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

by

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ABSTRACT

In order to determine the hazards posed by hydrophobic organic compounds (HOCs) in sediment beds, the following areas of research were explored: (1) the use of polyethylene (PE) sheets as passive sampling devices in sediments, using performance reference compounds (PRCs) in order to reduce deployment times to the order of days, (2) the use of limited PRC data to calibrate mass-transfer models for the exchange of a suite of compounds between polymer strips and sedimentary porous media, and (3) the use of *in-situ* passive sampling methods to deduce chemical activities of HOCs in sediments and the tissues of soft shelled clams (*Mya arenaria*) , in order to measure bioaccumulation potential.

First, the use of PE passive samplers, *in-situ*, to measure freely dissolved HOC concentrations, is demonstrated. PRCs, impregnated into the PE before use, allow porewater concentrations to be deduced after exposure times much shorter than would be required for sampler equilibration (days instead of months). Next, the method is expanded for measuring suites of compounds of the same class. A one-dimensional diffusion model of chemical exchange between a polymer sheet of finite thickness and an unmixed sediment bed is employed. Porewater concentrations for seventeen polycyclic aromatic hydrocarbons (PAHs) are measured using samplers deployed for 3 to 10 days in homogenized sediment from a coal-tar contaminated site.

Finally, the samplers are used to determine the potential for HOCs to bioaccumulate in *Mya arenaria* in sediments from six sites near Boston, MA. PE-deduced porewater PAH concentrations are compared to lipid-normalized tissue PAH concentrations in samples taken from twelve stations distributed throughout the sites. Additionally, tissue concentrations are compared to bulk sediment concentrations and porewater concentrations deduced from equilibrium partitioning models that include sorption to both organic carbon and black carbon fractions. Results show correlations only between PE-deduced porewater concentrations and tissue concentrations, illustrating the usefulness of PE passive samplers for gauging risk to benthic organisms associated with HOC contaminated sediments. Also, porewater concentrations estimated using equilibrium partitioning methods overestimated porewater concentrations by one to three orders of magnitude at all but one site.

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Special thanks are also extended to the members of the Gschwend Lab, past and present, and members of the Parsons "Supergroup" for sharing ideas, lending advice, and offering support.

Chapters 2 and 3 of this thesis are based on coauthored work. Chapter 2 coauthors are John MacFarlane, Alexandra Patricia Tcaciuc and Phil Gschwend. Chapter 3 coauthors are Charles Harvey and Phil Gschwend. Thanks are extended to Anne Giblin and Charles Hopkinson of the Marine Biological Laboratory, Wood Hole, MA for their assistance observing sampler deployment and collecting sediment cores in the field. Thanks also to Danny Reible (Univ. of Texas), Dave Nakles (ENSR), and Kathleen McDonough (ENSR) for providing sediment samples from Hunter's Point, CA, and Russ Boles (Division of Marine Operations, Univ. of Massachusetts, Boston) for piloting the boat during sampler recovery.

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Chapter 1: Introduction

Hydrophobic organic chemicals (HOCs) are present in most aquatic environments, often at high concentrations near urban centers, and may have significant negative effects on the ecology of those environments and on human health. Understanding the fate and biological availability of HOCs in different environmental systems is important for predicting their toxic effects to resident biota, and the risks they pose to humans. Among HOCs of environmental concern are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), low solubility pesticides, and dioxins. These largely anthropogenic compounds may enter waterways through runoff, atmospheric deposition, rainout, spills or direct dumping. HOCs accumulate in aquatic sediments due to their higher affinity for settling particles than the water phase (Eisenreich 1987; Fowler et al. 1989; Baker et al. 1991). Even as HOC inputs are reduced to surface waters through efforts to limit their discharges, sediments may remain a source of contamination to overlying waters and continue to affect organisms living within and above them (Zeng et al. 1998).

The broad extent of contaminated sediments underlying US waters illustrates the need for a system to rank sediments in order to focus remediation resources to those sites which pose the highest risks to environmental and public health. The United States Environmental Protection Agency (EPA) has identified 6.5% of the nation's river reaches as being areas where sediments would have probable or possible adverse affects on aquatic life or human health (U.S.EPA 2004b). Additionally, 35% of the country's estuarine areas have been described as degraded due to sediment contamination (U.S.EPA 2004a). These sediments vary widely in the type of

contamination (including HOC, heavy metal, and pesticide), contaminant concentrations, and in the physical and chemical properties of the sediments themselves.

A method of measuring the potential for HOCs to be transferred from sediments to other environmental compartments is necessary for prioritizing areas for remediation. For chemicals that strongly sorb to sediment solids, determining the chemical's potential to partition to biota is central to calculating the risk contaminated sediments pose to the natural environment and human health. The importance of this "bioavailability" in accurately calculating risk has driven decades of research into its definition and measurement; however, there has been little consensus on the topic (Ehlers and Loibner 2006). Of the many measures of bioavailability that have been proposed, freely dissolved porewater concentration, C_{PW}, and chemical activity, a, can be most clearly defined (not operationally defined fractions of the total concentration) and accurately measured (McGroddy and Farrington 1995; Ramos et al. 1998; Cornelissen et al. 2006; Reichenberg and Mayer 2006). C_{PW} and a are also very closely related. If one chooses a reference concentration for any chemical, i, as the saturated water concentration of that chemical's liquid in water, $C_{i,w}^{sat}(L)$, then a_i is the concentration of chemical i freely dissolved in the water, normalized to its reference concentration:

$$a_i = \frac{C_{i,PW}}{C_{i,w}^{sat}(L)} \tag{1.1}$$

There are several reasons why chemical activity may be a more convenient measure of sediment quality than C_{PW}. First, chemical activity in any equilibrated system will be equal in all phases of that system. If one can measure the concentration in any phase, while knowing the equilibrium partition constant between that phase and water, $K_{phase\text{-}w}$, then one can measure a in that system (Schwarzenbach et al. 2003):

$$a_i = \frac{C_{i,phase}}{K_{i,phase-w} C_{i,w}^{sat}(L)} \quad (1.2)$$

This makes the concept of chemical activity especially useful in complex systems such as sediments that contain many difficult-to-separate and characterize fractions. In systems that are not equilibrated, the chemical activities of different phases will be not be the same. One can know, however, that chemical mass will be transfered from the phases of higher activity to the phases of lower activity. Finally, others have shown that cumulative chemical activities of hydrophobic organic contaminants (HOCs), $\sum a_i$, of 0.1 to 0.01 correlate with narcotic toxicity effects for organisms living in air and water (Hansen et al. 2003; Reichenberg and Mayer 2006). Knowing the chemical activities of as many HOCs as possible would be very useful in trying to determine if a sediment will cause narcotic effects.

Passive sampling techniques have been sought for measuring C_{PW} and a of hydrophobic organic contaminants (HOCs) in sediments because of difficulties encountered using more traditional measurement methods. These difficulties include the need to account for HOC sorption to colloidal, and/or particulate organic material remaining in porewaters that have been physically separated from sediment solids through squeezing or centrifuging (Chin and Gschwend 1991). Other alternatives to direct porewater extraction, such as the application of equilibrium partitioning models (EqP), have their own limitations due to the need for accurate knowledge of fractions and partitioning coefficients for all major sorbents present in a sediment sample, including difficult-to-measure black carbon (BC) fractions (Accardi-Dey and Gschwend 2002; Accardi-Dey and Gschwend 2003).

Passive sampling tools are able to directly measure chemical activity in complex media, such as sediments, by taking advantage of the fact that, in equilibrated systems, a in any phase is equal to a in any other phase. Solid phase micro extraction (SPME) and polyethylene (PE) strips have been used to make *ex situ* measurements of sediment chemical activities by allowing the passive sampling tool to equilibrate with sediment samples (Mayer et al. 2000; Booij et al. 2003; Lohmann et al. 2004). In simpler systems, like the water column, performance reference compounds (PRCs) have been used in PE to allow for exposure times shorter than those that would be required for the sampler to reach equilibrium with their surroundings (Booij et al. 2002; Adams et al. 2007).

In this work, PRCs are used with PE strips deployed into the more complex systems of sediment beds. In Chapter 2 three PRCs (d10-phenanthrene, d10-pyrene, and d12-chrysene) are used to calibrate a mass transfer model allowing for the measurement of C_{PW} for six polycyclic aromatic hydrocarbons (PAHs) which match the PRCs in terms of diffusivities and partitioning coefficients (phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, and chrysene), in the sediments, after exposure times of just 3 to 14 days. The results of these measurements are compared with those made by directly extracting porewaters and correcting for particulate organic carbon in the water, and by measuring the sediment concentrations and using EqP models (organic carbon (OC) only and OC + BC).

Because it would be impractical to have to include a matching PRC for every chemical one would like to measure in porewaters, the PE-PRC method is expanded to allow the measurement of chemicals that do not match PRCs in terms of diffusivities and partitioning coefficients. In Chapter 3, the mass transfer model is refined to account for a no-flux boundary

at the center of the PE thickness. By doing so, three PRCs can be used to calibrate the model to allow for the measurement of C_{PW} for 17 PAHs after exposure times of up to 10 days.

Finally, in Chapter 4, PE strips are used to measure C_{PW} and a in intact sediment beds, and results are compared to concentrations and chemical activities measured in the tissues of *Mya arenaria* harvested from the same sediment. Correlations of chemical activities measured in porewaters and organism tissues from six sites near Boston, MA are compared with those obtained through the application of equilibrium partitioning models to sediment samples collected from the same sites. General conclusions and areas for future work are described in Chapter 5.

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Chapter 2: Measurement of freely dissolved PAH concentrations in sediment beds using passive sampling with low-density polyethylene strips

(based on work published in *Environmental Science and Technology* with John MacFarlane, Alexandra Patricia Tcaciuc and Philip Gschwend)

Abstract

In order to assess hydrophobic organic chemical (HOC) contamination in sediments, a method was developed using polyethylene (PE) passive samplers inserted directly in the intact sediment beds to measure freely dissolved HOC concentrations. Performance reference compounds (PRCs: d10-phenanthrene, d10-pyrene, and d12-chrysene), impregnated into the PE before use, allowed porewater concentrations to be deduced after exposure times much shorter than would be required for sampler equilibration (days instead of months). Using three diverse sediments in the laboratory, PE-deduced porewater concentrations of six native PAHs (phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, and chrysene) matched results from airbridge testing and from direct porewater extractions after correcting for colloid effects. PE strips, deployed from a boat in Boston Harbor, yielded concentrations that were like those measured in porewaters from a sediment core collected nearby. Notably, porewater concentrations estimated using an equilibrium partitioning (EqP) model were always much higher (up to 100x) than those measured using the other methods, suggesting the large inaccuracy of that approach.

Introduction

Sediment beds contaminated with hydrophobic organic compounds (HOCs) like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are widespread, and assessing the hazard they pose is problematic since the mobility and bioavailability of the HOCs is so uncertain. Such situations may be evaluated by quantifying the HOCs in the bed's porewater via modeling or measurement. Modeling approaches such as equilibrium partitioning (EqP, (Bierman 1990; Hansen et al. 2003)), normalize sediment concentrations using the relevant sorption coefficients, but these coefficients are still not known very well in many cases (DiToro et al. 1991; Accardi-Dey and Gschwend 2003; Hansen et al. 2003). Traditional techniques for measuring freely dissolved concentrations, C_{PW}, of HOCs in porewaters also present many challenges. Notably, the porewater must be separated through centrifugation, squeezing, or filtration while avoiding air contact, and then trace HOCs must be measured in relatively small water volumes. Colloidal matter must be removed (Hawthorne et al. 2005) or its effect on HOCs must be estimated (Chin and Gschwend 1991; McGroddy and Farrington 1995):

$$C_{PW} = \frac{C_W}{1 + [TOC] K_{OC}} \tag{2.1}$$

where C_W is the sum of both truly dissolved and colloid-bound species of compound in the porewater, $[TOC]$ is the concentration of colloidal organic carbon in the water (kg/L), and K_{OC} is the colloidal organic carbon-water partition coefficient (L/kg). Due to these complexities, neither modeling nor measuring has readily enabled accurate assessments of contaminated sediments.

In order to improve this situation, passive sampling methods have been developed to allow C_{PW} to be deduced from concentrations accumulated in an easily separable, and well

defined, synthetic phase. For example, semi-permeable membrane devices (SPMDs) have been used to measure HOCs in the water column for many years (Huckins et al. 1990); unfortunately their deployment disrupts sediments due to their protective cages. Solid-phase micro extraction fibers (SPMEs) and polyethylene (PE) strips have been equilibrated with sediment samples in the laboratory over periods of up to 60 days (Mayer et al. 2000; Booij et al. 2003b; Lohmann et al. 2004; Vinturella et al. 2004). Samplers made of polyoxymethylene (POM) and polydimethylsiloxane (PDMS) have been used *in situ*, equilibrating with sediments over periods of up to 119 days (Cornelissen et al. 2008). Hence, a variety of polymeric materials can be inserted into intact sediments and used to accumulate HOCs in proportion to their presence.

However, since these polymeric materials cannot be generally assumed to equilibrate within intact sediments, performance reference compounds (PRCs) are needed. PRCs have been used in passive samplers to shorten deployment times in the water column by allowing mass transfer coefficients to be gauged (Booij et al. 2002; Huckins et al. 2002; Adams et al. 2007). The same physical model was used by Tomaszewski and Luthy (Tomaszewsky and Luthy 2008) for PE inserted into sediments to measure total PCBs. Sediment systems, however, differ from the water column by not being well mixed. In this case one may need to consider transfer resistances in both the polymer and sediment. Therefore, in order to use PRCs accurately for sediments, a more complex mass transfer model is needed.

To advance the use of PE passive samplers in contaminated sediment beds, several activities were pursued. First, a diffusion model for compounds exchanging between PE and a porous medium (sediments) was developed and utilized to examine the factors controlling HOC uptake (and PRC release) by PE passive samplers. Next, replicate PE strips, containing deuterated PRCs, were deployed in the laboratory to assess C_{PW} of several target PAHs

(phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, and chrysene) after exposure times that were far too short to attain PE-sediment equilibration. The accuracy of the PE method was assessed using (a) concentrations measured in porewaters separated from sediment solids, (b) concentrations measured in waters equilibrated with sediments across an airbridge, and (c) concentrations measured in the sediments themselves when they were normalized according to the EqP approach (Hansen et al. 2003). Finally, a PE-carrying vehicle was constructed and deployed from a boat in Boston Harbor; and after a one-week incubation, the accuracy was checked by comparison with PAHs measured in porewaters from a nearby diver-recovered core.

Mass transfer model

A one-dimensional diffusion model was employed for deducing C_{PW} in sediment porewaters from PE deployments that were too short for PE-sediment equilibration. First, diffusion in a system consisting of two contacting media, a finite PE strip of thickness $2l$ and semi-infinite sediment on both sides was considered, following Fick's second law:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2}, \qquad -l < x < l \tag{2.2}$$

$$\frac{\partial C_{SED}}{\partial t} = D_{SED}\frac{\partial^2 C_{SED}}{\partial x^2}, \qquad x < -l \text{ and } x > l \tag{2.3}$$

where C_{PE} (mol/cm^3 of PE) and C_{SED} (mol/cm^3 of sediment) are concentrations in PE and sediments, respectively, D_{PE} (cm^2/s) is diffusivity within the PE, D_{SED} (cm^2/s) is diffusivity within the sedimentary porous medium, and t is time (s). Diffusivity within the sediments was

assumed to involve diffusion through the water-filled pores affected by the tortuous path and sorptive exchanges (Schwarzenbach et al. 2003):

$$D_{SED} = \frac{1}{1 + r_{sw} K_d} \frac{D_W}{\tau} \tag{2.4}$$

where r_{sw} is the solid-to-water phase ratio (g solid/cm^3 water), K_d is the sediment-water partition coefficient (C_{sed}/C_{PW}), D_W is the diffusivity in water (cm^2/s), and τ is tortuosity. At the PE-sediment interfaces, partitioning equilibrium was assumed:

$$\frac{C_{PE}}{C_{SED}} = K_{PESED}, \qquad \text{at } x = l \text{ and } x = -l \text{ for } t > 0 \tag{2.5}$$

and fluxes into and out of the contacting media were set equal:

$$D_{PE} \frac{\partial C_{PE}}{\partial x} = D_{SED} \frac{\partial C_{SED}}{\partial x}, \qquad \text{at } x = l \text{ and } x = -l \tag{2.6}$$

Since the problem is symmetrical, we also assume a no-flux condition at x=0. Crank (1975) gave an analytical solution across a boundary between two semi-infinite media with different diffusivities and partitioning coefficients. Hence, if initially $C_{SED}(x, t=0) = C^0_{SED}$ (mol/cm^3) for all $x > l$, and $C_{PE}(x, t=0) = 0$ (mol/cm^3) for $0 < x < l$, then for suitably short times ($t << l^2/D_{PE}$):

$$C_{SED}(x,t) = \frac{C^0_{SED}}{1 + K_{PESED}(D_{PE}/D_{SED})^{1/2}} \left[1 + K_{PESED}(D_{PE}/D_{SED})^{1/2} \operatorname{erf}\left(\frac{x - 1}{2 D_{SED}^{1/2} t^{1/2}} \right) \right] \tag{2.7}$$

$$C_{PE}(x,t) = \frac{K_{PESED} C^0_{SED}}{1 + K_{PESED}(D_{PE}/D_{SED})^{1/2}} \operatorname{erfc}\left(\frac{|x - 1|}{2 D_{PE}^{1/2} t^{1/2}} \right) \tag{2.8}$$

Integrating over x, the HOC and PRC masses that have crossed the boundary per unit area are:

$$M_{HOC}(t) = 2\left(\frac{t}{\pi}\right)^{1/2} \frac{K_{PESED} C^0_{HOC,SED}}{1/D_{PE}^{1/2} + K_{PESED}/D_{SED}^{1/2}} \tag{2.9}$$

and $$M_{PRC}(t) = 2\left(\frac{t}{\pi}\right)^{1/2} \frac{C^0_{PRC,PE}}{1/D_{PE}^{1/2} + K_{PESED}/D_{SED}^{1/2}} \quad (2.10)$$

This short-term solution contains a time-dependent, but initial-concentration-independent, expression for mass transfer that is a function of diffusivities and partitioning:

$$k = 2\left(\frac{t}{\pi}\right)^{1/2} \frac{1}{1/D_{PE}^{1/2} + K_{PESED}/D_{SED}^{1/2}} \quad (2.11)$$

Depending on the diffusate and sediment properties, it is possible for either the PE or sediment side to dominate this term. Because D_{PE}, D_{SED}, and K_{PESED} can be assumed virtually equal for a given deuterated PRC and its corresponding non-deuterated target compound, we can use Eqs. 2.9 and 2.10 to find:

$$C^0_{HOC,SED} = \frac{M_{HOC}(t)}{M_{PRC}(t)} \frac{C^0_{PRC,PE}}{K_{HOC,PESED}} \quad (2.12)$$

and since $K_{HOC,PESED}$ is equal to $K_{HOC,PEW}/K_{HOC,d}$, where K_{PEW} is the polyethylene-water partition coefficient (L_{PE}/L_W), we find:

$$C_{HOC,PW} = \frac{M_{HOC}(t)}{M_{PRC}(t)} \frac{C^0_{PRC\,PE}}{K_{HOC,PEW}} \quad (2.13)$$

Thus, measuring the changes in target and PRC concentration in the PE, one can deduce $C_{HOC,PW}$ in porewaters. For longer times (i.e., when $C_{HOC,PE} \neq 0$ at x = 0), Eq. 2.13 is still accurate based on tests using a finite difference model (Appendix A).

Materials and Methods

All solvents were Baker Ultraresi-analyzed (Philipsburg, NJ, USA). Laboratory water was treated with an ion-exchange and activated carbon system (Aries Vaponics, Rockland, MA,

USA) until 18 MOhm-cm resistance was achieved. All PAH standards were purchased from Ultra Scientific in methanol, acetone, or dichloromethane (North Kingston, RI, USA).

Polyethylene strips were prepared from low-density polyethylene (PE) sheets (Trimaco, Durham, NC, USA). PE was soaked twice in dichloromethane for 24 hr and twice in methanol for 24 hr, before soaking twice in water for 24 hr. PE was then placed in water containing the PRCs and equilibrated 6 months. Modeling indicated that 2 months would be sufficient to achieve an initially even distribution of PRCs throughout the PE thickness.

Water, PE, and sediment extractions

Water samples 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. 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.

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. Swabbing and exposure to laboratory air is not expected to affect absorbed PAH concentration in PE based on tests using multiple swabs and solvents (Appendix B). Strips were then cut into approximately 2 cm sections, surrogate standards were added, and then they 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 GCMS analysis.

Dried (60 °C for 24 hr) 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.

All extracts were analyzed using gas chromatography-mass spectrometry (GCMS, JEOL GCmate, 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 305 °C. The column temperature began at 70 °C and was raised 20 °C/min until a temperature of 180 °C was reached, the temperature was then raised 6 °C/min until a temperature of 300 °C was reached, and remained there for 7.5 min. The MS was operated in selected ion monitoring (SIM) and EI+ modes. A standard mixture containing 25 aromatic compounds including each of the PRCs, target compounds, surrogates and internal standards used in this study, was run every 3 to 5 sample measurements to monitor instrument stability, determine response factors, and confirm measurements remained in the linear range for the instrument. Repeated measurements (n=6) of the calibration standard indicated the measurement uncertainty for the instrument was typically between 3% and 9% relative error for the PAHs used in this study. Percent recoveries for the surrogate standards (± 1 RSD) were: (a) 77 ±15% to 82 ±13% for PE extracts, (b) 57 ±16% to 74 ±11% for porewater, and (c) 57 ±21% to 79 ±19% for sediments. PRC and target compound concentrations were corrected for recoveries of the corresponding closest-eluting surrogate standard.

K_{PEW} for 25μm thick PE

As sorptive properties of PE have been observed to vary (Adams et al. 2007), K_{PEW} (21 °C) values specific to the PE used in this study were measured for 13 parent and alkylated PAHs and 16 PCBs (Table 2.1). K_{PEW} (in L_W/kg_{PE} for the remainder of this chapter) for each compound, *i*, was calculated from one to five water measurements and four to six PE measurements. Propagating the error (one standard deviation) on the PE and water measurements resulted in an uncertainty of ±13% (or a little less than ±0.1 log units) on each measured K_{PEW}. K_{PEW} values measured for two PE batches were the same within uncertainty.

K_{PEW} values were adjusted for temperature and salinity in each experiment as described by Adams et al. (2003). The salt concentration of the porewaters at our test sites was assumed to be 0.4 M as typical for the overlying estuarine water. For laboratory testing, the temperature of sediment samples was 21 °C. Although sediment temperature was not measured at the Boston Harbor field site at the time of collection, previous investigators reported sediment temperature there to be 17 °C in August (measured in 1992, 93, and 94) (Nowicki et al. 1997), and this value was used since the water temperature at the time of deployment was 16 °C.

Carbon analyses

Total organic carbon (TOC) in the water samples was measured using a Shimadzu TOC 5000 analyzer (Shimadzu Scientific Instruments, Colombia, MD, USA). Samples were acidified with phosphoric acid (Phosphoric Acid GR, EM Science, Gibbstown, NJ, USA) to a pH of 2 and sparged with TOC grade air (Airgas, Radnor, PA, USA) until TOC measurements stabilized.

Dried (60 °C for 24 hr) and ground sediment sub-samples (~10 mg each) were analyzed for their mass fractions of organic carbon (OC) and black carbon (BC) using a CHN elemental

analyzer (Vario EL III, Elementar, Hanau, Germany). BC sub-samples were pre-combusted, under excess air, at 375 °C for 24 hr to remove the OC fraction (Gustafsson et al. 1997). Subsequently, OC and BC sub-samples were acidified with 0.35 M sulfurous acid (H_2SO_3) (Baker Analyzed, Philipsburg, NJ, USA) to remove carbonates and dried at 60 °C for 24 hr before CHN analysis. The total carbon fraction (f_{OC}), including both OC and BC, was taken to be the non-pre-combusted, acidified, carbon fraction. The black carbon fraction (f_{BC}) was taken to be the fraction remaining in samples after pre-combustion and acidification (Table 2.2).

Sampling sites

To avoid variability due to natural heterogeneity in the sediment beds, sediment samples were collected and thoroughly homogenized before use (Table 2.2). Two samples were collected from 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 these sites, approximately 40 L of sediments were collected from just above the low tide lines. In the lab, each sample was homogenized in a large galvanized steel tub by mixing with a metal hoe for 1 hr. Approximately 20 L of the homogenized sediments were transferred to cylindrical, seamless, glass tanks. 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 from a third site near a former navy ship yard were collected by colleagues at the Univ. of Texas (D. Reible) from Hunter's Point (HP), San Francisco Bay, homogenized by colleagues at ENSR (D. Nakles & K. McDonough), and sent to us in 1 L jars on ice. Sediments and water were allowed to sit undisturbed in the laboratory tanks for 1 to 2 weeks before PE strips were inserted using PE

frames (Figure 2.1). In the case of HP, PE was inserted into the sediments using stainless steel forceps after the jars had equilibrated with lab temperature (21 °C). Samplers were removed from the IE sediments after 3 days and from DB and HP sediments after 7 days. It was assumed that there was no significant biodegradation over these sampling periods. Following PE retrieval, surface waters were then siphoned out of the tanks; sediments were scooped out and centrifuged (30 to 60 min at 900g) 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.

PE deployment frames and platform

Frames were constructed to hold the PE, allowing strips to be inserted into the sediments while only minimally disturbing the bed. Aluminum sheet metal (1.27 mm thick) was cut to form two "E-shaped" plates, between which the PE was held (Figure 2.1). PE was secured in place, between the two plates, at the top and bottom of the frame, by machine screws. The frames allowed exposure of the PE on two sides, with a lower window of PE inserted to a depth of 16 cm into the sediments, and a second window exposing the PE to the water above the sediment-water interface.

A deployment vehicle (Figure 2.1), which could hold two PE frames, was constructed of aluminum angle bar. The large footprint (24 in. x 18 in.) was designed so that the vehicle would not sink into soft sediments. Rods on either end of the sampler can accommodate 50 lbs of removable weight to aid penetration into stiff sediments. For deployment at a relatively sandy site near the mouth of Boston Harbor, the sampler carried 30 lbs of iron weights.

