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A passive sampler based on solid phase microextraction (SPME) for sediment-associated organic pollutants: Comparing freely-dissolved concentration with bioaccumulation

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HIGHLIGHTS

- An encased SPME passive sampler was used to measure C_{free} in contaminated sediments.
- Samplers were co-exposed with benthic invertebrates under lab and field conditions.
- Invertebrate tissue concentrations of organochlorines were highly correlated with C_{free}.
- SPME samplers can serve as a proxy for bioaccumulation *in situ*.

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ABSTRACT

The elevated occurrence of hydrophobic organic chemicals (HOCs) such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs) and legacy organchlorine pesticides (e.g. chlordane and DDT) in estuarine sediments continues to poses challenges for maintaining the health of aquatic ecosystems. Current efforts to develop and apply protective, science-based sediment quality regulations for impaired waterbodies are hampered by non-concordance between model predictions and measured bioaccumulation and toxicity. A passive sampler incorporating commercially available solid phase microextraction (SPME) fibers was employed in lab and field studies to measure the freely dissolved concentration of target HOCs (C_{free}) and determine its suitability as a proxy for bioaccumulation. SPME deduced C_{free} for organochlorines was highly correlated with tissue concentrations (C_b) of *Macoma* and *Nereis* spp. co-exposed in laboratory microcosms containing both spiked and naturally contaminated sediments. This positive association was also observed *in situ* for endemic bivalves, where SPME samplers were deployed for up to 1 month at an estuarine field site. The concordance between C_b and C_{free} for PAH was more variable, in part due to likely biotransformation by model invertebrates. These results indicate that SPME passive samplers can serve as a proxy for bioaccumulation of sediment-associated organochlorines in both lab and field studies, reducing the uncertainty associated with model predictions that do not adequately account for differential bioavailability.

1. Introduction

The protection and utilization of coastal aquatic resources require an integrated approach among scientists, regulators, dischargers and the public. The accumulation of chemical contaminants in estuarine sediments poses a substantial risk to the coastal marine environment (Johnson et al., 2002). As a critical step toward this endeavor, federal, State, regional and local regulators are working in collaboration with scientists and industry professionals to establish quantitative sediment quality guidelines and/or objectives (SQG/SQOs) to limit future damage to estuarine resources and to protect the environmental quality of the coastal zone. The two most commonly used approaches to establish SQGs/SQOs are through use of chemical specific thresholds based on theoretical or empirical relationships among bulk sediment chemistry, toxicological effects, and in some cases measures of *in situ* ecological condition. It is evident, however, that universal, single value criteria may poorly represent the fraction of sediment contaminants that is available for uptake by exposed organisms. This is particularly true for HOCs that are influenced by dissolved organic constituents (Means and Wijayaratne, 1982), total organic

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carbon (Karickhoff et al., 1979) and soot or "black carbon (Gustafsson and Gschwend, 1997). In the latter case, the presence of black carbon in field sediments decreased PAH partitioning to sediment porewater (McGroddy and Farrington, 1995) and reduced bioavailability to sediment-dwelling organisms (Maruya et al., 1997). Moreover, sediment porewater distribution coefficients (K_{oc}) for PCBs and chlorinated dioxins and furans were invariably greater than those predicted by partitioning to bulk organic matter (Bucheli and Gustafsson, 2001). Not surprisingly, enhanced sorption and reduced bioavailability for non-PAH classes of HOCs to sediment containing soot carbon have also been reported (Jonker et al., 2004).

As bioavailability is defined as the fraction of a contaminant that is available for uptake, bioaccumulation by benthic organisms can be effectively modeled as bioconcentration of freely dissolved HOCs in porewater (Kraaij et al., 2003). It follows that measurement of the freely dissolved concentration (C_{free}) in sediment porewater is preferred over the use of bulk chemistry (or C_{total}) for more accurately assessing bioavailability of sediment-associated HOCs (Lu et al., 2011). Historically, determination of C_{free} required relatively large sample volumes and several processing steps, i.e. *ex situ* filtration, extraction and pre-concentration steps that may introduce artifacts and that are labor and materials intensive (Lydy et al., 2014).

