Experimental verification of a model describing solid phase microextraction (SPME) of freely dissolved organic pollutants in sediment porewater

Ze-Yu Yang1, Keith A. Maruya, Darrin Greenstein, David Tsukada and Eddy Y. Zeng

ABSTRACT
To verify a theoretical mass balance and multiple compartment partitioning model developed to predict freely dissolved concentrations (FDCs) of hydrophobic organic chemicals (HOCs) using negligible depletion-solid phase microextraction (nd-SPME), a series of sediment slurry experiments were performed using disposable poly(dimethyl)siloxane (PDMS) coated solid phase microextraction (SPME) fibers and 14C-radiolabeled HOC analogs. First, pre-calibration of disposable PDMS coated fibers for four model compounds (phenanthrene, PCB 52, PCB 153 and \( p,p' \)-DDE) with good precision (≤10%) was achieved. Second, sediment slurries spiked and aged with the radiolabeled analogs were extracted by SPME with manipulation of the sediment slurry mass or the PDMS coating volume. The measured extent of depletion by SPME \( (x_e) \) decreased with increasing sediment mass \( (m_s) \); conversely, \( x_e \) increased with increasing PDMS coating volume \( (V_f) \), which is consistent with the theoretical prediction from our previous model (Yang et al. 2007b). Moreover, the SPME-measured FDCs \( (C_{pw,SPME}) \) followed the order of phenanthrene > PCB 52 > \( p,p' \)-DDE > PCB 153, and the measured and predicted \( C_{pw} \) values were not substantially different from empirically determined values except for \( p,p' \)-DDE.

INTRODUCTION
The bioavailability of contaminants is a critical component for evaluation of risks associated with contaminated soils or sediments. The bioavailable fraction of contaminants, and in particular for hydrophobic organic chemicals (or HOCs), is defined as the freely dissolved concentration (FDC; Krajai et al. 2002). However, it is a nontrivial task to measure FDCs due to the inherently ultralow aqueous solubility for HOCs, coupled with the incomplete phase separation of FDCs from competing phases in natural systems, e.g., dissolved organic matter (DOM) in sediment porewater. Therefore, the potential for highly variable biological impacts due to differential contaminant bioavailability is often ignored in risk assessment. As a result, the assessment of contaminated sediments and soils is often based on total HOC concentrations.

Solid phase microextraction (SPME) devices have been applied as a tool to measure the FDCs of HOCs (Vaes et al. 1996, Urrestarazu-Ramos et al. 1998, Mayer et al. 2000), and as a surrogate for bioavailability, to represent bioaccumulation by organisms directly exposed to contaminated media (Verbruggen et al. 2000, Leslie et al. 2002a, Leslie et al. 2002b). SPME fibers are coated with a small volume (nL-µL range) of a hydrophobic phase (e.g., poly(dimethyl)siloxane or PDMS) to sorb the freely dissolved fraction of target HOCs. With a large surface area to volume ratio, these fibers comprise a relatively fast sorption medium that does not affect the chemical equilibrium present in soil/sediment.

For both direct immersion and headspace sampling techniques, three conditions must be attained for appropriate application of SPME in measuring FDCs in complex matrices identified by Heringa and Hermens (2003). First, equilibration between the
bound and free fractions of the analyte must be established. Second, the amount of HOC sorbed by the SPME fiber should be negligible, compared to the total pool available for sorption. This condition is known as non-depletive SPME (nd-SPME). Lastly, the binding matrix should not affect the SPME measurements.

In our previous study (Yang et al. 2007b), a theoretical mass balance framework that utilized equilibrium partitioning theory was presented to model the behavior of HOCs in a simplified three component system consisting of solid, aqueous (e.g., porewater) and SPME phases. The key parameters for this model were sediment volume, moisture content and organic carbon (OC) content of the slurry under consideration, as well as SPME coating volume. Relationships predicting the minimum sediment volume necessary to achieve nd-SPME as functions of properties such as target chemical hydrophobicity (i.e., $K_{ow}$) and SPME coating volume were generated.

The objective of this study was to experimentally verify the above-mentioned three conditions needed for equilibrium, nd-SPME in measuring the FDCs of HOCs in sediment. Cost-effective, disposable PDMS-coated fibers were exposed in sediment slurries spiked with $^{14}$C radiolabeled HOC analogs. These experimental results were than compared with our previous theoretical predictions (Yang et al. 2007b).