Airbridges

Airbridges (van Wezel et al. 1996; Bucheli and Gustafsson 2000) were assembled using 2-L glass desiccators with ground glass lids (without 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 clean water (Figure 2.2). To maintain sediment anoxia, the headspace in the 2-L jar 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.

Results and Discussion

Modeling results

A finite-difference model for the transfer of chemicals between PE and sediments was used to examine the use of PRCs (Appendix A). Assuming reasonable values for diffusivity and partitioning parameters for a compound like pyrene in a sediment like that at the DB site (D_{PE} from Adams (2003), D_{SED} calculated following Schwarzenbach et al. (2003) assuming $K_d=10^{4.1}$, $D_W=6\text{x}10^{-6}$ cm^2/s, porosity=0.7, and tortuosity=2), the mass transfer model indicates the fractional uptake of pyrene from the sediment and fractional release of the d10-pyrene PRC from the PE are both 50% after 75 hr (Figure 2.3). The fractions continue to match when the model is run for shorter or longer times.

Next, the model was used to ascertain the accuracy of using a single-resistance to calibrate mass transfer. While the model showed that HOCs approach equilibrium in order of

increasing molecular weight, it also showed that diffusion in the polyethylene becomes less rate-limiting for larger HOCs, as implied by Eqn 2.11, when the second term in the denominator begins to dominate the mass transfer resistance. Testing the modeled results against a single resistance exponential model with a molar volume adjustment (Booij et al. 2003a; Tomaszewsky and Luthy 2008) indicated that using d10-phenanthrene to calibrate for the mass transfer of larger chemicals, pyrene and chrysene, would lead to C_w values that are 40% and 60% too low, respectively. This indicates that molar volume adjustments are not sufficient to account for large differences in diffusivities of PRC and target chemical in both polymer and porous medium.

Finally, the model was employed to optimize use of PE in the sediment. Concentration profiles for the d10-pyrene PRC as a function of position, x, show the fractional approach to equilibrium slows with time (Figure 2.3). After 75 hr, half the mass of this PRC has left the PE and diffused about 300 μm into the sediment. To halve the remaining PRC load in the PE (reach 75% loss of PRC) required an additional 410 hr (17 d), and to halve it again (reach 87.5% loss) would take about another 1800 hr (75 days). In each case, the model indicated the PRC diffused less than 0.1 cm into the adjacent sediment bed. As fractional pyrene accumulation matches fractional PRC loss in PE, the model also illustrated how longer exposure times allowed only modest additional pyrene "signal" to be acquired. Longer exposures, therefore, offer little benefit for subsequent chemical analysis while making recovery of sampling apparatus less likely. Using site-specific information, the model suggested that, after an exposure of 3 days in IE sediments and 7 days in DB sediments, phenanthrene would be more than 80% equilibrated, pyrene would be 60 to 70% equilibrated, and chrysene would only be 30 to 50% equilibrated (Figures 2.4 and 2.5). In light of such expectations, PE exposure times could be chosen so as to

ensure seeing statistically significant decreases in d12-chrysene (the slowest exchanging PRC) in the PE strips.

K_{PEW} for 25μm thick PE

Despite differences in manufacturer and sheet thickness, K_{PEW} in this work matched those measured by Adams et al. (2007) (Table 2.1) for phenanthrene, fluoranthene, and 2,2',5,5'-tetrachloro biphenyl. Adjusting for temperature, K_{PEW} for phenanthrene and fluoranthene are also in agreement with those seen by Booij et al. (2003a). Phenanthrene's K_{PEW} also matched that measured by Huckins et al. (1993). Differences, however, were observed for other PAHs with those determined by Adams et al. (2007) (pyrene, benz(a)anthracene, and chrysene), and Booij et al. (2003a) (pyrene and chrysene), and for the one PCB measured by Huckins et al. (1993) (2,2',5,5'-tetrachloro biphenyl). Because it is possible that differences in manufacturing process and laboratory handling could change a particular PE (e.g., its crystallinity) and thereby affect K_{PEW}, it is recommended that K_{PEW} be evaluated for any PE source before it is used for passive sampling.

As noted previously (Adams et al. 2007), K_{PEW} values increase with HOC hydrophobicity (Table 2.1). To enable estimates of new K_{PEW} values, measured log K_{PEW}s were compared to corresponding log K_{OW}s (Figure 2.6). K_{OW} values for PAHs were from Sangster (1989), while K_{OW} for PCBs were from Hawker and Connell (1988). As expected, the K_{PEW} values were of similar magnitudes as the corresponding K_{OW}s. When all compounds were considered together, $\log K_{PEW} = 0.97 (\pm 0.06) \log K_{OW} - 0.05 (\pm 0.35)$, $R^2=0.91$, where uncertainties are one standard deviation.

Dynamic range and detection limits of PE strips as passive samplers

Freely dissolved concentrations of PAHs in the three homogenized sediments were observed using PE to range over five orders of magnitude (Figure 2.7). As expected, since it is a coal-tar affected site, IE porewaters had the highest freely dissolved PAH concentrations (up to 5200 ng/L for fluoranthene). In contrast, DB and HP porewaters had much lower porewater PAHs (down to 0.1 ng/L for benz(a)anthracene). Uncertainty in the measurements ranged from 16% to 45% based on propagating one standard deviation of the measurements in each of six sampler sections through calculations for C_{PW}.

Detection limits of the method depend on the size of PE sections analyzed. In this study, approximately 30 mg pieces of 25-μm thick PE were used. With samplers of this size, it would have been possible to see down to 3 ng/g PE using GCMS analysis of 100 μL extracts. This translates to being able to measure PAH concentrations in porewaters near picograms per liter (1 pg/L for a PAH like benzo(a)pyrene). Smaller concentrations could be measured using larger sections of PE.

Use of PRCs to estimate equilibrium HOC uptake by PE and comparison to equilibrated (tumbled) PE

To test the effectiveness of the PRCs for estimating target compound equilibrium concentrations, sediments from Island End were also tumbled with PE until equilibrium was reached as described elsewhere (Lohmann et al. 2004). Three sub-samples (~100 g wet wt) of IE sediments were mixed with 150 mL of 0.5 M sodium chloride solution, and 20 mg pieces of PE, in 250 mL round-bottom flasks and placed on a tumbling apparatus for 2 weeks. Previous time series tumbling experiments have shown that IE sediments and PE in this ratio were equilibrated,

in terms of PAHs of molecular weight 178 to 228, in less than 2 weeks. After tumbling, the PE, sediments, and porewaters were separated and extracted. In parallel, a strip of PE was inserted into a bed of this same sediment sample for 2 weeks, a time that is not sufficient to equilibrate, before being removed and extracted.

Use of Eqn. 2.13 to calculate $C_{equil,PE}$ (= C_{PW} * K_{PEW}) was confirmed by comparing $C_{equil,PE}$ measured in PE tumbled to equilibrium for IE sediments and $C_{equil,PE}$ deduced from the $C_{t,PE}$ and fraction of PRC loss in each case (Figure 2.8). Four sub-samples of PE exposed to sediments in a jar had concentrations of 3 (± 2) $\mu g/g_{PE}$, 55 (± 3) ug/g_{PE}, and 10 (± 2) $\mu g/g_{PE}$ for phenanthrene, pyrene, and chrysene, respectively. PE tumbled to equilibrium with sediments, however, had concentrations of 2 (± 0.3) $\mu g/g_{PE}$, 99 (± 17) $\mu g/g_{PE}$, and 25 (± 5) $\mu g/g_{PE}$, for the same three HOCs, respectively. When the concentrations in each sub-sample were divided by the fraction of PRC lost from each section, the calculated equilibrated concentrations were 4 (± 2) $\mu g/g_{PE}$, 89 (± 6) $\mu g/g_{PE}$, and 23 (± 5) $\mu g/g_{PE}$, respectively. Hence, within error the fully equilibrated PE and the PRC-corrected PE-insertion results were the same concentrations.

Correcting extracted porewater concentrations for colloidal TOC effects

Freely dissolved concentrations deduced from PE measurements were first compared to concentrations measured in waters that had been separated from sediment solids for each of the three samples using a centrifuge (Figure 2.9). These "raw" porewater concentrations, C_W were all higher than the PE-deduced C_{PW}, sometimes by more than an order of magnitude. Others have observed similarly higher-than-expected porewater concentrations and have shown that colloidal organic carbon, which is not separated from water when centrifuged, carried sorbed

chemicals (Chin and Gschwend 1992; McGroddy and Farrington 1995). Since PAHs that are sorbed to organic carbon are not "freely dissolved", it is necessary to correct for this sorbed fraction. Because of the labor involved in alum flocculation, and out of concern that sorption properties of flocs may be different from the naturally present colloids (Hur and Schlautman 2004), we used a TOC correction method (Eqn 2.1) to calculate the freely-dissolved concentrations. TOC-corrected C_{PW}, came much closer to matching PE-deduced C_{PW} than C_W, but had large uncertainties (Figure 2.7). Most of the uncertainty in TOC-corrected C_W is due to uncertainty in the K_{OC} value used in its calculation. K_{OC} values have been reported by many researchers for different types of OC found in natural waters and sediments (both particle-associated OC and humic materials) (Karickhoff 1981; Landrum et al. 1984; Chin and Weber 1989; Eadie et al. 1990; Chin and Gschwend 1992; Chiou et al. 2000; Perminova et al. 2001; Hawthorne et al. 2005). Wide variation in these reported K_{OC} values (by up to a factor of five) is likely due to compositional differences in the various types of organic matter involved. In this work, we used K_{OC} values reported by Karickhoff 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. For phenanthrene, anthracene, fluoranthene, and pyrene, the Karickhoff values fall within the mid-range of reported values. For benz(a)anthracene, and chrysene, the Karickhoff values are at the high end of the range of reported values.

In order to check the appropriateness of using Karickhoff K_{OC} values at the IE site, which was affected by coal tar, a fluorescence quenching (FQ) experiment was performed to test pyrene sorption to the porewater colloids (Gauthier et al. 1986; Backhus and Gschwend 1990; Chin and Gschwend 1992; Schlautman and Morgan 1993; Perminova et al. 2001). The K_{OC} needed to fit the quenching data, assuming 100% quench on sorption, closely matched the Karickhoff value

for pyrene. So these values were applied for the rest of the experiment, but the reader is cautioned that such values may still be inaccurate for other cases.

Comparison of porewater and airbridge concentrations with PE-deduced C_{PW}

In general, either TOC-corrected C_{PW} or airbridge-measured C_W matched PRC-corrected PE-deduced C_{PW} within uncertainty across five orders of magnitude, implying the PE passive samplers were yielding accurate results. Within uncertainties, TOC-corrected porewater concentrations always matched PE-deduced C_{PW}, for the six PAHs in all three sediments (Figure 2.7). Most of the uncertainty in TOC-corrected C_{PW} was due to uncertainty in the K_{OC} value used in its calculation. Freely dissolved concentrations were also measured using an airbridge method (Bucheli and Gustafsson 2000; Hong et al. 2003) (Figure 2.10). In general, the rate at which the HOCs equilibrated across the airbridge decreased in order of molecular weight, with the light chemicals equilibrating before heavier ones (Figure 2.11). All six PAHs from each of the sediment slurries had equilibrated with the water side by approximately 30 days. Water concentrations agreed, within uncertainty, with PE-deduced C_{PW} for IE and HP samples. The DB airbridge C_W values, however, were greater than PE-deduced C_{PW} by about a factor of five on average. It is possible that the DB results suffered from a modest PAH carryover in the Teflon seal from the previous use of the equipment for the IE coal-tar sediments.

Of particular interest, are the results from IE site. As noted, these sediments are from a coal-tar contaminated sediment and were swabbed to remove a dark residue from some sections of the PE (Appendix B). On those sections PRCs and target chemical were exchanging with, and possibly across, an additional phase (not just PE and bulk sediment). Resulting equivalent chemical activities in PE and porewater indicate that the mass-transfer model also works for

exchange of chemical between PE and coal tar (which is also equilibrated with porewater), and/or between PE and bulk sediment, across an additional phase (coal-tar film). As both PRCs and target chemicals have to cross any film coating the PE, additional, thin, diffusive layers are not expected to interfere with application of the PRC-correction method.

Use of equilibrium partitioning models and sediment concentrations to estimate HOC concentrations truly dissolved in porewater

Because of the difficulty involved in sampling sediment porewaters, the current practice for measuring HOC contamination of sediments is to measure sediment concentrations and apply an equilibrium partitioning (EqP) model to estimate C_{PW} (Hansen et al. 2003). The EqP model currently recommended by the EPA only includes partitioning to the organic carbon fraction of sediments.

$$C_{PW} = C_{SED} / K_d \tag{2.14}$$

where

$$K_d = f_{OC} K_{OC} \tag{2.15}$$

Other researchers have shown the importance of including additional sorptive phases to EqP models including black carbon (Accardi-Dey and Gschwend 2003; Cornelissen et al. 2005; Lohmann et al. 2005; Khalil and Ghosh 2006).

To assess the efficacy of the EqP approach at our study sites, OC and BC fractions, f_{OC} and f_{BC}, were measured in IE, DB and HP sediments (Table 2.2). These data were used along with measured C_{SED} in EqP models to calculate C_{PW} in the three sediments for phenanthrene, pyrene, and chrysene (Figure 2.12). The EqP model results for C_{PW} were consistently much higher than PE-deduced C_{PW} values for the three compounds, sometimes by more than two

orders of magnitude. For only one chemical in one sediment did the modeled C_{PW} match the PE-deduced C_{PW} within uncertainty, pyrene in IE sediment. This site had high f_{OC} (0.24, compared to 0.004 in DB). It is possible that much of what was included in f_{OC} was pitch. Khalil et al. measured similar fractions of pitch at other manufactured gas plant sites, and measured partitioning relationships between pitch and water that were between those observed for ordinary OC and BC. Generally, the EqP model performed poorly in sediments that were both relatively clean (DB) and relatively dirty (IE).

Finally, black carbon measurements were included into the EqP model (Accardi-Dey and Gschwend (Accardi-Dey and Gschwend 2002)):

$$K_d = f_{OC} K_{OC} + f_{BC} K_{BC} C_W^{n-1} \quad (2.16)$$

where K_{BC} is the black carbon-water partitioning coefficient, and n is the Freundlich exponent (we assumed 0.7 following Lohmann et al.). Although there is still substantial uncertainty in the BC-sorption parameters, including BC in the EqP model brought the calculated C_{PW} much closer to the PE-deduced C_{PW} for all three compounds (Figure 2.12). Clearly, efforts to use sediment concentrations to deduce truly dissolved porewater concentrations requires a better understanding of K_d values than is given by the $f_{OC} K_{OC}$ model.

Field trial in Boston Harbor

PE-deduced C_{PW} in the Boston Harbor sediments were like those at the DB site (Figure 2.13). TOC-corrected C_{PW} were slightly higher, for every PAH measured, when compared to C_{PW} deduced using the PE method. This may be due to the error associated with the TOC

corrections for colloids. But since the PE and sediment core were not co-located, these differences may simply reflect heterogeneity of harbor sediments. This trial confirmed that PE could be carried by a vehicle, dropped from the side of a boat into stiff, low OC sediments, and easily retrieved for analysis after a 1-week exposure.

Of the three methods used to measure or deduce C_{PW} (TOC-corrected C_{PW}, airbridge-measured C_W, and PE-deduced C_{PW}), PE strips were the easiest tool to use in estimating freely dissolve PAH concentrations. Porewater measurement at the field site required divers to collect and cap a core before bringing it to the surface. Once in the laboratory, the sediment core required careful (e.g., redox protective) and time consuming handling to prevent changes in partitioning between phases. In addition, centrifuging 0.4 L of sediments produced only 62 mL of porewaters that could be solvent extracted and measured for TOC content. The airbridge measurement technique required very careful handling of the apparatus and long experiment duration with multiple subsamples in order to confirm equilibrium was reached.

In contrast, PE strips can probe *in situ* sediments while minimally disturbing the system. Samplers can be deployed and retrieved from the side of a boat by a single person. The strips can then be extracted and analyzed within a single day. Although the field site was strewn with cobbles, divers confirmed that the frames penetrated the sediments and strips were intact when the sampler was recovered. The PE sheeting used in this experiment was inexpensive and easy to handle, which would allow for many probes to be deployed in the same area in order to assess the vertical and lateral extent of contamination at a site. Each strip provided multiple samples that allowed us to collect statistical information regarding probe performance, and by deploying the strip across the bed-water interface, we could easily assess the gradients driving bed-to-water

column transfers. In summary, we believe PE passive samplers with PRCs to be a simpler option for sediment assessment than current practices, and could provide a more detailed picture of HOC contamination in sediments.

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Table 2.1. Partition coefficients for selected PAHs and PCBs, polyethylene-water (K_{PEW}), octanol-water (K_{ow}), organic carbon-water (K_{OC}), and liquid-chemical water solubility (C_w^{sat}(L)).

Compound	log K_{PEW}[a]	log K_{ow}	log K_{oc}[d]	- log C_W^{sat}(L)[e]
PAHs				
phenanthrene	4.3 ± 0.1	4.52[b]	4.17	4.8
1-methyl phenanthrene	4.7 ± 0.1	5.08[b]		
3,6-dimethyl phenanthrene	5.2 ± 0.1			
anthracene	4.3 ± 0.1	4.50[b]	4.28	3.8
2-methyl anthracene	5.0 ± 0.1	5.07[b]		
9,10-dimethyl anthracene	5.3 ± 0.1	5.69[b]		
fluoranthene	4.9 ± 0.1	5.20[b]	4.83	5.4
pyrene	4.7 ± 0.1	5.00[b]	4.73	5.3
benz(a)anthracene	5.5 ± 0.1	5.91[b]	5.50	6.3
chrysene	5.5 ± 0.1	5.86[b]	5.40	6.1
benzo(b)fluoranthene	6.3 ± 0.1	5.78[b]		
benzo(k)fluoranthene	6.3 ± 0.1	5.78[b]		
benzo(a)pyrene	6.4 ± 0.1	6.35[b]		
PCBs				
2,2',5 trichloro biphenyl (#18)	4.9 ± 0.1	5.24[c]		
2,4,4' trichloro biphenyl (#28)	5.4 ± 0.1	5.67[c]		
2,2',3,5 tetrachloro biphenyl (#43)	5.5 ± 0.1	5.75[c]		
2,2',5,5' tetrachloro biphenyl (#52)	5.5 ± 0.1	5.84[c]		
2,3',4,4' tetrachloro biphenyl (#66)	5.9 ± 0.1	6.20[c]		
2,2',4,5,5' pentachloro biphenyl (#101)	6.2 ± 0.1	6.38[c]		
2,3,3',4,4' pentachloro biphenyl (#105)	6.3 ± 0.1	6.65[c]		
2,3,3',4',6 pentachloro biphenyl (#110)	6.1 ± 0.1	6.48[c]		
2,3',4,4',5 pentachloro biphenyl (#118)	6.4 ± 0.1	6.74[c]		
2,2',3,3',4,4' hexachloro biphenyl (#128)	6.5 ± 0.1	6.74[c]		
2,2',3,3',4,5 hexachloro biphenyl (#129)	6.6 ± 0.1	6.73[c]		
2,2',3,4,4',5' hexachloro biphenyl (#138)	6.6 ± 0.1	6.83[c]		
2,2',4,4',5,5' hexachloro biphenyl (#153)	6.4 ± 0.1	6.92[c]		
2,2',3,3',4,4',5 heptachloro biphenyl (#170)	6.9 ± 0.1	7.27[c]		
2,2',3,4,4',5,5' heptachloro biphenyl (#180)	7.0 ± 0.1	7.36[c]		
2,2',3,4',5,5',6 heptachloro biphenyl (#187)	7.1 ± 0.1	7.17[c]		

[a] K_{PEW} for 25 μm thick PE (Trimaco, Inc.) (L_w/kg_{PE})

[b] from Sangster (1989) (L_w/L_O)

[c] from Hawker and Connell (1988) (L_w/L_O)

[d] from Karickhoff (1981) (L_w/kg OC)

[e] calculated from $C_w^{sat}(s)$ values using $C_w^{sat}(L) = C_w^{sat}(s)\, e^{\Delta fusG/RT}$ as given in Schwarzenbach et al. (2003) for (25 degC) (in mol/L). $C_w^{sat}(s)$ values also from Schwarzenbach et al. (2003)

Table 2.2. Sampling locations including site descriptions, OC and BC fractions, and sediment concentrations (ng/gdw).

Station	site description	f_{OC}[a]	f_{BC}	C_{SED} phenanthrene	C_{SED} pyrene	C_{SED} chrysene
Dorchetser Bay (DB) Quincy, MA	42° 17.90' N/ 71° 01.02'W suburban harbor, clamming bed	0.0040/ 0.0047 (n=2)	0.0004 (n=1)	79 ± 23 (n=3)	41 ± 12 (n=3)	48 ± 26 (n=3)
Island End (IE) Chelsea, MA	42° 23.39' N/ 71° 03.17' W urban harbor, former manufactured gas plant	0.24 ±0.02 (n=4)	0.09 ±0.01 (n=4)	52,000 ± 28,000 (n=3)	156,000 ± 43,000 (n=3)	95,000 ± 41,000 (n=3)
Hunter's Point (HP) San Francisco, CA	urban harbor, naval shipyard	0.030 ±0.007 (n=3)	0.016 ±0.004 (n=4)	110 / 150 (n=2)	670 / 240 (n=2)	800 / 160 (n=2)
outer Boston Harbor (BH) off Long Island, Boston, MA	42° 19.85' N/ 70° 57.72' W across channel from former sewage outfall	0.016[b]	-			

[a] includes measured OC and BC

[b] Tucker et al. 2007, f_{BC} not measured separately

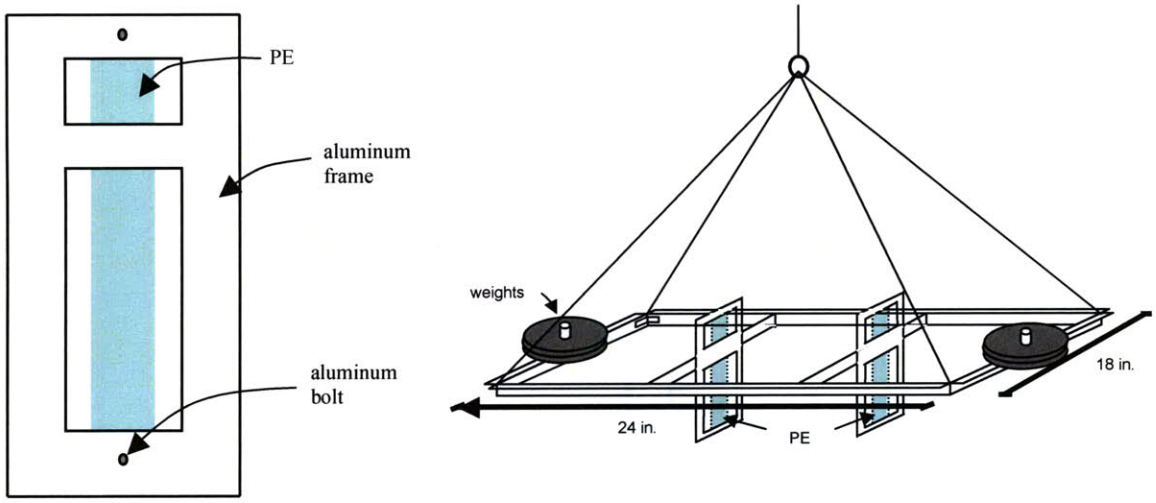

Figure 2.1. PE holder and deployment vehicle.

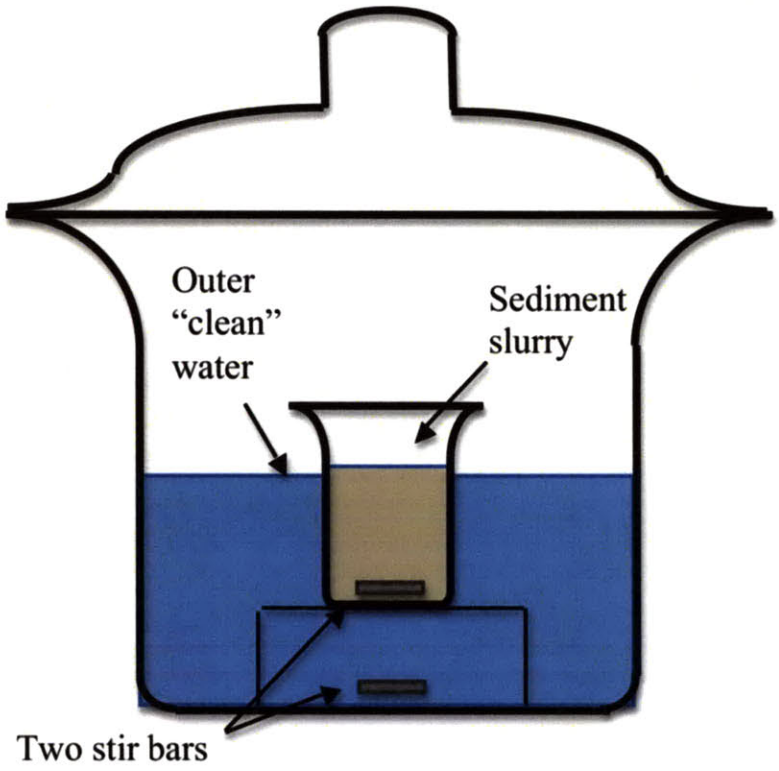

Figure 2.2. Airbridge diagram.

