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A PASSIVE SAMPLER BASED ON SOLID-PHASE MICROEXTRACTION FOR QUANTIFYING HYDROPHOBIC ORGANIC CONTAMINANTS IN SEDIMENT PORE WATER

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Abstract—Sediment-quality assessment often is 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 the present study, we developed and tested a pore-water sampler that uses solid-phase microextraction (SPME) to measure freely dissolved (bioavailable) HOC concentrations. A single polydimethylsiloxane (PDMS)-coated SPME fiber is 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 HOCs of current regulatory concern. Precalibrated samplers were exposed to spiked estuarine sediment in laboratory microcosms to determine the time to equilibrium and the equilibrium concentrations across a range of sediment contamination. Time to equilibrium ranged from 14 to 110 d, with 30 d being sufficient for more than half the target HOCs. Equilibrium SPME measurements, ranging from 0.009 to 2,400 ng/L, were highly correlated with but, in general, lower than HOC pore-water concentrations determined independently by liquid–liquid extraction. This concept shows promise for directly measuring the freely dissolved concentration of HOCs in sediment pore water, a previously difficult-to-measure parameter that will improve our ability to assess the impacts of contaminated sediments.

Keywords—Contaminated sediments Persistent organic pollutants Bioavailability Solid-phase microextraction Sediment pore water

INTRODUCTION

Accumulation of hydrophobic organic compounds (HOCs) to high levels in sediments poses a risk to both ecological and human health via direct and indirect pathways. Some legacy HOCs (e.g., chlordane) may be toxic to benthic organisms that inhabit contaminated sediments, whereas marine and terrestrial mammals (including humans) are indirectly exposed to HOCs via food-web transfer. The biomagnification of toxicants like DDT, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers can result in and/or exacerbate reproductive and immunosuppressive impacts. The bulk sediment concentration is a logical and, thus, commonly used indicator of potential HOC exposure for benthic organisms. Coupled with biological endpoints like benthic community condition and toxicity (e.g., median lethal concentration), bulk sediment chemistry has been widely used in sediment-quality assessment [1,2]. To account for the affinity of HOCs with organic matter [3], models relating aqueous- and solid-phase partitioning were created to help explain differences in bioavailability observed in ecotoxicological endpoints [4].

More recently, heterogeneity within the organic subcomponent of soils and sediments has been shown to have a profound effect on the partitioning and bioavailability of HOCs. Condensed, sooty materials, known collectively as black carbon (BC), were shown first to reduce the bioavailability of PAH in contaminated harbor sediments [5] and subsequently to influence similarly the bioavailability of PCBs [6] as well as legacy and current-use, chlorinated pesticides [7]. The effectiveness of BC in altering HOC bioavailability, at least in the short term, has resulted in its consideration for remedial strategies for highly contaminated sediments [8]. A growing body of evidence suggests that the freely dissolved phase of HOCs (C_{free}) represents the highly bioavailable fraction [9,10]. Determination of this parameter, however, must be made at ultralow levels, and it is made difficult by the presence of dissolved organic matter (DOM), a competing binding phase for HOCs in natural waters [11], including sediment interstitial or pore water [12]. Because separation of freely dissolved from colloidal and particulate HOC fractions is exceedingly difficult, little data are available, and measurements of total aqueous HOC concentrations are much more common. Unfortunately, this latter parameter can be of limited utility in quantifying bioavailable HOCs.

Solid-phase microextraction (SPME) is a passive sampling technology [13] that senses C_{free} in complex aqueous matrices [9]. As evidence, in situ samplers with polydimethylsiloxane (PDMS)-coated SPME fibers [14] were deployed for several weeks in coastal seawater [15]. Subparts-per-trillion concentrations of DDT as determined by this sampler agreed well with independently measured, operationally defined, dissolved-phase measurements. Based on this concept, a mass-balance and partitioning model predicted that the minimum sediment volume required to maintain nondepletive conditions for a SPME-based, pore-water sampler was independent of HOC concentration (both solid and aqueous phases) and that relatively small sediment volumes (<10 ml) participated in exchange equilibria [16]. More importantly, that work also demonstrated that sub-ng/L detection limits were possible for

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Table 1. Log polydimethylsiloxane (PDMS)–water partition coefficients (K_f) of study analytes for three commercially available coating thicknesses