Passive sampling methods (PSMs) have the potential to eliminate logistical, cost and sediment disturbance pitfalls associated with traditional sediment porewater assessment methods (Parkerton and Maruya, 2014). Debate over the utility and interpretation of PSM data generated *in situ* vs. *ex situ* rages; however, there is little doubt that successful deployment *in situ* provides highly relevant data (Ghosh et al., 2014). *In situ* PSMs based on dialysis have been used for geochemical research (Doig and Liber, 2004); however, this multi-barrier concept suffers from a lack of HOC-compatible membranes and an inherent difficulty in modeling non-steady conditions (Grigg et al., 1999). Solid phase microextraction (SPME) developed by Arthur and Pawliszyn (1990), on the other hand, has been shown to be effective in quantifying C_{free} for a wide range of HOCs in extracted sediment porewater (King et al., 2004; Hawthorne et al., 2005, 2009), in the water column (Zeng et al., 2004; Fernandez et al., 2012) and in predicting bioavailability and acute toxicity (Parkerton et al., 2000; Hawthorne et al., 2007). In contrast to other sorptive materials (Jonker and Koelmans, 2001; Vinturella et al., 2004), two clear benefits of SPME are the uniformity and commercial availability of fiber material, and the minimal post-collection processing required.

Prior to widespread application of PSMs, demonstration of their utility for serving as a proxy for bioaccumulation and toxicity is needed (You et al., 2011). The objective of this study was to assess the concordance between tissue residue concentrations (C_b) and C_{free} for HOCs using a SPME sampler developed specifically for sediment applications (Maruya et al., 2009). To maximize the application potential of this sampler, we investigated concordance under both under lab and field exposure conditions. We first co-exposed SPME samplers and benthic invertebrates in 28 d lab experiments with spiked and naturally-contaminated sediment. We subsequently deployed SPME samplers for one month at an estuarine field site, and collected endemic bivalves for comparison to *in situ* bioaccumulation.

2. Materials and methods

Twelve HOCs spanning a wide range of hydrophobicity were selected for sediment spiking experiments based on frequency of occurrence in contaminated sediments and relevance to environmental regulations and monitoring requirements (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). SPME fibers coated with 100 μm polydimethylsiloxane (PDMS) were obtained from Supelco (Bellafonte, PA, USA). Fibers (as-received) were thermally pre-treated in a GC injector heated to 300 °C for 15 min. All solvents of the highest purity available and reagents of ACS 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 and solvent rinsed with acetone and hexane before and after use.

Table 1
Octanol–water ($\log K_{ow}$) and fiber-water partition coefficients ($\log K_f$) of target analytes for SPME fibers coated with 100 μm polydimethylsiloxane (PDMS).

Analyte	$\log K_{ow}$[a]	$\log K_f$[b]
Phenanthrene	4.46	3.90 ± 0.07
Fluoranthene	5.16	4.26 ± 0.09
Benzo[*a*]pyrene	6.13	5.82 ± 0.29
Heptachlor epoxide	4.98	4.48 ± 0.05
α-chlordane	6.22	5.37 ± 0.07
trans-nonachlor	6.35	5.68 ± 0.08
p,p′-DDE	6.96	6.17 ± 0.07
p,p′-DDD	6.22	6.11 ± 0.17
p,p′-DDT	6.91	5.24 ± 0.11
PCB 52	5.84	5.52 ± 0.09
PCB 153	6.92	6.25 ± 0.09
PCB 180	7.36	6.10 ± 0.09

[a] From Maruya et al. (2009).
[b] Average ± SD for triplicate ($n = 3$) extraction.

2.1. Co-exposure of SPME and benthic invertebrates in laboratory microcosms

SPME samplers were co-exposed with bivalves (*Macoma nasuta*) and polychaetes (*Nereis virens*) in estuarine sediments spiked with the 12 target HOCs. Intertidal sediment collected from the Upper Newport Bay Ecological Reserve were spiked at nominal concentrations ranging from 50 to 5000 ng/g dry and aged on a roller table for 8 h/day for a period of 2 months, storing in the dark at 4 °C when not being rolled. Five specimens per species were pre-acclimated for >72 h at 15 °C in glass aquaria containing 5 cm sediment and overlying filtered seawater (Supplemental Information, Fig. S1). Triplicate aquaria for each of five spiked concentrations plus unspiked sediment were subject to static seawater exchange of ~2.8 L/day. Water quality (temp, pH, DO and NH_3) was measured and recorded in each tank periodically during the 28 d exposure period with more frequent monitoring for randomly selected tanks.

In a second experiment, SPME samplers were co-exposed with *M. nasuta* and *N. virens* in glass aquaria containing field-collected sediments without any fortification of target HOCs in accordance with the protocol described above, except that flow-through instead of static seawater exchange was instituted (Table S1). Field collected sediments were homogenized by hand prior to layering into aquaria. Animals were not fed during the 28 day exposure. Historical data on field-collected sediments from six coastal stations in southern California indicated that mortality of estuarine amphipods at these stations ranged from a low of 15% to a high of 92%, and that concentrations of HOCs also varied widely, e.g. up to a factor of >200 for total PCBs.

