A passive sampler based on solid phase microextraction (SPME) for quantifying hydrophobic organic contaminants in sediment porewater

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ABSTRACT

Sediment quality assessment is often hindered by the lack of agreement between chemical and biological lines of evidence. One limitation is that the bulk sediment toxicant concentration, the most widely used chemical parameter, does not always represent the bioavailable concentration, particularly for hydrophobic organic compounds (HOCs) in highly contaminated sediments. In this study, a porewater sampler that utilizes solid phase microextraction (SPME) to measure freely dissolved ("bioavailable") HOC concentrations was developed and tested. A single polydimethylsiloxane (PDMS) coated SPME fiber was secured in a compact protective housing that allows aqueous exchange with whole sediment while eliminating direct contact with sediment particles. Fibers with three PDMS coating thicknesses were first calibrated for 12 model polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), DDTs, and chlordanes, representing HOCs of current regulatory concern. Pre-calibrated samplers were exposed to spiked estuarine sediment in lab microcosms to determine the time to equilibrium and equilibrium concentrations across a range of sediment contamination. Time to equilibrium ranged from 14 to 110 days, with 30 days being sufficient for more than half of the target HOCs. Ranging from 0.009 to 2400 ng/L, equilibrium SPME measurements were highly correlated with, but generally lower than HOC porewater concentrations determined independently by liquid-liquid extraction. This concept shows promise for directly measuring the freely dissolved concentration of HOCs in sediment porewater, a previously difficult-to-measure parameter that will improve frameworks for assessing the impacts of contaminated sediments.

INTRODUCTION

Sediments are the largest sink of HOCs in the aquatic environment. Accumulation of HOCs to high levels in sediments poses a risk to both ecological and human health via direct and indirect pathways. For example, chlordanes are associated with toxic effects exerted on benthic organisms that directly inhabit contaminated sediments. Conversely, marine and terrestrial mammals (including humans) are indirectly exposed to HOCs via food web transfer. The resulting biomagnification of toxicants like DDT, PCBs, and brominated flame retardants (e.g., polybrominated diphenyl ethers (PBDEs)) can result in and/or exacerbate reproductive and immunosuppressive impacts.

The bulk sediment concentration of a suspected toxicant is a logical and thus commonly used indicator of potential HOC exposure for benthic organisms. Coupled with biological endpoints like benthic community condition and sediment toxicity, bulk "sediment chemistry" has been widely used in sediment quality assessment (Chapman *et al.* 1987, Bay *et al.* 2007). To account for the affinity of HOCs with organic matter (Karickhoff *et al.* 1979), models relating aqueous and solid phase partitioning were created to help explain differences in bioavailability observed in toxicological and bioaccumulation endpoints (DiToro *et al.* 1991).

More recently, heterogeneities within the organic subcomponent of soils and sediments have also been shown to have a profound effect on the partitioning and bioavailability of HOCs. Condensed, sooty materials known collectively as black carbon (BC) were first shown to reduce the bioavailability of PAH in contaminated harbor sediments (McGroddy

and Farrington 1995). Several subsequent studies have shown a similar influence of BC on the binding strength and bioavailability of additional classes of HOCs, including PCBs (Jonker *et al.* 2004), as well as legacy and current-use pesticides (Xu *et al.* 2008). The effectiveness of BC in altering HOC bioavailability, at least in the short term, has resulted in its consideration in remedial strategies for highly contaminated sediments (Tomaszewski *et al.* 2007).

A growing body of evidence suggests that the freely dissolved phase of HOCs represents the highly bioavailable fraction (Mayer *et al.* 2000a, Kraaij *et al.* 2003). By definition, however, determination of this parameter must be made at ultralow levels (e.g., in the sub-parts per billion range). Moreover, this determination is made difficult by the presence of dissolved organic matter (DOM), a competing binding phase for HOCs in natural waters (Means and Wijayaratne 1982), including sediment interstitial or "porewater" (Brownawell and Farrington 1986). Because separation of freely dissolved from colloidal and particulate HOC fractions is exceedingly difficult, little data is available and measurements representing total aqueous phase HOC concentrations are much more common. Unfortunately, this latter parameter can be of limited utility in assessing bioavailability of HOCs in highly impacted, urban sediments containing elevated levels of soot carbon.

Solid phase microextraction is a passive sampling technology (Arthur and Pawliszyn 1990) that has shown promise for ultralow level detection of HOCs in aqueous media. Moreover, SPME is selective for the freely dissolved fraction in complex aqueous matrices (Mayer *et al.* 2000a). As evidence of this phenomenon, in situ samplers incorporating hydrophobic PDMS coated SPME fibers (Zeng *et al.* 2004) were deployed for several weeks to detect subparts per trillion concentrations of DDT in coastal seawater (Zeng *et al.* 2005). Concentrations determined by this sampler agreed well with independently measured, operationally defined dissolved phase measurements.

Based on this concept, a mass balance and HOC partitioning model predicted that the minimum sediment volume (V_s^{min}) required to maintain non-depletive conditions for a SPME based porewater sampler was independent of HOC concentration in both sediment and porewater, and that relatively small sediment volumes (<10 ml) participate in exchange equilibria among the solid, aqueous and SPME phases

(Yang *et al.* 2007a). This work also demonstrated that the sensitivity of such a sampler was proportional to K_{ow}, increased with increasing sorbent volume (V_f), and most importantly, that sub ng/L detection limits were possible.

