FINAL REPORT

Using Passive Polyethylene Samplers to Evaluate Chemical Activities Controlling Fluxes and Bioaccumulation of Organic Contaminants in Bed Sediments

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Massachusetts Institute of Technology

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Many sediment beds are contaminated by hydrophobic organic compounds (HOC) like PAH and PCB. Evaluating the hazard posed remains a difficult challenge. The HOC' presence must be measured in terms that reflect their availability to move to other locations (e.g., overlying waters), to receptors (e.g., shellfish and fish), and to microorganisms that might facilitate degradation. The objective of this project was to demonstrate the efficacy of using polyethylene (PE) strips to assess HOC in sediment beds. The method involves insertion of PE strips, pre-loaded with internal standards, across the bed-water interface at sites of concern, leaving the PE to absorb HOC, and then retrieving the samplers and measuring the HOC accumulated in the PE by solvent extraction and gas chromatographic-mass spectrometry. After using the internal standards to extrapolate observed HOC loads to their equilibrium levels, PE-water partition coefficients can be used to calculate contaminant pore water concentrations (or chemical activities) as a function of depth into the bed. Independent measures of such pore water concentrations showed good correspondence with the PE-inferred results. Moreover, PE-inferred pore water concentrations of PAH at six intertidal field sites were consistent with levels needed to explain PAH tissue burdens in soft-shelled clams living at those locations. Given the relative ease of the PE passive sampling method, these results strongly support the conclusion that future efforts to assess the risks posed by organic contaminants in sediments can be effectively determined using PE passive samplers.

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Many sediments are contaminated by hydrophobic organic compounds (HOCs) like PAHs and PCBs. The objective of this project was to demonstrate the efficacy of using polyethylene (PE) strips to assess HOCs in such sediment beds. The method involves insertion of PE, loaded with internal standards, into sediment at sites of concern, leaving the PE to absorb HOCs, and then retrieving the strips and measuring the HOCs accumulated in the PE. After using the internal standards to extrapolate observed HOC loads to their equilibrium levels, PE-water partition coefficients are used to calculate pore water concentrations. Independent measures of such pore water concentrations showed good correspondence with the PE-infered results. Moreover, PE-infered pore water concentrations of PAHs at six intertidal field sites were consistent with levels needed to explain PAH tissue burdens in soft-shelled clams living at those locations. The results support the conclusion that future efforts to assess the risks posed by organic contaminants in sediments can be effectively determined using PE passive samplers.

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List of Acronyms, Abbreviations, and Symbols

ASE	accelerated solvent extraction
BSAF	biota-sediment accumulation factors
D_{PE}	diffusivities of PAH within PE
$C_{sediment}$	chemical concentration in sediment
C_w	chemical concentration in water
DB	Dorchester Bay
EqP	equilibrium partitioning
f_{bc}	fraction black carbon
f_{lipid}	fraction lipid
f_{oc}	fraction organic carbon
$f_{protein}$	fraction protein
GCMS	Gas Chromatography-Mass Spectrometry
HP	Hunter's Point
HOC	hydrophobic organic compounds
IE	Island End
$K_{clam\text{-}w}$	clam-water partition coefficient
$K_{lip\text{-}oc}$	lipid-organic carbon partition constants
$K_{lipid\text{-}w}$	lipid-water partition coefficient
$K_{protein\text{-}w}$	protein-water partition coefficient
K_{oc}	organic carbon normalized sorption coefficient
K_{PEW}	polyethylene-water partition coefficients
K_d	solid-water or sorption coefficient
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PE	polyethylene
PRC	performance reference compounds
SRM	standard reference material
TOC	total organic carbon
V	molar volume

Keywords

passive sampling, polyethylene, sediments, pore water concentrations, PAH, PCB

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Using Passive Polyethylene (PE) Samplers to Evaluate Chemical Activities Controlling Fluxes and Bioaccumulation of Organic Contaminants in Bed Sediments

Abstract

Many sediment beds are contaminated by hydrophobic organic compounds (HOC) like PAH and PCB. Evaluating the hazard posed remains a difficult challenge. The HOC' presence must be measured in terms that reflect their availability to move to other locations (e.g., overlying waters), to receptors (e.g., shellfish and fish), and to microorganisms that might facilitate degradation.

The objective of this project was to demonstrate the efficacy of using polyethylene (PE) strips to assess HOC in sediment beds. The method involves insertion of PE strips, pre-loaded with internal standards, across the bed-water interface at sites of concern, leaving the PE to absorb HOC, and then retrieving the samplers and measuring the HOC accumulated in the PE by solvent extraction and gas chromatographic-mass spectrometry. After using the internal standards to extrapolate observed HOC loads to their equilibrium levels, PE-water partition coefficients can be used to calculate contaminant pore water concentrations (or chemical activities) as a function of depth into the bed. Independent measures of such pore water concentrations showed good correspondence with the PE-inferred results. Moreover, PE-inferred pore water concentrations of PAH at six intertidal field sites were consistent with levels needed to explain PAH tissue burdens in soft-shelled clams living at those locations. Given the relative ease of the PE passive sampling method, these results strongly support the conclusion that future efforts to assess the risks posed by organic contaminants in sediments can be effectively determined using PE passive samplers.

1. Objective

Our objective was to demonstrate the efficacy (accuracy and precision of results) of using PE strips to assess the hazard posed by organic pollutants such as polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in sediment beds.

2. Background

Many sediment beds in the United States are highly contaminated by HOC. HOC such as PAH and PCB are persistent and tend to bioaccumulate. Some of these compounds are mutagens and/or carcinogens, and all of them contribute to disruption of membrane functions (e.g., DiToro et al., 2000a and b). HOC-contaminated sediments may cause long-term pollution of their surroundings (Larsson, 1985; Salomons et al., 1987; Burgess and Scott, 1992; Ko and Baker, 1995; Achman et al., 1996; Latimer et al., 1999; Mitra et al., 1999; Schneider et al., 2002). Currently, assessment of the extent of contamination requires expensive sediment sampling and analyses, often yielding uncertain information regarding the degree of hazard and the spatial extent of the problem. Subsequent remediation commonly involves costly dredging of the hazardous solids and may unnecessarily expend funds on clean materials since it is currently hard to know the depth and boundaries of the truly hazardous bed.

Much of the problem of assessing these hazards derives from conceptual issues. In an effort to manage such contaminated solids, regulators try to set permissible concentrations for solid-associated HOC. These concentrations are chosen in an effort maintain HOC mobility to overlying waters and dose to benthic faunal at acceptable levels. Currently, this evaluation is performed by assuming equilibrium partitioning (EqP) of HOC among the solid phases, pore water, and benthic organisms. Moreover, such partitioning estimates are made assuming that only HOC absorption into the natural organic matter of the sediments and HOC accumulation in the lipids of the organisms are important. Such EqP modeling has recently been used to set sediment quality benchmarks for the protection of benthic organisms living in sediments that contain PAH (Hansen et al., 2003).

However, this form of EqP modeling has been found to be very inaccurate for estimating HOC mobility and bioavailability at many sites and for many HOC. If EqP were accurate, then biota-sediment accumulation factors (BSAF) should match the corresponding lipid-organic carbon partition constants, $K_{lip\text{-}oc}$ [$(mol_{HOC}/L_{lipid})/(mol_{HOC}/kg_{oc})$]. But BSAF measured for a wide range of benthic infauna are commonly 1 to 2 orders of magnitude below this EqP expectation (e.g., Tracey and Hansen, 1996; Hellou et al., 2002: Kraaij et al., 2002). Likewise, PAH biodegradation observations demonstrate that these rates are not consistent with the assumption that sorption equilibria are maintained (e.g., Rijnaarts et al., 1990; Amellal et al., 2001; Guthrie-Nichols et al., 2003).

These results suggest one of the following problems. First, estimates of solid-water partition coefficients, K_d values, based on the $f_{oc}K_{oc}$ model, underestimate sorption of HOC in many real-world cases. Consequently, subsequent calculations that use such K_d values with measured HOC concentrations in sediments fail badly with respect to establishing sedimentary HOC chemical activities (or fugacities), the parameter that actually drives contaminant mobility and bioaccumulation. We now know that the sediments include very important reduced carbon sorbents such as soots, biomass chars, and coal residues, and these components of the "f_{oc}" must

be specifically treated to estimate K_d values accurately (e.g., Gustafsson et al., 1997; Ghosh et al., 2000, 2001, 2003; Accardi-Dey and Gschwend, 2002, 2003; Lohmann et al., 2005.)

Secondly, it is likely that HOC desorption kinetics, which involve diffusive mass transfers on sub-millimeter scales, may limit mobility/bioavailability of HOC and cause the assumption of phase equilibration in EqP to be wrong (e.g., McGroddy and Farrington, 1995). This appears true for surface sediments even after efforts to use a soot-corrected K_d values (Accardi-Dey and Gschwend, 2003). Time scales of such transfers appear to involve days to months, while fluid-solid and biota-solid contacts can be are commonly of much shorter duration.

Finally, it is clear that benthic animals do not simply exchange HOC with the bed sediments, as they may also interact with suspended solids via feeding and the overlying water column via respiration (e.g., Lohmann et al., 2004). Hence, a more holistic view of bioaccumulation requires treatment of all HOC exchanges between the animal and all the subsystems (e.g., bed sediment, water column) of a particular ecosystem to which a given organism is exposed.

Besides these conceptual difficulties, it is hard to evaluate a region of suspect sediments because the chemical contamination is heterogeneous and the physical extent of the problem is poorly constrained. This information limitation derives, in large part, from the difficulty and expense of measuring the relevant contamination in sufficient detail. Composite sediment samples are frequently used to save money spent on chemical analyses, thus losing information on the spatial extent of contamination. Also, relatively few samples are obtained since subsequent analyses are time-consuming and expensive. Finally, sampling the bed is usually performed in a manner that does not allow straightforward comparison with the overlying water quality regarding the same target HOC. Hence, ecosystem level understandings of sources and fluxes are not obtained. In recent work in Boston Harbor (Lohmann et al., 2004), we found evidence that the bed sediments may still be the primary source of PAH to infauna such as *Mya arenaria*, but the overlying water column may now be the source of PCB to these same clams! Clearly, our efforts need to be directed to cleaning up ecosystems, and not just the media that we suspect are the dominant contamination sources.

These conceptual and practical problems must be addressed if we ever hope to improve our risk-based assessments of the need to clean up contaminated sediment beds. Hence, it was the objective of this research to develop a passive sampler methodology, suited to sampling organic contaminants across bed-water interfaces and down into the sediment bed. The methodology must yield data that are more readily applicable to assessing contaminant mobility and bioavailability than current procedures based on sediment concentrations. Further, the procedures should be cost-effective, enable an expansion of the data sets we can acquire, and be useful for making risk assessments and clean up decisions. This report shows that passive samplers made from PE strips are able to satisfy these data needs.

3. Materials and Methods

3.1 Low Density Polyethylene (PE) Preparation and Testing.

Polyethylene strips were prepared from 1-mil (25.4 um), low-density polyethylene (PE) sheet purchased from local hardware stores. The PE was cleaned by sequentially soaking twice in

dichloromethane for 24 hr, twice in methanol for 24 hr, and then twice in water for 24 hr. The PE was then placed in water containing performance reference compounds (PRC, deuterated and ^{13}C-labeled forms of the PAH and PCB of interest) and equilibrated for 6 mo in order to achieve an initially even distribution of PRC throughout the PE thickness.

In order to deploy such PE strips in the field, an aluminum frame was designed to support and expose the PE strips on both sides (Figure 1). The frame consisted of two "C shaped" pieces cut from aluminum sheet. The PE strip(s) could be stretched across the frame. Further, the frame was constructed so it could be mounted on a platform for deployment from a boat (Figure 1).

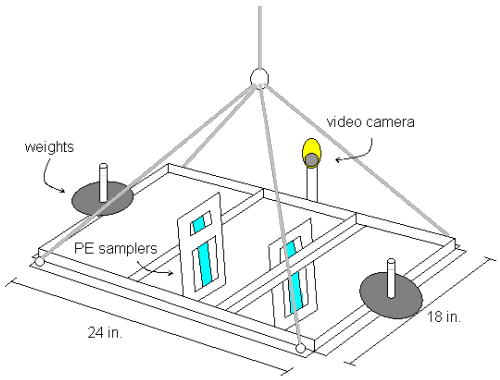

Figure 1. PE sampler (a) shown schematically in an aluminum frame, (b) pictured in a frame that is held by a paint roller on the end of an extendable paint pole for deployment in shallow water from a boat, and (c) mounted on the cross members of a rectangular vehicle with rope attachments to enable lowering into deeper waters from a boat.

To enable PE concentrations to be used to infer equilibrated water concentrations, K_{PEW} (21 ^{o}C) values were measured for 13 parent and alkylated PAH and 16 PCB (Table 1). A K_{PEW} (L_W/kg_{PE}) value for each compound was calculated from one to five water measurements and four to six PE measurements. K_{PEW} values measured for two PE batches were the same within uncertainty. When all PAH and PCB were considered together, we found: log K_{PEW} = 0.96(±0.07)*log K_{ow} + 0.00 (±0.42), R^2 = 0.88.