2.2. In situ deployment of SPME samplers in intertidal sediments

A simple deployment fixture to maintain SPME samplers at a fixed depth beneath the sediment–water interface was designed, fabricated and successfully tested for intertidal applications. SPME samplers were deployed at five sites in the main channel of the Tijuana River (Fig. 1) within NOAA's Tijuana River National Estuarine Research Reserve (near San Diego, CA, USA) in October 2008 and again in March 2009. Whole sediment was screened for benthic macroinvertebrates and both media were analyzed for a broad suite of HOCs using methods described below.

2.3. Analysis of SPME fibers, sediment porewater and tissue

HOCs sorbed onto SPME fibers were thermally desorbed into an Agilent 7890 digital gas chromatograph coupled to a 5975C quadrupole mass spectrometer operating in the electron ionization mode. For SPME samplers deployed in the Tijuana River NERR in 2009, negative chemical ionization GC–MS was performed on recovered fibers to lower the detection limit for PCBs and organochlorine pesticides. Tissue samples were homogenized with kiln-fired Na_2SO_4 and extracted with dichloromethane/methanol (90:10 v/v) at 100 °C and 3000 psi using an Accelerated Solvent Extraction (ASE 300) system (Dionex, Salt Lake City, UT, USA). Tissue extracts were exchanged to DCM and further cleaned up using silica gel/alumina column chromatography, eluting the target HOCs in the initial eluant fractions of DCM and hexane. Procedural blanks and matrix spikes were analyzed with each batch of 12 tissue samples. Dibromooctafluorobiphenyl (DBOFB), PCB-208, naphthalene-d8, acenaphthene-d10, pyrene-d10 and perylene-d12 were added to each sample prior to extraction as recovery surrogates. The results for analysis of blanks (no analyte detected above the method detection limit) and recovery surrogates (73–90%) indicated satisfactory analytical performance was achieved (Supplemental Information, Table S2). The freely dissolved concentration determined by SPME (C_{free}) was computed as

$$C_{free} = C_f/K_f = N_f/V_fK_f$$

where N_f is the mass of HOC sorbed to the SPME fiber as determined by GC–MS, V_f is the volume of PDMS coating (0.612 μl), and HOC-specific K_f values are taken from Table 1.

3. Results and discussion

3.1. Co-exposure of SPME and benthic invertebrates in laboratory microcosm

Mortality among test organisms at the end of the 28 d exposure to spiked sediments and SPME samplers was low (2 of 180; <2%). DOC in sediment porewater isolated by centrifugation and subsequently filtered was relatively high at the start of the experiment (160 ± 10 mg/L) but decreased to much lower levels (6.4 ± 3.0 mg/L) by the end of the 28 d exposure. As reported in Maruya et al. (2009), total concentrations of spiked HOCs in sediment (C_s) and porewater (by liquid–liquid extraction or LLE) were correlated with C_{free} estimated by the SPME samplers, with LLE-based concentrations higher (as expected) than C_{free}.

Tissue concentrations (C_b) for most HOCs in *M. nasuta* and *N. virens* were positively associated with SPME. The high degree of correlation for DDTs (as one example) indicates that our SPME sampler is an excellent predictor of HOC body burdens. Moreover, the regression slope (0.927) suggests a near 1:1 relationship between body burden and SPME measurements (Fig. 2). Similar results were observed for chlordanes in *N. virens* (Fig. S2) as well as for PCBs in both test species (data not shown).

For co-exposure of test invertebrates and SPME samplers to the field-collected sediments, water quality in all test aquaria for the field-collected sediment experiment was maintained within recommended guidelines, except for depressed DO levels in two of the 18 replicate aquaria. Survival of *M. nasuta* was 100% and was greater than 87% for 5 of the 6 treatments for *N. virens*. Survival of *N. virens* in the only sediment that had not been pre-characterized for HOC levels and or sediment toxicity (Sample 6) was 47%. Total organic and black carbon content varied by a factor of 25 whereas HOC levels varied by as much as two orders of magnitude (Table 2). By day 28, dry wt., TOC and BC-normalized sediment PAH concentrations were correlated with freely dissolved porewater (SPME) concentrations (Supplemental Information, Table S3). Surprisingly, TOC and BC normalization did not substantially improve the correlation between bulk sediment concentrations and SPME measurements. Lipid-normalized tissue concentration (C_b) for both test species was positively associated with SPME for some (e.g. Pearson's R for fluoranthene in *Macoma* was 0.68, $p = 0.002$) but not all PAH (e.g. phenanthrene in Fig. 3); however, we observed fewer significant positive associations for *Nereis* (see below). Passive samplers made from PDMS tubing overestimated C_{free} for PAH in lab bioaccumulation experiments with *N. virens* (marine sediments) and *Lumbriculus variegatus* (Barthe et al., 2008). Biotransformation by benthic invertebrates including polychaetes like *Nereis* spp. may affect accumulation of selected PAH (Rust et al., 2009), and thus limit the utility of predictive relationships between C_b and C_{free}. The 28 d exposure period may also have been insufficient to achieve equilibrium for the more hydrophobic HOCs (Barthe et al., 2008; Muijs and Jonker, 2012). Fewer detections of organochlorines were afforded by SPME, ostensibly due to their ultra-low concentrations; however, measurements of C_{free} were clearly more predictive of measured tissue concentrations than porewater concentrations determined by LLE (Supplemental Information, Fig. S3).