The objective of this study was to develop and test the performance of a compact SPME passive sampler that can measure freely dissolved HOCs of regulatory concern in sediment porewater. With a focus on in situ measurement, an additional requirement for this sampler was to protect the SPME fiber from damage, fouling, and/or sediment contact. To achieve this, a prototype sampler adapted from a previous water column design (Zeng *et al.* 2004) was developed and fabricated. Key parameters (effect of PDMS coating thickness on sensitivity, time to equilibrium, and agreement with alternative porewater measurements) were then determined for selected prototypes using spiked sediment exposures.

METHODS

Twelve PAH, PCBs, DDTs and chlordanes spanning a wide range of hydrophobicity were selected as target HOCs based on frequency of occurrence in contaminated sediments and in environmental regulations (Table 1). Purified compounds were obtained from AccuStandard (New Haven, CT), UltraScientific (North Kingston, RI) and Sigma-Aldrich (St. Louis, MO). PDMS coated SPME fibers (7-, 30-, and 100-μm coating) were obtained from Supelco (Bellafonte, PA). Fibers (as-received) were thermally pre-treated in a gas chromatograph (GC) injector heated to 300°C for 15 minutes. All solvents of the highest purity available and reagents of ACS grade or better were purchased from Fisher Scientific (Fair Lawn, NJ). All glassware was exhaustively hand washed, kiln-fired at 550°C for ≥4 hours and solvent rinsed with acetone and hexane before and after use.

Effect of PDMS coating thickness on the fiber-water partition coefficient (K_f*)*

Compound-specific K_fs were determined for 7-, 30- and 100-μm PDMS coated SPME fibers following the methods developed by Yang *et al.* (2006). Briefly, double-distilled water containing all target HOCs at a single concentration (~0.2 ng/ml) was prepared in triplicate 2-L glass flasks with sodium azide to inhibit biotransformation. A single SPME fiber and Teflon-coated magnetic stir-bar were placed into each flask, which was then sealed with a

Analyte	log K_{ow}	log K_f*		
		7 μm	30 μm	100 μm
Phenanthrene (PHEN)	4.46	4.32 ± 0.11	4.10 ± 0.10	3.90 ± 0.07
Fluoranthene (FLUA)	5.16	4.69 ± 0.15	4.55 ± 0.08	4.26 ± 0.09
Benzo[a]pyrene (BAP)	6.13	6.06 ± 0.11	6.06 ± 0.15	5.82 ± 0.29
Heptachlor epoxide (HE)	4.98	4.64 ± 0.20	4.70 ± 0.03	4.48 ± 0.05
α-chlordane (aCHL)	6.22	5.59 ± 0.21	5.66 ± 0.03	5.37 ± 0.07
trans-nonachlor (tNON)	6.35	5.94 ± 0.24	6.14 ± 0.07	5.68 ± 0.08
p,p'-DDE	6.96	6.27 ± 0.20	6.50 ± 0.12	6.17 ± 0.07
p,p'-DDD	6.22	6.04 ± 0.30	6.66 ± 0.11	6.11 ± 0.17
p,p'-DDT	6.91	5.83 ± 0.24	6.06 ± 0.16	5.76 ± 0.11
PCB 52	5.84	5.66 ± 0.19	5.71 ± 0.03	5.52 ± 0.09
PCB 153	6.92	6.68 ± 0.20	6.59 ± 0.20	6.45 ± 0.09
PCB 180	7.36	6.76 ± 0.22	6.37 ± 0.34	6.54 ± 0.09

* average ± sd for triplicate (n = 3) batch calibration determinations

solvent-rinsed PTFE-lined cap. After exposing the fiber to the spiked water, the flask was agitated at 700 rpm and maintained at 23 ±2°C for 24 or 40 days, the longer time period for 100-μm coated fibers only. Fibers were analyzed using thermal desorption GC-MS (see "Sample analysis" below), while aqueous samples were liquid-liquid extracted (LLE). The accuracy of LLE was evaluated using a one-to-one recovery correction strategy employing a ^{13}C or deuterated-labeled surrogate for each target HOC.

Sampler design

The configuration of this study's prototype sampler was adapted from a previously designed water column sampler that had been tested and field-validated for sub-ppb levels of DDT in seawater (Zeng et al. 2004, Zeng et al. 2005). To protect and stabilize the SPME fiber assembly, a cylindrical housing was constructed of 1 mm thick copper (Cu) tubing with holes drilled into the walls to allow free water exchange with the fiber surface. The fiber assembly was attached to a Cu end cap that was secured onto one end of the cylindrical housing. A second end cap was fitted to the housing opposite of the fiber.