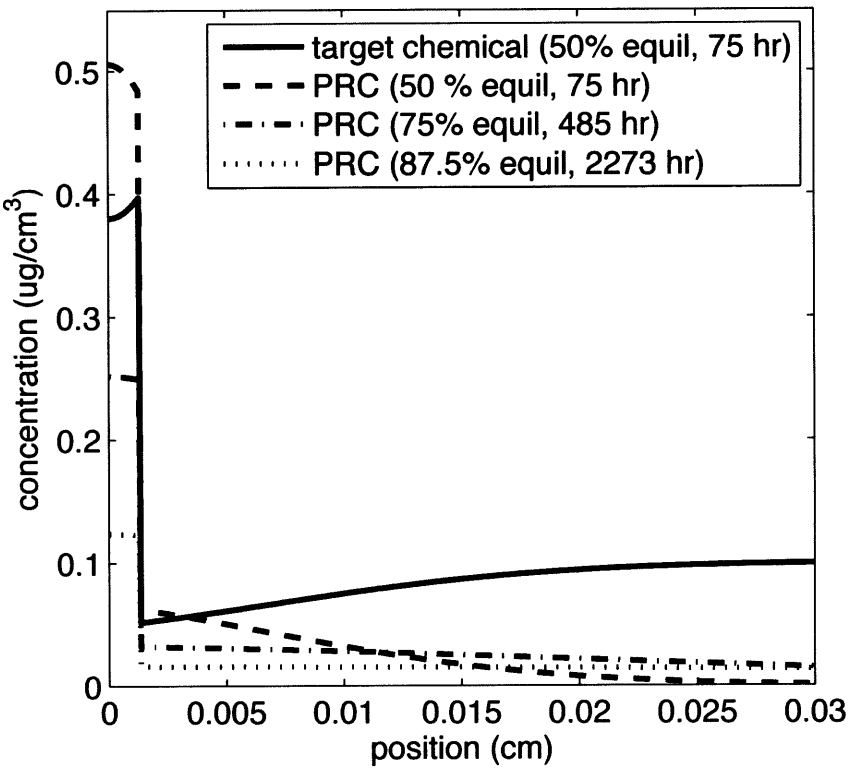

Figure 2.3. Spatial profiles of a representative PRC (d10-pyrene) and its corresponding target chemical diffusing between PE and Dorchester Bay sediments ($C^0_{PE,PRC}$=1, $C^0_{SED,target}$=0.1, $C_{equil,PE,PRC}$=0, $C_{equil,PE,target}$=0.77) obtained by numerical modeling (Appendix A).

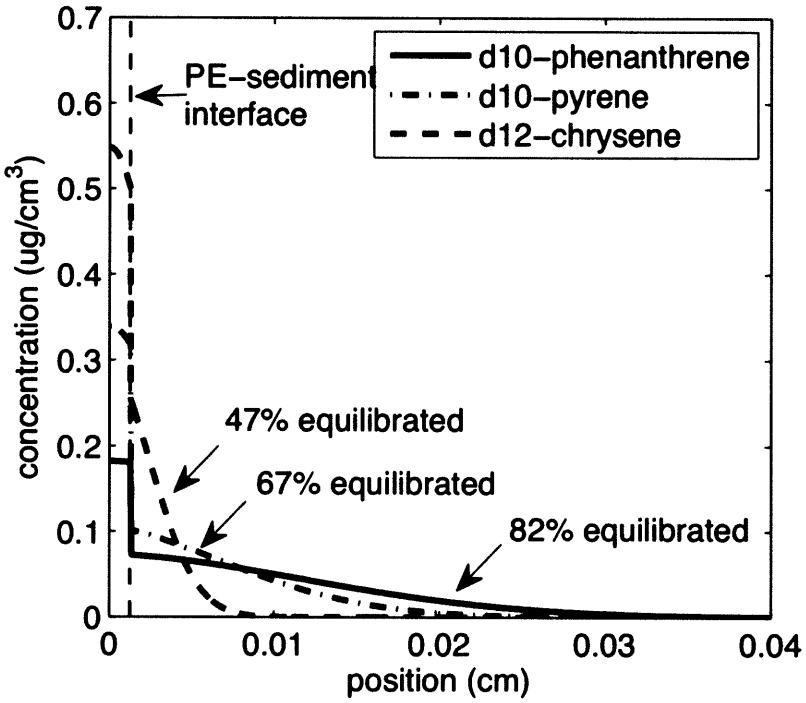

Figure 2.4. Model-inferred profiles of three PRCs, deuterated-phenanthrene, -pyrene and -chrysene, diffusing from PE to IE sediment after 3 days (C^0_{PE}=1μg/cm^3).

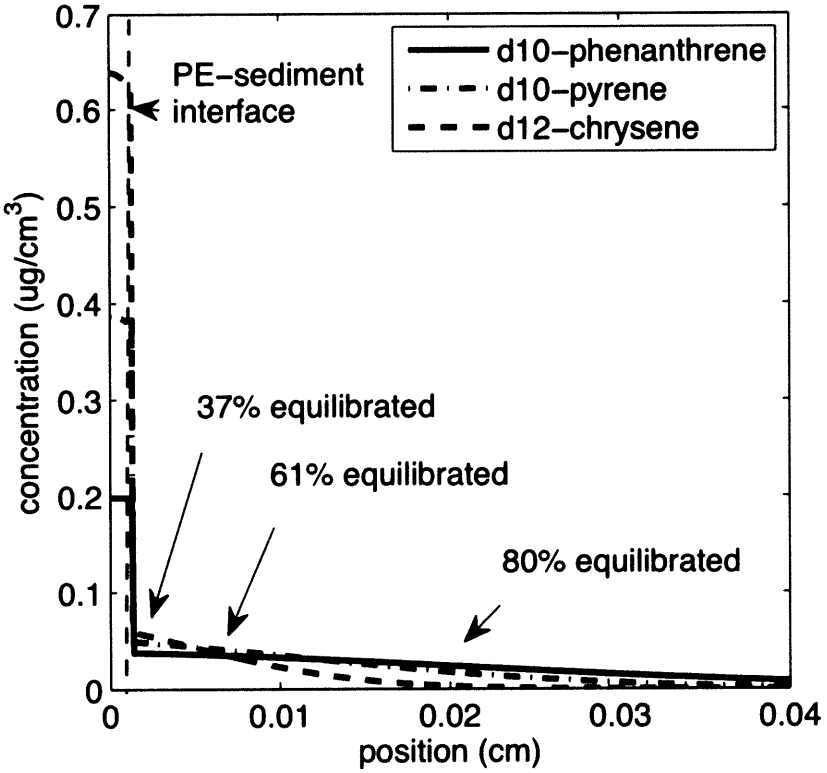

Figure 2.5. Model-inferred profiles of three PRCs, deuterated-phenanthrene, -pyrene, and -chrysene, diffusing from PE to DB sediment after 7 days (C^0_{PE}=1 μg/cm^3).

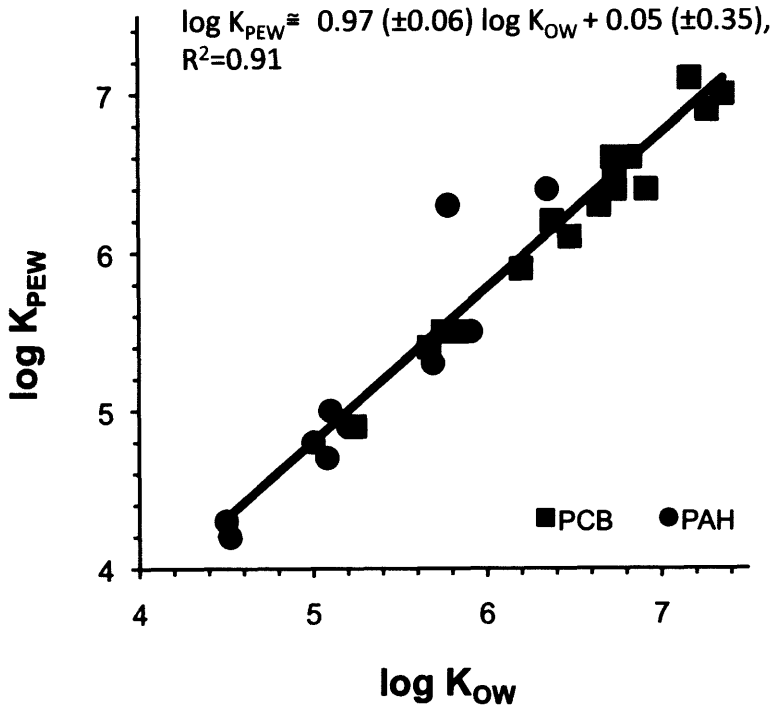

Figure 2.6. Relation of log K_{PEW} vs. log K_{OW} for 13 PAHs and 16 PCBs.

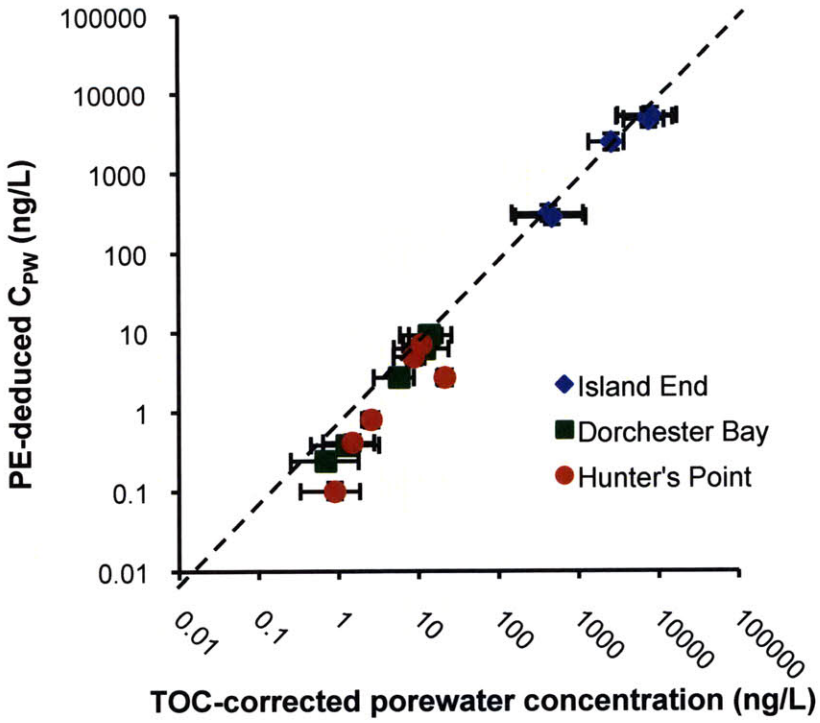

Figure 2.7. PE-deduced C_{PW} vs. porewater concentrations found by solvent extraction and corrected for TOC-sorption for Island End, Dorchester Bay, and Hunters Point samples used in the laboratory.

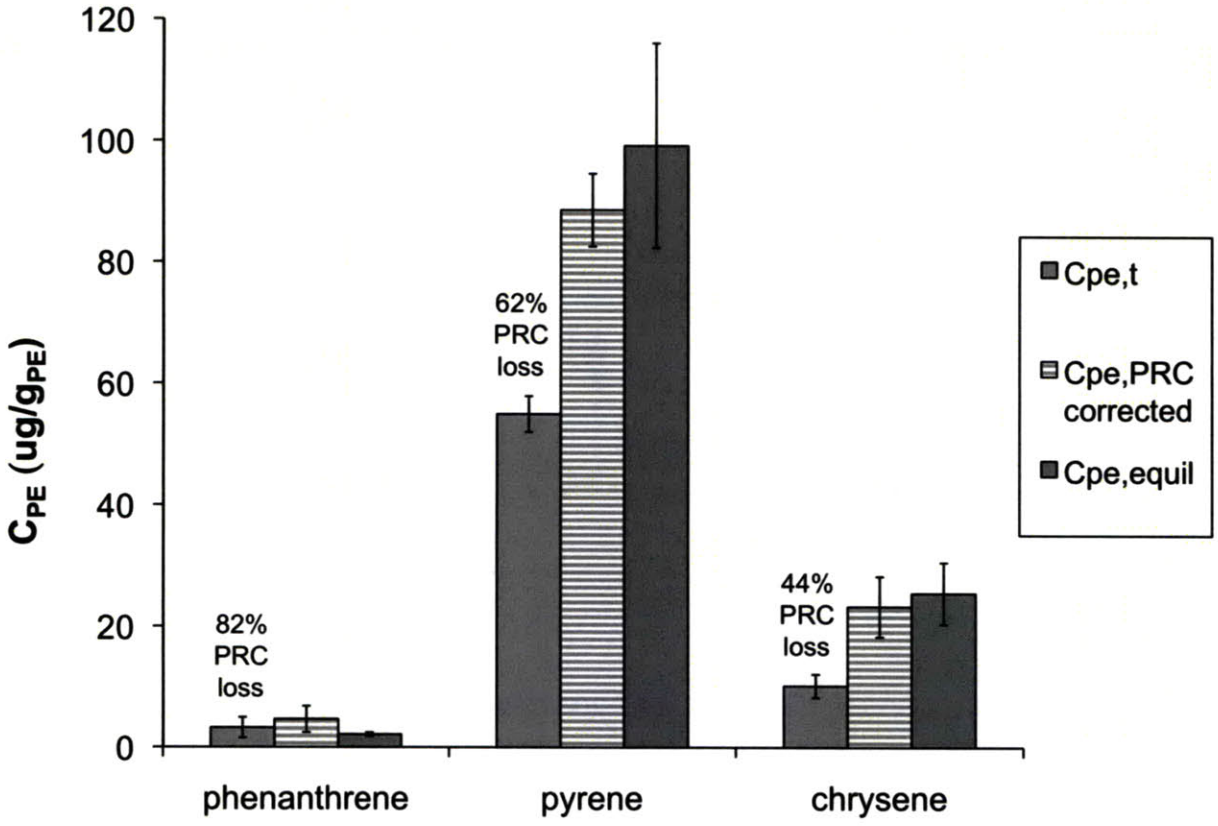

Figure 2.8. Phenanthrene, pyrene, and chrysene measured in PE exposed to Island End sediments for 14 days ($C_{PE,t}$), PRC-corrected PE concentrations ($C_{PE,PRC\ corrected}$), and concentrations measured in PE tumbled to equilibrium with the same sediments ($C_{PE,equil}$).

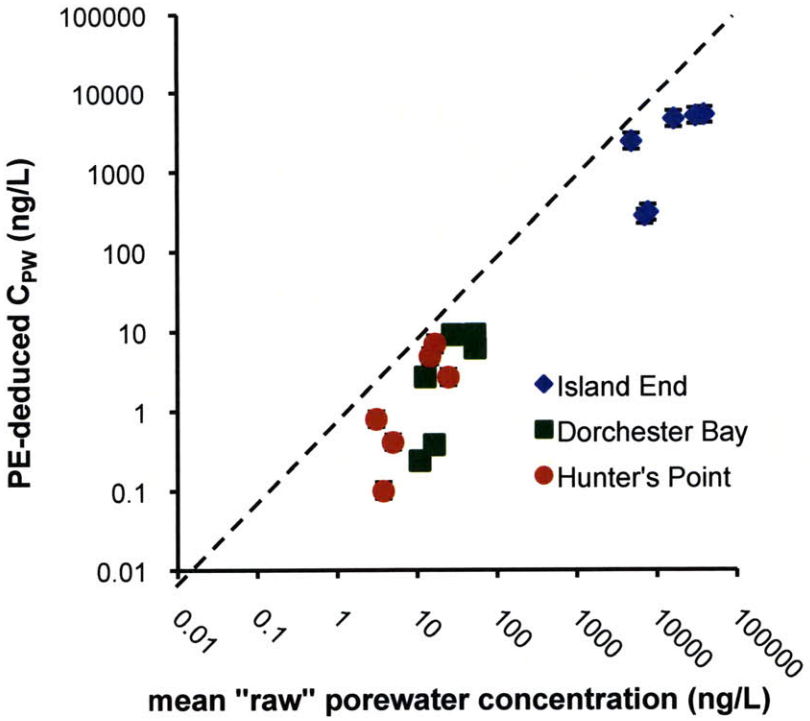

Figure 2.9. PE-deduced C_{PW} vs. "raw" porewater concentrations for Island End, Dorchester Bay, and Hunter's Point samples.

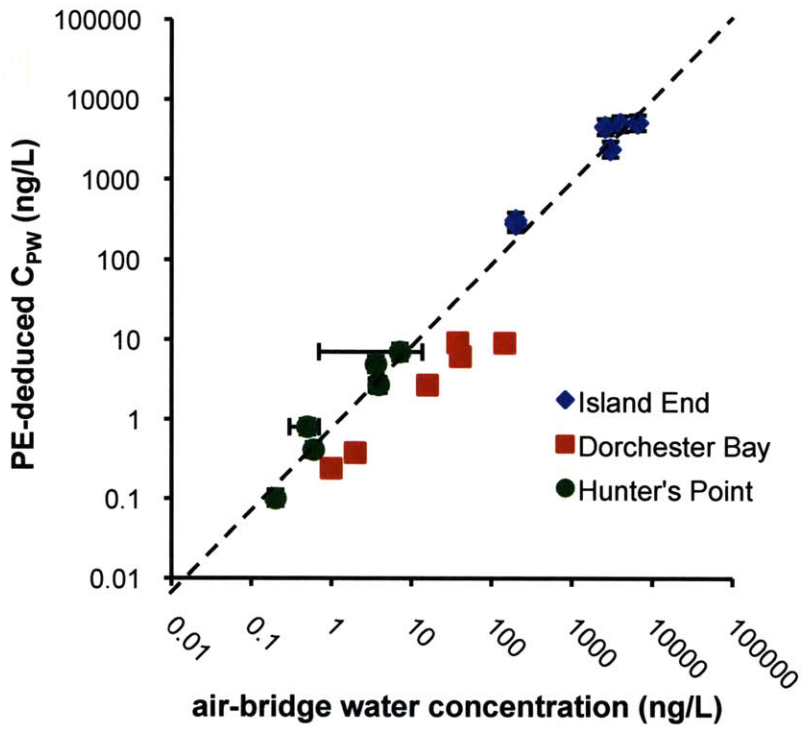

Figure 2.10. PE-deduced C_{PW} vs. airbridge water concentrations for Island End, Dorchester Bay, and Hunters Point samples.

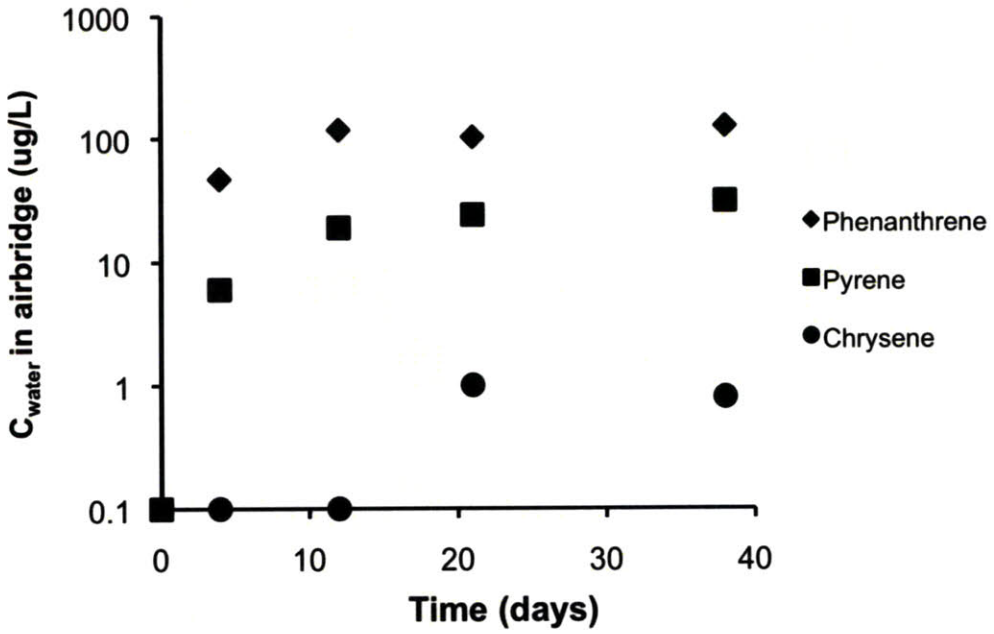

Figure 2.11. Timecourse data for C_W in Dorchester Bay airbridge exposed water.

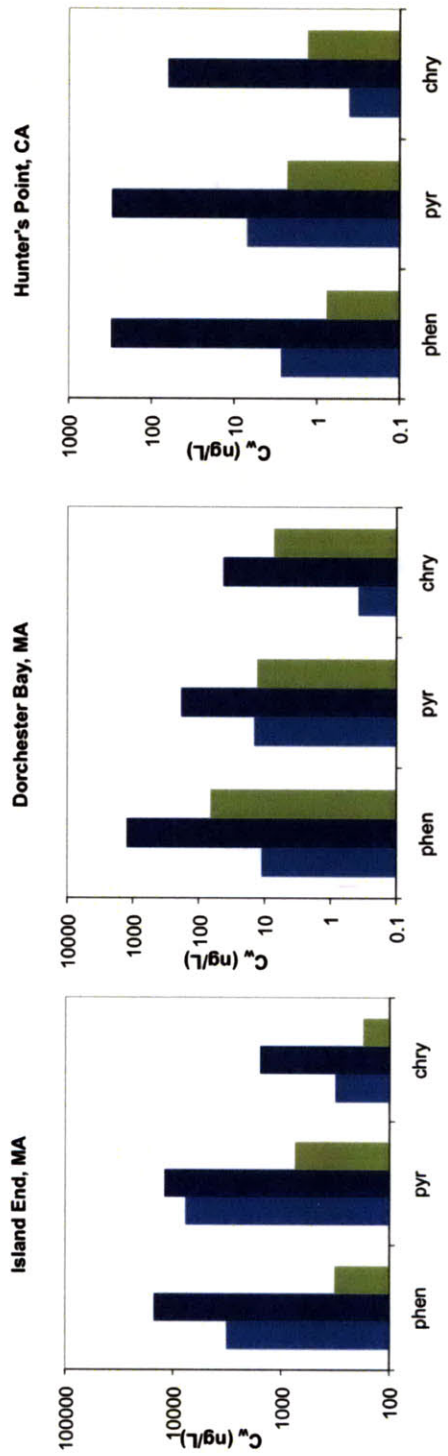

Figure 2.12. PE-deduced C_{PW} ( ), EqP calculated C_{PW} (OC + BC treated as OC) ( ), and EqP calculated C_{PW} (OC and BC treated as different sorbents) ( ) for Island End, Dorchester Bay, and Hunters Point sediments.

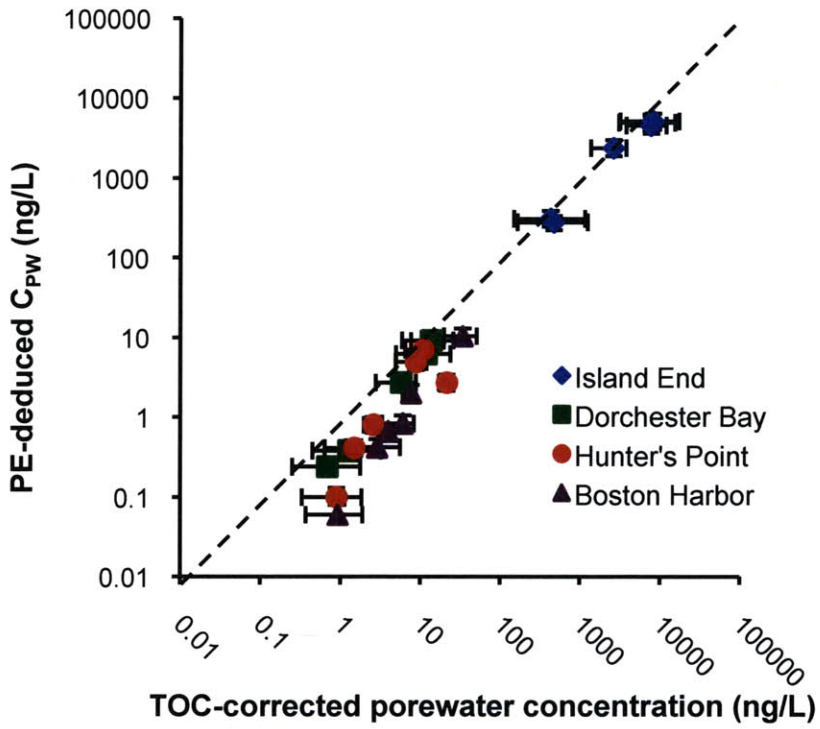

Figure 2.13. PE-deduced C_{PW} vs. TOC-corrected porewater concentrations for Boston Harbor field trial with homogenized samples for reference.

Chapter 3: Using performance reference compounds in polyethylene passive samplers to deduce sediment porewater concentrations for numerous target chemicals

(based on work published in *Environmental Science and Technology* with Charles Harvey and Philip Gschwend)

Abstract

Polymeric passive samplers are useful for assessing hydrophobic organic chemical contamination in sediment beds. Here, an improved method is described for measuring concentrations of contaminants in porewater by using performance reference compounds (d10-phenanthrene, d10-pyrene, and d12-chrysene) to calibrate sampler/site-specific mass transfer behavior. The method employs a one-dimensional diffusion model of chemical exchange between a polymer sheet of finite thickness and an unmixed sediment bed. The model is parameterized by diffusivities and partition coefficients for both the sampler and sediment. This method was applied to estimate porewater concentrations for seventeen PAHs from polymeric samplers deployed for 3 to 10 days in homogenized sediment from a coal-tar contaminated site. The accuracy of the method was verified by comparing the passive sampler results to concentrations measured through liquid-liquid extraction of physically-separated porewaters, with corrections for sorption to colloidal organic carbon. The measurements made using the two methods matched within about a factor of 2.0 (± 0.9) for the seventeen target PAHs.

Introduction

Polymer-based passive samplers are valuable tools for quantifying hydrophobic organic contaminants in environmental media such as sediment porewaters, air, and surface waters

(Huckins et al. 1993; Shoeib and Harner 2002; Wania et al. 2003; Adams et al. 2007; Cornelissen et al. 2008). Several materials, deployment procedures, and analysis techniques have been developed specifically for use in sediments. Mayer et al. (2000) incubated solid-phase microextraction fibers (SPME), coated with polydimethylsiloxane (PDMS), with whole sediments in the laboratory over a period of 30 days to measure PCB concentrations in porewaters. Hawthorne et al. (2005) extracted PAHs from carefully separated porewater samples of as little as 1.5 mL with SPME. Polyethylene (PE) strips have been tumbled with sediment slurries in the laboratory over periods of up to 4 weeks to measure PAHs, PCBs, and dioxins (Booij et al. 2003; Lohmann et al. 2004). Much longer equilibration times were used for deployments of polyoxymethylene strips (POM), PE, and PDMS directly into sediment beds (Booij et al. 2003; Cornelissen et al. 2008). While these efforts have been very informative, it is desirable to have a passive sampling approach that does not require returning samples to the laboratory for equilibration or use of protracted *in situ* deployment times.

