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Aeration Effects on the Partitioning of a PCB to Anoxic Estuarine Sediment Pore Water Dissolved Organic Matter

JOEL A. PEDERSEN,[†]
CHRISTOPHER J. GABELICH,[†]
CHEN-HUNG LIN,[‡] AND I. H. SUFFET*,[‡]

Environmental Science and Engineering Program, School of Public Health, University of California, Los Angeles, California 90095-1772

Pore water dissolved organic matter (DOM) plays an important role in the distribution, mobility, and bioavailability of hydrophobic organic chemicals (HOCs) in sediment environments. The effect of aeration on the partitioning of 2,2′,4,4′-tetrachlorobiphenyl (TeCB) to anoxic pore water DOM from three estuarine sites was investigated. Pore water DOM was fractionated into molecular size and polarity fractions by ultrafiltration and XAD-8 resin chromatography. Total organic carbon analysis was utilized to determine shifts in molecular size and polarity distributions. Changes in functional groups and aromaticity were evaluated for whole and fractionated pore waters by specific UV absorbance at 254 nm ($SUVA_{254}$). The solubility enhancement method was used to determine the partitioning of TeCB to whole and fractionated pore water DOM. At two sites, the overall TeCB-DOM distribution coefficient decreased by an order of magnitude after aeration. The higher molecular size and all polarity fractions exhibited a decrease in partitioning behavior upon aeration. The aromaticity and TeCB-DOM distribution coefficient of the lowest molecular size fraction (<1000 Da) decreased upon aeration. The highest (>10 000 Da) and lowest (<1000) molecular size fractions contributed the most to overall partitioning. The observed aeration effects in anoxic estuarine sediment pore waters differed significantly from those previously reported in freshwater systems.

Introduction

Estuarine and marine sediments represent an important reservoir for recalcitrant hydrophobic organic pollutants, such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (*1, 2*). Assessment of the environmental risk posed by these pollutants and evaluation of alternative management strategies require an accurate understanding of the distribution of hydrophobic organic chemicals (HOCs) in sediment environments. The distribution and bioavailability of HOCs in natural and disturbed sediment environments depends on their association with various sediment phases, i.e., mineral surfaces, sediment-bound organic matter, pore water, and pore water dissolved organic matter (DOM) (*1, 3−8*). The association of HOCs with the various sediment phases is affected by sorbent and sorbate properties (*1*), as well as matrix effects (*8, 9*).

Pore water DOM represents a pool of organic matter that plays an important role in the distribution, mobility, and bioavailability of HOCs. The association of HOCs with DOM results in higher pore water concentrations (*10−18*) and reduced bioavailability (*2, 14, 19, 20*). Only freely dissolved HOCs appear to be taken up by benthic organisms through ventilation of sediment interstitial water and contaminated overlying water. The measured concentration of a chemical in sediment pore water, or the apparent solubility (C_{pw}), is the sum of the freely dissolved (C_{aq}) and DOM-associated chemical concentrations (C_{pwdom}) expressed in μg/L (*21, 22*):

$$C_{pw} = C_{aq} + C_{pwdom} \quad (1)$$

The partitioning of a HOC between the aqueous and DOM phases is expressed as an equilibrium distribution coefficient (K_{pwdom}) defined as the ratio of the bound (μg/L) to dissolved (μg/L) concentration normalized by the DOM concentration (mg-C/L) found in the pore water:

$$K_{pwdom} = C_{pwdom}/C_{aq}\,[DOM_{pw}] \times 10^6 \quad (2)$$

where 10^6 is a unit conversion factor so that K_{pwdom} has units of L/kg to be more directly comparable to sediment organic carbon partition coefficient (K_{oc}).

Pore water DOM is derived from the decomposition of aquatic and terrestrial organisms and the byproducts of microbial metabolism, and is composed of a heterogeneous mixture organic molecules including humic acids, fulvic acids, hydrophilic acids, carbohydrates, amino acids, carboxylic acids, and hydrocarbons (*23, 24*). These molecules differ in size, polarity, functional groups, degree of branching, and macromolecular configuration. Various analytical techniques (e.g., field flow fractionation, resin chromatography, size exclusion chromatography, ultracentrifugation, ultrafiltration) have been employed to fractionate DOM on the basis of one or more of these properties (*1, 25*). Each DOM fraction binds HOCs to a different extent (*26, 27*). Structural characteristics, such as degree of aromaticity, polarity, C/H ratio, molecular size, and molecular configuration differ between the various fractions and are responsible for the differing sorptive capacities of pore water DOM fractions.

Changes in ionic strength can alter the molecular configuration of humic substances (*28*). Ghosh and Schnitzer (*29*) proposed that, at high concentrations of neutral electrolytes, DOM molecules exist as rigid "spherocolloids" with hydrophobic interiors and hydrophilic exteriors (Figure 1). The macromolecular structure of humic substances can also be altered by changes in pH. As the hydrogen ion concentration increases, the molecular diameter of humic macromolecules was found to increase (*30*). Ghosh and Schnitzer (*29*) described humic substances as "flexible linear colloids" under neutral pH conditions with coiling to rigid "spherocolloids" at low pH (Figure 1). Engebretson and von Wandruszka (*31*) found that the spherocolloid, or pseudomicellar, conformation of humic acids were of transitory nature. Their studies, however, were conducted at ionic strengths far lower than that of seawater (i.e., $I = 7.24 \times 10^{-5}$ to 2.60×10^{-4} M compared to 0.7 M for seawater).

The interaction of HOCs with pore water DOM should differ markedly in freshwater and saltwater. HOCs interact

* Corresponding author telephone (310) 206-8230; fax: (310) 206-3358; e-mail: msuffet@ucla.edu.
[†] Environmental Science and Engineering Program.
[‡] Environmental Health Science Department.

