
17-19	5.46	3.84	6.91	2.97	7.01	8.23	1.22	0.316	1.83	1.95	4.16	1.65	3.28	4.21	0.435	0.277
19-21	3.11	2.52	5.05	2.95	5.06	5.87	0.984	0.245	1.06	1.31	2.61	0.946	2.33	2.61	0.419	—
21-23	—	1.76	3.26	1.85	2.89	3.12	0.874	0.316	1.49	1.43	2.29	0.786	2.36	2.52	0.265	0.279
23-25	1.03	1.08	1.71	0.799	1.50	1.77	0.267	0.333	1.07	1.11	1.74	0.780	1.52	2.00	0.367	0.208
25-29	—	0.681	1.02	0.505	1.05	1.27	0.259	0.294	0.448	0.491	0.625	0.252	0.739	0.528	—	—
29-35	—	0.431	0.518	0.265	0.501	0.648	0.144	0.154	0.367	0.350	0.509	0.239	0.470	0.450	—	—
35-43	—	0.095	0.112	0.086	0.078	0.164	—	—	0.211	0.128	0.249	0.141	0.183	0.194	—	—

Figure 3-12 A (page 194) and B (page 195). Depth profiles of individual chlorobiphenyls in the sediments and in interstitial waters at Station M. The concentration axes are changed for the three congeners shown in Figure 3-12A. The corresponding structures of the PCB #'s are given in Table 3-1.

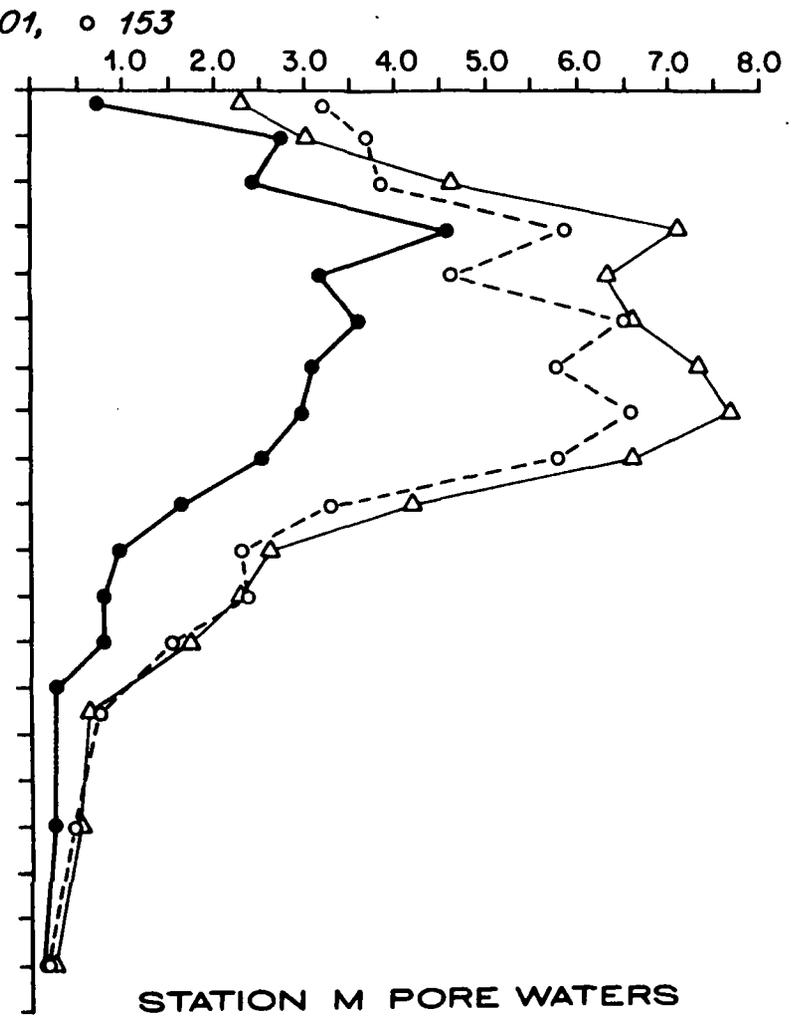
5 1454



Sediment Concentrations (ng/g)



Pore Water Concentrations (ng/L)



5 1455

suggests that the source of PCBs may have substantially decreased in recent years. The nearly three-fold increase in Aroclor 1254 with depth at Station 67 supports this observation. The concentrations of the major chlorobiphenyls decreases rapidly below 15 or 17 cm at Station M and are barely observable in the 35-43 cm section. This is consistent with the ^{210}Pb profile and the hypothesis that biological mixing processes are largely responsible for the PCB distributions in the sediments at this site.

The concentration profiles of the most highly chlorinated biphenyls (nC1 = 7-10) do not decrease as rapidly with depth in the sediments (Figure 3-11, Table 3-6). This may indicate that the time history of supply of these congeners to the sediments may be different than PCBs transported from New Bedford. It should be mentioned that the concentrations and peak areas are smaller for this group of compounds and baseline interference increases the errors in their quantification. This is particularly true in deeper samples.

Interstitial water concentrations of total PCBs and individual chlorobiphenyls with depth in the core are also given in Tables 3-5 and 3-6 and illustrated in Figures 3-9A and 3-12. Total PCB concentrations increase from 62 to 170 ng/L over the upper 15 cm and are lower than the levels measured in New Bedford Harbor sediments. Interstitial water concentrations are again much higher than those expected in the water column and can be compared to filtered water column concentrations of 0.20 to 1.6 ng/L measured at four sites in Buzzards Bay (de Lappe et al., 1980).

The concentrations of individual chlorobiphenyls shown in Figure 3-12 are primarily related to the sediment sorbed concentration of PCB and the DOC (Figure 3-9B) at each depth interval. However, the interstitial water

concentrations do not increase greatly at 1-3 cm depth where the DOC has a large spike. The DOC concentration measured at this depth is somewhat higher than concentrations found in the subsurface DOC maxima at this site by McNichol (1986) and probably represents very recent production of DOC. This DOC may be low molecular weight in nature or represent very new production from a source of labile organic matter which had recently been deposited in the sediment and had not yet approached sorptive equilibrium with PCBs.

The profiles of K'_d for several chlorobiphenyls are given in Table 3-7 and selected profiles are illustrated along with TOC/DOC in Figure 3-13. Measured K'_d s are low (400-7000) and do not increase with K_{ow} . With the exception of the low TOC/DOC at 1-3 cm, measured K'_d s are very well described by the three-phase equilibrium sorption model. These results provide additional support to the contention that interstitial water PCBs are substantially sorbed to organic colloids and that measured distributions closely approach sorptive equilibrium.

Measured distribution coefficients are congener specific but less so than at Station 67. In the upper 13 cm, K'_d s tend to be higher and more variable for the less chlorinated biphenyls. The trend of increasing K'_d with decreasing nCl observed at Station 67 is generally observed in the upper sediments. Below 13 cm, K'_d s of all congeners converge and tend to be slightly lower than predicted values. It is tempting to ascribe lower K'_d values in the deeper sediments to diffusion of PCBs in interstitial waters from above into layers of lower concentration. However, there is not a good correspondence of measured K'_d s at a given sediment depth with the relative diffusive fluxes of individual chlorobiphenyls estimated from the pore water profiles.

Figure 3-13. The depth profiles of K'_d for four representative chlorobiphenyls are shown along with that of TOC/DOC at Station M.

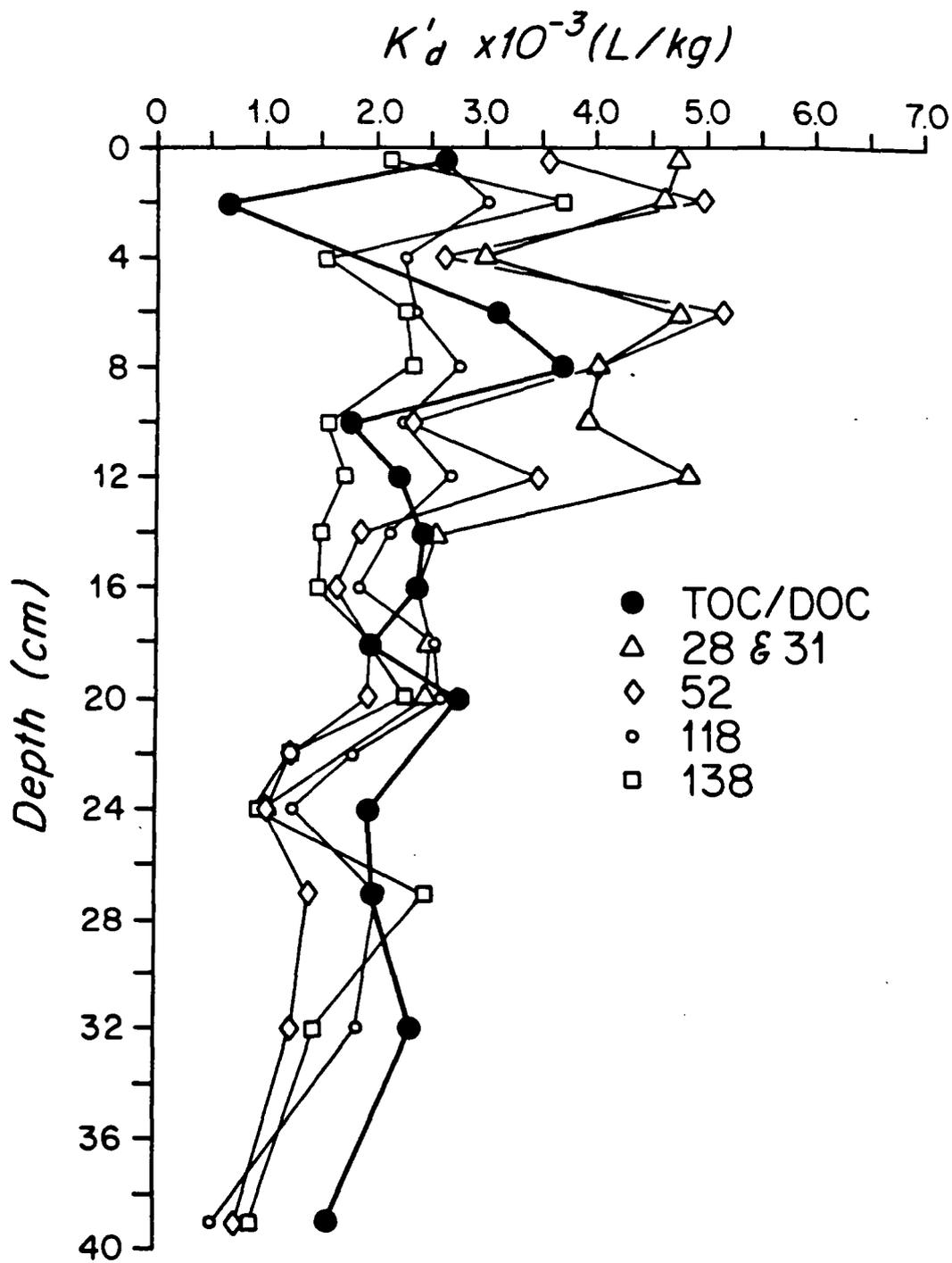


Table 3-7. K'_d s of selected individual chlorobiphenyls at Station M.
Structures of PCB #'s are given in Table 3-1
and Figure 3-10.

Depth	$K'_d \times 10^{-3}$ (L/Kg)											
	8	18	28 + 31	49	52	101	110	108	138	153	170	196
0-1	5.91	5.99	4.74	3.20	3.55	3.04	3.19	2.62	2.12	1.97	2.02	1.66
1-3	1.56	3.42	4.61	4.66	4.97	3.71	3.12	3.03	3.70	2.90	5.62	5.76
3-5	3.69	3.48	2.94	2.25	2.60	1.54	2.18	2.26	1.54	1.53	1.38	1.13
5-7	2.86	4.04	4.78	4.42	5.15	1.49	2.72	2.36	2.27	2.06	1.85	1.81
7-9	3.81	3.22	4.01	3.53	3.99	1.60	2.95	2.78	2.32	2.23	2.21	2.34
9-11	5.50	2.85	3.90	2.08	2.29	1.65	2.12	2.22	1.55	1.85		
11-13	6.43	3.87	4.84	2.93	3.47	1.59	2.66	2.68	1.71	2.04	2.03	1.57
13-15	2.65	2.12	2.51	1.84	1.87	1.42	2.39	2.11	1.49	1.62	1.90	1.42
15-17	3.45	2.00	2.36	1.72	1.64	1.29	2.36	1.85	1.46	1.52	1.33	1.19
17-19	3.95	1.71	2.99	2.19	1.97	1.66	2.85	2.53	1.95	2.02	2.86	1.66
19-21	5.86	1.74	2.94	2.20	1.92	1.93	2.96	2.58	2.25	2.08	2.35	0.860
21-23	1.91	0.904		1.42	1.23	1.42	2.05	1.78	1.24	1.46	1.64	0.602
23-25	1.33	0.769	0.968	1.20	0.978	0.982	1.16	1.22	0.885	1.02	0.728	0.583
25-29	2.21	1.00	—	1.81	1.39	1.64	2.27	2.00	2.41	2.34	—	—
29-35	1.49	0.634	—	1.44	1.23	1.02	1.52	1.81	1.44	1.42	—	—
35-43	—	—	—	0.680	0.743	0.644	0.853	0.530	0.845	0.494	—	—

Three-phase Sorption Model for PCBs

It is useful to further evaluate the assumptions involved in the simple three-phase equilibrium sorption model given by equations (3-8) and (3-10) with the combined partitioning results from the three sediment cores, and experimental results from Chapter 2 and the literature (Chapters 1 and 2). Equation 3-8 can be rewritten as:

$$K'_d = \frac{\text{TOC } K_{oc}s}{1 + \alpha \text{ DOC } K_{oc}c} \quad (\text{eqn. 3-12})$$

where α is the fraction of DOC which is colloidal. $K_{oc}s$ for PCBs can be estimated by substituting the $\log K_{ow}s$ for chlorobiphenyls given in Table 3-1 into equation 3-2, and using values of a and b determined from laboratory sorption studies of PCBs and other HOC with freshwater sediments and soils (Table 1-1 or 3-9).

Comparisons of measured sediment interstitial water data from Stations 84 and 67 and model predictions of K'_d from two-phase and three-phase partitioning models are presented in Figures 3-14 and 3-15. The three solid lines are predictions of two-phase sediment water partitioning given by equation 3-1 and the predictions of $K_{oc}s$ based on experimentally determined $\log K_{oc}$ vs. $\log K_{ow}$ relationships published by three groups of workers (Means et al., 1980; Schwarzenbach and Westall, 1981; Chiou et al., 1983). Line 1 from Means et al. (1980) is nearly identical to a relationship reported by Karickhoff et al. (1979) (Table 1-1), and most nearly fits the PCB sorption data of Gschwend and Wu (1985) (see Figure 1-2). The PCB sorption data of

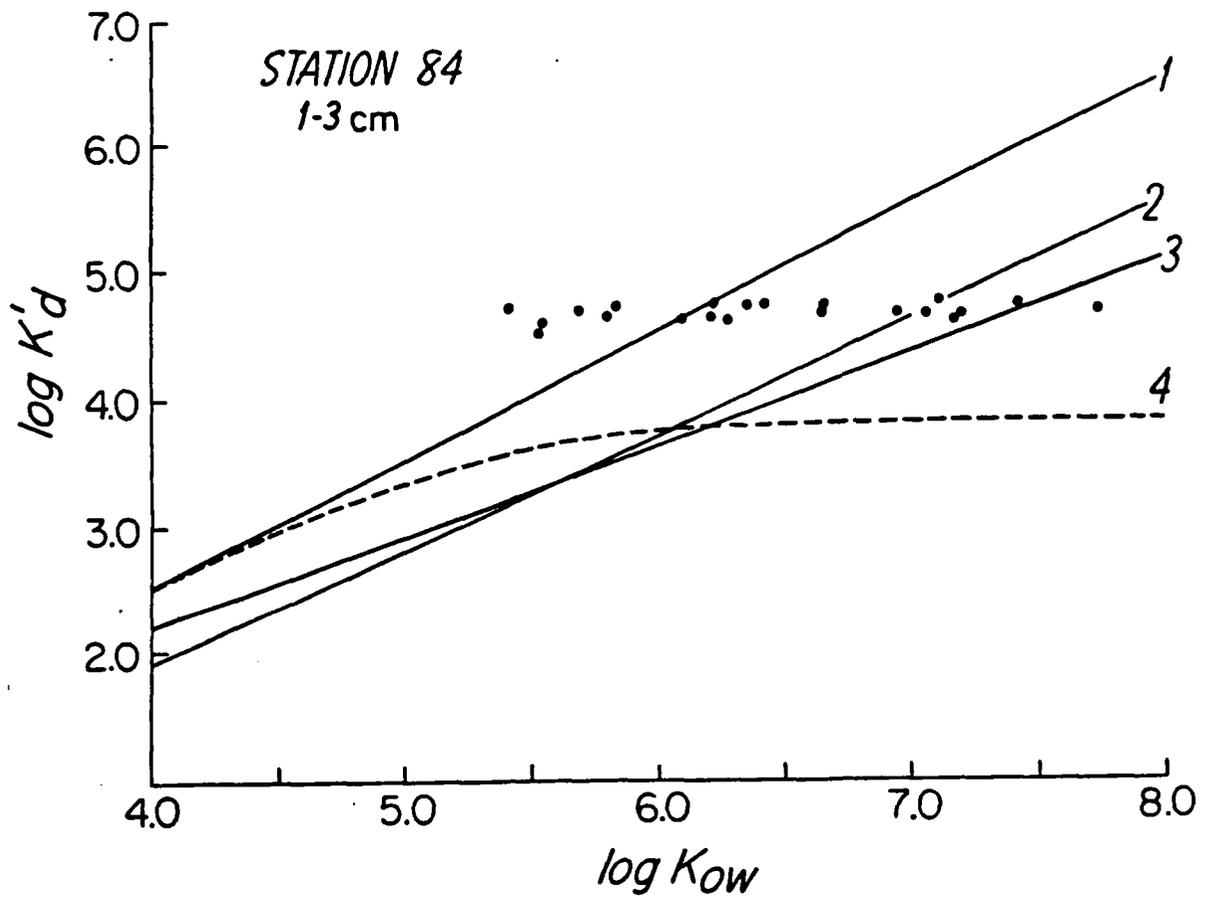
Gschwend and Wu (1985) may be more accurate due to the experimental conditions used (see Chapter 1). Lines 2 (Chiou et al., 1983) and 3 (Schwarzenbach and Westall, 1981) are primarily based on chlorinated aromatic compounds including PCBs and result in predictions of K'_d of PCBs which are significantly lower than line 1.