Table 1. Logarithms of low density polyethylene-water partition coefficients, K_{PEW} (L_w/kg_{PE}) measured for polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB).

Compound	**log K_{PEW}**	**Compound**	**log K_{PEW}**
PAH		**PCB**	
phenanthrene	4.3 ± 0.1	2,2',5 trichloro biphenyl	4.9 ± 0.1
1-methyl phenanthrene	4.7 ± 0.1	2,4,4' trichloro biphenyl	5.4 ± 0.1
3,6-dimethyl phenanthrene	5.2 ± 0.1	2,2',5,5' tetrachloro biphenyl	5.5 ± 0.1
anthracene	4.3 ± 0.1	2,2',3,5 tetrachloro biphenyl	5.5 ± 0.1
2-methyl anthracene	5.0 ± 0.1	2,3',4,4' tetrachloro biphenyl	5.9 ± 0.1
9,10-dimethyl anthracene	5.3 ± 0.1	2,2',4,5,5' pentachloro biphenyl	6.2 ± 0.1
fluoranthene	4.9 ± 0.1	2,3,3',4',6 pentachloro biphenyl	6.1 ± 0.1
pyrene	4.7 ± 0.1	2,3',4,4',5 pentachloro biphenyl	6.4 ± 0.1
benz(a)anthracene	5.5 ± 0.1	2,3,3',4,4' pentachloro biphenyl	6.3 ± 0.1
chrysene	5.5 ± 0.1	2,2',4,4',5,5' hexachloro biphenyl	6.4 ± 0.1
benzo(b)fluoranthene	6.3 ± 0.1	2,2',3,4,4',5' hexachloro biphenyl	6.6 ± 0.1
benzo(k)fluoranthene	6.3 ± 0.1	2,2',3,3',4,5 hexachloro biphenyl	6.6 ± 0.1
benzo(a)pyrene	6.4 ± 0.1	2,2',3,3',4,4' hexachloro biphenyl	6.5 ± 0.1
		2,2',3,4',5,5',6 heptachloro biphenyl	7.1 ± 0.1
		2,2',3,4,4',5,5' heptachloro biphenyl	7.0 ± 0.1
		2,2',3,3',4,4',5 heptachloro biphenyl	6.9 ± 0.1

Diffusivities of PAH within PE were estimated using published diffusivity data for aromatic compounds (Saleem et al. 1989; Yeom and Huang 1992; Rusina et al. 2007). A log-linear relationship (Figure 2) was assumed between log D_{PE} and each compound's molar volume (Ruelle 2000) resulting in a relation:

$$\log D_{PE} = -0.026 \times V - 4.8 \qquad \text{where } D_{PE} \text{ is in cm}^2\text{/s and } V \text{ is in cm}^3\text{/mol.}$$

To perform laboratory testing of the PE samplers (Fernandez et al, 2009a), sediments were collected from two sites in Boston Harbor, the first near a former manufactured gas plant at Island End (IE), Chelsea, MA, and the second, from a relatively cleaner site at an active clamming bed near the mouth of the Neponset River in Dorchester Bay (DB). At each site, approximately 40 L of sediments were collected and homogenized in a large galvanized steel tub by mixing with a metal hoe for 1 hour. Sediments from a third site, Hunter's Point (HP), San Francisco Bay, were collected and homogenized by colleagues (D. Reible, D. Nakles & K.

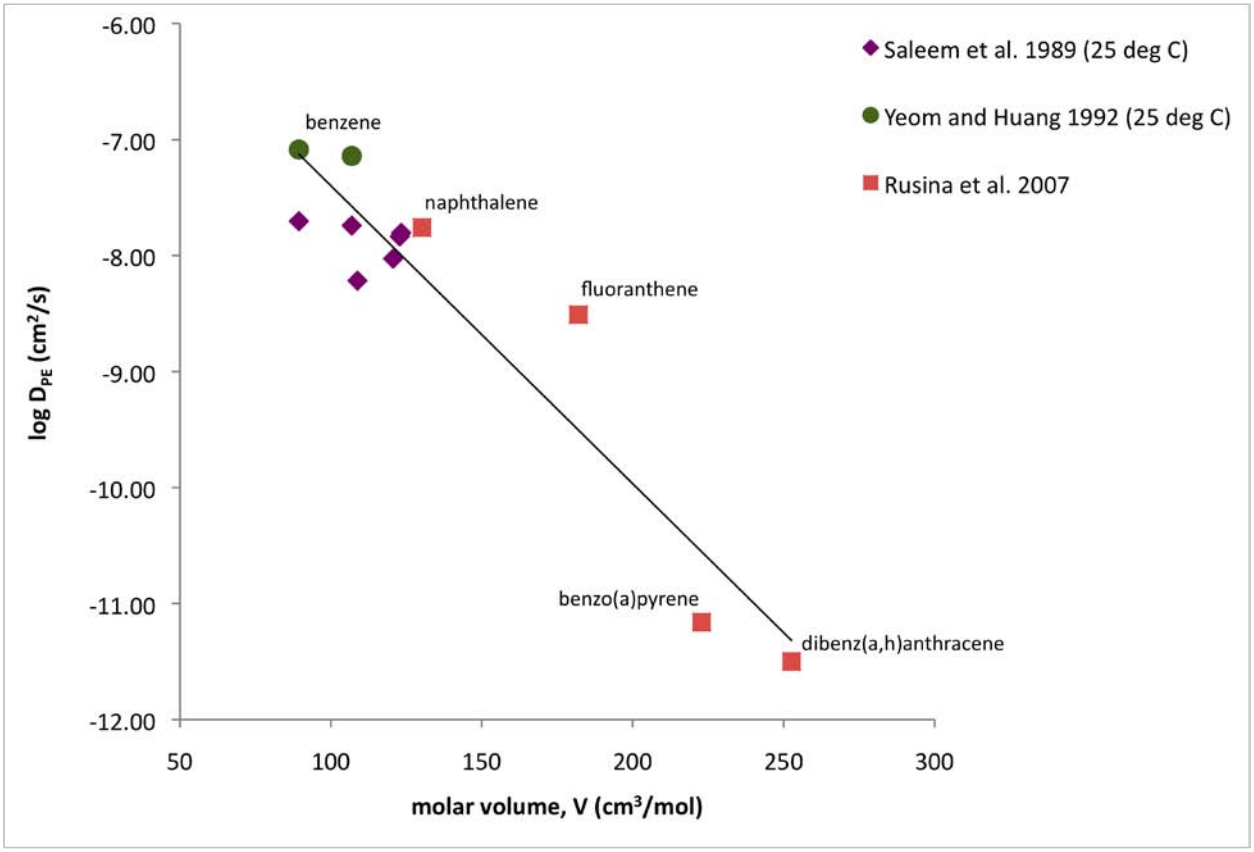

Figure 2. Published log D_{PE} values versus molar volumes (*1*) for ten aromatic compounds. The best-fit log-linear relationship, log D_{PE} = -0.026 × V − 4.8, was used to estimate D_{PE} for PAH in this study.

McDonough), and sent to us in jars on ice. Approximately 20 L of the homogenized sediments were transferred to cylindrical, seamless, glass tanks and covered with approximately 8 cm water collected at the site of sediment collection. Sediments and water were allowed to sit undisturbed in the laboratory tanks for 1 to 2 weeks before PE strips were inserted using long stainless steel forceps. Samplers were removed from the IE sediments after 3 days and from DB and HP sediments after 7 days. Upon removal from sediments, PE strips were rinsed in clean water. PE strips used in the Island End sediments were swabbed with a hexane-soaked wipe to remove any coal tar residues adhering to the PE surface. Strips were then cut into approximately 2 cm sections, surrogate standards were added, and then they were extracted by soaking in 15 mL of dichloromethane overnight. The extracts were concentrated to approximately 1 mL under a gentle stream of ultra pure grade nitrogen. Internal standards were added to the extracts before gas chromatography-mass spectrometry (GCMS) analysis. GCMS was done using a JEOL GCmate instrument (JEOL Ltd., Tokyo, Japan). Splitless 1-µL injections were made onto a 30 m J&W Scientific HP-5MS capillary column (0.25 mm internal diameter with a 0.25 µm film thickness). The injection port temperature was held at 305ºC. The initial column temperature of 70ºC was raised at 20ºC/min until a temperature of 180ºC was reached, and then the temperature was raised 6ºC/min until a temperature of 300ºC was reached, and remained there for 7.5 min. The MS was operated in selected ion monitoring (SIM) and EI+ modes. Calibration standards

containing at least 25 aromatic compounds including each of the PRC, target compounds, surrogate and injection standards used in this study, were run every 3 to 5 sample measurements to monitor instrument stability, determine response factors, and confirm that measurements remained in the linear range for the instrument. Repeated observations using the calibration standard indicated the measurement uncertainty for the instrument was typically ±10% relative error. For PE samples, percent recoveries for the surrogate standards (± 1 RSD) were 77 ±15% to 82 ±13%.

As passive sampling incubations of the PE strips in the sediment were typically insufficient to achieve equilibration, the losses of the PRC were used to estimate the degree of equilibration of structurally similar target compounds (Fernandez et al., 2009a). When other target compounds were assessed in the same compound class, a diffusive mass transfer model (see below and Fernandez et al., 2009b) was tuned with PRC data and then employed to extrapolate measured PE concentrations of other target PAH to expected equilibrated loads. Finally, pore water concentrations were deduced using this extrapolated equilibrium estimate and the relation, $C_w = C_{polyethylene} / K_{PEW}$.

3.2 Pore Water Analyses and Corrections for Colloids

In order to evaluate the accuracy of the PE-inferred pore water concentrations, direct measures of pore water concentrations were made. To this end, sediments were centrifuged (30 to 60 min at 900*g*) to compact the sediment solids. Supernatants were removed, and they were run through a glass column containing glass wool if necessary to remove globules of tar and "floatable" particles before pore water extractions. Pore water samples were extracted in a separatory funnel after adding surrogate standards (d10-anthracene, d12-fluoranthene, and d12-benz(a)anthracene in acetone) before the first extraction. The combined extracts were dried using anhydrous sodium sulfate and reduced to approximately 1 mL using a rotary evaporator and to smaller volumes (~100 to 200 µL) under a gentle steam of N_2. Finally, internal standards (d10-acenaphthene, *m*-terphenyl, and d12-perylene in dichloromethane) were added to the extracts before final analyses. All extracts were analyzed using GCMS as described above. Percent recoveries for the surrogate standards (± 1 RSD) were 57 ±16% to 74 ±11% for pore water samples.

Total organic carbon (TOC) concentrations in the water samples were measured using a Shimadzu TOC 5000 analyzer (Shimadzu Scientific Instruments, Colombia, MD). Samples were acidified with phosphoric acid (Phosphoric Acid GR, EM Science, Gibbstown, NJ) to a pH of 2 and sparged with TOC grade air (Airgas, Radnor, PA) until TOC measurements stabilized. Dissolved PAH concentrations, C_w, were calculated from the values measured in raw pore waters, C_{tot}, by correcting for sorption to colloidal organic matter, estimated using the TOC data: $C_w = C_{tot}/(1+[TOC]\ K_{oc})$ where C_w is the TOC-corrected pore water concentration, [TOC] is the concentration of organic carbon in the water (kg/L), and K_{oc} is the organic carbon-water partition coefficient (L/kg). In this work, we used K_{oc} values reported by Karickhoff (1981) and assigned an uncertainty of a factor of three on those values to reflect our uncertainty regarding the type of material making up our measured TOC. In order to check the appropriateness of using Karickhoff's K_{oc} values for pore water colloids, a fluorescence quenching experiment was

performed to test pyrene sorption to the pore water colloids (Fernandez et al., 2009a). The K_{oc} that we needed to fit the quenching data matched the Karickhoff value for pyrene within 3%.

3.3 Air Bridge Testing

Air bridges (Figure 3) were assembled using 2L glass desiccators with ground glass lids (scrupulously cleaned to remove any sealant grease). Each system contained a 250-mL glass beaker containing ~200 mL of sediment slurry (15-25 g wet sediment in 0.4 M sodium chloride solution and a glass covered stir bar) surrounded by 1100 mL of "clean" water (0.4 M sodium chloride and 10 mM sodium azide solution). A stir plate, under the desiccator, motivated stirring in both the slurry and surrounding clean water. To maintain sediment anoxia (and thereby inhibit contaminant oxidation), the headspace in the 2L dessicator was flushed with argon for 20 min through the desiccator's vacuum outlet in the lid, after each water sample was taken. Samples (50 to 100 mL) of the outer "clean" water were analyzed at intervals until dissolved concentrations stabilized. Procedures of these water analyses were the same as described above for pore waters, except TOC measures were unnecessary.

Data for PAH and PCB showed "plateau" concentrations after about 1 month (Figure 4). Hence all data in this "plateau" were averaged to establish estimates of the pore water concentrations for each specific sediment sample tested in this way.