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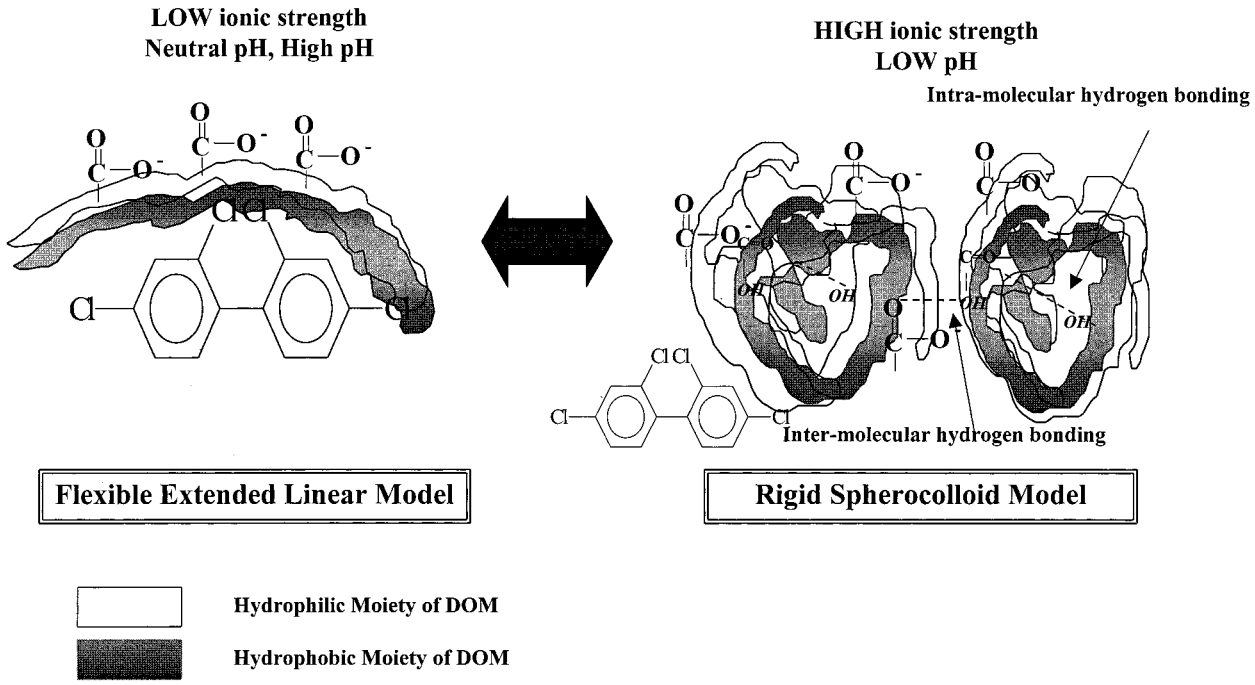

FIGURE 1. Influence of ionic strength and pH on the macromolecular structure of a model of humic substance.

primarily with the hydrophobic domains of DOM macromolecules. The water of hydration along linear polyfunctional macromolecules differs around charged and hydrophobic segments. Charged sites are surrounded by α-structure water which participates in hydrogen bond formation, while hydrophobic segments are enveloped by β-structure water. The binding of a HOC to a DOM macromolecule involves the displacement of the water of hydration (*4*). The displacement of β-structure water by an HOC is thermodynamically favored over the removal of the tightly bound α-structure water (*4*). In freshwater systems, DOM macromolecules exist in a linear configuration with the hydrophobic domains surrounded by β-structure water. In high ionic strength solutions, DOM macromolecules fold upon themselves and the hydrophobic domains are concentrated in the interior of the coiled macromolecules. To bind to the hydrophobic domains in the interior of these DOM molecules, HOCs must displace the α-structure water of hydration surrounding the hydrophilic moieties on the exterior of the spherocolloids. Thus, in saltwater solutions, the hydrophobic domains are less accessible and HOCs must interact with a macromolecule with more highly charged/polar surface.

Just as Karickhoff (*32*) described a composite partition coefficient for the binding of HOCs to sediment organic matter, the sediment pore water DOM−HOC distribution coefficient may be considered a linear combination of the interactions of the constituent DOM fractions:

$$K_{\text{pwdom}} = \sum K_i f_i \tag{3}$$

where K_i is the distribution coefficient of the ith DOM fraction, and f_i is the mass fraction of the ith DOM fraction. This relationship, however, has not been found to hold for freshwater sediment systems (*27*). The total or initial unfractionated K_{pwdom} did not equal the mass-weighted sum of the individual fractions.

Many environmental processes, such as transport across the saltwater wedge, sediment resuspension during storms, and bioturbation, alter the chemistry of the aqueous matrix in which DOM resides. Ionic strength, pH, divalent cation concentration, and redox potential (Eh) influence the structure (*29*) and composition of DOM (*7, 22*), as well as the association of HOCs with pore water dissolved organic matter (*9, 22, 33*). Previous studies have examined the influence of pH and ionic strength on the association of HOCs with DOM (*22, 27, 33*). Relatively few have investigated the role of redox potential on the partitioning of HOCs to pore water DOM (*22, 34*). Oxidation of organic matter in anoxic pore water, for example, during the dredging of sediments, seasonal migration of the redoxcline, or sediment resuspension by storm events, changes the macromolecular structure, molecular weight distribution, and total concentration of pore water DOM, as well as its propensity to bind HOCs (*34, 35*). An understanding of these changes in pore water DOM structure and HOC partitioning can contribute to the evaluation of the environmental risks posed by in-place contaminants and alternative sediment remediation strategies.

In this study, anoxic pore waters from three estuarine sediment environments were aerated and the resultant changes in the DOM structure, composition, and association with a model HOC (2,2′,4,4′-tetrachlorobiphenyl) examined. Pore water DOM was fractionated into molecular size fractions by sequential batch ultrafiltration and into polarity fractions by XAD resin chromatography. Total organic carbon (TOC) analysis was utilized to determine shifts in molecular size and polarity distributions. Changes in functional groups and aromaticity were evaluated for whole and fractionated pore waters by specific UV absorbance at 254 nm ($SUVA_{254}$). The effect of aeration on the partitioning of HOCs to pore water DOM was evaluated using the solubility enhancement method (*27, 34*).

The normalization of ultraviolet absorbance (A_{254}) by the dissolved organic carbon (DOC) concentration provides a measure of the aromatic content of the DOM and is termed the specific UV_{254} absorbance or $SUVA_{254}$ (*36*−*38*). $SUVA_{254}$ is the ratio of the absorbance to the DOC concentration (mg-C/L) with units of L/mg-C/m:

$$\text{SUVA}_{254} = \text{A}_{254}/\text{DOC} \times 10^2 \tag{4}$$

where 10^2 is a unit conversion factor. Higher $SUVA_{254}$ values

correspond to DOM that is more hydrophilic, aromatic and of higher molecular weight (*36*). These molecules more hydroxyl-, carbonyl-, ester-, and carboxyl-substituted aromatic rings than DOM with lower $SUVA_{254}$ value (*39*).

Experimental Methods

Sample Collection. Three estuarine sites with anoxic sediments were selected in southern California. Two sites (Newport 1 and 2) were located in the Upper Newport Bay Ecological Reserve. Newport 1 was located in a small tidal channel in a pickleweed (*Salicornia*) marsh, while Newport 2 was in a shallow tidal channel on a mudflat. The third estuarine site was located in a pickleweed marsh at Point Mugu Naval Air Weapons Station. All three sites had pore water DOM concentrations of at least 15 mg-C/L.

Anoxic sediment samples were collected in 1-L and 2-L glass jars fitted with Teflon-lined closures. Care was taken to prevent sample contact with atmospheric oxygen. Samples were stored at 4 °C in the dark until processed.

