Comparing solid phase microextraction and polyethylene passive samplers for measuring ultra-low aqueous concentrations of regulated organic pollutants

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Abstract

Solid phase microextraction (SPME) fibers and low-density polyethylene (PE) passive samplers were co-exposed in spiked water experiments and in an impacted urban waterway to compare their performance in detecting ultra-trace levels of waterborne organic pollutants. Detections of nine model hydrophobic organic compounds (HOCs) using PE was greater than for SPME for spiked aqueous concentrations (C_w) less than 0.1 ng/L. The greater sensitivity of PE was confirmed *in situ*, with detectable levels as low as 1 pg/L for selected polychlorinated biphenyl (PCB) congeners. In laboratory studies, concentrations of targeted polycyclic aromatic hydrocarbons (PAHs), PCBs and chlorinated pesticides detected by SPME were within a factor of 2 on average to those measured using liquid-liquid extraction (LLE), while PE measurements were within a factor of 4 of LLE and were biased low, possibly due to uncertainties in PE equilibrium-partitioning coefficients. When *in situ* PE-measured concentrations were corrected for disequilibrium using performance reference compounds, the average ratio of SPME to PE for *in situ* concentrations was 1.8, indicating good overall agreement between the two passive samplers. *In situ* C_w values for SPME and PE were 70% (n = 4) and 210% (n = 6) on average of operationally dissolved C_w values determined on XAD resin with values for individual chemicals ranging from 20 to 140% (SPME/XAD) and from 27 to 590%. (PE/XAD). Although uncertainties (e.g., error associated with laboratory-measured equilibrium constants and corrections for disequilibrium) surrounding calibration parameters and equilibrium have not been fully resolved, these results indicate that both SPME and PE show promise as ambient sampling tools for contaminants of regulatory concern in the aquatic environment.

Introduction

Within aquatic systems, it is the freely dissolved aqueous concentration that controls the bioavailability or activity of HOCs (Mayer *et al*. 2003). Historically, measuring the freely dissolved phase (without particle-bound or dissolved organic matter-bound HOCs) has required various separation techniques (e.g., filtering, centrifugation) followed by liquid-liquid or solid phase extraction. Additionally, the ultralow concentrations of HOCs present in the dissolved phase may require the extraction of large volumes of water to ensure detection. Passive samplers, including SPME fibers and low-density PE, have recently allowed for measurement of freely dissolved HOC concentrations (Mayer *et al*. 2003, Vrana *et al*. 2005), which are directly correlated to the bioavailable fraction (Friedman *et al*. 2009). In comparison with off-line extraction techniques, they provide a cost-effective sampling and pre-concentration alternative for measuring HOCs currently regulated under legislation such as the United States Environmental Protection Agency (USEPA) Clean Water Act.

Several studies have used SPME samplers to measure freely dissolved HOCs, including dichlorodiphenyl trichlorethane (DDT) and its

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metabolites, in surface waters (Zeng *et al*. 1999, 2005a; Xing *et al*. 2009). Polyethylene samplers have also been used to measure surface water PCB and PAH concentrations (Booij *et al*. 2003, Adams *et al*. 2007). Cornelissen *et al*. (2008) compared SPME (28.5 µm), and polyethylene (100 µm) to polyoxymethylene (55 and 500 µm) and found disequilibrium for higher molecular weight PAHs sampled with thicker sorptive samplers. For this study, SPME and PE were compared *in situ* with the use of performance reference compounds in the slower-diffusing PE (Rusina *et al*. 2007) to allow for possible disequilibrium correction.

Solid phase microextraction is based on the association of HOCs with a polymeric phase, e.g., polydimethylsiloxane (PDMS) coated onto a fused silica support or "fiber" (Arthur and Pawliszyn 1990). Analytes extracted by the SPME fiber are then desorbed directly into the analyzing instrument, e.g., gas chromatography-mass spectrometry (GC-MS), eliminating the need for sample processing. Direct injection of SPME, however, requires fibers with relatively small sorptive coating volumes (commercial fibers used in this study were < 1 µl). Technical grade optical fibers may also be used to provide for larger sorptive volumes (~ 10 µl) at less cost (Mayer *et al*. 2000). Solid phase microextraction fibers are also available in varying thicknesses (7 - 100 µm); the smaller thicknesses allow for faster equilibration times; however, as thickness decreases, the volume of PDMS decreases and sensitivity decreases (Mayer *et al*. 2003).

In contrast, low-density PE samplers made with ~2 ml of PE have been used in the field (Adams *et al*. 2007). The larger volume of these samplers allows for greater sensitivity, but requires solvent extraction prior to GC analysis. Like SPME fibers, PE can be purchased in varying thicknesses (25 - 100 µm) with the smaller thicknesses allowing for faster equilibration times. For PE, chemicals diffuse into both sides of the sheet so that the diffusion path length (12.5 - 50 µm) is half of the total thickness. For both samplers, smaller thicknesses will allow for faster equilibration times while smaller overall sampler volumes will limit the detection of chemicals of interest as smaller masses of these chemicals will be sorbed.

The goal of this study was to compare the sensitivity and accuracy of SPME and PE for determination of aqueous phase HOCs. Freely dissolved concentrations of PAH, PCBs and organochlorine pesticides that are currently regulated in the US were measured via SPME and PE in controlled laboratory exposures. To determine their performance under field conditions, both types of samplers were co-deployed at several locations in an estuarine waterbody listed as impaired due to organic pollutants.