3.2. In situ deployment of SPME samplers in intertidal sediments

Freely dissolved porewater concentrations of PAH, PCBs and pesticides determined by SPME samplers deployed at the Tijuana River NERR are summarized in Supplemental Information (Table S4). Individual PAH that were detectable by SPME included (in order of decreasing abundance) naphthalene, phenanthrene, pyrene and fluoranthene. The sum of PAH ranged from ⩽21 to 40 ng/L. In 2008, PCBs were largely non-detectable, save for PCB 49, -52 and 153/168 which were all barely above MDLs (∼0.05 ng/L). When switching to GC-NCI-MS in 2009, several congeners were detected (e.g. PCB-101, 110, 128, 138, 153/168) due to the increased sensitivity for analytes with >4 chlorines. Once again, detectable concentrations were at or near MDLs (∼0.001 ng/L). The sum of PCBs ranged from non-detect (<0.05 ng/L) to 0.18 ng/L. For pesticides, diazinon (∼20 ng/L) and chlorpyrifos (1–2 ng/L) dominated in 2008 and 2009, respectively. Barely detectable traces of p,p′-DDE were also observed in both deployment years. For all three classes of HOCs, *in situ* C_{free} was higher at the two stations furthest from the river mouth, i.e. 6010 and 6012 (Fig. 1).

Tissue concentrations (C_b) for the bivalves *Protothaca* and *Tagelus* spp. on a dry weight and lipid weight basis were positively correlated with C_{free} for total PCBs (Fig. 4). Interestingly, the correlation was not improved when normalizing to lipid weight, and the slope of the log–log regression were similar (0.540 vs. 0.547). For pesticides, this relationship was not significant (Supplemental Information, Fig. S4), however, this is not surprising as the sample size was small owing to few detections and the fact that the detected concentrations were very near or at the MDL. Additionally, the pesticides with the highest C_{free} (i.e. diazinon and chlorpyrifos) are not known for their bioaccumulation potential, particularly relative to the DDTs. Correlation between PAH was not attempted due to the possibility of biotransformation.

A number of lab studies comparing tissue concentrations with C_{free} determined by passive samplers have been published. Vinturella et al. (2004) exposed *N. virens* to field collected sediments in static microcosms and simultaneously measured uptake

Fig. 1. SPME sampler deployment stations in the NOAA Tijuana River National Estuarine Research Reserve (CA). Site selection coincided with an assessment of sediment chemistry, toxicity and benthic community condition.

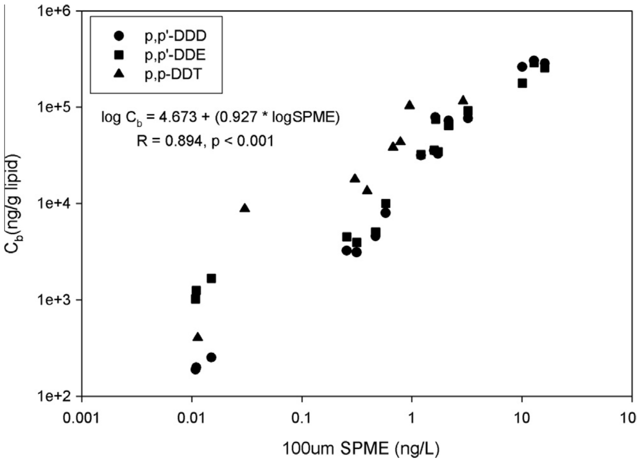

Fig. 2. Concentration of DDTs in *Macoma nasuta* (C_b) vs. freely dissolved (C_{free}) concentration in sediment porewater measured using SPME after 28 days exposure to spiked sediment. Regression analysis showed a highly significant, 1:1 log–log relationship between C_b and C_{free}.