Analyte[a]	log K_{OW}	log K_f[b]		
		7 μm	30 μm	100 μm
Phenanthrene	4.46	4.32 ± 0.11	4.10 ± 0.10	3.90 ± 0.07
Fluoranthene	5.16	4.69 ± 0.15	4.55 ± 0.08	4.26 ± 0.09
Benzo[*a*]pyrene	6.13	6.06 ± 0.11	6.06 ± 0.15	5.82 ± 0.29
Heptachlor epoxide	4.98	4.64 ± 0.20	4.70 ± 0.03	4.48 ± 0.05
α-Chlordane	6.22	5.59 ± 0.21	5.66 ± 0.03	5.37 ± 0.07
trans-Nonachlor	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

[a] DDD = 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; DDE = 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene; PCB = polychlorinated biphenyl.
[b] Values are presented as the average ± standard deviation for triplicate (n = 3) batch calibration determinations.

HOCs with log octanol–water partition coefficient (K_{OW}) values of six or greater.

The objective of the present study was to develop and test the performance of a compact, SPME-based passive sampler that can measure C_{free} for HOCs of regulatory concern in sediment pore water. With a focus on in situ measurement, an additional requirement for our sampler was to protect the SPME fiber from damage as well as from fouling and/or sediment contact. To achieve this, a prototype sampler adapted from a previous water-column design [14] was designed and fabricated. Key parameters (effect of PDMS coating thickness on sensitivity, time to equilibrium, and agreement with alternative pore-water measurements) were then determined for selected prototypes using spiked sediment exposures.

MATERIALS AND METHODS

Twelve PAHs, 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). High-purity (≥95%) compounds were obtained from AccuStandard (New Haven, CT, USA), UltraScientific (North Kingston, RI, USA), and Sigma-Aldrich (St. Louis, MO, USA). Solid-phase microextraction fibers coated with 7, 30, and 100 μm of PDMS were obtained from Supelco (Bellafonte, PA, USA). Fibers (as-received) were thermally pretreated at 300°C for 15 min. All solvents of the highest purity available and reagents of American Chemical Society grade or better were purchased from Fisher Scientific (Fair Lawn, NJ, USA). All glassware was exhaustively hand-washed, kiln-fired at 550°C for 4 h or more, and solvent-rinsed with acetone and hexane before and after use.

Effect of PDMS coating thickness on fiber–water partition coefficient

Compound-specific, fiber–water partition coefficient (K_f) values were determined for SPME fibers coated with 7, 30, and 100 μm of PDMS following the methods developed by Yang et al. [17]. 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 solvent-rinsed, Teflon®-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 d, with the longer time period for 100-μm fibers only. Fibers were analyzed by thermal desorption gas chromatography–mass spectrometry (GC-MS; see *Sample analysis*), whereas aqueous samples underwent liquid–liquid extraction (LLE). The accuracy of LLE was evaluated using a 1:1 recovery correction strategy employing a ^{13}C- or deuterated-labeled surrogate for each target HOC.

Sampler design

The configuration of our prototype sampler was adapted from a previously designed water-column sampler that was tested and field-validated for sub-ng/L levels of DDT in seawater [14,15]. To protect and stabilize the SPME fiber assembly, a cylindrical housing was constructed of thin-walled (thickness, 1 mm) copper tubing with holes drilled into the walls to allow free water exchange with the fiber surface. The fiber assembly is attached to a copper end cap that is secured onto one end of the cylindrical housing. A second end cap is fitted to the housing opposite of the fiber. To prevent direct contact of the fiber with sediment particles, a glass-fiber filter (GF/F; Whatman, Maidstone, UK) is wrapped around the housing exterior followed by a single layer of 270-mesh (opening, 0.053 mm), T316 stainless-steel screen held in place by No. 6 (diameter, 0.406 mm), single-strand, stainless-steel wire (Fig. 1). To check for effects on sampler performance because of housing size, a small prototype (length, 110 mm; internal diameter [i.d.], 7.5 mm; internal cavity volume, 4.9 cm^3) and a large prototype (length, 150 mm; i.d., 14 mm; internal cavity volume, 23 cm^3) were constructed.

Sediment exposure experiments

Sampler toxicity. To test for toxicity resulting from the sampler itself, polychaetes (*Nereis virens*) and bivalves (*Macoma nasuta*) obtained from Brezina and Associates (Dillon Beach, CA, USA) were exposed in 19-L, glass aquaria, each containing a 5-cm layer of sieved marine sediments and overlying filtered seawater. Duplicate aquaria containing sediment, organisms, and a single large-prototype sampler, as well as 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 28-d bioaccumulation assay guidance manuals [18].