Following the lead of Huckins et al. (2002) in their development of semipermeable membrane devices (SPMDs), passive samplers can be deployed for times that are too short to attain environment-sampler equilibrium by impregnating performance reference compounds (PRCs) into the sampler before deployment. The concentration of the reference compound in the sampler after it is retrieved can then be used to gauge the system's compound-dependent approach to equilibrium and hence to extrapolate the measured contaminant concentrations to their equilibrium values. When a PRC and target chemical have the same diffusivities and partitioning properties, the prediction of $C^{\infty}_{polymer}$, the concentration in the polymer when

equilibrated with the sediments ($ng/kg_{polymer}$), is straightforward (Booij et al. 2002; Adams et al. 2007; Tomaszewsky and Luthy 2008; Fernandez et al. 2009):

$$C^{\infty}_{polymer} = \frac{C_{polymer(t)} C_{PRC,init}}{C_{PRC,init} - C_{PRC(t)}} \tag{3.1}$$

where $C_{polymer(t)}$ is the concentration of target chemical accumulated in the polymer after an exposure time that is too short to reflect equilibration, $C_{PRC(t)}$ is the concentration of PRC in the polymer after the same time, and $C_{PRC,\ init}$ is the initial concentration of PRC in the polymer before deployment. Subsequently, partition coefficients can be used to deduce porewater concentrations:

$$C_{PW} = \frac{C^{\infty}_{polymer}}{K_{polymer-water}} \tag{3.2}$$

where C_{PW} is the porewater concentration (ng/L), and $K_{polymer\text{-}water}$ is the equilibrium partition coefficient between the polymer and water ($L/kg_{polymer}$).

However, when PRC and target chemical have different diffusivities and/or partitioning properties, a method for extrapolating PRC behavior to other compounds is required. Tomaszewsky and Luthy (2008) compared two approaches for using a single PRC to measure a suite of PCBs: a molar value adjustment (Huckins et al. 2006) and an exposure adjustment factor (Huckins et al. 2002). Both approaches yielded uptake rates by PE samplers, after 28-day exposures, that matched field-measured uptake rates within a factor of two for most congeners, but tended to overestimate rates for smaller compounds while underestimating uptake rates for larger compounds.

In this work, an alternative method is presented. First, a mass transfer model was developed which accounts for compound-specific diffusivities within both the sampler and the

environmental medium being assessed. Using this generic model, the data from only the PRCs were used to infer key mass transfer properties, the bed-sampler partition coefficients and the effective diffusivities in the sediment, for the polymer-environmental medium of interest. Subsequently, adjusting for the physical and chemical properties of targets (diffusivities and partition coefficients), site-specific and target-specific information were combined to deduce environmental concentrations of a broad range of individual target compounds without waiting for the samplers to approach equilibration with their surroundings. The method was tested by applying it to passive samplers made of PE sheets, impregnated with three PRCs, which were inserted into a tank of homogenized sediments obtained from a coal-tar site to simulate an intact sediment bed. Porewater concentrations of 17 PAHs were deduced from the PRC-calibrated PE measurements, and the accuracy of this approach was confirmed by comparing the results to concentrations measured through liquid-liquid extraction of porewater samples with corrections for sorption to colloidal organic carbon.

Passive sampler-sediment bed mass transfer theory

Fickian diffusion in and out of a sheet of polymer film of finite thickness (=2l) embedded in an infinite thickness of sediment was modeled as:

$$\frac{\partial C_{PE}}{\partial t} = D_{PE}\frac{\partial^2 C_{PE}}{\partial x^2}, \qquad -l < x < l \tag{3.3}$$

$$\frac{\partial C_{SED}}{\partial t} = D_{SED}\frac{\partial^2 C_{SED}}{\partial x^2}, \qquad -\infty < x < -l \text{ and } l < x < \infty \tag{3.4}$$

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). In the case of a fully saturated sediment bed, D_{SED} reflects molecular diffusion through the porewater, retarded due to sorptive exchanges with non-moving bed particles; in this case, sorption/desorption to/from the sediment solids is assumed to be fast compared to diffusion through the bed. This assumption is supported by modeling the desorption of the slowest diffusing, and most highly drawn down PAH measured in this work, dibenz(a,h)anthracene. Using Wu and Gschwend's (Wu and Gschwend 1988) model of intra-particle desorption, the time for fully depleted porewaters to reach 90% equilibrium with sediment particles is on the order of hours, while PE samplers were in place for days. At the interface of the polymer film and the sediment, the diffusive fluxes match so that mass is conserved:

$$D_{PE}\frac{dC_{PE}}{dx} = D_{SED}\frac{dC_{SED}}{dx}, \qquad \text{at } x = +l \text{ and } x = -l \tag{3.5}$$

and a local equilibrium distribution is assumed:

$$C_{PE} = K_{PESED}\, C_{SED}, \qquad \text{at } x = l \text{ and } x = -l \tag{3.6}$$

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

$$\frac{dC_{SED}}{dx} = 0, \qquad \text{at } x = \infty \text{ and } -\infty$$

Concentrations of PRCs are initially set to a uniform value in the polymer and zero in the sediment. The initial conditions for target chemicals are switched from those of a PRC, to zero concentration in the polymer and uniform concentration in the sediment. Because the system is

linear, the solution for one of these two types of initial condition can be calculated directly from the solution for the other initial condition (Appendix C).

The solution for this boundary value problem was found in the Laplace domain (Appendix C). The fractional equilibration of target chemical accumulated in the polymer film, and the PRC remaining in the film, were found by integrating the Laplace-domain chemical concentrations across the polymer film:

$$\overline{\hat{M}}_{target} = \frac{\sqrt{\psi}}{s^{3/2}\left(K_{PESED} + \sqrt{\psi}\coth\left(\sqrt{s}\right)\right)} \tag{3.7}$$

$$\overline{\hat{M}}_{PRC} = \left(\frac{1}{s} - \overline{\hat{M}}_{target}\right) \tag{3.8}$$

where overbar denotes Laplace transform and $\hat{M}_{target}$ is the mass of target compound normalized by the equilibrium mass, and $\hat{M}_{PRC}$ is the mass of PRC compound normalized by the initial mass within the film. The dimensionless Laplace parameter, *s,* is based on a dimensionless time variable:

$$T = \frac{\mathrm{t}D_{PE}}{l^2} \tag{3.9}$$

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 (Eqns. 3.7 and 3.8) back to the time domain, we used a numerical method (Hollenbeck 1998; Hollenbeck et al. 1999). In this way, $\hat{M}_{target}$ ($=M_{target}/M_{inf}$) or $\hat{M}_{PRC}$ ($= M_{PRC}/M_{init}$) are obtained as functions of time. One goal of this work was to present results so that others may interpret their data with these methods. To that end, both a MATLAB code for inversions and families of curves that serve as type curves for

determining parameters, are given in appendices D and E. The accuracy of the model was checked by comparing results to those obtained using a finite-difference model of chemical exchange between the two phases (Chapter 2), which had previously been checked for accuracy against analytical solutions available for special cases (e.g. uniform diffusivity in two phases, or short times before centerline concentration changes).

The model parameters, ψ and K_{PESED}, are both functions of K_d, expressed here in non-traditional units of cm^3 water/cm^3 sediment:

$$\psi = \frac{D_{SED}}{D_{PE}} = \frac{D_W}{(1 + r_{sw} K_d)\tau D_{PE}} \approx \frac{D_W}{r_{sw} K_d \tau D_{PE}} \tag{3.10}$$

$$K_{PESED} = \frac{K_{PEW}}{K_d} \tag{3.11}$$

where D_W is a chemical's diffusivity in water (cm^2/s) (Hayduk and Laudie 1974),

r_{sw} is the volume ratio of whole sediment to water calculated from porosity, n,

$$r_{sw} = \frac{1}{n} \tag{3.12}$$

τ is tortuosity (also estimated from n for marine sediments) (Weissberg 1963; Boudreau 1996),

$$\tau = 1 - \ln(n^2) \tag{3.13}$$

K_{PEW} is the polymer-water partition coefficient (expressed here in units of cm^3 water/cm^3 polymer), and

K_d is equal to the "normal" sorption coefficient (e.g., in units of cm^3 water/g dry sediment) multiplied by the sediment's bulk density in g dry sediment/cm^3 sediment.

For any moderately hydrophobic compound (K_{OW}>10^3) in a sediment containing about 1% organic carbon content, r_{sw} K_d will be much greater than 1, hence allowing the approximation shown in Eqn. 3.10.

Given this model, a family of curves for various K_d values may be produced by numerically inverting Eqn. 3.8 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}) (Figures 3.1, 3.2, and 3.3).

Since one can usually assume a relationship between log K_d and other compound properties like log K_{OW} for specific compound classes, then for a given sediment and class of chemicals, using data from at least two PRCs, 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 Eqn. 3.7 at T_{exp}, or read from a curve (Appendix E). Finally, C_{PW} may be calculated as:

$$C_{PW} = \frac{C_{polymer(t)} M_{inf}}{K_{polymer-water} M_{(t)}} \tag{3.14}$$

Materials and Methods

All solvents were Baker Ultraresi-analyzed (Philipsburg, NJ, USA). Laboratory water was treated with an ion-exchange and activated carbon system (Aries Vaponics, Rockland, MA, USA) until 18 MOhm-cm resistance was achieved, followed by UV exposure (TOC reduction

unit, Aquafine Corporation, Valencia, CA, USA). All PAH standards were purchased from Ultra Scientific (North Kingston, RI, USA) in methanol, acetone, or dichloromethane.

Polyethylene strips were prepared from low-density polyethylene (PE) sheets (25 μm from Trimaco, Durham, NC, USA, 51 μm from Carlisle Plastic, Inc, Minneapolis, MN, USA). All PE was soaked twice in dichloromethane for 24 hr and twice in methanol for 24 hr, before soaking twice in water for 24 hr. Finite difference model calculations for diffusion of d12-chrysene from stirred water, through a 1-cm water-side boundary layer, and into PE indicated that 1 month is sufficiently long for 51 μm thick PE to equilibrate with the solution; but to be sure of even PRC distribution throughout the polymer films, the PE used in this study was in contact with PRC solution for >6 months (approximately 400 mg PE in 1 L aqueous PRC solution). K_{PEW} values for individual PAHs exchanging between these polymers and deionized water have been reported previously (Adams et al. 2007; Fernandez et al. 2009).

Sediment sampling site

Sediments for this study were collected from a site in Boston Harbor, near a former manufactured gas plant at Island End (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 hr. 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 (Chapter 2). The PE passive samplers were removed from the sediments after 3 (25 μm) or 10 (51 μm) days. Since PAHs 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 and polyethylene 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.

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. Swabbing and exposure to laboratory air is not expected to affect absorbed PAH concentration in PE based on tests using multiple swabs and solvents (Appendix B). 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 analysis.

All extracts were analyzed using gas chromatography-mass spectrometry (GCMS, JEOL GCmate, 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 305°C. The initial column temperature of 70°C was raised at 20°C/min until a temperature of 180°C was reached, and then the temperature was raised 6°C/min until a temperature of 300°C 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 PRCs, 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 porewater. Recoveries from porewater samples suffered due to spillage of second extract volume. 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 porewater and PE samples, which were approximately 130 ng/L and 250 ng/g PE, respectively, for these samples.

Carbon analyses and organic carbon-correction of porewater concentration

Total organic carbon (TOC) was measured in unfiltered porewater samples using a Shimadzu TOC 5000 analyzer (Shimadzu Scientific Instruments, Colombia, MD, USA). Samples were acidified with phosphoric acid (phosphoric acid GR, EM Science, Gibbstown, NJ, USA) to a pH of 2 and sparged with TOC grade air (Airgas, Radnor, PA, USA) for 20 minutes.

Dissolved PAH concentrations, C_{PW}, were calculated from the values measured in raw porewaters, C_W, by correcting for sorption to colloidal organic matter, estimated using the TOC data:

$$C_{PW} = \frac{C_W}{1 + [TOC]K_{OC}} \tag{3.15}$$

where C_{PW} is the TOC-corrected porewater 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 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 (Chapter 2). In order to check the appropriateness of using Karickhoff's K_{OC} values for this site's porewater colloids, a fluorescence quenching (FQ) experiment was performed to test pyrene sorption to those colloids (Gauthier et al. 1986; Backhus and Gschwend 1990; Chin and Gschwend 1992; Schlautman and Morgan 1993; Perminova et al. 2001). The K_{OC} that we needed to fit the quenching data matched the Karickhoff value for pyrene within 3%. We continued to apply these values for the rest of the experiment, but caution the reader that such values may be inaccurate for other cases where colloidal organic carbon may have different sorption properties.

Polyethylene diffusivities

PE diffusivities for the PAHs were estimated using published diffusivity data for aromatic compounds (Saleem et al. 1989; Yeom and Huang 1992; Rusina et al. 2007). None of the data used were calculated using methods of sorption/desorption from/to fluids which may lead to errors due to boundary layer effects (Reynolds et al. 1990). A log-linear relationship (Figure 3.4) was assumed between log D_{PE} and each compound's molar volume (Ruelle 2000). Relating diffusivities to molar volumes is consistent with free-volume theory of diffusive transport in polymers (Fujita 1961; Aboul-Nasr and Huang 1979). Estimated D_{PE} values were used to convert exposure times (seconds) to non-dimensional T_{exp} and to calculate ψ for each chemical.

One key outcome of the modeling work reported here is that we need to determine the diffusivities of environmentally important chemicals in polymers, and how these diffusivities change with temperature and pressure, in order to make future improvements to the accuracy of such passive sampling methods. In this work, D_{PE} reported for 25 °C (near the ambient temperatures in the laboratory) were used. Saleem et al. (1989) and Yeom and Huang (1992) observed diffusivity decreasing by about an order of magnitude over a 20 °C decrease in temperature (45 °C to 25 °C). In order to use PE samplers with the method described above, in submerged sediment beds, diffusivities of HOCs at temperatures much lower than those measured so far (0-10 °C) must be determined.

Results and Discussion

Accuracy of few-PRC method for assessing multiple target compounds

To evaluate the accuracy of the PE method, albeit using only three PRCs, we contrasted PE-inferred porewater concentrations of PAHs with direct measures of these concentrations. First, the fractional loss of the PRCs after known exposure times (i.e., known T values) were used to find the K_d for each PRC. 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 the 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, T values for these exposures were calculated to be 50 and 41 in the 25 μm thick and 51 μm thick PE, respectively (Figure 3.2). The intersections of these two $M_{PRC(t)}/M_{PRC,init}$ ratios and T combinations correspond with 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 other PRCs, d10-phenanthrene and d12-chrysene, K_ds for these two compounds were found ($10^{3.7}$ and $10^{5.5}$, respectively) (Figures 3.1, and 3.3). 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 here, cm^3 water/cm^3 sediment) and our own measures of organic contents of the sediment at this site.

K_d values found using this PE-PRC method can also be compared to values found using measurement of C_{SED} and C_W, and estimates based on sorption to OC and BC fractions. PE-PRC determined K_d values for pyrene and chrysene are consistent with K_d measured in these sediments using solvent extraction of sediment and porewaters ($10^{4.4 \pm 0.5}$, and $10^{5.6 \pm 0.6}$, respectively) (Chapter 1). Sediment and water extraction measured K_d for phenanthrene was $10^{4.5 \pm 0.5}$. K_d values calculated using the f_{OC} K_{OC} approximation (Eqn. 2.15) (and converted to

units of cm^3 water/cm^3 sediment) are similar to those measured using the PE-PRC method for phenanthrene and pyrene, ($10^{3.7}$ and $10^{4.0}$, respectively) while the f_{OC} K_{OC} approximated value is lower than the PE-PRC method value for chrysene ($10^{5.0}$). Including sorption to BC in K_d estimation (Eqn. 2.16) yields K_d values (L_W/L_{SED}) higher than the PE-PRC method values for the three PAHs ($10^{5.4}$, $10^{5.5}$, and $10^{5.9}$ for phenanthrene, pyrene and chrysene, respectively). In general, the PE-PRC method K_d values are bracketed by values measured or estimated using more traditional methods.

Next, the log K_ds for d10-phenanthrene, d10-pyrene, and d12-chrysene in IE sediment were used along with their tabulated log K_{OW} values (Sangster 1989) to establish a relationship between log K_d and log K_{OW} for this particular sediment, log K_d = 1.4 (± 0.3) × log K_{OW} − 2.7 (± 1.5). The use of additional PRCs (e.g., 5 or 6 bracketing the hydrophobicities of the target analytes of interest) would improve this step by providing more data with which to establish a relationship. Finally, this site-specific result was used to estimate log K_d for seventeen target PAHs using their log K_{OW}s . These estimated K_d values were then used to calculate each target compound's ψ (Eqn. 3.10), and K_{PESED} (Eqn. 3.11). By numerically inverting Eqn. 3.7, $M_{(t)}/M_{inf}$ was calculated for each of the target chemicals (Matlab code in Appendix D). Alternatively, $M_{(t)}/M_{inf}$ could have been estimated by using the appropriate $M_{(t)}/M_{inf}$ vs. T curve (Appendix E) and read off of the plot for the exposure time used. For example, Eqns. 3.10 and 3.11 yield ψ and K_{PESED} for pyrene in the IE sediments of 0.6 and 5, respectively. Using Figures E.1 and E.2 in Appendix E, one can find the $M_{(t)}/M_{inf}$ on the y-axis, corresponding to the points between the ψ = 0.3 and ψ = 1 curves for T= 50 (25 μm thick PE) and 41 (51 μm thick PE). While numerical inversion of Eqn. 3.7 yielded $M_{(t)}/M_{inf}$ of 68% and 66% for pyrene in the two samplers, using Figures E.1 and E.2 to estimate $M_{(t)}/M_{inf}$ yielded values of 60-70%.

Finally, C_{PW} values were deduced using measured $C_{polymer(t)}$ and Eqn. 3.14. For pyrene, the 25 μm thick PE yielded C_{PW} of 7300 ng/L while the 51μm thick PE yielded C_{PW} of 8100 ng/L, two results differing by only 10% for a compound with physical and chemical properties exactly matching one of our PRCs. Likewise, we estimated corresponding porewater concentrations for the target chemicals including eleven PAHs that lie between the PRCs 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 PRCs (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). For all 17 target compounds, the PE-deduced C_{PW} and TOC-corrected C_{PW} matched well (agreement within a factor of 2.0 ± 0.9, n=16), with TOC-corrected values most often higher than PE-deduced C_W (Table 3.1 and Figure 3.5). For chemicals that match the PRCs in terms of diffusivities and partition coefficients (phenanthrene, pyrene, and chrysene), the PE-deduced and TOC-corrected values matched within an average factor of 1.2 ± 0.06 (n=3). The method performed better when interpolating between the PRCs (average agreement within a factor of 1.5 ± 0.7, n=11) than when extrapolating to larger chemicals (average agreement within a factor of 2.9 ± 1.1, n=5). Including larger PRCs might improve the PE-inferred results for the largest target chemicals. However, if larger HOCs are targeted, longer passive sampler exposure times would likely be needed to transfer measurable amounts of PRCs to sediments. Even an estimated 4 week deployment time, however, for a PRC the size of dibenz(a,h)anthracene, is much shorter than the estimated years that would be required for the sampler to approach equilibrium with the sediments for chemicals of that size.

While some of the difference between the two sets of measured C_{PW} may be due to the difficulties associated with measuring small PAH masses extracted from porewater samples, error could also be introduced by uncertainty in the polymer diffusivities of the compounds, which were used to shape the M_t/M_{inf} vs. T curves, and to locate case-specific positions on the T axis (Appendix E). Fractional equilibration (M_t/M_{inf}) is more sensitive to changes in T in areas where the curve is steep (short T) than areas where the curve is more shallow (long T). While it would be preferable to work with T for all chemicals that are in the shallow areas of the curves, if one is interested in a broad range of chemicals, this may not always be possible. Following any single deployment time, larger chemicals with slower diffusivities will appear in the steeper areas of M_t/M_{inf} vs. T curves while smaller, faster diffusing chemicals will appear in more shallow areas. Longer deployments or thinner polymer films may be used to achieve desired T for deployments.

Comparison of diffusion model to two alternative approaches

Previously, other calculation approximations with simpler mathematical forms have been used for analyzing target compounds accumulated in a passive sampler embedded in sediment; here, we consider the accuracies of those approaches. In Chapter 2 of this work the no flux boundary at the sampler's center was ignored, thus representing a situation in which the sampler is taken to be infinitely thick. At short-times, before the concentration at the centerline of the sampler begins to change, the mass of target chemical or PRC transferred across the interface may be described as follows (derived from Crank (1975)):

$$M_{target}(t) = 2\left(\frac{t}{\pi}\right)^{1/2}\left(\frac{K_{PESED}C_{SED}}{D_{PE}^{-1/2} + K_{PESED}D_{SED}^{-1/2}}\right) \tag{3.16}$$

$$M_{PRC}(t) = 2\left(\frac{t}{\pi}\right)^{1/2}\left(\frac{C_{PRC,init}}{D_{PE}^{-1/2} + K_{PESED}D_{SED}^{-1/2}}\right) \quad (3.17)$$

where $M_{target}(t)$ is the mass of target chemical per cm^2 that has crossed the polymer-sediment boundary, $M_{PRC}(t)$ is the mass of PRC per cm^2 that has crossed the polymer-sediment boundary. A similar simplification is made by Booij et al. (2003) who describe a model for uptake by PE which acts as an "infinite sink", but does not account for diffusivity within the PE. The infinite sampling medium approximation (Eqns. 3.16 and 3.17) increasingly diverges from the complete solution at later times (Figure 3.6). The fraction equilibrated would be overestimated by using a semi-infinite medium approximation by 5% by the time the polymer has actually equilibrated 20%. Overestimation increases as the sampler continues to equilibrate. These effects are cancelled out when using PRCs and target chemicals that exactly match in terms of partition coefficients and diffusivities (Chapter 2), but the model would be inappropriate for measuring any target chemical which does not have a diffusion and sorption matching PRC.

A second approximation other investigators have used derives from an extension of models used to interpret data from use of semipermeable membrane devices (SPMDs) suspended in water. In this case, chemical transfers have been modeled as exchange between well-mixed lipid (triolein) separated by a diffusive barrier (PE) from a well-mixed aqueous environment. This view yields exponential uptake expressions (Huckins et al. 1993; Booij et al. 1998; Booij et al. 2003)

$$M_{target}(t) = 2\,l\,K_{PEW}C_{PW}(1 - e^{-k_e t}) \quad (3.18)$$

$$M_{PRC}(t) = 2\,l\,C_{PRC,init}\,e^{-k_e t} \quad (3.19)$$

where k_e is the exchange rate coefficient and is fitted to time-course data. Unfortunately, this view neglects mass transfer limitations within the bed. Comparing the exponential uptake model (Eqns. 3.18 and 3.19) to the complete solution reveals important differences between the two. If we fit an exponential uptake model by matching the complete solution at 50% of its equilibrium value, the exponential model underestimates the equilibrium polymer concentration for all exposure times before 50% equilibration is reached and overestimates for all times after that (Figure 3.6). Again, these results imply that this approximation is only accurate if one has tuned the exchange rate coefficient, k_e, to a PRC that exactly matches a target chemical in terms of both sediment and polymer diffusivity and partitioning behavior. Previous modeling experiments have shown that adjustments to k_e based on the molar volumes of target and PRC compounds (Tomaszewsky and Luthy 2008) are not sufficient to correct for inaccuracies of applying an exponential model for diffusion from stagnant sediments (Chapter 2).

Applicability of method to other samplers and environments

The one-dimensional diffusion model used to describe a thin layer of diffusive material embedded in a thick (or infinite) bed of a second diffusive material could be used to describe many situations of practical importance. These include polymer sheets inserted into sediment beds, soils, or sludges. In order to apply the model to these situations, one would need to know the molecular diffusivities within the polymer and medium being sampled, and a target chemical's partition coefficient between sampler and sampled medium.

One important use of the mass transfer model is to help determine appropriate deployment times. As one would like measurable amounts of PRCs to be transferred from the sampler during a given deployment, estimates of K_d and porosity can be used along with Eqns

3.10 and 3.11, and type curves (Appendix E) to find the time after which measurable amounts of compound ($\geq$ 20% given measurement uncertainty) have been transferred from the sampler. For application in soils, diffusive transport in the air phase must also be considered in calculation of D_{SED} (Table 3.2). PRCs from one compound class may be used to deduce porewater concentration of a target chemical from a different compound class as long as (a) the target's D_{PE} is known or can be estimated from data for similarly shaped compounds, and (b) the target obeys the same log K_d vs. log K_{OW} relationship as the PRCs.

Finally, if one were to use diffusive samplers to measure K_d in sediments, one may ask whether sediment properties like porosity should be measured. As it would be inconvenient to have to measure porosity of every *in situ* sediment horizon for every passive sampler deployment, the method was tested for its sensitivity to this parameter. The method described above was followed assuming two additional porosity cases, 40% and 80%, and results were compared to the case of the measured porosity, 60%. While the different porosities resulted in variations in PRC K_ds of up to an order of magnitude, the deduced porewater concentrations were all within 5% of the base, 60% porosity, case. Hence, porosity should be measured when accurate measures of K_d are desired without sediment extractions, but are not necessary for measuring C_{PW}, where reasonable estimates of porosity are sufficient.

Since sediment beds are always contaminated with a myriad of HOCs, having a means to assess the mobile and bioavailable fractions of a wide array of compounds in the same sampling exercise will be a great advantage for site and media evaluations. Compared to passive sampling methods where sampler and sediment are allowed to equilibrate, the method described here requires additional steps in sampler preparation and data analysis. The benefit, however, is shortened deployment time, which is often important when the chances of loss of deployment

apparatus increases with time, as in urban environments or high traffic marine areas, or when sediment data are time critical. Unfortunately, application of first-order mathematics to correct for such incomplete mass transfer data undoubtedly leads to substantial inaccuracy in the results. Our approach rectifies this concern.

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Table 3.1. Measured and PE-deduced porewater concentrations for selected PAHs in Island End sediment samples (ng/L). Measured TOC concentrations in porewater samples were 53 mg/L and 67 mg/L.