of PAH by polyethylene (PE). Log–log regressions of lipid-normalized tissue vs. PE concentrations (not converted to C_{free}) of 3–5 ring PAH resulted in a slope of 0.6 and intercept of 1.8 and 2.4 for individual and total PAH, respectively. These parameters are remarkably similar to the regression parameters determined for the *in situ* $\log C_b$ (ng/g lipid) vs. $\log C_{free}$ relationship for PCBs in the present study (Fig. 4). You et al. (2006) utilized disposable SPME fibers in freshwater sediments spiked with radiolabeled p,p′-DDE and phenanthrene and, similar to Vinturella et al. (2004), related the SPME-sorbed contaminant to bioaccumulation by co-exposed oligochaetes (*L. variegatus*). The resulting highly significant $\log C_b$–log SPME relationship had a slope of 0.89, similar to the slope for our spiked experiment with DDTs (Fig. 2). In a recent study where investigators exposed earthworms to soil spiked with model HOCs similar to those investigated herein, linear regressions of lipid-normalized concentrations and C_{free} determined by SPME

Table 2
Physicochemical characteristics of field-collected sediments for 28 day co-exposure of SPME samplers and benthic invertebrates.

Sample	TOC (%)	BC (%)	DOC mg/L	ΣPAH ng/g dry	ΣPCB ng/g dry	ΣDDT ng/g dry	ΣCHL ng/g dry
1	4.9	0.48	5.5	6860	nd	126	31
2	3.1	0.74	5.5	3800	nd	73	8.3
3	1.6	0.23	3.3	17,800	1070	nd	nd
4	1.8	0.32	2.2	24,500	363	nd	nd
5	1.0	0.19	3.0	1230	3.6	54	nd
6	0.2	0.03	5.9	na	na	na	na
Min	0.2	0.03	2.2	1230	nd	nd	nd
Max	4.9	0.74	5.9	24,500	1070	126	31
Max/min	25	25	2.7	20	>300	>2	>4

ΣCHL – sum of seven chlordane analytes.
TOC – total organic carbon; BC – black carbon; DOC – dissolved organic carbon in porewater.
nd – not detected; na – data not available.

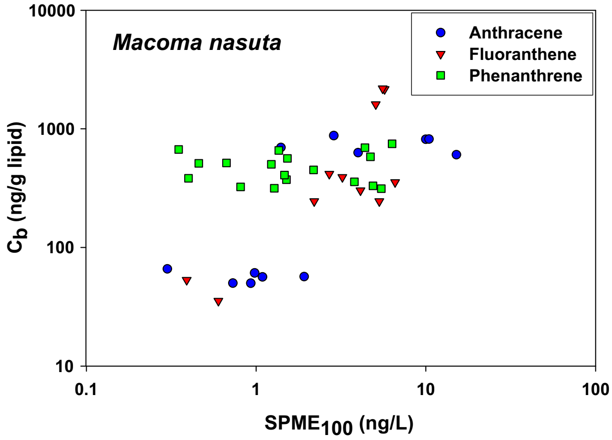

Fig. 3. Lipid-normalized tissue concentration (C_b) for *Macoma nasuta* exposed to field-collected sediments for 28 d was positively associated with the freely dissolved (C_{free}) concentration in sediment porewater measured using SPME for some but not all PAH.