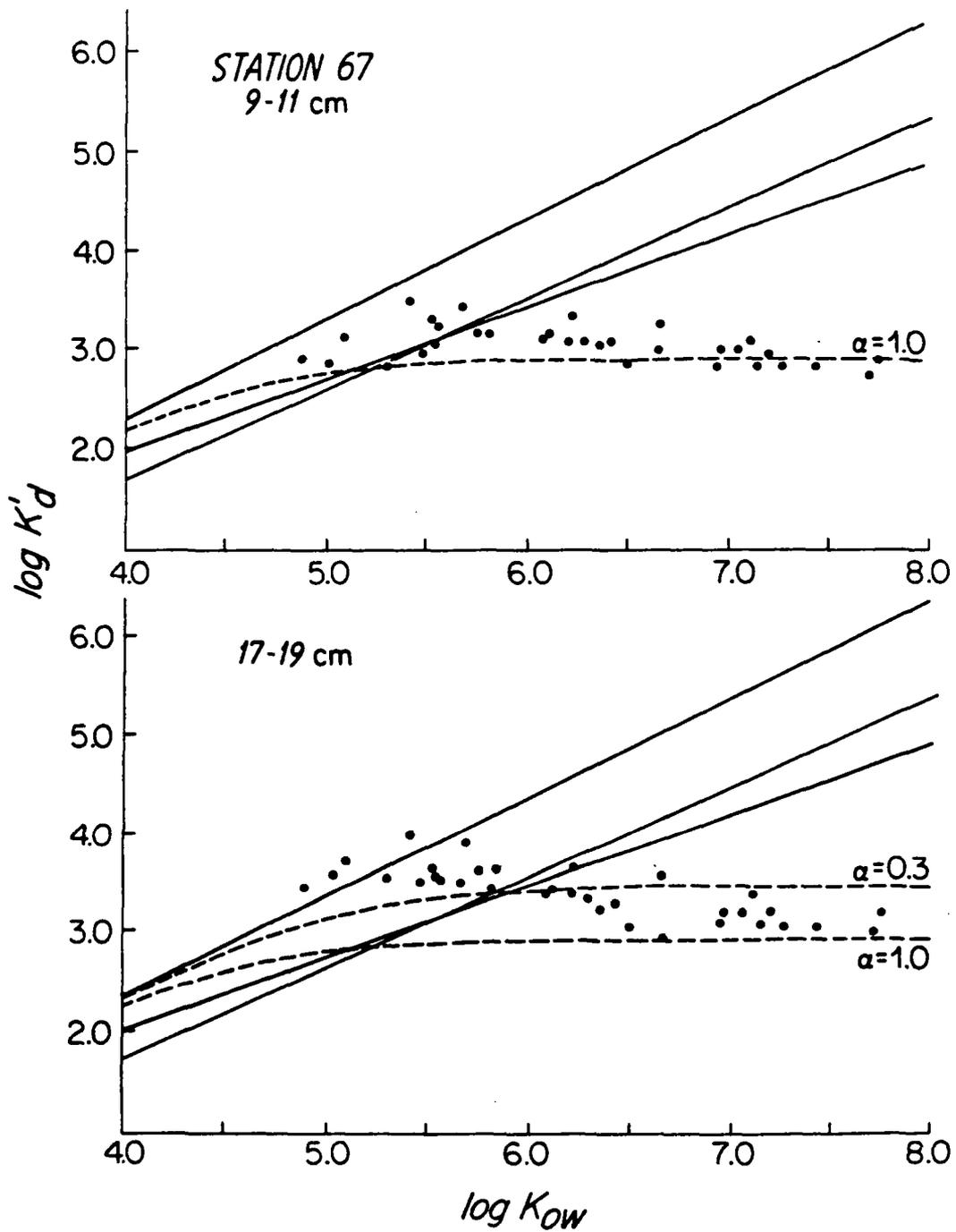
Two other points need to be made in comparing these predictions to the data reported here. First, for the most part, these relationships are based on solutes with $\log K_{ow} < 6.0$ while the PCBs considered here have $\log K_{ow}$ s ranging from 4.89 to greater than 7.75. The validity of the extrapolations 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 (McDevit and Long, 1952; Gordon and Thorne, 1967) 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 (see Appendix 1). In the sediment organic matter phase, salinity increases could possibly change sorbate activity coefficients by affecting the configuration or water content of the organic matter.

A model of three-phase partitioning (equation 3-12) is represented in Figure 3-14 by line 4. This curve assumes $f_{oc} = 10$ mg/L in the pore water at Station 84 at 1-3 cm (DOC was not measured at this site). The major assumption is that both K_{oc} s and K_{oc} can be predicted by the regression defining line 1 ($\log K_{oc} = 1.0 \log K_{ow} - 0.32$). This assumption is

Figure 3-14. $\log K'_d$ vs $\log K_{ow}$ of individual chlorobiphenyls from the 1-3 cm section at Station 84. Solid lines 1 (Means et al., 1980), 2 (Chiou et al., 1983), and 3 (Schwarzenbach and Westall, 1981) are predictions of two-phase partitioning based on laboratory sediment sorption experiments. Line 4 represents the three-phase equilibrium sorption model (Equation 3-12) predicted using assumptions given in the text. Solid circles are data points.

Figure 3-15. $\log K'_d$ vs $\log K_{ow}$ for two representative sediment intervals at Station 67. Model lines are the same as Figure 3-14. The plot for the 17-19 cm section illustrates the effect of assuming a lower α (0.3) in Equation 3-12.





somewhat arbitrary for the reasons stated above, but fits the sediment and water column data better than the other lines and does illustrate the effect of colloidal organic matter on the observed distribution of PCBs. The effect of salinity on the model predictions is to raise the two-phase partitioning predictions of K'_d (on the order of 0.1 to 0.4 log units) but would not raise the limiting value of K'_d which is predicted in the three-phase model (line 4 in Figure 3-14) as long as $K_{oc,c} = K_{oc,s}$. 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 underpredicts 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 3-3). These high K'_d values at Station 84 are not easily explained.

Possible explanations include saturation of PCBs in the sediment phase, due to the high concentrations of PCBs at Station 84, or sorptive disequilibrium between sediment phases and interstitial waters. Pore water concentrations of PCBs suggest that saturation is unlikely. Dexter and Pavlou (1978b) have reported that the seawater solubilities of total trichlorobiphenyls in a mixture of Aroclor 1242 and total tetrchlorobiphenyls in Aroclor 1254 are 8.9 and 2.2 $\mu\text{g/L}$, respectively. The concentrations of total PCBs in pore waters of the upper 15 cm at Station 84 range from 0.22 to 1.6 $\mu\text{g/L}$ and include not only dissolved but also colloid-sorbed PCBs. Thus, pore water PCBs are well below equilibrium with a saturated PCB phase. Furthermore, when K'_d s of PCBs are normalized to organic carbon of the

sediments, apparent $\log K_{oc}$'s are 5.77 to 6.97 which exceeds $\log K_{ow}$ for at least tri- and tetrachlorobiphenyls. This makes it unlikely that pore water PCBs are in equilibrium with any organic solvent-type phase which might have coated the sediment at this organic-rich site.

Disequilibrium of PCBs between sediment and pore water phases might occur by advection of pore water or changes of the sediment organic matter matrix over time at Station 84. 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 readily 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 3-15A and B). The three-phase model curves incorporate measured values of DOC and assume $\alpha = 1$ in equation 3-12. These results demonstrate a 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 that site.

Figure 3-15B shows the effect of assuming less than 100% of the DOC is colloids ($\alpha = 0.3$) on model calculations. The calculation of α from equation 3-12 and the observed K'_d 's of 101 for all sediment depths yields values of 0.223 to 0.967 and an average of 0.573. These estimates of organic colloid concentrations are consistent with those operationally defined by ultrafiltration at Station M (Table 2-1) and other studies mentioned above.

Measured and model K'_{ds} are plotted for one sediment depth at Station M in Figure 3-16 and illustrate the effect of various assumptions concerning $K_{oc,s}$ and $K_{oc,c}$. In this case, line 1 is again the two-phase partitioning prediction from Means et al. (1980). Line 2 is a three-phase partitioning model where $K_{oc,s}$ is described by line 1, $\alpha = 0.8$ (determined at Station M in Chapter 2), and

$$\log K_{oc,c} = 0.818 \log K_{ow} + 0.193 \quad (\text{eqn. 3-13})$$

Equation 3-13 was derived from literature reports of HOC sorption with dissolved humic substances in Chapter 1 and closely predicted the partitioning results of PCBs with colloidal organic matter from coastal water determined in Chapter 2. It is seen that these assumptions over-predict the K'_{ds} of chlorobiphenyls in sediment-interstitial waters. Furthermore, it is evident that any assumption of the slope of the dependence of $\log K_{oc}$ on $\log K_{ow}$ (a in eqn. 3-2) which is smaller for colloidal than sedimentary organic matter will not predict a constant limiting value of K'_{ds} with increasing $\log K_{ow}$ which is apparent in most of the sediment-pore water samples in this study.

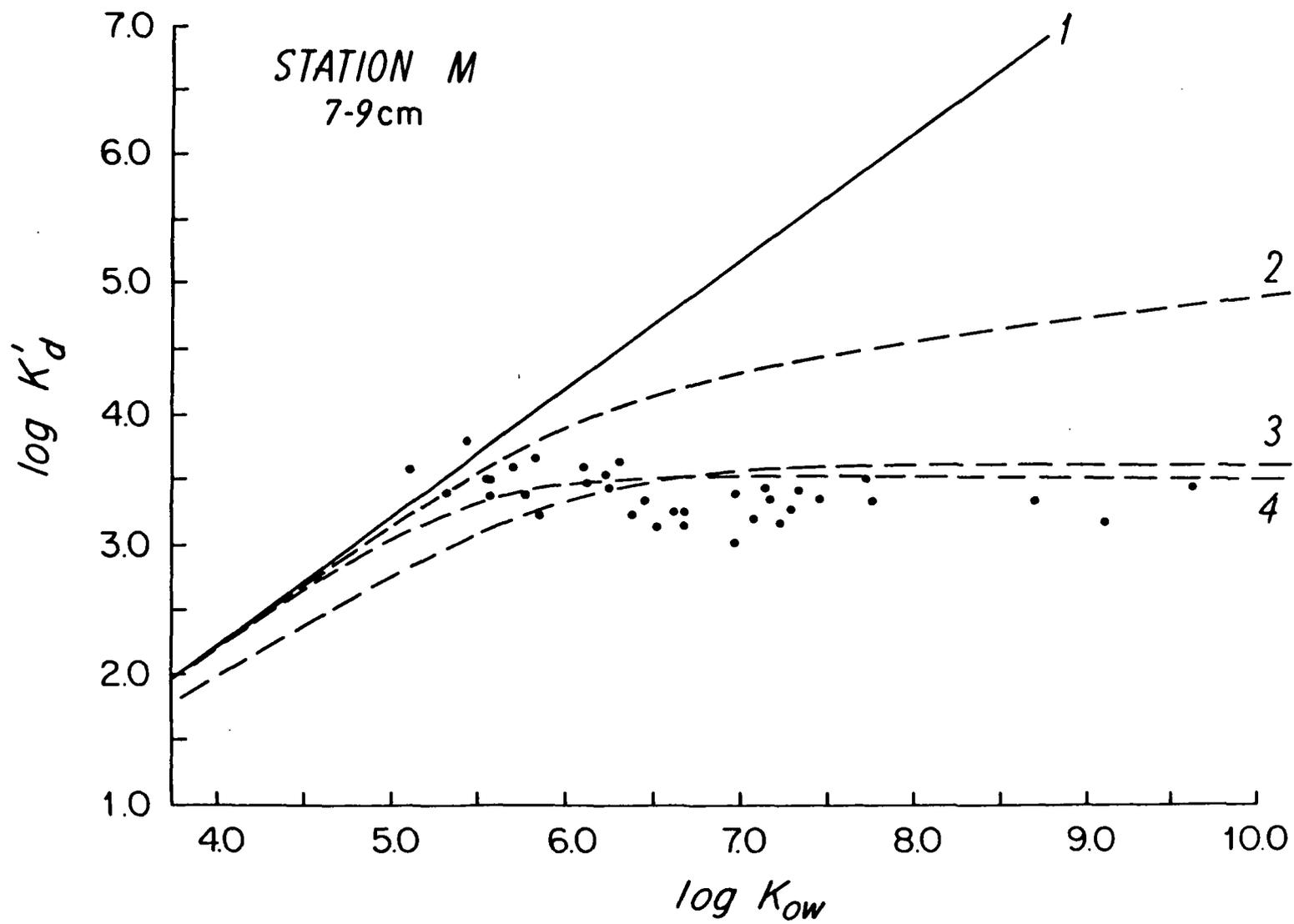
Line 3 in Figure 3-16 is the same as line 2 except that $K_{oc,s}$ is also described by equation 3-13. Any assumption of $K_{oc,s}$ lower than those predicted by line 1 results in model K'_{ds} of many tri- and tetrachlorobiphenyls lower than those measured in these sediments. Finally, line 4 is the same three-phase partitioning model given in Figures 3-14 and 3-15 and most closely predicts the observed data, including the partitioning of octa- through decachlorobiphenyls which were measured at Station M.

Chlorobiphenyl-specific K'_d s which result in the enrichment in pore water of more highly chlorinated congeners relative to lesser chlorinated ones in Station 67 samples and in the upper 13 cm at Station M are not easily explained. There are at least three possible processes which can be considered to explain these observations:

1) Microbial degradation of chlorobiphenyls occurs in the sediments and is limited by desorption into interstitial waters, such that the rates of degradation are comparable to timescales of sediment desorption. This would explain the apparent depletions of more soluble congeners in pore waters, as these compounds are also degraded more rapidly. Figure 3-17 illustrates that K'_d s of individual PCBs tend to increase with their degree of relative depletion to 170 with depth at Station 67. Chlorobiphenyl specific K'_d s are less pronounced at Station M and K'_d converges below 13 cm. There are fewer indications of microbial degradation at this site and rates of microbial activity are probably much lower due to different microbial populations and a lower supply of organic matter to the sediments. It would be useful to compare the results from these two cores to samplings made in late winter or spring when temperatures and microbial activity are much lower (Martin, 1985).

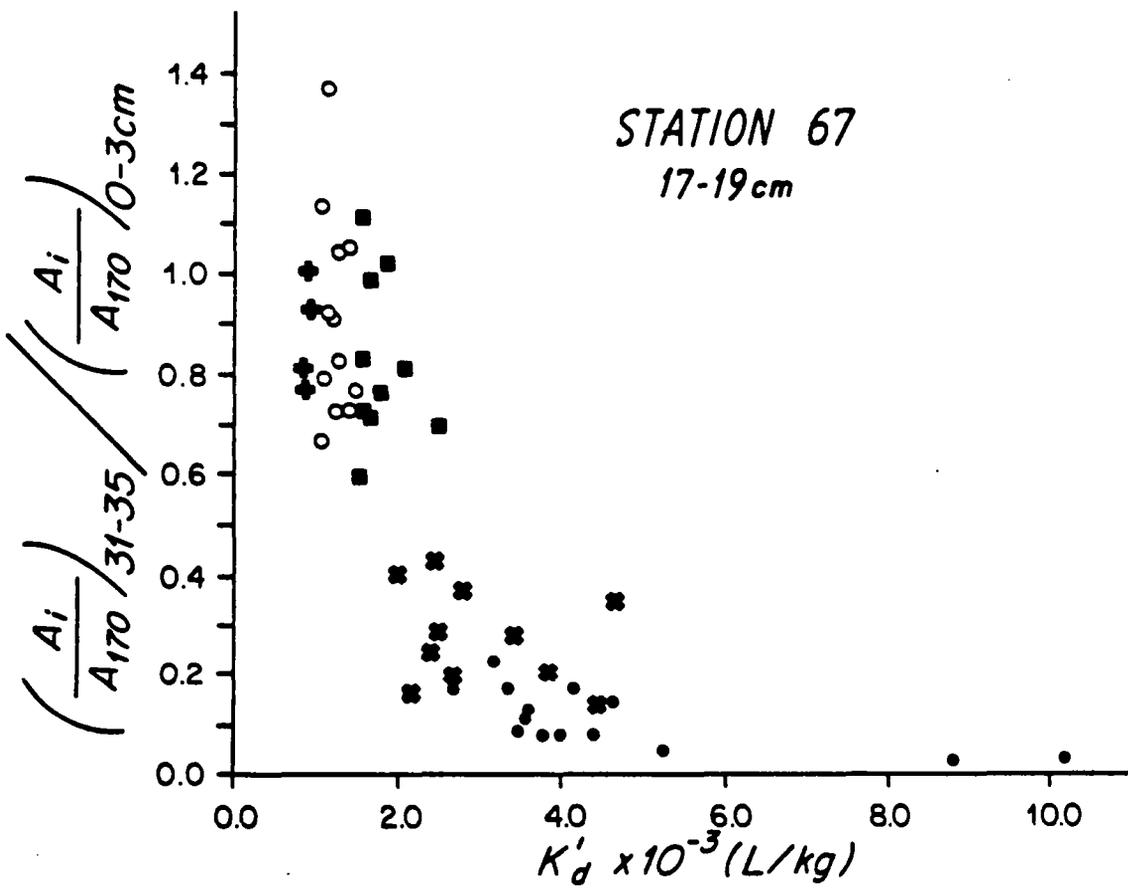
2) Sorptive disequilibria may also be caused by pore water diffusion, or irrigation of interstitial waters by benthic organisms. Both of these mechanisms are unlikely to explain the trends in K'_d s observed at Station 67 because similar chlorobiphenyl specific K'_d s exist at all sediment depths down to 41 cm. Pore water irrigation might explain the higher than expected and variable K'_d s in the upper 13 cm at Station M. However, if interstitial water concentrations were affected only by removal by irrigation, and sediment

Figure 3-16. A plot of $\log K'_d$ vs $\log K_{ow}$ for one sediment depth at Station M. Line 1 is the same as the two-phase predictions given in Figures 3-14 and 3-15. Dashed lines 2-4 are three-phase models based on different assumptions of K_{oc} and K_{oc} described in the text. This figure includes the partitioning results of chlorobiphenyls 194, 206, and 209. The reported $\log K_{ow}$ s of these compounds are 8.68, 9.14, and 9.60 respectively (Bruggeman et al., 1982).



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Figure 3-17. K'_d of individual chlorobiphenyls at 17-19 cm at Station 67 plotted vs their relative depletions in the solid phase with depth (see Figures 3-8 and 3-15). The congeners which show the greatest apparent losses in the sediments tend to have highest K'_d . Isomeric groups of PCBs are shown with the following symbols: nCl = 3 (\bullet), 4 (\otimes), 5 (\blacksquare), 6 (\circ), and 7 (\oplus).



desorption, it is expected that compounds with low K_{ow} s would desorb at faster rates and have lower measured distribution coefficients. This is not the case. From these observations, it is suggested that disequilibria caused by PCB transport in interstitial waters would not explain the departures of lower chlorinated biphenyls from model predictions of K'_{ds} .

3) Another explanation which is consistent with congener-specific K'_{ds} s is that there are effects of molecular size and structure of PCBs on sorption with sedimentary and colloidal organic matter. The possible effects of solute structure on organic colloid binding were discussed in Figure 2. These effects might become increasingly important as the size of colloidal organic matter decreases. The size or molecular weight range of interstitial water colloidal organic matter is unknown.

One 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 steric hindrance to sorption sites, it could be expected that as molecular size increased with increasing nCl (also increasing K_{ow}) the effective volume of accessible organic matter decreases. This would explain why $\log K_{oc}$ seems to have a greater dependence (the slope a) on $\log K_{ow}$ than does $\log K_{oc}$ s in Figures 3-15 and 3-16. This proposed mechanism would appear from the results from the three cores to be dependent on the sediment organic matter source. Steric hindrance to sorption sites might also be influenced by interstitial water salinity and major ion chemistry (see Chapter 1).