Compound	**TOC-corrected C_W** (average, n=2)	**PE deduced C_W** (average, n=7)	**+/-** (1 σ)	**Ratio of TOC-corrected C_W to PE-deduced C_W**
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)- plus benzo(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

Table 3.2. Estimated ψ and K_{PESED} for six example compounds in low OC and high OC sediments and a soil. Low OC sediments assumed to have f_{OC} = 0.005, and f_{BC} = 0.0005. High OC sediments and soil assumed to have f_{OC} = 0.05, and f_{BC} = 0.005. Diffusion in soil is assumed to occur through both air and water phases.

Compound	low OC sed ψ	high OC sed ψ	soil ψ	low OC sed K_{PESED}	high OC sed and soil K_{PESED}
phenanthrene	10	1	9,000	20	2
benzo(a)pyrene	1	0.1	600	3	0.3
2,2',5,5'-PCB	40	4	30,000	300	30
2,2',3,4,4',5,5-PCB	50	5	40,000	400	40
atrazine	7,000	900	7,000,000	100	20
p,p'-DDT	6	1	5,000	3	0.3

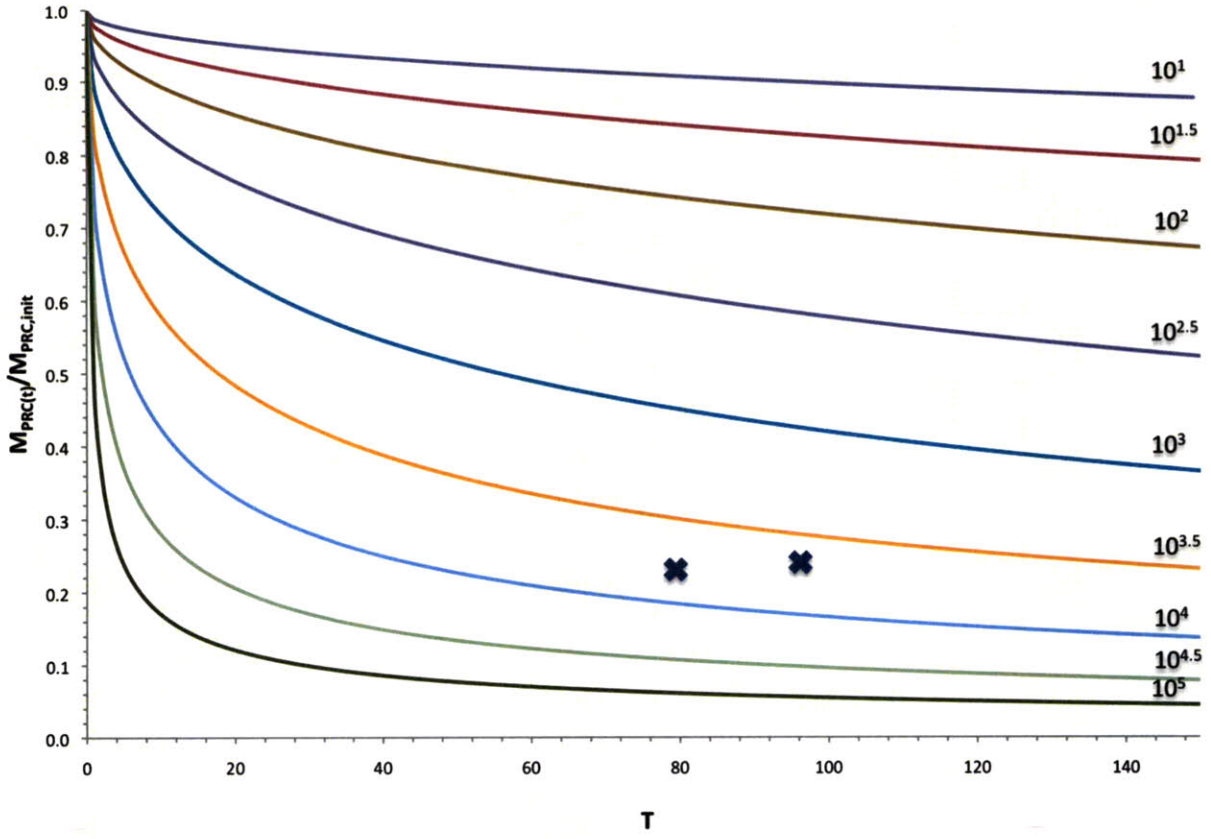

Figure 3.1. Fractions remaining for a PRC, d10-phenanthrene, vs. non-dimensional exposure time in sediments like those from IE (60% porosity) for a wide range of K_ds. With 25 µm thick PE exposed for 3 days (T=96) 24% remained, while 51 µm thick PE exposed for 10 days (T=79) had 23% remaining. The intersections of these loss data and the dimensionless times indicated two estimates of d10-phenanthrene K_d of $10^{3.6}$ and $10^{3.8}$, respectively, for this site's sediment.

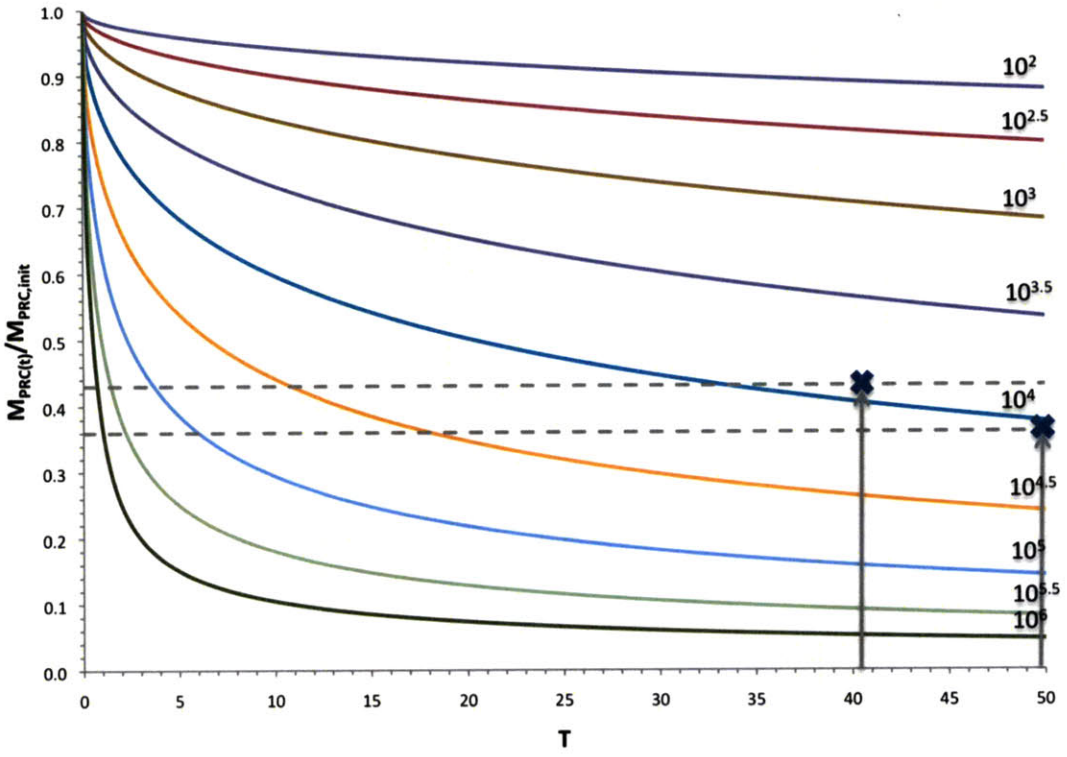

Figure 3.2. Fractions remaining for a PRC, d10-pyrene, vs. non-dimensional exposure time in sediments like those from IE (60% porosity) for a wide range of K_ds. With 25 μm thick PE exposed for 3 days (T=50) 36% loss was measured, while 51 μm thick PE exposed for 10 days (T=41) had 43% loss. The intersections of these loss data and the dimensionless times indicated two estimates of d10-pyrene K_d of $10^{4.0}$ and $10^{3.9}$, respectively, for this site's sediment.

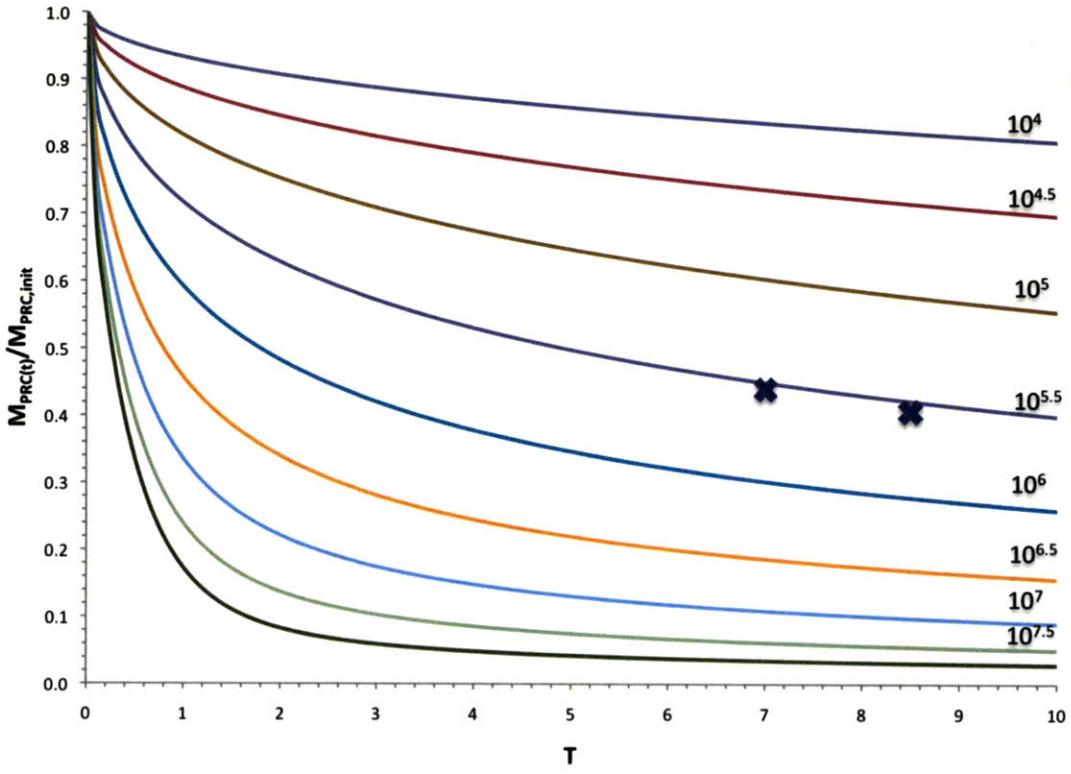

Figure 3.3. Fractions remaining for a PRC, d12-chrysene, vs. non-dimensional exposure time in sediments like those from IE (60% porosity) for a wide range of K_ds. With 25 μm thick PE exposed for 3 days (T=8.5) 41% remained, while 51 μm thick PE exposed for 10 days (T=7.0) had 44% remaining. The intersections of these loss data and the dimensionless times indicated an estimate of d12-chrysene K_d of $10^{5.5}$ for this site's sediment.

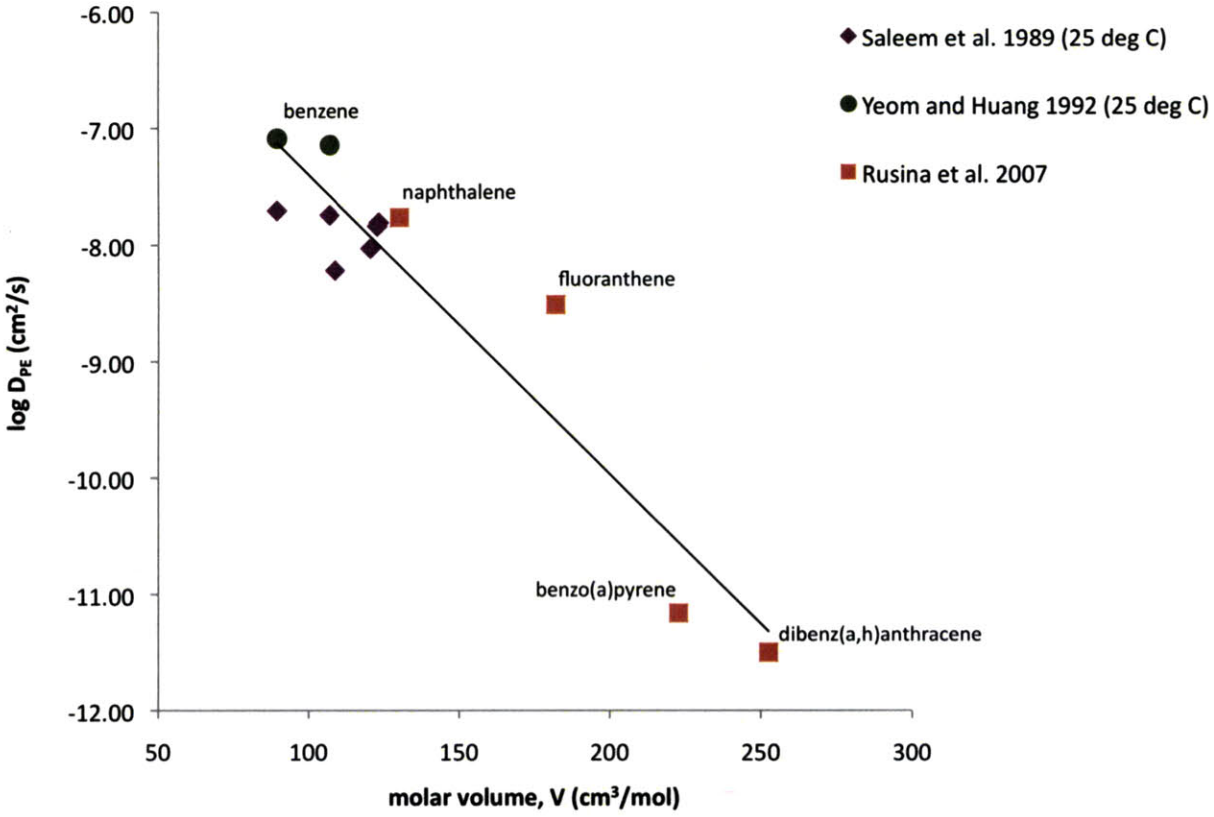

Figure 3.4. Published log D_{PE} values versus molar volumes (Ruelle 2000) for ten aromatic compounds. The best-fit log-linear relationship, log D_{PE} = -0.026 (±0.003) × V − 4.8 (± 0.4), was used to estimate D_{PE} for PAHs in this study.

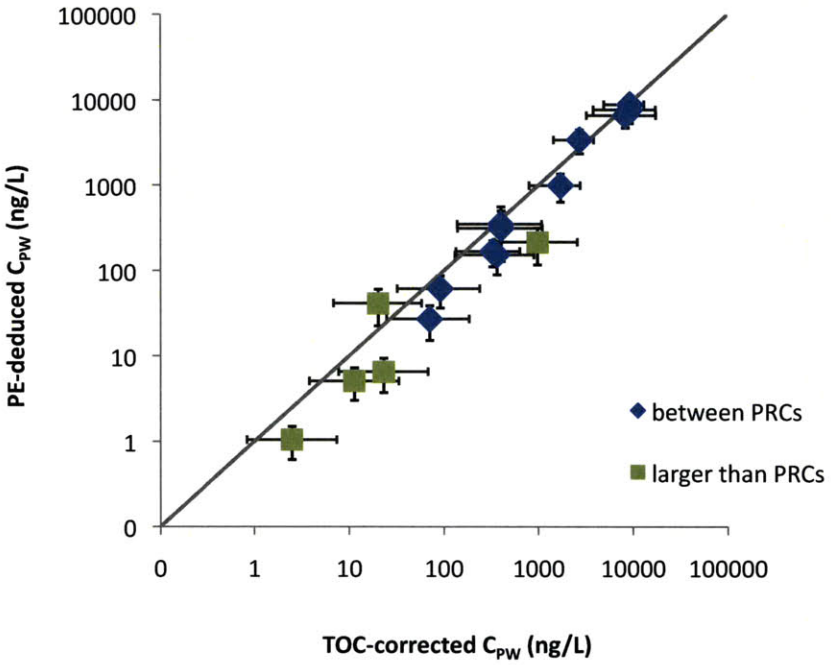

Figure 3.5. PE-deduced C_{PW} vs. porewater concentrations found by solvent extraction and corrected for sorption to colloidal organic carbon for Island End sediments. The 1:1 line is shown, and the error bars represent ±1σ.

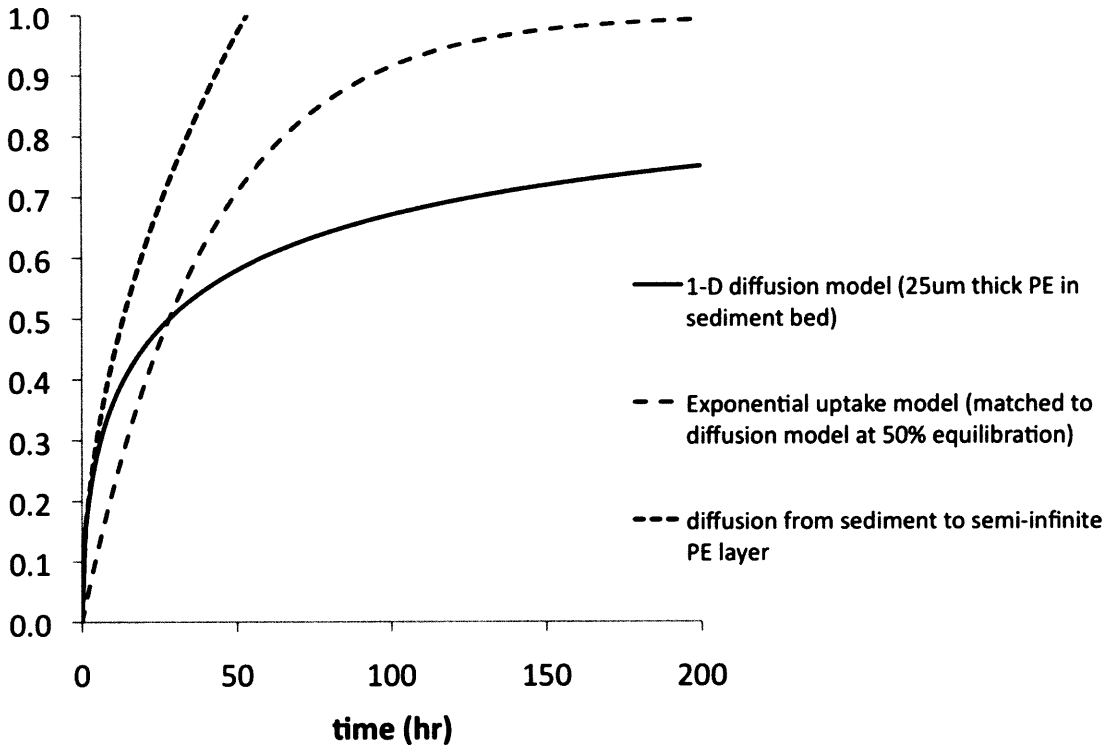

Figure 3.6. Modeled pyrene uptake by a sampler using the diffusion model used in this work (solid curves), an exponential uptake model (dashed curves), and diffusion to a semi-infinite layer of PE (short-dash curves).

Chapter 4: Chemical activities measured directly in sediment beds to predict PAH bioaccumulation by soft-shelled clams (*Mya arenaria*)

Abstract

Freely-dissolved porewater PAH concentrations and chemical activities have been suggested as measures of the bioavailability of PAHs in contaminated sediment beds. In this work polyethylene (PE) passive samplers, containing performance reference compounds (PRCs) (d10-phenanthrene, d10-pyrene, and d12-chrysene), were deployed in sediment beds near Boston, MA for a one-week period. Clams (*Mya arenaria*) and sediments were then collected from the same sediments (directly adjacent to samplers). Concentrations and chemical activities of three PAHs that match the PRCs (phenanthrene, pyrene, and chrysene) were measured in the porewaters (using PE-PRC method), in clam tissues, and in the bulk sediment. Chemical activities in clams were compared to (a) those measured in porewaters using PE samplers and those calculated using sediment measurements, and (b) an equilibrium partitioning (EqP) model that includes sorption to organic carbon and black carbon fractions. Porewater concentrations measured using PE samplers were more predictive of clam tissue concentrations than those determined using an EqP model. Correlations between PE-deduced porewater chemical activity and clam tissue chemical activity, were found for pyrene and chrysene, and had R^2 values of 0.29 and 0.93 and p-values of 0.05 and 3×10^{-5}, respectively. Also, EqP models overestimated porewater concentrations for the three chemicals by one to three orders of magnitude at all but one site.

Introduction

Many approaches have been taken to measuring the environmental risks associated with contaminated sediments. Investigations often begin with determining the effects of contamination on benthic and demersal organisms that are in direct contact with sediments and can be a route of exposure to humans and the larger food web. One approach, taken by the U.S. Environmental Protection Agency, is to apply an equilibrium partitioning (EqP) model to measurements of sediment concentrations and organic carbon fractions to determine the incremental narcotic toxicity risks posed by hydrophobic organic chemicals (HOCs) to fish and benthic invertebrates (Hansen et al. 2003). In this method, sediment concentrations are normalized to their organic carbon content and equilibrated organism concentrations are calculated. Researchers have shown, however, that accumulation of HOCs in organisms is often much lower than what is predicted by EqP models (Bierman 1990; Paine et al. 1996; Tracey and Hansen 1996). Results have been improved by including additional sorptive materials in the EqP model (Gustafsson et al. 1997; Accardi-Dey and Gschwend 2003; Cornelissen et al. 2006a). As sediments may contain different sorptive fractions, each with different affinities for HOCs, it is very difficult to get accurate results using EqP models (Cornelissen et al. 2006b; Khalil and Ghosh 2006).

Another approach to the problem of predicting how much of a chemical will be transferred to benthic organisms is to calculate uptake and removal to and from the organism through multiple routes (Boese et al. 1990; Morrison et al. 1996; Thomann and Komlos 1999). Steady-state mass balance models, which include terms for uptake (across gills, dermally, and

through diet) and for removal (metabolic transformation, dermally, and through excretions), have been examined. In order to calculate steady-state concentrations, however, rates for each uptake and removal pathway, for each species and chemical, are required, making this method difficult to apply outside of the laboratory.

While the mass balance approach may be a more accurate description of what is occurring within organisms, the concept of thermodynamic potential for exchange, as used in EqP is still useful, and may be more easily applied. Many researchers, for example, have found correlations between freely-dissolved porewater concentrations and organism tissue concentrations (Ramos et al. 1998; Kraaij et al. 2003; Cornelissen et al. 2006a; Hawthorne et al. 2007). Others have found correlations between the PAH concentrations in organism gut fluids and their uptake to benthic organisms through the gut (Voparil and Mayer 2000; Ahrens et al. 2001). Normalizing either of these concentrations to the solvent's capacity to hold the chemical yields the chemical activity, *a*, in that phase, a measure of the chemical's energetic state that may be used to determine bioaccumulation potential (Schwarzenbach et al. 2003; Reichenberg and Mayer 2006).

The PE-PRC method, described in Chapters 2 and 3, allows porewater chemical activity of polycyclic aromatic hydrocarbons (PAHs) to be measured in sediment porewaters over periods of days to weeks. This work will examine if porewater chemical activities measured in in-place sediments are predictive of tissue concentrations in organisms living within those sediments.

Mya arenaria, or soft-shelled clams, are often included in bioaccumulation studies (Gardner and Pruell 1988; McDowell and Shea 1997; Rhodes et al. 1997; Lohmann et al. 2004;

Galassi et al. 2008). The easily harvested bivalves commonly live up to 10-12 years in sand and silty sands in intertidal zones (as well as deeper waters) throughout the world (Abraham and Dillon 1986; McDowell and Shea 1997). The clams are also a commercially important species with 3.9 million pounds of clams, worth $22 million, harvested in 2008 in the United States (NOAA 2010).

The species is exposed to contaminants in sediments and the water column through numerous routes. Unlike other clams, *M. arenaria* have shells that gape at both ends, exposing soft tissues to sediments. They live at depth (up to 30 cm deep in sediments) and extend long necks just to the sediment-water interface (Thorin et al. 1998). Taking in food from this interface results in the ingestion of sediment particles along with plankton (Kaag et al. 1997). The clams respire by pumping water from the water column through the siphon and across their gills. In laboratory testing, Frouin et al. (2007) observed the uptake of PAHs to *M. arenaria* from dosed food, sediment beds, suspended solids, and water-column water. Radiolabeled pyrene in sediments, food and water were observed to progress through the clam over a period of a month. Initially the compound is seen on gills, in intestines, and on digestive glands, before being transferred to lipid-rich areas of the gonad, along the siphon, and to nephridia (organs that perform similar functions to our kidneys).

Due to the multiple routes of exposure and disequilibria between sediment porewaters, food, and the water-column, *M. arenaria* are not usually equilibrated with sediments as EqP models would predict (Lohmann et al. 2004). Mass-balance models applied to the clams have included terms for uptake and elimination of PAH to/from the water column across the gills, uptake from sediment particles and food across the gut, transformation through metabolism, and elimination through excretion of wastes. Using their mass balance model, where sources and

sinks to/from filter feeders and benthic detritivores are described in terms of fugacities, Morrison et al. (1996) calculated that the importance of uptake/elimination through the gut relative to uptake/elimination across the gills increases as the hydrophobicity of the compound increases. Using this model and chemical activities in the water column and sediments as endpoints, one would expect organisms living within and ingesting sediments, while breathing water from water column would have tissue chemical activities somewhere between the two endpoints with the contribution of sediments to tissue activities increasing with hydrophobicity of the compound.

With this in mind, a field study was designed to measure porewater chemical activities *in situ*, directly adjacent to clams. Clams and sediments would then be collected to compare activities measured in each medium. While it was not expected that activities would be equivalent in clam tissues and porewaters, it was expected that the two measures would correlate assuming that clams are taking up chemicals from the sediment bed and that differences in water column activities from site to site are small compared to differences in porewater activities. By measuring porewater activities directly, using PE, difficulties encountered when applying EqP models to sediment concentrations would be avoided. Also, depth profiles of a_{PW} could be measured by slicing PE at intervals following sediment exposure, allowing for the comparison of both surface and deeper sediments to a_{org}.

