

# Partitioning of 2,2',4,4'-Tetrachlorobiphenyl by the Dissolved Organic Matter in Oxic and Anoxic Porewaters

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Until recently, the dissolved organic matter (DOM) of pore waters was an overlooked pool of organic matter important to the fate and transport of hydrophobic organic chemicals (HOCs). The aqueous solubility enhancement and the porewater DOM partition coefficient ( $K_{PDOM}$ ) of 2,2',4,4'-tetrachlorobiphenyl (TeCB) were compared in samples of anoxic porewater and that same porewater after aeration. Aeration of anoxic porewater increased TeCB partitioning by porewater DOM. Despite a decrease in DOM concentration (coagulated by precipitated iron(III) oxidized during porewater aeration), oxic (aerated) porewaters had greater solubility enhancement and up to an order of magnitude larger  $K_{PDOM}$  than anoxic (unaltered) porewaters. Anoxic porewaters with no detectable dissolved oxygen and 45 mg/L dissolved iron(II) had the smallest TeCB solubility enhancement and  $K_{PDOM}$ . Using experimentally determined  $K_{PDOM}$  values, a three-phase equilibrium-partitioning model predicts the following: (1) the distribution of HOC freely dissolved and associated with porewater DOM will change when anoxic sediments are aerated; (2) HOC mobility will increase with anoxic sediment aeration because HOC concentration in the aquatic phase will increase; and (3) HOC bioavailability will be less in anoxic porewaters as compared to oxic systems because a smaller concentration of HOC will be freely dissolved.

## Introduction

Within the sediment environment, the distribution and bioavailability of hydrophobic organic chemicals (HOCs) such as polychlorinated biphenyls, polyaromatic hydrocarbons, and chlorinated pesticides may be influenced by the dissolved organic matter (DOM) of sediment porewater (1). DOM, defined as the fraction of organic matter that can pass through a 0.45- $\mu$ m filter, is a heterogeneous mixture of organic compounds of which about 50% are high molecular weight humic substances, humic and fulvic acids (2). Natural organic matter on sediments and soils (3) and as DOM (4) can behave conceptually as a separate phase into which dissolved HOCs can partition (3). Interactions with DOM can alter some properties of HOCs, e.g., increase solubility (4–10), slow volatilization (11, 12), decrease sediment partitioning (13–20), and alter reactivity (21) and bioavailability (22–24). Few

studies have examined the role of porewater DOM (e.g., refs 1, 16, and 20).

Factors influencing DOM partitioning of an HOC include (1) HOC hydrophobicity; (2) DOM nature and "quality" (e.g., aromatic content, molecular size, and configuration); and (3) physical–chemical properties of the environment (7, 25). In a study of anoxic freshwater sediments, the abundance, distribution, and configuration of isolated humic substances depended on the ionic strength of the sample during analysis (26). DOM of different environments is not always similar and will associate to different degrees with HOCs (7, 27–32). Many bottom sediment environments are anoxic (33) and have very different water chemistry than surface waters because of steep physical, chemical, and biological gradients at the sediment–water interface (34, 35). Physical disturbances such as dredging and high flows from heavy rain can mix underlying anoxic porewater with overlying aerated surface water. Changes to the porewater can include the following: (1) oxidation of reduced metal species as the dissolved oxygen concentration is increased; (2) a decrease in ionic strength and conductivity as ions are removed by coagulation; and (3) changes to inorganic parameters such as pH,  $E_h$  (redox potential), and alkalinity as the porewater is mixed with the overlying water of different chemical composition (2).

At present, it is unknown how aeration of anoxic sediment environments will change porewater DOM concentration and quality and in turn affect the distribution and mobility of HOCs. Any increase or decrease in the partition coefficient would be significant when considering the mass loading of contaminants mobilized into the water column when sediments are disturbed and aerated. This implies a change in the bioavailability. This is important since biological systems can be quite sensitive to relatively small changes in concentration in their response to toxic compounds. Also, the procedure of collecting and transporting sediment samples from the field to the laboratory for analysis should maintain the sample at ambient conditions, especially if the sampling site was anoxic. Several studies have reported changes in concentration and characterization of porewater DOM with exposure to the atmosphere (7, 36, 37).

To characterize the partitioning of an HOC by porewater DOM and to examine the effects of anoxic porewater aeration, the solubility enhancement of TeCB (2,2',4,4'-tetrachlorobiphenyl) by the DOM of anoxic and oxic porewaters was measured and used to determine the porewater DOM partition coefficients ( $K_{PDOM}$ ) in each system. The partition coefficients and representative TeCB and DOM concentrations in anoxic and oxic porewaters were used in a three-phase equilibrium-partitioning model to compare the TeCB dissolved phase distribution and to predict HOC mobility and bioavailability in anoxic and oxic porewaters.

## Experimental Methods

**Sample Preparation.** Surface water and sediment samples were collected during the spring, summer, and fall from the Brandywine River in Chadds Ford, PA, and stored headspace-free in 2–5-L amber bottles at 4 °C. Extraction and handling of porewater samples and measurements of dissolved oxygen concentration, pH, and  $E_h$  were performed inside a glovebox or anaerobic glovebag (Saranex Model X-27-17, Instruments for Research and Industry, Cheltenham, PA). Figure 1 shows a schematic of the glovebox and equipment setup. To create an oxygen-free environment for sample handling, the atmosphere of the glovebox or glovebag was replaced three times with high-grade nitrogen passed through a molecular sieve gas purifier (Alltech Associates, Deerfield, IL), activated

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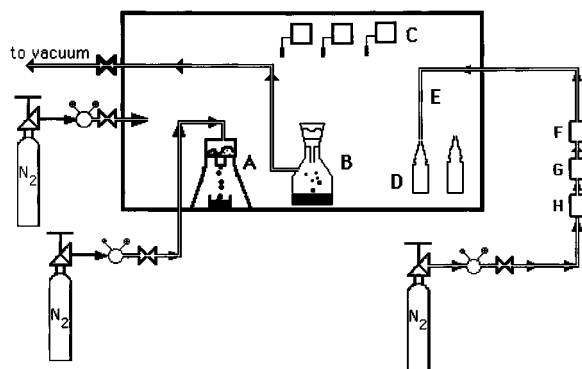


FIGURE 1. Schematic of the glovebox and equipment setup: A, sediment filtration unit; B, vacuum filtration unit; C, electrodes (dissolved oxygen, pH, and  $E_h$ ); D, equilibration vials; E, molecular sieve gas purifier; G, oxygen trap; H, activated carbon trap.

carbon, and an oxygen trap before entering the box or bag. Oxygen in the glovebox and glovebag was monitored by anaerobic indicator strips (Gas-Pak Strips, Becton Dickinson and Co., Cockeysville, MD).