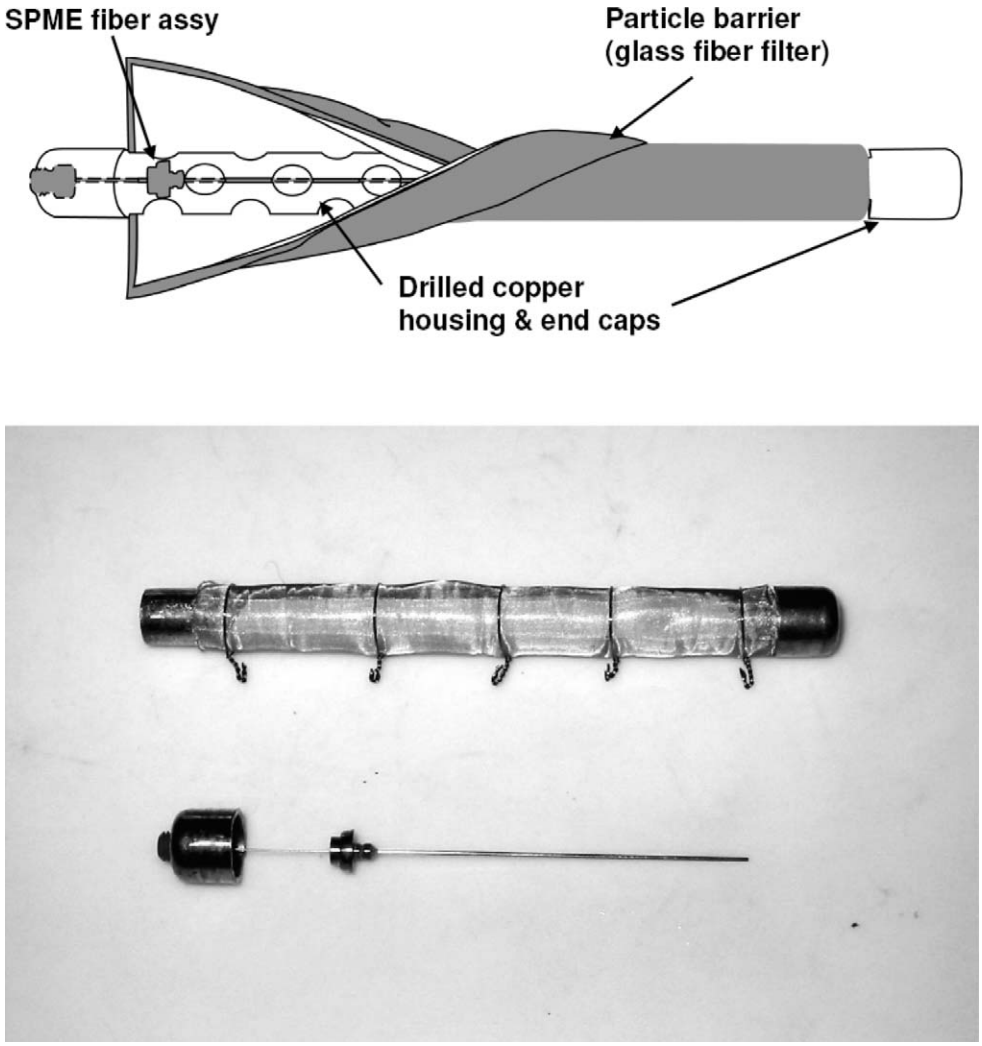

Fig. 1. Schematic of the solid-phase microextraction (SPME)–based pore-water sampler (**top**) and photograph of small-prototype casing (length, 110 mm; outside diameter, 9.5 mm) with stainless-steel mesh/glass-fiber filter and SPME fiber assembly attached to removable end cap (**bottom**).

Preparation of spiked test sediments. Intertidal sediments from Newport Bay (NB; CA, USA) 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 with all 12 target compounds at nominal concentrations of 50, 100, 500, and 1,000 ng/g each in precleaned, 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 were maintained at room temperature during homogenization. After equilibration, spiked sediments were kept in the dark at 4°C until use.