Pore Water Extraction. Pore water was extracted from sediment samples by pressure filtration through a PreSep TCLP 0.7 μm glass fiber filter (Cat. No. G07WP14225, MSI, Westboro, MA) under a maximum pressure of 35 psig N_2 (oxygen-free grade) in a Teflon-lined hazardous waste filtration unit (Cat. No. YT30142HW, Millipore Corp., Bedford, MA). For the Newport sites, pore water to be aerated was collected without regard to contamination by atmospheric oxygen. Newport site pore water to be treated anoxically and all Pt. Mugu pore water was collected in nitrogen-purged amber bottles and stored under nitrogen in a glovebag at 4 °C in the dark. Care was taken to avoid excessive agitation of samples to minimize coagulation of colloidal components (*35*). Pt. Mugu samples were split, and half the pore water volume was treated under oxic conditions and half under anoxic conditions. All subsequent processing of anoxic samples was performed in an anoxic glovebox (LabCono, Inc.).

"Oxic" pore water was prepared by bubbling zero-grade air (first passed through a moisture trap, GAC column, and organic carbon-free water) through anoxic pore water for 4−13 days. The prolonged exposure of pore water DOM to oxidative conditions was not intended to mimic conditions in estuarine or marine environments, but to achieve a level of oxidation that would enable the measurement of changes in partitioning of TeCB to pore water DOM. Although the length of aeration time affects the absolute magnitude of changes in partitioning, the direction of change remains the same. This was verified by aerating the same pore waters for different time periods. Prior to use, oxic samples were filtered through a 0.7 μm glass fiber filter to remove precipitated iron and coagulated DOM. Seawater passed through a GAC column was used as reference water. The DOC concentration in the reference water was 0.8 mg-C/L.

Water Quality Measurements. Pore water conductivity was measured with a Model 1484 conductivity meter (Chemtrix, Inc., Hillsboro, OR). An Accumet 950 pH/ion meter (Cat. No. 13-636-950, Fisher Scientific, Pittsburgh, PA) equipped with Accumet combination pH electrode with calomel reference (Cat. No. 13-620-270, Fisher Scientific, Pittsburgh, PA) was used to measure pH. Redox potential was measured with an ORP (Redox) combination electrode (Cat. No. 05990-55, Cole-Parmer Instrument Co., Vernon Hills, IL). Ferrous and total iron were measured using the bathophenanthroline method (*40*−*42*). Alkalinity was determined by titration (*43*). Metal concentrations in the sediment pore water were determined by inductively coupled plasma/atomic emission spectrometry (ICP/AES) using a Perkin-Elmer Optima 3000 DA ICP/AES spectrometer (*43*).

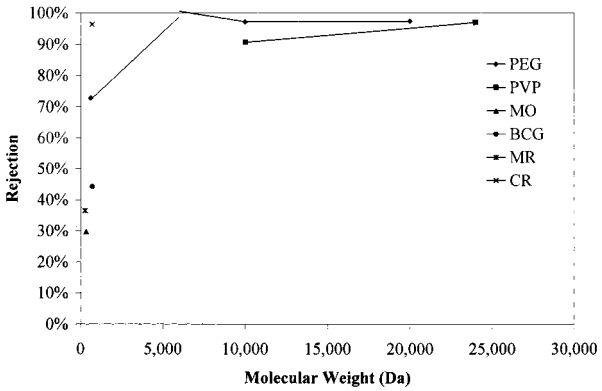

FIGURE 2. Rejection of probe solutes by an Amicon YM10 (10 kDa MWCO) ultrafiltration membrane. PEG = poly(ethylene glycol); PVP = polyvinyl pyrolidone; MO = methyl orange; BCG = bromocresol green; MR = methyl red; CR = Congo red. All solutions were prepared in 0.01 M orthophosphate buffer (pH 7.3).

Ultrafiltration. Samples of anoxic and oxic sediment pore water were fractionated by sequential ultrafiltration through 76 mm diameter Amicon YM10, YM3, and YM1 membranes (Amicon, Inc., Beverly, MA). These membranes have nominal molecular weight cutoffs (MWCO) of 10 000, 3000, and 1000 Da, respectively (*44*). The membranes were characterized using several homologous series of probe compounds. Example results of this characterization are shown in Figure 2; details are reported elsewhere (*45*). Ultrafiltration was performed in a 400-mL, Teflon-lined, stainless steel, stirred ultrafiltration cell pressurized with nitrogen at 35 psig.

Prior to use, ultrafiltration membranes were soaked in a 5% NaCl solution for at least 30 min to remove the glycerin preservative added by the manufacturer. This was followed by at least a 60 min soaking in deionized (DI) water (Milli-Q Plus water system, ZD 40 115 95, Millipore Corp., Bedford, MA) with three water changes. After placement in the ultrafiltration cell, membranes were rinsed with 100 mL of DI water prior to running a 100 mL DI water blank. These pretreatment steps reduced the amount of organic carbon leached from the membranes to a level below experimental error. Because the literature is unclear whether ultrafiltration membranes can be reused without leaching or interference of previously sorbed material (*46, 47*), membranes were used only once and then discarded.

Pore waters were fractionated sequentially by ultrafiltration to achieve >10 kDa, 3−10 kDa, 1−3 kDa, and <1 kDa molecular size fractions. Filtration was discontinued once approximately 67% of the initial volume had passed through the membrane to minimize breakthrough (*1*). Sequential fractionation was used to minimize concentration polarization and filter clogging (*35, 48*).

XAD Resin Fractionation. XAD-8 resin, an acrylic ester nonionic polymeric adsorbent, (40/60 mesh beads; Alltech Associates, Inc. Deerfield, IL) was rinsed with 0.1 N NaOH and then Soxhlet extracted for 24 h sequentially with methanol, diethyl ether, acetonitrile, and methanol (*49*). Prior to each sample application the cleaned XAD-8 resin was rinsed with 0.1 N NaOH followed by 0.1 N HCl three times (*50*). Oxic and anoxic samples were fractionated into hydrophobic acid (HbA), hydrophobic neutral (HbN), and hydrophilic (Hl) subcomponents by the method detailed in Kukkonen et al. (*51*).

Solubility Enhancement Method. 2,2′,4,4′-Tetrachlorobiphenyl (TeCB, PCB-47) was used as model hydrophobic organic chemical to evaluate pollutant association with pore water DOM. Radiolabeled ^{14}C-TeCB (1.0 μCi/mL) was pur-

TABLE 1. Aeration Effects on Estuarine Sediment Pore Water pH, Alkalinity, Total and Ferrous Dissolved Iron Concentrations (mg/L)[a]

	pH		alk (mg/L as $CaCO_3$)		Fe^{2+} (mg/L)		Fe_T (mg/L)	
site	anoxic	oxic	anoxic	oxic	anoxic	oxic	anoxic	oxic
Newport 1	8.0	8.9	891.5	534.9	5.1	0.3	8.6	2.1
Newport 2	8.2	9.0	891.5	490.3	1.3	0.9	3.5	2.4
Pt Mugu	7.8	8.8	852.7	668.6	4.4	0.6	4.9	0.9

[a] Iron measurements were made by the bathophenanthroline method (*40*−*42*).

chased as a toluene solution from Sigma Chemical Co. (Cat. No.29751-8). Unlabeled TeCB was purchased from Chem Service Inc. (Cat. No. 7822G, West Chester, PA). TeCB solubility in reference seawater and solubility enhancement were determined following the method of Hunchak-Kariouk and co-workers (*27, 34*). Ecolite (+) (Cat. No. 882475, ICN Biomedical, Inc., Costa Mesa, CA) was used as the liquid scintillation cocktail, and apparent solubility determined using a Beckman LS1800 liquid scintillation counter (Beckman Instruments, Palo Alto, CA).