**METHODS**

**Target Analytes and Other Materials**

$^{14}$C-labeled phenanthrene, 1,1-bis-(4-chlorophenyl)-2,2-dichloroethene ($p,p'$-DDE), 2,2', 4,4'-tetrachlorobiphenyl (PCB 52), and 2,2', 4,4', 5,5'-hexachlorobiphenyl (PCB 153) with specific activities of 55.7, 12.7, 7.2, and 12.6 Ci mol$^{-1}$, respectively, were purchased from Sigma (St. Louis, MO). Logarithmic octanol/water partition coefficients ($\log K_{ow}$; Table 1) are 4.46 for phenanthrene (Neff and Burns 1996), 6.96 for $p,p'$-DDE (de Bruijn et al. 1989), and 5.84 and 6.92 for PCB 52 and PCB 153 (Hawker and Connell 1988), respectively. Ultra resi-analyzed grade hexane and reagent grade sodium azide ($\text{NaN}_3$) were obtained from Mallinckrodt Baker (Phillipsburg, NJ). Optima grade acetone and hexane were obtained from Fisher Scientific (Pittsburgh, PA). EcoLite$^{TM}(+) $ scintillation fluid was obtained from ICN Biomedicals (Costa Mesa, CA). Disposable SPME (optical) fiber with a 430-µm core and a 35-µm PDMS coating thickness was purchased in bulk from Polymicro Technologies (Phoenix, AZ).

**Table 1. Log $K_{f}$ values and ratios of $K_{f}/K_{ow}$ for disposable PDMS-coated SPME fibers.**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\log K_{ow}$</th>
<th>$\log K_{f}$</th>
<th>$K_{f}/K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenanthrene</td>
<td>4.46</td>
<td>3.66 (0.04)</td>
<td>0.16</td>
</tr>
<tr>
<td>PCB 52</td>
<td>5.84</td>
<td>5.04 (0.05)</td>
<td>0.16</td>
</tr>
<tr>
<td>PCB 153</td>
<td>6.92</td>
<td>5.99 (0.03)</td>
<td>0.12</td>
</tr>
<tr>
<td>$p,p'$-DDE</td>
<td>6.96</td>
<td>5.29 (0.06)</td>
<td>0.02</td>
</tr>
</tbody>
</table>

$^a$ Values of log $K_{ow}$ of phenanthrene, PCB 52 and PCB 153, and $p,p'$-DDE were from the previous studies of Neff and Burns (1996), Hawker and Connell (1988), and de Bruijn et al. (1989), respectively.

$^b$ Obtained with 35-µm PDMS coating thickness and 3-cm fiber length.

**Spiked Sediment Slurry Preparation**

Wet-sieved (500-µm mesh) estuarine sediment with TOC content of 0.66% collected using a Van Veen grab from upper Newport Bay (Newport Beach, CA) was suspended in filtered seawater to a final water content of 60% (w/w) and a density of 1.5 g ml$^{-1}$. Four 155-g aliquots of this slurry were spiked with an acetone solution containing 2 µCi each of $^{14}$C-labeled phenanthrene, $p,p'$-DDE, PCB 52, and 3 µCi $^{14}$C-labeled PCB 153. After addition of NaN$_3$ to inhibit biodegradation, spiked slurries were homogenized on a roller table for two hours every day in the following two months, and stored at 4°C for seven months in the dark.

**Calibration of Disposable SPME Fibers**

Prior to initial use, SPME fibers, cut into 3-cm lengths, were sonicated for 30 minutes with distilled water, and acetone. Similarly, glass scintillation vials (25 ml) were washed with detergent and tap water, rinsed with distilled water, and kilned at 450°C for ≥4 hours. PTFE-coated stir bars were rinsed with distilled water, sonicated in CH$_2$Cl$_2$ for 10 min, and dried at 100°C. Pre-conditioned fibers were inserted into 25-ml distilled water (dissolved organic carbon (DOC) <0.03 mg L$^{-1}$) spiked with different $^{14}$C-labeled target chemicals following the procedures described previously for commercially available fibers (Yang et al. 2007a). Briefly, the ini-
tial radioactivity of the four analytes in 25 ml of water was 0.005 μCi, and the times to equilibrium for phenanthrene, PCB 52, PCB 153, and p,p’-DDE were four, four, eight, and eight days, respectively. The radioactivities of SPME fiber sorption \( (N_f^e) \) and in residual spiked water \( (N_w^e) \) after SPME equilibrium extraction were counted by a 1214 RackBeta ‘Excel’ liquid scintillation counter (LSC; LKB Wallac, Wallac, Turku, Finland), and the partition coefficient \( (K_f) \) of a 3-cm disposable PDMS fiber is expressed as:

\[
K_f = \frac{C_f^e}{C_w^e} = \frac{N_f^e V_w}{V_f N_w^e}
\]

where \( C_f^e \) and \( C_w^e \) are the analyte concentrations in the PDMS coating and water after equilibrium SPME extraction; and \( V_f \) and \( V_w \) are the volumes of the PDMS coating and water, respectively.

The coating volume \( (V_f) \) of disposable fibers with different lengths and thicknesses can be expressed as: \( V_f = \pi L (R^2 - r^2) \), where \( L \) is the length of the fiber, \( R \) is the sum of the radius of the glass core and the coating thickness (250 μm), and \( r \) is the radius of the glass core (215 μm). \( V_f \) for a 3-cm disposable fiber is, for example, 1.53 μl.

**Sediment Slurry Experiments**

**Time to equilibrium \( (t_{eq}) \)**

Time-series experiments were performed to determine \( t_{eq} \) for an aged sediment slurry spiked with \(^{14}\)C-labeled PCB 153. Triplicate fibers of the same length (3 cm long, \( V_f = 1.53 \mu l \)) were inserted into flasks containing 25 ml of spiked slurry to ensure nd-SPME. After fiber insertion, flasks were secured on a roller table rotating at 6 rpm in a water bath maintained at 25 ±2°C. At 1, 2, 4, 8, 16, 20, 24, and 30 days, fibers in triplicate were carefully removed from the vial, gently wiped with a Kimwipe tissue and rinsed with distilled water to remove residual sediment. Loaded fibers were then extracted with hexane in a sonication bath for two hours (Yang et al. 2007a). The fiber desorbing (hexane) solutions were analyzed by LSC and \( t_{eq} \) determined from plots of \( N_f \) vs. extraction time.

**Effect of PDMS coating volume and sediment mass on extent of depletion**

Two sets of experiments were designed to test the effects of \( V_f \) and sediment mass \( (m_s) \) on the extent of depletion \( (x_e) \), where \( x_e = \frac{(C_{pw} - C_{pw0})}{C_{pw0}}, \) and \( C_{pw} \) and \( C_{pw0} \) are the FDCs in porewater before and after SPME extraction, respectively. First, disposable fibers of different length and thus increasing \( V_f \) (1.53, 4.59, 9.2, 18.4, and 36.8 μl) were inserted into five spiked and aged slurries with a volume of 5 ml to test the effect of \( V_f \) on \( x_e \), respectively. Five identical 5-ml slurries (spiked with four \(^{14}\)C-chemicals) without SPME fibers were prepared independently to determine \( C_{pw0} \). Second, 18 cm long fibers \( (V_f = 9.2 \mu l) \) were exposed in spiked and aged slurries of different volumes (3, 5, 10, and 20 ml) to test the effect of \( m_s \) on \( x_e \), respectively. Similarly, 3-, 5-, 10-, and 20-ml slurry samples spiked with the \(^{14}\)C-labeled analytes without SPME fibers were also prepared under the same controlled environment to determine \( C_{pw0} \). All slurries were shaken on a roller table at 6 rpm and maintained at 25 ±2°C.

Loaded fibers were removed from slurries after 24 days, cleaned completely of any residual sediment with distilled water, sonicated in 10 ml of hexane for 2 hours, and analyzed by LSC. Approximately 100 mg of sediment slurry was weighed and counted by LSC to determine radioactivity associated with sediment before \( (C_s) \) and after \( (C_s) \) SPME extraction. Porewater was obtained from sediment slurry samples by centrifugation at 3500 rpm for 30 minutes; 1 ml of porewater was used to determine total porewater concentrations before \( (C_{pw0}) \) and after \( (C_{tot}) \) SPME. In these experiments, \( C_{tot} \) and \( C_{tot0} \) were considered the precursors of \( C_{pw} \) and \( C_{pw0} \), respectively. \( C_{tot} \) and \( C_{tot0} \) also represent comparative values before SPME for mass balance purposes. It should be noted that no replicate experiments to measure \( N_f \) were undertaken in the present study because good precision in calibrating disposable SPME fibers was obtained. On the other hand, porewater radioactivity was measured in duplicate or triplicate for a given sample except for four samples with a slurry volume of ~3 ml that did not provide sufficient porewater for repeated measurements (1 ml of porewater was needed for each measurement). For instance, less than 2 ml of porewater could be squeezed from a 3-ml slurry sample, while approximately 2 ml of porewater could be separated from the 5- to 10-ml samples. As a result, all data points in Figures 2 and 3 were the averages of repeated porewater measurements before and after extraction.
Data Analysis