To prevent direct contact of the fiber with sediment particles, a glass fiber filter (Whatman GF/F) was wrapped around the housing exterior followed by a single layer of 270 mesh (0.053 mm opening) T316 stainless steel screen held in place by No. 6 (0.406 mm dia) single-strand stainless steel wire (Figure 1). To check for effects on sampler performance due to housing size, a "small" (length = 110 mm; housing id = 7.5 mm; internal cavity volume = 4.9 cm³) and a "large" (length = 150 mm; housing id = 14 mm; internal cavity volume = 23 cm³) prototype were constructed.

Sediment Exposure Experiments

Sampler toxicity

To test for toxicity due to the sampler itself, polychaetes (Nereis virens) and bivalves (Macoma nasuta) obtained from Brezina and Associates (Dillon Beach, CA) were exposed in 19-L glass aquaria, each containing a 5-cm layer of sieved marine sediment and overlying filtered seawater. Duplicate aquaria containing sediment, organisms, and a single large prototype sampler, and sediment and organisms only were prepared. A fifth aquarium served as a sediment only control. Flow-through conditions and water quality were maintained and measured as prescribed in ASTM/EPA 28-day bioaccumulation assay guidance manuals (ASTM 1995).

Preparation of spiked test sediments

Intertidal sediments from Newport Bay (NB),
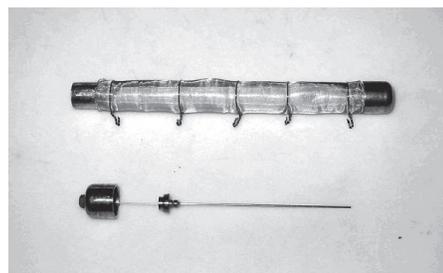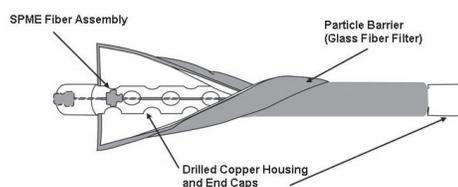
Figure 1. Schematic of the SPME-based porewater sampler (top) and photograph of "small" prototype casing (110 mm L x 9.5 mm od) with stainless steel mesh/glass fiber filter and SPME fiber assembly attached to removable end cap (bottom).

Newport Beach, CA, were collected, sieved, homogenized, and analyzed for several parameters, including BC, total organic carbon (TOC) and bulk HOC concentrations. Five-liter sieved aliquots were spiked at nominal concentrations of 50, 100, 500, and 1000 ng/g each in pre-cleaned, sealed glass bottles that were homogenized daily on a roller table for two months. Bottles were covered with aluminum foil to minimize ambient light exposure and maintained at room temperature during homogenization. After equilibration, spiked sediments were kept in the dark at 4°C until use.

Time to equilibrium

Four hundred ml of a composite of spiked and aged NB sediment prepared as described above was layered into 1-L borosilicate glass graduated cylinders. The nominal concentration for each analyte was 300 ng/g, with the exception of heptachlor epoxide which was spiked at a lower level (~60 ng/g). Two small samplers and a single large sampler each outfitted with 100-µm PDMS fibers were inserted below the sediment surface in each of the cylinders; the outfitted cylinders were then maintained at 25 ±3°C in an enclosed cabinet, shielded from ambient light. All three samplers in a single cylinder were removed for analysis at 14, 30, 60, 110, and 240 days. Filtered seawater was added as needed to maintain a constant level of overlying water. After removal, SPME fibers were inspected for damage, carefully wiped with tissue to remove residual water, and analyzed by thermal desorption GC-MS for the 12 target analytes. Porewater and spiked sediments sub-sampled at each time point were processed and analyzed by GC-MS as described below (see "Sample analysis").

Equilibrium SPME concentrations

Based on the previous time-series experiment, the prototype samplers were exposed to a concentration series of spiked NB sediment to determine porewater concentrations under static, equilibrium conditions. Two small and a single large sampler were exposed to 500 ml of spiked NB sediments in 1-L glass graduated cylinders for 60 days. Treatments included one unspiked and the four nominal spiked sediment concentrations described above. Ambient conditions during exposure were similar to those described previously (see "Time to equilibrium" above). At the end of the exposure period, SPME fibers were processed and analyzed for target HOCs. Porewater and spiked sediments sub-sampled at

Day 0 and Day 60 were processed and analyzed by GC-MS as described below.

Sample analysis

Fifty- to 100-ml aliquots of porewater were isolated from 100 to 150 g of whole sediment in a Teflon bottle centrifuged at 1800 rpm for 30 minutes, filtered through a glass fiber filter (Whatman GF/F), and subsequently extracted with triplicate aliquots of CH_2Cl_2 in a glass separatory funnel. Organic extracts were combined, concentrated, and exchanged to hexane using a rotary evaporator prior to GC-MS analysis. Frozen aliquots of whole sediment were thawed at room temperature, freeze-dried, extracted with CH_2Cl_2 under elevated temperature and pressure using a Dionex 300 ASE system (Salt Lake City, UT), and cleaned with silica gel/alumina column chromatography. Eluted extracts containing target HOCs were analyzed by GC-MS (see below). Sediment TOC was determined by catalytic combustion of an oven-dried decarbonized aliquot of wet sediment using a Carlo Erba CHN analyzer. Sediment BC was estimated per Gustafsson *et al.* (1997) on an oven-dried (60°C) aliquot of wet sediment ground to a fine powder and decarbonized with 1 M HCl. After re-drying, samples were combusted at 375°C for 24 hours in the presence of excess air and BC quantified on a CHN analyzer. A 1-ml aliquot of isolated porewater was acidified and analyzed for dissolved organic carbon (DOC) using a Shimadzu DOC (catalytic) analyzer.