DOM Characterization. Each pore water DOM fraction was characterized using a combination of techniques. The dissolved organic carbon concentration in each fraction (mg total dissolved nonpurgable organic carbon/L) was measured with a DC-80 automated laboratory TOC analyzer (Xertex Corp., Santa Clara, CA) using mercuric chloride/mercuric nitrate/potassium persulfate oxidation (proprietary method for chloride complexation, *52*). Except for the anoxic Pt. Mugu fractions, duplicate DOC measurements were usually within 0.2 mg-C/L of each other. Ultraviolet absorbance at 254 nm of whole and fractionated pore waters was measured using a Hewlett-Packard 8451A diode array spectrophotometer. With the exception of the anoxic Pt. Mugu fractions, duplicate measurements generally ranged between 0.02 and 0.2 L/mg-C/m.

Results and Discussion

Aeration Effects on Water Quality Parameters. Anoxic pore water collected from all three sites showed a 0.8−1.0 unit pH increase upon aeration (Table 1). The increase in pH was probably primarily due to the removal of the weak Lewis acid Fe^{2+}($pK_a = 9.5$) from solution by the precipitation of ferric hydroxide (see below). During the aeration process, hydrogen sulfide ($pK_a = 7.1$) may have been stripped out of solution, further increasing the pH. Hunchak-Kariouk et al. (*34*) also noted a pH increase of comparable magnitude when anoxic freshwater sediment pore water containing appreciable dissolved iron (45 mg/L) was aerated.

Pore water alkalinity, the acid neutralizing capacity (ANC) of the aqueous system, decreased in all three samples (Table 1). In addition to the carbonate buffer system, other protolysis systems, such as borates, phosphates, silicates, and sulfides, contribute to the ANC of estuarine sediment pore waters (*53*). ICP data revealed that the observed decrease in alkalinity upon aeration was probably due to the precipitation of calcium phosphates and calcium, strontium, and manganese carbonates. The precipitation of these species was apparently in response to the increase in pore water pH due to aeration. The decrease in alkalinity was greater for the Newport sites (357−401 mg/L as $CaCO_3$) than for the Pt. Mugu site (184 mg/L as $CaCO_3$).

Aeration of anoxic pore water resulted in a decrease in both total and ferrous dissolved iron concentration for all sites (Table 1). Previous investigators noted a decrease in total dissolved iron levels when anoxic sediments were exposed to atmospheric oxygen during sample handling (*35*). The increase in redox potential brought about by the introduction of oxygen into the anoxic system caused the oxidation of iron from the Fe(II) to Fe(III) state. The dissolved iron concentration and pH of the system were within the range for $Fe(OH)_3$ precipitation (*53*). Ferric hydroxide precipitation removed a weak Lewis acid from solution and resulted in an increase in pH.

Ionic strength remained approximately the same for the two Newport pore waters but decreased significantly for the Pt. Mugu sample. The decrease in ionic strength observed upon aeration of Pt. Mugu pore water was probably due to the precipitation of ferric hydroxide, calcium and strontium carbonates, and calcium phosphates upon aeration. Total iron concentration decreased nearly one order of magnitude for this sample. Aeration of anoxic pore water resulted in an order of magnitude decrease in phosphorus concentration (4.6 mg/L in anoxic pore water to 0.46 mg/L after aeration). Orem and Gaudette (*35*) also noted a large decrease in phosphate concentration when anoxic pore water was oxidized during laboratory handling.

Whole Pore Waters. Sediment pore water DOM was characterized by TOC analysis and UV absorbance at 254 nm to correlate DOM structure and composition with observed pore water DOM distribution coefficients. Slightly different values for whole pore water DOC, $SUVA_{254}$, and K_{pwdom} were obtained from the ultrafiltration and XAD resin fractionation experiments. The variability of the results was probably due to differences in the particular jars of sediment used for each method. Ultrafiltration and XAD resin chromatography were performed on different days, using separate bottles of pore water from the same batch of composited sediment. Complete mixing of the entire batch of pore water was not possible because of the difficulty of manipulating large volumes of anoxic water in a glovebox. While the absolute values of the measured parameters differed slightly for the whole pore waters, the general trends observed were consistent between both treatments.

DOC concentrations in whole (unfractionated) pore waters decreased by over 24% for two sites (Newport 2 and Pt. Mugu) upon aeration (Table 2). This decrease in DOC concentration was probably a consequence of coagulation with precipitating Fe(III) hydroxides. The pore water iron concentration and pH were within the sweep coagulation range (*54*). DOM has been shown to participate in complexation or adsorption reactions with iron oxides and hydroxides (*37, 39*). Several researchers noted similar decreases in estuarine and riverine pore water DOC concentrations attributable to coagulation with $Fe(OH)_3$ (*34, 35*). The DOC concentration in pore water from Newport 1 did not significantly decrease.

Aeration of anoxic pore waters caused a 0.8−2.2 L/mg-C/m decrease in $SUVA_{254}$ at all sites (Table 2). This decrease in specific absorbance occurred regardless of whether the DOM concentration was altered by aeration. The decrease in $SUVA_{254}$ can therefore be interpreted as resulting from both the selective coagulation of DOM molecules rich in oxygenated functional groups and the oxidative cleavage of aromatic groups (*39*). The ferric/ferrous iron system has been shown to catalyze the oxidation of organic molecules containing hydroxy carboxylic functional groups (e.g., phe-

TABLE 2. Effect of Aeration on the DOC Concentration and Specific Absorbance at 254 nm, $SUVA_{254}$, of Whole and Fractionated Anoxic Pore Waters[a]