Theoretical background of nd-SPME conditions

As described previously (Yang et al. 2007b), the governing equation relating the minimum sediment volume \( V_{s\,\text{min}} \) for nd-SPME in a slurry system to other experimental parameters is as follows:

\[
V_{s\,\text{min}} = \frac{K_f V_f (1 - x)}{x \delta_s \left( K_{oc} f_{oc} + \frac{f_{pw}}{1 - f_{pw}} \delta_{pw} \right)}
\]

where \( \delta_s \) and \( \delta_{pw} \) are the densities of sediment and porewater, respectively; \( f_{pw} \) is the moisture content of the slurry, \( f_{oc} \) is the TOC content in the sediment, \( K_{oc} \) is the partition coefficient of the analyte between sediment TOC and water; \( K_f V_f \) is the analyte-specific product of the PDMS coating-water partition coefficient and coating volume, and \( x \) (\( = x \) in Equation 2) is the theoretical extent of depletion.

In the present study, two parameters were updated in Equation 2. First, the amount of HOCs associated with DOC maybe significant relative to that which is freely dissolved (i.e., the FDC). Second, the sediment volume \( V_{s\,\text{min}} \) was replaced by sediment mass \( m_s \). Accordingly, Equation 2 can be updated and expressed as:

\[
\frac{K_f V_f}{m_s} = \frac{K_{doc} f_{pw} m_s}{1 - f_{pw}} \left( \rho_{doc}^0 - \rho_{doc} \right)
\]

where \( K_{doc} \) is the partition coefficient of the analyte between DOC and water, and \( \rho_{doc}^0 \) and \( \rho_{doc} \) are the DOC concentrations in porewater before and after SPME, respectively. The remaining parameters in Equation 3 represent properties of the slurry (e.g., \( f_{pw} \) and \( f_{oc} \)) and/or target analytes and can be assumed to be constant.

Estimation of freely dissolved concentrations \((C_{pw})\) in porewater

The innocuity of matrix effects, e.g., association of HOCs with DOM, is the third condition for justifying the use of nd-SPME to measure the FDCs. The freely dissolved concentration in porewater \((C_{pw})\) can be predicted using the theory of equilibrium partitioning for three simplified dual component systems: PDMS coating and water; DOC and water; and sediment TOC and water. These concentrations are designated as \( C_{pw,\text{SPME}} \), \( C_{pw,\text{doc}} \), and \( C_{pw,\text{oc}} \), respectively. \( C_{pw,\text{SPME}} \) can be expressed as:

\[
C_{pw,\text{SPME}} = \frac{N_s}{K_f V_f}
\]

where all the parameters have been defined previously. In porewater containing colloidal organic matter, \( C_{pw,\text{doc}} \) can be estimated from a three-phase partitioning model (Chin and Gschwend 1992, Burkhard 2000).

\[
C_{pw,\text{doc}} = C_{tot} \left( 1 + \frac{\rho_{poc} K_{poc}}{1 + \rho_{doc} K_{doc}} \right)
\]

where \( \rho_{poc} \) and \( \rho_{doc} \) are the concentrations of particulate organic carbon (POC, \( \rho_{poc} \approx 0 \) due to the filtration using GF/F membrane with a 0.7-µm nominal pore size after centrifugation) and DOC, respectively. Similarly, the radioactivity \((N_s)\) of a certain amount of SPME extracted sediment slurry \((m_s)\) was measured before centrifugation.