SPME fibers, sediment, and porewater extracts were analyzed using a Varian 3800 gas chromatograph coupled to a Saturn 2200 ion trap mass spectrometer (Varian, Walnut Creek, CA). The GC was equipped with a 1079 split/splitless injector operated isothermally at 280°C and an 8200 autosampler. A 60 m x 0.25 mm id DB-5 fused silica column (0.25-µm film thickness; J&W Scientific, Folsom, CA) was used for chromatographic separation. The injector temperature was programmed from 100 to 280°C at ~100°C/minute with a 20-minute hold time at the maximum temperature. SPME fiber assemblies were manually injected using the splitless mode. After a 1-minute hold at 100°C, the column temperature was increased to 220°C at 8°C/minute, followed by a second increase at 10°C/minute to 290°C (10-minute hold). The carrier gas was ultra-high purity helium with a constant flow rate of 1.3 ml/minute. The ion trap, manifold, and transfer line temperatures were maintained at 220, 80, and

280°C, respectively. The ion trap was operated in the positive electron impact (70 eV) mode and a single quantitation ion per target compound was acquired using the selected ion storage (SIS) mode. A 5-point external standard calibration curve was generated to quantify target HOCs sorbed to SPME fibers. The internal standard method was employed for quantitation of target HOCs in sediment and porewater extracts based on a 6-point (25- to 2000-ppb) calibration curve.

Quality control

New SPME fibers were used for all work described in this study. Target HOCs were not detected in any procedural blank analyzed in parallel with sediment and porewater samples. Acenaphthylene-d_{10}, phenanthrene-d_{10}, perylene-d_{12}, benzo(g,h,i)perylene-d_{12}, tetrachloro*meta*xylene (TCMX), PCB65, and PCB209 were spiked into each sample prior to extraction as recovery surrogates. Mean surrogate recoveries were 91 ±12 and 86 ±23% for sediment and porewater samples, respectively. Sample concentrations were not corrected for surrogate recovery.

Data analysis

K_f values were calculated using the ratio of the equilibrium concentrations in the PDMS coating (C_f^∞) and in the aqueous phase (C_w^∞):

$$K_f = \frac{C_f^\infty}{C_w^\infty} = \frac{N_f^\infty}{V_f C_w^\infty} \tag{1}$$

where N_f^∞ is the absolute analyte amount sorbed to the SPME fiber at equilibrium and V_f is the volume of the PDMS coating.

Aqueous phase concentrations determined by SPME ($C_{w,spme}$) were computed using HOC-specific K_f values by rearranging Equation 1:

$$N_f = K_f V_f C_w \tag{2}$$

where N_f is the mass of HOC sorbed to the SPME fiber.

Theoretical considerations and underlying assumptions justifying the use of Equations 1 and 2 are given in Zeng and Noblet (2002). Statistical analyses including linear regression were performed using SigmaStat v2.03, and plots were generated using Sigma Plot 2002 for Windows v8.02.

RESULTS

Sediment Exposure Experiments

Sampler toxicity

Temperature, pH, salinity, dissolved oxygen (DO), and total NH_3 measured on Days 1, 5, 12, 19, 22 and 26, of the 28-day test remained within acceptable ranges. Survival of *M. nasuta* after 28 days was 100% (10 of 10) for both aquaria with the large prototype sampler. Recovery of *N. virens* was highly variable among aquaria; however, survival was greatest in the two aquaria with samplers.

Effect of PDMS coating thickness on K_f

With the exception of *p,p'*-DDD, compound specific mean K_fs for the 7-µm PDMS coating were greater than those corresponding to the 100-µm coating (Table 1). Moreover, a decreasing trend in K_f with increasing coating thickness was observed for all three PAH as well as for PCB 153. In addition, the variability in mean K_f was roughly twice as high on average for 7-µm PDMS fibers compared to the 30- and 100-µm PDMS fibers. Although higher in magnitude on average, K_fs for the 30-µm PDMS fibers were not substantially different than for 7-µm fibers when considering the variability associated with the thinner coating (Table 1).

Time to equilibrium

The time required for target HOCs to reach steady state between the 100-µm PDMS fibers and spiked NB sediments under static conditions ranged between 14 and 110 days. Steady state was achieved by Day 14 for PHEN; Day 30 for α-chlordane (aCHL) and *p,p'*-DDE; and Day 60 for PCB 180 (Figure 2). Corresponding times for the remaining target HOCs were 30 days for *trans*-nonachlor (tNON) and PCBs 52 and 153; 60 days for fluoranthene (FLUA) and heptachlor epoxide (HE); and 110 days for benzo[a]pyrene (BAP; data not shown). *p,p'*-DDD did not reach steady state over the duration of the 240-day experiment, and *p,p'*-DDT was not detectable at any time.