		DOC (mg-C/L)		$SUVA_{254}$ (L/mg-C/m)	
site	DOM fraction	anoxic	oxic	anoxic	oxic
Newport 1	whole pore water	18.6−18.8	17.7−18.0	5.06−5.44	4.14−4.22
	> 10 kDa	0.4−0.5	0.7−0.8	3.80−3.99	2.83−3.11
	3−10 kDa	2.1−2.1	2.4−2.5	3.30−3.40	3.20−3.36
	1−3 kDa	10.0−10.4	5.5−5.7	2.54−2.69	3.13−3.20
	<1 kDa	10.4−10.6	5.1−5.2	1.02−1.04	1.90−2.14
	HbA	14.4	11.0- 11.0	3.73	2.65−2.67
	HbN	5.8−5.9[b]	2.1−2.1	−[b]	1.68−1.71
	HI	2.9	7.7−7.9	2.26	0.86−0.92
Newport 2	whole pore water	15.9−15.9	11.6−11.6	4.94−5.05	2.87−2.93
	> 10 kDa	1.2−1.3	1.3−1.4	3.67−3.80	2.52−2.60
	3−10 kDa	2.1−2.2	1.6−1.7	3.40−3.44	3.04−3.12
	1−3 kDa	8.6−8.8	3.2−3.3	2.74−2.76	2.75−2.84
	<1 kDa	5.1−5.1	4.5−4.6	1.21−1.30	2.19−2.36
	HbA	9.5−9.5	9.1−9.2	2.27−2.29	2.50−2.56
	HbN	15.3−15.6[b]	2.4−2.6	−[b]	6.0[c]
	HI	1.8−1.8	9.6−9.7	1.46−1.77	0.34−0.44
Pt. Mugu	whole pore water	32.6−34.3	14.4−15.1	5.59−5.96	4.45−4.70
	> 10 kDa	3.4−5.0	1.3−2.1	4.07−4.90	3.69−4.17
	3−10 kDa	4.9−5.8	7.2−7.2	3.46−3.88	2.99−3.11
	1−3 kDa	3.4−4.9	8.2−8.4	3.07−3.63	2.71−2.78
	<1 kDa	6.8−12.5	5.9−6.3	1.23−2.17	2.50−2.57
	HbA	11.2−11.9	10.0−10.1	3.63−4.16	3.53−3.65
	HbN	2.2−2.5	2.0−2.1	1.52−2.87	1.79−2.12
	HI	11.7−12.0	10.2−10.3	2.54−2.66	2.53−2.55

[a] Pore waters were fractionated by molecular size and polarity. Molecular size fractions were obtained by sequential ultrafiltration through Amicon YM10 (MWCO = 10 kDa), YM3 (MWCO = 3 kDa), and YM1 (MWCO = 1 kDa) membranes. The DOC concentration for each molecular size fraction was obtained by mass balance calculations. The $SUVA_{254}$ values reported are for the fractions enriched in the molecular size fraction indicated. Polarity fractions were obtained by XAD-8 resin chromatography. Pore waters were fractionated into three polarity fractions: hydrophobic acid (HbA), hydrophobic neutral (HbN), and hydrophilic (HI) fractions. Duplicate and triplicate analyses are reported as ranges of DOC and $SUVA_{254}$ values. Single values indicate single measurements. [b] Contaminated with methanol. [c] Probable experimental error.

nols, tannic acid, gallic acid) (*53*). The Fe(II)/Fe(III) system may have catalyzed the oxidative cleavage of π-bonds during aeration of the anoxic pore waters. Both selective coagulation and oxidation seem to have been operative during aeration of the Newport 2 and Pt. Mugu samples. Although the overall DOM concentration decreased (implying coagulation), an examination of the $SUVA_{254}$ data for the molecular size and polarity fractions reveals that both mechanisms probably played a role (see discussion below). The decrease in absorbance observed in the Newport 1 sample may have been primarily due to the selective oxidation of aromatic groups highly substituted with oxygenated functional groups because the large drop in $SUVA_{254}$ was accompanied by only a small decrease in overall DOM concentration. Previous researchers working in freshwater systems noted decreases in A_{253} and A_{254} when oxic reservoir water was coagulated with alum (*39*) or anoxic interstitial water was aerated (*34*).

The observed changes in aromaticity and polar functional groups were expected to result in altered affinity of DOM for the model hydrophobic organic chemical, TeCB. Aeration of the anoxic samples resulted in a substantial (order of magnitude) decrease in the pore water DOM distribution coefficient, K_{pwdom}, for the two Newport sites (Figure 3). The Pt. Mugu site showed no significant change in overall partitioning behavior. This lack of change in the distribution coefficient after aeration may be due to the effects of selective coagulation and oxidative cleavage of aromatic moieties being offset by the significant drop in ionic strength. The drop in ionic strength may have resulted in conformational changes to the DOM making hydrophobic domains more accessible to TeCB. While the results from these three sites indicate that alterations in TeCB-DOM partitioning behavior under different redox conditions were site specific, the observed behavior contrasted dramatically with data from freshwater systems. Hunchak-Kariouk et al. (*34*) observed an order of magnitude increase in K_{pwdom} upon aeration of anoxic riverine interstitial waters. The dramatic difference in the direction of change in partitioning behavior between fresh and estuarine systems was probably attributable to ionic strength effects (see Figure 1) and site specificity. Assuming both selective coagulation and oxidative cleavage of aromatic moieties occurred in the freshwater and estuarine pore water systems, the different results of aeration on partitioning behavior may be due to the conformation of the DOM macromolecules under differing ionic strength conditions (*9, 29*).

TeCB solubility and binding to DOM differed in freshwater and saltwater. In reference seawater, the absolute TeCB solubility (i.e., C_{aq} in eq 1) was 12 μg/L, five times less than that observed in freshwater (62 μg/L) (*34*). The surface hydrophobicity of DOM molecules in high ionic strength solutions is expected to be dramatically less because of the conformational changes discussed above and illustrated in Figure 1. Thus, under both oxic and anoxic conditions, TeCB binding to DOM was expected to be less in saltwater solutions than in freshwater systems because both before and after aeration the ionic strength of the matrix remained high.

Molecular Size Fractions. DOM recoveries for the sequential ultrafiltration were generally between 76 and 97%. For the anoxic Newport samples, recovery was greater than 100%, probably because of contamination in the anoxic glovebox. Lower molecular size fractions (<3 kDa) made up the bulk of the DOM (> 48−81%) at all sites under both oxic and anoxic conditions (Table 2). Previous researchers also noted the predominance of lower molecular weight DOM in marine and estuarine systems (*55, 56*). As was the case for whole pore waters, most molecular size fractions showed a decrease in DOC concentration upon aeration (Table 2). This was especially pronounced for the lower (<3 kDa) molecular size fractions from the Newport sites (9−63% reduction). No