Porewater was extracted from the sediment by pressure filtration with nitrogen at a maximum of 35 psi using a Teflon-lined hazardous waste filtration unit (Catalog No. YT30142HW, Millipore Corp., Bedford, MA). During the extraction, the porewater was filtered through two glass fiber prefilters and a 0.45- $\mu\text{m}$  filter (127 mm coarse filter: AP25; 124 mm fine filter: AP15; 142 mm mixed cellulose ester: HAWP; Millipore Corp., Bedford, MA). Manipulation difficulties within the confines of the glovebox occurred: some pore water samples became contaminated with sediment, and a second 0.45- $\mu\text{m}$  filtration step was required.

"Anoxic porewater" refers to porewater extracted from sediments and used immediately in solubility enhancement experiments. "Oxic porewater" was prepared by bubbling air (first passed through organic carbon-free water and a glass wool trap pre-extracted with ultra-pure quality hexane) through anoxic pore water for up to 12 days; prior to use, samples were filtered through a 0.45- $\mu\text{m}$  glass fiber filter to remove precipitated iron and coagulated DOM. "Aged anoxic porewater" was prepared by storing 0.45- $\mu\text{m}$  filtered aliquots of anoxic pore water in nitrogen-flushed flame-sealed ampoules for several days at 4 °C; prior to use, samples were centrifuged at 5000 rpm to remove any precipitate. "DOM-free porewater" was prepared by treating anoxic and oxic porewater with Filtrasorb-400 granular activated carbon (Calgon Corp., Pittsburgh, PA) to remove DOM. Surface water was filtered through 0.45- $\mu\text{m}$  glass fiber filters prior to use.

**Solubility Measurements.** TeCB aqueous solubility and solubility enhancement were measured by equilibrating small volumes (<15 mL) of water samples with TeCB-coated micro glass beads in small crimp-top vials or flame-sealed ampoules (Wheaton Glass Co., Millville, NJ). The advantage of this method was that a known amount of TeCB could be equilibrated with a small amount of water in a closed system with minimal or no headspace. Crimp-top vials were replaced with flame-sealed ampoules because anoxic samples were altered by atmospheric oxygen leaking through the vial caps. Micro glass beads, 60/80 mesh (Alltech Assoc., Inc., Applied Science Labs, Deerfield, IL) and 250  $\mu\text{m}$  (Supelco Inc., Bellefonte, PA) were cleaned and coated with a mixture of  $^{14}\text{C}$ -labeled (Sigma Chemical Co., St. Louis, MO) and unlabeled (Chem Services, West Chester, PA) TeCB. Separate stock solutions of the  $^{14}\text{C}$ -labeled and unlabeled TeCB were prepared in methanol and stored at 4 °C in amber bottles. The beads were coated with TeCB by adding known amounts of  $^{14}\text{C}$ -labeled and unlabeled TeCB to methanol slurries of beads and heating gently to evaporate the methanol. Coated beads were stored at 4 °C.

The amount of TeCB-coated beads added to each ampoule was adjusted to provide a source of TeCB many times greater than aqueous solubility (>1500  $\mu\text{g/L}$  final concentration). Ampoules containing the TeCB-coated beads were flushed with nitrogen before filling with anoxic porewater inside the glovebox or glovebag. After sealing, the vials were wrapped in foil and equilibrated by end-over-end rotation at 15 rpm at room temperature. Samples from each sediment extraction were equilibrated for different times to determine when equilibrium was achieved. Beads and any precipitate were separated by centrifugation for 1 h at 5000 rpm. A 0.5–2-mL aliquot from each ampoule was mixed with 10 mL of liquid scintillation cocktail (Packard Ultima Gold LSC), and the  $^{14}\text{C}$  radioactivity was counted in a Packard Tri-Carb 4530 scintillation counter (United Technologies, Downers Grove, IL). After equilibration, the beads and vessel walls were washed with three 5-mL methanol washes analyzed by liquid scintillation. The sum of the TeCB amounts in the washes and equilibration samples was always 90% or greater of the initial amount of TeCB added to each vial. TeCB aqueous solubility was measured in Brandywine River surface water, DOM-free porewaters, 0.005 M phosphate buffer, and organic carbon-free water. TeCB solubility enhancement was measured in anoxic, aged anoxic, and oxic porewaters.

**Porewater and DOM Characterization.** Ultraviolet absorption at 254 nm was measured with a Perkin-Elmer 556 spectrophotometer using a 1-cm path length cell. DOM concentration, milligrams per liter of total dissolved non-purgeable organic carbon (mg of C/L), was measured by potassium persulfate oxidation with DC-8 TOC analyzer (Xertex-Dohrmann Corp., Santa Clara, CA). The ratio of the 254-nm absorbance to the DOM concentration is an estimate of the aromatic nature of the DOM termed  $\text{SUVA}_{254}$ , the specific ultraviolet absorbance at 254 nm [ $\text{L}(\text{m} \cdot \text{mg of C})^{-1}$ ] (38).  $\text{SUVA}$  is expressed as per meter (m) absorbance divided by the DOC in mg of C/L.