Using the definitions of \( K_{oc} = C_{oc}/C_{pw} \), \( C_s = \frac{N_s}{m_s (1 - f_{pw})} \), and \( C_{oc} = C_s f_{oc} \), where \( C_{oc} \) and \( C_s \) are the analyte concentrations in OC and slurry, \( C_{pw,\text{oc}} \) can be expressed as:

\[
C_{pw,\text{oc}} = \frac{N_s}{m_s (1 - f_{pw}) f_{oc} K_{oc}}
\]

Assumptions and conditions for model simulation

In the present study, \( f_{oc} \) and \( f_{pw} \) are 0.66 ±0.10% and 60% and \( \rho_{doc}^0 \) and \( \rho_{doc} \) were determined with a Shimadzu TOC-VCPH/CPN analyzer (Columbia, MD) to be 274 and 485 mg L\(^{-1}\), respectively. The equilibrium partitioning parameters \((K_{oc} \) and \( K_{doc} \)) were estimated from their empirical relationships to the octanol-water partition coefficient \((K_{ow})\), i.e., \( K_{doc} = 0.08 K_{ow} \) (Burkhard 2000) and \( K_{oc} = 0.41 K_{ow} \) (Karickhoff 1981). Incorporating these parameters...
Verification of SPME model for organic pollutants in porewater - 33

(7)

It is evident that $x_t$ is governed by analyte-specific values of $K_{ow}$ and $K_f$, PDMS coating volume ($V_f$), and slurry mass ($m_s$). Similarly, Equations 5 and 6 can be revised to:

$$C_{pw,doc} = C_{tot}/(1 + 3.88 \times 10^{-5} K_{ow}) \quad (8)$$

and

$$C_{pw,oc} = \frac{923 N_f}{m_t K_{ow}} \quad (9)$$

RESULTS AND DISCUSSION
Calibration of Disposable Fibers
The measured log $K_f$ values for the four model HOCs using the disposable PDMS coated fibers (3 cm long) are summarized in Table 1. In general, the measured values were proportional to log $K_{ow}$, with $K_f/K_{ow}$ ratios of 0.16, 0.16, and 0.12 for phenanthrene, PCB 52, and PCB 153, respectively. These latter ratios were similar to the empirical value of 0.123 reported by Mayer et al. (2000). For $p,p'$-DDE, however, the measured log $K_f$ of 5.29 was almost two orders of magnitude less than its reported $K_{ow}$ value, resulting in a $K_f/K_{ow}$ of 0.02. This discrepancy for $p,p'$-DDE may partially be due to the inaccuracy of the cited $K_{ow}$ value (Pontolillo and Eganhouse 2001). Another important attribute for pre-calibration of SPME fibers is precision. Extraction precision for the disposable fibers in this study was better than 10% ($n = 7$), indicating their appropriateness for quantitative determinations.

Variation of DOC and OC Contents with Incubation Time
DOC in centrifuged porewater increased with agitation time in the slurry experiments, from 274 mg L$^{-1}$ at the beginning of SPME exposure to 485 mg L$^{-1}$ after 24 days of loading. Koelmans and Prevo (2003) also reported that turbulence (agitation) caused DOC to increase, especially for sediment with low TOC content and high water to sediment ratio, which yielded high liberated DOC. The high water to sediment ratio and low OC content ($f_{pw}$ and $f_{oc}$ of 60% and 0.66 ±0.10% ($n = 7$), respectively) coupled with the continuous shaking in this experiment likely facilitated the release of organic matter from sediment into the aqueous phase, resulting in the observed increase in DOC over time. To account for this in model prediction, $\rho_{doc}$ and $\rho_{doc0}$ in Equation 3 were assigned their time dependent values. However, the sediment TOC content in the present study did not change measurably during the test period, and thus its value was assumed constant.

Extraction Kinetics and Attainment of Equilibrium
Radioactivity ($N_f$) of $^{14}$C-labeled PCB 153 on disposal fibers increased with extraction time rapidly for the first 10 days, followed by a slower rate of change, and finally reaching a plateau at Day 20 (Figure 1). The equilibrium time for PCB 153 was clearly in the range of 20 - 30 days. Because $t_{eq}$ is proportional to the molecular weight of an analyte (Pawliszyn 1997), this amount of time should be sufficient to obtain equilibrium for the other three target analytes since PCB 153 has the highest molecular weight among the four analytes. An extraction time of 24 days was thus chosen for all four analytes.