Six sites near Boston, MA, which had been observed to be clam habitats (McDowell and Shea 1997; Chase et al. 2002), and where sediment concentrations and OC and BC fractions were expected to vary (based on previous measurements, proximity to industry and historical land use), were chosen for sampling. Chemical activities were measured in sediment porewaters using PE samplers, in organism tissues, and in sediments using an EqP model which includes

sorption to OC and BC. Compiled data for all sites were queried for correlations between a_{PW} and a_{org}. These correlations were then compared to those between porewater chemical activities calculated by applying an EqP model to sediment measurements and a_{org} to see if the PE method is an improvement over the existing method for estimating bioaccumulation potential.

Materials and Methods

All solvents were Baker Ultraresi-analyzed (Philipsburg, NJ, USA). Laboratory water was treated with an ion-exchange and activated carbon system (Aries Vaponics, Rockland, MA, USA) until 18 MOhm-cm resistance was achieved, followed by UV exposure (TOC reduction unit, Aquafine Corporation, Valencia, CA, USA). All PAH standards were purchased from Ultra Scientific (North Kingston, RI, USA) in methanol, acetone, or dichloromethane.

Polyethylene (PE) strips were prepared from low-density polyethylene (LDPE) sheets (25 μm from Trimaco, Durham, NC, USA). All PE was soaked twice in dichloromethane for 24 hr and twice in methanol for 24 hr, before soaking twice in water for 24 hr. Finite-difference model calculations for diffusion of d12-chrysene from stirred water, through a 1-cm water-side boundary layer, and into PE indicated that 1 month is sufficiently long for 25 μm thick PE to equilibrate with the solution; but to be sure of even PRC distribution throughout the polymer films, the PE used in this study was in contact with PRC solution for >7 months (approximately 20 g PE in 1 L aqueous PRC solution).

Field sampling

PE strips were deployed and clams and sediments were collected from six locations near Boston, MA (Figure 4.1, Table 4.1) 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 include the following: (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 19th 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 (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.

Sampling of all sites was conducted over a period of two weeks, in November 2008, during low tides, in the intertidal zone. First, 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 -20°C until extraction, sediments were stored at 4°C until extraction, and PE were sectioned at 4 cm intervals and

immediately extracted. 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.

PE extraction

Upon return 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 gas chromatography/mass spectrometry (GC/MS) analysis.

Clam extractions

Extraction of PAHs from clams was performed using a 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 mussels 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. Three precombusted GF/B filters (Whatman International Ltd., Maidstone, England) were used

in the bottom of each 33 mL stainless steel extraction cell. The clam mixture was added to cells between two layers of precombusted Ottawa sand (EMD Chemicals, Gibbstown, NJ, USA). 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 Dionix ASE 200 (Dionix Corporation, Sunnyvale, CA). Each cell was extracted three times, using dichloromethane:methanol (1:1), heated for 5 minutes (125°C) at 1500 psi, and flushed with 60% of 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 4°C. 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.

Sediment extractions

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 4°C 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.

OC and BC fraction analysis

Dried (60°C for 24 hr) and ground sediment sub-samples (~10 mg each) were analyzed for their mass fraction of BC and OC as well as C/N and C/H ratios, using a Vario EL III CHN elemental analyzer (Elementar, Hanau, Germany). BC samples were combusted at 375° C for 24 hr to remove the OC fraction (CTO375) (Gustafsson et al. 1997; Lohmann et al. 2004; Flores-Cervantes 2008). Both OC+BC and BC samples were acidified with 200 µL of 0.35 M sulfurous acid (H_2SO_3) (Baker Analyzed, Phillipsburg, NJ) and then dried at 60°C for 24 hours to remove carbonates before CHN analysis.

Three analyses of each sediment sub-sample were performed for each of the two measurements (BC and OC+BC). Acetanilide (Elemental Microanalysis Limited, Okehampton, UK) was used as a calibration standard for the analytical method. Blanks were run between every six samples.

Column chromatography

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 °C 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. PCBs and PAHs 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 GC/MS analysis to determine each sample volume.

Gas chromatography/mass spectrometry analysis

All extracts were analyzed using gas chromatography-mass spectrometry (GCMS, JEOL GCmate, 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 305°C. The initial column temperature of 70°C was raised at 20°C/min until a temperature of 180°C was reached, and then the temperature was raised 6°C/min until a temperature of 300°C 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.

Quality control

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. Large ranges in recovery of surrogate standards were expected due to the many transfers and manipulations of the extracts. 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 clam, PE, and sediment samples.

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 were 134% of the reported value. Repeated measurements yielded the same result. 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.

Calculation of chemical activities

Chemical activities were calculated from concentrations measured in clams, PE, and sediments. In clams, for which tissue concentrations, C_{org}, are reported on a dry weight basis, compounds were assumed to be associated with both the lipids and proteins in the extracted tissues:

$$a_{org} = \frac{C_{org}}{(f_{lip} K_{lip-w} + f_{prot} K_{prot-w}) C_W^{sat}(L)} \tag{4.1}$$

where f_{lip} and f_{prot} are the fractions (dry weight basis) of lipids and proteins in the clam tissues, $K_{lip\text{-}w}$ and $K_{prot\text{-}w}$ are the lipid-water, and protein-water partitioning coefficients, and $C_w^{sat}(L)$ is a liquid chemical's solubility in water, which will serve as the reference point for all activities used in this work. Similarly, chemical activities in sediment porewaters were calculated using the PE method from calculated equilibrium PE concentrations, C_{PE}, and PE-water partition coefficients, K_{PEW},

$$a_{PW} = \frac{C_{PE}}{K_{PEW} C_w^{sat}(L)} \tag{4.2}$$

Sediment chemical activities were calculated from bulk sediment concentrations and sediment-water partition coefficients, K_d,

$$a_{sed} = \frac{C_{sed}}{K_d C_w^{sat}(L)} \tag{4.3}$$

and

$$K_d = (f_{OC} + f_{BC})\, K_{OC} \quad \text{(treating all organic carbon as one sorbent) or,} \tag{4.4}$$

$$K_d = f_{OC}\, K_{OC} + f_{BC}\, K_{BC}\, C_w^{n-1} \quad \text{(treating OC and BC as separate sorbents)} \tag{4.5}$$

where K_{OC} is the organic carbon-water partitioning coefficient, K_{BC} is the black carbon-water partitioning coefficient, C_w is the water concentration, and n is the Freundlich exponent. Here an n=0.7 is assumed (following Lohman et al.(2005)). Partition coefficients and water solubilities used in this work are given in Table 4.2.

Results and Discussion

Chemical activities of three PAHs (phenanthrene, pyrene, and chrysene) were measured in sediments, clams, and porewaters of twelve stations throughout the six sites: 3 stations at Collins Cove, 1 station at Pioneer Village, 2 stations at Lead Mills, 3 stations at Pines River, 1 station at Island End, and 2 stations at Dorchester Bay.

Sediments

Three subsamples of Collins Cove 2 surface sediments were measured to determine reproducibility of the sediment measurement method. PAH concentrations in these subsamples had coefficients of variance (CV) (using 1σ, n=3) for phenanthrene, pyrene, and chrysene of 13%, 10%, and 4%, respectively. These fractions were used as the uncertainties for each PAH concentration for the rest of the sediment measurements.

All three target chemicals were found in both surface and deeper sediment samples from all 12 stations (n=23) (Table 4.3). Pyrene was most often at the highest concentration in each sample. Exceptions include four surface layer samples (two from Collins Cove, and two from Pines River) and three deeper sediment samples (one each from Collins Cove, Lead Mills, and Pines River) where phenanthrene was measured at higher concentrations. Chrysene was most often measured at the lowest concentrations, always lower than pyrene, and never the highest concentrations. In three samples chrysene was measured at higher concentration than phenanthrene (two surface samples from Lead Mills and Island End, and one deeper layer sample from Dorchester Bay).

Sediment concentrations measured in this work were similar to those previously measured by other researchers. Concentrations of phenanthrene and pyrene in Dorchester Bay

samples were similar to those measured by Lohmann et al. in 2001(2004). For phenanthrene, Lohmann et al. report a range of 180-220 ng/gdw with a mean of 200 ng/gdw, while in this work a range of 52-160 ng/gdw were measured. Lohmann et al. measured pyrene over a range of 440-480 ng/gdw with a mean of 460, while in this work a range of 120-330 ng/gdw was measured. Concentrations measured for all three PAHs at Island End were the within the range observed in 4 size fractions of sediments from the same site by Wang et al. (2001).

Sediment concentrations across all stations ranged over 4 orders of magnitude and were higher in sediments with greater fractions of OC and BC. The highest concentrations were measured at Collins Cove and Island End. These stations also had high fractions of OC and BC and higher ratios of methyl-phenanthrene + methyl-anthracene to phenanthrene + anthracene (molecular weight 192/178) than other sites (1.0 to 1.7 in Collins Cove and Island End while only <1 at other stations) (Table 4.4). These ratios indicate contributions from petrogenic sources to PAH loads in Collins Cove and Island End (Gschwend and Hites 1981). The lowest PAH concentrations were measured at Pioneer Village, an area with low OC and BC fractions.

While stations at Collins Cove, Lead Mills, Dorchester Bay and Pines River were all narrowly spaced (covering areas of 2-3 m^2), sediment concentrations over these areas were sometimes similar and sometimes highly variable. Sediments from the Dorchester Bay stations matched within uncertainty and those from Collins Cove varied by only about a factor of 2. Sediments from the Pines River and Lead Mills sediments, however, varied by over an order of magnitude between stations 1 to 2 m apart. These results reflect the heterogeneity of many sediment beds, making the collection of many samples from a single site necessary to measure the range of sediment contamination levels.

Organic carbon fractions (f_{OC}), black carbon fractions (f_{BC}), as well as C/N and C/H mole ratios, were measured in at least one sediment sample from each site (Table 4.3). Organic carbon fractions ranged from 0.07% in the Pioneer Village sands to 13% in the lower layer of Collins Cove station 1. Black carbon fractions ranged from 0.01%, also in Pioneer Village sands, to 6.3%, also in sediments from Collins Cove. Unlike most sediments reported in the scientific literature, f_{BC} values were higher than f_{OC} values in some samples from Collins Cove and Lead Mills. The range of C/N and C/H ratios in the black carbon fractions at Collins Cove, Lead Mills, and Island End suggest that a portion of these materials are like NIST Diesel soot (having C/N between 12 and 69 and C/H between 2 and 8) (Accardi-Dey and Gschwend 2002). Even higher C/N ratios (28 – 70) in combined organic carbon and black carbon fractions than in black carbon fractions, observed at Collins Cove and Island End, may indicate the presence of coal, oil, tar, or other petrogenic materials. Dick et al. (2006) report C/N mole ratios for bituminous coal of 35 to 41 while Gustafsson et al. (1997) report nearly complete combustion of lignite, seam coal, and anthracite using the CTO 375 method. These two measures combined suggest that the large f_{OC} values measured in Collins Cove may be due to the presence of coal dust. This is not surprising considering the proximity of the site to a large, uncovered coal storage pile adjacent to the Salem Harbor Power Station. The large f_{OC} values and high C/N ratios at Island End are likely due to the presence of coal tar at this site. Lower C/N ratios in material surviving CTO 375 method in sediments from other sites including Lead Mills, Pines River, Dorchester Bay and Pioneer Village suggest that these materials are not soots. Other materials making up these fractions may include pollen and tire waste from road runoff (Gustafsson et al. 1997; Accardi-Dey and Gschwend 2002; Descolas-Gros and Scholzel 2007).

Again, f_{OC} and f_{BC} values measured in this work at Dorchester Bay are similar to those previously measured. Lohmann et al. report a range of 1.3-1.5% with a mean of 1.4%, and 0.13-0.19% with a mean of 0.16% for f_{OC} and f_{BC}, respectively. Accardi-Dey and Gschwend (2002) report 1.4 ± 0.13% for $f_{OC} + f_{BC}$, and 0.26 ± 0.07% for f_{BC} in a nearby area of Dorchester Bay, while Flores-Cervantes et al. found f_{OC} of 1.04 ± 0.14% and f_{BC} of 0.16 ± 0.05%. In this work the ranges were 1.1 to 4% and 0.29 to 0.47% for f_{OC} and f_{BC}, respectively. At Island End, f_{OC} values and C/N ratios were measured by Wang et al. (2001), ranging between 4.82 and 27.9% TOC and 17.5 and 44.5 C/N for four size fractions, values similar to those measured in this work for whole sediments.

Clams

Phenanthrene, pyrene, and chrysene were measured in each of the clams sampled in this work. Uncertainty in clam measurements was determined by measuring tissue concentrations in six clams taken from the Collins Cove, station 3 (approximately 3 dm^3 of sediments). CVs of 51%, 34%, and 50% for phenanthrene, pyrene, and chrysene, respectively, were measured in the six clams. These are all higher than the CV measured in three subsamples of one of the six Collins Cove, station 3 clams, (46%, 13%, and 8% for phenanthrene, pyrene, and chrysene, respectively). As, frequently, only a single clam was collected from a given station, the CV for the six clam sample was used as the uncertainty for clam measurements in order to capture likely variability between clams.

Clam tissue concentrations ranged over two orders of magnitude for the 26 clams extracted in this work (Table 4.5). As with the sediments, pyrene was most often at the highest concentration, of the three PAHs measured, in each clam. A clam from Pioneer Village had the

lowest concentrations, and a clam from Island End had the highest. In some cases clams from the same stations had concentrations that matched each other within uncertainty (e.g. pyrene in Collins Cove, station 1). In other cases, clams from the same station had concentrations of individual PAHs that varied by 1 to 2 orders of magnitude (e.g. Island End).

There are many possible explanations for clams from the same station having very different measured concentrations. Frouin et al. (2007) exposed clams to radiolabeled pyrene through sediment and diet, then observed anatomical areas of high pyrene concentration. These areas included a strip along the siphon, and gills, both of which were included in extractions in this work. If a clam was not well homogenized before subsampling for extraction, it may be possible that an area of high or low concentration was extracted in the outlier clams. Also, Frouin et al. observed tissue concentrations to be higher in male clams than in female clams due to accumulation in gonads. Clam genders were not recorded in this work, and it is expected that spawning had not occurred near the time of sampling (Abraham and Dillon 1986). It is also possible that the clams are reflecting heterogeneity in the sediment beds; although the clams were collected from the same station, sediments may be heterogeneous within the volume of the station (approximately 3 dm3 of sediment). In comparing clam tissue activities to porewater activities in this work, data will be compared for both individual clams and station averages.

Because accelerated solvent extraction, the method used in this work to extract PAHs from clam tissues, also extracted lipids and some proteins from the tissues, a lipid fraction could not be measured by drying an aliquot of the extract as is normally done when using a Soxhlet extraction method, which extracts lipids but not proteins. In this work, lipid and protein fractions for all clams are assumed to be 5% and 50%, respectively, based on measurements by other researchers (McDowell and Shea 1997; Schwarzenbach et al. 2003; Lohmann et al. 2004).

Lohmann et al. (2004) measured lipid fractions between 5.3 and 9.0% in clams from Dorchester Bay and 5.8 and 7.6% in clams from the Saugus River (near Pines River) in 2001 on a dry weight basis, while protein fractions were calculated to be 48%. McDowell and Shea (1997) measured lipid fractions between 3.7 and 6.1% for whole clams from the Massachusetts Bay, while Galassi et al. measure an average of 5.1% in clams from the Gulf of Gdansk, in the Baltic Sea. Protein fractions for other aquatic invertebrates have been measured in the range of 50-70% (Schwarzenbach et al. 2003).

Porewater

Porewater chemical activities were measured at each station using PE samplers. By slicing the PE into 4 cm intervals, porewater activities, integrated over 4 cm depths into sediments, could be calculated, using PRC loss to correct for disequilibrium between PE and sediment beds (Chapter 1) (Tables 4.6, 4.7, and 4.8). The highest fractional equilibrations were seen in samplers exposed to Island End sediments (high K_d sediment), while the lowest fractional equilibrations were seen in samplers exposed to Dorchester Bay and Pioneer Village sediments (low K_d sediments). Such a trend is predicted by the mass-transfer model used in this work.

While little variation in porewater chemical activity with depth was observed at most stations, chemical activity increased with depth in some cases. Pyrene activities in Collins Cove stations 3 and 4, Island End, and Pines River station 2 increased with depth, with the 8-12 cm depth section being ~2.5 times higher than surface (0-4 cm) sections. In Island End sediments all three compounds increased with depth by at least a factor of three, with phenanthrene increasing with depth by a factor of 16. Increasing chemical activities in porewaters indicate upward flux of the chemical.

While the sites with the lowest and highest PAH sediment concentrations also had the lowest and highest porewater chemical activities, interesting differences between the two measures can be seen. Pines River and Collins Cove had sediment PAH concentrations that differed by a factor of 8 on average. Porewater chemical activities, however, only differed by a factor of 1.5 on average. This may be due to the large carbon fractions in the Collins Cove site, which serve to lower the chemical activities of PAHs in those sediments. Conversely, sediment PAH concentrations in Collins Cove and Island End were similar, with Island End having higher f_{OC} and f_{BC} than Collins Cove. While one would expect Collins Cove to have higher chemical activities than Island End due to a smaller sorptive fraction, the opposite was observed, with Island End having higher porewater chemical activities by 1-2 orders of magnitude. One reason for this observation may be that the material which is measured as OC and BC at Collins Cove is more sorptive than the material being measured as OC and BC at Island End. Alternatively, high chemical activities at Island End may be due to the presence of coal tar at the site. Coal tars from ten manufactured gas plant sites in the Eastern United States have been measured to have pyrene chemical activities averaging 2.6×10^4 ppm (assuming ideal behavior in coat-tar, γ=1) (Brown et al. 2006). Partitioning between water and coal tars may be contributing to porewater concentrations (and chemical activities). It is also possible that the porewaters in these surface sediments are equilibrated with weathered coal tars that have shed low molecular weight compounds (such as those measured in this work) leading to equilibrated water concentrations that are lower than those which would be equilibrated with "fresh" tars by about a factor of 10.

Differences in the ratios of mw192 to mw178 compounds in sediment and PE extracts also suggest that the sources of PAHs being measured are different at the different sites (Table 4.4). For example, the ratio of mw192 to mw178 compounds in sediment extracts from Island

End is 1.1 (n=1), while the average ratio measured in PE extracts is 6 ± 2 (n=12). This may be an indication that PAHs from source material with fast desorption kinetics (e.g. petrogenic materials) are equilibrating more quickly with the samplers than PAHs from source material with slower desorption kinetics (e.g. pyrogenic materials) (Kuo et al. 2007).

PE-PRC method and EqP method for measuring a_{PW}

Porewater chemical activities measured using PE can be compared to those calculated using EqP models. Using sediment concentrations, f_{OC} and f_{BC} measured at each station, and Eqns. 4.3, 4.4 and 4.5, chemical activities, a_{sed}, were calculated for each station. Comparing a_{sed} to PE-deduced a_{PW} illustrates the difficulties of measuring porewaters activities in highly heterogenous environments and calculating K_d accurately when including only one or two sorbent pools. First, comparing a_{PW} to a_{SED} calculated using an EqP model which regards f_{OC} plus f_{BC} as a single organic carbon fraction (Eqn. 4.4), as is recommended in many EPA methods, differences of one to three orders of magnitude were observed in the three PAHs at many sites (Figure 4.2). This would mean that sediments such as those at Collins Cove would be considered up to 1000 times more dangerous to benthic organisms than the PE-derived result would indicate. Similar results were seen at every site investigated except for Island End. This indicates that using current methods for estimating the bioaccumulation potential of sediments significantly overestimates the extent of HOC contaminated sediments that exceed any benchmark threshold.

By considering two sorbent pools (OC and BC) (Eqn 4.5) differences between the two measures were reduced but large differences are still observed at some sites (Figure 4.3). The Pines River 2 site had a high phenanthrene activity in the sediment that was not seen in the clams

or PE at that station. Of greater interest are the data from the Island End and Lead Mills 1 stations. At these stations, large fractions of black carbon were measured (4.9 and 2.1% in the surface layer), fractions that are in the range of those measured in Collins Cove. While calculating K_d using f_{OC} and f_{BC} appears to do a good job for the Collins Cove sediments, K_d appears to be overestimated in Lead Mills and Island End sediments. Since C/N mole ratios for the Lead Mills and Island End samples are in the same range as those measured in Collins Cove, it is difficult to say that the OC or BC material was different, with different sorption properties at the three stations. It may be possible that these sediments were heterogenous at the scale that the PE sampler and our sediment grab were separated in space. Alternatively, it may be possible that a mixture of materials, which survive CTO 375, and have C/N ratios in the range measured here (e.g. carbon black, chars, or pollen) (Gustafsson et al. 1997; Fernandes et al. 2003; Descolas-Gros and Scholzel 2007), have sorption properties that differ from those of diesel soot, which was used to determine K_{BC}s used in this work.

Agreements between a_{sed} (calculated using OC and BC fractions) and a_{PW} varied between chemicals with phenanthrene having the greatest variability (Figures 4.3 and 4.4). The ratio of a_{sed} to a_{PW} for phenanthrene varied by an average factor of 21 ± 29 (± 1 σ). For pyrene the ratio varied by an average factor of 46 ± 105 (± 1 σ) when including the Lead Mills outlier, or by an average factor if 12 ± 14 when leaving the Lead Mills site out. For chrysene the ratio varied by an average factor of 7 ± 4 (±1 σ). These data indicate that there is no linear correlation between a_{sed} and a_{PW}. This is likely due to inaccurate estimation of K_d, leading to inaccurate a_{sed}. Estimating K_d could be improved by better identifying the sorptive fractions in a sediment, and using partition coefficients tuned to each fraction.

Predicting a_{org} from a_{sed} or a_{PW}

The goal of this research was to determine if porewater chemical activities could be used to predict chemical activities in clam tissues. And further, to determine if the PE-PRC method performed better or worse than the EqP method at making this prediction. By converting concentrations to chemical activities, different phases can be directly compared, and equivalent chemical activities would indicate equilibrium in the partitioning of chemical between the phases. Higher chemical activities in one matrix would indicate the direction of transfer (from areas of higher chemical activity to areas of lower chemical activity).

First, chemical activities in sediments (a_{SED}), calculated using an EqP model, were compared to chemical activities measured in organism tissues (a_{org}). Data for phenanthrene show a great deal of scatter with a_{SED} ranging over 4 orders of magnitude, while a_{org} range over only 2 orders of magnitude (Figure 4.5). Chemical activities of pyrene and chrysene also show a great deal of scatter, with no clear correlations. While breaking f_{OC} and f_{BC} into more specific fractions of carbonaceous materials and applying partition coefficients tuned to those fractions might help reduce the scatter in these data, getting K_d correct would require much more effort.

Comparisons of a_{PW} to a_{org} show very different results than comparisons of a_{sed} to a_{org}. Within uncertainty for phenanthrene activities in clams, about half of the clams showed equivalent chemical activities in porewaters from the 0-4 cm depth and clam tissues (Figure 4.6). The average ratio of a_{PW} to a_{org} for the 26 samples was 1.5 ± 4.3 (± 1σ). The range of chemical activities, however, was very narrow, and there were outliers, including Collins Cove station 1, where high phenanthrene activities were measured in porewaters. Greater scatter were oberserved in the data when comparing a_{PW} from the 4-8 cm and 8-12 cm depths to a_{org} (Figures 4.7 and 4.8). The large scatter in data from the three depths could be an indication that steady

state phenanthrene activity in clams is dominated by exchange across the gills with the water column, with uptake from sediments and metabolism being less important.

While the range of chemical activities of pyrene in clams was larger than for phenenthrene, only three clams appeared to be equilibrated with porewaters from the 0-4 cm depth within uncertainty (Figure 4.9). Scatter in the data for pyrene were similar at the 4-8 cm depth and greater at the 8-12 cm depth (Figures 4.10 and 4.11). In general, chemical activities of pyrene were higher in the porewater than in clams with an average a_{PW} to a_{org} ratio of 19 ± 72 (±1 σ) (0-4 cm depth) when including Island End, or 6 ± 4 (±1 σ) when not including Island End. This could be an indication of high metabolism or elimination rates for pyrene. Simpson et al. (2002) observed the metabolism of pyrene by *M. arenaria*. The presence of radiolabeled pyrene in the nephridia of *Mya*, as observed by Frouin et al. (2007) may also be an indication that clams are actively removing pyrene.

Excluding the Island End station, chemical activities of chrysene in porewaters spanned just over a single order of magnitude (Figures 4.12, 4.13, and 4.14). As for phenanthrene, chemical activities in porewaters and clam tissues match for over half of the samples at the 0-4 and 4-8 cm depths, with an average a_{PW} to a_{org} ratio of 9 ± 31 (±1 σ) (4-8 cm depth) when including Island End, or 1 ± 0.6 (±1 σ) when not including Island End. Differences in solubility between pyrene and chrysene may make metabolism and/or removal of pyrene easier, leading to a larger a_{PW}/a_{org} ratio for pyrene.

In order to limit the effects of clam variability at individual stations, clam chemical activities were averaged for each station before comparison to porewater activities measured at each of 3 depths where PE were sectioned (0-4 cm depth, 4 – 8 cm depth, and 8-12 cm depth) (Figure 4.15, 4.16, and 4.17). Chemical activities of each PAH, in the two phases, were

examined for linear correlations. Data from Island End were left out of linear regressions because of the large gap in values between this site and all of the others for pyrene and chrysene. No correlation was seen in the data for phenanthrene ($p > 0.05$). For pyrene, the only statistically significant correlation found was between clams and porewaters from the 0-4 cm depth, $a_{org} = 0.21 (\pm 0.10)\ a_{PW} + 1.2 (\pm 2.6)$ ($r^2 = 0.29$, n=13, $p = 0.05$). For chrysene, the strongest correlation was found between a_{PW} from the 4-8 cm depth and a_{org}, $a_{org} = 1.8 (\pm 0.20)\ a_{PW} - 0.99 (\pm 0.50)$ with an r^2 of 0.93 (n=9, $p=3\times10^{-5}$). Using chrysene data for the top sediment layer (0-4 cm) the correlation had an r^2 value or 0.66 (n=13, $p=8\times10^{-4}$). Using these relationships, if porewater were measured using PE to have chemical activities of pyrene and chrysene of 50 ppm, average clam tissue activities could be expected to be 12 ppm (± 65%) for pyrene, and 89 ppm (± 12%) for chrysene.