$E_h$  was measured in millivolts (mV) with a platinum redox combination electrode (Model 97-78-00, Orion, Framington, MA) and an Accumet meter (Model 630, Fisher Corp., Pittsburgh, PA). Dissolved iron(II) concentration, used to monitor the oxidation–reduction state of the porewater, was measured by the bathophenanthroline method of Lee and Stumm (39) as modified by McMahon (40, 41). The method of Greenberg et al. (42) was modified to measure the dissolved oxygen concentration in small volumes of porewater.

## Results and Discussion

The measured total concentration of an HOC dissolved in porewater,  $[\text{HOC}]_{\text{PW}}$ , is the sum of the freely dissolved concentration,  $[\text{HOC}]_{\text{Aq}}$ , and the dissolved concentration of HOC associated with the porewater DOM,  $[\text{HOC}]_{\text{PWDOM}}$

$$[\text{HOC}]_{\text{PW}} = [\text{HOC}]_{\text{Aq}} + [\text{HOC}]_{\text{PWDOM}} \quad (1)$$

For eq 1, concentration units are the same for all values but can be any unit (e.g.,  $\mu\text{g/L}$ ). The porewater DOM partition coefficient,  $K_{\text{PWDOM}}$  (L/kg), [normalized for organic carbon] for TeCB was determined as

$$K_{\text{PWDOM}} = \frac{[\text{TeCB}]_{\text{PWDOM}}}{[\text{TeCB}]_{\text{Aq}}[\text{PWDOM}]} \times 10^6 \quad (2)$$

where  $[\text{TeCB}]_{\text{PWDOM}}$  is the concentration of dissolved TeCB associated with the porewater DOM ( $\mu\text{g/L}$ ) or equals  $[\text{TeCB}]_{\text{PW}} - [\text{TeCB}]_{\text{Aq}}$ ;  $[\text{TeCB}]_{\text{PW}}$  is the measured total concentration of dissolved TeCB in the porewater ( $\mu\text{g/L}$ );  $[\text{TeCB}]_{\text{Aq}}$  is the concentration of TeCB freely dissolved ( $\mu\text{g/L}$ ) (the freely dissolved TeCB aqueous concentration is at its maximum solubility in distilled water);  $[\text{PWDOM}]$  is the porewater DOM concentration (as mg of C/L); and  $10^6$  is the unit conversion of mg/L to Kg/L of organic carbon. The unit conversion is done to make the data more directly comparable to  $K_{\text{oc}}$ , the

TABLE 1. Measured TeCB and Porewater DOM Concentrations and Calculated  $K_{P_{WDOM}}$  in Five Samples of Brandywine River Porewater<sup>a</sup>

	sample	porewater DOM concn (mg of C/L)	change in porewater DOM concn by aeration (mg of C/L)	TeCB concn ( $\mu\text{g/L}$ )	$K_{P_{WDOM}} \times 10^{-5}$ (L/kg)
I	anoxic porewater	15.1		150	1.0
	oxic porewater	10.8	4.3	331	4.1
II	anoxic porewater	15.0		98	0.4
	oxic porewater	12.6	2.4	373	4.0
III	anoxic porewater	11.8		149	1.2
	oxic porewater	10.1	1.7	275	3.4
IV	anoxic porewater	13.2		152	1.1
	oxic porewater	6.9	6.3	234	4.1
V	anoxic porewater	15.0		108	0.5
	oxic porewater	12.4	2.6	480	5.5
	average		3.5		
	oxic porewater			$303 \pm 53$	$4.2 \pm 0.7$
	anoxic porewater			$131 \pm 23$	$0.8 \pm 0.3$

<sup>a</sup> Sample I was collected in the spring; samples II, III, and IV were collected in the summer; sample V was collected in the fall; samples I, II, III, and V were equilibrated in flame-sealed ampoules; sample V was equilibrated in crimp-top vials; TeCB is 2,2',4,4'-tetrachlorobiphenyl; DOM is dissolved organic matter;  $K_{P_{WDOM}}$  is the porewater dissolved organic matter partition coefficient.

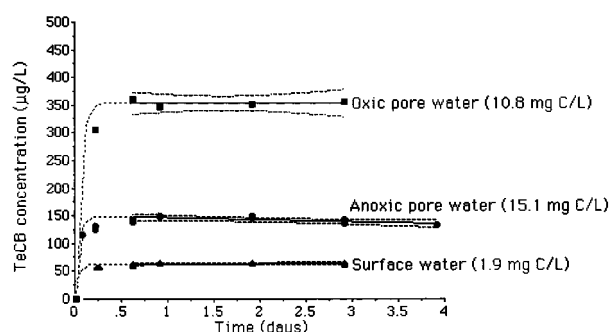


FIGURE 2. TeCB concentration in Brandywine River anoxic and oxic porewaters and surface waters (95% confidence interval shown; spring sample).

partition coefficient between sediment and water normalized to kg/L of organic carbon.

Figure 2 shows one example of the measured TeCB solubilities in anoxic and oxic Brandywine River porewater samples equilibrated for up to 4 days (all waters were extracted from the same sediment sample). The equilibration is initially rapid, levels off after 1 day, and thereafter remains constant; 95% confidence intervals are shown. Similar results were measured for porewaters extracted from other Brandywine River sediments collected during different seasons. Table 1 lists the TeCB and DOM concentrations and the calculated  $K_{P_{WDOM}}$  for five Brandywine River porewaters. (Samples were collected in the spring, summer, and fall. Reported concentrations are for 1-day equilibrations; concentrations did not change significantly during equilibration up to 10 days.)