Although sampler uptake of *p,p'*-DDE was similar to the other model HOCs, *p,p'*-DDD and *p,p'*-DDT did not behave in a similar fashion. In fact, *p,p'*-DDT in whole sediment decreased from a mean
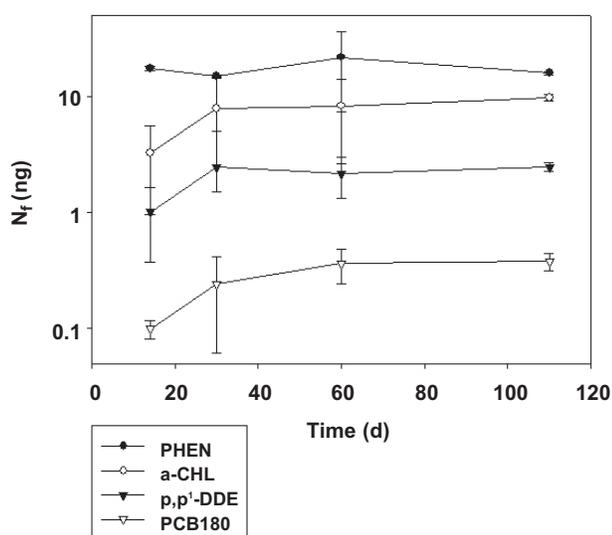
Figure 2. Mass of target HOC sorbed by the SPME sampler outfitted with a 100 µm PDMS fiber (N_f) vs. exposure time in spiked sediment. PHEN = phenanthrene; a-CHL = α-chlordane; PCB180 = 2,2',4,4',5,5'6-heptachlorobiphenyl.

of 324 ng/g (Day 0) to 92 ng/g (Day 240), a 72% decrease over the duration of the experiment. The disappearance of *p,p'*-DDT was corroborated in the subsequent concentration-series equilibrium experiment (see below) with only 11 to 24% of the Day 0 concentration present in the spiked sediment treat-

ments by Day 60. In contrast, sediment concentrations of *p,p'*-DDD and *p,p'*-DDE were relatively stable (<30% decrease over 240 days).

Sampler sensitivity and performance

Using the K_fs determined herein, estimated method detection limits (MDLs) for the sampler with 100-µm PDMS fibers calculated using Equation 2 ranged from 0.024 ng/L for PCB 180, the most hydrophobic study compound, to 10.3 ng/L for PHEN, the least hydrophobic study compound (Table 2). At 60 days, mean porewater concentrations determined by SPME ($C_{w,spme}$) for PHEN ranged from 43 to 2400 ng/L for the lowest and highest spiked sediment concentration, respectively (Table 2). For PCB 180, $C_{w,spme}$ ranged from 0.009 to 0.43 ng/L, with the lower value roughly 2.5 times lower than the estimated MDL. Levels of *p,p'*-DDE determined by SPME ranged between 0.08 and 4.4 ng/L. With the exception of *p,p'*-DDT, all target analytes were detectable by both the small and large prototype samplers at the lowest spiked sediment concentration (Table 2).

The effect of K_{ow} (or K_f) on sampler sensitivity was clearly demonstrated by the decrease in $C_{w,spme}$ for HOCs of increasing hydrophobicity (Figure 3). In contrast, SPME porewater concentrations for the

Table 2. Comparison of target HOC porewater concentrations ($C_{w,spme}$) determined by small and large prototype samplers after 60-day exposure to spiked estuarine sediment. Units are ng/L. Mean ±sd (n = 2) are reported for small samplers. See Table 1 for analyte abbreviations. MDL = estimated method detection limit based on Equation 2. C_{sed} = nominal spiked sediment concentration (each analyte); * indicates value <MDL. S/L = ratio of $C_{w,spme}$ determined by small (7.5 mm id x 15 cm Length) and large (14 mm id x 150 mm Length) samplers.

Analyte	MDL	C_{sed} ~50 ppb		S/L	C_{sed} ~500 ppb		S/L
		Small	Large		Small	Large	
PHEN	10.3	42.5 ± 5.91	56.6	0.75	2120 ± 334	2388	0.89
FLUA	4.29	11.0 ± 1.0	14.5	0.76	508 ± 96	610	0.83
BAP	0.247	0.04* ± 0.02	0.04	0.84	0.39 ± 0.25	1.51	0.25
HE	2.71	4.65 ± 1.07	6.39	0.73	269 ± 51	330	0.81
aCHL	0.349	1.37 ± 0.67	3.92	0.35	87.9 ± 44.7	79	1.11
tNON	0.171	0.46 ± 0.26	1.79	0.26	28.0 ± 16.9	20.3	1.38
p,p' -DDD	0.063	0.13 ± 0.04	0.18	0.7	4.47 ± 0.76	6.83	0.65
p,p '-DDE	0.055	0.08 ± 0.04	0.43	0.19	4.38 ± 2.79	2.89	1.52
p,p '-DDT	0.113	0.04* ± 0.07	<0.13	n/a	0.24 ± 0.13	0.36	0.67
PCB 52	0.123	1.04 ± 0.68	3.05	0.34	76.6 ± 46.4	53.9	1.42
PCB 153	0.029	0.023* ± 0.006	0.14	0.17	1.16 ± 0.74	0.92	1.26
PCB 180	0.024	0.009* ± 0.004	0.04	0.24	0.36 ± 0.21	0.43	0.83
Mean				0.48			0.97

DDT compounds were not distinguishable for the same spiked sediment concentration due to similar fiber-water partitioning behavior (see K_fs in Table 1). Moreover, porewater concentrations determined by the samplers after 60 days exposure to spiked NB sediment increased with increasing bulk sediment concentration (TOC: 0.66 ±0.031%) for all model HOCs (Figure 3).