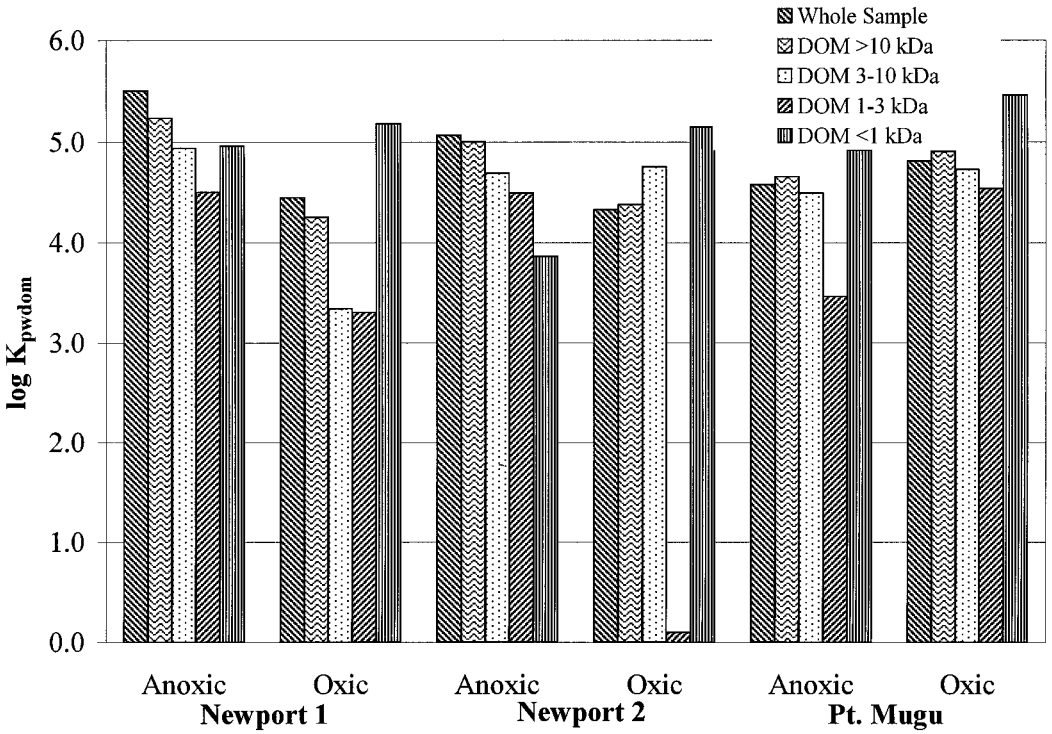

FIGURE 3. Effect of aeration on the 2,2′,4,4′-tetrachlorobiphenyl-DOM distribution coefficient (K_{pwdom} [L/kg]) for whole and molecular size fractionated anoxic pore waters.

systematic shifts in overall dissolved organic matter DOM molecular size distribution were observed; changes in pore water DOM molecular size composition were site specific. Previous researchers also observed site specific changes in interstitial water DOM molecular weight composition in response to the oxidation of anoxic estuarine sediments (*35*). As noted above, much of the decrease in DOM concentration of the molecular size fractions may be attributable to coagulation with precipitating $Fe(OH)_3$.

Although their conformation differs, preferential coagulation of the larger (>1 kDa) DOM molecules in freshwater systems has been demonstrated (*57, 58*). Davis and Gloor (*57*) examined the effects of alumina coagulation on the molecular weight distribution of DOM isolated from a Swiss lake. These authors found DOM molecules with molecular weights greater than 1000 were preferentially removed by coagulation. Most of the DOM removed had molecular weights between 1000 and 3000. Randtke (*58*) summarized the results of a large number of coagulation studies and found almost universal agreement that higher molecular weight, hydrophobic, acidic macromolecules were preferentially removed by coagulation with metal hydroxides.

For all three sites, anoxic $SUVA_{254}$ values decreased with molecular size fraction. This indicates that on a mass basis the larger molecular size fractions were richer in aromatic rings substituted with oxygenated functional groups than were the lower size fractions. The absorptivity of the highest molecular size fraction (>10 kDa) generally decreased upon aeration, while that of the lowest fraction increased (0.3−1.3 L/mg-C/m increase) at all sites (Table 2). For the largest size fraction at the Newport sites, absorptivity decreased while the DOM concentration remained approximately the same. This suggests that UV absorbance changes for these size fractions were due primarily to the cleavage of aromatic rings substituted with polar functional groups (*39*). On the other hand, the reduction in $SUVA_{254}$ of the highest molecular size fraction (>10 kDa) for the Pt. Mugu site may have been due to the selective coagulation of the larger, activated aromatic humic macromolecules, as evidenced by the concomitant decrease in DOM concentration. The increase in $SUVA_{254}$ of the lower molecular size fractions may be due to increased activation of aromatic rings caused by oxidation (*39*) or by the oxidative cleavage of larger, more highly aromatic molecules (*35*). Although the conformation of DOM molecules differs in low ionic strength conditions, similar studies in freshwater systems showed a consistent decrease in aromaticity for all molecular size fractions when anoxic interstitial waters were aerated (*27*).

At the two Newport sites, aeration of anoxic pore waters resulted in a decrease in K_{pwdom} for the largest (0.6−1.3 log unit reduction) and 1−3 kDa (1.1−4.5 log unit reduction) size fractions (Figure 3). A 0.2−1.3 log unit increase in partitioning was observed for the smallest size fraction at all three sites. This increase is consistent with the increased aromaticity of the smallest molecular size fraction (*59*). The decrease in partitioning behavior for the larger molecular size fractions was probably due to the oxidative cleavage of aromatic rings and the selective removal of macromolecules rich in oxygenated functional groups (*39*). These mechanisms would result in the disruption of hydrophobic domains or their removal from solution, and effectively reduce the number of regions capable of sequestering the hydrophobic probe molecule. A similar phenomenon has been observed in freshwater systems. The results of numerous freshwater coagulation studies show that the natural organic matter fractions most likely to be removed by coagulation are hydrophobic and exhibit a greater affinity for synthetic organic chemicals (*58*).

Polarity Fractions. XAD-8 fractionation of anoxic and aerated pore waters revealed that the HbA and Hl fractions comprised the bulk of the DOM (>79% combined) (Table 2). Several studies in freshwater systems showed similar results (*38, 60*). Although aeration produced site specific changes in polarity fraction DOC concentrations, some general trends were observed. The concentration of the Hl fraction tended to increase (up to 500% increase; the Pt. Mugu sample was an exception), while that of the HbA fraction usually decreased (3−24% reduction). These results indicate that