Reported TeCB aqueous solubility ranges from 50 to 68  $\mu\text{g/L}$  (43–46). The average TeCB aqueous solubility in Brandywine River surface water, DOM-free porewaters, organic carbon-free water, and 0.005 M phosphate buffer was 61  $\mu\text{g/L}$  ( $\pm 3$   $\mu\text{g/L}$ ,  $n = 16$ ). The TeCB concentrations reported in Table 1 are statistically different for anoxic and oxic porewater samples. The TeCB concentration in anoxic porewaters ranged from about 100 to 150  $\mu\text{g/L}$ , and TeCB solubility was enhanced by the porewater DOM. However, the TeCB solubility was more enhanced in oxic porewaters aerated for 12 days; TeCB concentration ranged from about 230 to 480  $\mu\text{g/L}$ . The average  $K_{P_{WDOM}}$  for oxic samples,  $4.2 \times 10^5$  L/kg is almost 1 order of magnitude greater than the average  $K_{P_{WDOM}}$  for anoxic samples,  $0.8 \times 10^5$  L/kg. This increase in  $K_{P_{WDOM}}$  is attributed to the increase in TeCB solubility by the DOM even though the DOM concentration decreased 20–50% when the anoxic porewater was aerated. Reported DOM partition coefficients for TeCB vary, depending

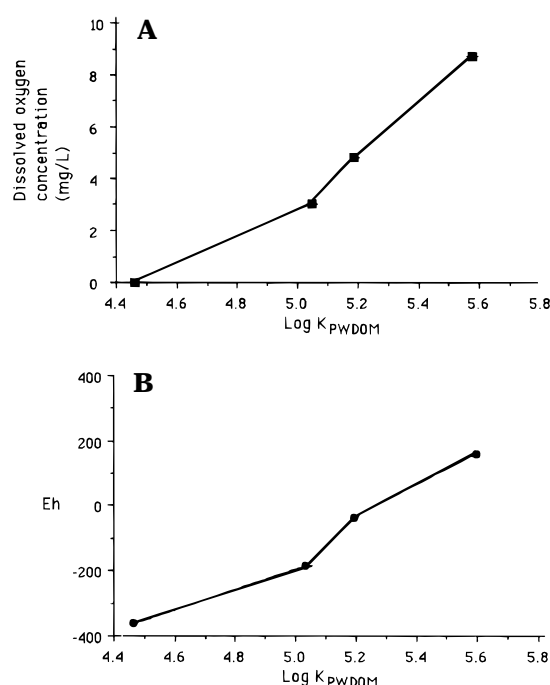


FIGURE 3. Panel A shows the relationship between dissolved oxygen concentration and  $K_{P_{WDOM}}$ . Panel B shows the relationship between  $E_h$  and  $K_{P_{WDOM}}$  in four Brandywine River porewaters.

on sample source and analysis technique, ranging from  $7.76 \times 10^5$  L/kg in surface water (29) to  $1.47 \times 10^5$  L/kg in porewater (36). Caron (16) reported a  $K_{P_{WDOM}}$  of  $2.23 \times 10^5$  L/kg of organic carbon for Brandywine River porewater but did not attempt to maintain sample anoxic conditions.

Figure 3A shows the relationship between dissolved oxygen concentration and  $K_{P_{WDOM}}$ ; as the dissolved oxygen increases the  $K_{P_{WDOM}}$  increases. Figure 3B shows the relationship between  $E_h$  and  $K_{P_{WDOM}}$ ; as the  $E_h$  increases,  $K_{P_{WDOM}}$  also increases.  $E_h$  takes into account all redox couples in the system including the iron(II)/iron(III) and sulfide/sulfur/sulfate couples that are significant in this study. DO takes into account only oxygen concentration within the environmental system. Thus, DO concentrations and  $E_h$  values do not correspond exactly with each other. Some of the anoxic porewater samples were exposed to small amounts of atmospheric oxygen during sample handling, which increased the initial  $E_h$  and dissolved oxygen concentration. Anoxic porewater with the smallest measured  $E_h$  (–350 mV) and no detectable dissolved oxygen had the smallest partition

TABLE 2. Measured TeCB and Porewater DOM Concentrations,  $SUVA_{254}$ , and  $K_{PDOM}$  in Aged Anoxic and Oxic Brandywine River Porewaters

sample	time (days)	porewater DOM concn (mg of C/L)	TeCB concn ( $\mu\text{g/L}$ )	$K_{PDOM} \times 10^{-5}$ (L/kg)	$SUVA_{254}$ ( $\text{L}(\text{m}\cdot\text{mg of C})^{-1}$ )
anoxic porewater	0	16.6	117	0.54	3.0
	4	15.8	130	0.70	2.8
	12	10.5	127	1.02	2.6
oxic porewater	0	15.8	181	1.23	1.5
	2	14.2	209	1.69	1.5
	4	13.2	284	2.74	1.5
	12	8.7	331	4.07	1.9

coefficient ( $\log K_{PDOM} > 5.5$ ). This indicates that the DOM is changed to different forms under different aeration conditions. This change in the nature of the DOM appears to be very complex and needs further study.

**Effect of Iron on TeCB Partitioning by Anoxic and Oxic Pore Water DOM.** Anoxic Brandywine River porewater contained 45 mg/L dissolved iron(II), which may have influenced TeCB sorption by porewater DOM. An iron(II) precipitate formed during the aging of anoxic porewater and during the equilibration of some anoxic porewaters in the flame-sealed ampules. Figure 4A shows the total dissolved iron, dissolved iron(II), and precipitated iron concentrations in anoxic porewater with time. The TeCB solubility in anoxic porewaters was constant for up to 13 days despite the decrease in dissolved iron(II) concentration and the formation of the iron(II) precipitate (Figure 4B). The change in iron(II) form does not appear to influence the DOM sorption of TeCB.

In certain environments, the concentration of dissolved iron(II) is controlled by solid phases such as siderite ( $\text{FeCO}_3$ ), amorphous iron sulfide ( $\text{FeS}$ ), and vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) (35). Extraction of the porewater from the sediment can change this equilibrium. When a new equilibrium was established in the sediment-free porewater, iron(II) coordinated species such as  $\text{FeS}_2^{2-}$  could not be sustained and probably re-equilibrated to form  $\text{FeS}$ . During aging and equilibration of the anoxic porewater, the equilibrium is re-established by the formation of the iron(II) precipitate.