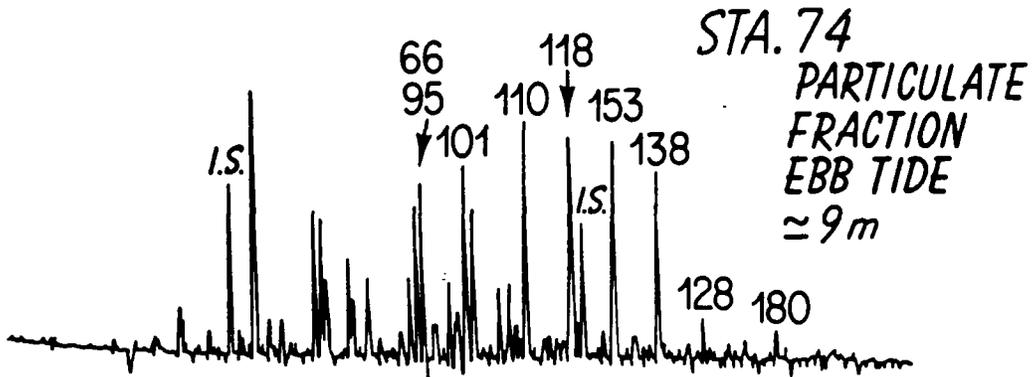
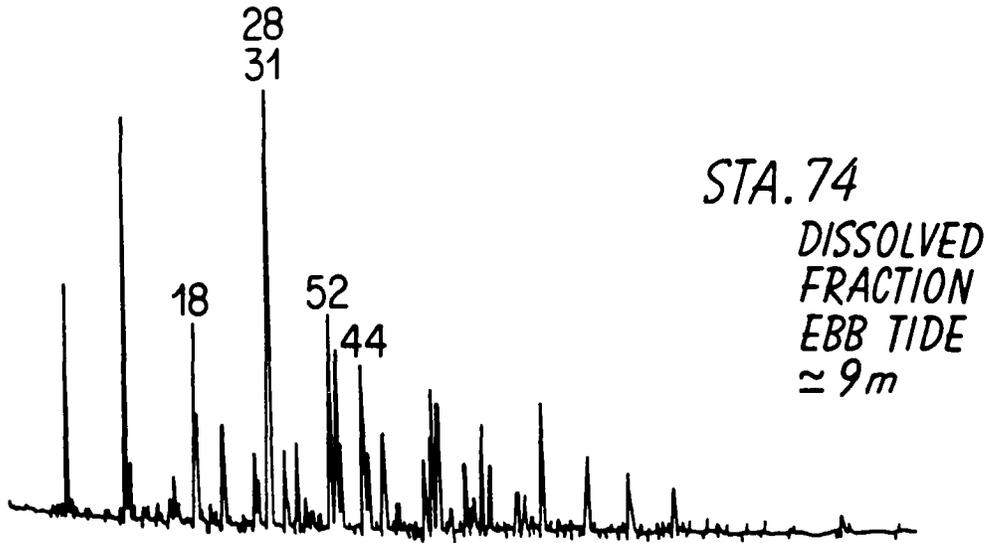
Water Column Partitioning Studies

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 3-8). 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 particulate fractions and filtrates 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 filtered water fractions of one sample (Figure 3-18). Not all of the peaks in the gas chromatograms are PCBs, some of which have been labeled with IUPAC chlorobiphenyl numbers (Table 3-1). The trend of K'_d increasing with degree of chlorination or K_{ow} agrees with observed partitioning of PCBs in the Hudson River (Bopp, 1979), Puget Sound (Dexter and Pavlou, 1978a), and Pacific Ocean (Tanabe and Tatsukawa, 1983), 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_{oc} s were not made on the water samples, values of these properties are assumed to be in the range of those measured in an extensive survey of New Bedford Harbor (Summerhayes et al., 1977), which covered tidal and seasonal cycles. Assumed

Figure 3-18. Capillary gas chromatograms of filtrate ("dissolved") and particulate PCB samples from New Bedford Harbor Station 74. Not all peaks are PCBs and selected PCB numbers are given in Table 3-1. I.S.: internal standard.



Minutes
25 40 50
Retention Time

Table 3-8. Tidal Cycle Concentrations of Total PCBs

Sample	Particulate Fraction ng/L	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

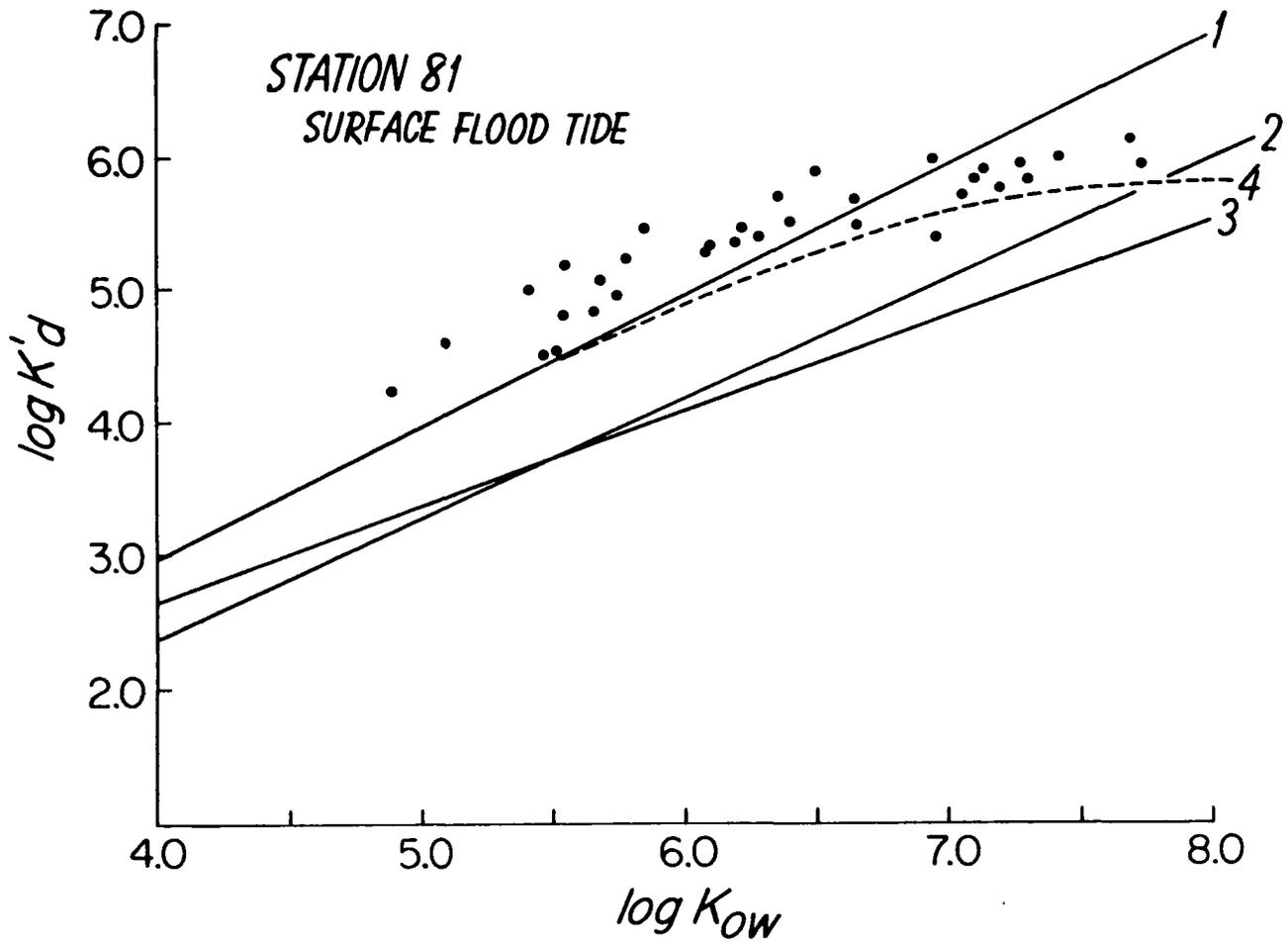
values for suspended solids concentrations and f_{oc} s are 3.0 mg/L and 0.20 for surface samples, and 5.0 mg/L and 0.15 for bottom samples. These assumptions are probably valid within a factor of three and do not affect calculated slopes of $\log K'_d$ vs $\log K_{ow}$ presented later.

Figure 3-19 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 $\log K_{ow}$ s. The three-phase model depicted by Line 4 assumes an f_{oc} of 0.25 mg/L, which is consistent with reported measurements made in coastal waters (Zsolnay, 1979) and results from Nantucket Sound reported in Chapter 2. The three-phase model calculations do show that reasonable assumptions of f_{oc} s and f_{oc} c can explain the observed partitioning of PCBs and that, under these conditions, the quantitative role of organic colloids on observed K'_d s is minimal until $\log K_{ow}$ s exceed 6.0. This is not the case in pore waters or in other organic rich waters where organic colloid concentrations can be many times higher.

The linear regression parameters, a and b, from the data of $\log K'_d$ vs $\log K_{ow}$ have been calculated. In Table 3-9, these parameters are first derived by considering all data points, and comparing 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 have been made. However, both of these observations are interpreted to be consistent with the expected

Figure 3-19. $\log K'_d$ vs $\log K_{ow}$ for a Station 74 water column sample.

Lines are as given in preceding Figures 3-14, 3-15, and 3-16, and assumptions of particulate and colloidal organic carbon are given in the text.



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Table 3-9. 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			
Line 1. Means et al.(1980)	1.00	-0.32	0.990
Line 2. Chiou et al.(1983)	0.904	-0.55	0.994
Line 3. Schwarzenbach and Westall (1981)	0.72	0.49	0.975

curvilinearity of this relationship when considering chlorobiphenyls with high K_{ow} . The linear regressions have also been calculated by only considering data for chlorobiphenyls 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 (Wu and Gschwend, 1986). 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 chlorobiphenyls. It is not possible to distinguish whether equilibrium partitioning of PCBs is established in the water column, within the limitations of both the data here and models of seawater partitioning. The results do suggest that dissolved PCB phases are more important than colloid-sorbed PCBs in observed water column distributions as is predicted by the three-phase partitioning model.

GENERAL DISCUSSION

The results from these field studies coupled with experimental results reported in Chapter 2 and other studies in the literature suggest that the biogeochemistries of PCBs are affected significantly by sorption with organic colloids in coastal sediments. Interactions of PCBs and other HOC with organic colloids will influence remobilization of these compounds in sediments and affect their distribution and transport in the water column. The three sediment cores studied have concentrations and profiles of interstitial water PCBs which indicate a diffusional flux into overlying waters. Estimation of these fluxes and the migration of PCBs in sediments is complicated by uncertainties concerning the nature and biogeochemical cycling of organic colloids in sediment pore waters. Chapter 4 addresses the problem of predicting PCB transport in sediments.

Sorption reactions of HOC with colloidal and sedimentary organic matter are also likely to influence the rates of chemical and biological transformations. Further studies should be aimed at developing a better understanding of the role of sorption in the bioavailability of HOC to organisms in contact with sediment interstitial waters.

CONCLUSIONS

Highly elevated concentrations of PCBs are reported in the interstitial waters of coastal sediments from New Bedford Harbor and Buzzards Bay, Massachusetts. Several lines of evidence support the hypothesis that sorption

of PCBs with colloidal organic matter in interstitial waters is important in controlling the distribution of these compounds.

a) PCB concentrations in interstitial waters at all three sites were much higher than that in overlying water column. PCBs increased with depth at Station 67 to supersaturated levels for many chlorobiphenyls. This increase correlated with the DOC profile.

b) The composition of PCBs in pore waters at all three stations are very similar to the compositions in the sediment phase. If two-phase aqueous sorption with the sediments were controlling the observed distribution then the more soluble, less chlorinated congeners would have lower K'_d s and be enriched in interstitial waters. This is the case in the water column where organic colloids are in lower concentrations. In Station 67 sediments and the surface sediments at Station M, the more highly chlorinated biphenyls are actually enriched in interstitial waters when compared to the sediments. A large fraction of many chlorobiphenyls in interstitial waters must be sorbed to organic colloids to explain these distributions.

c) A three-phase equilibrium sorption model in which dissolved PCBs approach a dynamic equilibrium with both sediment and colloidal organic matter can describe the partitioning results at Stations 67 and M, and predicts the near constancy of K'_d with increasing K_{ow} at all three stations. However, the depth profiles and high values of K'_d at Station 84 are not presently understood.

d) Laboratory studies of HOC-organic colloid sorption reported in Chapter 2, and in the literature, predict that a high percentage of most PCBs that are in pore waters will be sorbed to colloidal organic matter.

2) Three-phase partitioning models indicate that K_{oc} 's for PCB-organic colloid sorption must be relatively high and close to those for sediment organic matter in these sediment interstitial waters. Furthermore, the slope, a , in the dependence of $\log K_{oc}$ on $\log K_{ow}$ must be very close to, or slightly greater than that for the sediment organic matter. The higher partition coefficients predicted from line 1 in Figures (3-15)-(3-17) and (3-20) more closely describe the results than do other predictive correlations presented for HOC-sediment or HOC-organic colloid sorption. Congener specific K'_{ds} of PCBs in some sediments in this study may reflect an effect of solute size and shape on either sediment or colloidal organic matter sorption. The reason for congener specific K'_{ds} which tend to decrease with nCl in Station 67 and Station M sediments are most likely due to steric constraints on sediment sorption or to microbial degradation of PCBs in the interstitial waters of those sediments.

3) The three-phase partitioning model for PCBs in the water column predicts the greater importance of dissolved PCBs in the filtered phase due to lower concentrations of colloidal organic matter. Measured K'_{ds} approach predictions of two-phase, water/particle partitioning when the effect of colloids on high K_{ow} PCBs is considered. The preferential solubilization of low K_{ow} PCBs observed in the water column explains the lower relative

abundances of those congeners in sediments at Station M which have probably been transported on suspended sediments from New Bedford.

4) Congener specific depletions of di-, tri-, and tetrachlorobiphenyls were observed with increasing depth at Station 67. This is probably the result of microbial degradation of PCBs at that site, although lack of oxic conditions requires the presence of microbial degradation pathways yet to be characterized. Results from the other sites studied here and in other environments indicate that this degradation must be specific to conditions at the Station 67 site.

CHAPTER IV
TRANSPORT OF PCBs IN COASTAL SEDIMENTS

INTRODUCTION

Many hydrophobic organic compounds (HOC) are highly sorbed to sediment organic matter and accumulate in estuarine and coastal sediments. The ability of sediments to act as a short- or long-term sink for HOC depends on the rates of transport of HOC within sediments and across the sediment-water interface. There are many processes which can affect the transport of particle-reactive compounds in sediments (Berner, 1980). Particle-sorbed species are transported relative to the sediment-water interface by sediment accumulation, and sediment mixing caused by waves, currents, or the activities of benthic organisms. Resuspension of the sediment bed will result in transport and possibly dispersal of sediment-sorbed materials. HOC are also present in interstitial waters in dissolved or colloidal phases and may be transported by diffusive or advective processes.

There have been relatively few studies concerning the rates or mechanisms of HOC transport in sediments. Berner (1976, 1980) and Schink and Guinasso (1978) have shown how the effect of equilibrium sorption of dissolved compounds with sediments can be included in the modelling of early diagenesis. The flux of HOC out of undisturbed sediments into clean water has been measured in two studies (Fisher et al., 1983; Karickhoff and Morris, 1985), and DiToro et al. (1985) have measured the diffusion of 2,2',4,4',5,5'

hexachlorobiphenyl in a Saginaw Bay sediment. These studies have shown that migration in sediments by diffusion of dissolved HOC can be highly impeded by sorption to sediments, and that the amount of retardation is related to the extent of partitioning with sediments. Processes other than diffusion which affect transport of HOC in sediments increase in importance relative to diffusion as the amount of sorption to sediments increases. Karickhoff and Morris (1985) found that the feeding and burrowing behavior of tubificid worms greatly enhanced the redistribution of HOC in the biologically mixed zone and resulted in a four- to six-fold increase in the flux of HOC into the overlying water when contrasted with undisturbed sediments where diffusion was the only process affecting transport.

Model predictions (Chapters 2 and 3) and field results (Brownawell and Farrington, 1985, 1986; Chapter 3) suggest that an important fraction of PCBs and other HOC of similarly low aqueous solubilities are sorbed to colloidal organic matter in interstitial waters of coastal marine sediments. This results in higher total concentrations of chlorobiphenyls in pore waters and affects the mobility of PCBs by diffusive or advective processes. Means and Wijayarathne (1982) proposed that colloid sorption might increase transport of HOC. The effect of a mobile colloid phase on the transport of particle-reactive solutes has not been considered in transport models. Unfortunately, the biogeochemical cycling and migrational properties of colloidal organic matter in sediments are not well understood. The importance of HOC sorption with colloids to a general diagenetic description of the distribution and transport of HOC in sediments is evaluated in this chapter. This model is then applied to PCB data from Station M in Buzzards Bay and

other sediment transport parameters determined here and in other studies to illustrate the role of colloids in the flux of PCBs across the sediment water interface.

TRANSPORT MODEL FOR HOC IN SEDIMENTS

A generalized one-dimensional model which considers diffusion, advection, sediment accumulation, sorption, and biological mixing to describe the transport and distribution of HOC in sediments is presented. The primary premise of this model is that dissolved HOC in interstitial waters are sorbed reversibly to both sediment organic matter and colloidal organic matter in pore solution. It is further assumed that colloidal organic matter is able to migrate in pore waters. The former assumption is supported by the agreement of observed PCB partitioning in coastal sediments with three-phase equilibrium sorption models presented in Chapter 3.

The change with time in HOC concentration C_T (per volume of bulk sediment; e.g., ng/cm³) at a given depth, x , below the sediment-water interface can be given by the sum of equations describing dissolved (C_d), sediment (C_s) and colloid-sorbed (C_c) HOC:

$$\partial C_T / \partial t = \partial(\phi C_d) / \partial t + \partial[(1-\phi)\rho_s C_s] / \partial t + \partial(\phi C_c) / \partial t \quad (\text{eqn. 4-1})$$

where ϕ is the porosity of interconnected pore water and ρ_s is the dry sediment density (see Berner, 1980). Note that C_c in this chapter is in units of volume (e.g., ng/cm³). To assess the effect of colloids on the

total transport of HOC it is necessary to write expressions for the last three terms in equation 4-1 and solve them simultaneously. Following the example of Berner (1976, 1980) a complete general diagenetic equation for dissolved HOC can be written:

$$\frac{\partial (\phi C_d)}{\partial t} = \frac{\partial [\phi D_d \frac{\partial C_d}{\partial x} + D_B \frac{\partial (\phi C_d)}{\partial x}]}{\partial x} + I \quad (\text{eqn. 4-2})$$

$$- \frac{\partial (\phi v C_d)}{\partial x} + (\frac{\partial (\phi C_d)}{\partial t})_{\text{Sed Sorption}}$$

$$+ (\frac{\partial (\phi C_d)}{\partial t})_{\text{Col Sorption}} + \phi \Sigma R_d$$

which corresponds to the aqueous diffusivity corrected for sediment porosity and tortuosity, D_B is a bioturbation coefficient which describes random mixing of sediments (and associated pore water) by the feeding and burrowing behavior of benthic organisms (Goldberg and Koide, 1962; Berner, 1980), I represents any transport of solutes in surface sediments by irrigation, v is velocity or advection of pore water, and ΣR_d is the sum of any production or transformation reactions affecting dissolved HOC. The terms $(\frac{\partial (\phi C_d)}{\partial t})_{\text{Sed Sorption}}$ and $(\frac{\partial (\phi C_d)}{\partial t})_{\text{Col Sorption}}$ represent the gain or loss of dissolved HOC due to sorption-desorption reactions with sediments and colloids, respectively. Irrigation is often an important process in coastal sediments having large populations of benthic infauna, and can result in enhanced exchange of solutes from interstitial waters of biologically active surface sediments with overlying water (Goldhaber et al., 1977; Aller, 1980c, 1982; Berner, 1980; Martin, 1985).