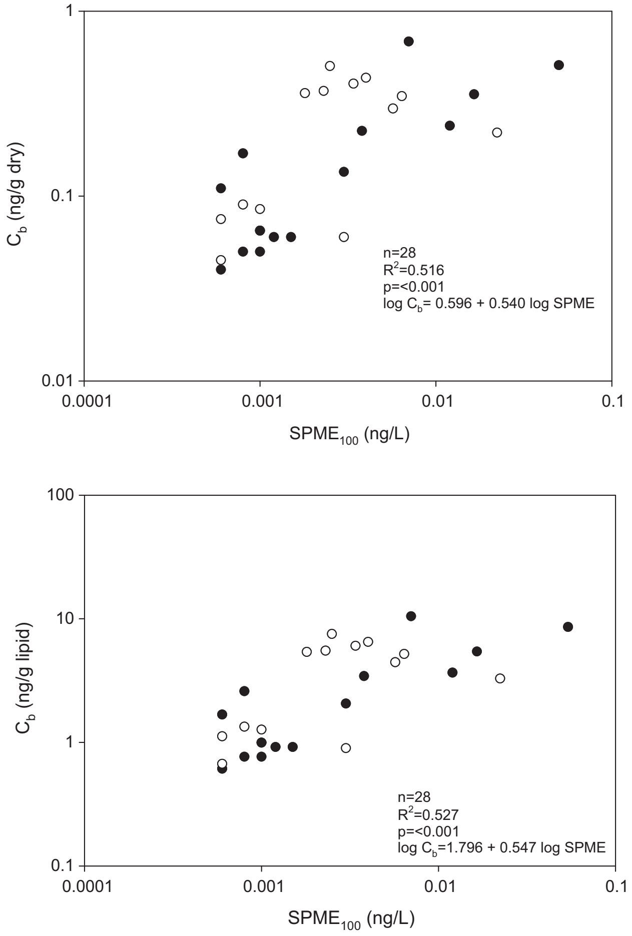

Fig. 4. Tissue (C_b) vs freely dissolved sediment porewater (C_{free}) concentration of total PCBs for field-collected bivalves (*Protothaca* and *Tagelus* spp.) from the Tijuana River National Estuarine Research Reserve. (top) dry weight and (bottom) lipid normalized tissue concentrations. *Protothaca* – filled circles; *Tagelus* – open circles.

for phenanthrene, pyrene, p,p′-DDT, PCB-153 and lindane were significant, with correlation coefficients ranging between 0.63 and 0.84 (Bielska et al., 2014).

Fewer data comparing C_b for benthic invertebrates and C_{free} in sediment porewater under field conditions are available. In a comparison of SPME and polyoxymethylene (POM), another commonly used passive sampler sorbent, a 1:1 relationship between equilibrium-predicted bioaccumulation based on C_{free} and bioaccumulation measured in the field was observed (Van der Heijden and Jonker, 2009). A study with *L. variegatus* and SPME exposed *in situ* at several sites contaminated with PAHs concluded that SPME effectively predicted the bioaccumulation of the worms within a factor of four by accounting for site-specific bioavailability (Muijs and Jonker, 2012). Using POM, decreases in C_{free} for PCBs after remedial action (activated carbon treatment) *in situ* corresponded with decreases in tissue concentrations of *L. variegatus* (Beckingham and Ghosh, 2013). Thomas et al. (2014) incorporated SPME in assessing the effectiveness of remedial activities on sediment contaminated with PAH and PCBs. For a tidal estuarine site, these investigators observed a positive relationship between C_b for the polychaete *Neanthes arenaceodentata* and $C_{free} * K_{ow}$ for sediment-associated PCBs, with a slope of 0.68. The impact of spatial placement of the sampler to represent bioaccumulation can also be detected with PSMs. A difference between *in situ* and *ex situ* uptake into passive sampling devices and biota for POM samplers was found to depend on the sediment depth represented by the experimental design. Samplers deployed in the top 0.5 cm *in situ* correlated with *in situ* bioaccumulation data for *Neanthes arenaceodentata*, but were not as well correlated to laboratory bioaccumulation, because the samples used in the laboratory exposures represented an integrated depth sample (Janssen et al., 2011).

Attainment of equilibrium by passive samplers and biological processes are two major considerations for interpreting similarities and differences among empirical relationships reported between $\log C_b$ (ng/g lipid) vs. $\log C_{free}$. In particular, the slope of log–log regression equations can indicate the degree of equilibrium achieved by the passive sampler relative to the model organism. Slopes of unity indicate parity in uptake efficiency between the sampler and tissue. If the model HOC is readily biotransformed but comparatively persistent in abiotic matrices, the slope can be expected to be less than unity (Vinturella et al., 2004). Likewise, if attainment of equilibrium by the passive sampler is slower than for the organism, a slope of less than one would result (You et al., 2011; Thomas et al., 2014). Clearly, achievement of equilibrium (or nearly so) in both compartments simplifies the interpretation of log–linear relationships, and thus maximizes their utility to predict bioaccumulation across scenarios (Ghosh et al., 2014). This is demonstrated in the spiked sediment lab exposures in the present study (Figs. 2 and S2). When equilibrium is not sufficiently achieved, such relationships are limited to case- or scenario-specific applications (e.g. Fig. 4). Performance reference compounds (PRCs) pre-loaded into passive samplers prior to exposure have been proposed as a remedy to correct for non-equilibrium, however, this practice adds complexity and cost (Ghosh et al., 2014). Depletion of freely dissolved HOCs by a passive sampler with excess sorptive mass relative to sediment TOC can also alter the kinetics of exchange resulting in an underestimation of C_{free}. In our sediment experiments, the ratio of sorbent to TOC mass (<1 μg PDMS; >1 g TOC) was kept well below 1%, the threshold considered acceptable for maintaining negligible depletion conditions (Ghosh et al., 2014).