The $N_f$ with 24-day extraction was about 0.66% of the total radioactivity of the slurry, which is negligible relative to the experimental system because the PDMS coating volume was substantially smaller than that of the slurry. In addition, the time to equilibrium of 24 days in the present study was far less than that in static experiments (our unpublished results show that a longer time to equilibrium was
Variation of Theoretical and Experimental Extents of Depletion with Sediment Mass ($m_s$)

The criterion for nd-SPME is typically met by restricting the SPME extraction to a negligible fraction of the FDC, i.e., the extent of depletion is confined to a preset threshold (Vaes et al. 1996). Although researchers have chosen thresholds ranging from 1 to 10% (Górecki and Pawliszyn 1997, Poerschmann et al. 1997, Górecki et al. 1998, Parkerton et al. 2000), a thorough examination of the extent of depletion under specific experimental conditions is the key for ensuring the validity of nd-SPME. By fixing the length of a PDMS coated fiber at 18 cm ($V_f = 9.2$ µl) and varying the slurry volume (3 to 20 ml), the corresponding $m_s$ and $m_w$ values were 1.8, 3.0, 6.0, and 12.0 g, respectively.

Substituting the above parameters and the measured $K_f$ and cited $K_{ow}$ values (Table 1), the resulting theoretical extent of depletion computed using Equation 7 was in the range of 0.293 - 0.044, 0.298 - 0.045, 0.0435 - 0.0065, and 0.186 - 0.033 for phenanthrene, PCB 52, PCB 153, and $p,p'$-DDE, respectively. It is clear that the predicted percent of depletion decreased with increasing $m_s$ for all four model analytes (Figure 2). To examine the effect of $m_s$ experimentally, the measured extent of depletion was also determined for the four different slurry sizes (3, 5, 10, and 20 ml). Figure 2 shows that both the theoretical and experimental extents of depletion decreased with increasing sediment mass ($m_s$) for all analytes except for $p,p'$-DDE (see below).

Values of $x_e$ were consistently higher than $x_t$ (Figure 2). Additionally, theoretical modeling (Yang et al. 2007b) concluded that the minimum theoretical $V_s$ values reach a plateau as log $K_{ow}$ approaches 4 - 5 when $x_t$ is assumed to be 5%. All log $K_{ow}$ values of the target chemicals in the present study are higher than 4. When $x_t$ is assumed to be 5%, the minimum $m_s$ values from Equation 7 are 8.3, 8.4, 6.3, and 1.2 g for phenanthrene, PCB 52, PCB 153, and $p,p'$-DDE, respectively. The corresponding $x_e$ values in Figure 2 at these $m_s$ are close to or slightly higher than 15%, except for that of $p,p'$-DDE. The $x_e$ of $p,p'$-DDE was less than 15% at all tested $m_s$ (from 1.8 to 12.0 g), which is consistent with its theoretical minimum $m_s$ values (1.2 g) with the assumption of $x_t = 5%$. Consequently, the minimum experimental $m_s$ values are similar to each other except for that of $p,p'$-DDE. Possible reasons for this deviation are the much lower measured $K_f$ value for $p,p'$-DDE, which is far less than empirical predictions based on the relationship $K_f = 0.123 K_{ow}$ (Mayer et al. 2000). In addition, literature values of log $K_{ow}$ for this compound may be grossly overestimated (Pontolillo and Eganhouse 2001).

Several points can be made from the data in Figure 2. First, data for $x_e$ mirrors the decreasing trend in $x_t$ with increasing $m_s$, indicating that the the-
theoretical framework described previously (Yang et al. 2007b) adequately represents the effects of analyte specific properties (e.g., $K_{ow}$ and $K_{oc}$) and sediment mass on the extent of depletion. Second, the general $x_e > x_t$ trend suggests a fixed bias in experimental measurements (e.g., error in LSC counting, centrifugation, and other sample preparation procedures) or in literature $K_{ow}$ values. Third, a sediment mass approaching 10 g is needed to maintain acceptable extent of depletion ($\leq 10\%$) for three of the four test compounds. Lastly, the measured extent of depletion for $p,p'$-DDE did not exceed 0.12 even though no discernable trend with sediment mass was observed. Additional work with this compound is needed to fully understand these observations.

