Correlation between SPME-measured sediment porewater and benthic invertebrate concentrations of hydrophobic organic contaminants (HOCs)

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Abstract -- The quality of sediments can profoundly affect the beneficial uses of waterways subject to anthropogenic contamination. To assess the bioavailability of sediment-associated hydrophobic organic contaminants (HOCs), we previously developed a compact in situ passive sampler that employs solid phase microextraction (SPME). In this study, we co-exposed *Macoma nasuta* and *Nereis virens* and SPME samplers to spiked estuarine and field-collected sediments for 28 d. HOCs of regulatory concern were analyzed by GC-ECD and GC-MS in SPME fibers, invertebrate tissues and bulk sediment. A 1:1 relationship was observed between freely dissolved porewater (SPME) and body burdens of target organochlorines and PAH spiked into test sediment. For field-collected sediments, SPME was correlated with bulk sediment concentration and with body burdens of selected PAH. Although promising, additional testing is needed to fully characterize the potential of this approach for quantifying the bioavailable fraction of sediment-associated HOCs.

BACKGROUND

The accumulation of hydrophobic organic chemicals (HOCs) in estuarine sediments poses a risk to the health of coastal marine ecosystems. Sediment associated PAH, PCBs, DDTs and chlordanes are currently listed by regulatory agencies as causes for impairment in contaminated waterbodies. However, efforts to assess sediment quality in impaired systems are frequently hampered by non-concordance among bulk sediment chemistry, toxicity and in situ benthic condition [1]. Passive in situ methods for determining freely dissolved HOCs, e.g. solid phase microextraction (SPME), offer clear advantages over traditional ex situ techniques. Previously, we developed a compact, SPME sampler for in situ quantification of freely dissolved HOCs in sediment porewater [2]. The objective of this study was to compare our sampler's measurements with invertebrate body burdens in laboratory exposures of spiked and field-collected sediments.

METHODS

Sampler design (Fig. 1)

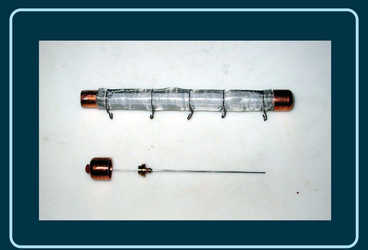


Fig. 1. SCCWRP's porewater sampler for HOCs (unassembled). (top) Copper housing with glass fiber filter and stainless steel mesh particle barrier; (bottom) SPME fiber (100 um PDMS) assembly attached to housing end cap.

Co-exposure of SPME samplers and benthic invertebrates

- 5 cm spiked or field collected sediment in glass aquaria (triplicates per treatment)
- 7- and 100um PDMS samplers co-exposed with *Macoma nasuta* & *Nereis virens* (5 ea.)
- 28 d test; 16:8 L/D cycle; water quality (temp; pH; DO; ammonia) per ASTM guidelines

Experiment #1 – Spiked estuarine sediments

- Newport Bay (CA) sediment spiked w/12 model HOCs (Table 1)
- Five spiked concentrations (5 to 5000 ng/g) + unspiked; rolled & aged for 60 d
- Static seawater renewal (50% water change every 3 d)

Table 1. Sampler method detection limits (MDLs) for target HOCs in sediment porewater.

Target HOC	C_{sat} (µg/L)	log K_{ow}	log $K_{f\text{-}100}$	MDL_{100} (ng/L)
phenanthrene (PHEN)	1200	4.46	3.90	2.1
fluoranthene (FLUA)	260	5.16	4.26	1.5
benzo[a]pyrene (BAP)	1.5	6.13	5.82	0.16
PCB-52	15	5.84	5.52	0.04
PCB-153	0.95	6.92	6.45	0.02
PCB-180	0.37	7.36	6.54	0.02
heptachlor epoxide	280	4.98	4.48	1.3
α–chlordane (α-CHL)	56	6.22	5.37	0.18
Trans-nonachlor (*t*-NON)	32	6.35	5.68	0.09
p,p'-DDE	1.3	6.96	6.17	0.02
p,p'-DDD	160	6.22	6.11	0.02
p,p'-DDT	3.1	6.91	5.76	0.13

Experiment #2 – Field-collected estuarine and marine sediments

- Five contaminated & one reference sediment from the SoCal coast (Table 2)
- Flow through (4 mL/min); 15 ± 1°C; 33 ± 2 ppt salinity 16:8 light/dark cycle
- Expanded list of target HOCs (PAH; organochlorines; pyrethroids/fipronil)
- Black carbon (BC) estimated using previously published methods

Table 2. Total HOC concentrations (ng/g dry) for field-collected test sediments (Experiment #2).