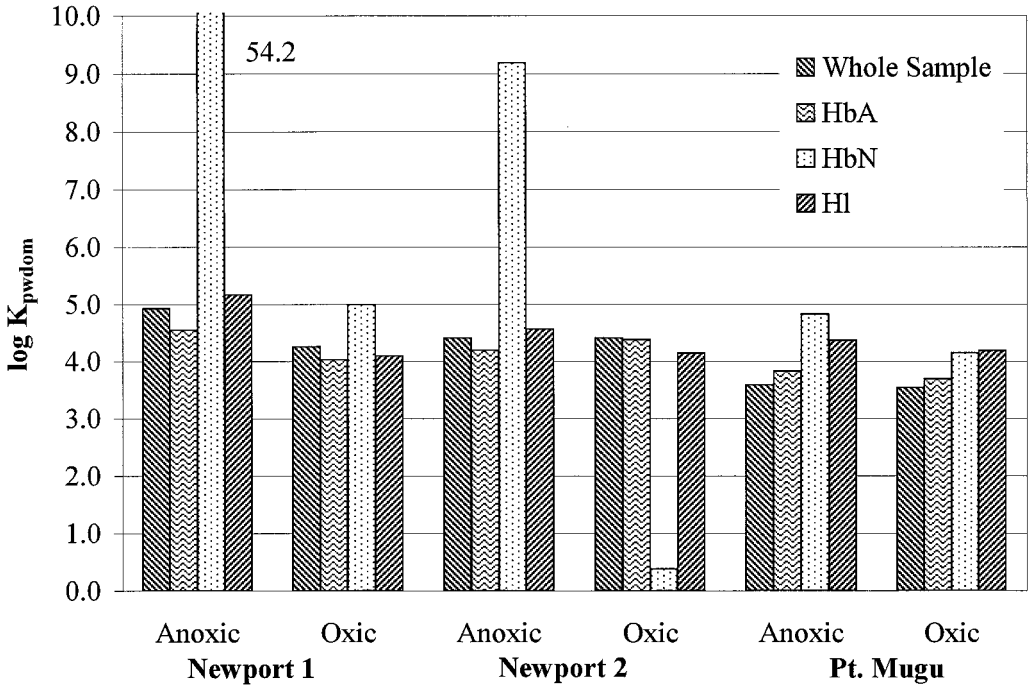

FIGURE 4. Effect of aeration on the 2,2′,4,4′-tetrachlorobiphenyl-DOM distribution coefficient (K_{pwdom} [L/kg]) for whole and polarity fractionated anoxic pore waters.

while some DOM molecules were removed by selective coagulation, those remaining in solution increased in functionality (*35*). Previous researchers working in freshwater systems found the Hl fraction to be composed primarily of lower molecular weight organic acids (*50*, *61*, *62*). Our size fractionation results do not indicate an increase in the concentration of the lower molecular size fractions, suggesting that lower molecular size fractions may contain HbA and HbN molecules in addition to Hl substances. Orem and Gaudette (*35*) observed structural changes in estuarine sediment pore water DOM following oxidation as evidenced by a significant reduction or loss of the liquid chromatogram peak representing the least polar fraction, indicating a possible increase in functionality.

The anoxic HbN fractions from the two Newport sites were found to be contaminated with residual methanol. Reprocessing resulted in insufficient sample for further analysis. However, the DOC data are displayed in Table 2 for illustrative purposes. The contribution of the HbN fraction to the overall DOM concentration was comparable between the uncontaminated samples. The Pt. Mugu HbN fraction constituted less than 10% of the total DOM and displayed no significant decrease in concentration upon aeration. These data were similar to those obtained by Krasner et al. (*38*) in freshwater systems.

$SUVA_{254}$ values were consistently higher for HbA fractions indicating that on a mass basis these fractions were richest in hydroxyl-, carboxyl-, and ester-substituted aromatic moieties (Table 2) (*39*). The aromaticity of HbA and Hl fractions tended to decrease upon aeration. The HbA fraction at Newport 2 was an exception to this trend. Selective coagulation of molecules richer in aromatic chromophores and the oxidative cleavage of aromatic rings (*39*) appeared responsible for the reduction in $SUVA_{254}$ for the HbA fractions. The decrease in $SUVA_{254}$ for the Hl fraction contrasts with the increase observed for the lowest molecular size fractions (Table 2), indicating the Hl fraction included molecules larger than those passing through a 1 kDa ultrafilter. The aromaticity of the oxic Newport 2 HbN fraction was extremely high (6.0 L/mg-C/m) and may have been due to experimental error.

The distribution coefficients for the polarity fractions decreased slightly upon aeration in almost all cases (Figure 4). The magnitude of the drop in K_{pwdom} was much less than that observed for the molecular size fractions. The reductions were consistent with the observed decreases in aromaticity (*59*), with the only fraction showing an increase in K_{pwdom} (Newport 2 HbA fraction) displaying the only verifiable increase in $SUVA_{254}$. These results support the findings of others that the ability of humic substances to bind HOCs increases with DOM aromaticity (*59*). The large values obtained for the anoxic Newport HbN fraction distribution coefficients were due to the cosolvency effect of methanol (*4*). The general decreases in aromaticity and fractional distribution coefficients for the polarity fractions lend further support to the interpretation that the number of regions capable of binding the hydrophobic probe molecule were effectively reduced by both the disruption of hydrophobic domains and their removal from solution.

Composite Nature of K_{pwdom}. To test the hypothesis that the overall TeCB-DOM distribution coefficient could be expressed as a linear combination of the component fractions weighted by mass, we summed the contributions of each fraction following eq 3 for both molecular size and polarity fractions. General agreement between the overall distribution coefficient and that obtained from the weighted sum of the molecular size fractions was apparent for the oxic Newport 1 sample and all Pt. Mugu samples (Figure 5). For these samples, the difference between the overall and composite distribution coefficients was less than 20%. The summed distribution coefficient from the anoxic Newport 1 and Newport 2 sites departed markedly from that of the whole pore water. This discrepancy between the whole and composite distribution coefficients may have been due to apparent contamination of these samples in the anoxic glovebox as noted above. Alternatively, weighting by mass fraction may not be appropriate. Weighting by surface area, density of hydrophobic domains, or some other parameter may be more relevant. These other weighting possibilities pose serious analytical challenges.