Time to equilibrium. The SPME samplers were exposed to spiked sediment under static conditions in a time-series experiment to determine the time to equilibrium for the target HOCs. A composite of test NB sediment (400 ml), prepared as described above, was layered into 1-L, borosilicate glass, graduated cylinders. The nominal concentration for each analyte was 300 ng/g except for heptachlor epoxide, which was spiked at a lower level (~60 ng/g). Two small and a single large sampler outfitted with 100-μm PDMS fibers were inserted below the sediment surface in each of five cylinders 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 d. 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 a tissue to remove residual water, and analyzed by thermal desorption GC-MS for the 12 target analytes. Pore-water and spiked sediments 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, prototype samplers were exposed to a concentration series of spiked NB sediment to determine pore-water 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 d. 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*). At the end of the exposure period, SPME fibers were processed and analyzed for target HOCs. Pore-water and spiked sediments subsampled at days 0 and 60 were processed and analyzed by GC-MS as described below (see *Sample analysis*).

Sample analysis. Aliquots (50–100 ml) of pore water were isolated from 100 to 150 g of whole sediment in a Teflon bottle

centrifuged at 1,800 *g* for 30 min, filtered through a glass-fiber filter (Whatman), 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 before 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 accelerated solvent extraction system (Dionex, Salt Lake City, UT, USA), and cleaned up 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 an elemental analyzer. Sediment BC was estimated as described by Gustafsson et al. [19] on an oven-dried (60°C) aliquot of wet sediment ground to a fine powder and decarbonized with 1 M HCl. After redrying, samples were combusted at 375°C for 24 h in the presence of excess air and BC quantified using the elemental analyzer. A 1-ml aliquot of isolated pore water was acidified and analyzed for dissolved organic carbon (DOC) using a Shimadzu (Columbia, MD, USA) DOC (catalytic) analyzer.

Solid-phase microextraction fibers and sediment and pore-water extracts were analyzed using a Varian 3800 gas chromatograph coupled to a Saturn 2200 ion-trap mass spectrometer (Varian, Walnut Creek, CA, USA). The gas chromatograph was equipped with a 1079 split/splitless injector operated isothermally at 280°C and an 8200 autosampler. A DB-5 fused silica column (length, 60 m; i.d., 0.25 mm; film thickness, 0.25 μm; J&W Scientific, Folsom, CA, USA) was used for chromatographic separation. The injector temperature was programmed from 100 to 280°C at 100°C/min with a 20-min hold time at the maximum temperature. The SPME fiber assemblies were manually injected using the splitless mode. After a 1-min hold at 100°C, the column temperature was increased to 220°C at 8°C/min, followed by a second increase at 10°C/min to 290°C (10-min hold). The carrier gas was ultrahigh-purity helium with a constant flow rate of 1.3 ml/min. 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 mode. A five-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 pore-water extracts based on a six-point (25–2,000 ng/ml) calibration curve.

Quality control. New SPME fibers were used for all work described in the present study. Target HOCs were not detected in any procedural blank analyzed in parallel with sediment and pore-water samples. Acenaphthylene-d_{10}, phenanthrene-d_{10}, perylene-d_{12}, benzo[*ghi*]perylene-d_{12}, tetrachloro-*meta*-xylene PCB 65, and PCB 209 were spiked into each sample before extraction as recovery surrogates. Mean surrogate recoveries were 91% ± 12% and 86% ± 23% for sediment and pore-water samples, respectively. Sample concentrations were not corrected for surrogate recovery.

Data analysis

The 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^∞):

$$K_f = \frac{C_f^\infty}{C_w^\infty} = \frac{N_f^\infty}{V_f C_w^\infty} \quad (1)$$

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

$$N_f = K_f V_f C_w \quad (2)$$

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 by Zeng and Noblet [20]. Statistical analyses including linear regression were performed using SigmaStat® (Ver 2.03) and plots generated using Sigma® Plot 2002 for Windows® (Ver 8.02; SYSTAT, Point Richmond, CA, USA).

RESULTS AND DISCUSSION

Sampler toxicity

Temperature, pH, salinity, dissolved oxygen, and total NH_3 measured on days 1, 5, 12, 19, 22, and 26 of the 28-d test remained within acceptable ranges. Survival of *M. nasuta* after 28 d was 100% (10 of 10) for both tanks with the large-prototype sampler. Recovery of *N. virens* was highly variable among tanks; however, survival was greatest in the two tanks with samplers. We concluded that the prototype sampler did not cause mortality and, thus, was compatible with species typically used in long-term, sediment bioaccumulation evaluations.