Irrigation is caused by diffusion or advection of solutes across burrow walls providing a more rapid exchange of solutes with overlying waters (Aller, 1980c). Flushing of burrows may involve multiple mechanisms of exchange and several approaches have been applied to the modelling of exchange by vertical molecular diffusion plus irrigation (see Aller, 1982; Martin, 1985). Due to uncertainties involved in modelling the irrigation of HOC and organic colloids in surface sediments, its effect is neglected for the purposes of this model. However, the possible importance of irrigation on exchange across the sediment-water interface is discussed in a later section.

In the absence of irrigation and production or transformation reactions of HOC in sediments, the governing equations for the distribution and transport of HOC can be considerably simplified. In the case of constant porosity and solute sediment diffusion coefficients, the governing equations for dissolved, sediment-sorbed, and colloid-sorbed HOC concentrations are:

$$\phi \frac{\partial C_d}{\partial t} = \phi D_d \frac{\partial^2 C_d}{\partial x^2} + \phi \frac{\partial D_d (\partial C_d / \partial x)}{\partial x} - \phi \frac{\partial v C_d}{\partial x} - (\frac{\partial C_d}{\partial t})_{\text{sed sorption}} - (\frac{\partial C_d}{\partial t})_{\text{col sorption}} \quad (\text{eqn. 4-3})$$

$$(1-\phi) \rho_s \frac{\partial C_s}{\partial t} = (1-\phi) \rho_s \frac{\partial D_s (\partial C_s / \partial x)}{\partial x} - (1-\phi) \rho_s \frac{\partial \omega C_s}{\partial x} + (\frac{\partial C_d}{\partial t})_{\text{sed sorption}} + (\frac{\partial C_c}{\partial t})_{\text{sed sorption}} \quad (\text{eqn. 4-4})$$

$$\phi \frac{\partial C_c}{\partial t} = \phi D_c \frac{\partial^2 C_c}{\partial x^2} + \phi \frac{\partial D_c (\partial C_c / \partial x)}{\partial x} - \phi \frac{\partial v C_c}{\partial x} + (\frac{\partial C_d}{\partial t})_{\text{col sorption}} - (\frac{\partial C_c}{\partial t})_{\text{sed sorption}} \quad (\text{eqn. 4-5})$$

where ω is the sediment accumulation rate, D_c is the sediment diffusion

coefficient of colloidal organic matter; and analogous to sorption of dissolved HOC, $(\partial C_c / \partial t)_{\text{sed sorption}}$ represents the change of colloid-sorbed HOC due to sorption-desorption of colloidal organic matter with sediments. Note that the above equations are written to conform to mass balance considerations which dictate that there be no net change of HOC in a volume of bulk sediment due to sorption alone.

The assumption of local equilibrium between all three phases allows for equations 4-3, 4-4, and 4-5 to be combined and solved for C_d , C_c , or C_s . This assumes that sorption is rapid compared to other processes affecting HOC and reversible. The validity of this assumption is supported by studies of migration of HOC in sediments (Schwarzenbach and Westall, 1981; Di Toro et al., 1985), and the agreement of equilibrium sorption models to sediment-pore water distributions of PCBs described in Chapter 3. Local equilibria can be described by the following equations:

$$C_s = \text{TOC } K_{oc,s} C_d \quad (\text{eqn. 4-6})$$

$$C_c = C_c' K_{oc,c} C_d \quad (\text{eqn. 4-7})$$

where $K_{oc,s}$ and $K_{oc,c}$ are the organic carbon normalized partition coefficients of individual HOC (see Chapters 1-3) with sediment and colloidal organic matter, respectively, and C_c' is the concentration of colloidal organic carbon in pore waters. Addition of the left hand sides of equations 4-3, 4-4, and 4-5 gives C_T (equation 4-1). Applying the conditions of local equilibrium yields:

$$\frac{\partial C_s}{\partial t} = \phi \frac{\partial [C_s / (TOC \cdot K_{oc} s)]}{\partial t} + (1-\phi) \rho_s \frac{\partial C_s}{\partial t} + \phi \frac{\partial (K_{oc} C_c' / K_{oc} s TOC) C_s}{\partial t} \quad (\text{eqn. 4-8})$$

A simple solution for $\partial C_s / \partial t$ exists when TOC, C_c' , and the partition coefficients are constant with time and depth. The latter is a reasonable assumption (Chapters 1-3). TOC does not often change with depth by more than a factor of two in coastal sediments. However, it is known that C_c' changes by as much as a factor of five as a function of time (Hines et al., 1982; McNichol, 1986) and depth (Krom and Sholkovitz, 1977). Assuming constant sediment properties, and that compaction or other externally driven pore fluid flows can be neglected (i.e., $v = \omega$) gives the following solution of equations 4-3 through 4-7 for C_s :

$$\frac{\partial C_s}{\partial t} = \frac{\partial D_B \frac{\partial C_s}{\partial x}}{\partial x} + \left(\frac{D_d + C_c' K_{oc} c D_c}{1 + [(1-\phi) \rho_s / \phi] TOC K_{oc} s} \right) \frac{\partial^2 C_s}{\partial x^2} - \frac{\omega \partial C_s}{\partial x} \quad (\text{eqn. 4-9})$$

The first term in equation 4-9 represents the transport of bulk sediments by biological mixing. The second term is the migration of HOC by diffusion of dissolved and colloid-sorbed HOC, which is impeded by sorption of HOC to the sediments, and the third term is the advection of HOC by sediment burial. Because of the assumption of local equilibria within the sediments, an equivalent expression can be written for C_d by substituting $C_d \cdot K_{oc} s \cdot TOC$ for C_s into both sides of equation 4-9 and dividing by $K_{oc} s \cdot TOC$. Several important points can be made in regard to the solution of this model.

1) The solution to the three-phase transport model reduces to two-phase transport when $D_d \gg K_{oc} \cdot C_c' \cdot D_c$. In other words, when either organic colloids do not significantly affect the speciation of HOC (i.e., $K_{oc} \cdot C_c' \ll 1$) or when colloids are not appreciably mobile because of very low diffusivities, the effect of colloids on transport can be ignored. In that case, the following diagenetic equation can be written:

$$\frac{\partial C_s}{\partial t} = \frac{\partial D_B \partial C_s / \partial x}{\partial x} + \left(\frac{D_d}{1 + [(1-\phi)\rho_s/\phi]K_p} \right) \frac{\partial^2 C_s}{\partial x^2} - \frac{\omega \partial C_s}{\partial x} \quad (\text{eqn. 4-10})$$

where $K_p = K_{oc} \cdot \text{TOC}$. This expression is equivalent to the equations solved by other workers to include dissolved phase-sediment sorption in the general diagenetic equation (Berner, 1976, 1980; Schink and Guinasso, 1978). More general solutions than equation 4-10, which do not assume constant sediment properties are found in those references.

2) Under these conditions, the role of colloids in transport is to increase the diffusion of HOC in pore waters. The relative enhancement of transport by diffusion of colloid-sorbed HOC depends both on the fraction of pore water HOC sorbed to colloids and to the relative diffusion coefficients of dissolved HOC and that of colloids. An example of PCB transport is given later to illustrate these points.

3) Bioturbation of surface sediments will often be important in controlling the transport and distribution of HOC in sediments, when HOC are highly sorbed to sediments. In the absence of sediment sorption, biological mixing of bulk sediment (not including irrigation) has always been observed to

be a slower mechanism of solute transport than molecular diffusion. Measured bioturbation coefficients in coastal sediments are on the order of 10^{-8} to up to 10^{-6} cm^2/sec (Berner, 1980; Aller, 1982) while the sediment diffusion coefficients of dissolved PCB, for example, are calculated to be approximately 2 to 4 $\times 10^{-6}$ cm^2/sec . However, equations 4-9 and 4-10 show that the apparent diffusivities (D_{app}) of pore water HOC which are highly sorbed to sediments are greatly reduced

$$D_{app} = \frac{D_d + C_c' \cdot K_{oc} \cdot D_c}{1 + [(1-\phi)\rho_s/\phi] \text{TOC} \cdot K_{oc} \cdot C_c'} \quad (\text{eqn. 4-11})$$

since the factor $[(1-\phi)\rho_s/\phi] \text{TOC} \cdot K_{oc} \cdot C_c'$ usually dominates in the denominator of equation 4-11 for HOC in sediments. Examples of model calculations of D_{app} for PCBs in coastal sediments are given later. Given reasonable estimates of the properties in equation 4-11, apparent diffusivities are 10^{-3} to less than 10^{-6} times D_d for PCBs in sediments. Therefore bioturbation, and sometimes sediment burial, will be more important than pore water diffusion in affecting the distributions of PCB-like compounds within the biologically mixed zone of surface sediments.

4) The solution of the three-phase transport model has a more complicated form when solved for non-constant C_c' . If C_c' changes only with depth, but not with time (i.e., steady state is assumed for $\partial C_c'/\partial t$), the solution is straightforward but includes additional terms for the transport of C_c caused by gradients in C_c' . An interesting result from solutions assuming steady-state C_c' is that adsorption-desorption, production, and

consumption of C_e' in pore waters does not affect the total transport equation for HOC in sediments. When $\partial C_e'/\partial t$ cannot be assumed to be zero, the solution to transport becomes more complicated and an explicit equation describing $\partial C_e'/\partial t$ must be included.

EXAMPLE CALCULATION FOR PCBs

Application of equation 4-9 to a simple case of PCB transport in sediments illustrates the effect that colloidal organic matter has on diffusive transport of HOC. In the case where sediment mixing can be neglected, and sediment properties (ϕ , ρ_s , D_d , D_c , $K_{oc}s$, $K_{oc}c$, TOC, and C_e') are constant as a function of depth and time:

$$\frac{\partial C_B}{\partial t} = D_{app} \frac{\partial^2 C_B}{\partial x^2} - \frac{\omega \partial C_B}{\partial x} \quad (\text{eqn. 4-12})$$

When ω is negligible, or when x is referenced to a fixed layer instead of the sediment-water interface (see Berner, 1980), the sedimentation term can be neglected. The migration of PCBs over time can be easily shown in a hypothetical situation where PCBs exist in a uniform layer of sediment having a constant concentration, $C_{s,0}$, down to a depth at which the concentration drops immediately to zero at a reference depth $x = 0$. This problem has been considered by Di Toro et al. (1985) and the boundary conditions are that at time = 0:

$$\begin{aligned} C_s &= C_{s,0} & x &\leq 0 \\ C_s &= 0 & x &> 0 \end{aligned}$$

where x is the distance below the boundary. When sediment properties provide an infinite spatial domain, i.e., they are uniform over several cm in this case, then the solution for C_s as a function of time and depth is given by Crank (1975) as:

$$C_s(t,x) = C_{s0}/2 [1 - \operatorname{erfc}(x/2\sqrt{D_{spp}t})] \quad (\text{eqn. 4-13})$$

where D_{spp} is given by equation 4-11, and t is time.

D_{spp} is estimated for two PCBs having a range of hydrophobicities: 2,4,4'-trichlorobiphenyl (PCB No. 28) and 2,2',4,4',5,5'-hexachlorobiphenyl (PCB No. 153) with respective $\log K_{ow}$ s of 5.68 and 7.20 (Table 1-2). For the purposes of this discussion the sorptive properties of colloidal organic matter are assumed to be the same as sediment organic matter. Further assume that K_{oc} can be estimated by the predictive equation of Means et al. (1980) for the sorption of neutral HOC with sediments and soils (see Chapters 1-3 for the support of this assumption). Typical values for ϕ , ρ_s , TOC, and C_c from deep sediments (10-40 cm) at Station M are 0.758, 2.60, 20 g/kg, and 10 mg/L (Chapters 2 and 3; Martin, 1985; McNichol, 1986), and are used in model calculations here. Sediment diffusion coefficients can be calculated from molecular diffusion coefficients in water and corrected for the effect of sediment porosity and tortuosity by

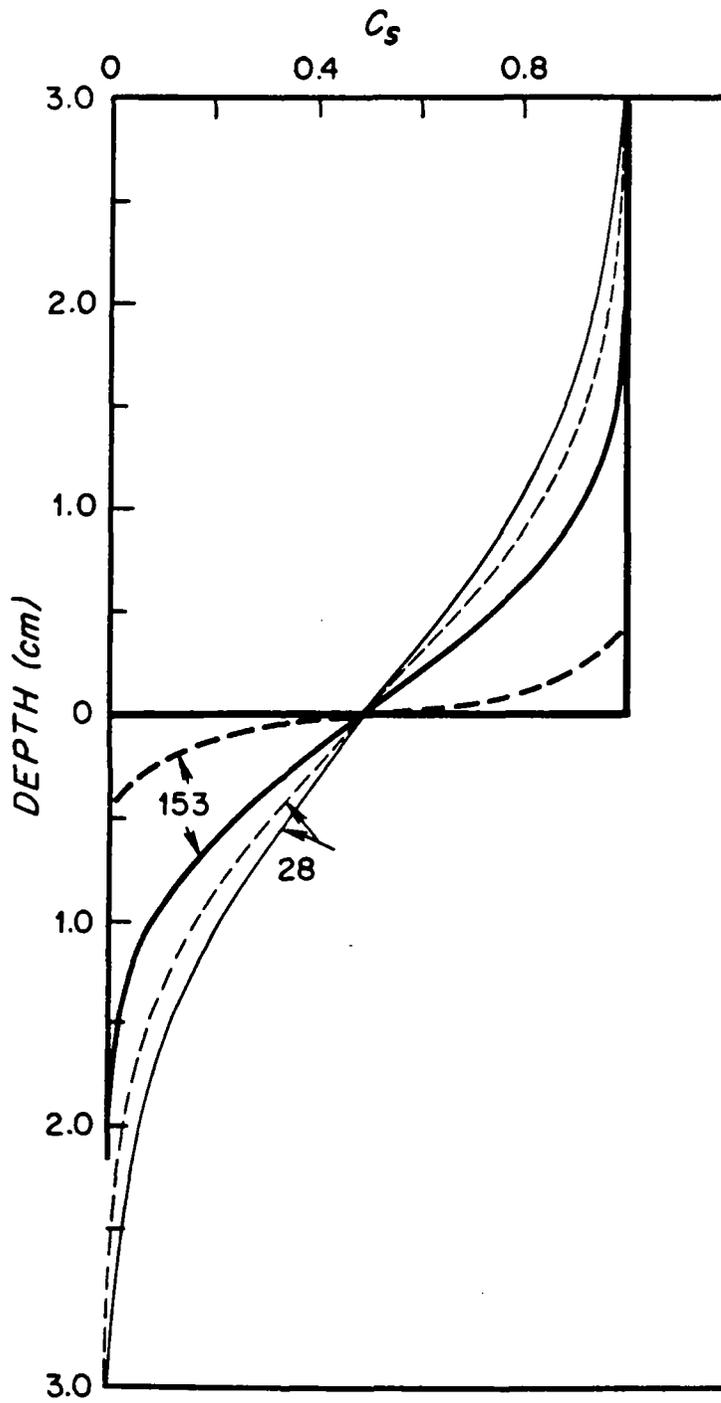
$$D_{sSed} = D_{sWater}/(\phi F) \quad (\text{eqn. 4-14})$$

where F is the formation factor, which can be measured from the electrical

resistivity of the sediment (see Berner, 1980). At Station M in Buzzards Bay, porosity and resistivity measurements give average sediment diffusion coefficients which are 0.64 times aqueous diffusivities (Martin, 1985). Aqueous diffusivities of PCBs are estimated by the method of Hayduk and Laudie (1974) using Le Bas molal volumes of PCBs. The resulting sediment diffusivities are 3.3 and 2.9×10^{-6} cm^2/sec at 20°C for 28 and 153 respectively. Finally, estimation of the diffusivity of organic colloids in interstitial waters is a major uncertainty. The aqueous diffusion constants of non-electrolyte macromolecules are given in Perry (1962). If colloidal organic matter in pore waters has a molecular weight of 10,000, then an appropriate sediment diffusion coefficient for these macromolecules may be estimated at 7.0×10^{-7} cm^2/sec . This indicates that diffusion of colloid-sorbed materials is roughly four to five times slower than that of dissolved PCBs. Further work is needed to estimate the molecular size and diffusivity of pore water colloids to validate their importance in migration.

The distributions of the two chlorobiphenyls injected into a sediment column and allowed to diffuse for 20 years can be estimated (Figure 4-1) with the property estimates and assumptions given above. Since a similar load of trichlorobiphenyl diffused in the dissolved and colloid-sorbed phases, this less hydrophobic compound migrates somewhat further than hexachlorobiphenyl. The migration for 153 is approximately the limiting case for diffusion of HOC which are not appreciably mobile in the dissolved phase under these conditions. While the migration of 153 is no further than about 1 cm in 20 yr, it is greatly enhanced over that predicted if there was no colloid effect. This is seen by comparison with dashed lines in Figure 4-1 (showing

Figure 4-1. The normalized distributions of chlorobiphenyls 28 and 153 after diffusing in typical coastal sediments for 20 years. The heavy line denotes the initial distribution at $t = 0$; the solid lines give the solutions for diffusion of these two congeners given by equations 4-11 and 4-13 including the effect of organic colloids; and the dashed lines show the migration of the chlorobiphenyls in the absence of a mobile colloid phase. The assumptions and parameters used in these model calculations are given in the text.



the migration of the two PCBs if colloid sorption is negligible or colloids are not mobile in pore solution). It is seen that the migration of 28 is greater than that for 153 because of higher dissolved concentrations of trichlorobiphenyl in pore waters.

An enhancement factor of D_{app} due to colloid sorption is given by:

$$\frac{D_{app} \text{ 3-phase}}{D_{app} \text{ 2-phase}} = 1 + \frac{f_s \cdot D_c}{(1-f_s)D_d} \quad (\text{eqn. 4-15})$$

where f_s is the fraction of HOC in pore water sorbed to colloids. Because D_c is several times less than D_d , a major fraction (> 80%) of HOC must be sorbed to influence mobility to a measurable extent. Figure 4-1 shows that the diffusive migration of PCBs is expected to be small and probably difficult to detect with conventional sediment coring and subsampling methods. However, larger distances of migration are expected when the porosity of sediments is higher, when longer time scales are considered, when TOC is much lower (as in sandy sediments), or for HOC which have higher solubilities (lower K_{oc} s).