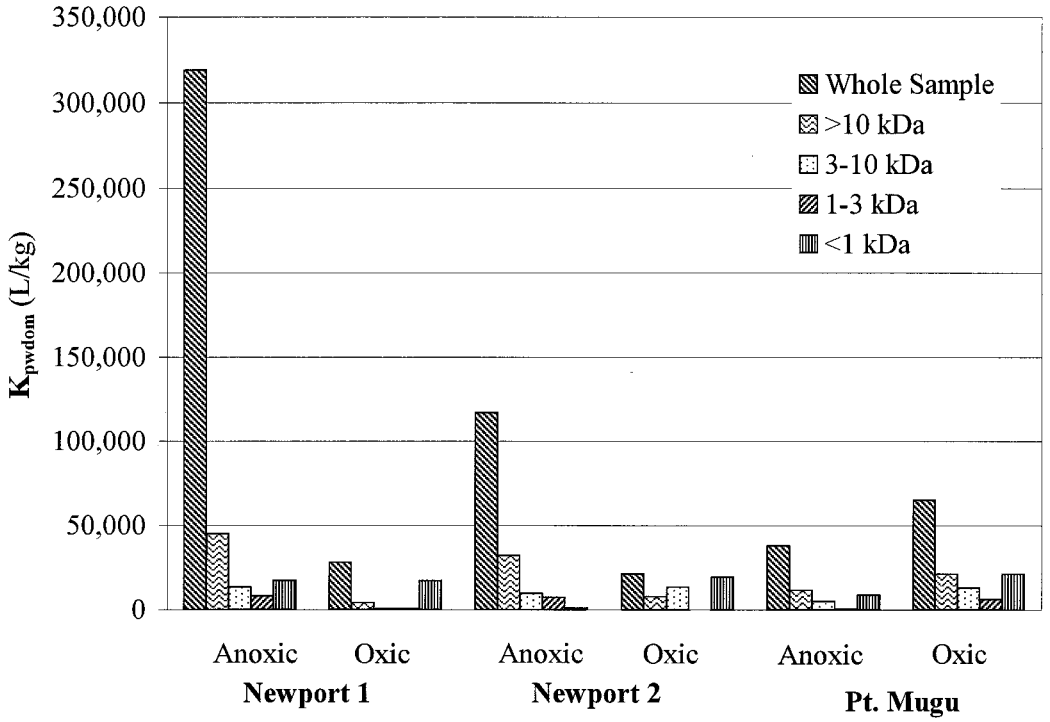

FIGURE 5. Overall and composite molecular size 2,2′,4,4′-tetrachlorobiphenyl-DOM distribution coefficients. Composite distribution coefficients were calculated as the mass-weighted sum of the fractional distribution coefficients using eq 3.

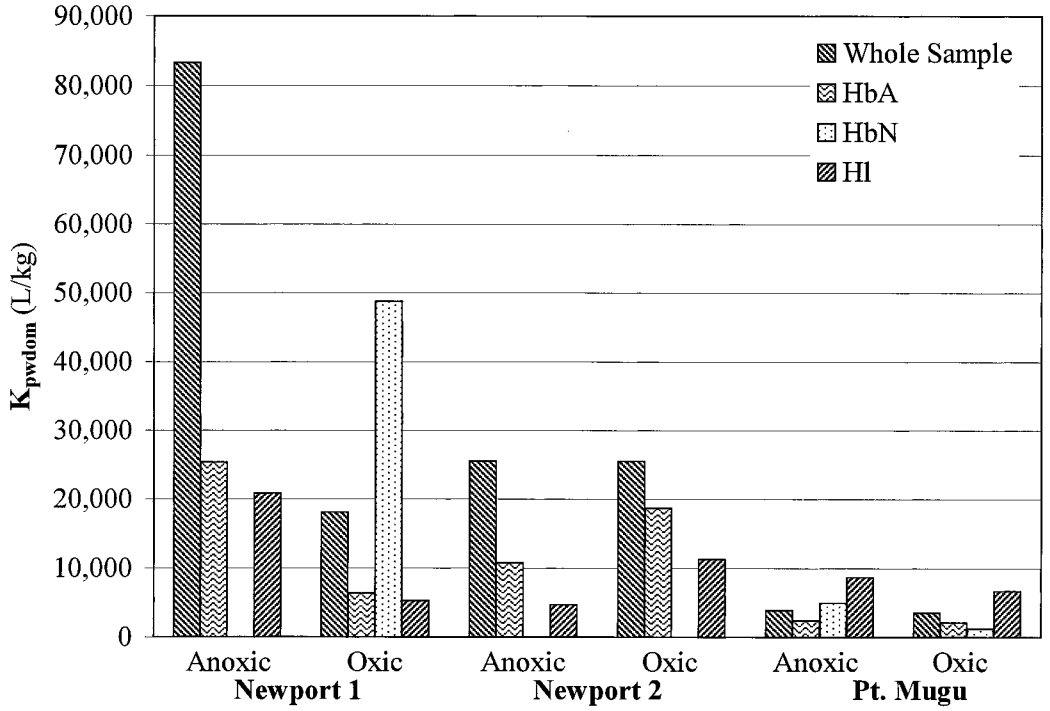

FIGURE 6. Overall and composite polarity 2,2′,4,4′-tetrachlorobiphenyl-DOM distribution coefficients. Composite distribution coefficients were calculated as the mass-weighted sum of the fractional distribution coefficients using eq 3.

The composite distribution coefficient calculated from the weighted sum of the polarity fractions differed significantly from the overall K_{pwdom} for most samples (Figure 6). For all samples evaluated, the distribution coefficient based on the sum of the individual components was greater than that measured for the whole pore water. Except for the oxic Newport 2 sample, the difference between the overall and composite distribution coefficient was greater than 20%. The two anoxic Newport samples could not be evaluated because of methanol contamination. The observed difference between the overall and composite distribution coefficients may be due to changes in the conformation or functional groups of the DOM brought about by its relatively harsh treatment during XAD resin chromatography. As mentioned above, the relevancy of alternative weighting possibilities may also warrant exploration.

Examination of the composite distribution coefficients also revealed the relative importance of individual fractions to the overall partitioning behavior of TeCB. For the two Newport sites the >10 kDa molecular size fraction contrib-

uted the most to overall partitioning in anoxic pore waters, while the <1 kDa fraction was most important in oxic sites. For the Pt. Mugu site the >10 kDa and <1 kDa molecular size fractions contributed approximately equally to the overall partitioning of TeCB to pore water DOM under both anoxic and oxic conditions.

No general trend existed for the relative importance of the polarity fractions to the overall partitioning behavior of TeCB. For the Newport 2 samples, the contribution of the HbA and Hl fractions to overall partitioning increased upon aeration, while that of the HbN and Hl fractions decreased for the Pt. Mugu samples. The HbN fraction contributed most to overall partitioning for the oxic Newport 1 sample, while the Hl fraction was the most important in the Pt. Mugu samples. Extremely high K_{pwdom} values were obtained for the anoxic Newport HbN fractions because of the cosolvency effect of methanol (*4*). The contribution of these fractions was not included in the composite distribution coefficients in Figure 6. The data from the remaining anoxic Newport fractions are displayed for illustrative purposes. Working in freshwater systems, Kukkonen and Oikari (*60*) concluded that the HbA fraction and degree of DOM aromaticity accounted for most of the variation in distribution coefficients for DOM from different boreal waters. Our data do not support the role these authors attributed to the HbA fraction. Matrix effects (e.g., conformational differences due to pH or ionic strength), as well as the source and diagenic state of the DOM may determine the relative importance of each polarity fraction to overall partitioning.

Environmental Significance. While the experimental conditions were not intended to mimic natural increases in redox potential, the results obtained indicate the trends in DOM structure, composition, and HOC partitioning expected to occur in response to the disturbance of in-place sediments in estuarine and marine environments. The aeration of anoxic estuarine sediments results in complex alterations to pore water chemistry and DOM structure and composition. Increases in the redox potential of estuarine sediments caused by the seasonal migration of the redoxcline, bioturbation, sediment resuspension in storm events, and dredging may result in the mobilization of DOM-bound hydrophobic organic pollutants. With exposure of anoxic sediment pore water to dissolved oxygen, DOM-bound HOCs are released into the aqueous phase, thereby increasing their mobility. The aeration of anoxic sediments may therefore also result in increased HOC bioavailability to water column organisms and benthic invertebrates via the diffusion route of exposure (*63*).

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