Effect of PDMS coating thickness on K_f

Except for 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p′*-DDD), compound-specific mean K_f values 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 PAHs 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, compound-specific K_f values for the 30-μm fibers were not substantially different than those for the 7-μm fibers, taking into consideration the greater variability associated with mean K_f values determined using the thinner PDMS coating (Table 1).

The values of K_f reported in the present 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 [21]. Our K_f values for phenanthrene and fluoranthene compared favorably (within 0.2 log units) with those reported previously [22]; however, our K_f values for 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p,p′*-DDE) were higher than previously reported [22,23]. Comparison of K_f values for chlordanes is difficult, because very few, if any, published data are available, particularly for heptachlor epoxide.

Previous studies have reported both substantial and little discernable coating thickness dependence on K_f for various HOCs. Paschke and Popp [24] reported a substantially lower K_f for PCB 153 using 100- versus 7-μm PDMS, although K_f values for PCB 52 and *p,p′*–DDE in their study were not substantially different for the two coating thicknesses. The values of K_f determined using ^{14}C-labeled analogues of se-

lected HOCs (including six of those targeted herein) and 100-μm PDMS fibers were compared with literature values for native compounds [23]. For four of six common analytes, K_f values determined in this latter study were within 0.3 log units of those measured herein, with greater deviations for phenanthrene and benzo[*a*]pyrene (B*a*P). Ter Laak et al. [21], however, recently reported virtually no difference in K_f for PCB congeners among 7-, 30-, and 100-μm PDMS disposable fibers. In this latter study, fibers with the 100-μm coating were exposed for 152 d, compared with less than 60 d for most previous experiments.

Several theories have surfaced to explain the effect, or lack thereof, of coating thickness on compound-specific K_f values. 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, which have a lower surface area to volume ratio than their thinner counterparts, 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_f values. Ter Laak et al. [21], on the other hand, suggest that nonuniformity in K_f is an artifact of nonequilibrium in previous calibration studies; this would explain the lower values reported for thicker coatings that require longer exposure times to achieve equilibrium. Regardless, accurate determination of K_f values for fibers with different PDMS formulations and/or coating thicknesses coupled with compatibility in selecting deployment times is essential for obtaining accurate and consistent results. Moreover, these critical calibration procedures need to be carefully documented to allow cross-validation by multiple practitioners.

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 or less and 110 d. Steady state was achieved by day 14 for phenanthrene, by day 30 for α-chlordane and *p,p′*-DDE, and by day 60 for PCB 180 (Fig. 2). Corresponding times for the remaining target HOCs were 30 d for PCBs 52 and 153 and *trans*-nonachlor, 60 d for fluoranthene and heptachlor epoxide, and 110 d for B*a*P (data not shown). The *p,p′*-DDD did not reach steady state over the duration of the 240-d experiment, and *p,p′*-DDT was not detectable at any time.

Except for 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 fluoranthene and BAP were among the longest, even though their K_{OW} values are among the lowest of all target analytes (Table 1). Stronger-than-anticipated binding of PAH to highly condensed forms of organic matter, such as BC, has been well documented [5,19,25]. 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%; 17% of TOC as BC) in this matrix. Moreover, the delayed approach to steady state for B*a*P in particular is consistent with multiphase (fast and slow) partitioning and desorption models (see, e.g., Pignatello and Xing [26]). Competing sorbing phases, such as DOM, also may influence aqueous–sediment exchange kinetics. Although DOC was relatively high throughout the time series, it did not change substantially over the 240-d exposure period (day 0, 680 mg/L; day 240, 780 ± 12 mg/L). This also was true for sediment TOC (day 0, 0.60%; day 240, 0.77%).