Differences in correlations between clams and porewaters from the 0-4 cm and 4-8 cm depths may indicate that for pyrene, intake of surface sediments through ingestion is more important or as important as dermal exposure through the siphon to steady state clam concentrations, while for chrysene, dermal exposure across the siphon is the more important route. As the samplers were not exposed to sediments at the depths that many clams were found (up to ~20 cm deep), it is not possible to determine the relative importance of dermal exposure near the gaping shell.

Slopes for correlations that included data from Island End were also calculated and compared to those calculated without data from this station. Because of the large gap in values between Island End chemical activities and those from other stations for pyrene and chrysene, the r^2 values on correlations for those chemicals were both near 1 (0.97 and 0.92, respectively). For pyrene, slopes and intercepts for the correlations are with the uncertainties of the correlations

calculated without Island End data: $a_{org} = 0.17\ (\pm\ 0.01)\ a_{PW} + 2.0\ (\pm\ 1.5)$ (n=14, $p=2\times10^{-10}$). In the case of chrysene, both the slope and intercept change, $a_{org} = 0.09\ (\pm\ 0.01)\ a_{PW} + 2.3\ (\pm\ 0.9)$ (n=10, $p=1\times10^{-5}$). Since the Island End clam tissue activity is the average of two clams that differed by more than an order of magnitude, the reliability of these relationships would be improved by sampling more organisms from Island End, and by sampling areas which have porewater and organism chemical activities that fall in the gap between the Island End and the rest of the stations.

Finally, chemical activities calculated using EqP models for the upper sediment layers were compared to clam tissue chemical activities. No linear correlations of the two measures were found (r^2 values always < 0.05, and p values always > 0.05). Thus, PE-deduced chemical activities were better predictors of tissue concentrations or chemical activities for these three PAHs in *M. arenaria* than sediment porewater activities calculated by applying EqP models.

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Table 4.1. Sampling sites including location, general description, sediment temperature and porosity.

site	no. stations	lat./long.	general description	sediment temperature (°C)	porosity[a]
Collins Cove Salem, MA	4	42° 31.724' N/ 70° 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	42° 30.466' N/ 70° 53.041' W	coarse sand beach, ~ 1.5 km south of Salem Harbor Power Station	9.6	0.29
Lead Mills Marblehead, MA	2	42° 29.821' N/ 70° 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	42° 26.033' N/ 70° 59.671' W	silty sand along shallow tidal estuarie, adjacent to land fill	12	0.52
Island End Chelsea, MA	1	42° 23.392' N/ 71° 03.148' W	silty sand in coal-tar contaminated cove	11.5	0.57
Dorchester Bay Quincy, MA	2	42° 17.852' N/ 71° 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

[a] Porosities were calculated from laboratory measured water content, assuming a solids density of 2.5 g/cm^3. As sediments may have partially drained during sampling and/or lost moisture during storage, reported porosities should be considered a lower bound of field conditions.

Table 4.2. Partition coefficients and water solubility for selected target PAHs and PRCs.

	log K_{OW}[a]	log K_{PEW}	log $K_{lip\text{-}w}$[b]	log $K_{prot\text{-}w}$[b]	log K_{OC}[c]	log K_{BC}[d]	- log C_w^{sat}(L)[e]
phenanthrene/ d10-phenanthrene	4.52	4.3	4.6	3.2	4.2	6.1	4.35
pyrene/ d10-pyrene	5.00	4.6	5.1	3.5	4.6	6.4	4.95
chrysene/ d12-chrysene	5.86	5.5	5.8	4.1	5.4	6.9	5.76

[a] Sangster (1989)
[b] Schwarzenbach et al. (2003), adjusted for temperature (10 °C) and salinity (assumed 0.4 M)
[c] Karickhoff (1981), adjusted for temperature (10°C) and salinity (assumed 0.4 M)
[d] Lohmann et al. (2004)
[e] Calculated from $C_w^{sat}(s)$ values using $C_w^{sat}(L) = C_w^{sat}(s)\, e^{\Delta fusG/RT}$ as given in Schwarzenbach et al. (2003) for (10 °C) (in mol/L). $C_w^{sat}(s)$ values also from Schwarzenbach et al. (2003)

Table 4.3. Concentrations (ng/g dry wt) of PAHs in sediments, organic carbon fractions (f_{OC}s), black carbon fractions (f_{BC}s), C/N and C/H mole ratios

Site / Station	surface layer (approx. top 10 cm)									lower layer (approx. 20 cm depth)								
				f_{OC}			f_{BC}						f_{OC}			f_{BC}		
	phen	pyr	chry	(%)	C/N ratio	C/H ratio	(%)	C/N ratio	C/H ratio	phen	pyr	chry	(%)	C/N ratio	C/H ratio	(%)	C/N ratio	C/H ratio
Collins Cove																		
1	13000	9400	3500	3.3	51	1.66	1.8	12	2.33	23000	9000	2800	13	77	1	5.7	54	6
2	5400	9400	4400	0.8	6	1.6	4.2	43	1.92	5400	9400	4300	4.3	22	<0.2	6.3	69	4
3	6600	5800	4300	2.6	36	<0.2	3.6	22	3.54	4000	5800	2300	3.7	51	0.4	2.6	23	2
Pioneer Village																		
1	5	6	5	0.07	4.5	0.04	0.01	0.5	<0.2	3	5	8	0.06	1	<0.2	0.02	0.6	<0.2
Lead Mills																		
1	42	90	46	0.5	37	<0.2	2.1	16	1.34	420	420	190	1.1	1	<0.2	1.5	39	2
2	200	400	240	-	-	-	-	-	-	2900	2200	850	-	-	-	-	-	-
Pines River																		
1	2400	1400	1200	-	-	-	-	-	-	450	320	230	-	-	-	-		
2	2400	2400	830	1.5	13	0.2	0.44	7	0.36	64	150	65	1.7	11	0.3	0.25	6	0.2
3	140	230	88	1.1	6	0.2	0.06	0.7	<0.2	130	260	69	1.0	14	0.2	0.30	2	0.3
Island End																		
1	2400	16000	5500	9.1	47	<0.2	4.9	30	3.74	-	-	-	-	-	-	-	-	-
Dorchester Bay																		
1	52	120	54	4.0	21	0.5	0.47	9	0.26	77	300	130	1.1	11	0.2	0.29	5	<0.2
2	82	130	49	-	-	-	-	-	-	160	330	100	-	-	-	-	-	-

Table 4.4. Methyl-phenanthrene and -anthracene to phenanthrene and anthracene ratios (Σ192/Σ178) in extracts of PE, clams, and sediemnts for selected stations.

Site	Station	PE	clam	sediment
Collins Cove				
	1	0.5	<0.01	0.7
	2	1.2	1.0	1.7
	3	1.0	<0.01	1.6
Lead Mills				
	1	<0.1	<1	0.6
	2	<0.1	<1	0.8
Pines River				
	1	<0.3	<0.1	0.4
	3	1.0	0.9	0.6
Island End				
	1	6.0	2.4	1.1
Dorchester Bay				
	1	1.0	4.4	0.4
	2	1.4	<0.1	0.4

Table 4.5. Concentrations (ng/gdw) measured in Mya arenaria, water fraction (f_{wat}), and shell length.

Site	Station	Clam	Concentration (ng/gdw) phen	pyr	chry	f_{wat} (%)	shell length (mm)
Collins Cove							
	1	a	310	62	27	84.0	70
		b	110	90	21	85	78
		c	120	70	25	84	76
	2	a	1100	900	374	86	67
		b	77	100	31	86	78
		c	78	110	35	87	82
	3	a	53	150	54	85	70
		b	130	250	110	87	70
		c	85	140	52	85	60
		d	23	91	29	82	52
		e	60	130	38	88	85
		f	97	170	53	86	64
Pioneer Village							
	1	a	26	23	14	82	58
		b	10	10	3	80	74
		c	17	12	3	80	74
Lead Mills							
	1		29	28	13	77	53
	2		36	39	19	83	44
Pines River							
	1	a	58	31	15	84	93
		b	94	84	26	85	90
	2		47	74	24	79	75
	3	a	240	290	110	82	87
		b	28	79	15	81	64
Island End							
	1	a	25	27	33	81	54
		b	156	1730	841	79	52
Dorchester Bay							
	1		40	66	32	77	59
	2		19	38	16	81	56

Table 4.6. Equilibrium PE concentrations (ng/g PE) for selected PAHs, calculated from measured PE concentrations and loss of matching PRC.

		phenanthrene			pyrene			chrysene		
Site	Station	0-4 cm	4-8 cm	8-12 cm	0-4 cm	4-8 cm	8-12 cm	0-4 cm	4-8 cm	8-12 cm
Collins Cove										
	1	1,100	3,000	-	3,900	4,700	-	160	160	-
	2	340	480	-	3,200	4,400	-	260	230	-
	3	190	94	120	4,700	6,700	12,000	280	250	460
	4	260	240	110	2,900	3,600	8,400	200	190	700
Pioneer Village										
	1	62	-	23	220	-	330	140	-	150
Lead Mills										
	1	130	68	120	1,100	2,500	5,800	150	76	140
	2	160	150	-	700	820	-	120	110	-
Pines River										
	1	310	200	78	3,700	1,900	2,400	82	57	37
	2	110	93	57	3,000	3,600	9,100	340	630	180
	3	83	-	92	2,600	-	2,800	230	-	360
Island End										
	1	520	3,300	8,600	57,000	98,000	180,000	7,900	28,000	34,000
Dorchester Bay										
	1	230	110	83	1,800	1,300	1,400	310	140	180
	2	120	-	-	1,100	-	-	180	-	-

Table 4.7. Porewater activities (ppm) for selected PAHs, calculated from measured PE concentrations of target and PRC compounds, K_{PEW} and $C_w^{sat}(L)$ using Eqn. 4.2.

		phenanthrene			pyrene			chrysene		
Site	Station	0-4 cm	4-8 cm	8-12 cm	0-4 cm	4-8 cm	8-12 cm	0-4 cm	4-8 cm	8-12 cm
Collins Cove										
	1	14	39	-	71	86	-	2.8	2.8	-
	2	4.4	6.1	-	58	81	-	4.3	4.1	-
	3	2.4	1.2	1.5	86	122	210	5.7	4.3	8.0
	4	3.3	3.1	1.4	53	66	150	5.1	3.3	12
Pioneer Village										
	1	0.80	-	0.30	4.1	-	6.1	2.4	-	2.6
Lead Mills										
	1	1.9	1.0	1.7	21	46	110	2.6	1.3	2.4
	2	2.1	2.0	-	13	15	-	2.1	1.9	-
Pines River										
	1	4.0	2.5	1.0	67	36	44	1.4	1.0	0.7
	2	1.4	1.2	0.73	55	67	170	5.9	11	3.1
	3	1.1	-	1.2	47	-	51	4.1	-	6.2
Island End										
	1	6.6	42	110	1,100	1,800	3,300	140	500	590
Dorchester Bay										
	1	3.0	1.4	1.1	34	23	25	5.4	2.4	3.1
	2	1.5	-	-	19	-	-	3.0	-	-

Table 4.8. Fractional equilibration of PE samplers after 1 week exposures, calculated from initial and t=7 d concentrations of PRCs in PE. Uncertainty is assumed to be ± 28% based on propagation of error on two PE concentration measurements.

		phenanthrene			pyrene			chrysene		
Site	Station	0-4 cm	4-8 cm	8-12 cm	0-4 cm	4-8 cm	8-12 cm	0-4 cm	4-8 cm	8-12 cm
Collins Cove										
	1	0.78	0.72	-	0.73	0.71	-	0.89	0.88	-
	2	0.64	0.54	-	0.47	0.58	-	0.79	0.70	-
	3	0.59	0.58	0.62	0.47	0.44	0.49	0.64	0.55	0.60
	4	0.81	0.78	0.76	0.76	0.70	0.33	0.85	0.81	0.40
Pioneer Village										
	1	0.69	-	0.69	0.40	-	0.40	0.26	-	0.26
Lead Mills										
	1	0.34	0.45	0.42	0.70	0.71	0.73	0.83	0.82	0.84
	2	0.87	0.40	-	0.73	0.74	-	0.90	0.88	-
Pines River										
	1	0.66	0.64	0.65	0.90	0.81	0.69	0.93	0.90	0.83
	2	0.66	0.70	0.74	0.54	0.73	0.55	0.84	0.92	0.85
	3	0.96	-	0.56	0.78	-	0.43	0.53	-	0.16
Island End										
	1	0.86	0.92	0.92	0.84	0.87	0.86	0.87	0.96	0.94
Dorchester Bay										
	1	0.34	0.39	0.54	0.71	0.66	0.75	0.69	0.65	0.78
	2	0.40	-	-	0.71	-	-	0.69	-	-

Figure 4.1. Map of sampling locations, 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).

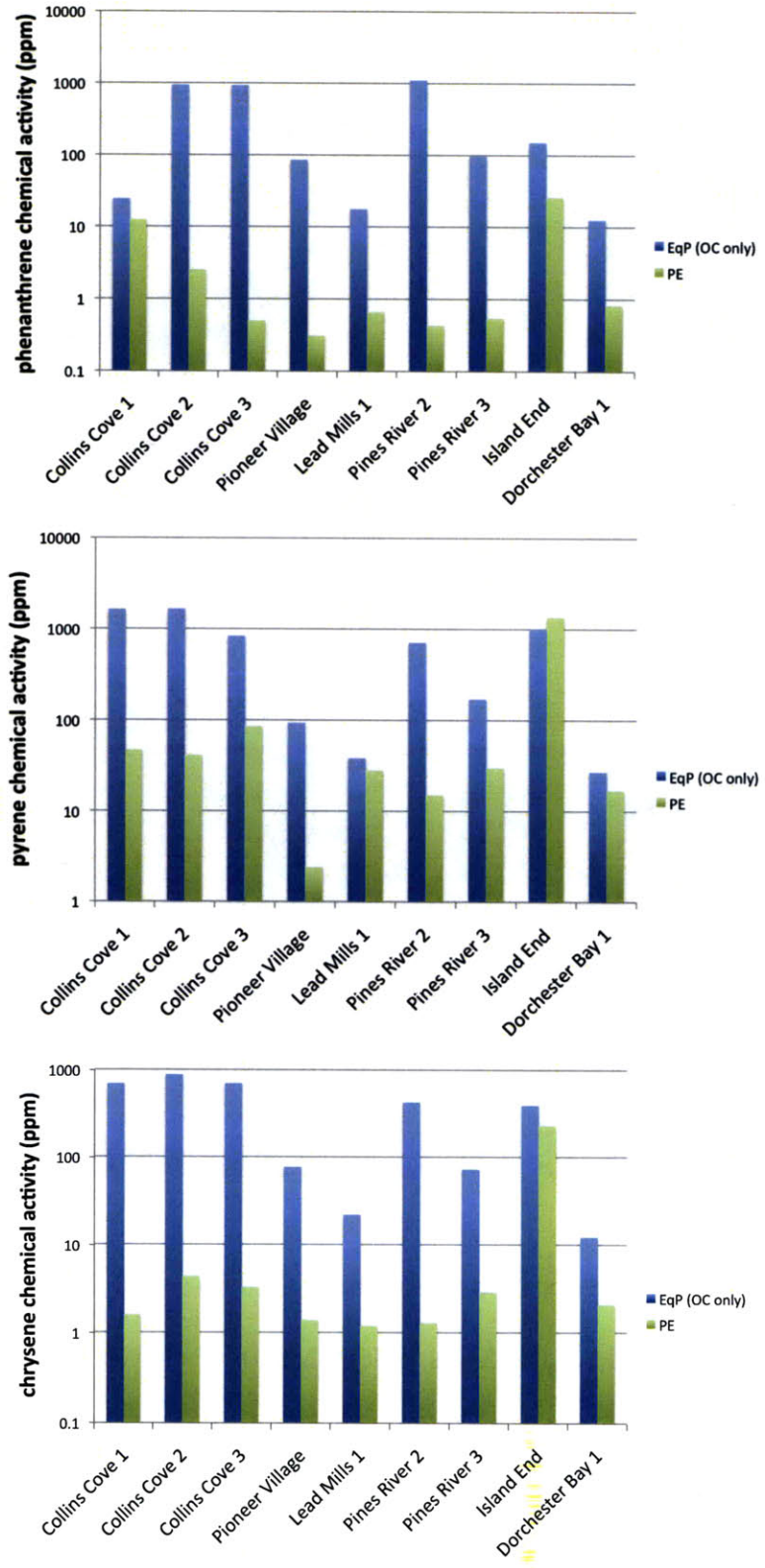

Figure 4.2. Comparison of chemical activities of three PAHs measured in porewaters using PE passive samplers and calculated using an EqP model considering only organic carbon ($f_{OC} + f_{BC}$).

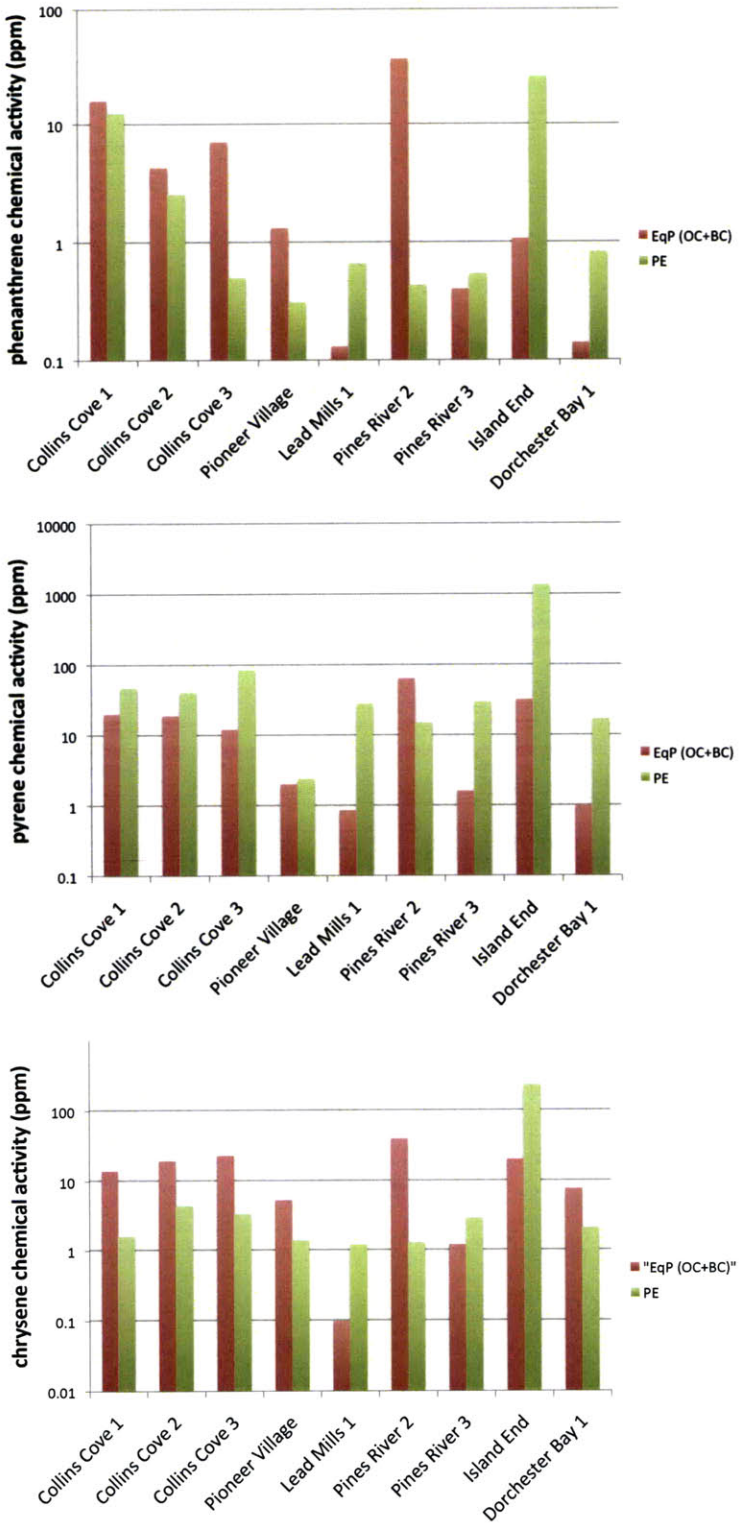

Figure 4.3. Comparison of chemical activities of three PAHs measured in porewaters using PE passive samplers and calculated using an EqP model considering both organic carbon and black carbon.

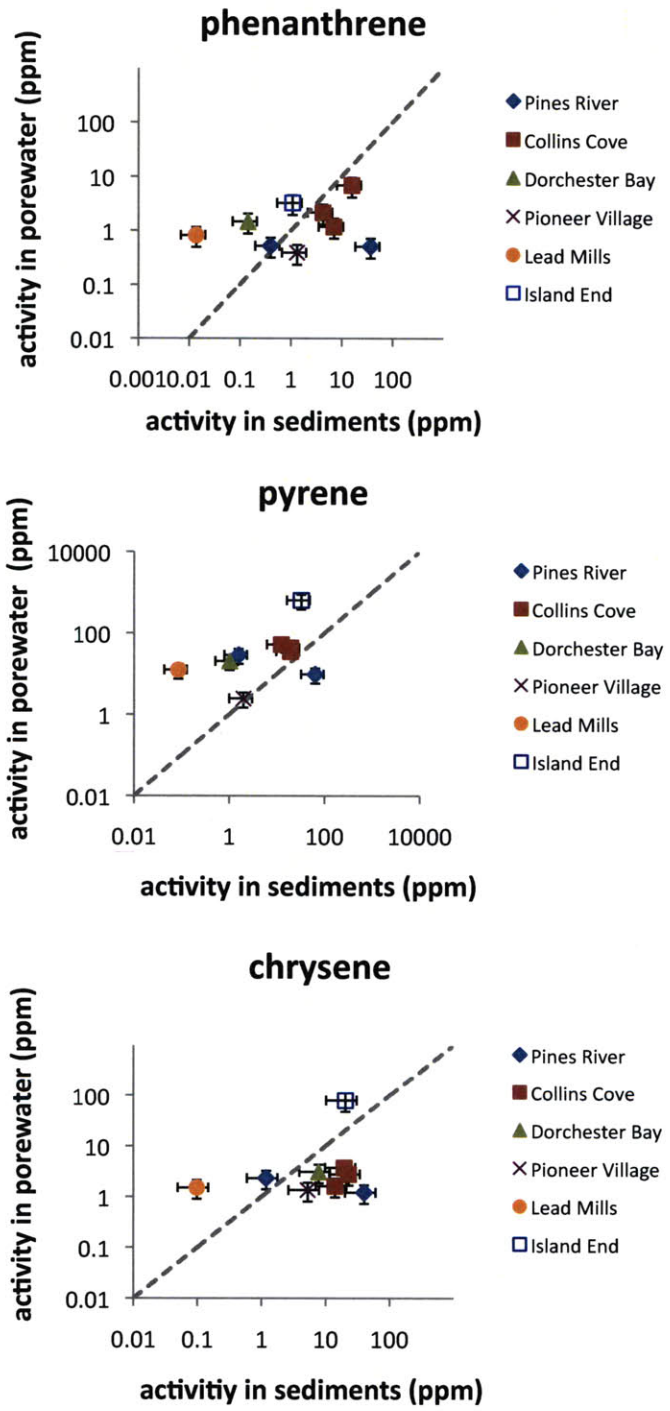

Figure 4.4. Chemical activities of three PAHs measured in porewaters using PE passive samplers and calculated using EqP model (including f_{OC} and f_{BC}) and measured sediment concentrations at six sites near Boston, MA.

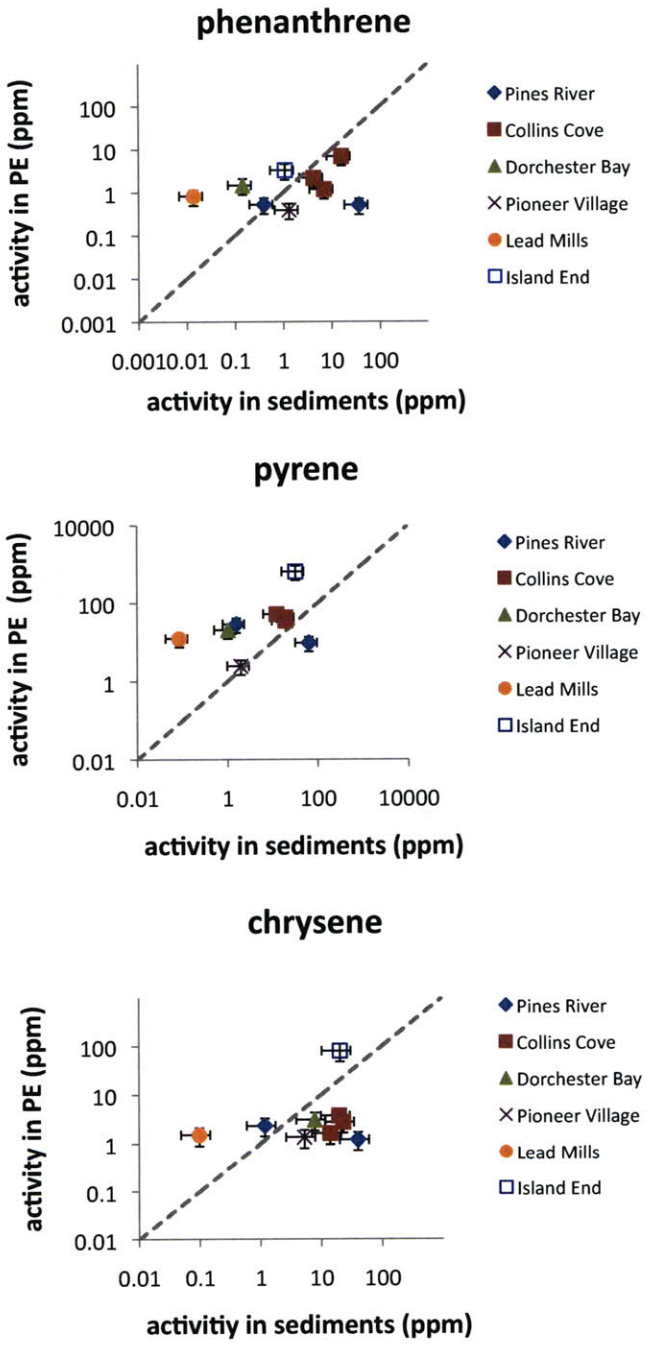

Figure 4.5. Chemical activities of three PAHs calculated using EqP model and measured sediment concentrations and measured in clam tissues (averaged for each station) at six sites near Boston, MA.