Methods

Materials

Methanol (MeOH), acetone, dichloromethane (DCM), and hexane were all JT Baker ultra-resi-analyzed grade (Phillipsburg, NJ). Low carbon reagent water (TOC < 6 µg/L) was from a Milli-Q purification system (Millipore, Billerica, MA). Nine model HOCs (PCB 52, PCB 101, PCB 153, PCB 180, phenanthrene, pyrene, benzo[a]pyrene, 4,4'-DDE, and *cis* chlordane) were purchased from Ultra Scientific (N. Kingstown, RI). SPME fibers coated with 100-µm PDMS manufactured by Supelco (Bellefonte, PA) were purchased through Sigma-Aldrich.

Low-density PE (30 + 4 µm thick; Carlisle Plastics, Inc., Minneapolis, MN) was cut into strips ~ 6 cm x 120 cm (~ 2 g each). After cleaning by soaking in DCM (24 hours), MeOH (24 hours), and Milli-Q water, each strip was preloaded with six performance reference compounds (PRCs): phenanthrene-d_{10}, pyrene-d_{10}, benzo[a]pyrene-d_{12}, PCB 51, PCB 155, and PCB 185 at concentrations (µg/g PE = 0.36 ±0.06, 2.6 ±0.3, 0.44 ±0.12, 2.9 ±0.6, 1.8 ±0.4, and 7.5 ±1.0, respectively) similar to those used previously for semi-permeable membrane devices (SPMDs; Booij *et al*. 1998, Huckins *et al*. 2002). Preloading was accomplished by placing PE strips in a MeOH-water solution (80:20) spiked with the PRCs for 12 days (Booij *et al*. 2002).

Spiked Water Laboratory Exposures

Preloaded PE strips and SPME fibers were co-exposed in five 20-L glass carboys containing Milli-Q water spiked to achieve four different concentrations of the nine model HOCs, ranging from 0.001 ng/L for the most hydrophobic compounds to 1000 ng/L for phenanthrene. Three PE strips and SPME fibers each were placed into each of the spiked water carboys (wrapped in Al foil to exclude light), with the fifth serving as a non-spiked blank. After spiking with acetone as the carrier solvent (0.02 - 20 ml for Carboy #1 through Carboy #4), the carboys were stirred for 24 hours prior to addition of the passive samplers. PE strips were suspended using 32 gauge

copper wire cleaned and sonicated in DCM. SPME fibers were supported inside the carboy with a thin sheet of pre-cleaned polytetrafluoroethylene (PTFE), draped over the mouth of the carboy. Each carboy was continuously stirred for 47 days and maintained at 23 ±2°C.

Co-Deployment of PE and SPME Samplers in an Urban Waterway

Both types of samplers were co-deployed in Ballona Creek and Marina del Rey, CA, USA at five locations (Figure 1) for 23 days in Sept-Oct 2007. A single PE strip (~2 g) and either one or two SPME fibers encased in a perforated 15 x 1.5 cm cylindrical copper housing (Zeng *et al*. 2004) were deployed at two depths: 0.5 m above the sediment-water interface and 0.5 m below the water surface. Triplicate PE strips and an Infiltrex 100 *in situ* pump system were deployed at Site 5. Included for validation of PE and SPME measurements, the battery powered pump system was deployed for four days during the 23-day sampler exposure period at a depth of 1.5 m above the sediment-water interface. Prior to deployment, copper SPME housings were sonicated for 20 minutes each DCM:MeOH (1:1) and hexane, dried at room temperature, and wrapped in aluminum foil until installation of SPME fibers.

Immediately before deployment, SPME fibers were extruded from their protective sleeve and cleaned in hexane. PE strips were woven accordion style onto solvent-cleaned 18 gauge copper wire and a small square (≤0.05 g) was removed for subsequent determination of PRC initial concentrations. The copper wire/PE assembly was threaded through and secured to polypropylene rope suspended in the water column with a subsurface float and anchored in place by iron chain links. SPME samplers were attached to the rope with stainless steel hose clamps (Zeng *et al*. 2004).

The Infiltrex system pumped 944 L of ambient water first through a 0.7-µm glass fiber filter and subsequently through a PTFE column packed with XAD-2, exhaustively pre-extracted with DCM and MeOH. Upon retrieval, the XAD column was wrapped with aluminum foil and stored in an ice chest for transport to the laboratory. During sampler retrieval, water depth, temperature, specific conductivity, salinity, and pH were measured using a YSI Data Sonde (Yellow Springs Instruments, Yellow Springs, OH; data not shown). Water column samples were collected in 40-ml amber glass scintillation vials pre-