The difference in $C_{w,spme}$ measured by the small and large prototypes was within a factor of 2 on average at the lowest spiked sediment concentration (50 ng/g), whereas the agreement between the two samplers averaged 97% for the second highest concentration tested (500 ng/g; Table 2). The relative difference between the two sampler sizes averaged 11%, and was less than 52% for all target HOCs with the exception of BAP (Table 2). Variability between duplicate samplers (measured only for the small prototype) approached 50% for $C_{w,spme} \leq 1$ ng/L but was routinely <20% for concentrations in the

higher parts per trillion range (Figure 3). The single measurement by the large prototype generally fell within the uncertainty associated with the duplicate small samplers. For lower bulk sediment concentrations (e.g., 50 ng/g), the relative difference increased to 77% largely due to lower absolute mean concentrations and higher variability among SPME measurements.

SPME vs. liquid liquid extraction (LLE)

Porewater concentration determined by our SPME sampler was strongly correlated with that determined by liquid-liquid extraction of filtered centrifugate of whole sediment ($C_{w,LLE}$; Figure 4). The slope of the highly significant linear regression equation relating $C_{w,spme}$ and $C_{w,LLE}$ (n = 48; $R^2 = 0.998$; p <<0.001) was 0.94, indicating a near 1:1 correspondence between the two measurements. SPME measured concentrations were also lower in magnitude in general than those measured by LLE,
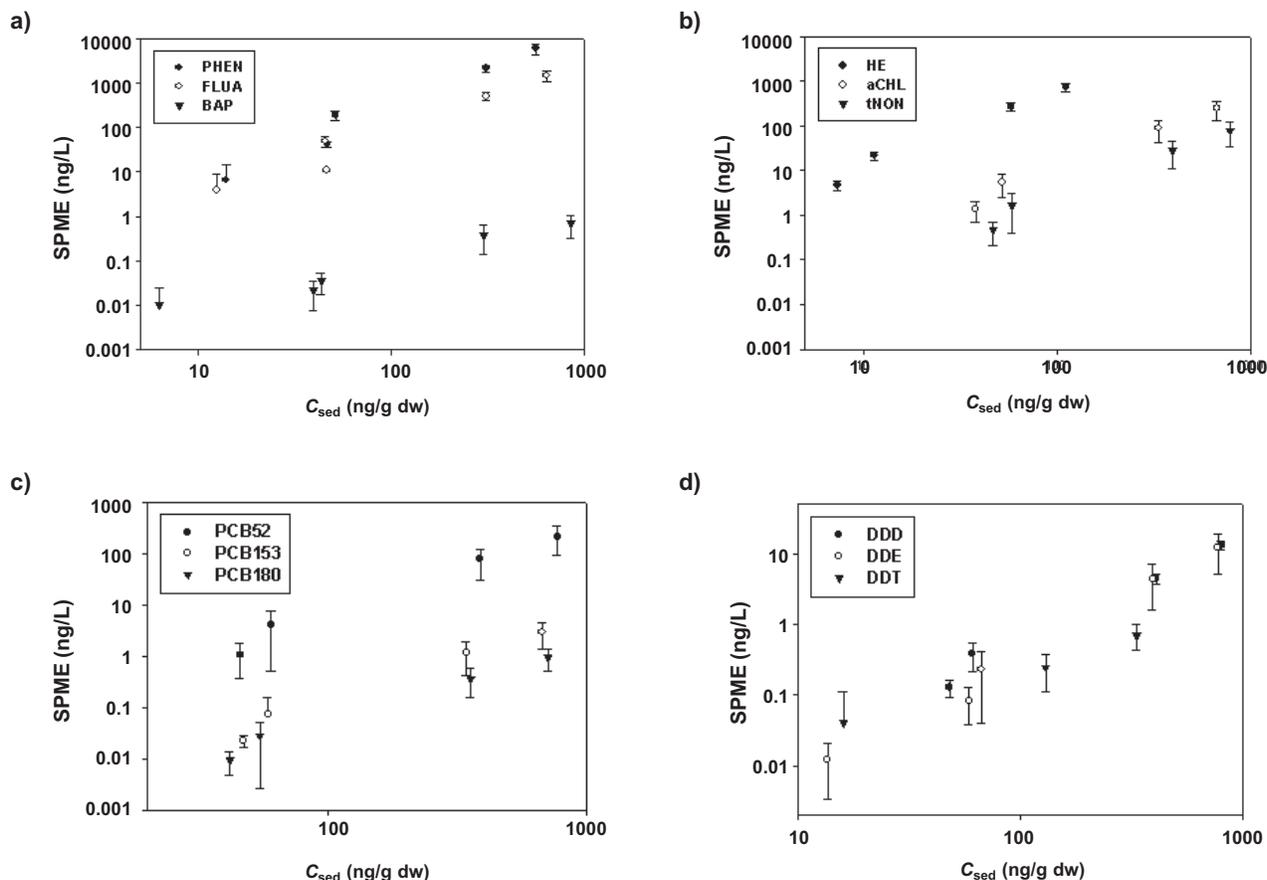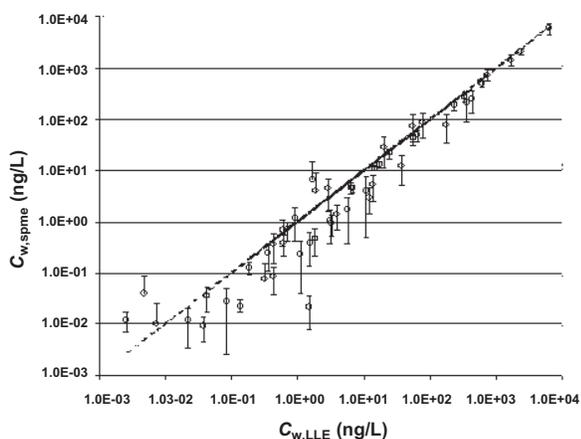