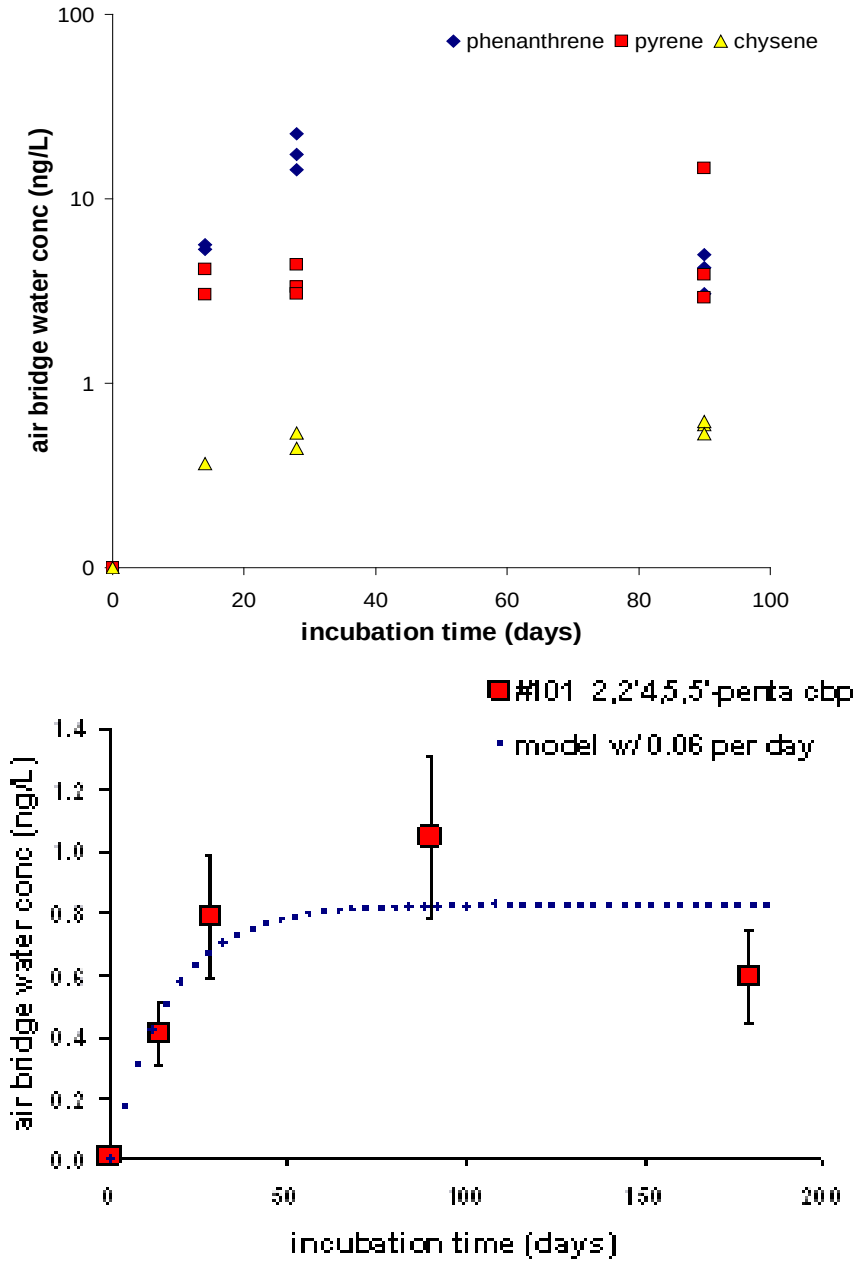

Figure 4. Example time courses of air bridge results showing build up of representative PAH (upper panel**), and a representative PCB, 2,2'4,5,5'-pentachlorobiphenyl (**lower panel**), in the initially pure water outside the sample-containing beaker. The PAH case involved use of the coal-tar-contaminated sediment from the Island End site in Boston Harbor, while the PCB case involved Hunter's Point sediment.**

3.4 Sediment Analyses and Equilibrium Partitioning (EqP) Estimates of Pore Water Concentrations

Dried sediment samples and surrogate standards were Soxhlet extracted for 24 hr using 450 mL of dichloromethane. Extracts were reduced to approximately 10 mL using the rotary evaporator. Injection standards were added to the final extract. GCMS analyses of these extracts were performed as described above. Percent recoveries for the surrogate standards (± 1 RSD) were 57 ±21% to 79 ±19% for sediment analyses. Target compound concentrations were corrected for recoveries of the corresponding closest-eluting surrogate standard.

Dried (60 ºC for 24 hr) and ground sediment sub-samples (~10 mg each) were analyzed for their mass fractions of organic carbon (f_{oc}) and black carbon (f_{bc}) using a CHN elemental analyzer (Vario EL III, Elementar, Hanau, Germany) using the methods of Gustafsson et al. (1997). The sediment concentration data, $C_{sediment}$, together with measure of the f_{oc} and f_{bc}, allowed estimates of the pore water concentrations as performed using the EqP model. Hence, one estimates the pore water concentration as:

$$C_w = C_{sediment} / f_{oc}*K_{oc}$$

Additionally, one may use a more complex sorption coefficient that attempts to reflect the role of black carbons as a sorbent (e.g., Accardi-Dey and Gschwend, 2002, 2003). In this case, one estimates the pore water concentration:

$$C_w = C_{sediment} / (f_{oc}*K_{oc} + f_{bc}*K_{bc}*C_w^{-0.3})$$

where the Freundlich coefficient has been assumed to be 0.7. This expression is solved iteratively since C_w appears on both sides.

3.5 Mass Transfer Modeling to Use a Few Performance Reference Compounds (PRC) for Assessing Many Target Contaminants

When PRC and target chemicals have different diffusivities and/or partitioning properties, a method for extrapolating PRC behavior to other compounds is required. Consequently, we developed a one-dimensional diffusion model of chemical exchange between a polymer sheet of finite thickness and an unmixed sediment bed (Fernandez et al., 2009b). Fickian diffusion in and out of a sheet of polymer film of finite thickness (=2l) embedded in an infinite thickness of sediment was modeled:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2}, \qquad -l < x < l \qquad (1)$$

$$\frac{\partial C_{SED}}{\partial t} = D_{SED}\frac{\partial^2 C_{SED}}{\partial x^2}, \qquad -\infty < x < -l \text{ and } l < x < \infty$$

where C_{PE} (mol/cm^3 PE) and C_{SED} (mol/cm^3 sediment) are concentrations in the polymer and sediment in units of mass per volume, respectively, D_{PE} (cm^2/s) is diffusivity within the polymer, D_{SED} (cm^2/s) is diffusivity within the porous sedimentary medium, 2l is the polymer thickness

(cm), and t is time (s). This formulation can be parameterized using molecular diffusivities and partition coefficients for both the sampler and sediment. At the interface of the polymer film and the sediment, the diffusive fluxes match so that mass is conserved:

$$D_{PE}\frac{dC_{PE}}{d\mathrm{x}} = D_{SED}\frac{dC_{SED}}{d\mathrm{x}}\ , \qquad \text{at x = } +l \text{ and x = } -l \tag{2}$$

and an equilibrium distribution is assumed at the contact boundary of the PE and the sediment:

$$C_{PE} = K_{PESED}\, C_{SED}, \qquad \text{at x = } l \text{ and x = } -l \tag{3}$$

where K_{PESED} is the polymer-sediment partition coefficient (cm^3 sediment/cm^3 PE). The remote boundary conditions are:

$$\frac{d\,C_{SED}}{d\,\mathrm{x}} = 0, \qquad \text{at x = } \infty \text{ and } -\infty \tag{4}$$

Concentrations of PRC are initially set to a uniform value in the polymer and zero in the sediment. The initial conditions for target chemicals are set to be zero concentrations in the polymer and uniform concentrations in the sediment.

The solution for this boundary value problem was found in the Laplace domain (Fernandez et al., 2009b). The Laplace-domain masses of target chemical accumulated in the polymer film and the PRC remaining in the film were found by integrating the chemical concentrations across the polymer film:

$$\overline{M}_{target} = \frac{M_{inf}\sqrt{\psi}}{s^{3/2}\left(K_{PESED} + \sqrt{\psi}\coth\left(\sqrt{s}\right)\right)} \tag{5}$$

$$\overline{M}_{PRC} = M_{init}\left(\frac{1}{s} - \frac{\overline{M}_{target}}{M_{inf}}\right) \tag{6}$$

where M_{inf} is the mass of the target in the film that would be in equilibrium with the sediment, and $M_{,init}$ is the initial mass of PRC in the film. The dimensionless Laplace parameter, s, is based on a dimensionless time variable:

$$T = \frac{t\,D_{PE}}{l^2} \tag{7}$$

This solution contains two dimensionless parameters: the ratio of diffusion coefficients, $\Psi = D_{SED}/D_{PE}$, and the polymer-sediment partition coefficient, K_{PESED}. To invert the Laplace-domain solutions back to the time domain, we used a numerical method (see Fernandez et al. 2009b). In this way, we obtain $M_{(t)}$ or $M_{PRC(t)}$, the target and PRC masses as functions of time.

Both Ψ and K_{PESED} are functions of K_d, expressed here in non-traditional units of cm^3 water/cm^3 dry sediment:

$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw}K_d)\tau D_{PE}} \approx \frac{D_W}{r_{sw}K_d\,\tau D_{PE}} \tag{8}$$

$$K_{PESED} = \frac{K_{PEW}}{K_d} \tag{9}$$

where D_W is a chemical's diffusivity in water (cm^2/s), r_{sw} is the volume ratio of whole sediment to water calculated from porosity, τ is tortuosity, and K_{PEW} is the polymer-water partition coefficient (expressed here in units of cm^3 water/cm^3 polymer. For any moderately hydrophobic compound in a sediment containing even 1% organic carbon, the product, $r_{sw} K_d$, will be much greater than 1, allowing the final approximation show in Eq. 8. The K_d for a PRC compound in a sediment may then be found from its fractional loss during deployment of known non-dimensionalized time of deployment (T_{exp})

To invert the Laplace-domain solutions back to the time domain, we used a numerical method (Hollenbeck 1998; Hollenbeck et al. 1999). In this way, the fractional approaches to equilibrium of target compounds, M_{target}/M_{inf}, or PRC, M_{PRC}/M_{init} , were obtained as functions of time. Fernandez et al. (2009b) present both a MATLAB code for inversions and families of "type curves" that allow estimates of the necessary parameters. Given this model, a family of curves for various K_d values may be produced for varying values of dimensionless time, T. The K_d values for each PRC may then be found by finding the intersection of the fraction of PRC lost during a particular passive sampler use and the non-dimensionalized time of the deployment (T_{exp}).

Since one can usually assume a relationship between log K_d and other compound properties like log K_{OW} for specific HOC compound classes, then for a given sediment and class of chemicals, using data from at least two PRC, one can estimate the K_d for any target chemical whose sorption behavior is captured by that relationship. The estimated K_d values for target compounds can then be used to calculate ψ and K_{PESED} values for that chemical and $M_{(t)}/M_{inf}$ may be either calculated by numerically inverting the Laplace value at T_{exp}, or read from a type curve. Finally, the pore water concentration may be calculated as:

$$C_{PW} = \frac{C_{polymer(t)} M_{inf}}{K_{polymer-water} M_{(t)}} \qquad (10)$$

To test the effectiveness of this approach, sediments were collected from near a former manufactured gas plant at IE, Chelsea, MA. Approximately 40 L of sediments were collected from just above the low tide line. In order to allow replicate observations, the sediments were thoroughly homogenized in a large galvanized steel tub by mixing with a metal hoe for 1 hour. Approximately 20 L of the homogenized sediments were transferred to a darkened, cylindrical, seamless, glass tank. The sediments filled the tank to a height of approximately 25 cm and were covered with approximately 8 cm water collected at the site of sediment collection. Sediments and water were allowed to sit undisturbed in the laboratory tank for 2 weeks before PE strips of either 25 µm or 51 µm thickness (i.e., 1 mil or 2 mil, respectively) were inserted using aluminum support frames. The PE passive samplers were removed from the sediments after 3 (25 µm) or 10 days (51 µm). Since PAH have been present in these sediments for decades, we assume no significant biodegradation of target chemicals occurred during these sampling periods. Following PE retrieval, surface waters were then siphoned out of the tank; sediments were scooped out and centrifuged (30 to 60 min at 900*g*) to compact the sediment solids; and supernatants were removed and run through a glass column containing glass wool to remove globules of tar and "floatable" particles before porewater extractions. Water samples (75 mL) were extracted three times by shaking with 20-40 mL of dichloromethane for 5 min in a

separatory funnel. Surrogate standards (d10-anthracene, d12-fluoranthene, and d12-benz(a)anthracene in acetone) were added to the samples before the first extraction to enable evaluation of method recoveries. The combined extracts were dried using anhydrous sodium sulfate and reduced to approximately 1 mL using a rotary evaporator (Buchi Rotavapor-R, Brinkman Instruments, Westbury, NY). Finally, injection standards (d10-acenaphthene, m-terphenyl, and d12-perylene in dichloromethane) were added to the extracts to allow accurate assessment of the final extract volumes before GCMS analyses.