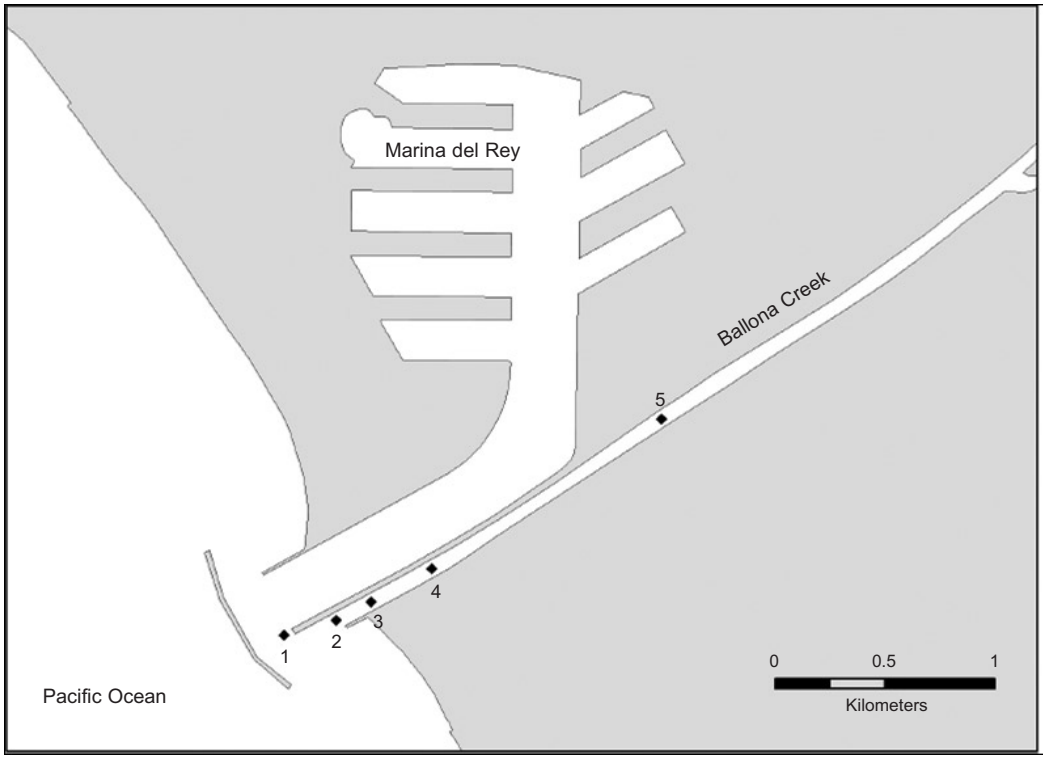

Figure 1. Sampling sites in Ballona Creek, Los Angeles County, CA, USA.

rinsed with acetone and DCM. After filtration with a kiln-fired glass fiber filter (Whatman GFF; Maidenstone, England), a 1-ml aliquot was acidified and analyzed for dissolved organic carbon (DOC) using a Shimadzu elemental analyzer (Shimadzu Scientific Instruments, Colombia, MD) with the oxidation catalyst heated to 680°C.

Laboratory Sample Preparation

At the predetermined time for the laboratory exposures, SPME fibers were retracted, placed in a glass vial, and stored at -20°C until analysis by GC-MS. Laboratory-exposed PE strips were placed in a solvent rinsed 300 ml glass bottle, spiked with between 3 and 120 ng of anthracene-d_{10}, chrysene-d_{10}, perylene-d_{12}, PCB 50, PCB 143, and PCB 189 (as recovery surrogates) and extracted twice with 300 ml of DCM over 24 hours at room temperature (~23ºC). The PE extracts were filtered through Na_2SO_4 combusted at 500°C to remove water and concentrated to ~10 ml using a Rotovap and solvent exchanged to hexane. The PE extracts were then concentrated to final volumes appropriate for the initial water concentrations in each carboy using a gentle stream of high purity N_2.

Carboy water remaining after all samplers were removed was extracted in 1.5-L increments by shaking with three 100-ml aliquots of DCM in a 2-L separatory funnel and combining the organic extracts. An increasing volume of residual water was extracted as the initial nominal spiking concentration decreased. Anthracene-d_{10}, chrysene-d_{12} and PCBs 30 and 205, were added as recovery surrogates prior to extraction. Extracts were concentrated and exchanged to hexane using a Rotovap, then carefully reduced to ~25 µl using N_2.

In Situ Sample Preparation

SPMEs retrieved from the field sites were removed from their copper casing, gently rinsed with DI water to remove any biofilm growth, retracted, and placed in an amber glass vial for transport back to the laboratory (on ice) for processing within 24 hours. Fibers that could not be analyzed within this period were stored at -20°C. The PE strips were removed from the copper wire and stored in a solvent cleaned 120-ml amber jar for transport back to the laboratory (on ice). After gently rinsing with Milli-Q water to remove biofilm growth, PE strips were spiked with anthracene-d_{10}, chrysene-d_{10}, perylene-d_{12}, PCB 50, PCB 143, and PCB 189 as recovery surrogates and extracted twice with 300 ml of DCM for 24 hours. Concentrated extract was cleaned via a silica gel-alumina column (30 x 1.1 cm) packed bottom to top with neutral silica gel (12 cm, ~4.8 g dry weight, 3% deactivated), neutral alumina (6 cm, ~5.8 g dry weight, 3% deactivated), and anhydrous sodium sulfate (1 cm). Fractions of 15 ml hexane and the subsequent 50 ml of hexane/DCM (70:30, v/v) were collected. The eluate was exchanged to hexane and concentrated to 1 ml for GC analysis.

The XAD-2 resin from the *in situ* pump system was spiked with surrogate standards and eluted consecutively with 200 ml of MeOH and DCM at a flow rate of 5 ml/minute within 24 hours after retrieval as described previously (Zeng *et al*. 1999). The MeOH fraction was back-extracted three times with 50-ml aliquots of DCM and all extracts combined, exchanged to hexane and concentrated to 1 ml. Internal standards were added to final extracts before GC-MS analyses (Zeng *et al*. 1999, 2004).