Station ID	Location	TOC (%)	BC (%)	%MORT	ΣPAH	ΣDDT	ΣCHL
5012	Dominguez Ch.	4.9	0.48	92	6300	120	<10
5108	Dominguez Ch.	3.1	0.74	54	4400	84	24
NS-24	San Diego Bay	1.6	0.37	40	5800	4.8	<10
NS-11	San Diego Bay	1.8	0.36	21	7200	4.1	<10
4370	LA/LB Harbor	1.0	0.19	15	390	51	<10
OCR	San Pedro Shelf	0.2	0.03	na	26	2.5	<10

BC = black carbon; ΣCHL = total chlordane
%MORT = percent mortality (96 h amphipod test)

Analytical and QA/QC

- Bulk sediment, depurated tissue by ASE, silica/alumina cleanup
- Sequential CH_2Cl_2 extraction of porewater isolated by centrifugation ("LLE")
- GC-ECD (HP5890) or GC-MS analysis (Varian Saturn 2000, SIS mode)
- Performance-based QA/QC including analysis of blanks, matrix spikes, SRM

RESULTS & DISCUSSION

Experiment#1 – Spiked sediments

Both *M. nasuta* and *N. virens* accumulated all 12 target HOCs spiked into test sediment in proportion to the spiked concentration, with good precision within treatments (Fig. 2).

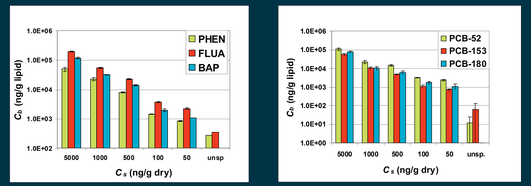
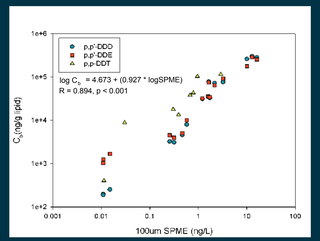


Fig. 2. Tissue concentrations of target PAH (left) and PCBs (right) spiked into estuarine sediment (Experiment#1). See Table 1 for compound abbreviations.

Lipid-normalized tissue concentration (C_b) for both test species was positively associated with freely dissolved porewater concentration (SPME) (Fig. 3).

The high degree of correlation for DDTs and chlordanes (R > 0.89) indicates that our SPME sampler is an excellent predictor of HOC body burdens. Moreover, the regression slopes (0.927 to 1.07) suggest a 1:1 relationship between body burden and SPME (Fig. 3). Similar results were observed for target PAH and PCBs (Table 1).



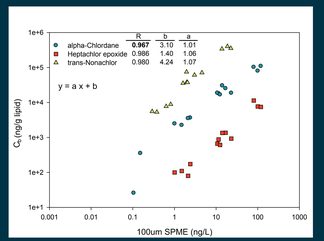
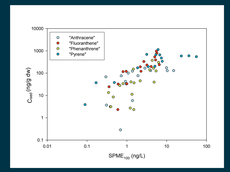


Fig. 3. Lipid-normalized tissue concentration (log C_b) was highly correlated with freely dissolved porewater concentrations (log SPME) for DDTs in *M. nasuta* (left) and chlordanes in *N. virens* (right) in spiked sediment exposures (Experiment#1).

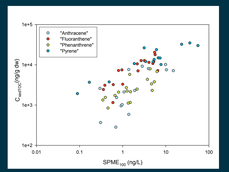
Experiment#2 – Field collected sediments

Test sediments were expected to exhibit differential HOC bioavailability based on previous work [3]. BC (a known HOC sequestrant) varied by a factor of 4 whereas HOC levels varied by as much as 140 (Table 2). "OCR" sediment was included as a reference sample.