FLUX OF PCBs ACROSS THE SEDIMENT-WATER INTERFACE

The flux of individual chlorobiphenyls across the sediment-water interface is given by:

$$F_{x=0} = -\phi(D_B + D_d)(\partial C_d / \partial x)_{x=0} - \phi(D_B + D_c)(\partial C_c / \partial x)_{x=0} - I_d - I_c + \phi v(C_d + C_c)_{x=0} \quad (\text{eqn. 4-16})$$

where flux out of the sediments is negative and I_d and I_c are solute exchange of dissolved and colloid-sorbed PCBs with the overlying water by irrigation of the sediment bed. The irrigation terms here do not include solute transport which is already accounted for in the biodiffusion terms, where D_b is calculated from the mixing of bulk sediments by biological processes (any physical mixing of the bed by waves or currents is implicitly included in D_b).

Estimates of the fluxes of four PCBs from surface sediments into the overlying water are made from field measurements of PCBs in sediments and pore waters at Station M in Buzzards Bay to illustrate the role of colloidal organic matter in affecting transport of HOC in typical coastal sediments. Chlorobiphenyls 28 (plus unresolved 31) and 153 are considered again along with 2,2',5,5'-tetrachlorobiphenyl (PCB No. 52) and 2,2',4,5,5'-pentachlorobiphenyl (PCB No. 101). The log K_{ow} s (from Table 1-2) for 52 and 101 are 6.05 and 6.49, respectively. Log K_{oc} s, D_d , and D_c for the four chlorobiphenyls are calculated as in the previous example. The gradients of C_d and C_c at the interface have large uncertainties because of insufficient resolution in depth near the interface. The overlying water concentrations of total PCBs have been reported to be 0.20 to 1.0 ng/L (De Lappe et al., 1980) and can be considered an infinite sink for diffusion of PCBs out of pore waters at Station M (Chapter 3). The concentration gradient of C_c and C_d at the interface is assumed to be the concentration determined in the upper (0-1 cm) section divided by the mid-point of the depth of that sample from the interface. Those gradients are greater than those over the upper 10 cm of sediment but probably represent lower limits of the

gradients at the interface. The concentrations C_d and C_c in the upper 1 cm section of sediment are calculated from the measured sediment and total pore water concentrations in the following manner:

$$C_d = C_s / (\text{TOC} \cdot K_{oc} s) \quad (\text{eqn. 4-17})$$

$$C_c = C_{pw} - C_d \quad (\text{from eqn. 4-17}) \quad (\text{eqn. 4-18})$$

where C_s and C_{pw} are the measured sediment and pore water concentrations of chlorobiphenyls in the upper 1 cm given in Table 3-6 and TOC is 0.0317 kg/kg (Table 3-5).

The biodiffusion coefficient is calculated in the next section to be about 3.0×10^{-7} cm²/sec over the upper 10 cm from the ²¹⁰Pb profile. Values for D_b of $0.9 - 8.1 \times 10^{-7}$ cm²/sec were calculated from ²³⁴Th over two seasonal cycles at this station (Martin, 1985) and compare well with the ²¹⁰Pb result which is integrated over a much longer time scale than ²³⁴Th. Compaction and any externally compressed flow in pore waters are neglected and v is assumed to equal the net sediment accumulation rate of 0.5 mm/yr determined at this site by ¹⁴C dating of four sediment sections (McNichol, 1986).

The resulting calculations of the diffusive and advective flux of the four chlorobiphenyls is given in Table 4-1. The relative importance of transport of colloid-sorbed PCBs compared to dissolved PCBs increases with increasing hydrophobicity and colloid-enhanced transport is predicted to surpass the dissolved solute flux at hydrophobicities corresponding to those between the tetra- and pentachlorobiphenyls considered (i.e., when $C_c \cdot K_{oc} c / C_d >$

Table 4-1. Fluxes of 4 chlorobiphenyls across the sediment-water interface at Station M in Buzzards Bay, considering molecular diffusion (F_{DIP}), bioturbation (F_{BIO}) and advection (F). $D_c = 7.0 \times 10^7 \text{ cm}^2/\text{sec}$; $\phi = 0.850$; $\omega = 1.59 \times 10^{-9} \text{ cm}^2/\text{sec}$; $D_B = 3.0 \times 10^{-7} \text{ cm}^2/\text{sec}$. Other assumptions and data are given in Table 3-5 and in the text.

PCB No.	C_d (pg/cm^3)	C_c (pg/cm^3)	D_d ($\times 10^6 \text{ cm}^2/\text{sec}$)	$\partial C_d/\partial x$ (pg/cm^4)	$\partial C_c/\partial x$ (pg/cm^4)	Fluxes ($\times 10^6 \text{ pg}/\text{cm}^2 \cdot \text{sec}$)						
						Dissolved			Colloid-Sorbed			Total
						F_{DIP}	F_{BIO}	F_U	F_{DIP}	F_{BIO}	F_U	F_T
28+31	1.94	0.23	3.30	3.88	0.46	-10.9	-0.989	3×10^{-3}	-0.276	-0.117	3×10^{-4}	-12.3
52	0.321	0.809	3.14	0.642	1.62	-1.71	-0.163	4×10^{-4}	-0.969	-0.413	1.1×10^{-3}	-3.26
101	0.202	2.11	3.01	0.404	4.22	-1.03	-0.103	3×10^{-4}	-2.53	-1.08	2.0×10^{-3}	-4.74
153	0.0357	3.86	2.86	0.0174	7.72	-0.174	-0.018	4×10^{-5}	-4.62	-1.97	5.2×10^{-3}	-6.78

$\text{pg} = 10^{-12} \text{g}$

D_a/D_e). Equations 4-17 and 4-18 appear to underpredict C_e for 28 + 31 (due to the difference of two large numbers) since the ratio of C_e to C_a is much less than expected based on K_{oc} . Nonetheless, this will not have a dominant effect since the predicted flux of dissolved solute by diffusion will still control the flux of trichlorobiphenyl (from taking D_a to be nearly five times D_e in these calculations). The dissolved solute flux by diffusion is approximately ten times that caused by bioturbation. However, biodiffusion may be relatively more important for PCBs which are primarily colloid-sorbed because of the closer similarity of D_a and D_e . For all four chlorobiphenyls the effect of sediment advection may be ignored, unless there is an externally compressed flow which is 10^2 to 10^4 times faster than sediment burial or compaction.

Crude estimates of the residence times of these four chlorobiphenyls in the 15 m water column at Station M with respect to the pore water fluxes calculated in Table 4-1 can be made from the water column concentrations in Buzzards Bay reported by De Lappe et al. (1980). Assuming water column inventories of 5 to 100 $\mu\text{g}/\text{cm}^2$ for these four congeners, the water column residence times are on the order of 5 days to 1 year. These residence time calculations have large errors due to the gross uncertainties in the actual water concentrations of the four chlorobiphenyls considered, and the large lateral gradients in PCB concentrations which exist in Buzzards Bay waters and sediments (Chapter 3). Residence times of PCBs in the water column with respect to volatilization (by the method outlined in Lyman et al., 1982), and water mixing in Buzzards Bay (R. Signell, personal communication) are on the order of one week, and one month respectively. Despite their uncertainties, these

calculations do suggest that pore water fluxes of dissolved and colloid-sorbed PCBs can be important in resupplying a shallow water column with PCBs.

The effect of enhanced PCB transport by irrigation of pore water PCBs across the burrow walls of macrobenthos has not been treated here. The flushed burrows provide conduits for rapid exchange of non-adjacent overlying water. This horizontal exchange of pore waters cannot adequately be described by one-dimensional diffusion descriptions (Aller, 1980, 1982; Martin, 1985). Burrow walls and muddy sediments are apparently impermeable to advection (Aller, 1980c) and models which treat the exchange of pore water solutes as a depth dependent diffusional process exchanging pore water at depth directly with overlying water have proved successful (Aller, 1980c; Martin, 1985). Unfortunately, these non-local exchange models require detailed understanding of burrow density and geometry (Aller, 1980c) or a known "calibration" solute such as measuring the ^{222}Rn deficit. Martin (1985) has shown that the depth and intensity of irrigation varied tremendously over a seasonal cycle at Station M, and probably is related to the temperature and supply of labile organic matter to the sediments.

One major uncertainty which will affect the modelling of HOC transport by irrigation concerns the permeability or reactivity of burrow walls to HOC and particularly colloidal organic matter. Both the radial diffusion model of Aller (1980c) and empirical non-local exchange models (e.g., Martin, 1985) predict that the irrigation rate will be directly proportional to the sediment diffusion coefficient. This suggests that as in the case of vertical molecular diffusion, the exchange rate by irrigation or colloid-sorbed HOC will be considerably slower than that of dissolved HOC due to lower

diffusivity. The permeability of burrow walls to organic colloids will be a difficult but important factor to test in future studies.

The importance of irrigation to the total flux across the sediment-water interface is uncertain but for some dissolved solutes can be comparable or even greater than the flux from vertical diffusion across the sediment-water interface for small dissolved solutes in some coastal sediments (Berner, 1980; Aller, 1982). In general, irrigation will be most important when the gradient of pore water solute is not great at the interface but increases sharply in the irrigated zone with depth. This might be the case for HOC which have subsurface maxima due to in-situ production or burial, and in the case when colloid concentrations increase with depth.

SEDIMENT MIXING OF ^{210}Pb AND PCBs AT STATION M

It is evident from the preceding discussions that highly sorbed HOC are not expected to migrate appreciably in sediment interstitial waters. In the absence of pore water migration, the distribution of a non-degrading, particle-sorbed compound with depth will be controlled by its history of deposition to the sediment, subsequent sediment burial, and bulk sediment mixing caused by the feeding and burrowing activities of benthic macrofauna.

Sediment mixing processes have been modelled as being analagous to Fickian-type eddy diffusion, where the sediment mixing term in diagenetic equations can be described by biodiffusion coefficients (D_b) within the upper mixed layer of sediments (Goldberg and Koide, 1962; Guinasso and Schink, 1975; Benninger et al., 1979). This approach has had some success in modelling the

sediment profiles of natural radioactive elements with appropriate half-lives, such as ^{210}Pb ($t_{1/2} = 22.3$ yrs.) and ^{234}Th ($t_{1/2} = 24.1$ days), and for certain bomb-generated fallout radionuclides (especially $^{239,240}\text{Pu}$ and ^{137}Cs). A diffusion analogy for sediment mixing is not strictly valid for sediment mixing which involves transfer of non-adjacent parcels of sediment, which may occur in the feeding of some benthic organisms or from the infilling of relic burrow structures with surface sediments (Benninger et al., 1979; Ailer, 1982). However, if the number of non-local mixing events is large and randomly distributed over the lifetime of solid-phase property being measured, then an eddy diffusion modelling approach may be applicable. In this section the sediment distribution of ^{210}Pb is compared to that of PCBs to evaluate the mixing of these two different types of particle tracers.

The distribution of ^{210}Pb has been modelled here in terms of a one-dimensional steady-state model following the example of Nozaki et al. (1977) and Benninger et al. (1979). The unsupported ^{210}Pb activity (A ; $A = ^{210}\text{Pb} - ^{226}\text{Ra}$ in dpm/g) can be given by:

$$\frac{\partial}{\partial x} D_B \frac{(1-\phi)\rho_s A}{\partial x} - \frac{\omega \partial (1-\phi)\rho_s A}{\partial x} - \lambda (1-\phi)\rho_s A = 0 \quad (\text{eqn. 4-19})$$

where λ is the decay constant for ^{210}Pb , and assumes that ^{210}Pb does not migrate by any other processes. When D_B , ϕ , ρ_s , and ω are constant in the biologically mixed zone the solution to equation 4-19 is:

$$A = A_0 \exp\left(\frac{\omega - \sqrt{\omega^2 + 4D_B\lambda}}{2D_B} \cdot X\right) \quad (\text{eqn. 4-20})$$

where A is the activity of unsupported ^{210}Pb at depth x , and A_0 is the activity at $x = 0$. Without independent measurements of ω or D_b , equation 4-20 cannot be solved uniquely by plotting $\ln A$ vs depth. It is seen from this equation that the effect of sedimentation can be ignored when $4D_b\lambda \gg \omega^2$. Likewise, the sediment accumulation rate may be calculated if there is negligible mixing.

The data for unsupported ^{210}Pb at Station M are given in Chapter 3. When all data are considered for ^{210}Pb and the effect of sedimentation is neglected, applying equation 4-20 yields a constant biodiffusion coefficient of $1.3 \times 10^{-7} \text{ cm}^2/\text{sec}$. However there is a factor of two break in the slope of $\ln A$ vs x at 10 cm for ^{210}Pb , suggesting that there is slower mixing below that depth. If it is assumed that the excess ^{210}Pb below 10 cm is only due to sediment accumulation (i.e., no mixing below 10 cm) an ω of 0.329 cm/yr is calculated. This value agrees well with a sediment accumulation rate of 0.295 cm/yr calculated at Station P in Buzzards Bay using the same approach (Farrington et al., 1977). However, this ω is unreasonably high at Station M because it gives an apparent age of 118 years for the 35-43 cm section into which PCBs have penetrated (Chapter 3). PCB contamination in Buzzards Bay probably dates back only 40 years from the time that this core was collected (Farrington et al., 1985). An independent estimate of 0.05 cm/yr for the sediment accumulation rate at Station M has been made by McNichol (1986) using the ^{14}C age of three sediment sections below 30 cm. This latter estimate can be used to solve for D_b .

A two-layer model for unsupported ^{210}Pb is applied to account for an apparently lower mixing rate in the deeper mixed zone below 10 cm. The model

assumes that the ^{210}Pb distribution in the upper layer is only controlled by mixing, which can be described by a constant D_{b1} over that interval, and radioactive decay. In the second layer both mixing (with a constant biodiffusion coefficient, D_{b2}) and sedimentation are considered:

$$\text{layer 1: } D_{b1}(\partial^2 A / \partial x^2) - \lambda A = 0 \quad (\text{eqn. 4-21})$$

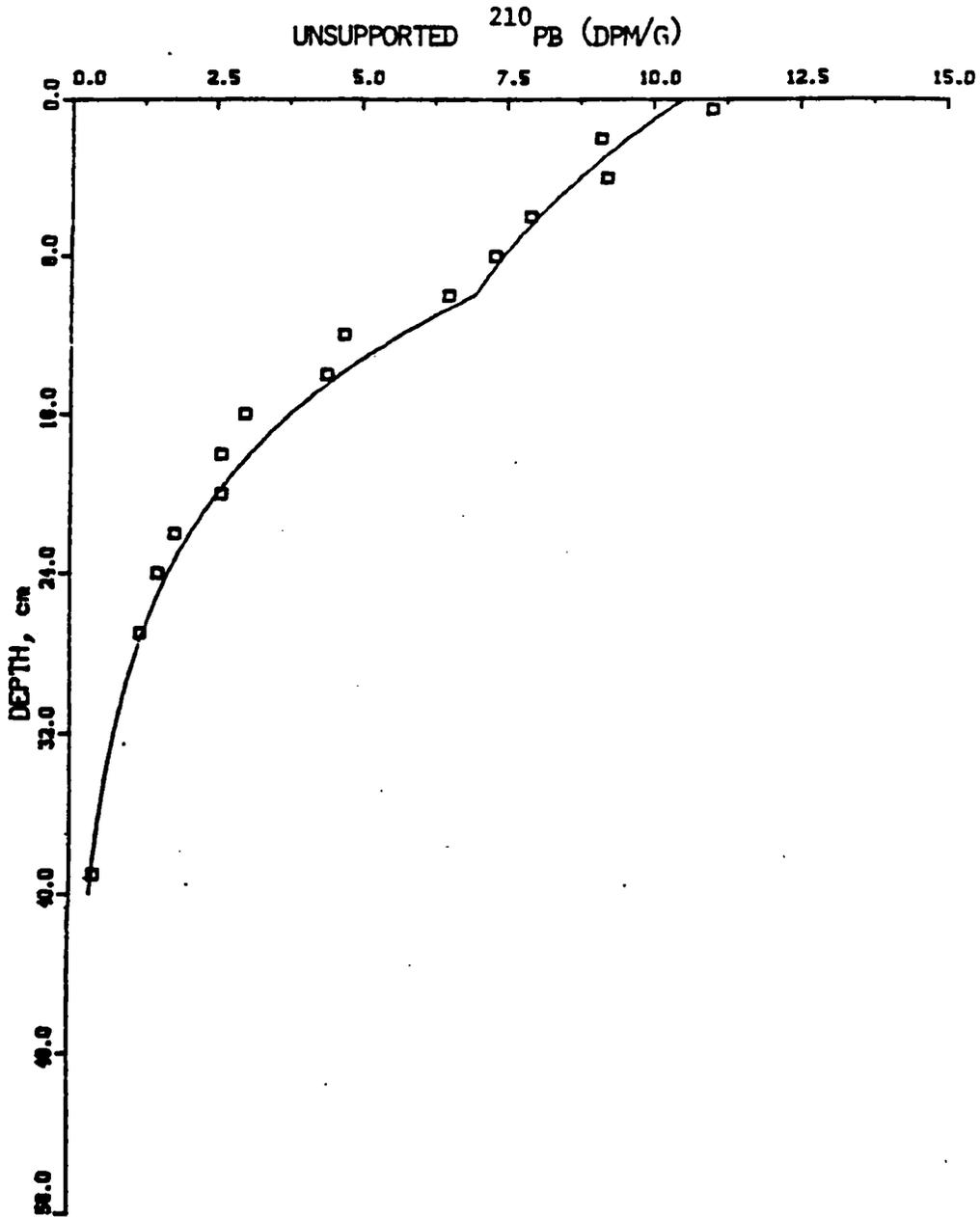
$$\text{layer 2: } D_{b2}(\partial^2 A / \partial x^2) - \omega \partial A / \partial x - \lambda A = 0 \quad (\text{eqn. 4-22})$$

boundary conditions:

$$x = 0, \quad A = A_0$$
$$x = x_1, \quad A_1 = A_2 \quad J_1 = J_2$$
$$x = \infty, \quad A = 0$$

where x_1 is the depth of the first layer and J_1 and J_2 are the fluxes across that depth from above and below. This problem has been solved for the mixing of solid-phase organic carbon by McNichol (1986). Figure 4-2 shows the fit of this model to the data assuming $D_{b1} = 3.0 \times 10^{-7} \text{ cm}^2/\text{sec}$, $D_{b2} = 8.0 \times 10^{-8} \text{ cm}^2/\text{sec}$, $\omega = 0.05 \text{ cm/yr}$, $x_1 = 10 \text{ cm}$, and $A_0 = 10.5 \text{ dpm/g}$. This is not a unique or best fit for the model, but adequately describes the data. The biodiffusion coefficient of 3.0×10^{-7} is well within the range of $(0.9 - 8.1) \times 10^{-7} \text{ cm}^2/\text{sec}$ determined in the upper few cm by ^{234}Th at this site (Martin, 1985) and suggests that the depth of rapid mixing may be deeper than that indicated by the shorter-lived tracer. In the second layer the biodiffusion coefficient is still large enough to dominate the assumed sedimentation rate. The values of D_b in both layers are well within the range of those determined in other muddy coastal sediments (see Berner, 1980;

Figure 4-2. The depth profile of unsupported ^{210}Pb given by the two-layer model . The small squares are the actual data for ^{210}Pb measured at Station M. The model and parameter assumptions are found in the text.