GC-ECD and -MS Analyses

A Varian 3800 GC/Saturn 2000 ion trap MS (Varian, Walnut Creek, CA) was used to analyze SPME fibers, water, and PE extracts for PAH. The injector temperature was programmed from 100 to 280°C at ~100°C/minute with a 40-minute hold time at 280°C. Carrier gas was ultra-high purity helium with a flow rate of 1.0 ml/minute. Chromatographic separation was achieved with a 60 m x 0.25 mm id (0.25-µm film thickness) DB-5MS column (J&W Scientific, Folsom, CA) programmed from 80°C (1 minute hold) to 176°C at 8°C/minute, ramp to 230°C at 1.5°C/minute, and a final increase to 290°C at 5°C/minute (21 minute hold). The temperatures of the ion trap, manifold, and transfer line were 220, 120, and 280°C, respectively. Mass spectra were acquired in the electron impact mode at 70 eV by selected ion storage (SIS) method. Extracts were quantified using a six point calibration curve (50 to 2000 ng/ml) with an internal standard to calculate a relative response factor (RRF). The SPME fibers and extracts were analyzed using a six point external calibration curve and an external standard.

A Hewlett Packard 5890 Series II plus gas chromatograph (Palo Alto, CA, USA) equipped with a ^{63}Ni electron capture detector and a 7683 autosampler was employed for quantitation of PCB

and chlorinated pesticides in PE and water extracts. A 60-m DB-5MS GC column similar to the one used for GC-MS analysis was used. Helium (1.5 ml/minute) and nitrogen were used as carrier and makeup gas, respectively. The injector was operated in the splitless mode at 280˚C and the detector temperature was 300˚C. The column temperature was programmed at 170˚C for 20 minutes, increased to 290˚C at 4˚C/minute, and held at 290˚C for 20 minutes. Two microliters of sample extract were injected and a nine point external standard calibration curve (1, 2, 5, 10, 25, 50, 100, 250, and 500 ng/ml) was generated to quantify target analytes.

Quality Assurance/Quality Control

The nine model HOCs were nondetectable in carboy, SPME, and PE blanks as well as in procedural blanks representing the extraction of PE and residual carboy water. The lone exception was the detection of phenanthrene, 4,4'-DDE and PCBs 52 and 101 in the carboy water blank. Respectively, these blank levels were 1, 10, 16 and 57% of the corresponding concentrations measured in the residual water from the lowest spiked treatment. Detectable concentrations in residual water samples were blank-corrected for these HOCs only. Atmospheric PE blanks exposed at each of the field sites also showed no detectable target analytes.

Surrogate recoveries (mean ±1 sd) for residual carboy water extracts ranged from a low of 70 ±31% to a high of 107 ±8%. Corresponding values for PE extracts ranged from 91 ±15% to 96 ±18%. Recoveries for the XAD-2 resin were 70% for naphthalene-d_8, 94% for acenaphthylene-d_{10}, 98% for phenanthrene-$d_{10,}$ 107% for chrysene-d_{12}, 84% for benzo[ghi]perylene-d_{12}, 90% for tetrachloro-m-xylene, and 96% for PCB 65. Sample concentrations were not corrected for surrogate recovery.

Data Analysis

For SPME at equilibrium with the surrounding water (Zeng and Noblet 2002), the dissolved aqueous concentration of the target chemical, C_w can be calculated as:

$$C_w = \frac{C_f}{K_f} = \frac{n_f}{K_f V_f} \quad (1)$$

where C_f is the concentration of the chemical in the SPME fiber, K_f is the SPME-water equilibrium partitioning coefficient, n_f is the mass of the chemical on the fiber, and V_f is volume of fiber coating (0.612 µl for Supelco 100-µm PDMS fibers). The K_f values for the model HOCs are taken from previous work (Zeng *et al*. 2005b, Yang *et al*. 2006, Maruya *et al*. 2009). Similarly, the equilibrium aqueous concentration determined by PE ($C_{W\infty}$) is calculated using (Adams *et al*. 2007):

$$C_{W\infty} = \frac{C_{PE\infty}}{K_{PEW}} \quad (2)$$

where K_{PEW} is the PE-water equilibrium partitioning coefficient and $C_{PE\infty}$ the concentration of chemical in the polyethylene at equilibrium. The K_{PEW} values for the model HOCs were determined for thicker polyethylene material (51 ±3 µm) from the same manufacturer (Sayre *et al*. 2007).

Preloaded PRCs may be used to check for attainment of equilibrium by PE and also to correct for disequilibrium (Adams *et al*. 2007). Assuming 1st-order kinetics, the exchange rate coefficient, k_e can be calculated according to the following:

$$k_e = \ln\left(\frac{C_{PE0,r} - C_{PE\infty,r}}{C_{PEt,r} - C_{PE\infty,r}}\right) \cdot t^{-1} \quad (3)$$

where $C_{PE0,r}$ $C_{PE\infty,r}$ and $C_{PEt,r}$ are the initial, equilibrium and time t concentration of the PRC (denoted with an r subscript) in the PE, respectively. Assuming infinite bath conditions (i.e., PRC concentration in the PE is zero after infinite time), Equation 3 becomes:

$$k_e = \ln\left(\frac{C_{PE0,r}}{C_{PEt,r}}\right) \cdot t^{-1} \quad (4)$$

Assuming the rates of exchange for the target chemical and the corresponding PRC are first-order and equivalent in magnitude, $C_{W\infty}$ can be expressed as:

$$C_{W\infty} = \frac{C_{PEt}}{\left(1 - e^{-k_e t}\right) \cdot K_{PEW}} \quad (5)$$