Figure 3. Porewater concentration of target HOCs determined by SPME samplers vs. bulk sediment concentration (C_{sed}). PAH (a), chlordanes (b), PCBs (c), and DDTs (d). Exposure time for 100-μm PDMS fibers was 60 days. Error bars represent one standard deviation for small prototype sampler (n = 2; internal cavity volume = 4.9 cm³).

Figure 4. Porewater concentration of target HOCs determined with SPME samplers ($C_{w,spme}$) vs. liquid-liquid extraction ($C_{w,LLE}$). Error bars represent one standard deviation for "small" prototype configuration (n = 2; internal cavity volume = 4.9 cm³).

as indicated by the trend data relative to the 1:1 (unity) relationship (Figure 4). The average percent difference between SPME and LLE ranged from -3.1 to -56%, indicating that as much as 50% of the LLE measured HOC was not detected by the SPME sampler.

DISCUSSION

Because survival of test animals in aquaria containing the prototype samplers was essentially 100%, it was concluded that the prototype sampler did not cause mortality, and was thus compatible with species typically used in long-term sediment bioaccumulation evaluations.

K_fs reported in this study were within 0.1, 0.23 and 0.4 log units of those determined for PCB 52, 153 and 180, respectively, using disposable PDMS fibers with virtually equivalent coating thicknesses (ter Laak *et al.* 2008). The K_fs for phenanthrene (PHEN) and fluoranthene (FLUA) compared favorably (within 0.2 log units) with those reported previously (Mayer *et al.* 2000b); however, the K_fs for *p,p'*-DDE in this study were somewhat higher than those previously reported (Mayer *et al.* 2000b, Yang *et al.* 2007b). Comparison of K_fs for chlordanes is difficult as very few, if any, published data are available, particularly for heptachlor epoxide (HE).

Previous studies have reported both substantial and no discernable coating thickness dependence on K_f for various HOCs. Paschke and Popp (2003)

reported a substantially lower K_f for PCB 153 using 100- vs. 7-µm PDMS, although K_f values for PCB 52 and *p,p'*–DDE in that study were not substantially different for the two coating thicknesses. K_fs determined using ^{14}C labeled analogs of selected HOCs (including six of those targeted herein) and 100-µm PDMS fibers were compared with literature values for native compounds (Yang *et al.* 2007b). For four of six common analytes, K_fs determined in the latter study were within 0.3 log units of those measured herein, with greater deviations for PHEN and BAP. However, ter Laak *et al.* (2008) recently reported virtually no difference in K_f for PCB congeners among 7-, 30- and 100-µm PDMS disposable fibers. In the latter study, fibers with 100-µm coating were exposed for 152 days, compared with <60 days for most previous experiments.

Several theories have surfaced to explain the effect, or lack thereof, of coating thickness on compound-specific K_fs. According to the manufacturer, the PDMS coating for commercially available 7-µm fibers is bonded to the fused silica support, whereas the 100-µm version is hot-dipped, potentially resulting in different sorbent morphology and thus overall sorptive capacity. Alternatively, extremely slow diffusion across thicker (e.g., 100 µm) coatings may render the layer of PDMS closest to the glass support ineffective for sorption, resulting in less HOC per volume of coating sorbed, and thus lower K_fs. On the other hand, ter Laak *et al.* (2008) suggest that nonuniformity in K_f is an artifact of nonequilibrium in previous calibration studies; which would explain the lower values reported for thicker coatings that require longer exposure times to achieve equilibrium. In all cases, accurate determination of K_f values for fibers with different PDMS formulations and/or coating thicknesses, coupled with compatibility in selecting deployment times are essential in obtaining accurate and consistent results. Moreover, these critical calibration procedures need to be carefully documented to allow cross-validation by multiple practitioners.