**Variation of Theoretical and Experimental Extents of Depletion with Coating Volume ($V_f$)**

Varying $V_f$ experimentally (by using fibers of different length) while fixing $m_s$ (5-ml slurry volume corresponding to $m_s$ and $m_w$ of 3.0 and 4.5 g, respectively) resulted in the increasing trend in $x_e$ for the model HOCs (Figure 3). This is reasonable since the extraction capacity (or $N_f$) of a SPME fiber increases with increasing PDMS coating volume. When exposed to a fixed reservoir of HOC in the aqueous (porewater) phase, increasing $N_f$ by using longer fibers thus results in greater extent of depletion (or $x_e$). Furthermore, very good agreement between $x_e$ and $x_t$ was observed for phenanthrene and a fixed positive bias, similar to that observed with $m_s$ (Figure 2), was observed for PCBs 52 and 153 (Figure 3). Values of $x_e$ were also greater than $x_t$ for $p,p'$-DDE, but any increasing trend with $V_f$ was less obvious.

From the previous experiment, predicted minimum $m_s$ values from Equation 7 at $x_t = 5\%$ were similar to the experimental minimum $m_s$ with a 15\% extent of depletion. Therefore, 5\% is assumed to be the threshold for $x_t$. Using Equation 7 and assuming $x_e = 15\%$ for $m_s = 3$ g, the corresponding theoretical maximum values of $V_f$ for phenanthrene, PCB 52, PCB 153, and $p,p'$-DDE, were 2.3, 2.3, 3.0, and 16.5 µl, respectively. By comparison, the experimentally measured maximum $V_f$ obtained from the linear regression of the observed experimental data (Figure 3) were 13.4, -0.6, 6.7, and 26.5 µl, respectively.

Inspection of Figure 3 reveals that the extent of depletion ($x_e$ or $x_t$) can be maintained below 0.1 for $V_f$ less than 10 µl for phenanthrene, PCB 52 and PCB 153. The corresponding data for $p,p'$-DDE indicates a doubling of the critical $V_f$, i.e., at approximately 20 µl. Because commercially available SPME fibers have a fixed length (1 cm) and a maximum PDMS coating of 0.612 µl, this finding suggests that the use of disposable fibers with more than 10 times greater sorptive volume can be utilized without depleting a fixed sediment mass (~3 g). In either case, the experimental data presented herein show good agreement with the trends predicted by the theoretical framework (Equation 7). Additional work remains, however, to fully explain the deviations observed for $p,p'$-DDE.

**Effect of Dissolved Organic Matter**

Aqueous phase concentrations of the target HOCs in the spiked slurries determined by SPME (Equation 4; $C_{pw,SPME}$) from all verified nd-SPME systems are plotted against concentrations estimated from the relationships defined by partitioning to DOM (Equation 8; $C_{pw,doc}$) and TOC (Equation 9; $C_{pw,oc}$). It should be noted that $C_{pw,SPME}$ and $C_{pw,doc}$ were estimated with nd-SPME requirements detailed in previous sections. For example, the minimal $m_s$ and maximal $V_f$ to achieve nd-SPME conditions were 10 g and 13.4 µl, respectively, for phenanthrene in the present study; therefore, a system with $m_s = 12$ g

---

**Figure 3.** Variation of experimentally measured ($x_e$) and theoretically predicted ($x_t$) extents of depletion ($t_{eq} = 24$ days) with PDMS coating volume ($V_f$). Sediment slurry mass ($m_s$) was fixed at 3 g; $V_f$ values were 1.5, 4.6, 9.2, 18, and 37 µl, respectively.
Verification of SPME model for organic pollutants in porewater - 36

(with a slurry volume of 20 ml) and \( V_f = 18.4 \) or 36.8 \( \mu l \) presumably satisfies the nd-SPME conditions to evaluate the corresponding average \( C_{pw,SPME} \) and \( C_{pw,doc} \). All measured slurry analyte concentrations were averaged to estimate \( C_{pw,oc} \) because the analyte amount extracted by SPME was negligible for the entire slurry system. \( C_{pw} \) values follow the order of phenanthrene > PCB 52 > \( p,p' \)-DDE > PCB 153 (Figure 4), indicating that the FDCs decrease with increasing \( \log K_{ow} \). This clearly shows that HOC-specific hydrophobicity largely governs the amount of HOCs associated with (dissolved phase) DOC/(particulate phase) TOC and as a direct result of partitioning, the amount that is the FDC (Kraaij et al. 2002). Moreover, the measured and predicted \( C_{pw} \) values for phenanthrene were within a factor of two, with the DOM prediction and SPME-measured values nearly identical (Figure 4). For the two PCB congeners, on the other hand, \( C_{pw,SPME} \) and \( C_{pw,oc} \) were coincident with each other with the predicted \( C_{pw,doc} \) much lower than the others. Possible errors in estimating \( K_{oc} \) are likely higher than similar determinations of \( K_{oc} \).