For the 47-day laboratory experiments under non-infinite bath conditions, equilibrium was evaluated by measuring the PRC concentration in the PE

at time t ($C_{PEt,r}$). This value was compared to the expected equilibrium PRC concentration in the PE ($C_{PE\infty,r}$):

$$C_{PE\infty,r} = \frac{K_{PEW} \cdot C_{PE0,r} \cdot M_{PE}}{V_W + K_{PEW} \cdot M_{PE} + K_f V_f} \quad (6)$$

where $C_{PE0,r}$ and $C_{PE\infty,r}$ are the initial and equilibrium PRC concentrations in the PE, respectively, M_{PE} is the mass of the PE and V_w is the volume of water.

Results

Sensitivity

The HOC-specific method detection limits (MDLs) for SPME and PE were estimated using K_f and K_{PEW} values listed in Table 1. Due to the much larger sorptive mass (~2 g), the estimated MDLs for PE are several orders of magnitude lower than for SPME (0.612 µl) and range from 3.8 x 10^{-5} ng/L for PCB 180 to 0.015 ng/L for phenanthrene (Table 1), compared with 0.024 ng/L (PCB 180) and 10.3 ng/L (phenanthrene) for SPME. Because C_w is inversely proportional to K for both samplers (Equations 1 and 2), MDLs decrease with increasing hydrophobicity as measured by K_{ow}. All nine model HOCs were detected by PE in the 47-day laboratory exposures whereas SPME did not detect any of the target HOCs for the lowest concentration treatment.

The same general result was observed for the side-by-side *in situ* deployment, where PE again detected all nine target analytes in all samplers and SPME detected the targets with variable frequency (Table 2). SPME detected phenanthrene, pyrene and 4,4'-DDE with high frequency (≥15 detections/16 samplers) to levels < 1 ng/L and PCB 52 and *cis*-chlordane in roughly 50% of the samples to levels < 0.1 ng/L. SPME did not detect the more hydrophobic analytes (most PCB congeners and benzo[a]pyrene). In contrast, PE was able to detect even the most hydrophobic target analytes to levels as low as 0.0006 ng/L (for PCB 180) that were out of the range for XAD-2 (Table 2). Although not directly comparable, the range of SPME and PE measurements in general bracketed the single measurements (Figure 3).

Comparison of PE and SPME Laboratory Concentrations

When SPME and PE-measured dissolved concentrations ($C_{W,SPME}$ and $C_{W,PE}$, respectively), ranging over nearly four orders of magnitude in spiked laboratory exposures were plotted vs. concentration determined on residual water subject to liquid-liquid

Table 1. Partition coefficients and estimated method detection limits for nine model organic pollutants using SPME and PE passive samplers.

Chemical	Log K_{OW} [a]	Log K_f [b]	Log K_{PEW} [c]	Estimated Method Detection Limit (ng/L)	
				SPME[d]	PE[e]
Phenanthrene	4.52	3.9	4.33	10.3	0.015
Pyrene	5	4.31	5.02	2	0.003
Benzo[a]pyrene	6.35	5.82	6.61	0.25	7.7 x 10^{-5}
PCB 52	6.17	5.52	5.51	0.11	0.00097
PCB101	6.65	6.08	6.16	0.034	0.00022
PCB153	7.09	6.45	6.71	0.029	6.1 x 10^{-5}
PCB180	7.21	6.54	6.91	0.024	3.8 x 10^{-5}
Cis-chlordane	6.1	5.37	5.53	0.17	0.00092
4,4'-DDE	6.96	6.17	6.25	0.055	0.00018

[a] From Sangster (1989), Ruelle (2000), Simpson *et al*. (1995), de Bruijn *et al*. (1989)

[b] 100 µm PDMS coating from Zeng *et al*. (2005b), Yang *et al*. (2006) and Maruya *et al*. (2009)

[c] 51 µm polyethylene; Sayre *et al*. (2007)

[d] Maruya *et al*. (2009) except for pyrene and PCB 101, which were estimated assuming minimum detection of 25 pg by GC-MS and Eq. 1

[e] Estimate assumes 25 pg/µl minimum detection by GC-MS, 25 µl final extract volume, and 2 g PE

Table 2. Aqueous concentrations of target analytes in the Ballona Creek estuary[a] measured using SPME, PE, and in a large volume sample extracted by XAD-2 resin[b].

Chemical	SPME		PE		XAD-2[d]
	Range (ng/L)	# Detects[c]	Range (ng/L)	# Detects[c]	(ng/L)
Phenanthrene	≤0.50 – 19	16/16	0.31 – 5.3	13/13	1.9
Pyrene	≤0.68 – 9.2	15/16	0.23 – 1.7	13/13	NA
Benzo[a]pyrene	<0.25	0/16	0.0029 – 0.042	13/13	0.15
PCB 52	≤0.010 – ≤0.020	16-Nov	0.037 – 0.19	13/13	0.021
PCB 101	<0.034	0/16	0.0060 – 0.029	13/13	NA
PCB 153	<0.029	0/16	0.0045 – 0.018	13/13	0.011
PCB 180	<0.024	0/16	0.00056 – 0.0046	13/13	< 0.010
Cis -chlordane	≤0.008 – ≤0.016	16-Jul	0.052 – 0.24	13/13	0.069
4,4'-DDE	≤0.0061 – 0.029	15/16	0.023 – 0.074	13/13	0.089
4,4'-DDT	≤0.044 – 1.5	16/16	0.048 – 0.17	13/13	0.028
	Total:	**80/160**	**Total:**	**130/130**	