When the anoxic porewater was aerated, the dissolved iron(II) was oxidized and the porewater DOM was coagulated by the iron(III) precipitate. The DOM concentration was reduced, and the DOM of the oxic porewater represents only a fraction of the initial DOM in the anoxic porewater. The amount of DOM coagulated depended on the aeration time. The samples reported in Table 1 were aerated for 12 days and had the largest change in DOM concentration. (DOM concentration decreased 20–50%.) The measured dissolved iron concentration of the Brandywine River porewaters (45 mg/L) is within the sweep coagulation range (porewater pH ranged from 7.5 in anoxic samples to 8.8 in oxic samples) (47).

**Characterization of Anoxic and Oxic Porewater DOM.** Table 2 compares the measured TeCB and DOM concentrations, the  $K_{PDOM}$ , and the  $SUVA_{254}$  for several anoxic and oxic porewaters. The TeCB solubility enhancement and  $K_{PDOM}$  changed only slightly if the anoxic sample was aged before equilibration with the TeCB-coated beads. The slight increase in DOM partitioning may be due to unintentional oxygen contamination of the anoxic porewater during the extensive sample manipulations in the glovebag. In contrast, the TeCB solubility enhancement and  $K_{PDOM}$  changed significantly as the aeration time was increased. Although smaller for oxic than anoxic porewaters,  $SUVA_{254}$  remained fairly constant in both sample types with time.

Because  $SUVA_{254}$  is a measure of the aromatic content of the DOM, larger  $SUVA_{254}$  values [ $>3 \text{ L}(\text{m}\cdot\text{mg of C})^{-1}$ ] would indicated the presence of DOM that was more hydrophilic, aromatic, and of higher molecular weight than the DOM of waters with smaller  $SUVA_{254}$  (38).

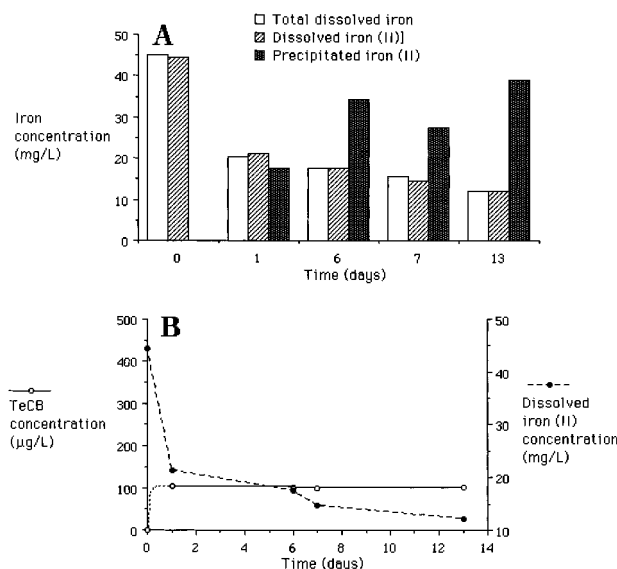


FIGURE 4. (A) Total dissolved iron, dissolved iron(II), and precipitated iron(II) concentrations in anoxic Brandywine River porewater with time. (B) Changes in TeCB and dissolved iron(II) concentrations in anoxic Brandywine River porewater with time (porewater DOM (15 mg of C/L),  $SUVA_{254}$  3.0  $\text{L}(\text{m}\cdot\text{mg of C})^{-1}$ ,  $E_h$  (–350 mV), and pH (7.65) remained constant with time).

The larger  $SUVA_{254}$  of the anoxic pore water [ $3.0 \text{ L}(\text{m}\cdot\text{mg of C})^{-1}$ ,  $\pm 0.36 \text{ L}(\text{m}\cdot\text{mg of C})^{-1}$ ,  $n = 5$ ] suggests a more aromatic DOM as compared to the aerated porewater [4-day aeration,  $1.5 \text{ L}(\text{m}\cdot\text{mg of C})^{-1}$ ,  $\pm 0.03 \text{ L}(\text{m}\cdot\text{mg of C})^{-1}$ ,  $n = 2$ ; 12-day aeration,  $1.9 \text{ L}(\text{m}\cdot\text{mg of C})^{-1}$ ,  $\pm 0.24 \text{ L}(\text{m}\cdot\text{mg of C})^{-1}$ ,  $n = 5$ ]. However in this study, the  $K_{PDOM}$  is smallest for anoxic samples with higher  $SUVA_{254}$ .

Increased sorption of HOCs has been correlated to the aromaticity of humic substances (48). Although anoxic porewater DOM is more aromatic (higher  $SUVA_{254}$ ), it has a lower sorptive capacity of TeCB (Table 2). Conversely, when the anoxic porewater is aerated, the lower  $SUVA_{254}$  indicates that this oxic porewater DOM is less aromatic than the original anoxic porewater DOM, but in spite of this has a greater sorptive capacity for TeCB. Therefore, the predicted direct correlation of aromaticity and sorption of HOCs does not hold in this case. The phenomena appears to be very complex, and the physiochemical nature of how the DOM changes during aeration needs extensive evaluation before an explanation can be given.

**Modeling the Bottom Sediment Environment.** One approach to understanding the environmental fate and transport of HOCs is to use equilibrium-partitioning models. These models can predict HOC mobility, distribution, and bioavailability in sediment environments. Several investigators (14, 30, 49–51) have used equilibrium-partitioning models to visualize the sediment environment as a series of three compartments: (1) the sediment with its associated organic coat; (2) the porewater; and (3) the porewater DOM, among which an HOC can distribute itself in a dynamic

equilibrium. The distribution models of Mackay et al. (52) and McCall et al. (53) use the equilibrium-partitioning concept to describe the fate of an HOC in the aquatic environment. Caron (16, 31) expanded the McCall et al. model (53) to include the water column DOM, the porewater, and the porewater DOM as available compartments for chemical partitioning.