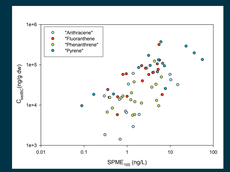
Dry wt., TOC and BC-normalized sediment PAH concentrations were correlated with freely dissolved porewater (SPME) concentrations (Fig. 4). TOC and BC normalization did not improve the correlation between bulk sediment and SPME measurements.



	n	R^2	b	a	P
Anthracene	15	0.27	1.44	0.77	0.046
Fluoranthene	17	0.74	1.62	1.47	<0.001
Phenanthrene	18	0.5	1.26	1.19	0.001
Pyrene	15	0.74	1.94	0.73	<0.001
Σ$_p$PAH	65	0.52	1.55	1.01	<0.001



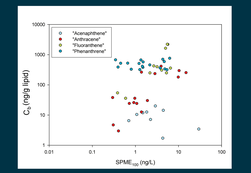
	n	R^2	b	a	P
Anthracene	15	0.53	3.19	0.74	0.002
Fluoranthene	17	0.69	3.67	0.64	<0.001
Phenanthrene	18	0.52	3.28	0.49	<0.001
Pyrene	15	0.85	3.84	0.44	<0.001
Σ$_p$PAH	65	0.52	3.46	0.63	<0.001



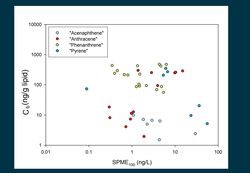
	n	R^2	b	a	P
Anthracene	15	0.37	4.01	0.68	0.016
Fluoranthene	17	0.44	4.47	0.65	0.004
Phenanthrene	18	0.25	4.12	0.43	0.036
Pyrene	15	0.62	4.62	0.47	<0.001
Σ$_p$PAH	65	0.41	4.28	0.62	<0.001

Fig. 4. Log SPME was correlated with bulk sediment concentration (log C_{sed}) on a dry wt basis (left); normalized to TOC (middle) and black carbon (BC) (right) for PAH in field-collected sediments (Experiment #2).

Lipid-normalized tissue concentration (C_b) for both test species was positively associated with SPME for some but not all PAH (Fig. 5). Biotransformation [4] may affect accumulation of selected PAH by benthic invertebrates, including polychaetes like *Nereis* spp. The 28 d exposure period may also be insufficient to achieve equilibrium for the more hydrophobic HOCs [5].



	n	R2	b	a	P
Acenaphthene	9	0.17	1.02	-0.29	0.27
Anthracene	12	0.6	2.00	0.88	0.003
Fluoranthene	11	0.68	2.03	1.17	0.002
Phenanthrene	18	0.00001	2.67	-0.001	0.99
Σ$_p$PAH	50	0.021	2.15	0.25	0.32



	n	R2	b	a	P
Acenaphthene	7	0.45	0.91	-0.42	0.098
Anthracene	13	0.50	1.27	1.03	0.007
Phenanthrene	17	0.050	2.30	-0.18	0.39
Pyrene	7	0.23	2.06	-0.38	0.27
Σ$_p$PAH	44	0.0068	1.76	-0.11	0.59

Fig. 5. Log C_b was correlated with log SPME for some but not all PAH in *M. nasuta* (left) and *N. virens* (right) exposed for 28 d in field-collected sediments (Experiment#2).

SUMMARY & CONCLUSIONS

Invertebrate body burdens were highly correlated with SPME measurements of freely dissolved levels in sediment porewater for 12 model HOCs in spiked sediment exposures

The slopes of log-log regressions of C_b vs. SPME were near unity, indicating a 1:1 relationship between SPME and body burdens

SPME measurements were correlated with bulk sediment concentrations for PAH in unamended, field-collected samples; TOC and BC normalization, however, did not improve these correlations

Correlation between C_b and SPME were variable for PAH in unamended, field-collected samples, perhaps due to non-attainment of equilibrium and/or species-specific biotransformation. Results for organochlorines are pending.

Field trials are underway to determine if our sampler can quantify the in situ bioavailability of sediment-associated HOCs of regulatory concern.

Acknowledgements

This work was funded in part by the Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET). We also thank V. Raco-Rands for graphics support.

Literature cited

[1] Bay et al. 2007. Integ Environ Assess Mgmt 3, 491; [2] Maruya et al. Environ Toxicol Chem in press; [3] Bay et al. 2005. SCCWRP Tech. Rep. 451; [4] Varanasi et al. 1985. Environ Sci Technol 19, 836; [5] ter Laak et al. 2008. Anal Chem 80, 3859.