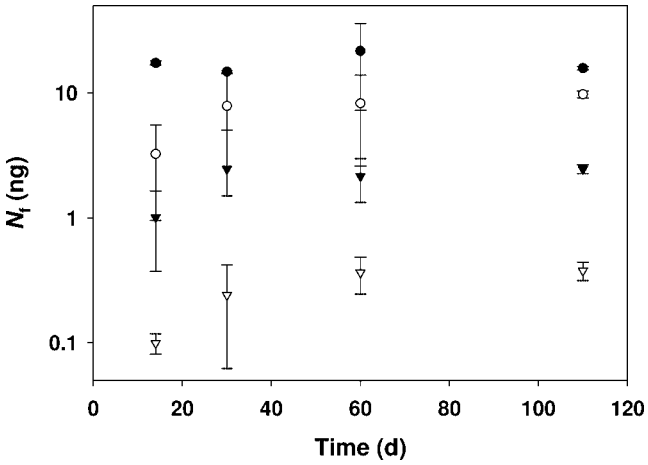

Fig. 2. Mass of target hydrophobic organic compounds sorbed by the solid-phase microextraction sampler outfitted with a 100-μm polydimethylsiloxane fiber (N_f) versus exposure time in spiked sediment. a-CHL = α-chlordane (○); PCB 180 = 2,2′,4,4′,5,5′,6-heptachlorobiphenyl (▽); PHEN = phenanthrene (●); *p,p′*-DDE = 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (▼).

The recent study by ter Laak et al. [21] incorporated long-term (>100 d) 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. For HOCs with log K_f of between four and seven, diffusion across aqueous thin films and through the polymeric (i.e., PDMS) sorbent resulted in a predicted $t_{95\%}$ of from 1 to more than 100 d. Our time-to-equilibrium observations (Fig. 2) thus are consistent with those predicted by these investigators.

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 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 still present in the spiked sediment treatments by day 60. In contrast, sediment concentrations of *p,p′*-DDD and *p,p′*-DDE were relatively stable (<30% decrease over 240 d). It has long been known that sediment-associated *p,p′*-DDT is reductively dechlorinated to *p,p′*-DDD under anaerobic conditions (see, e.g., Eganhouse and Pontolillo [27]). If active in our microcosms, which were not poisoned to minimize biotransformation, these processes would explain the nondetectable concentrations of *p,p′*-DDT and non–steady state concentrations of *p,p′*-DDD associated with the sampler. Thus, compounds that are subject to significant transformation within the time frame needed to achieve water–fiber equilibrium are not amenable to this technique.

Sampler sensitivity and performance

Using the K_f values 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 target compound, to 10.3

Table 2. Comparison of target analyte pore-water concentrations ($C_{w,spme}$) as determined by small- and large-prototype samplers after 60 d exposure to spiked estuarine sediment[a]

		C_{sed} (50 ppb)			C_{sed} (500 ppb)		
Analyte	MDL	Small	Large	S/L	Small	Large	S/L
Phenanthrene	10.3	42.5 ± 5.91	56.6	0.75	2,120 ± 334	2,388	0.89
Fluoranthene	4.29	11.0 ± 1.0	14.5	0.76	508 ± 96	610	0.83
Benzo[*a*]pyrene	0.247	0.04 ± 0.02[b]	0.04	0.84	0.39 ± 0.25	1.51	0.25
Heptachlor epoxide	2.71	4.65 ± 1.07	6.39	0.73	269 ± 51	330	0.81
α-Chlordane	0.349	1.37 ± 0.67	3.92	0.35	87.9 ± 44.7	79.0	1.11
trans-Nonachlor	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	0.70	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[b]	<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[b]	0.14	0.17	1.16 ± 0.74	0.92	1.26
PCB 180	0.024	0.009 ± 0.004[b]	0.04	0.24	0.36 ± 0.21	0.43	0.83
Mean				0.48			0.97

[a] Units are ng/L. Values for small samplers are reported as the mean ± standard deviation ($n = 2$). C_{sed} = nominal spiked sediment concentration (each analyte); DDD = 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane; DDE = 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene; MDL = estimated method detection limit based on Equation 2; PCB = polychlorinated biphenyl; S/L = ratio of $C_{w,spme}$ as determined by small (internal diameter, 7.5 mm) and large (internal diameter, 14 mm) samplers.
[b] Value less than the MDL.