Upon removal from sediments, PE strips were rinsed in clean water and swabbed with a hexane-soaked wipe to ensure that only absorbed molecules, but not those associated with adhering sediment particles or tarry films, would be quantified. Strips were cut into approximately 2 cm sections, surrogate standards were added, and then the strips were extracted three times by soaking in 15 mL of dichloromethane overnight. The combined extracts were concentrated to approximately 1 mL under a gentle stream of ultra pure grade nitrogen. Injection standards were added to the extracts before final GCMS analysis.

All extracts were analyzed using GCMS as described above. Calibration standards containing at least 25 aromatic compounds including each of the PRC, target compounds, surrogate and injection standards used in this study, were run every 3 to 5 sample measurements to monitor instrument stability, determine response factors, and confirm that measurements remained in the linear range for the instrument. Repeated observations using the calibration standard indicated the measurement uncertainty for the instrument was typically ±10% relative error. Percent recoveries for the surrogate standards (± 1 RSD) were 77 ±15% to 82 ±13% for PE extracts and 57 ±16% to 74 ±11% for pore water. PRC and target compound concentrations were corrected for recoveries of the corresponding closest-eluting surrogate standard. All target chemicals were found to be above detection limits in pore water and PE samples, which were approximately 130 ng/L and 250 ng/g PE, respectively, for these samples.

3.6 PE Sampling to Infer PAH Bioaccumulation by *Mya arenaria*

PE strips were deployed and clams and sediments were collected from six locations near Boston, MA (Figure 5) in November 2008. The sites were selected based on the presence of *M. arenaria*, previous measurements of PAH concentrations in sediments, and historical information concerning industrial use of the areas. From north to south, the locations included:

(a) Collins Cove, Salem, MA – a large but shallow cove approximately 600 m east if the Salem Harbor Power Station, a coal- and oil-fired power plant,
(b) Pioneer Village, Salem, MA – a sandy beach along Salem Harbor, approximately 1500 m south of Salem Harbor Power Station,
(c) Forest River (Lead Mills), Marblehead, MA – at the mouth of a tidal river down-stream of a 19^{th} century lead mill that burned down in 1968,
(d) Pines River, Saugus, MA – along a tidal river adjacent to a closed land fill and a waste-to-energy plant,
(e) Island End, Chelsea, MA – a coal-tar contaminated site, and

Figure 5. Map of sampling locations used in this study, listed from north to south: Collins Cove, Salem, MA; Pioneer Village, Salem, MA; Lead Mills, Salem, MA; Pines River, Saugus, MA; Island End, Chelsea, MA; and Dorchester Bay, Quincy, MA (Google maps 2009**)**.

(f) Dorchester Bay, Quincy, MA – downwind of the Southeast Expressway (I-93) and near the site of a former garbage incinerator on Spectacle Island. It was expected that these sites would provide a wide range of PAH chemical activities in the sediments.

Samplings of all sites were conducted over a period of two weeks, in November 2008, during low tides, in the intertidal zone. PE samplers were deployed at each site directly adjacent to what appeared to be siphon holes in the sediment. PE samplers in aluminum frames were pushed into sediments to a depth of between 4 and 12 cm depending on how far they would go in before meeting resistance. One week later, PE samplers were collected. At the same time, clams from the adjacent sediments were collected using a spade, and sediment samples were taken from the surface (approximately top 10 cm) and from a lower layer (approximately 10-20 cm deep). PE strips were rinsed with clean water in the field and placed between aluminum plates, which were

then wrapped in aluminum foil. Clams and sediments were placed in glass jars. All samples were returned to the lab on ice. Clams were stored at -20ºC until extraction, and sediments were stored at 4ºC until extraction. PE samplers deployed at Pioneer Village were not found on the retrieval trip. Instead, clams and adjacent sediment were collected and returned to the lab where PE was inserted directly into jarred sediment and exposed for 32 days.

Upon returning to the laboratory, PE strips were again rinsed in clean water and swabbed with a wipe (a hexane-soaked wipe in the case of Island End samplers) to ensure that only absorbed molecules, but not those associated with adhering sediment particles or tarry films, would be quantified. Strips were cut into approximately 4 cm sections, surrogate standards (d10-anthracene, d10-fluoranthene, and d12-benz(a)anthracene) were added, and strips were extracted three times by soaking in 15 mL of dichloromethane overnight. The combined extracts were exchanged into hexane and concentrated to approximately 0.5 mL under a gentle stream of ultra pure grade nitrogen. Injection standards (d10-acenaphthene, *m*-terphenyl, and d12-perylene) were added to the extracts before GC/MS analysis as described above.

Extraction of PAH from clams was performed using a accelerated solvent extraction (ASE) method modified from that described by Yusa et al. (2005). Partially thawed clams were measured for shell length and whole-clam mass. Clams were then shucked, reweighed, and dissected to remove stomach, intestines, and most internal organs. The remaining neck, foot, and adductor muscles were then sliced and chopped using two razor blades until a mushy consistency was achieved. Approximate 2 g of the chopped clam were then ground with 1-2 g of precombusted diatomaceous earth (Hyflo Supercel, Sigma Aldrich, St. Louis, MO) until dry and crumbly. The clam mixture was added to the 33-mL stainless steel extraction cell between two layers of precombusted Ottawa sand (EMD Chemicals, Gibbstown, NJ). Surrogate standards were added to the top of the second sand layer before accelerated solvent extraction (ASE) was performed. The remaining homogenized clam tissue was weighed and dried to determine its water fraction. ASE was performed using a Dionex ASE 200 (Dionex Corporation, Sunnyvale, CA). Each cell was extracted three times, using dichloromethane: methanol (1:1), heated for 5 min (125ºC) at 1500 psi, and flushed with 60% of the ASE cell volume between each extraction. Extracts were collected in amber glass vials with aluminum-lined caps. Approximately 20 g activated Na_2SO_4 were added to each vial, and extracts were stored overnight at 4ºC. Combined extracts were exchanged into approximately 2 mL hexane using a rotary evaporator (Buchi Rotavapor-R, Brinkman Instruments, Westbury, NY) before column chromatography and GC/MS analysis.

Sediments were homogenized in their collection jars by stirring with a spatula for 5 min, while removing large stones and shells. Subsamples were taken for drying and weighing to determine water content. Additional subsamples (3-10 g) were taken for ASE. Two pre-combusted GF-B filters were used in the bottom of each 11-mL stainless steel extraction cell. Wet sediments were added to the cell between two layers of pre-combusted Ottawa sand. Surrogate standards were added to the top sand layer before ASE using the same method described above for clam extractions. Again, extracts were dried overnight at 4ºC using approximately 20 g Na_2SO_4. Extracts were exchanged into hexane and reduced to approximately 2 mL using a rotary evaporator before column chromatography and GC/MS analysis. Chromatography columns were prepared in 20 cm long, 1 cm outside diameter, glass columns with ~ 30 mL reservoirs. A

small plug of glass wool, followed by ~2 cm of activated granular Cu^0 (20-30 mesh, Baker Analyzed Reagent, J.T. Baker, Phillipsburg, NJ) for columns for use with sediment extracts, followed by 5 g fully activated (475 ºC for 24 hr) silica gel (100-200 mesh, EMD Chemicals, Gibbstown, NJ), followed by ~6 g anhydrous Na_2SO_4 were dry packed into each column (Long 1995). Hexane, 30 mL, was used to flush each column before clam or sediment extracts were charged onto the column. PCB and PAH were collected together, by running 100 mL of hexane:dichloromethane (9:1 v:v) through the column under slight pressure. The solvent mixture was exchanged into hexane and reduced to ~0.5 mL for clam extracts and ~10 mL for sediment extracts. Injection standard (*m*-terphenyl) was added to each extract immediately before GCMS analysis to determine each sample volume. Splitless 1-µL injections were made onto a 30 m J&W Scientific HP-5MS capillary column (0.25 mm internal diameter with a 0.25 µm film thickness). The injection port temperature was held at 305ºC. The initial column temperature of 70ºC was raised at 20ºC/min until a temperature of 180ºC was reached, and then the temperature was raised 6ºC/min until a temperature of 300ºC was reached, and remained there for 7.5 min. The MS was operated in selected ion monitoring (SIM) and EI+ modes. Calibration standards containing 20 aromatic compounds including each of the target compounds, surrogates, and injection standards used in this study, were run every 3 to 5 sample measurements to monitor instrument stability, determine response factors, and confirm that measurements remained in the linear range for the instrument. Repeated observations using the calibration standard indicated the measurement uncertainty for the instrument was typically ±10% relative error. Percent recoveries for the surrogate standards (± 1 RSD) were 73 ± 39%, 71 ± 24%, and 60 ± 31% in PE extracts for d10-anthrancene, d10-fluoranthene, and d12-benz(a)anthracene, respectively. Recoveries in clams were 54 ± 36%, 75 ± 26%, and 81± 29% for d10-anthrancene, d10-fluoranthene, and d12-benz(a)anthracene, respectively. Recoveries in sediment extracts were 73 ± 36%, 88 ± 32%, and 91 ± 33% for d10-anthrancene, d10-fluoranthene, and d12-benz(a)anthracene, respectively. Extraction and measurement methods were tested for accuracy by measuring standard reference materials (SRM), NIST SRM 1974b – Organics in Mussel Tissue (Mytilus edulis) and NIST SRM 1941a – Organics in Marine Sediment. While pyrene and chrysene matched within uncertainty for the mussel tissue, phenanthrene measurements averaged 134% of the reported value. The high recovery of phenanthrene in the mussel tissues may have been due to contamination of the sample before extraction. For the sediment SRM, phenanthrene matched the reported value within uncertainty, while pyrene and chrysene were recovered at 71% (± 4%) and 78% (±5%) of the reported values.

Finally, dried (60ºC for 24 hr) and ground sediment sub-samples (~10 mg each) were analyzed for their mass fraction of organic carbon, f_{oc}, and black carbon, f_{bc}, using a Vario EL III CHN elemental analyzer (Elementar, Hanau, Germany). BC samples were pre-combusted at 375º C for 24 hr to remove the OC fraction (CTO375) (Gustafsson et al. 1997; Lohmann et al. 2004). Both f_{oc} and f_{bc} samples were acidified with 200 µL of 0.35 M sulfurous acid (H_2SO_3) (Baker Analyzed, Phillipsburg, NJ) and then dried at 60ºC for 24 hours to remove carbonates before CHN analysis. Three analyses of each sediment sub-sample were performed for each of the two measurements (f_{oc} and f_{bc}). Acetanilide (Elemental Microanalysis Limited, Okehampton, UK) was used as a calibration standard for the analytical method. Blanks were run between every six samples.

4. Results and Discussion

4.1 Assessing the Accuracy and Precision of PE-Inferred Pore Water Concentrations

In order to assess the accuracy and precision of deductions made with the use of PE passive samplers, we performed a series of laboratory tests on well-mixed sediments obtained from diverse locations. Additionally, we used a diverse set of methods (pore water extractions, air bridges, sediment extractions and ancillary characterization with respect to f_{oc} and f_{bc}) to contrast the results to what was seen using the PE samplers and thereby seek to characterize the accuracy of this new passive sampling approach. Finally, the PE observations were made with replication so as to allow assessment of the method's precision.

Observations made for a representative PAH, pyrene, and a representative PCB, 2,2',4,5,5'-pentachlorobiphenyl (congener #101), using Hunters Point (San Francisco Bay) sediment are illustrative. Using the air bridge methodology, the concentration of pyrene in this sediment's pore water was about 4 ng/L (Figure 6; note: air bridge data for other PAH indicate that the result shown for air bridge #2 was an outlier.) Pore waters recovered from this sediment exhibited about 16 ng/L levels, although corrections for colloid-bound pyrene decrease that result to about 11 ng/L. This pore water result demonstrates the difficulties caused by colloidal phases with respect to assessing HOC. Also, sediment extracts normalized by two estimates of pyrene's sorption coefficient, K_d (one considering only absorption to organic matter, the second including potential effects of adsorption to black carbon) suggested pyrene's pore water concentration would be between 1 and 4 ng/L. This uncertainty in the sorption coefficient causes corresponding uncertainty in the EqP-type calculated pore water result.

Replicate observations made with PE passive samplers incubated in the sediment for a week or a month, resulted in pore water concentration estimates of 7±1 and 10±2 ng/L, respectively. These results imply the PE passive samplers were accurate to about a factor of 2 and precise to about 20% for this case. Similar results were seen for phenanthrene and chrysene (Fernandez et al., 2009a).

Similar observations were made for PCB congeners in this Hunters Point sample. For example, the mean of six air bridge results for PCB congener 101 indicated a pore water concentration of 1±0.5 ng/L (Figure 7). Pore water extraction indicated this congener's total presence in the water was about 5 ng/L, and estimates of the colloid-bound fraction lowered this to about 2 ng/L. Use of the measured sediment concentration and an estimate of the K_d value, without and with consideration of black carbon effects, suggested pore water concentrations of about 32 and 0.4 ng/L. Obviously, both the direct pore water extraction approach and the sediment-water equilibrium partitioning calculation approach suffer from some uncertainty as one must consider hard-to-quantify impacts of phases like colloids or black carbon.