Because phenanthrene is the least hydrophobic of the four model analytes, the concurrence between \( C_{pw,SPME} \) and \( C_{pw,oc} \) suggests a stronger relative interaction between DOM as opposed to sediment TOC. In contrast, the agreement between \( C_{pw,SPME} \) and \( C_{pw,oc} \) for the PCB congeners indicates that the solid phase (and not DOM) controlled the aqueous phase concentration. These latter findings further suggest that DOC is not an important binding phase in terms of measuring FDCs, i.e., that matrix effects contributed from DOM were negligible.

The fact that neither prediction corresponded to the measured \( C_{pw,SPME} \) for \( p,p' \)-DDE could be explained by two competing circumstances. Simple overestimation of \( K_{ow} \) value for \( p,p' \)-DDE, as pointed out previously by Pontolillo and Eganhouse (2001), may contribute to underestimated predicted values for both \( C_{pw,oc} \) and \( C_{pw,doc} \), since these quantities are indirect functions of \( K_{ow} \) (Equations 8 and 9). Another possible scenario is sorption of DOM/TOC directly to the PDMS coating, which in effect artificially increases the amounts of HOC sorbed to the fiber (Heringa and Hermens 2003). Since \( C_{pw,SPME} \) is modeled well for phenanthrene, PCB 52 and PCB 153, the only clear cut example of this scenario would be for \( p,p' \)-DDE, where \( C_{pw,SPME} \) was greater than both predicted values (Figure 4). Although DOC content was relatively high (485 mg L\(^{-1} \) at experiment’s end), sorption of DOM-associated HOC would likely have resulted in much higher \( C_{pw,SPME} \). Furthermore, several previous publications on direct-immersion SPME in matrix-containing samples did not report attachment of sample residues to SPME coatings or visual or quantitative proof of “DOM or TOC fouling” (Pawliszyn 1997, Urrestarazu-Ramos et al. 1998, Ohlenbusch et al. 2000, Hawthorne et al. 2005). Without evidence of enhanced fiber sorption for the other three analytes, we attribute the disconcordance in measured vs. predicted concentrations for \( p,p' \)-DDE to underestimated \( C_{pw} \), due to likely misrepresentation of partitioning properties based on \( K_{ow} \).

### Implications for Ultralow Level Detection in Sedimentary Environments

The experimental results presented herein suggest that the theoretical mass balance and multi-compartment partitioning model for describing the interaction of SPME fibers in HOC-contaminated sediment and/or sediment slurry environments presented previously by Yang et al. (2007b) can be used to guide the overall design of sediment porewater samplers based on SPME. Specifically, the effects of critical design parameters such as the minimum sediment volume and maximum sorptive coating volume \( (V_f) \) can be simulated without difficult and costly experimental validation. Moreover, characterization of the freely dissolved phase component of HOCs in sediment porewater is a highly relevant, yet elusive

![Figure 4. Comparison of SPME measured (\( C_{pw,SPME} \)) and predicted (\( C_{pw,doc} \) and \( C_{pw,oc} \)) freely dissolved concentrations in spiked sediment slurries (\( t_{eq} = 24 \) days). Sediment slurry mass (\( m_s \)) = 12 g; PDMS coating volume (\( V_f \)) = 9.2 μl.](image-url)
undertaking that can assist with directly quantifying the bioavailability of sediment associated HOCs. Lastly, this study highlighted the potential of disposable SPME fibers in increasing the sensitivity for ultralow level detection of dissolved phase HOCs.

**LITERATURE CITED**


Pontolillo, J. and R.P. Eganhouse. 2001. The search for reliable aqueous solubility (S_a) and octanol-water
partition coefficient ($K_{ow}$) data for hydrophobic organic compounds: DDT and DDE as a case study. Water-Resources Investigations Report 01-4201. US Geological Survey. Reston, VA.


**Acknowledgements**

Financial support of the present study by the National Natural Science Foundation of China (No. 20677061), the Cooperative Institute for Coastal and Estuarine Environmental Technology (Contract No. NA05NOS4191149), and the “One Hundred Talents” Program of the Chinese Academy of Sciences is gratefully acknowledged. The authors also thank Dr. Jian Peng and Dr. Wenjian Lao for their assistance.