Aller, 1982). The ^{14}C measured sediment accumulation rate is similar to another ^{14}C determined ω of 0.075 cm/yr measured at a Long Island Sound site (Benoit et al., 1979). It is not known how closely these long term estimates of ω approach contemporary sediment accumulation, but current rates can not be much higher and still reconcile the mixing of PCB at Station M and plutonium at the Long Island Sound site with those of ^{210}Pb in the same cores (Benninger et al., 1979).

The simplified equation describing PCB distributions with depth in the sediment is similar to that for ^{210}Pb and is given by:

$$\partial C_s / \partial t = \partial D_s (\partial C_s / \partial x) / \partial x - \omega \partial C_s / \partial x \quad (\text{eqn. 4-23})$$

and assumes no migration or other reactions of PCB after deposition. PCBs are not steady-state tracers and a source input function of PCBs to the sediment bed is required to solve Equation 4-23. This equation is further simplified here because sediment accumulation over the lifetime of PCBs in Buzzard Bay is calculated to be 2 cm at station M, and can be safely neglected for the purposes of model comparisons made here.

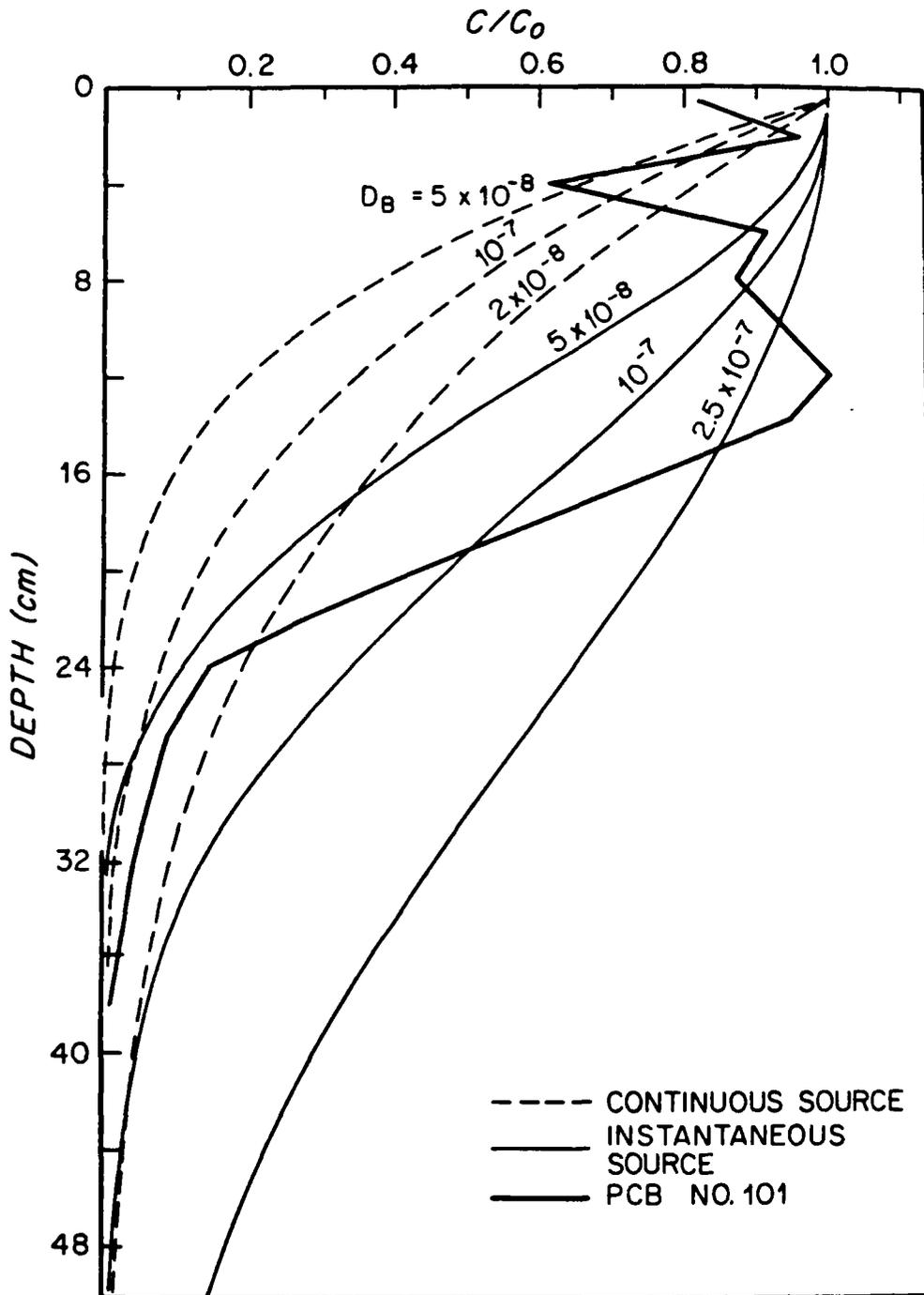
The resulting biodiffusion equation can be solved analytically as a function of time and depth by assuming a simple source function for PCBs. Cochran (1985) has reported the solutions of this problem for two situations which are considered here. The first is a continuous source function where the flux of individual chlorobiphenyls has been constant for the 40 yrs before the sediment was collected. Furthermore, mixing rates are assumed constant with depth in the core (i.e., an infinite spatial domain for mixing is

assumed). The second extreme case assumes that the source of PCBs to the sediment surface was instantaneous and was subsequently mixed into the sediment bed over 40 yrs without additional flux or sedimentation. Again, a constant mixing rate with depth is assumed in the solution. The normalized concentration profiles for both continuous and instantaneous source models is plotted (from the solutions given by Cochran, 1985) for a range of D_b in Figure 4-3. The normalized profile shapes are compared with that of 2,2',4,5,5'-pentachlorobiphenyl at Station M. The actual concentration data for this congener can be found in Table 3-6.

The depth profiles of 101 and other chlorobiphenyls (see Table 3-6) can not be completely described by the simple biodiffusion models shown in Figure 4-3. This is particularly true in the upper 14-16 cm where PCBs show a small subsurface maxima and appear to be more completely mixed than that predicted for a constant D_b with depth. Below this depth, the concave downward profile shape and depth of penetration of PCBs are consistent with the range of predicted biodiffusion profiles illustrated in Figure 4-3. The ^{210}Pb derived mixing rate below 10 cm was shown to be approximately 8.0×10^{-6} cm^2/sec and is not inconsistent with the deep mixing of PCBs.

It is difficult to suggest from the above models whether either of the extreme source functions considered above is more appropriate. If, as shown for ^{210}Pb , the mixing rate is faster in the upper 10 cm than that below, then there will be a build-up of PCBs in the first layer above that predicted by a model with D_b constant with depth. A more complicated model in which D_b decreases with depth (as in the 2-layer model for ^{210}Pb), and allows for a small amount of sedimentation (about 2 cm) would more closely predict

Figure 4-3. Bidiffusion profile shapes given by continuous and instantaneous source function models (solutions given in Cochran, 1985) for a range of D_b expected from ^{210}Pb modelling. The normalized profile for a representative chlorobiphenyl (PCB no. 101) in Station M sediments is compared to the simple model predictions.



the PCB data with both a continuous and instantaneous source function. However, any reasonable estimate of D_e in the upper layer will still predict a concave downward profile for PCBs in the upper mixed zone of sediment if a continuous constant input model is applied. The actual source function for the inputs of PCB to New Bedford Harbor, or to Station M with time can not be estimated at this time. The compositional changes of PCBs with depth at Station M noted in Chapter 3 indicate changing source functions with time. As mentioned in Chapter 3, the completion of the hurricane barrier in New Bedford Harbor resulted in a five-fold increase in sediment accumulation in the harbor (Summerhayes et al., 1977). If the flux of PCB out of New Bedford Harbor has also decreased since 1966, it could explain the increased mixing of PCBs in the surface sediments at Station M, and the lower PCB concentrations in the upper sediments at Station 67 in New Bedford's outer harbor (Chapter 3).

GENERAL DISCUSSION

A three-phase transport model has been presented in the preceding sections which includes the effect of colloid sorption on the total transport of pore water HOC in some cases. However, there are few field or experimental data available to test the predictions of this model. Organic colloid-enhanced migration was shown to be most important for HOC which have very slow rates of migration in typical sediments (see Figure 4-1). Sediment and new sampling methodology will be needed to sample the depth scales of expected migration in coastal sediments.

Two studies have measured the diffusion of high K_{oc} PCBs in the absence of competing processes, and might give some insight to a possible colloid effect (Fisher et al., 1983; Di Toro et al., 1985). In a syringe migration experiment Di Toro et al. (1985) measured an apparent diffusivity for PCB No. 153 of $3.95 \pm 1.12 \times 10^{-6}$ cm²/day. This can be compared to D_{app} calculated from equation 4-11 using the sediment properties reported by Di Toro et al. (1985) and K_{oc} which have been previously calculated for 153 in this chapter. A two-phase (no-colloid) D_{app} is predicted to be 1.28×10^{-6} cm²/day while that for colloid-enhanced migration is predicted to be 24.8×10^{-6} cm²/day assuming C_c' equals 10 mg/L in this experiment. The measured D_{app} is three times higher than that predicted for two-phase transport but about six times lower than the predicted D_{app} for three-phase transport. It is uncertain what concentrations of C_c' might be expected in their experimental design. To evaluate the possible role of colloid-enhanced migration in their experiments it would be useful to have data on a range of chlorobiphenyls which would have much different expected mobilities. If D_{app} does not approach a limiting value with increasing K_{oc} (K_{ow}) then the simple model presented in this chapter would predict that diffusive transport of colloid-sorbed HOC does not greatly exceed transport of dissolved HOC.

In a much different experiment, Fisher et al. (1983) have measured the flux of individual chlorobiphenyls out of undisturbed contaminated sediments into a continually purged water column. In this situation the concentrations of PCBs are depleted in the surface sediments with time. Surface sediments were not renewed by new inputs of PCBs from either the water column or from

mixing of sediments from below. Under these experimental conditions, the following expression for the flux of PCB as a function of time ($F_{c,t}$) is given by Karickhoff and Morris (1985) to be:

$$F_{c,t} = (m/L)(D_{app}/t)^{1/2} \quad (\text{eqn. 4-24})$$

where m is the total mass of PCB in the sediments initially, t is time, and L is the depth to which PCB is mixed in the sediment. This solution assumes that there is local-equilibria between C_s and C_d and colloid-sorbed PCB is not considered. The apparent diffusivities of four individual chlorobiphenyls were calculated by Fisher and co-workers to range from 1.2×10^{-9} cm²/day for 2,3',5-trichlorobiphenyl to 8.5×10^{-7} cm²/day for PCB No. 101. These values of D_{app} are roughly one to four orders of magnitude lower than those predicted from equation 4-11 for 2-phase sorption given the sediment properties in the experiment, and K_{oc} values predicted from K_{ow} (Table 3-1) for the individual chlorobiphenyls. Not only are the measured apparent diffusivities lower than predicted, they are directly related to the compound hydrophobicities, in apparent violation of the expected trend arising from retardation effects by sediment sorption. In other words, the most hydrophobic congeners appear to be depleted from the surface sediments at a faster rate.

The possible role of colloid-sorption on the observed trends in the results of the above study are not easily discerned because colloidal organic matter is surely also being depleted in the surface sediments. When the concentration of colloidal organic matter is not constant with depth the total flux of dissolved and colloid-sorbed PCBs can be written as

$$F_{x=0} = -\phi \left(1 + \left[\frac{f_B D_c}{(1-f_B) D_d} \right] D_d \right) (\partial C_d / \partial x)_{x=0} \quad (\text{eqn. 4-25})$$

$$-K_{oc} C_c \cdot C_d \cdot D_c (\partial C_c' / \partial x)_{x=0}$$

The gradients $(\partial C_d / \partial x)_{x=0}$ and $(\partial C_c / \partial x)_{x=0}$ at times greater than zero will both be of the form:

$$\partial C / \partial x = C_0 / \sqrt{\pi D_{app} t} \quad (\text{eqn. 4-26})$$

(Fisher et al., 1983) where C_0 is the initial concentration of chlorobiphenyl or colloidal organic matter in pore waters. When PCBs become increasingly associated with colloids, the total depletion of PCBs in sediments will depend more on the rate of depletion of organic colloids given by equation 4-26. Table 4-2 shows that reasonable assumptions predict that colloidal organic matter may have a higher apparent diffusivity than the chlorobiphenyls considered. This would result in faster losses of colloid-sorbed PCBs from surface sediments and might explain the anomalous increases in apparent diffusivities with increasing K_{ow} for PCBs calculated from equation 4-24 by Fisher et al. (1983).

Table 4-2 also shows the fluxes of the four chlorobiphenyls predicted from the sediment concentrations and sediment properties reported by Fisher et al. (1983) and estimates of K_{oc} s and K_{oc} c from K_{ow} (see previous examples). These estimates of PCB flux assume a gradient over the upper 0.5 cm.

Table 4-2. Comparisons of predicted fluxes and apparent diffusivities of four chlorobiphenyls measured by Fisher et al. (1983) with experimental observations. The structures and log K_{ow} s of the four PCBs are found in Table 3-1 and the log K_{oc} s have been calculated by the predictive equation of Means et al. (1980). Predicted D_{app} are for dissolved chlorobiphenyls and are calculated from equation 4-11 neglecting the colloid term and using the reported TOC of 2.9% and $\rho_s = 2.6 \text{ g/cm}^3$, and assuming $\phi = 0.75$. The diffusive fluxes of C_d and C_c predicted at zero time have been calculated in the same manner as in Table 4-1. The Concentrations of C_d and C_c have been calculated from the C_s values measured by Fisher et al. and the K_{oc} 's given below by : $C_d = C_s / (\text{TOC } K_{oc})$; $C_c = C_d K_{oc} C_c'$ and assumes $C_c' = 10 \text{ mg/L}$. These predicted fluxes across the interface are compared to measured fluxes integrated from days 4 to 12.

PCB no.	K_{oc} (L/Kg)	D_{app} predicted ($\text{cm}^2/\text{sec} \times 10^{10}$)	D_{app} observed	Fluxes ($\text{ng}/(\text{cm}^2\text{day}) \times 10^2$)			
				F_d	F_c	F_T	observed (t=4-12 days)
26	5.44	4.86	1.4×10^{-4}	4.92	2.88	7.80	0.563
49	5.90	1.57	1.5×10^{-3}	2.92	5.17	8.09	2.41
101	6.75	0.213	0.098	0.104	1.32	1.42	5.12
97	6.35	0.535	0.027	0.115	0.599	0.714	1.30
Organic collids	$K'_d=100$	81.2					

5
1522

Predicted fluxes for tetra- and pentachlorobiphenyls agree well with those found over days 4-12. The observed flux of PCB No. 26 is considerably lower than predictions and cannot be easily accounted for.

The D_{app} for colloidal organic matter estimated in Table 4-2 assumes an equilibrium distribution ratio (L/Kg) of 100. This represents the exchange of organic colloids with a fraction of the total TOC. This distribution ratio is in the range of those measured for artificial melanoidens (Hedges, 1978) and natural lacustrine DOM (Davis and Gloor, 1981) with clean model surfaces. The results for ratios of TOC/DOC determined for the coastal sediments studied in Chapter 3 are 700-4000 and indicate that roughly 10% of the sediment organic would have to be 'exchangeable' with colloidal organic matter to give a " K_d " of 100. As mentioned above, the adsorption of colloidal organic matter with sediments has not been studied, and must be determined to describe any non-steady-state behavior of colloidal organic matter in sediments.

CONCLUSIONS

A simple model for HOC transport which includes the effect of a mobile colloid phase was shown to have a straightforward solution when colloidal organic matter does not change with time. Several general conclusions can be drawn from the solutions considered:

1) When organic colloid and sediment properties are constant with time and depth, the effect of colloid-sorption on the total transport of HOC can be included in a colloid-enhanced apparent diffusion coefficient describing the diffusivity of both dissolved and colloid-sorbed HOC. These combined

diffusivities are retarded by sorption to sediments, and it was shown that the migration of total sediment chlorobiphenyls by pore water diffusion is still small (i.e., < 2 cm) over 20 yr timescales. However, consideration of colloid migration significantly enhanced the diffusion of very hydrophobic compounds which are not appreciably mobile in the dissolved phase.

2) Model calculations show that the flux of individual chlorobiphenyls across the sediment-water interface can be greatly enhanced by diffusion and bioturbation of colloidal organic matter. The calculated fluxes of PCBs from pore waters to the overlying water may provide a potentially important source of PCBs to Buzzards Bay. Accurate flux estimates are dependent on a better understanding of the size and diffusivity of organic colloids in interstitial waters, the gradients of C_a and C_c at the sediment-water interface, and the importance of irrigation in transporting both dissolved HOC and colloidal organic matter across the sediment-water interface. Of particular interest is the permeability of burrow walls to colloidal organic matter, a subject for future study.

3) It is difficult to use existing field or experimental data to test the expected role of colloidal-organic matter on migration. Critical evaluation of the PCB leaching experiments of Fisher et al. (1983) indicate that in the situation of non-steady-state loss of HOC and colloids from surface sediments, the rate of loss from sediment may be sensitive to the apparent diffusivity of colloidal organic matter in sediments. Experimental studies are necessary to determine the diffusivity and sediment adsorption of colloidal organic matter.

4) Sediment-mixing models suggest that the distribution of PCBs with depth at Station M in Buzzards Bay are consistent with biodiffusion parameters

determined from ^{210}Pb at the same site. Exact comparison of mixing of PCB and ^{210}Pb tracers are precluded by the unknown source function of PCBs to that site over the last 40 years. The PCB distributions are consistent with the hypothesis that sediment mixing, and not sedimentation or pore water diffusion, is primarily responsible for the observed profiles.

CHAPTER V

SUMMARY AND CONCLUDING REMARKS

PCBs were used as model compounds to study the physical-chemical behavior of hydrophobic organic compounds (HOC) in a coastal environment. The focus of this research has been on sorption of PCBs with colloidal organic matter, and the effect that sorption has on the speciation and geochemistry of PCBs in coastal sediments. Laboratory and field experiments were conducted, and integrated with results from other laboratory studies reported in the literature, to provide an understanding of sediment/interstitial water partitioning of PCBs.

The effect of colloidal organic matter on the speciation of PCBs in seawater could be directly determined by a static equilibrium headspace partitioning method. This method offers the advantage that it avoids operational phase separations which may be incomplete or alter equilibria during phase separation. It has been suggested here that several misconceptions concerning HOC sorption are due, in part, to experimental problems with phase separations. Headspace partitioning is an especially attractive technique for determining the speciation of HOC (such as PCBs) which appreciably sorb to container walls or other surfaces which might be used in phase separations. Adsorption of colloidal organic matter to container walls, changing the sorptive properties of those surfaces, is a problem which merits further investigation.