The results presented herein add strong evidence that C_{free} deduced from SPME equilibrated with sediment contaminated with HOCs can serve as a proxy for bioaccumulation by benthic invertebrates. Moreover, C_{free} deduced from SPME samplers has been used to derive toxicity benchmarks for other HOCs, such as pyrethroid pesticides (Harwood et al., 2013). Ideally, applications where equilibrium among the passive sampler (i.e. SPME), sediment and the organism of interest are readily achieved can best utilize 1:1 log–log relationships that predict body residues from

C_{free}. Such applications include well-mixed and/or readily bioavailable HOCs in sediments. For scenarios where equilibrium is not as easily attainable, e.g. fine grained sediment under static conditions *in situ*, site-specific characterization using carefully standardized protocols (i.e. highly constrained in time and space) or correction for equilibrium is needed.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2015.07.042.

References

Arthur, C.L., Pawliszyn, J., 1990. Solid-phase microextraction with thermal desorption using fused silica optical fibers. Anal. Chem. 62, 2145–2148.

Barthe, M., Pelletier, E., Breedveld, G.D., Cornelissen, G., 2008. Passive samplers versus surfactant extraction for the evaluation of PAH availability in sediments with variable levels of contamination. Chemosphere 71, 1486–1493.

Beckingham, B., Ghosh, U., 2013. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. Chemosphere 91, 1401–1407.

Bielska, L., Smidova, K., Hofman, J., 2014. Solid phase microextraction of organic pollutants from natural and artificial soils and comparison with bioaccumulation in earthworms. Ecotoxicol. Environ. Saf. 100, 44–52.

Bucheli, R.D., Gustafsson, O., 2001. Ubiquitous observations of enhanced solid affinities for aromatic organochlorines in field situations: are *in situ* dissolved exposures overestimated by existing partitioning models? Environ. Toxicol. Chem. 20, 1450–1456.

Doig, L., Liber, K., 2004. Dialysis minipeeper for measuring pore-water metal concentrations in laboratory sediment toxicity and bioavailability. Environ. Toxicol. Chem. 19, 2882–2889.

Fernandez, L., Lao, W., Maruya, K., White, C., Burgess, R.M., 2012. Passive sampling to measure baseline dissolved persistent organic pollutant concentrations in the water column of the Palos Verdes Shelf Superfund site. Environ. Sci. Technol. 46, 11937–11947.

Ghosh, U., Kane Driscoll, S., Burgess, R.M., Jonker, M.T.O., Reible, D., Gobas, F., Choi, Y., Apitz, S., Maruya, K.A., Gala, W.R., Mortimer, M., Beegan, C., 2014. Passive sampling methods for contaminated sediments: practical guidance for selection, calibration and implementation. Integr. Environ. Assess. Manage. 10, 210–223.

Grigg, N.J., Webster, I.T., Ford, P.W., 1999. Pore-water convection induced by peeper emplacement in saline sediment. Limnol. Oceanogr. 44, 425–430.

Gustafsson, O., Gschwend, P.M., 1997. Soot as a strong partitioning medium for polycyclic aromatic hydrocarbons in aquatic systems. In: Eganhouse, R.P. (Ed.), Molecular Markers in Environmental Geochemistry. American Chemical Society, Washington, DC, USA, pp. 365–381.

Harwood, A.D., Landrum, P.F., Lydy, M.J., 2013. Bioavailability-based toxicity endpoints of bifenthrin for *Hyalella azteca* and *Chironomus dilutus*. Chemosphere 90, 1117–1122.

Hawthorne, S.B., Grabanski, C.B., Miller, D.J., Kreitinger, J.P., 2005. Solid phase microextraction measurement of parent and alky polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of Kdoc values. Environ. Sci. Technol. 39, 2796–2803.

Hawthorne, S.B., Azzolina, N.A., Neuhauser, E.F., Kreitinger, J.P., 2007. Predicting bioavailability of sediment polycyclic aromatic hydrocarbons to *Hyalella azteca* using equilibrium partitioning, supercritical fluid extraction, and pore water concentrations. Environ. Sci. Technol. 41, 6297–6304.

Hawthorne, S.B., Miller, D.J., Grabanski, C.B., 2009. Measuring low pictogram per liter concentrations of freely-dissolved polychlorinated biphenyls in sediment pore water using passive sampling with polyoxymethylene. Anal. Chem. 81, 9472–9480.

Janssen, E.M.L., Oen, A.M.P., Luoma, S.N., Luthy, R.G., 2011. Assessment of field-related influences on polychlorinated biphenyl exposures and sorbent amendment using polychaete bioassays and passive sampler measurements. Environ. Toxicol. Chem. 30, 173–180.