The PE passive samplers indicated pore water concentrations for PCB 101 that were consistent with the air bridge observations. PE samples incubated for 1 week and 1 month indicated pore water concentrations to be 1±0.3 and 0.5±0.2 ng/L, respectively. As for the PAH, these data appear accurate to within a factor of two and have precisions near 30% relative error.

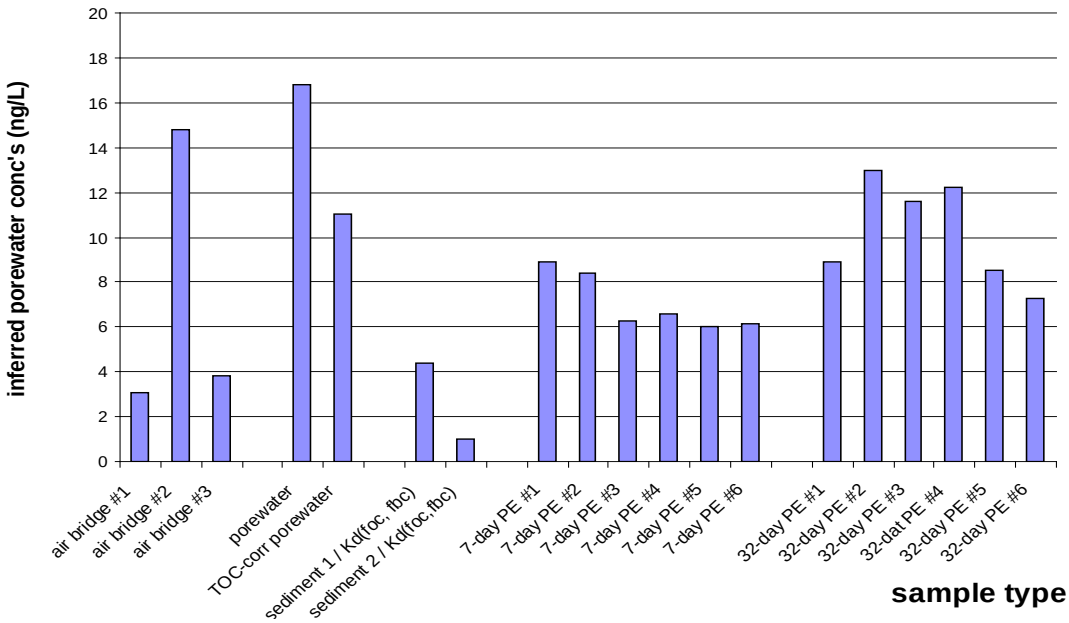

Figure 6. Comparison of four approaches for finding pore water concentrations of pyrene in Hunters Point sediments: (a**) three air bridges, (**b**) pore water extraction, without and with correction for colloids, (**c**) sediment extractions, normalized with sorption coefficients estimated without and with consideration of black carbon presence, (**d**) six PE strips incubated in the sediment for 7 days and normalized by K_{pew}(**pyrene**) and (**e**) six PE strips incubated in the sediment for 32 days and normalized by K_{pew}(**pyrene**).**

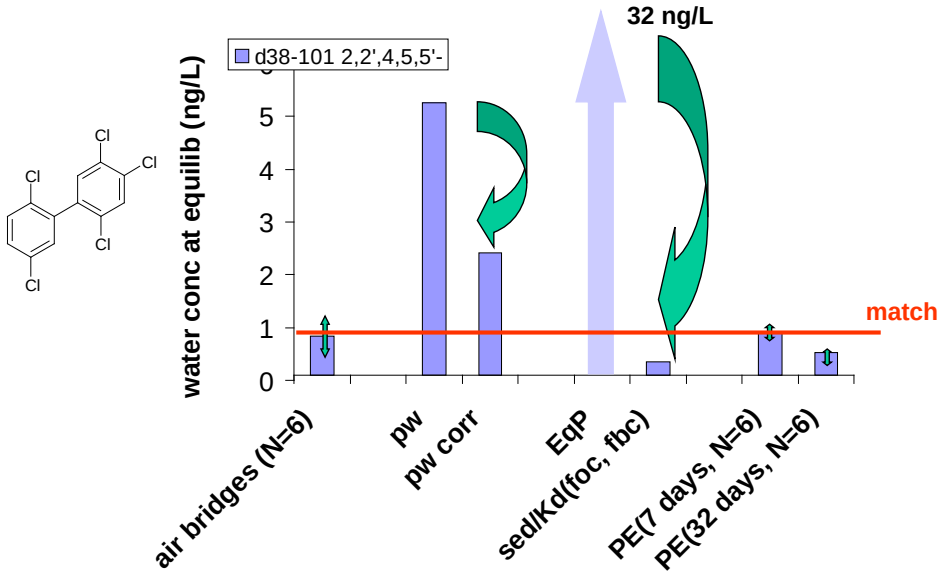

Figure 7. Comparison of four approaches for finding pore water concentrations of PCB congener 101 (2,2',4,5,5'-pentachlorobiphenyl**) in Hunters Point sediments: (**a**) mean and ±1σ for three air bridges, (**b**) pore water extraction, without and with correction for colloids, (**c**) sediment extractions, normalized with sorption coefficients estimated without and with consideration of black carbon presence, (**d**) mean and ±1σ of six PE strips incubated in the sediment for 7 days and normalized by K_{pew}(**PCB101**) and (**e**) mean and**

±1σ of six PE strips incubated in the sediment for 32 days and normalized by K_{pew}(PCB101).

Similar correspondence between PE-inferred pore water concentrations and those obtained via other approaches was also seen for sediments from other locations (Figure 8). Considering six PAH (phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, and chrysene) in three diverse sediments (Island End is a coal-tar affected site in northern Boston Harbor, Dorchester Bay is an active clamming region in southern Boston Harbor, and Hunters Point is a Naval Station in San Francisco Bay), we see a strong relation between PE-deduced pore water concentrations and those obtained by extracting pore water after correcting for colloid effects. And this correspondence was seen for concentrations ranging over about 6 orders of magnitude. As a result, the PE passive sampling methodology appears to be able to measure the presence of such hydrophobic organic contaminants at very diverse sites to within about a factor of 2 or 3 in accuracy and about ±30% relative error. Other common approaches (pore water analyses, EqP calculations using sediment concentrations) do not appear to be as accurate.

4.2 Testing the Deployment and Use of PE Samplers in the Field

In order to make the PE passive samples most useful (i.e., remove the need to collect and return sediment samples back to the lab), it is necessary to be able to deploy the samplers in the field.

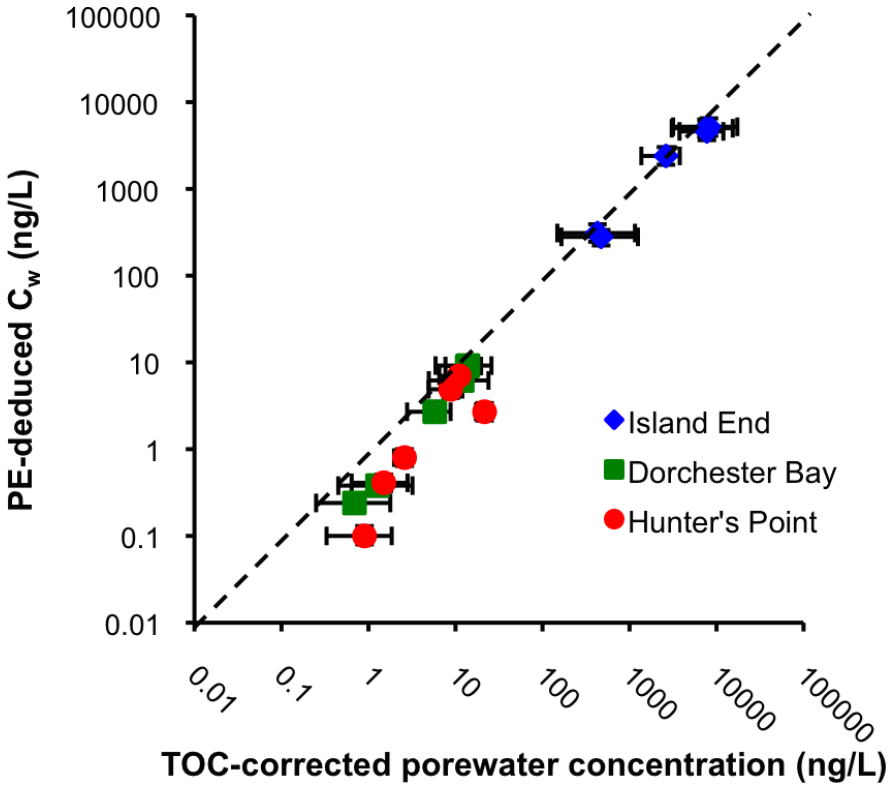

Figure 8. PE-deduced water concentrations C_w vs. pore water concentrations for six PAH (phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, and chrysene**) found by centrifugal compaction of the sediment followed by solvent extraction and corrected for TOC-sorption for Island End, Dorchester Bay, and Hunters Point samples.**
As a first step, an aluminum frame system was devised to enable insertion of the PE strips into a sediment bed by hand (Figure 1**). This "window" approach allowed exposure of the PE strips on both sides. Additionally, this frame system could be fixed to a paint roller and deployed using an extension pole to depths of ≤5 m.**

Next, in order to use the PE strips in still deeper waters, a deployment vehicle was built for deployment from a boat. Design criteria for the vehicle were:

(a) it must be able to be handled on, and deployed from, a small boat (<20 ft),
(b) it must withstand corrosion in salt water,
(c) it must have enough surface area to avoid over-penetration in soft sediments,
(d) it must have "adjustable" weighting to promote penetration in silty or sandy sediments, and
(e) it must be easy to retrieve.

To meet these criteria, we assembled a vehicle (Figure 1) and tested it from stationary docks overlying soft and hard sediment beds and from a vessel in Boston Harbor. The vehicle was rectangular and made from aluminum. PE frames could be bolted to cross members. Weights could be added on posts located on either end to encourage penetration of the PE into the sediment bed. Finally, lines were attached at each corner of the vehicle and collected at a single point for attachment to a line from the vessel. Recovery was achieved by use of attached buoys to locate the PE samplers upon return to the field site.

The PE-carrying vehicle was tested at a field site that is regularly monitored by the Massachusetts Water Resources Authority (MWRA) and their consultants (ENSR, Battelle, Ecosystems-MBL). We deployed the vehicle from the research vessel in several meters of water at a station near the mouth of Boston Harbor. The consultants observed the PE system deployment, and their divers observed the vehicle's descent and penetration into the bed. The vehicle was left in place with a tag line and a marker buoy. After 1 week, we returned to the site and successfully recovered the PE vehicle. The PE strips were returned to the laboratory and analyzed for target and tracer compounds. With the help of the divers, a small core was recovered near the vehicle, and it was returned to the laboratory for pore water analyses.

The PAH chemical activities deduced from these PE samplers matched the results obtained using the pore water sample obtained from the diver-retrieved core (Figure 9). The modest discrepancies may be due to spatial heterogeneity in the field since the recovered core could not be obtained from the exact location where the PE was inserted. We also contrasted the results from this first field deployment in Boston Harbor with our findings using heavily contaminated Island End sediment and lightly contaminated Dorchester Bay sediments (Figure 9, gray symbols). The field sampling observations (orange triangles) revealed that this field site exhibited a contamination level similar to that of Dorchester Bay, a very reasonable result given that both are fairly sandy, harbor stations.

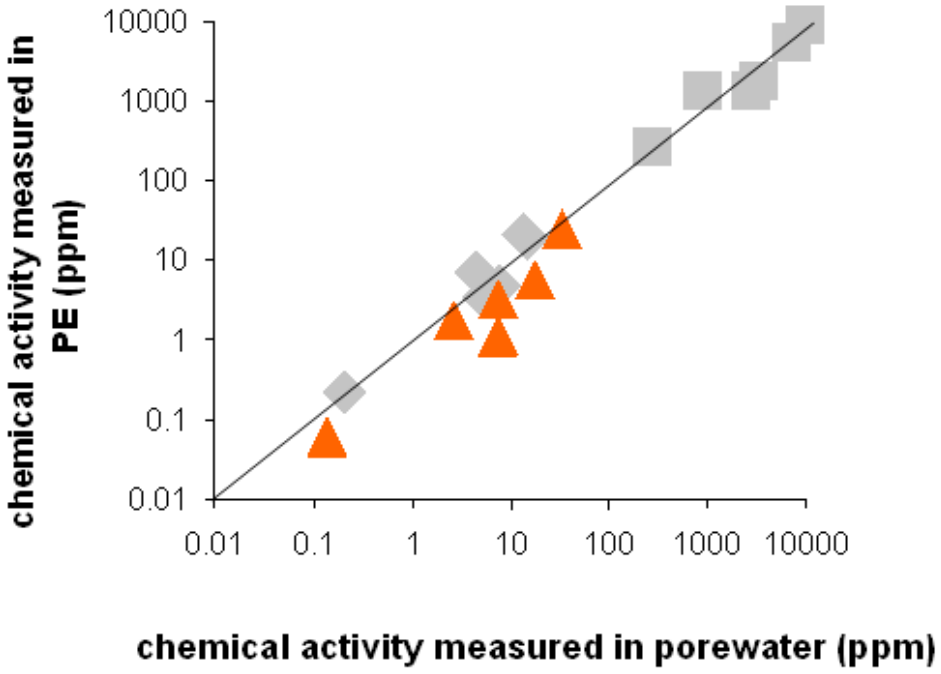

Figure 9. Comparison of PE-inferred pore water concentrations of six PAH when PE strips were deployed for 1 week in the field (orange symbols**) with corresponding pore water concentrations measured in cores retrieved by divers near the PE incubation position. Gray symbols show results for the same PAH using sediments from other harbor sites in the laboratory for comparison.**

The field deployment of PE samplers also allowed us to measure the vertical gradient of pyrene activity in the sediment bed and into the overlying water column (Figure 10). This type of data would, of course, be useful for estimating the bed-to-water flux of pyrene at this site recognizing that this PAH's chemical activity at all positions is equal to $conc_{pyrene}$ / sat'd $conc_{pyrene}$:

Flux (mol/m^2 sec) = - $D_{effective}$ * ($conc_{pyrene}$ in bed surface - $conc_{pyrene}$ in bottom water) / Δz

= - $D_{effective}$ (sat'd $conc_{pyrene}$)* (a_{pyrene} in bed surface - a_{pyrene} in bottom water) / Δz

Such flux information is necessary to estimate the mobility of pyrene from such a sediment bed contamination to the overlying water column and the animals living there.