With the exception of the chlordanes, the time to equilibrium increased with increasing hydrophobicity as measured by K_{ow}. It is interesting to note, however, that equilibration times for FLUA and BAP were among the longest, even though their K_{ow} values were among the lowest of all target analytes (Table 1). Stronger than anticipated binding of PAH to highly condensed forms of organic matter, such as soot or BC, has been well documented (McGroddy and

Farrington 1995, Gustafsson *et al.* 1997, Rust *et al.* 2004). Because NB sediments are largely derived from soils mobilized by stormwater runoff as well as particles depositing from the surrounding urban atmosphere, it is plausible that PAHs in particular are strongly associated with elevated levels of soot (TOC = 0.66 ±0.031%; BC = 16.8%) in this matrix. Moreover, the delayed approach to steady state for BAP in particular is consistent with multi-phase (fast and slow) partitioning and desorption models (e.g., Pignatello and Xing 1996). Competing sorbing phases such as DOM may also influence aqueous-sediment exchange kinetics. Although DOC was relatively high throughout the time series, it did not change substantially over the 240-day exposure period (Day 0: 680 mg/L; Day 240: 780 ±12 mg/L). This was also true for sediment TOC (Day 0: 0.60%; Day 240: 0.77%).

A recent study by ter Laak *et al.* (2008) incorporated long-term (>100 days) exposures to generate predictions of the time to reach 95% of the HOC equilibrium concentration in PDMS-water systems (or $t_{95\%}$) as a function of K_f. They found that for HOCs with log K_f between 4 and 7, diffusion across aqueous thin films and through the polymeric (PDMS) sorbent resulted in predicted $t_{95\%}$ of ~1 to >100 days. In the current study, time to equilibrium observations (Figure 2) are thus consistent with those predicted by ter Laak *et al.* (2008).

It has long been known that sediment-associated *p,p'*-DDT is reductively dechlorinated to *p,p'*-DDD under anaerobic conditions (e.g., Eganhouse and Pontolillo 2008). If active in the microcosms used for the current study, which were not poisoned to minimize biotransformation, these processes would explain the non-detectable concentrations of *p,p'*-DDT and non-steady concentrations of *p,p'*-DDD associated with the sampler. Thus, compounds that are subject to significant transformation within the timeframe needed to achieve water-fiber equilibrium are not amenable to this technique.

In the current study, MDLs estimated for the 100-µm PDMS sampler were comparable to previous studies using coatings of similar volume (e.g., Kraaij *et al.* 2003). Moreover, the sensitivity of this prototype equaled or exceeded that reported by other studies using SPME for *ex situ* measurement (Hawthorne *et al.* 2005, ter Laak *et al.* 2006). Previous investigations using PDMS coated fibers implanted directly into spiked or naturally contaminated sediment (i.e., without a protective housing),

commonly known as the "matrix SPME" approach (Kraaij *et al.* 2003, You *et al.* 2007), reported detectable porewater concentrations of HOCs ranging from 0.01 to 3.0 ng/L for PCBs; <4 to 60 ng/L for PAH; and 0.05 ng/L for *p,p'*-DDE. The current study's prototype measured similar ranges of concentrations for PCBs and *p,p'*-DDE while extending the lower detectable range for BAP and chlordanes to <0.5 ng/L (Table 2). In addition, this work is among the first to report SPME porewater results for chlordanes.

No trend or pattern was readily apparent between sampler size and HOC class. The larger deviations between the small and large sampler measurements for the high K_{ow} compounds at the lowest spiked sediment treatment were not unexpected, as measurements approached the sampler MDL . A higher degree of replication (e.g., triplicate samplers) should reduce the variability and improve the precision within experimental treatments or individual sample determinations.

The observed difference between $C_{w,spme}$ and $C_{w,LLE}$ was also as expected; SPME fibers sorb HOCs that are freely dissolved, whereas LLE measurements represent the HOCs bound to DOM (not removed by filtration) as well as the freely dissolved fraction. The relatively large discrepancy between these independently measured parameters (up to 50%) was also not surprising, as porewater DOC levels were high, ranging between 320 to 780 mg/L (mean ±sd: 620 ±180 mg/L) among the spiked sediment treatments. This effect, previously observed in experimental manipulations with binding proteins using SPME (Vaes *et al.* 1996), was more pronounced for the lower concentration range, as a higher percentage of HOC was bound to DOM.

Passive samplers that provide a direct measure of bioavailability of sediment-associated organic pollutants would be highly useful for resource managers and decision makers. The ability of the SPME-based sampler used in the current study to track independently measured porewater HOC concentrations and to discriminate between the dissolved or bioavailable fraction of HOCs in sediment porewater with high DOM background levels make it an attractive sampling alternative for sediment-associated contaminants. Data obtained by this technology could be used to complement, or in some cases replace bulk sediment chemistry as an essential line of evidence when assessing sediment quality. This is particularly true for highly modified sediments, e.g., those

impacted by pyrogenic sources of PAH where bioavailability has been shown to be highly correlated with dissolved phase concentrations and, in contrast, poorly predicted by bulk solid phase concentrations. However, before this concept is adopted for widespread use, additional characterization of its response and behavior and improvements/modifications for laboratory vs. *in situ* deployment are needed.

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ACKNOWLEDGEMENTS