In a three-phase bottom sediment system at equilibrium, the HOC fractions truly dissolved ( $\alpha_{\text{Aq}}$ ), associated with the porewater DOM ( $\alpha_{\text{PwDOM}}$ ), and associated with the sediment ( $\alpha_{\text{Sed}}$ ) can be expressed as eqs 3–5:

$$\alpha_{\text{Aq}} = \frac{[\text{HOC}]_{\text{Aq}}}{[\text{HOC}]_{\text{BSE}}} = \frac{1}{1 + K_{\text{PwDOM}}[\text{PwDOM}] + K_{\text{OC}}(f_{\text{OC}})} \quad (3)$$

$$\alpha_{\text{PwDOM}} = \frac{[\text{HOC}]_{\text{PwDOM}}}{[\text{HOC}]_{\text{BSE}}} = \frac{K_{\text{PwDOM}}[\text{PwDOM}]}{1 + K_{\text{PwDOM}}[\text{PwDOM}] + K_{\text{OC}}(f_{\text{OC}})} \quad (4)$$

$$\alpha_{\text{Sed}} = \frac{[\text{HOC}]_{\text{Sed}}}{[\text{HOC}]_{\text{BSE}}} = \frac{K_{\text{OC}}(f_{\text{OC}})}{1 + K_{\text{PwDOM}}[\text{PwDOM}] + K_{\text{OC}}(f_{\text{OC}})} \quad (5)$$

where  $[\text{HOC}]_{\text{BSE}}$  is the total concentration of an HOC in the bottom sediment environment or equals  $[\text{HOC}]_{\text{Aq}} + [\text{HOC}]_{\text{PwDOM}} + [\text{HOC}]_{\text{Sed}}$ ;  $[\text{HOC}]_{\text{Aq}}$  is the concentration of an HOC freely dissolved (aqueous solubility of HOC only when the system is at saturation);  $[\text{HOC}]_{\text{PwDOM}}$  is the concentration of dissolved HOC associate with the porewater DOM;  $[\text{HOC}]_{\text{Sed}}$  is the concentration of an HOC associated with the sediment organic carbon;  $K_{\text{PwDOM}}$  is the porewater DOM partition coefficient for the HOC (L/kg);  $K_{\text{OC}}$  is the organic carbon normalized sediment partition coefficient;  $[\text{PwDOM}]$  is the porewater DOM concentration (mg of C/L); and  $f_{\text{OC}}$  is the fraction of sediment organic carbon.

For eqs 3–5, concentration units are the same for all values but can be any unit (e.g.,  $\mu\text{g/L}$ ). When the partition coefficients,  $K_{\text{PwDOM}}$  and  $K_{\text{OC}}$ , and the concentration of the organic matter phases,  $[\text{PwDOM}]$  and  $f_{\text{OC}}$ , are known, predictions of distribution, mobility, and bioavailability can be determined for an HOC by evaluating its distribution in the three phases ( $\alpha_{\text{Aq}}$ ,  $\alpha_{\text{PwDOM}}$ , and  $\alpha_{\text{Sed}}$ ).

**Evaluation of a Bottom Sediment Distribution Model.** Equilibrium partitioning models allow a first estimation of the distribution of chemicals in various environmental media. This information is then used to estimate the overall chemical exposure of humans and other organisms. Using appropriate partition coefficients is essential in accurately predicting the magnitude of exposure. The five scenarios were presented to illustrate the potential error associated with the use of inappropriate  $K_{\text{PwDOM}}$  values in environmental models.

Five scenarios of the three-phase distribution model were evaluated for TeCB in Brandywine River sediments. The model results are indicative of HOC behavior in sediments similar to those of the Brandywine River. Using eq 2 and representative TeCB and DOM concentrations in anoxic porewater (100  $\mu\text{g/L}$  and 15 mg of C/L, respectively), a value of  $0.48 \times 10^5$  L/kg was calculated for  $K_{\text{PwDOM}}$  in anoxic porewater. Similarly, representative TeCB and DOM concentrations in oxic porewater (300  $\mu\text{g/L}$  and 7 mg of C/L, respectively) were used to calculate a value of  $4.07 \times 10^5$  L/kg for  $K_{\text{PwDOM}}$  in oxic porewater. (TeCB aqueous solubility of 58  $\mu\text{g/L}$  was assumed for the freely dissolved TeCB concentration in eq 2.) Table 3 lists the values used in eqs 3–5 to determine  $\alpha_{\text{Aq}}$ ,  $\alpha_{\text{PwDOM}}$ , and  $\alpha_{\text{Sed}}$ . In a separate investigation, the  $K_{\text{OC}}$  and  $f_{\text{OC}}$  were determined for TeCB partitioning in Brandywine River sediments (16). In all scenarios, the amount of TeCB associated with the sediment is greater than 98%; however, the fraction of the TeCB freely dissolved (free) and associated with the porewater DOM (bound) are different as shown in

**TABLE 3. TeCB Partition Coefficients and Organic Matter Concentrations of Brandywine River Sediments and Porewaters**

partition coefficients		organic matter concentrations	
anoxic $K_{\text{PwDOM}}$	$0.48 \times 10^5$ L/kg	anoxic $[\text{PwDOM}]$	15 mg of C/L
oxic $K_{\text{PwDOM}}$	$4.07 \times 10^5$ L/kg	oxic $[\text{PwDOM}]$	7 mg of C/L
$K_{\text{OC}}$	$0.36 \times 10^5$	$f_{\text{OC}}$	1.2%

Figure 5. Concentrations of free,  $[\text{TeCB}]_{\text{Aq}}$ , and bound,  $[\text{TeCB}]_{\text{PwDOM}}$ , are calculated as fractions the total dissolved TeCB concentration in the porewater,  $[\text{TeCB}]_{\text{pw}}$ .