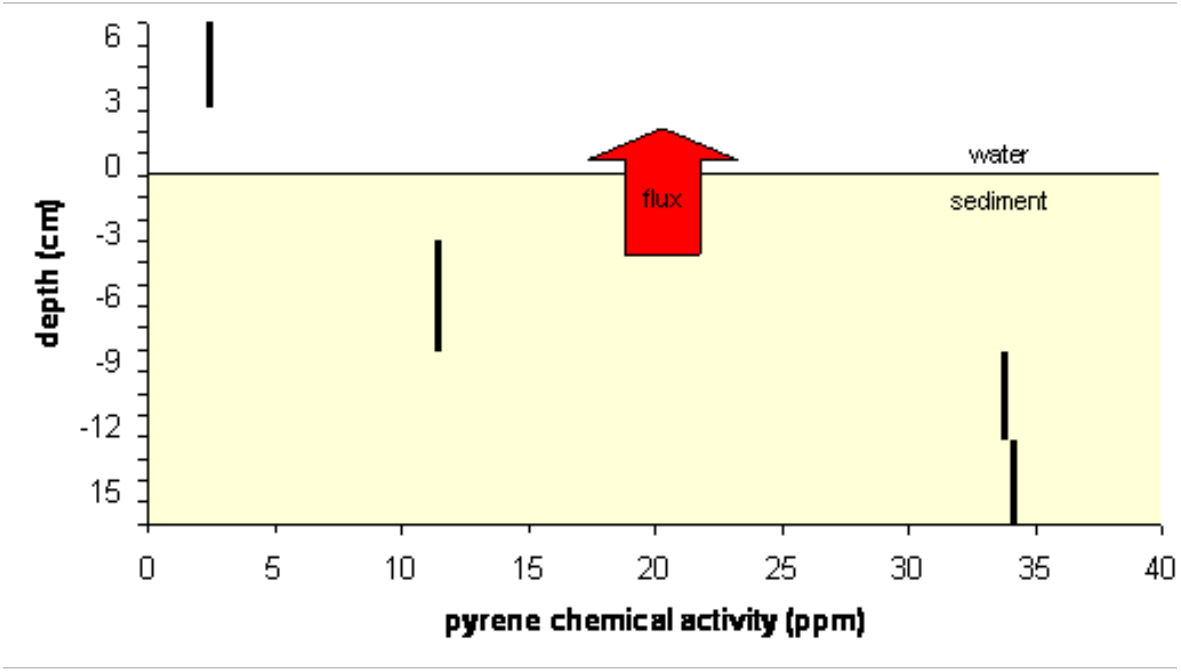

Figure 10. Profile of pyrene activities (= pore water concentration normalized by pyrene's liquid solubility of 900 ug/L**) across the sediment-water interface for a site in Boston Harbor. Values were deduced from a polyethylene strip inserted ~20 cm into the bed but still have ~6 cm above the bed-water interface.**

4.3 Mass Transfer Modeling to Enable Use of a Few PRC to Assess Many Target Contaminants

To evaluate the accuracy of the PE method using our new model with only three PRC, we contrasted PE-inferred pore water concentrations of PAH with direct measures of these concentrations in a sediment from our Island End "coal tar" contaminated station. To begin, the fractional losses of the three deuterated PRC (phenanthrene, pyrene, chrysene), after known exposure times, were used to find the K_d for each PRC (Fernandez et al., 2009b). For example, 36% of the d10-pyrene in the 25 µm thick sampler remained in the PE after a 3 day exposure, while 43% of this PRC remained in the 51 µm thick PE after 10 days. Using a D_{PE} of 3.1 × 10-10 cm^2/s for d10-pyrene, the non-dimensional time, T values (= time * D_{PE} / PE-half thickness squared) for these exposures were calculated to be 50 and 41 in the 25 µm thick and 51 µm thick PE, respectively. The intersections of the fractional losses and T values (Figure 11) corresponded to K_d values of $10^{4.0}$ and $10^{3.9}$, implying the K_d for d10-pyrene in this sediment was near $10^{4.0}$. Applying the same method to the two other PRC, d10-phenanthrene and d12-chrysene, K_ds for these two compounds were also found ($10^{3.7}$ and $10^{5.5}$, respectively). These values are consistent with those measured at other coal-tar contaminated sites (Khalil and Ghosh 2006) (assuming a solids density of 2.5 g/cm^3 to convert K_d from traditional units of L_w/kg dry sediment to those used in the mass transfer modeling, cm^3 water/cm^3 sediment) and our own measures of organic contents of the sediment at this site.

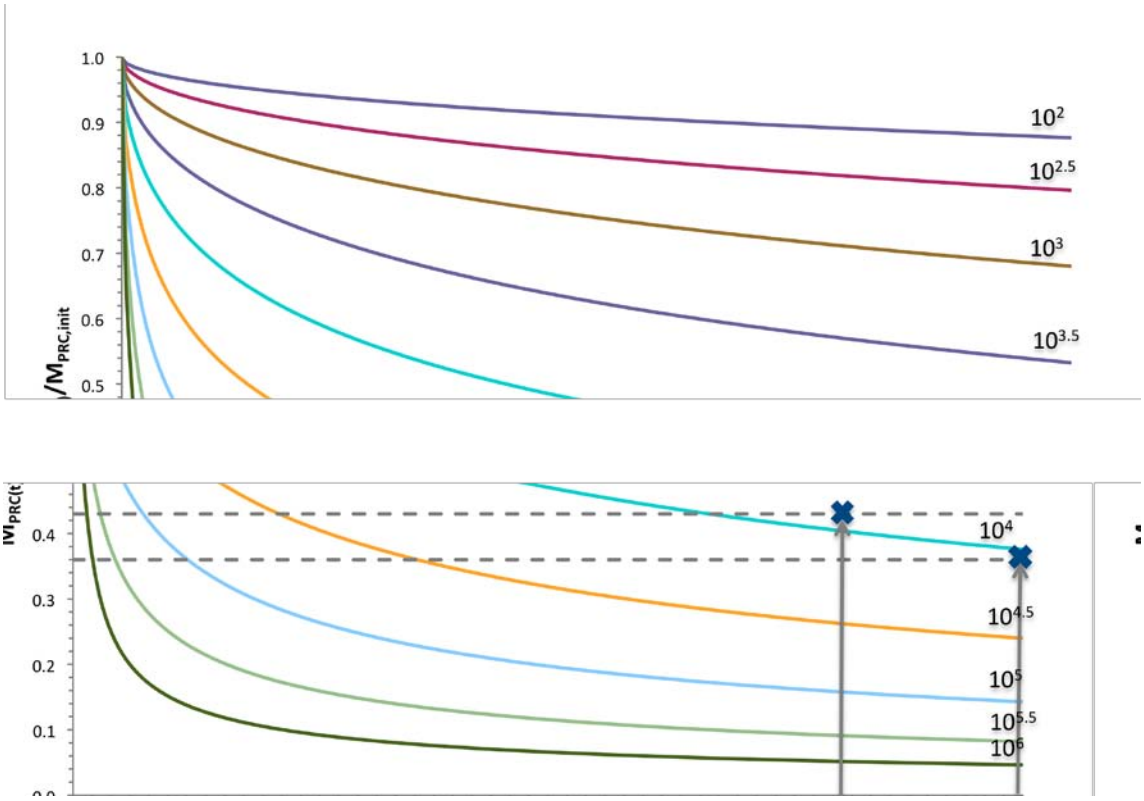

Figure 11. Measured fractional losses ($M_{PRC(t)}/M_{PRC,init}$**) of a PRC (**d10-pyrene**) from PE strips exposed to Island End sediments (**60% porosity**) for defined times (**setting the dimensionless time parameter, T = D_{PE}*time/PE thickness squared**). A 25 µm thick PE was exposed for 3 days (**T=50**) resulting in 36% loss, while a 51 µm thick PE was exposed for 10 days (**T=41**) and had 43% loss. The intersections of these (**T, $M_{PRC(t)}/M_{PRC,init}$ **) on this "type-curve" plot enables the K_d value for pyrene in this sediment to be estimated (**here, $10^{4.0}$ and $10^{3.9}$, respectively**) and this is done for each PRC used in the PE strips. The resultant K_d(**PRC**) values are then used to establish a relationship between the analytes' values of log K_d and log K_{ow}: log K_d = 1.4 × log K_{ow} -2.7. Subsequently, this relationship is then used to estimate site-specific K_d values for other compounds of the same class.**

Next, the log K_ds for d10-phenanthrene, d10-pyrene, and d12-chrysene in Island End sediment were used along with their K_{ow} values (Sangster 1989) to establish a relationship between log K_d and log K_{ow} for this sediment: log K_d = 1.4 × log K_{ow} − 2.7. Then this site-specific result was used to estimate K_d values for seventeen target PAH, including eleven PAH that lie between the PRC in terms of diffusivities and partition coefficients (phenanthrene, anthracene, 1-methylphenanthrene, 1-methylanthracene, fluoranthene, pyrene, 3,6-dimethylphenanthrene, 9,10-dimethylanthracene, 2-methylfluoranthene, benz(a)anthracene, and chrysene) and six that diffuse more slowly and have larger partition coefficients than the PRC (benzo(b) and benzo(k)fluoranthene (measured together), benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene and dibenz(a,h)anthracene). Using these site-specific and compound-specific K_d values, we estimated the effective diffusivities of each target compound in the sediment bed. Combined with the corresponding estimates of diffusivities in the PE, we used the mass transfer model to find the fractional approach of each target compound to bed-sampler

equilibrium. This result allowed us to correct the measured values of each target contaminant in the PE to estimate what they would be at bed-sampler equilibrium. Finally, pore water concentrations were deduced by normalizing these equilibrium estimates by the corresponding PE-water partition coefficients: $C_w = C_{PE}/K_{pew}$.

For chemicals with the same diffusivities and partition coefficients as the deuterated PRC (i.e., unlabelled phenanthrene, pyrene, and chrysene), the PE-deduced results and directly measured values (with TOC corrections) matched within an average factor of 1.2 ± 0.06 (N=3). For target compounds whose properties fall between those bounded by the three PRC, the method performed better (factor of 1.5 ± 0.7, N=11) than for larger chemicals whose diffusivities and partition coefficients fall outside the PRC range (factor of 2.9 ± 1.1, N=5). For all 17 target compounds, the PE-deduced C_ws and TOC-corrected C_ws matched within a factor of 2.0 ± 0.9, with TOC-corrected values most often higher than PE-deduced C_w (Figure 12). Including a larger PRC would improve the PE-inferred results for the largest chemicals, but would have required longer exposure times to transfer measurable amounts of that larger PRC to sediments.