[a] Five sites, two sampling depths per site

[b] NA—this chemical was not analyzed in this sample; < not detected (value listed is MDL); ≤ detected at level below MDL

[c] Number of times analyte was detected/number of samples analyzed

[d] Dissolved phase concentrations measured in 944 L sample collected at Site 5 only

extraction ($C_{W,LLE}$), a nearly 1:1 correlation for all three classes of target HOCs was observed (Figure 2). Considering all nine model HOCs, the slope for the linear regression between $C_{W,SPME}$ and $C_{W,LLE}$ was 0.96 (n = 24; R^2 = 0.82), while the corresponding value for $C_{W,PE}$ and $C_{W,LLE}$ was 1.1 (n = 34; R^2 = 0.90). For PCBs and PAHs, values of $C_{W,SPME}$ fall on both sides of the 1:1 correlation line, with SPME values within a factor of 2.5 and 2.3 of $C_{W,LLE}$ on average, respectively (Figure 2a,b). For *cis*-chlordane and 4,4'-DDE, both samplers showed a negative bias compared to $C_{W,LLE}$ (Figure 2c). However, the average deviation from $C_{W,LLE}$ for PE was three-fold greater than for SPME (7.0 vs. 2.3). $C_{W,PE}$ was also consistently lower than the $C_{W,LLE}$ by an average factor of 2.9 for PCBs and 3.6 for PAHs. These averages do not include detectable concentrations of benzo(a)pyrene (0.15 pg/L) and 4,4'-DDE (0.38 pg/L), which were more than ten times less than the corresponding LLE-measured concentrations (Figure 2). The discrepancy for these two data points may be attributed to high measurement uncertainty for both of these chemicals, which were detected near the estimated MDLs.

Comparison of PE and SPME *In Situ* Concentrations

In situ SPME and PE measurements for Ballona Creek, a tidal channel that drains a highly urbanized watershed in metropolitan Los Angeles and is listed as impaired in accordance with State and federal water quality criteria, bracketed the 1:1 correlation line for the five of nine target HOCs detected by SPME and 4,4'-DDT (Figure 3). The average ratio of SPME to PE estimated concentrations for the five target HOCs was 1.8, indicating good overall agreement between the two passive samplers. As was observed in the spiked laboratory exposures, SPME C_ws for phenanthrene and pyrene were higher overall than for PE (3.8 times larger on average). The PE- and SPME-measured concentrations lying closest to the 1:1 line were for DDE (SPME/PE = 0.43); for PCB 52 and *cis*-chlordane, SPME resulted in lower C_w than PE (SPME/PE = 0.22 and 0.17, respectively).

In situ PE and SPME measurements bracketed the XAD-measured operationally-defined dissolved concentrations for target HOCs and DDT at Site 5 in Ballona Creek (Figure 4). The average ratio of PE to XAD concentration was 2.1 for the six target HOCs detected (range: 0.27 for benzo(a)pyrene to 5.9 for