ng/L for phenanthrene, the least hydrophobic target compound (Table 2). At 60 d, mean pore-water concentrations as determined by SPME ($C_{w,spme}$) for phenanthrene ranged from 43 to 2,400 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-fold lower than the estimated MDL. Levels of *p,p′*-DDE as determined by SPME ranged between 0.08 and 4.4 ng/L. Except for *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 MDLs estimated for our 100-μm PDMS sampler were comparable to previous studies using coatings of similar volume (see, e.g., Kraaij et al. [10]). Moreover, the sensitivity of this prototype equaled or exceeded that reported by others who used SPME for ex situ measurement [28,29]. Previous investigations reported detectable pore-water concentrations of HOCs ranging from 0.01 to 3.0 ng/L for PCBs, less than 4 to 60 ng/L for PAH, and 0.05 ng/L for *p,p′*-DDE using PDMS-coated fibers implanted directly into spiked or naturally contaminated sediment (i.e., without a protective housing) with the so-called ''matrix SPME'' approach [10,30]. Our prototype measured similar ranges of concentrations for PCBs and *p,p′*-DDE while extending the lower detectable range for B*a*P and the chlordanes to less than 0.5 ng/L (Table 2). In addition, the present study is among the first to report SPME pore-water results for chlordanes.

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 (Fig. 3). Pore-water concentrations as determined by SPME for the DDT compounds, in contrast, were not distinct for the same spiked sediment concentration because of their similar fiber–water partitioning behavior (see K_f values in Table 1). Moreover, pore-water concentrations as determined by the samplers after 60 d of exposure to spiked NB sediment (TOC, 0.66% ± 0.031%) increased with increasing bulk sediment concentration for all model HOCs (Fig. 3).

The difference in $C_{w,spme}$ measured by the small and large prototypes was within a factor of two, 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 except B*a*P (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 less than 20% for concentrations in the higher parts-per-trillion range (Fig. 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%, in large part because of the lower absolute mean concentrations and the higher variability among SPME measurements. 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 was 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.

SPME versus LLE

Pore-water concentration as determined by our sampler was strongly correlated with that determined by LLE of filtered centrifugate of sediment ($C_{w,LLE}$) (Fig. 4). The slope of the highly significant linear-regression equation relating $C_{w,spme}$ and $C_{w,LLE}$ ($n = 48$, $r^2 = 0.998$, $p \ll 0.001$) was 0.94, indicating a near 1:1 correspondence between the two measurements. Concentrations as measured by SPME also were lower in magnitude than those measured by LLE, as indicated by the trend data relative to the 1:1 (unity) relationship (Fig. 4). This is to be expected, because SPME fibers measure C_{free} whereas LLE measurements represent the HOCs bound to DOM (not removed by filtration) as well as the freely dissolved fraction. In addition, the greater deviation from a 1:1 agreement for concentrations of less than approximately 1 ng/L may indicate that the most hydrophobic compounds may not have fully reached equilibrium by day 60.