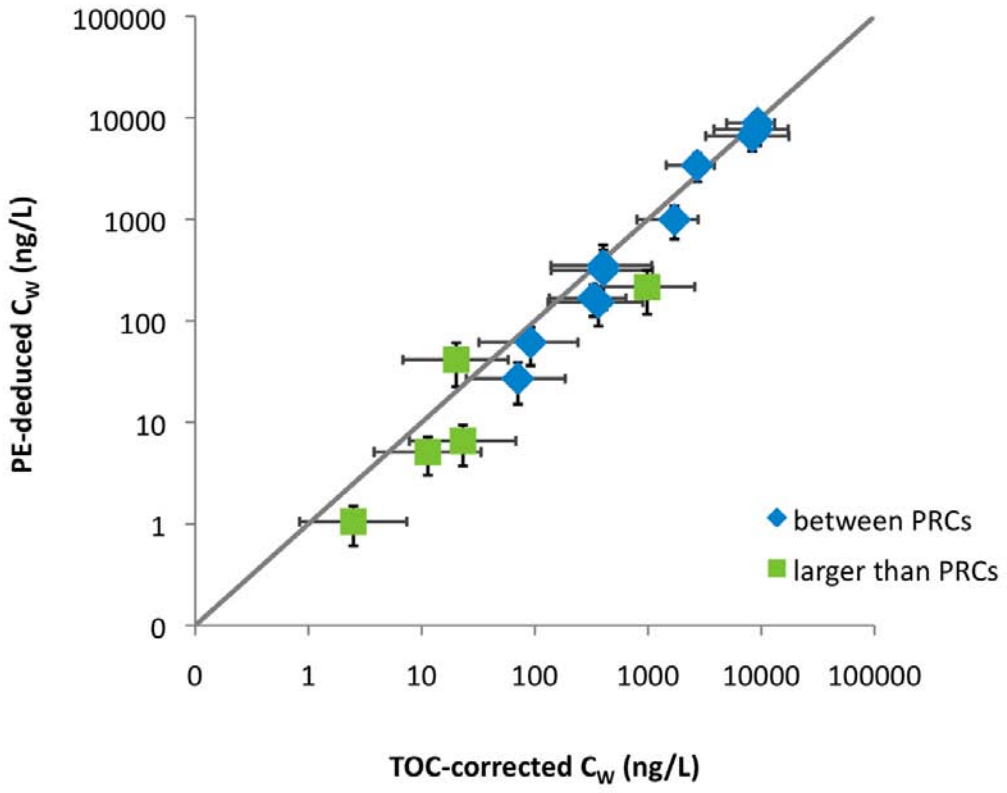

Figure 12. Use of a few PRC to adjust measured PE loads of PAH to values expected at sediment-PE equilibration for two sets of target contaminants (a**) those that exhibit partitioning properties between those of the three ^{13}C-labeled PRC (**phenanthrene, pyrene, and chrysene**) and (**b**) those that have partitioning properties outside those of the three PRC. The resultant PRC-corrected estimates are then normalized using K_{pew} values to deduce C_{pw} and compared to pore water concentrations found by solvent extraction and corrected for sorption to colloidal organic carbon for Island End sediments. The 1:1 line is shown, and the error bars represent ±1σ.**

Table 2. Comparison of Island End pore water results for 17 PAH deduce by pore water extractions and by PE passive sampling using a few PRC and the mass transfer model to estimate corrections for all target PAH.

Compound	**TOC-corrected pore water concentration (ng/L)** (average, N=2)	**PE-deduced pore water concentration (ng/L)** (average, N=7)	**PE-deduced** +/- σ	**Ratio of TOC-corrected to PE-deduced**
phenanthrene	2700	3400	1100	0.80
anthracene	9300	8900	2500	1.05
1-methylphenanthrene	1700	990	360	1.72
1-methylanthracene	330	170	57	1.96
fluoranthene	8300	6600	1900	1.26
pyrene	9200	7700	2400	1.19
3,6-dimethylphenanthrene	92	61	25	1.49
9,10-dimethylanthracene	71	27	12	2.62
2-methylfluoranthene	360	150	64	2.38
benz(a)anthracene	400	320	190	1.28
chrysene	400	350	210	1.14
benzo(b + k)fluoranthene	980	220	99	4.54
benzo(a)pyrene	20	41	19	0.49
indeno(1,2,3-c,d)pyrene	23	7	3	3.53
benzo(g,h,i)perylene	2	1	0.4	2.37
dibenz(a,h)anthracene	11	5	2	2.22

4.4 PE Passive Sampling to Infer Bioaccumulation of PAH by *Mya arenaria*

To examine the effectiveness of PE passive samplers for evaluating the bioaccumulation of organic contaminants like PAH and PCB by benthic fauna, we deployed PE samplers at several field sites where the soft-shelled clam, *Mya arenaria*, is known to live (Table 3 and Figure 5). The sites represent a wide array of nearby activities (coal burning electric power plant, landfill, coal tar disposal, incinerator) and sedimentary conditions in the vicinity of Boston.

Since the clams live burrowed in the sediment to depths between 10 and 20 cm, but extend their siphons up to the top of the bed, it was unclear which sediment horizon contributes most to clam exposures. Consequently, we measured properties of both the upper 10 cm and a deeper horizon (Table 4). PAH concentrations varied greatly from site to site. For example, pyrene concentrations in the upper 10 cm of sediment varied by more than a factor of 1000 ranging from only 6 ng/gdw up to 16,000 ng/gdw (Table 4). Factors influencing sediment sorption also varied widely. Organic carbon content (f_{oc}) ranged from only 0.07% by weight up to 9.1%, and black carbon concentrations (f_{bc}) went from 0.01% to 4.9%.

Table 3. Sampling sites used in assessing the ability of PE passive samplers to anticipate bioaccumulation in the soft shell clam, *Mya arenaria*.

site	no. stations	lat./long.	general description	sediment temperature (ºC)	porosity
Collins Cove Salem, MA	4	42º 31.724' N/ 70º 53.231' W	shallow tidal cove, dark silty sediments, ~ 700 m west of Salem Harbor Power Station	9.6	0.49
Pioneer Village Salem, Ma	1	42º 30.466' N/ 70º 53.041' W	coarse sand beach, ~ 1.5 km south of Salem Harbor Power Station	9.6	0.29
Lead Mills Marblehead, MA	2	42º 29.821' N/ 70º 53.176' W	coarse sand and shell fragments, at mouth of tidal river ~ 2.5 km south of Salem Harbor Power Station	9.6	0.46
Pines River Saugus, MA	3	42º 26.033' N/ 70º 59.671' W	silty sand along shallow tidal estuarie, adjacent to land fill	12	0.52
Island End Chelsea, MA	1	42º 23.392' N/ 71º 03.148' W	silty sand in coal-tar contaminated cove	11.5	0.57
Dorchester Bay Quincy, MA	2	42º 17.852' N/ 71º 01.154' W	coarse sand~2 km from I-93 and 3.8 km from Spectacle Island (site of former garbage incinerator)	9.6	0.53

Table 4. Sediment conditions for two zones (0-10 cm and ~20 cm) at sampling sites used to assess PE passive sampling to anticipate bioaccumulation, including PAH concentrations (ng/gdw), weight percent organic carbon (f_{oc}), and weight percent black carbon (f_{bc}). Not analyzed indicated by "na".

	Approx. upper 10 cm					**Approx. 20 cm depth**				
Site/Station	**phen**	**pyr**	**chry**	**f_{oc}**	**f_{bc}**	**phen**	**pyr**	**chry**	**f_{oc}**	**f_{bc}**
Collins Cove 1	13000	9400	3500	3.3	1.8	23000	9000	2800	13	5.7
Collins Cove 2	5400	9400	4400	0.8	4.2	5400	9400	4300	4.3	6.3
Collins Cove 3	6600	5800	4300	2.6	3.6	4000	5800	2300	3.7	2.6
Pioneer Village 1	5	6	5	0.07	0.01	3	5	8	0.06	0.02
Lead Mills 1	42	46	46	0.5	2.1	420	420	190	1.1	1.5
Lead Mills 2	200	240	240	na	na	2900	2200	850	na	na
Pines River 1	2400	1400	1200	na	na	450	320	230	na	na
Pines River 2	2400	2400	830	1.5	0.44	64	150	65	1.7	0.25
Pines River 3	140	230	88	1.1	0.06	130	260	69	1.0	0.30
Island End 1	2400	16000	5500	9.1	4.9	na	na	na	na	na
Dorchester Bay 1	52	120	54	4.0	0.47	77	300	130	1.1	0.29
Dorchester Bay 2	82	130	49	na	na	160	330	100	na	na

But concentrations of PAH did not vary so much with depth at any single site (generally <10x). Some sites had higher concentrations at depth (e.g., Lead Mills), while others had higher concentrations near the sediment surface (Pines River). Organic carbon and black carbon concentrations were usually similar in the 0-10 cm and 10-20 cm samples, with exceptions at Collins Cove where the deeper layer had 3 to 4 times higher f_{oc} than f_{bc} in two cases.

To begin to evaluate the effectiveness of the PE passive sampling for anticipating PAH bioaccumulation by *M. arenaria*, we transformed the PE and clam concentrations into chemical activities to allow direct comparisons. For the PE, this calculation simply uses the PRC-inferred equilibrium concentrations in the PE, C^{∞}_{PE}, and normalizes these by the PE-water partition coefficient, K_{PEW}, to obtain the corresponding pore water concentration. This result is then normalized by the compound's (liquid) solubility in water, C^{sat}_{w}. Hence, the calculation is:

$$\text{activity}_{\text{PE-inferred}} = C^{\infty}_{PE} / K_{PEW} / C^{sat}_{w}$$

The result is a dimensionless number reflecting the "fraction degree of saturation" of the sediment as reflected in the equilibrated PE or pore water.

Likewise, the clam's tissue concentrations were transformed to chemical activities. As for the PE, this process first involves normalizing the clam's tissue concentration, C_{clam}, by the chemical's clam-water partition coefficient, $K_{clam\text{-}w}$. While this coefficient has traditionally been estimated assuming only accumulation in the organism's lipids, we believe a more accurate approach for protein-rich organisms and only moderately hydrophobic compounds requires one to include partitioning into the proteins too (Lohmann et al., 2004). Hence, the values of $K_{clam\text{-}w}$ used here were deduced:

$$K_{clam\text{-}w} = f_{lipid} K_{lipid\text{-}w} + f_{protein} K_{protein\text{-}w}$$

For this calculation we used $f_{lip} = 0.05$ and $f_{protein} = 0.5$. Using the normalized result, $C_{clam}/K_{clam\text{-}w}$, with the compound's (liquid) solubility, one finds:

$$\text{activity}_{\text{clam-inferred}} = C_{clam} / K_{clam\text{-}w} / C^{sat}_{w}$$

Again, this resultant parameter simply reflects the degree of saturation of the clam tissue.

Using these two activities for one representative PAH, pyrene, the dependency of the clam tissue contents on contaminant presence at three depth intervals in the sediment (0-4 cm, 4-8 cm, and 8-12 cm) was examined (Figure 13). Aggregating the results from all six sites, one sees a closer correspondence between pyrene activities in the 0-4 cm horizon with the clam tissue than for the two deeper horizons. In general, the ratio of activity in the clam to activity in the PE was 0.67 for the 0-4 cm depths, while this ratio dropped to 0.48 for the 4-8 cm depths and to 0.36 for the 8-12 cm depths. This correspondence to the surface layer may reflect the clam's feeding behavior which involves taking in detritus using its siphon from the bottom water which undoubtedly includes solids suspended from the top of the bed.

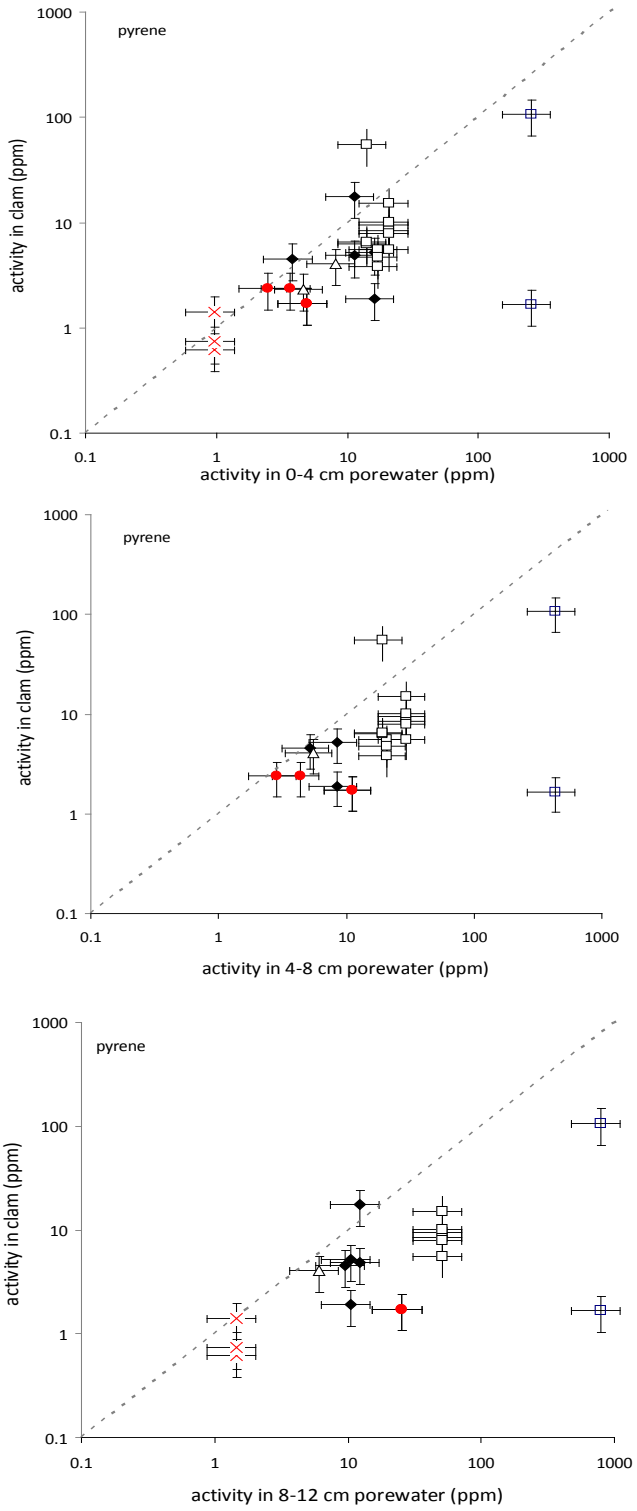

Figure 13. Pyrene chemical activities (ppm**) at three depths (**0-4, 4-8, and 8-12 cm**) inferred from PE passive samplers versus activities found in soft-shell clam tissues from six sites near Boston, MA. Average ratios at 0-4 cm were 67%, at 4-8 cm were 48%, and 8-12 cm were 36%.**

Based on this closer relation to the 0-4 cm depths at each site, activities of three representative PAH, phenanthrene, pyrene, and chrysene, in the clams were compared to corresponding activities from the PE at this near-surface depth (Figure 14). Since the data for phenanthrene and chrysene are "clumped", linear regression analysis is not very revealing on the question of how well the clam tissue concentrations of phenanthrene and chrysene can predicted from PE data. However, the pyrene data are somewhat more spread. The datum falling far below the 1:1 line for pyrene (and chrysene) is from the coal-tar contaminated site; we suspect one of the two clams was "unhealthy" and not feeding and respiring as it might normally. Hence, its body burden may have been especially under-equilibrated with its surroundings. Excluding this case, only 1 out of 27 points for pyrene fall more that a factor of three from the 1:1 line and only 4 out of 27 points for chrysene fall more than a factor of three from the 1:1 line. Even most of the phenanthrene data (20 out of 27) fall within a factor of five of the 1:1 line. Given, the propagated errors for both the PE-based and clam tissue-based chemical activities, it appears the PE passive sampler is almost always consistent with the bioaccumulation result from this burrowing clam.