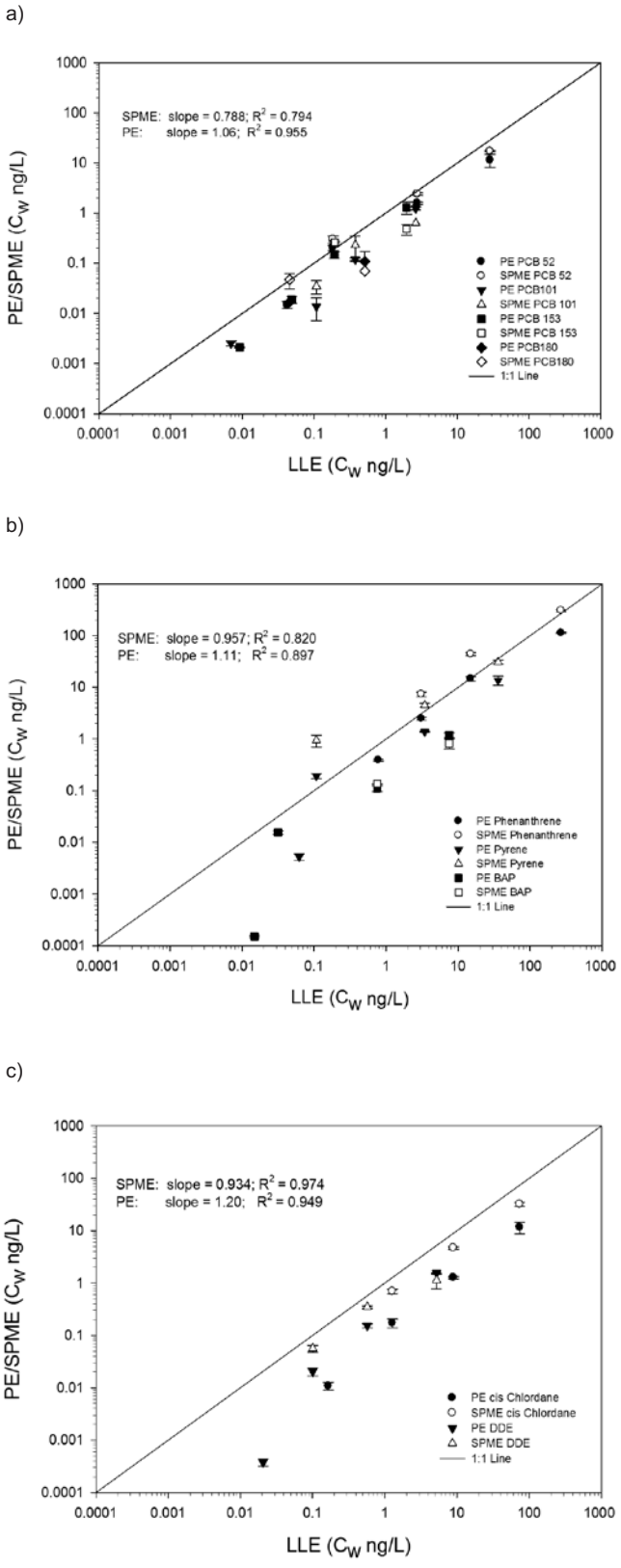

Figure 2. Aqueous concentrations of target HOCs (C_w) measured by SPME- and PE versus liquid-liquid extraction (LLE) in spiked water exposures. PCBs (a), PAHs (b), chlorinated pesticides (c), SPME (open symbols), and PE (closed symbols).

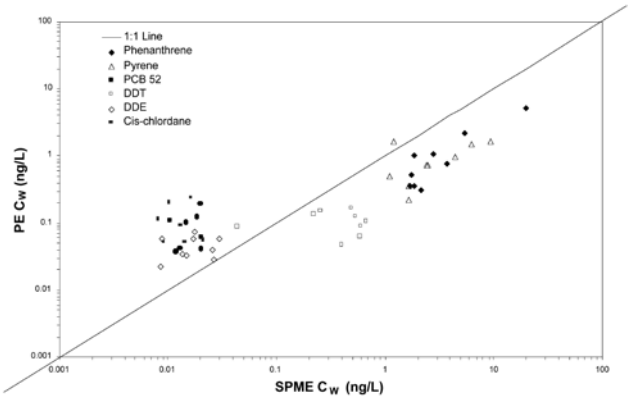

Figure 3. PE- vs. SPME-measured dissolved water concentrations (C_w) for phenanthrene, pyrene, PCB 52, 4,4'-DDE, 4,4'-DDT, and cis-chlordane for the Ballona Creek Estuary. Estimated C_ws for 4,4'-DDT were based on *K* values from Sayre *et al.* (2007) and Maruya *et al.* (2009).

PCB 52). The average ratio of SPME to XAD concentration was 0.70 for four mutually detectable HOCs (range: 0.20 for 4,4'-DDE to 1.4 for phenanthrene). Although not measured by XAD, PE and SPME C_ws for pyrene were comparable at 1.7 and 1.2 ng/L, respectively.

Assessment of Equilibrium

For the laboratory exposures, PRC concentrations in PE after 47 days were not substantially different than equilibrium predictions based on Equation 6. For example, measured ($C_{PEt,r}$) and predicted ($C_{PE\infty,r}$) concentrations for phenanthrene-d10 were 0.22 ±0.04 µg/gPE and 0.26 ±0.01 µg/gPE, respectively, and were 6.5 ±0.8 µg/gPE and 6.5 ±0.7 µg/gPE for PCB 185, respectively. Close agreement between $C_{PEt,r}$ and $C_{PE\infty,r}$ for the remaining four PRCs which were of intermediate hydrophobicity was also realized, indicating that equilibrium was achieved by the end of the 47-day exposure. This was not surprising as the continuous stirring action as well as the larger solid-to-water ratio would increase mass transfer rates within the carboys.

Discussion

Sensitivity

In this study, PE exhibited a greater sensitivity than SPME for the lower spiked water concentrations in the 47-day laboratory exposures. It should be noted that the use of technical grade optical fibers with larger volumes of PDMS has been demonstrated

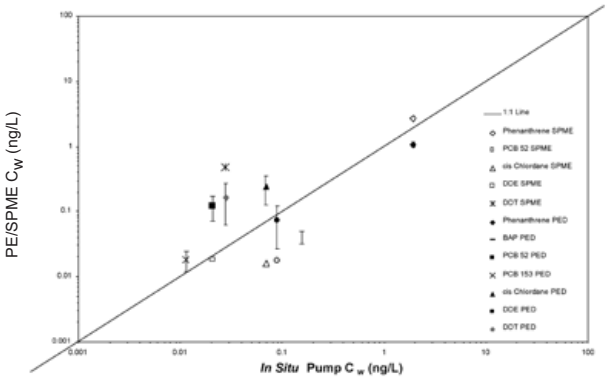

Figure 4. PE- and SPME-measured versus XAD-measured dissolved water concentrations (C_W) of target HOCs measured for Site 5, Ballona Creek estuary. SPME = open symbols and PE = closed symbols. PE error bars = 1 sd. BAP = benzo[a]pyrene. Estimated C_Ws for 4,4'-DDT were based on *K* values from Sayre *et al.* (2007) and Maruya *et al.* (2009).

to allow for lower detection in porewaters (e.g., 9 pg/L for PCB 180; Mayer *et al*. 2000). For both samplers, increasing the mass or volume of the sorptive material will result in greater sensitivity.