Johnson, L.L., Collier, T.K., Stein, J.E., 2002. An analysis in support of sediment quality thresholds for polycyclic aromatic hydrocarbons (PAHs) to protect estuarine fish. Aquat. Conserv. – Mar. Freshwater Ecosyst. 12, 517–538.

Jonker, M.T.O., Koelmans, A.A., 2001. Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. Environ. Sci. Technol. 35, 3742–3748.

Jonker, M.T.O., Hoenderboom, A.M., Koelmans, A.A., 2004. Effects of sedimentary sootlike materials on bioaccumulation and sorption of polychlorinated biphenyls. Environ. Toxicol. Chem. 23, 2563–2570.

Karickhoff, S.W., Brown, D.S., Scott, T.A., 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13, 241–248.

King, A.J., Readman, J.W., Zhou, J.L., 2004. Determination of polycyclic aromatic hydrocarbons in water by solid-phase microextraction-gas chromatography–mass spectrometry. Anal. Chim. Acta 523, 259–267.

Kraaij, R., Mayer, P., Busser, F.J.M., van Het Bolscher, M., Seinen, W., Tolls, J., Belfroid, A., 2003. Measured pore-water concentrations make equilibrium partitioning work – a data analysis. Environ. Sci. Technol. 37, 268–274.

Lu, X., Drake, B., Skwarski, A., Reible, D., 2011. Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. Environ. Toxicol. Chem. 30, 1109–1116.

Lydy, M.J., Landrum, P.F., Oen, A.M.P., Allinson, M., Smedes, F., Harwood, A.D., Li, H., Maruya, K.A., Liu, J., 2014. Passive sampling methods for contaminated sediments: state of the science for organic contaminants. Integr. Environ. Assess. Manage. 10, 167–178.

Maruya, K.A., Risebrough, R.W., Horne, A.J., 1997. The bioaccumulation of polynuclear aromatic hydrocarbons by benthic invertebrates in an intertidal marsh. Environ. Toxicol. Chem. 16, 1087–1097.

Maruya, K.A., Zeng, E.Y., Tsukada, D., Bay, S.M., 2009. A passive sampler based on solid phase microextraction (SPME) for quantifying hydrophobic organic contaminants in sediment porewater. Environ. Toxicol. Chem. 28, 733–740.

McGroddy, S.E., Farrington, J.W., 1995. Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts. Environ. Sci. Technol. 29, 1542–1550.

Means, J.C., Wijayaratne, R., 1982. The role of colloids in the transport of hydrophobic pollutants. Science 215, 968–970.

Muijs, B., Jonker, M.T.O., 2012. Does equilibrium passive sampling reflect actual *in situ* bioaccumulation of PAHs and petroleum hydrocarbon mixtures in aquatic worms? Environ. Sci. Technol. 46, 937–944.

Parkerton, T.F., Stone, M.A., Letinski, D.J., 2000. Assessing the aquatic toxicity of complex hydrocarbon mixtures using solid phase microextraction. Toxicol. Lett. 112, 273–282.

Parkerton, T.F., Maruya, K.A., 2014. Passive sampling methods for contaminated sediments: building consensus to improve decision-making. Integr. Environ. Assess. Manage. 10, 163–166.

Rust, A.J., Burgess, R.M., Brownawell, B.J., McElroy, A.E., 2009. Relationship between metabolism and bioaccumulation of benzo[*a*]pyrene in benthic invertebrates. Environ. Toxicol. Chem. 23, 2587–2593.

Thomas, C., Lampert, D., Reible, D., Janssen, E., Luthy, R.G., 2014. Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. Environ. Sci: Process. Impacts 16, 445–452.

Van der Heijden, S.A., Jonker, M.T.O., 2009. PAH bioavailability in field sediments: comparing different methods for predicting *in situ* bioaccumulation. Environ. Sci. Technol. 43, 3757–3763.

Vinturella, A.E., Burgess, R.M., Coull, B.A., Thompson, K.M., Shine, J.P., 2004. The use of passive samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polychaetes. Environ. Sci. Technol. 38, 1154–1160.

You, J., Landrum, P.F., Lydy, M.J., 2006. Comparison of chemical approaches for assessing bioavailability of sediment-associated contaminants. Environ. Sci. Technol. 40, 6348–6353.

You, J., Harwood, A.D., Li, H., Lydy, M.J., 2011. Chemical techniques for assessing bioavailability of sediment-associated contaminants: SPME versus Tenax extraction. J. Environ. Monit. 13, 792–800.

Zeng, E.Y., Tsukada, D., Diehl, D.W., 2004. Development of a solid-phase microextraction-based method for sampling of persistent chlorinated hydrocarbons in an urbanized coastal environment. Environ. Sci. Technol. 38, 5737–5743.