**Scenario 1.** The modeled system is an anoxic sediment system;  $K_{\text{PwDOM}}$  is known ( $0.48 \times 10^5$  L/kg),  $[\text{PwDOM}]$  is 15 mg of C/L, and  $[\text{TeCB}]_{\text{pw}}$  is 100  $\mu\text{g/L}$ . The free fraction is 58%, and the bound fraction is 42%. In this scenario, the  $[\text{TeCB}]_{\text{Aq}}$  is 58  $\mu\text{g/L}$  and  $[\text{TeCB}]_{\text{PwDOM}}$  is 42  $\mu\text{g/L}$ . This represents an actual result.

**Scenario 2.** The modeled system is an oxic sediment system;  $K_{\text{PwDOM}}$  is known ( $4.07 \times 10^5$  L/kg),  $[\text{PwDOM}]$  is 7 mg of C/L, and  $[\text{TeCB}]_{\text{pw}}$  is 300  $\mu\text{g/L}$ . The free TeCB fraction is 26%, and the bound fraction is 74%. The  $[\text{TeCB}]_{\text{pw}}$  and the bound fraction are greater in scenario 2 as compared to scenario 1 although the porewater DOM concentration is less. These results indicate that the mobility of TeCB is increased as anoxic bottom sediments are disturbed and aerated because  $[\text{TeCB}]_{\text{pw}}$  is increased (as indicated by the larger TeCB solubility enhancement in the oxic porewater, see also Table 1). TeCB bioavailability will also increase. The total concentration is increased from 100 to 300  $\mu\text{g/L}$ , and the free TeCB concentration will also increase. Although the free fraction is smaller in oxic porewater, the  $[\text{TeCB}]_{\text{pw}}$  is larger and therefore the  $[\text{TeCB}]_{\text{Aq}}$  will be larger. In this scenario,  $[\text{TeCB}]_{\text{Aq}}$  is 78  $\mu\text{g/L}$ . Reported TeCB aqueous solubility ranges from 50–68  $\mu\text{g/L}$  (43–46) and therefore a  $[\text{TeCB}]_{\text{Aq}}$  of 78  $\mu\text{g/L}$  is unrealistic. However, most systems are not at saturation. These results indicate that  $[\text{TeCB}]_{\text{Aq}}$  will increase as anoxic porewaters are aerated. Studies have shown that DOM association of HOCs reduces their bioavailability; the unassociated and freely dissolved HOC is considered to be the bioavailable and potentially toxic form (7).

**Scenario 3.** The modeled system is an anoxic sediment system;  $K_{\text{PwDOM}}$  in anoxic systems is unknown but assumed the same as in oxic systems ( $4.07 \times 10^5$  L/kg),  $[\text{PwDOM}]$  is 15 mg of C/L, and the  $[\text{TeCB}]_{\text{pw}}$  is 100  $\mu\text{g/L}$ . The free fraction is 14%, and the bound fraction is 86%.  $[\text{TeCB}]_{\text{Aq}}$  is 14  $\mu\text{g/L}$  as compared to 58  $\mu\text{g/L}$  in scenario 1. By using the wrong value for  $K_{\text{PwDOM}}$  in anoxic systems, the free fraction and  $[\text{TeCB}]_{\text{Aq}}$  are underestimated as compared to scenario 1.

**Scenario 4.** The modeled system is an anoxic sediment system;  $K_{\text{PwDOM}}$  in anoxic systems is unknown but assumed equal to  $K_{\text{OC}}$  ( $0.36 \times 10^5$ ),  $[\text{PwDOM}]$  is 15 mg of C/L, and the  $[\text{TeCB}]_{\text{pw}}$  is 100  $\mu\text{g/L}$ . The free TeCB fraction is 63%, and the bound fraction is 37%. The anoxic porewater DOM and the sediment organic matter are assumed to have the same partitioning capacity for TeCB. This assumption does not greatly alter the estimated free fraction in the porewater because the values of  $K_{\text{PwDOM}}$  in anoxic systems and  $K_{\text{OC}}$  are similar (see scenario 1). This assumption would not necessarily be valid for other compounds or other sediment systems.

**Scenario 5.** The modeled system is an anoxic sediment system;  $K_{\text{PwDOM}}$  in anoxic systems is unknown but is assumed equal to  $K_{\text{OC}}$ , which is estimated as  $0.411 \times K_{\text{OW}}$  (54) ( $K_{\text{OW}}$  is the octanol–water partition coefficient and is  $11.3 \times 10^5$  for TeCB (45)),  $[\text{PwDOM}]$  is 15 mg of C/L, and the  $[\text{TeCB}]_{\text{pw}}$  is 100  $\mu\text{g/L}$ . The free TeCB fraction is 5%, and the bound fraction is 95%. The free fraction is greatly underestimated as compared to the actual results of scenario 1. The distribution of TeCB in scenario 5 is very different from the distributions calculated in scenario 1 (anoxic porewater) and in scenario