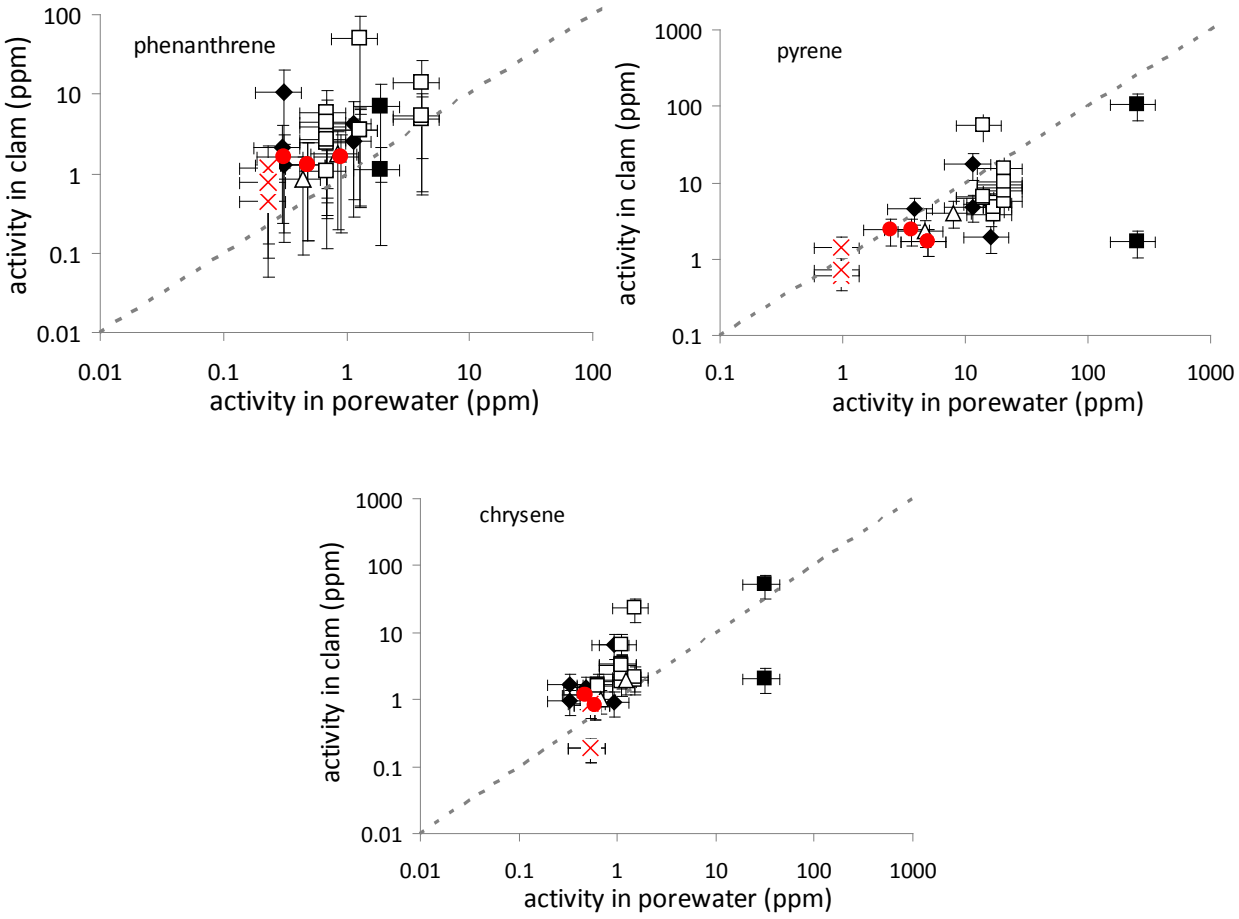

Figure 14. Chemical activities of three PAH measured in pore waters (0-4 cm depth**) using PE passive samplers and in clam tissues at six sites near Boston, MA.**

Finally, the PE passive sampling-inferred chemical activities were compared to expectations at those same sites using the equilibrium partitioning model (EqP). In the first case, the sorption coefficient was taken to be equal to the product of the total organic carbon content of the sediment, f_{oc}, and the PAH's organic carbon-normalized partition coefficient, K_{oc}. Hence, the chemical activities were estimated from sediment concentrations:

$$\text{activity}_{\text{sediment-inferred}} = C_{\text{sediment}} / (f_{oc}K_{oc}) / C^{\text{sat}}_{w}$$

For these calculations, the log K_{oc} was taken as 4.6. In almost every case, this EqP approach yielded pyrene activities that were substantially higher than what was found using PE passive samplers in the same sediment (Figure 15, upper panel). In fact, in 5 out of 9 cases, the EqP result was more than 10 times greater and would have implied a correspondingly greater exposures for benthic organisms.

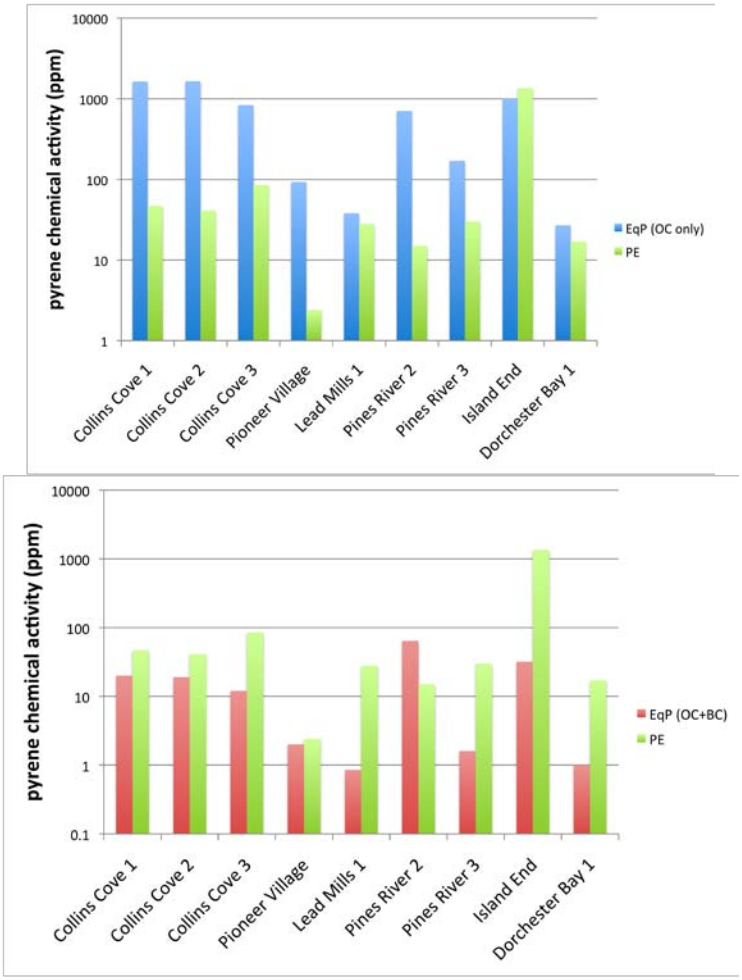

Figure 15. Comparison of pyrene's chemical activities (pore water concentration normalized by pyrene's liquid solubility**) measured in pore waters using PE passive samplers (green bars) and calculated using an EqP model (**upper panel**) assuming only equilibrium absorption into organic carbon (**i.e., $K_d = f_{oc}K_{oc}$**) and (**lower panel**) considering sorption to both organic carbon and black carbon (**i.e., $K_d = f_{oc}K_{oc} + f_{bc}K_{bc}C_w^{n-1}$**).**

In an effort to resolve this discrepancy, an improved estimate of the K_d value in each case was made by considering the sum of absorption to diagenetic organic matter plus adsorption to pyrogenic black carbon (Gustafsson et al., 1997; Accardi-Dey and Gschwend, 2002, 2003). In this case, the sorption coefficient is given:

$$K_d = f_{oc} K_{oc} + f_{bc} K_{bc} C_w^{(n-1)}$$

and the EqP approach becomes:

$$\text{activity}_{\text{sediment-inferred}} = C_{\text{sediment}} / (f_{oc} K_{oc} + f_{bc} K_{bc} C_w^{(n-1)}) / C^{sat}_w$$

Based on other work in the Boston Harbor area (Accardi-Dey and Gschwend, 2002; Lohmann et al., 2005), the log K_{bc} was taken to be 6.4 and n was assumed to be 0.7. Using this modification and measures of the f_{bc} content of each sediment (Table 4), the EqP calculations now move much closer to what was found using the PE passive samplers for the Collins Cove, Pioneer Village, and one of the Pine River sites (Figure 15, lower panel). However, this approach "over corrects" for the Lead Mills, Island End, Dorchester Bay, and the second Pine River sites. This result suggests that the original EqP method may not work well when pyrogenic black carbons are important sorbents, but that our current ability to estimate adsorption to BC in the environment is still rudimentary in that we assume all soots, chars, coals, etc. exhibit identical carbon mass-normalized adsorption parameters. Nonetheless, this exercise indicates that PE passive sampling-inferred contaminant activities may well be consistent with expectations from EqP-like approaches if we can get the sorption parameters right.

5. Conclusions and Implications for Future Research/Implementation

Given the relative ease of the PE passive sampling method and the belief that pore water concentrations are an excellent metric of contaminant mobility and bioavailability, these results strongly support the conclusion that future efforts to assess the risks posed by organic contaminants in sediments can be effectively determined using PE passive samplers.

These PE samplers offer several advantages. First, they can be prepared from cheap and widely available materials (hardware store LDPE sheet). Additionally, the extraction and analysis of the PE after deployment has proven to be much easier than corresponding sediment or organic tissue measures. Notably, there is little need to use normal phase liquid chromatography steps to clean up the extracts before gas chromatography. Next, the PE samplers can be loaded with internal standards or performance reference compounds (PRC) so adjustments are made for their use at every site in varying conditions (e.g., temperature, biofouling). Moreover, these PRC allow case-specific passive sampler calibration so that other target contaminants of interest can be quantified from the same sediment.

Despite all these advantages, some limitations remain. First, the physical chemical data, notably polyethylene-water partition coefficients for compounds besides PAH and PCB and compound diffusivities in polyethylene, are still quite limited. Perhaps more problematic, one finds that deployment times of 1 month or more may be necessary to achieve PRC losses that are sufficient

to measure precisely so the samplers can be accurately calibrated. Finally, deployments into beds below water that is deeper than divers can go (>30 m) have not been accomplished with enough repetition to be sure this will be an "easy" and dependable process.

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7. Appendices
List of Scientific/Technical Publications

Fernandez, L.A., J.K. MacFarlane, A.P. Tcaciuc, and P.M. Gschwend. Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low density polyethylene strips. *Environ. Sci. & Technol.*, 43, 1430-1436, 2009.

Fernandez L.A., C.F. Harvey, and P.M. Gschwend. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. *Environ. Sci. Technol.*, 43, 8888-8894, 2009.

Fernandez L.A. "Polyethylene Passive Samplers for Measuring Hydrophobic Organic Chemical Concentrations in Sediment Porewaters and their Use in Predicting Bioaccumulation in Soft-Shell Clams (*Mya arenaria*) from Sites Near Boston, MA." PhD dissertation, Dept. of Civil and Environmental Engineering, MIT, Cambridge, MA. 190 pp. 2010.