PE and SPME Laboratory Concentrations

The SPME measurements were in better agreement on average with dissolved concentrations determined by LLE. The negative bias observed for PE (all nine model HOCs; Figure 2) and for SPME (two organochlorine biocides; Figure 2c) may indicate a positive bias in K values. PE-water partition coefficients were determined for 51 µm thick material, whereas the PE used in the laboratory and field exposures was cut from 30 µm thick LDPE from the same manufacturer. Previously, K_{PEW} s for pyrene were found to vary by 0.3 log units for PE from different manufacturers (Fernandez *et al*. 2009), a degree of uncertainty which could result in a two-fold difference in $C_{W,PE}$. Differences among original PE material and their impact on K_{PEW}s need further study.

PE and SPME *In Situ* Concentrations

The discrepancy between SPME and PE for PCB 52 and *cis*-chlordane is not surprising as the SPME levels (although detectable on fibers) were lower than the corresponding MDLs (Table 1). Overall, the greater variability observed among PE- SPME-, and XAD-measured values in the field compared with the spiked laboratory measurements is to be expected considering that levels in the field were generally much lower and that the *in situ* pump was deployed for only 4 days, compared with 23 days for passive sampling devices (PSDs). Overall, the agreement between PE and SPME estimates and XAD results are well within an order of magnitude, indicating that these samplers are capable of reproducing operationally-defined dissolved HOC concentrations.

It has been hypothesized that XAD-measured concentrations may include DOC-bound HOCs (Schneider *et al*. 2006); however, XAD typically recovers small fractions of DOC (5 - 15% of the DOM or 10 - 30% of the DOC) in seawater and requires large manipulation of pH (Benner *et al*. 1992). In order to investigate the possibility of DOC-bound analytes, the percentage of chemical sorbed by DOC (0.92 mg/L at Site 5) was estimated to range from 1% for phenanthrene to as much as 63% for PCB 153 using a three-phase equilibrium partitioning model and organic matter-water equilibrium partition coefficients (K_{OM}) estimated using K_{ow} linear free energy relationships from Schwarzenbach *et al*. (1981). Using these corrections, it was observed that the DOC-corrected XAD measurements further under-predicted the dissolved concentration when compared to SPME- and PE-measured concentrations. This suggests that while DOC corrections are necessary for porewater samples, they are not appropriate for low-DOC samples measured using XAD.

Assessment of Equilibrium

Using Equations 1 and 2 to estimate C_w requires establishment of equilibrium between the PSD and the aqueous phase. If this assumption is violated, PE and SPME concentrations may be underestimated. In contrast, the extent of equilibrium reached for PRCs loaded into PE strips deployed for 23 days in Ballona Creek (Equations 4 and 5) suggested that the more hydrophobic analytes had not reached at least 90% of their final equilibrium values [$1 - e^{-k_e t} = 0.85 \pm 0.07$; 0.60 ± 0.14; and 0.54 ± 0.12 for benzo[a]pyrened-d_{12}, PCB 155 and PCB 185, respectively; n = 13]. Like the laboratory results, however, the lower molecular weight HOCs appeared to have reached equilibrium ($1\text{-}e^{-kt} = 0.99 \pm 0.01$; 0.97 ± 0.02; and 0.95 ± 0.04 for phenanthrene-d_{10}, pyrene-d_{10} and PCB 51, respectively; n = 13). PE estimated values of C_w were thus corrected for disequilibrium for corresponding target

HOCs (Figures 3 and 4). It can be argued that equilibrium (e.g., 90% or greater) for the more hydrophobic analytes may not have been achieved for SPME, which is consistent with the less than unity ratios of SPME to PE measurements for PCB 52 and 4,4'-DDE (Figure 3) and the apparent low bias for *cis*-chlordane and 4,4'-DDE by SPME (Figure 4). This is supported by field studies using SPME (28.5-µm coating thickness) where after 23 days, 5-ring and 6-ring PAHs had not reached equilibrium (Cornelissen *et al*. 2008).

Disequilibrium, however, does not explain the low bias associated with PE results from the laboratory exposures. Although no PRCs were selected to mimic *cis*-chlordane or 4,4'-DDE, the apparent equilibrium observed for PCB 185 (LeBas molar volume = 330.9 cm^3/mol; MacKay *et al*. 2006) suggests that both *cis*-chlordane or 4,4'-DDE (LeBas molar volumes of 319 and 340 cm^3/mol, respectively) have molecular diffusivities similar to PCB 185, and thus would be at equilibrium as well. Additionally, the larger equilibrium partitioning coefficient for PCB 185 (log K_{PEW} ~ 6.9) than *cis*-chlordane (5.5) and 4,4'-DDE (6.3) indicate that a larger mass of PCB 185 will be transferred to PE in order to reach equilibrium and will take more time than the transfer of the mass of *cis*-chlordane and 4,4'-DDE required to reach equilibrium. Another possible explanation for the low bias is uncertainty in PE-water partition coefficients. K_{PEW} values were determined for a 51-µm PE material, albeit from the same supplier (Carlisle Plastics) of the PE that was used in this study (30 µm). It is possible that varying thicknesses of PE material are produced during the manufacturing process that may result in materials of varying partitioning properties. Although no studies have investigated any such thickness dependence on K_{PEW}, others have reported a decrease in K_f for SPME with increasing PDMS coating thickness (Maruya *et al*. 2009). Neither PE nor SPME are immune to error caused by uncertainty in K values; thus it is important to determine these calibration parameters for the actual material used to ensure the maximum applicability of results.

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