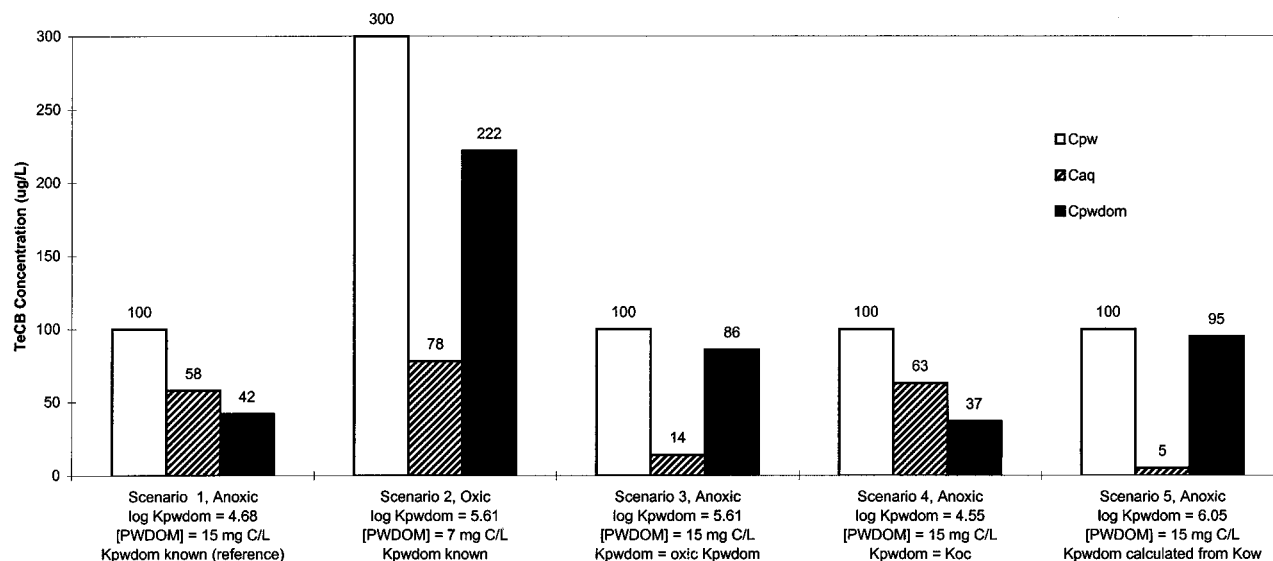


FIGURE 5. Evaluation of sediment distribution model bound and free TeCB fractions in Brandywine River porewater at saturation.

2 (oxic porewater), but is similar to results reported by Capel and Eisenreich (55). They measured the concentration of a range of chlorinated hydrocarbons in the bulk sediment, porewater, and *Hexagenia naiads* of Lake Superior sediments.  $K_{PWWDOM}$  values estimated from relations between estimated and calculated (from field data) lake sediment  $K_{OC}$  values were similar to but always less than either of the  $K_{OC}$  values. Using these estimated  $K_{PWWDOM}$  values in a three-phase distribution model, they reported less than 10% of the chlorinated hydrocarbons in the porewater were estimated to be freely dissolved. These results are similar to the results of scenario 5. Capel and Eisenreich (55) measured the concentration of chlorinated hydrocarbons in the pore water by extracting the samples with hexane. Apparently, hexane only recovered the free concentration, as described by Fish et al. (56). Also, the oxic/anoxic character of the sediment is not reported by Capel and Eisenreich (55). Capel and Eisenreich (55) may have underestimated the actual concentrations that might be more like scenarios 1 and 2.

The different porewater distributions of the free and bound fractions of dissolved TeCB in these five scenarios indicate that HOC mobility and bioavailability in anoxic and oxic sediment systems are different, and erroneous distributions will be assumed when incorrect partition coefficients are used to calculate porewater distributions of dissolved HOCs. Estimates of dissolved HOC distributions using aqueous solubility and  $K_{OW}$  values should be considered first approximations only of actual distributions. HOC distributions in the environment are site-specific and dependent on the type of organic matter in the system. Equilibrium partitioning models allow a first estimation of the distribution of chemicals in various environmental media. This information is then used to estimate the overall chemical exposure of humans and other organisms. Using appropriate partition coefficients is essential in accurately predicting the magnitude of exposure. The five scenarios were presented to illustrate the potential error associated with the use of inappropriate  $K_{PWWDOM}$  values in environmental models.

## Summary

Measured TeCB aqueous solubility enhancements and calculated  $K_{PWWDOM}$  values indicate that sample aeration has a measurable effect on TeCB partitioning by the porewater DOM of Brandywine River sediments. Even though aeration decreased its concentration and aromatic content, DOM in oxic porewater had greater partitioning for TeCB than the DOM in anoxic (unaltered) porewater. The high amounts of iron in the anoxic Brandywine River porewaters (45 mg/L)

acted as a natural coagulant to remove a fraction of the DOM when anoxic porewater was aerated. Although partitioning is greater for anoxic porewater DOM, its smaller  $SUVA_{254}$  suggests that the DOM is less aromatic compared to the anoxic porewater DOM. This finding is contrary to reported correlations of increased HOC partitioning with the aromatic content of humic matter (48).

The range of  $K_{PWWDOM}$  for TeCB in anoxic porewaters was  $0.40 \times 10^5$  to  $1.20 \times 10^5$  L/kg; for oxic porewater, the range was  $3.44 \times 10^5$  to  $5.49 \times 10^5$  L/kg. The variability of each data set shows the extent of the DOM differences in the two types of porewater. Literature values for TeCB partitioning by porewater DOM range from  $1.47 \times 10^5$  to  $2.23 \times 10^5$  L/kg and are dependent on the analytical method, sample source, and sample handling (16, 36). From this study, it is apparent that the DOM concentration and aromatic content are not the only criteria that determine the partitioning of TeCB by porewater DOM. The nature of the organic matter and its interaction with inorganic iron are also important.

When anoxic sediments are disturbed and mixed with aerated overlying water, a series of changes occur in the porewater matrix that can affect the distribution, mobility, and bioavailability of HOCs: the environmental redox potential, pH, and dissolved oxygen concentration are increased and reduced metal species are oxidized. The TeCB solubility enhancements and  $K_{PWWDOM}$  values determined in this study indicate that the distribution between free and DOM-associated TeCB species is different in anoxic sediment systems as compared to oxic systems. Mobility and bioavailability of HOCs are predicted to increase when anoxic sediments are disturbed and aerated because the total and freely dissolved HOC concentrations are increased.

## Acknowledgments

This work was presented at the American Chemical Society Meeting, New York, NY, August 1991. This paper is part of a Ph.D. dissertation presented at Drexel University, Philadelphia, PA, in 1992. The authors would like to thank Joel Pedersen for helping to edit the final draft of this paper.

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Received for review January 19, 1996. Revised manuscript received October 14, 1996. Accepted October 22, 1996.\*

ES9600542

\* Abstract published in *Advance ACS Abstracts*, January 15, 1997.