The average percentage difference between SPME and LLE

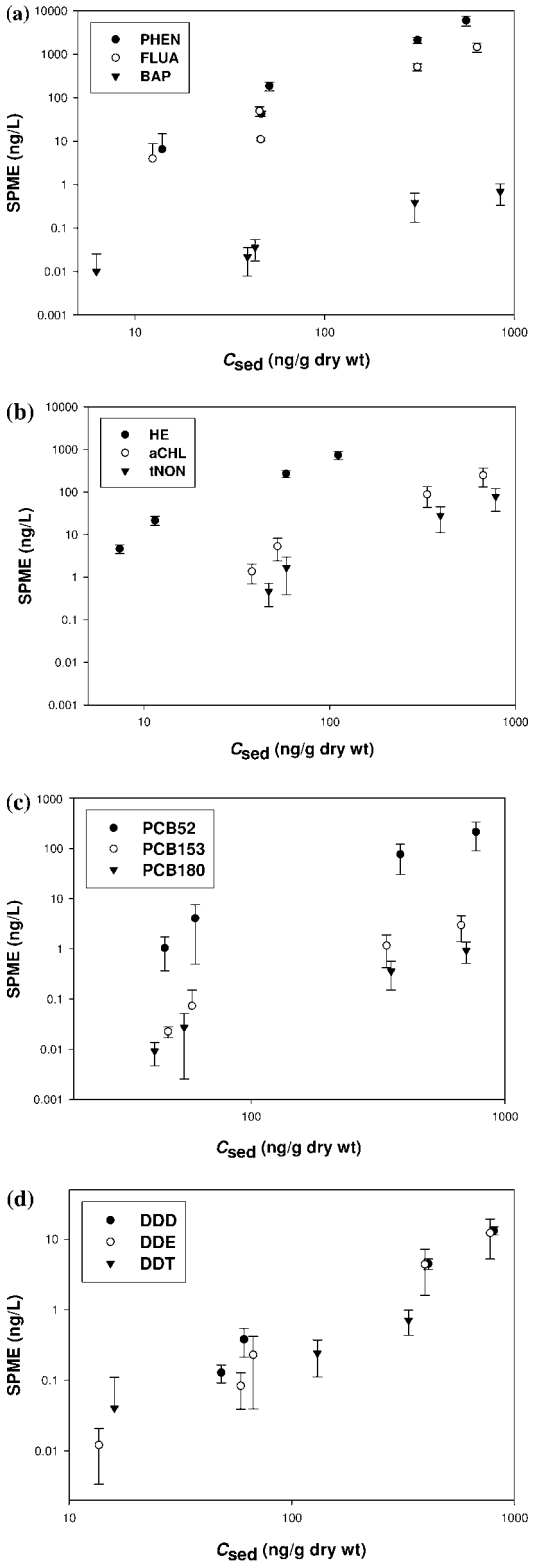

Fig. 3. Pore-water concentration of target hydrophobic organic compounds (HOCs) as determined by solid-phase microextraction (SPME) samplers versus bulk sediment concentration (C_{sed}): (**a**) phenanthrene (PHEN), fluoranthene (FLUA), and benzo[*a*]pyrene (B*a*P); (**b**) heptachlor epoxide (HE), α-chlordane (aCHL), and *trans*-nonachlor (tNON); (**c**) polychlorinated biphenyl (PCB) 52, PCB 153 and PCB 180; and (**d**) 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE), and DDT. Exposure time for 100-μm polydimethylsiloxane fibers was 60 d. Error bars represent one standard deviation for the small-prototype sampler (n = 2; internal cavity volume, 4.9 cm^3).

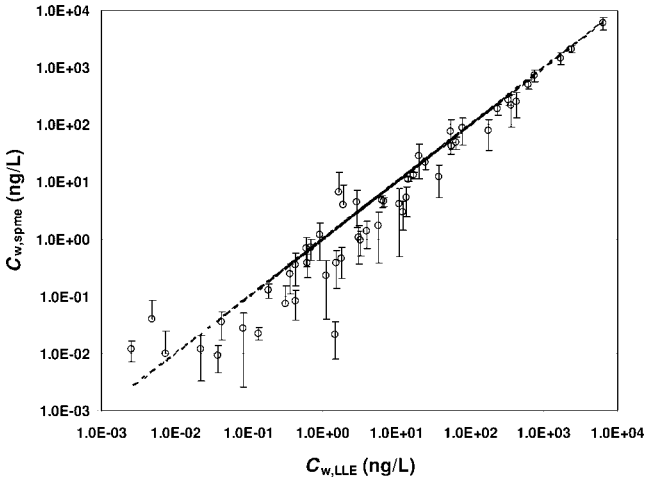

Fig. 4. Pore-water concentration of target hydrophobic organic compounds (HOCs) as determined with solid-phase microextraction (SPME) samplers ($C_{w,spme}$) versus liquid–liquid extraction ($C_{w,LLE}$). Error bars represent one standard deviation for the small-prototype configuration (n = 2; internal cavity volume, 4.9 cm^3). Data for HOCs detected at concentrations below the reported method detection limit were included.

ranged from −3.1 to −56%, indicating that as much as 50% of the LLE-measured HOC was not detected by the SPME sampler. This was not surprising, because pore-water DOC levels were high (mean ± standard deviation, 620 ± 180 mg/L), ranging between 320 to 780 mg/L among the spiked sediment treatments. This effect, as observed previously in experimental manipulations with binding proteins using SPME [31], was more pronounced for the lower concentration range, because a higher percentage of HOC was bound to DOM. Moreover, one would expect the more hydrophobic HOCs to preferentially associate with DOC and, thus, to exhibit the greatest differences between SPME (C_{free}) and LLE (total) concentrations.

Passive samplers that provide a direct measure of the bioavailability of sediment-associated organic pollutants would be highly useful for resource managers and decision makers. The ability of our SPME-based sampler to track independently measured pore-water HOC concentrations and to discriminate between the dissolved or bioavailable fraction of HOCs in sediment pore water with high DOM background levels makes 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, in which bioavailability has been shown to be highly correlated with dissolved-phase concentrations and, in contrast, poorly predicted by bulk solid-phase concentrations). Before this concept is adopted for widespread use, however, additional characterization of its response and behavior as well as improvements/modifications for laboratory versus in situ deployment are needed.

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