Organic carbon normalized partition coefficients (K_{oc}) were determined for four chlorobiphenyls with colloidal organic matter enriched from coastal seawater. Measured K_{oc} 's were similar to those reported in other studies of the sorption of PCBs with soils, sediments, and dissolved humic substances, and were also within a range of those predicted from $\log K_{ow} - \log K_{oc}$ correlations based on other HOC. When the partitioning results from this study are considered together with other data available in the literature, several conclusions concerning HOC-organic colloid sorption can be made:

- 1) The sorption of HOC with colloidal organic matter or dissolved humic substances (from soils) appears to be mechanistically similar to HOC sorption with sediment and soil organic matter. This is supported by linear sorption isotherms, non-competitive sorption, and the closeness of K_{oc} 's determined for colloid sorption to those measured with sediment and soil sorbents. These observations are consistent with an organic phase partitioning model, which predicts that HOC sorption is primarily controlled by the solutes incompatibility in the aqueous phase, and that interactions in the organic phase are nonspecific and weak. However, variability in HOC-organic colloid sorption may arise due to the size and polarity of colloidal organic matter.
- 2) The limited data which are presently available suggest that the sorption capacity of colloidal organic matter, which comes from different environments or has been collected by different methods, may be quite variable. The macromolecular organic matter in seawater is represented by a range of sizes and polarities. The effect of size and molecular configuration on the sorptive characteristics of colloids is expected to become increasingly important as the disparity in size between sorbate and sorbent decreases. The

second order mechanisms and factors influencing sorption could be studied with well characterized model sorbents of known size and composition. It may prove that additional properties of colloidal organic matter (in addition to colloid concentration and solute K_{ow}) are required to adequately predict the speciation of HOC in natural waters.

3) The range of K_{oc} 's which have been observed and predicted for individual chlorobiphenyls indicate that organic colloid sorption should strongly influence the speciation and distribution of PCBs in environments which contain high concentrations of colloids, such as the interstitial waters of reducing sediments. However, the effect of colloidal organic matter on the speciation of HOC in oligotrophic coastal and open ocean waters will be limited to very hydrophobic compounds ($\log K_{ow} > 6.0$).

Results from sediment-interstitial water studies provided strong evidence that a large fraction of the PCBs in interstitial water were sorbed to colloidal organic matter. This conclusion was based on the elevated concentrations of PCBs in pore waters, the composition of PCBs in pore waters (pore waters were not enriched in more soluble congeners), and the apparent distribution coefficients of individual chlorobiphenyls. The apparent distribution coefficients were explained by a three-phase partitioning model, which assumes local equilibrium between dissolved, colloidal organic, and sediment organic matter phases and predictions of K_{oc} 's based on correlations with K_{ow} determined in laboratory experiments. Observed partitioning was well described at Stations 67 and M by model predictions, and model considerations suggest that the sorptive characteristics of colloidal

organic matter must be very similar to sediment organic matter at those sites. The three-phase model underpredicts K'_d at Station 84, but does predict the constancy of K'_d with increasing K_{ow} . Differences in the pore water extraction methods used and a lack of DOC measurements at Station 84 prevent a critical explanation for the lower than expected pore water PCB concentrations at that site.

The apparent distribution coefficients of PCBs between suspended particles and filtered seawater in the water column increased twenty to sixty times with increasing K_{ow} at two stations in New Bedford Harbor and suggested a much greater importance of dissolved PCBs in speciation. Model calculations predicted that the effect of organic colloids could be neglected for HOC with $\log K_{ow} < 6.0$, due to lower concentrations of organic colloids in the water column. Because of limitations in the data sets and some uncertainties in predicting PCB partitioning in seawater, it was not possible to determine whether equilibrium conditions existed. In general, water column distributions of PCB-like compounds are more subject to nonequilibrium conditions due to air-sea exchange, spatial concentration gradients, and slow sorption kinetics which become more important at lower solids concentrations. An increased understanding of water column distributions and transport of HOC in coastal environments will require coupling of equilibrium and kinetic treatments of HOC sorption, physical transport models of sediment resuspension and transport, and further understanding of the transport of HOC from the sediment bed via pore water transport.

The effect of a mobile colloid-sorbed phase on a general sediment transport model is to enhance the diffusion of PCBs in interstitial waters and

can be included in an apparent diffusivity term when organic colloid concentrations and sediment properties are constant with time and depth. The migration of PCBs in typical coastal sediments is still expected to be small over 20 yr timescales, which is consistent with the similarity of PCB and ^{210}Pb profiles at Station M. Modelling of any non-steady-state behavior of organic colloids in sediments requires an understanding of organic colloid cycling and adsorption in sediments. The role of organic colloids in the flux of PCBs across the sediment water interface is predicted to be important for congeners which are highly sorbed. Diffusion, bioturbation, and physical mixing of colloid-sorbed PCBs in surface sediments can be of similar relative importance as transport processes in typical coastal sediments. Irrigation of colloid-sorbed compounds may also be an important transport process. Uncertainties involving the diffusivity of colloids, the permeability of burrow walls to organic colloids, and the mechanisms of irrigative transport are important unanswered questions which should be addressed in future studies.

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APPENDIX I

HENRY'S LAW CONSTANTS FOR PCBs

The Henry's Law constants (H) of several polychlorinated biphenyls in ultrafiltered seawater were determined by measuring the vapor phase and solution concentrations of PCBs in four sets of static headspace partitioning experiments conducted during this research. Henry's Law constants of the same congeners were measured in distilled water during three of those experiments. From these data, the influence of salinity on the aqueous phase activity coefficient ("salting out") can be evaluated.

Methods

The experimental protocols used in each of four experiments were similar to those detailed in Chapter 2, but were altered due to experimental problems in the first three experiments outlined in Appendix 2. In each set of experiments, four to five chlorobiphenyls (di- to hexachlorobiphenyl) were added to bottles containing ultrafiltered seawater or distilled water and PCBs were allowed to approach equilibrium over 2 to 5 days with dissolved (in water), vapor, and any sorbed phases. The temperatures of the room were $21 \pm 2^\circ\text{C}$. The distilled water was twice distilled in glass with K_2MnO_4 , and seawater was from the Chemotaxis Dock sampling site (Chapters 2 and 3). The salinity of two of the seawater samples was $32.6 \pm 0.3\%$ (by AgNO_3 titration).

Dimensionless Henry's Law constants (H/RT) were determined from the ratio of the vapor phase (C_v) and solution phase (C_T) concentrations of individual chlorobiphenyls in experimental bottles with the assumption that C_T is the truly dissolved concentration of PCB (C_d):

$$H/RT \text{ (mL/cm}^3\text{)} = C_v \text{ (ng/cm}^3\text{)}/C_T \text{ (ng/mL)} \quad \text{eqn. 1}$$

A series of bottles, containing ultrafiltered seawater and four or five chlorobiphenyls encompassing a range of PCB concentrations, was equilibrated in each set of experiments. C_v was determined two to five times over the course of the experiment and C_T was measured as replicate samples in each bottle at the end of the experiment (Chapter 2, Appendix 2). H/RT was calculated as the slope of the linear regression of C_v vs C_T . Separate distilled water bottles were equilibrated with PCBs and sampled five times in both phases during the 4-12-85 and 7-23-85 experiments. H/RT for distilled water bottles was then estimated as C_v/C_T .

The experimental problems involved in the first three experiments (Appendix 2) may significantly affect the results presented here for those experiments. The most important uncertainties involved the existence of high levels of DOC contamination in the experimental bottles for the August 29, 1985 and April 12, 1985 experiments, and the attainment of equilibrium between all phases in the experiments begun on March 21, 1984 and April 12, 1985. Non-equilibrium conditions in the later experiments were indicated by a decrease in the vapor phase concentrations over the course of the experiment. This was attributed in the first experiment to slow absorption of PCBs into a silicone seal which was employed in the initial experimental design (experimental bottles in the last three experiments were those illustrated in

Figure 2-1), and in the 4-12-85 experiment to possible re-precipitation of a PCB phase in bottles with the highest concentrations of PCBs. In these two experiments the single vapor phase PCB measurements taken at the end of the experiment are used for the vapor concentrations in the Henry's Law calculations. This assumes that the vapor phase was in equilibrium with the solution phase at the end of the experiment and that the dissolved phase concentration did not change during the time between the last vapor phase and solution sampling (2-10 hr prior to solution sampling for 3-24-84 samples and about 3 hr for 4-12-85 samples). This assumption would cause an overestimation of the true Henry's Law constants if the dissolved concentrations decrease after the final vapor phase sampling. The effect of contaminant DOC (Appendix 2) in ultrafiltrate bottles from 8-29-84 and 4-12-85 experiments would be to sorb PCBs in solution (if DOC was colloidal) or to decrease dissolved phase activity coefficients of PCBs when the concentration of low molecular weight organic co-solutes is great (Chiou et al., 1982). In this case, the air-sea partition coefficients would be below true Henry's Law constants in organic-free seawater.

Results and Discussion

C_v increased linearly with C_r (constant H) for each of the chlorobiphenyls in the ultrafiltrate equilibration experiments. Appendix Table 1-1 summarizes the headspace analysis results for ultrafiltrate and distilled water partitioning experiments. While there is general agreement in values of H/RT in ultrafiltrate experiments, there exists considerable variability (75 - 150%) in measured air-sea partitioning between the

Appendix Table 1-1. Summary of results for Henry's Law constants.
 DW = distilled water; USW = ultrafiltered seawater; errors on the distilled water experiment concentration are one standard deviation and the number of determinations is given in parenthesis; n refers to the number of ultrafiltrate bottles considered in the linear regressions of C_v vs C_T .

Experiment Sample Date M-D-Y	C_v (pg/cm ³)	C_T (ng/ml)	H/RT (ml/cm ³)	salting-out factor (H (USW)/H (DW))
PCB no. 8: 2,4'-dichlorobiphenyl				
3-21-84 DW	0.742	0.126	0.00589	
	11.1	1.46	0.00759	
3-21-84 USW			0.0118	n=2 1.75
8-29-84 USW			0.00690	n=4
4-12-85 DW	130 ± 16(3)	19.8 ± .23(5)	0.00657	
4-12-85 USW			0.0120	n=5 1.83
7-23-85 DW	17.4 ± 2.3(4)	2.44 ± .13(4)	0.00713	
7-23-85 USW			0.0102	n=5 1.43
PCB no. 28: 2,4,4'-trichlorobiphenyl				
3-21-84 DW	0.969	0.102	0.00950	
	12.7	1.52	0.00834	
3-21-84 USW			0.0137	n=2 1.53
8-29-84 USW			0.00737	n=7
4-12-85 DW	94.2 ± 2.5(4)	19.5 ± .11(5)	0.00483	
4-12-85 USW			0.00997	n=5 2.06
7-23-85 DW	18.5 ± 1.4(4)	3.11 ± (.061)	0.00595	
7-23-85 USW			0.00885	n=5 1.49
PCB no. 70: 2,3',4',5-tetrachlorobiphenyl				
3-21-84 DW	7.55	1.91	0.00441	
3-21-84 USW			0.00612	n=2 1.39
8-29-84 USW			0.00239	n=4
4-12-85 DW	24.0 ± 3.7(5)	9.31 ± .14(5)	0.00258	
4-12-85 USW			0.00622	n=5 2.41
7-23-85 DW	3.31 ± .32(4)	.928 ± .023(4)	0.00357	
7-23-85 USW			0.00461	n=6 1.29
PCB no. 87: 2,2',3,4,5'-pentachlorobiphenyl				
3-21-84 DW	0.722	0.135	0.00549	
	4.36	0.901	0.00484	
3-21-84 USW			0.00762	n=2 1.39
8-29-84 USW			0.00280	n=4
4-12-85 DW	8.70 ± 1.65(3)	3.67 ± .04(5)	0.00237	
4-12-85 USW			0.00387	n=6 1.63
7-23-85 DW	1.38 ± .11(3)	0.464 ± .020(4)	0.00297	
7-23-85 USW			0.00407	n=6 1.37
PCB no. 138: 2,2',3,4,4',5-hexachlorobiphenyl				
3-21-84 DW	0.221	0.0932	0.00237	
3-21-84 USW			0.00332	n=2 1.40
7-23-85 DW	0.577 ± .086(3)	0.195 ± .015(4)	0.00296	
7-23-85 USW			0.00397	n=5 1.34

experiments. This is particularly true for the first two experiments which had the largest problems in terms of potential artifacts. The values of H/RT are highest on 3-24-84, probably due to disequilibria, and are low (especially for tetra- and pentachlorobiphenyl) in the experiment started on 8-29-84, when DOC contamination may have had the most significant influence. There is better agreement (less than 35% difference) in Henry's Law constants determined on 4-12 and 7-23-85.

It can also be seen from the data in Appendix Table 1-1 that H/RT is fairly constant for the distilled water bottles, over a wide concentration range, run during different experiments. The notable exceptions to this are results for PCBs 70 and 87 which have higher Henry's Law constants for the 3-24-84 experiment. Again this could be attributed to disequilibria effects which were especially apparent in that experiment.

The Henry's Law constants determined in the 7-23-85 experiment are probably the most accurate due to experimental problems in other experiments noted above and in Appendix 2. H/RT in distilled water decreased from 0.0071 for PCB no. 8 to 0.0030 (ml/cm³) for 138. These values of H/RT are compared in Appendix Table 1-2 to other direct measurements of H (Murphy et al., 1983), to predictions based on vapor pressure (Bidleman, 1984) and aqueous solubility (Chiou et al., 1983; Mackay et al., 1980a) measurements of the same congeners corrected to the super-cooled liquid reference state (Chiou et al., 1982, 1983), and predictions of H for average n-chlorine substituted PCBs based on the dependence of solubility and vapor pressure on the number of chlorine substituents (Bopp, 1983). There is up to a factor of ten difference among measured H and between measured H and H from predictions based on vapor

Appendix Table 1-2. Measured and predicted Henry's Law constants for PCBs in distilled water. The predicted constants come from vapor pressures (at 25°C) reported by Bidleman (1984) and solubilities (at 20°C) given by Chiou et al. (1983) and Mackay et al. (1980a) and corrected to the super-cooled liquid reference state according to Chiou et al. (1982) assuming that the entropy of fusion is 13.5 cal/°C and using PCB melting points found in Mackay et al. (1980a).

PCB no.	H/RT (ml/cm ³)			
	This study	Murphy et al. (1983)	Predicted (V/S)	Bopp (1983) for nCL-2-6
<u>8</u>	0.0071	0.009	0.013	0.062
<u>28</u>	0.0060	0.008	0.016	0.033
<u>70</u>	0.0036	0.0076	0.0024	0.014
<u>87</u>	0.0030	0.0135	0.0015-0.0077	0.007
<u>138</u>	0.0030	0.020	-----	0.0027

pressures and solubilities. Potential errors exist in the predictive methods used, due to inaccuracies in estimating solubility and particularly vapor pressures of PCBs from parameters measured in experiments, and to a lesser extent on uncertainty involved in converting the solubilities of PCBs to their super-cooled reference state. Henry's Law constants have been predicted to decrease with increasing chlorine substitution by Bopp (1983), which is the trend seen in the ultrafiltered seawater and distilled water results reported here. However, the Henry's Law constants directly measured by Murphy et al. (1983) exhibit an increase in H with increasing chlorines. It is not at all clear why the determinations of H reported by Murphy et al. deviate from those reported here for PCBs bigger than trichlorobiphenyl. Sorption of PCBs to any residual dissolved organic matter is one possible effect which could lead to decreasing H for PCBs with increasing chlorine substitution. However, this is unlikely, given the low concentrations of DOC measured in distilled water (0 - 0.8 mg/L).

The effect of salinity on the aqueous phase activity coefficient can also be seen in Appendix Table 1-1. Henry's Law constants are 1.29 to 1.49 times higher for each chlorobiphenyl in ultrafiltered seawater than in distilled water for the 7-23-85 experiment. If the assumption that $C_T = C_a$ is valid (i.e., that none of the DOC in the ultrafiltrate or distilled water significantly sorbs PCBs), then the ratios of the Henry's Law constants given in Appendix Table 1-1 reflect the ratios of the respective aqueous phase activity coefficients in seawater and distilled water. The apparent salting-out of PCBs (23 - 32%) is similar to reported salting-out of 27-40% determined for five PAH in seawater of 33% salinity at 16.7°C (Whitehouse,

1984). Whitehouse also observed a 87% salting-in of 1,2-benzanthracene under the same conditions. The observations by Whitehouse (1984) and in this study contradict the expectation that the effect of salt on the aqueous phase activity coefficient increases with increasing size or decreasing solubility (McDevit and Long, 1952; Masterson and Lee, 1970) of nonpolar solutes. Further work is still necessary to understand the influence of molecular properties on the salting-out of large hydrophobic organic compounds.

APPENDIX II

EXPERIMENTAL PROBLEMS ENCOUNTERED IN HEADSPACE EXPERIMENTS

Chapter 2 describes the experimental procedures which were used in the static headspace partitioning method for determining the sorption of PCBs with colloidal organic matter for the experiment begun on July 23, 1985. Those procedures were adapted to correct for several methodological problems which became apparent after three earlier sets of experiments. Some of these problems were unfortunately not readily apparent at the time and may have invalidated, or at least complicated the interpretation of, the partitioning results from the earlier experiments. This Appendix briefly outlines the most important problems which were encountered, how they were corrected, and lists some of the partitioning results from the first three experiments.

(1) The initial bottle design used in the first experiment (3-24-84) employed 16 oz amber glass bottles and vapor was sampled and exchanged through brass 1/4" Swagelock fittings and 1/16" stainless steel tubing which were cemented to the plastic bottle caps. Silicone was then used inside the adapted caps to provide a seal with the experimental bottles. PCB concentrations were sampled two to six times between 24 and 96 hrs after the equilibrations were begun in that first experiment. The vapor concentrations in most of the bottles declined during the course of the experiment indicating non-equilibrium conditions. In bottles which were heavily sampled, this decrease in

concentration became slower or not apparent after 60 hr. The container walls and the silicone seal from one bottle were extracted with hexane after sampling the solution phase at the end of the experiment. The silicone seal contained 41 to 71% of the individual congeners accounted for in the bottle. The PCBs in the vapor phase were evidently being slowly absorbed into the silicone phase and the assumption of equilibrium between measured phases at the end of the experiment can not be verified. The partitioning results which are listed for this experiment later assume the final vapor phase measurement represents an equilibrium concentration with the solution phase sampled at the end of the experiment. The problem of silicone seals or other surfaces which might act to absorb PCBs was overcome with use of the all-glass experimental bottles (with a Teflon valve) which are illustrated in Figure 2-1 (Chapter 2).

(2) In the first three experiments, a mixture of four to five PCB congeners was introduced to the experimental bottles by adding 10 - 200 μ L of standard hexane solutions to the bottom of the bottles with a syringe. Solvent was then evaporated with a stream of N_2 for 90 seconds and then seawater was added and equilibrated. A range of PCB concentrations were used, maintaining the individual chlorobiphenyl concentration below their reported aqueous solubilities in the most concentrated bottles. However, in the experiment begun on 4-12-84 concentrations of the mixture of PCBs used in the most concentrated bottles were apparently in excess of the solubilities of those compounds in the mixture used. PCBs of tetra- through pentachlorobiphenyl reached saturation levels in solution and the amount of those compounds found in extracts of the container walls at the end of experiment increased

dramatically in the more concentrated bottles. This may have been due to the use of 3,3',4,4'-tetrachlorobiphenyl in that experiment. This compound appears to have low a solubility in seawater (a large range of solubilities for this compound are reported by Mackay, 1980a) and may have formed a PCB phase in these experimental bottles. Such a phase would have lowered the aqueous concentrations of the other congeners used. The vapor phase concentrations of the individual chlorobiphenyls decreased from the samplings at 36 hr to those at 60 hr in the most concentrated bottles (this was particularly true for the lower solubility compounds used). This is interpreted as a slow "reprecipitation" of PCBs into a PCB phase between the first and second sampling of the vapor. Once again, the partitioning results for this experiment assume that the vapor phase concentrations determined on the last (60 hr) sampling time are at equilibrium. The potential problem of PCB saturation in experimental systems was overcome in the 7-23-85 experiment by first pre-equilibrating ultrafiltered seawater with a standard PCB mixture and then using that as a stock solution to adjust PCB concentrations in the different bottles (Chapter 2).

(3) DOC samples from experimental bottles were taken after all experiments. The DOC determinations from the experiments conducted on 8-29-84 and 4-12-85 were unfortunately not analyzed until May 3, 1985. Those measurements indicated that there was a large DOC contamination in many of the experimental bottles. DOC concentrations ranged from 3.7 to 69.2 mg/L in the former experiment and from values near those anticipated to 55.5 mg/L in the latter experiment. The source of this contamination must have come from the Pyrex

brand low actinic glass bottles which were used for the first time in those experiments. The source of this DOC may have been leaching of an organic carrier phase used in the low actinic coating of the bottles. It is not known what the nature of this dissolved organic matter was or what its possible effect on partitioning results may have been (Appendix 1). This contamination was eliminated for the 7-23-85 experiment by chromic acid leaching of the bottles, followed by combustion overnight at 500°C.

4) Two samples of colloidal organic matter enriched by hollow fiber ultrafiltration on April 12, and June 13, 1985 (Chapter 2) were further concentrated by dialysis (using the same hollow fiber ultrafiltration apparatus) and roto-evaporation, and analysed by pyrolysis capillary gas chromatography (GC) and pyrolysis GC mass spectrometry. The mass spectra indicated that four of the largest peaks in the chromatograms were cyclic dimethylsiloxanes. It is likely that the source of this material was the silicone tubing which was used to pump and recycle the retentate through a Masterflex pump-head on a peristaltic pump during the hollow fiber ultrafiltration. It was not determined what fraction of the enriched colloidal organic matter was actually silicone, to what extent silicone may have contributed to the wet oxidation measurement of enriched colloidal organic matter reported in Table 2-1, or how much silicone affected the partitioning results observed in the first three experiments. The problem of silicone contamination was circumvented in later ultrafiltrations of seawater by using a magnetically-driven stainless steel and Teflon gear pump and stainless steel and glass transfer lines.

(5) Tenax-GC (35-60) mesh was used as an adsorbent in place of Florisil in experiments conducted on 3-24-84 and 8-29-84. Tenax was an effective adsorbent and PCBs could be determined by thermal desorption (300°C) in a Grob-type splitless injector by adapting a 15 cm capillary purge trap in front of the standard analytical column. This "cold-finger" was necessary to achieve higher flow rates ($75 \text{ cm}^3 \text{ min}^{-1}$) required to desorb the PCBs from the Tenax trap. This procedure worked well with the exception of blank and baseline problems which occurred when desorbing traps after exposure to the air. These problems were sporadic but often resulted in long periods of trap and column conditioning due to contamination. The differences in adsorbent traps and vapor analysis would not compromise comparison of results between experiments

The partitioning results determined in the first three experiments were calculated in a manner similar to the sorption isotherm approach outlined in Chapter 2. These results are summarized in Appendix Table 2-1 and compared to results given in Chapter 2 for the 7-23-85 experiment.

Appendix Table 2-1. Summary of partitioning results for static headspace partitioning experiments. The source of the log K_{ow} s are found in Table 2-4.

Chlorobiphenyl	Log K_{ow}	Log K_{oc}			
		3-24-84	8-29-84	4-12-85	7-23-85
2,4'-di CBP	5.11	4.47	4.80	4.72	4.28
2,4,4'-tri CBP	5.68	5.45	---	5.26	4.92
2,3',4',5-tetra CBP	6.19	5.82	---	5.58	4.79
2,2',3,4,5'-penta CBP	6.61	5.76	5.32	5.99	5.19

APPENDIX III

ADDITIONAL DATA TABLES

Complete data tables for K's at Station 67 in New Bedford Harbor, and for the concentrations of individual chlorobiphenyls in sediments and pore waters at Station M in Buzzards Bay are given in Appendix 3-1 and Appendix 3-2, respectively.

Appendix 3-1. A complete listing of the K_d's of PCBs at Station 67 which were not reported in Table 3-4. The Peak numbers reported here refer to PCB #'s and structures given in Table 3-1.

Depth (cm)	PCB Peak No. (See Table 3-1 for PCB identifications)																		
	4	5	7	8	9	10	12	13	14	17	18	19	20	21	22	23	24	25	26
0-3	24.0	8.71	16.4	9.37	14.8	14.8	14.5	22.3	11.3	10.9	15.7	19.4	15.2	16.2	16.3	18.0	14.8	19.9	12.8
3-5	10.1	6.14	3.60	4.46	5.71	2.94	3.94	3.26	4.42	3.58	4.97	3.89	4.67	3.09	3.17	3.54	4.71	6.27	3.86
5-7	4.90	3.40	4.23	4.03	3.85	4.32	4.48	4.72	2.57	2.67	2.78	3.69	2.92	2.62	3.19	3.62	3.01	3.30	2.39
7-9	2.14	1.11	1.84	2.02	2.27	1.91	2.59	3.41	1.71	1.36	1.71	2.12	1.64	2.08	1.92	2.40	1.73	2.35	1.37
9-11	1.35	.879	1.39	1.46	1.94	1.48	2.05	3.05	1.36	1.17	1.45	—	1.42	1.71	1.71	2.11	1.22	1.94	.960
11-13	4.78	2.45	3.29	2.63	3.54	3.22	3.58	6.43	1.96	1.92	2.67	3.09	2.48	3.07	3.30	4.47	2.13	3.99	1.67
13-17	3.08	2.05	2.41	2.61	3.33	2.39	6.17	8.17	1.95	2.14	3.16	3.80	2.80	3.82	4.93	3.48	2.79	4.17	1.99
17-19	5.25	3.17	4.00	3.37	4.41	4.14	4.60	10.1	2.52	2.16	2.81	3.47	2.68	3.44	3.87	4.65	2.00	4.59	1.55
19-21	6.35	6.75	4.39	6.34	4.09	4.98	7.74	9.62	2.16	2.07	2.50	3.62	2.07	3.10	4.50	4.76	1.96	4.27	1.52
21-23	10.9	8.45	5.92	10.0	5.75	5.36	9.36	13.4	3.09	—	3.45	4.64	3.16	3.64	4.64	3.14	2.49	3.92	1.93
23-25	1.52	1.39	1.60	2.11	2.80	1.75	3.95	1.22	4.06	2.82	3.45	4.46	3.34	4.59	5.92	5.65	2.53	3.73	2.07
25-27	1.76	1.73	1.80	2.65	3.58	2.16	4.63	12.1	4.23	3.25	4.89	5.57	4.29	6.01	7.10	7.52	3.13	8.08	2.63
27-29	2.64	2.43	3.21	7.51	5.96	4.44	7.87	12.8	7.54	5.54	6.51	6.92	6.33	8.29	7.80	8.57	3.87	9.80	3.24
29-31	1.03	1.42	1.02	1.73	1.98	1.70	3.78	5.34	5.63	3.74	5.13	3.79	4.61	7.18	6.36	6.56	3.08	6.65	2.68
33-41	2.35	1.89	2.29	1.61	1.60	2.01	2.48	1.69	2.32	1.92	2.25	1.18	1.60	3.40	2.87	2.51	1.43	1.74	1.63

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Appendix 3-1 continued. Missing K'_d in the 0-1 cm section are due to contamination of pore water sample (Chapter 3).

Depth (cm)	PCS Peak No. (Table 3.1)				$K'_d \times 10^{-3}$ (L/Kg)														
	28	29	30	31	32	33	35	36	37	39	41	42	43	44	45	46	47	48	49
0-3	10.4	11.1	12.1	13.5	12.0	9.08	—	—	—	—	—	—	—	—	—	—	—	—	—
3-5	3.24	2.31	3.68	4.21	3.78	3.15	4.80	3.19	3.42	4.27	3.13	3.13	3.14	3.53	3.46	2.77	2.68	3.19	3.30
5-7	2.27	2.88	2.56	2.90	2.55	2.25	2.16	1.96	2.08	2.66	2.01	1.98	2.08	2.43	2.03	2.13	1.82	2.45	2.74
7-9	1.22	1.39	1.46	1.59	1.42	1.13	1.67	.948	1.08	1.72	1.04	.970	1.08	1.52	1.23	.903	.890	1.25	1.38
9-11	.906	.882	.964	1.03	.948	.898	1.03	.620	.695	1.19	.697	.558	.668	—	.693	.536	.498	.729	.792
11-13	1.60	1.57	1.74	1.90	1.78	1.24	2.03	1.07	1.23	2.57	1.14	1.07	1.19	1.49	1.27	.907	.887	1.25	1.31
13-17	2.22	2.16	2.10	2.17	1.98	1.45	1.97	1.37	1.41	3.55	1.18	.928	1.70	1.64	1.39	1.11	1.27	1.61	1.76
17-19	1.39	1.58	1.64	1.77	1.70	1.17	1.86	1.08	1.22	2.50	1.14	1.07	1.20	1.40	1.79	.928	.904	1.28	1.40
19-21	1.62	1.54	1.53	1.74	1.63	1.05	1.76	1.16	1.28	2.90	1.15	—	1.52	1.26	1.39	1.11	1.10	1.58	1.88
21-23	1.66	2.10	1.91	2.08	1.76	1.30	2.33	1.14	1.27	2.86	1.12	1.02	1.54	1.81	1.71	1.06	1.13	1.56	2.06
23-25	2.17	2.88	2.14	2.23	2.14	1.69	2.45	1.55	1.75	2.88	1.34	1.16	3.82	1.43	1.39	1.09	1.10	1.38	1.62
25-27	2.58	2.46	2.81	3.08	3.00	2.08	3.24	1.49	2.16	4.05	2.02	1.88	2.12	2.40	2.38	1.82	1.74	2.34	2.43
27-29	3.29	2.94	3.29	3.37	3.24	2.52	3.51	2.19	2.52	4.29	2.09	2.02	2.30	2.43	2.21	1.74	1.77	2.28	2.57
29-31	2.69	2.61	2.79	2.96	2.90	2.02	3.16	1.88	2.07	3.68	1.85	1.64	1.91	1.86	2.04	1.44	1.47	1.92	2.21
33-41	2.05	1.34	1.28	1.43	1.35	1.13	1.38	1.67	1.55	2.26	1.75	1.77	1.40	1.19	1.10	1.24	1.33	1.73	1.29

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Appendix 3-2. Sediment and pore water concentration data for individual chlorobiphenyls at Station N. These data are for congeners which are not reported in Table 3-6 and whose response factors had been determined. Some of the data refer to PCBs which co-elute on the GC with one or more additional congeners, but are quantified as the PCB given. Structures of the PCB #'s are given in Table 3-1 and Figure 3-10.

Depth (cm)	Sample	PCB no.:	Concentration						Sediment (ng/g dry wt.)				
			18	48	44	40	60	86	131	105	141	137	129
0-1 sediment			2.71	4.78	3.15	1.05	2.05	3.15	.943	5.45	.859	.480	.735
0-1 pore water			.331	1.09	.617	.132	.491	.772	.336	1.39	.158	.138	.229
1-3 sed.			1.62	4.53	2.73	.566	2.60	6.01	1.05	6.21	1.04	.543	.817
1-3 p.w.			.474	.976	.620	.506	.684	1.82	1.06	1.83	.401	.117	.215
3-5 sed.			1.63	3.53	2.34	.596	1.50	3.69	.676	3.96	.600	.306	.520
3-5 p.w.			.468	1.57	.817	.208	—	2.74	.444	1.92	.264	.171	.328
5-7 sed.			3.38	9.84	7.09	1.60	2.38	5.25	1.18	6.91	1.05	.567	.906
5-7 p.w.			.835	2.23	1.23	.756	1.60	4.11	.511	2.37	.372	.193	.364
7-9 sed.			2.95	8.44	6.01	1.64	2.34	5.05	1.09	6.09	.963	.485	.759
7-9 p.w.			.918	2.39	1.29	.655	1.42	3.60	.455	1.92	.311	.148	.291
9-11 sed.			3.33	7.86	4.56	1.30	2.45	5.29	2.70	7.92	—	—	—
9-11 p.w.			1.17	3.78	3.01	1.77	1.14	4.68	1.51	1.75	—	—	—
11-13 sed.			3.98	11.2	8.80	2.01	2.04	5.50	3.05	7.54	.762	.390	.776
11-13 p.w.			1.03	3.81	2.61	1.44	1.25	3.79	.768	2.60	.245	.278	.565
13-15 sed.			2.81	8.16	3.68	1.24	1.58	5.06	2.83	6.74	.651	.365	.732
13-15 p.w.			1.32	4.43	1.79	.522	1.30	3.62	.857	2.91	.266	.223	.444
15-17 sed.			1.62	5.53	2.03	.730	.956	4.23	2.48	6.75	—	—	—
15-17 p.w.			.810	3.21	1.12	.357	1.11	3.17	.701	2.38	.231	.192	.365
17-19 sed.			1.52	5.63	2.24	1.03	.563	3.08	1.51	4.67	1.22	—	—
17-19 p.w.			.88	2.57	1.06	.295	.316	1.92	.480	1.59	.198	.228	.267
19-21 sed.			.899	3.71	1.31	.581	—	2.38	1.46	3.93	.689	—	—
19-21 p.w.			.518	1.89	.688	.243	.331	1.00	.390	1.24	.305	.193	.351
21-23 sed.			.608	2.52	.884	.389	—	1.49	.921	1.51	.212	.134	.209
21-23 p.w.			.673	1.77	.621	.185	.306	.667	.320	1.04	.217	.0847	.174
23-25 sed.			.379	1.49	.527	.212	—	.711	.217	.803	.0968	.115	.221
23-25 p.w.			.493	1.34	.566	.174	.220	.762	.228	.766	.151	.104	.185
25-29 sed.			.239	.921	.351	.157	—	.430	.274	.654	.233	—	—
25-29 p.w.			.238	.309	.233	.0546	.0989	.270	.0739	.273	.0486	.0337	.0712
29-35 sed.			.184	.505	.227	—	—	.247	.147	.345	.125	—	—
29-35 p.w.			.163	.350	.189	.0383	.0658	.234	.0677	.227	.0244	.0323	.0733
35-43 sed.			—	.0708	—	—	—	.0702	—	.0785	—	—	—
35-43 p.w.			.8687	.184	—	—	—	.126	.8405	.0974	.0370	.0256	.0474

Appendix 2-2 continued.

Depth (cm)	Sample	PCB no.:	Concentration										
			Sediment (ng/g dry wt.) Pore water (ng/L)										
			187	183	128	136	200	180	201	196	195	194	209
0-1 sediment			1.26	.663	2.39	1.57	.626	1.39	.648	.423	.326	.292	.366
0-1 pore water			.365	.280	.836	.506	.194	.581	.284	.186	.200	.128	.0935
1-3 sed.			1.48	.775	2.77	1.76	.715	1.79	1.30	.979	.569	.664	1.20
1-3 p.w.			.457	.238	.742	.421	.144	.301	.273	.170	.190	.178	.173
3-5 sed.			.881	.469	1.74	1.14	.509	.924	.443	.252	.201	.196	.385
3-5 p.w.			.696	.311	1.10	.675	.348	.673	.397	.223	.166	.234	.163
5-7 sed.			1.54	.844	3.15	1.94	.880	1.68	.770	.487	.315	.329	.315
5-7 p.w.			.819	.425	1.33	.760	.368	.893	.686	.269	.184	.192	.737
7-9 sed.			1.39	.741	2.77	1.68	.738	1.54	.706	.498	.275	.333	.371
7-9 p.w.			.699	.376	1.09	.609	.223	.694	.370	.213	.167	.167	.188
9-11 sed.			2.48	---	3.59	1.76	.780	1.66	.887	.500	---	---	1.04
9-11 p.w.			---	---	2.79	---	---	1.75	.914	.513	.264	.399	.149
11-13 sed.			1.41	.902	3.05	1.67	.779	1.58	.797	.501	.280	.286	1.02
11-13 p.w.			.976	.487	1.53	.798	.398	.910	.458	.322	.280	.412	.366
13-15 sed.			1.30	.951	2.86	1.57	.740	1.37	.722	.412	.309	.288	1.02
13-15 p.w.			.990	.654	1.74	1.05	.640	.928	.496	.290	.282	.242	.308
15-17 sed.			1.97	1.70	2.39	1.14	.575	.900	.469	.270	.203	.155	.395
15-17 p.w.			.828	.569	1.43	.889	.423	.822	.417	.227	.200	.178	---
17-19 sed.			1.32	1.28	2.46	1.69	1.43	1.24	.629	.362	.201	.185	.403
17-19 p.w.			.562	.425	1.04	.620	.387	.619	.328	.218	.171	.184	.314
19-21 sed.			1.16	1.34	1.95	1.86	1.35	.948	.496	.254	.172	.174	.362
19-21 p.w.			.482	.246	.699	.494	.314	.442	.363	.296	.197	.216	.151
21-23 sed.			.483	.385	.874	.609	.350	.380	.300	.199	.134	.0705	.428
21-23 p.w.			.357	.232	.356	.385	.280	.450	.254	.330	.0828	.110	.0869
23-25 sed.			.827	.232	.498	.328	.228	.288	.241	.158	.187	.114	.256
23-25 p.w.			.294	.221	.464	.374	.181	.336	.378	.271	.160	.0880	.111
25-29 sed.			.211	.260	.391	.297	.257	.222	.249	.190	.214	.137	.207
25-29 p.w.			.0982	---	---	.154	.186	.174	---	---	---	---	---
29-33 sed.			.186	.138	.203	.156	.145	.0893	.140	.0777	---	.0709	.0875
29-33 p.w.			.0738	---	.147	.136	.0971	.160	---	---	---	---	---
33-43 sed.			---	.188	.0833	---	---	---	---	---	---	---	---
33-43 p.w.			.0188	---	.0652	.0846	.0725	.0916	.172	.0926	---	.0383	.0891

BIOGRAPHICAL NOTE

The author was born on December 9, 1957 in Moline, Illinois and lived in nearby Orion until moving to Arlington Heights, Illinois in 1962, where he lived through college. He graduated from Rolling Meadows High School in 1976 and then attended DePaul University in Chicago from which he earned a Bachelor of Science in Chemistry in 1980. Since 1980, he has been a student in the MIT/WHOI Joint Program in Oceanography. He is a member of the American Chemical Society.

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