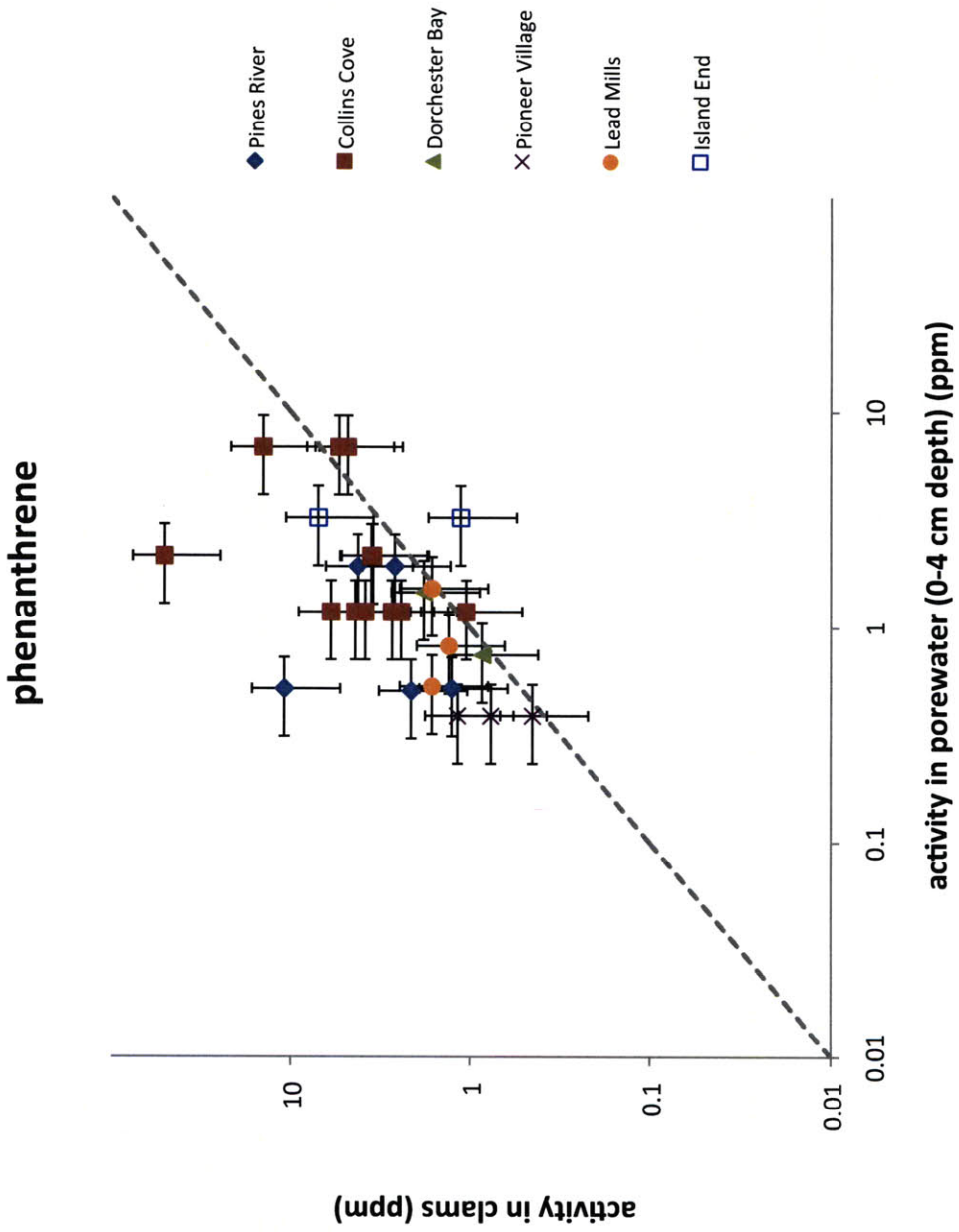

Figure 4.6. Chemical activities of phenanthrene measured in porewaters (0-4 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

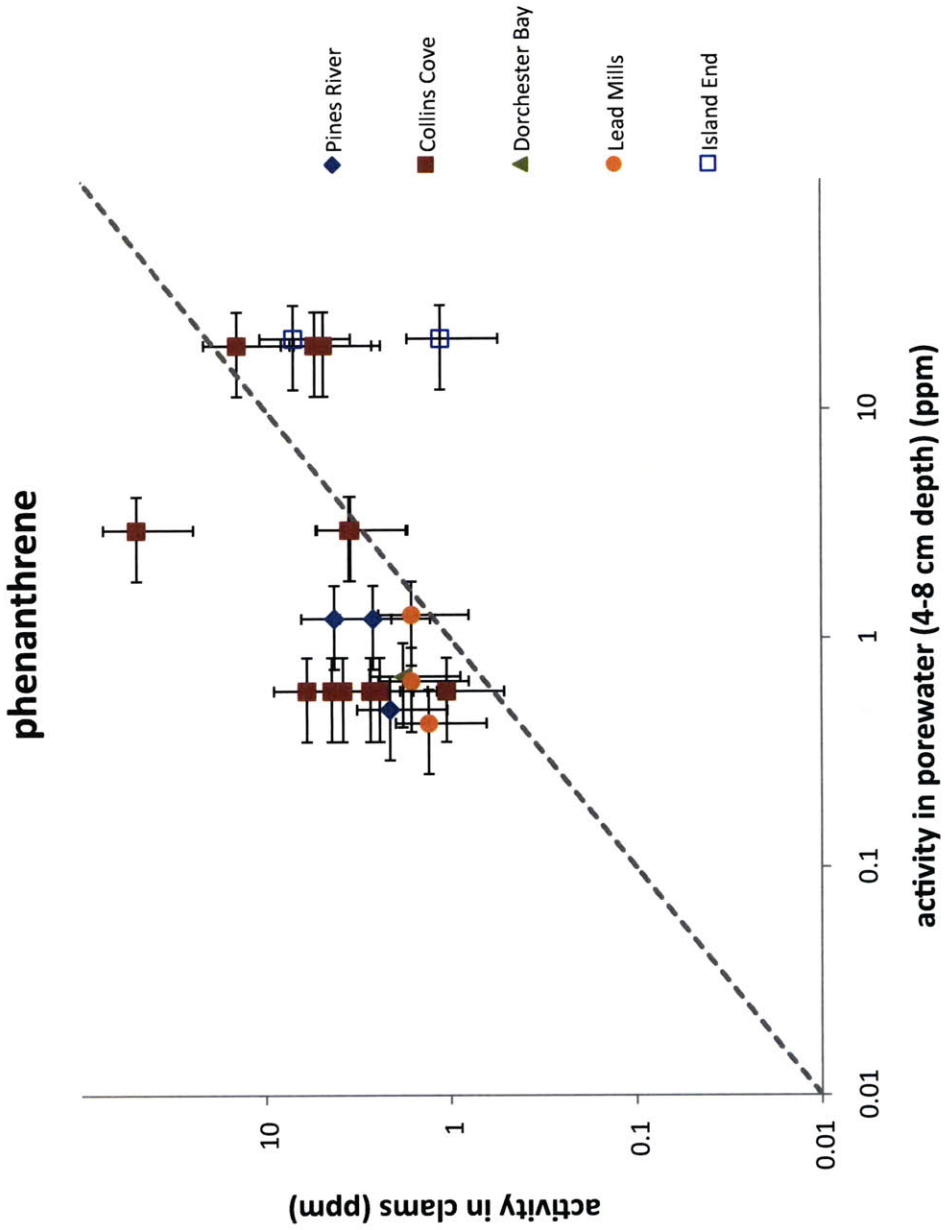

Figure 4.7. Chemical activities of phenanthrene measured in porewaters (4-8 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

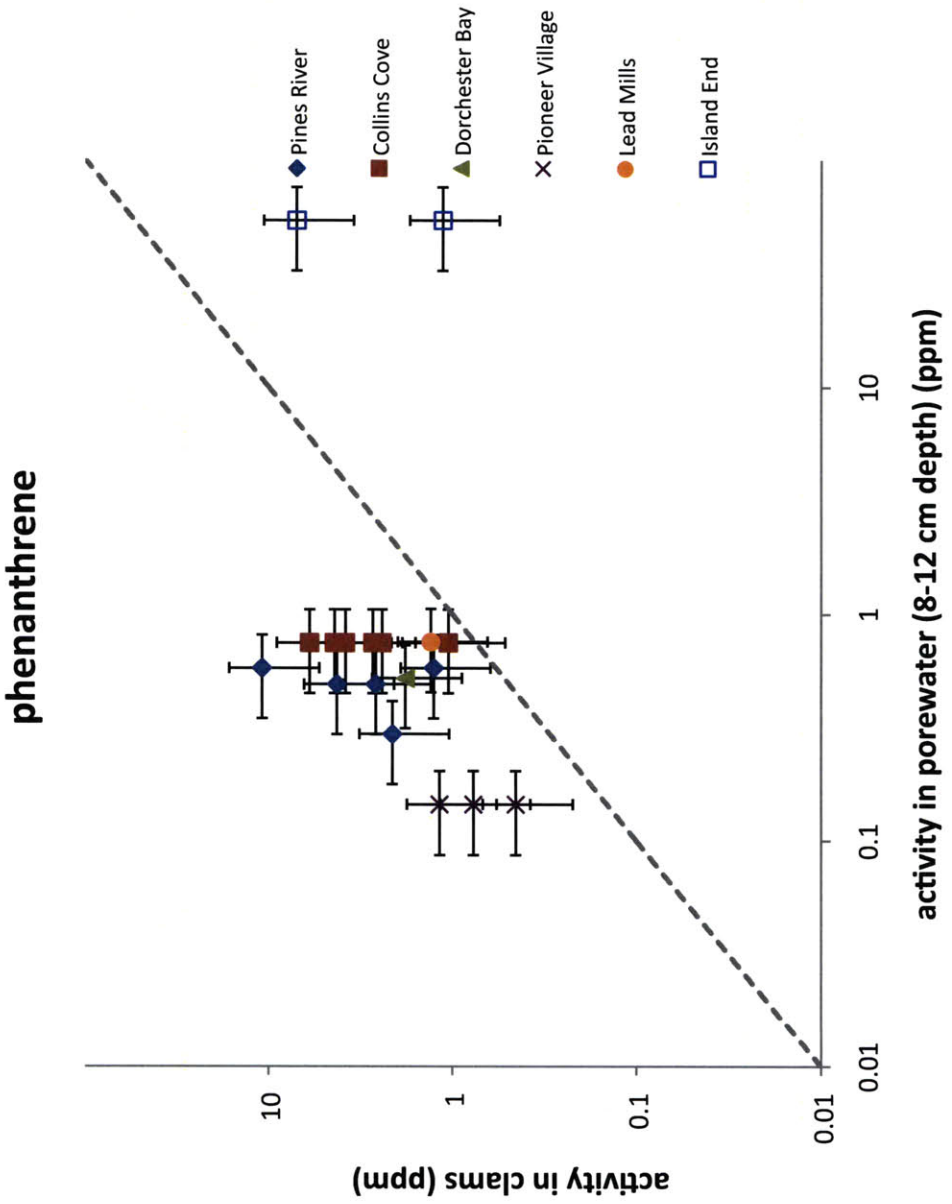

Figure 4.8. Chemical activities of phenanthrene measured in porewaters (8-12 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

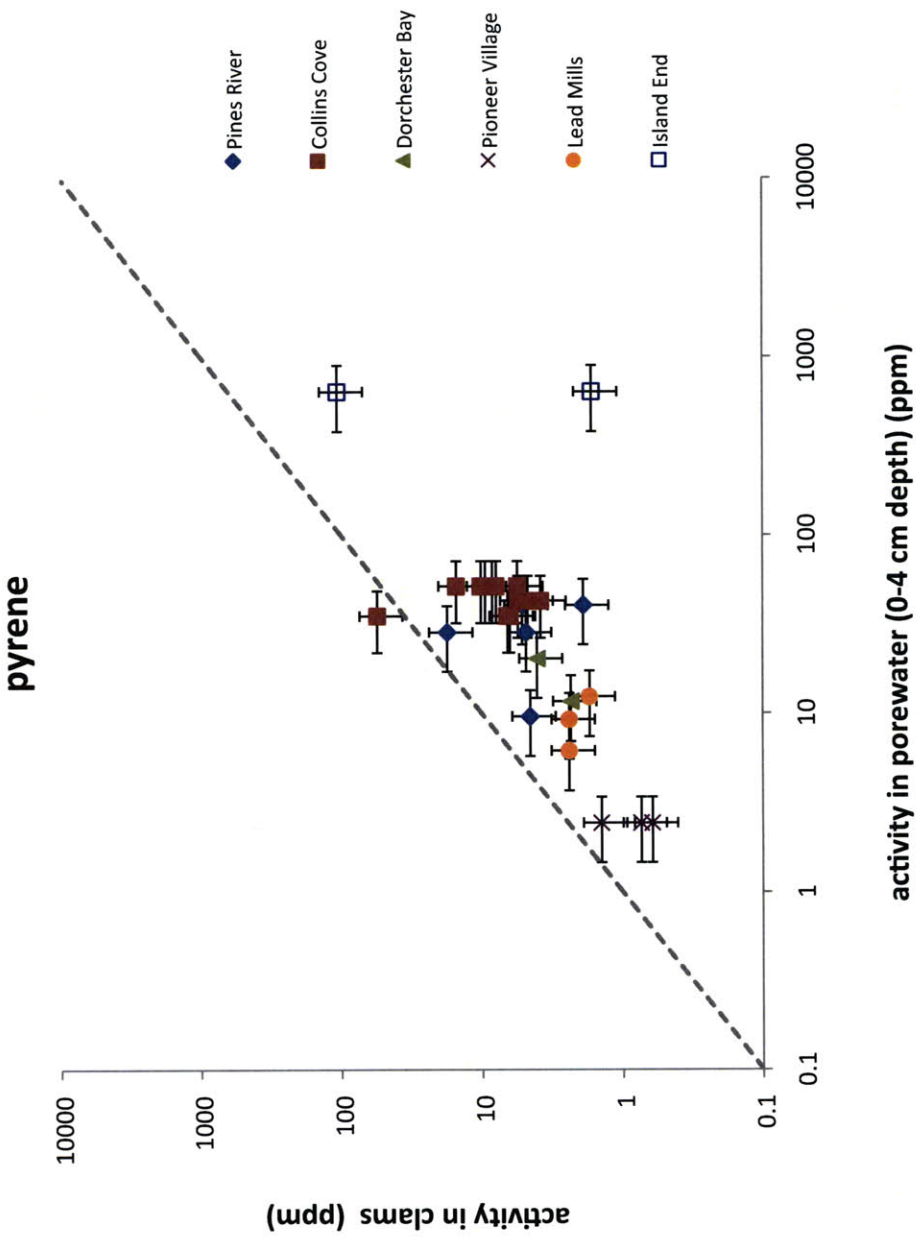

Figure 4.9. Chemical activities of pyrene measured in porewaters (0-4 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

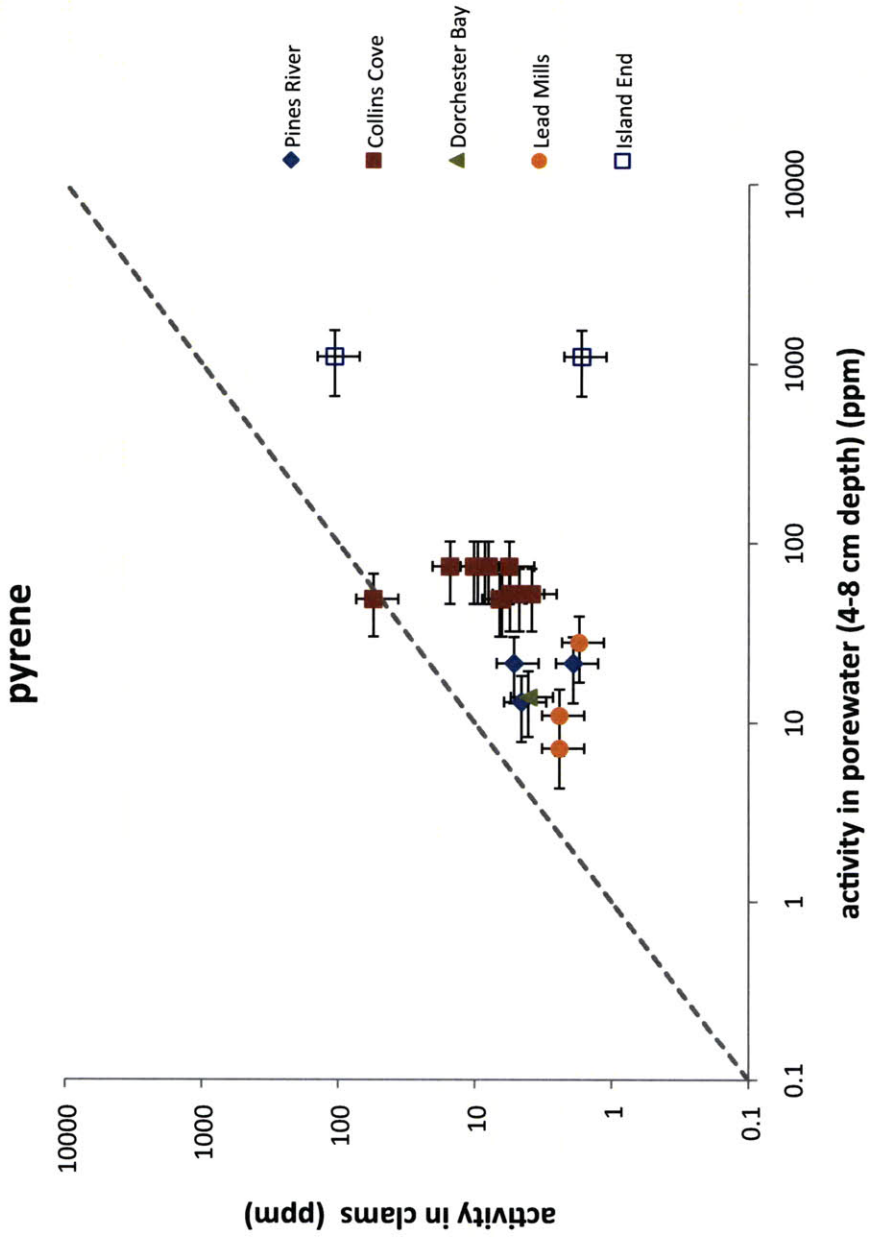

Figure 4.10. Chemical activities of pyrene measured in porewaters (4-8 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

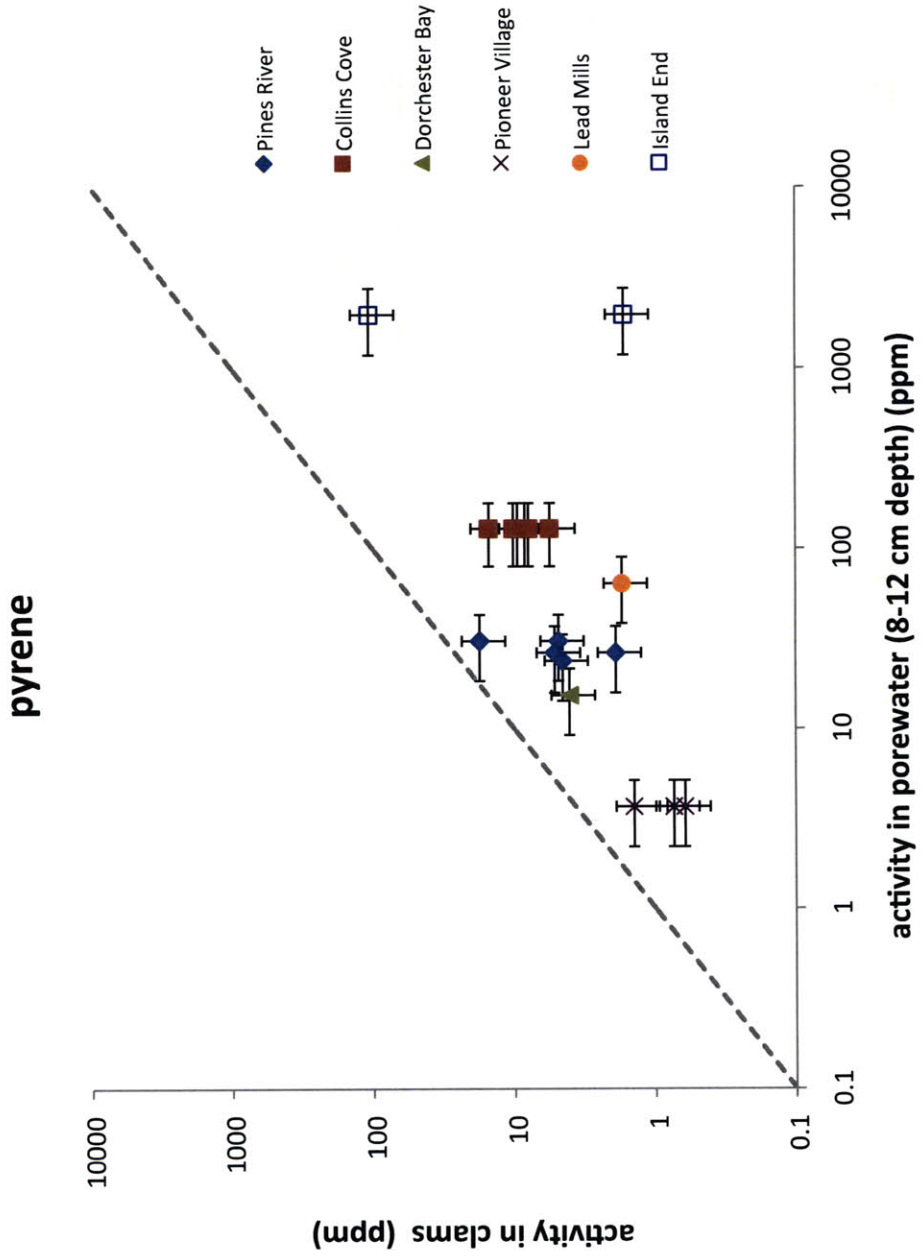

Figure 4.11. Chemical activities of pyrene measured in porewaters (8-12 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

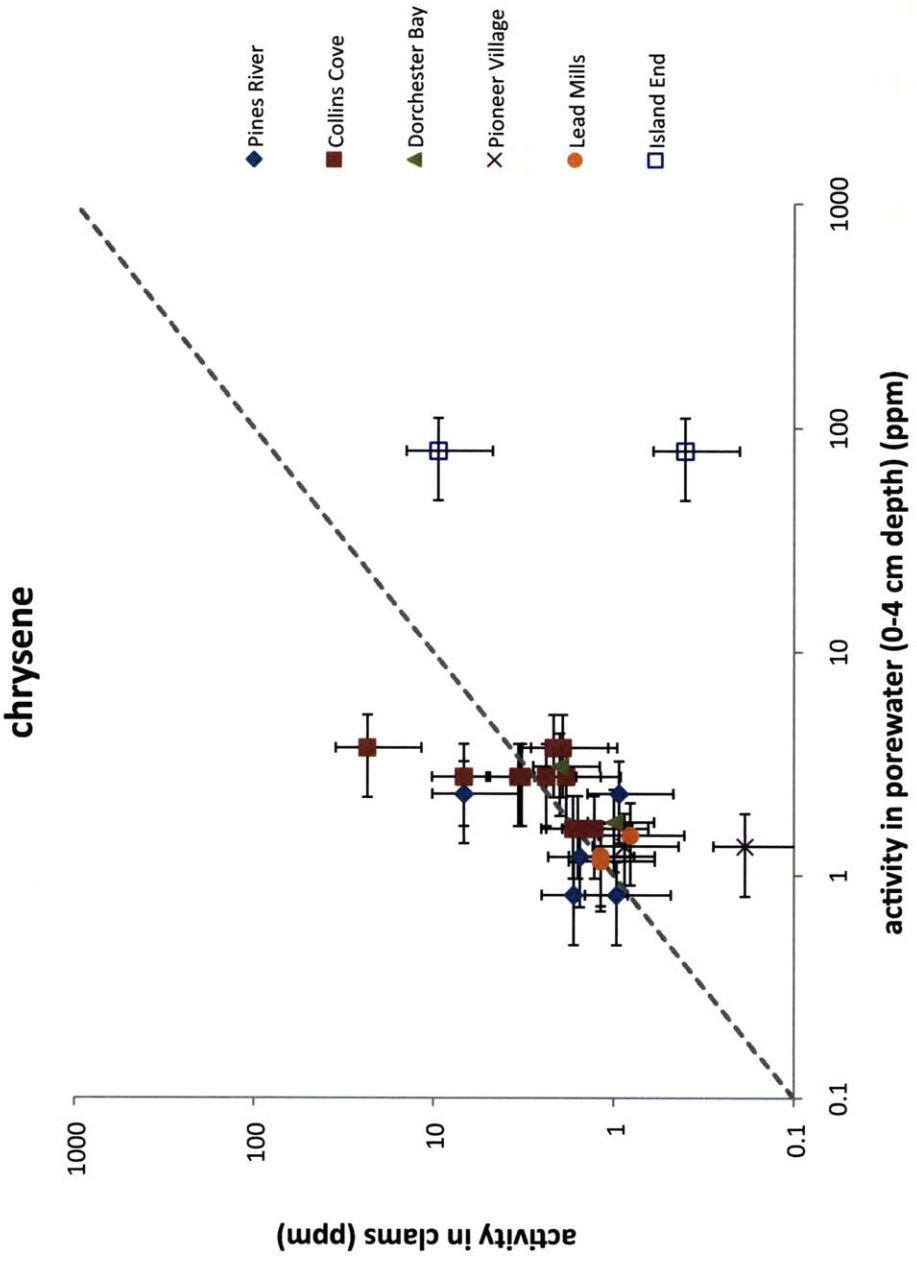

Figure 4.12. Chemical activities of chrysene measured in porewaters (0-4 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

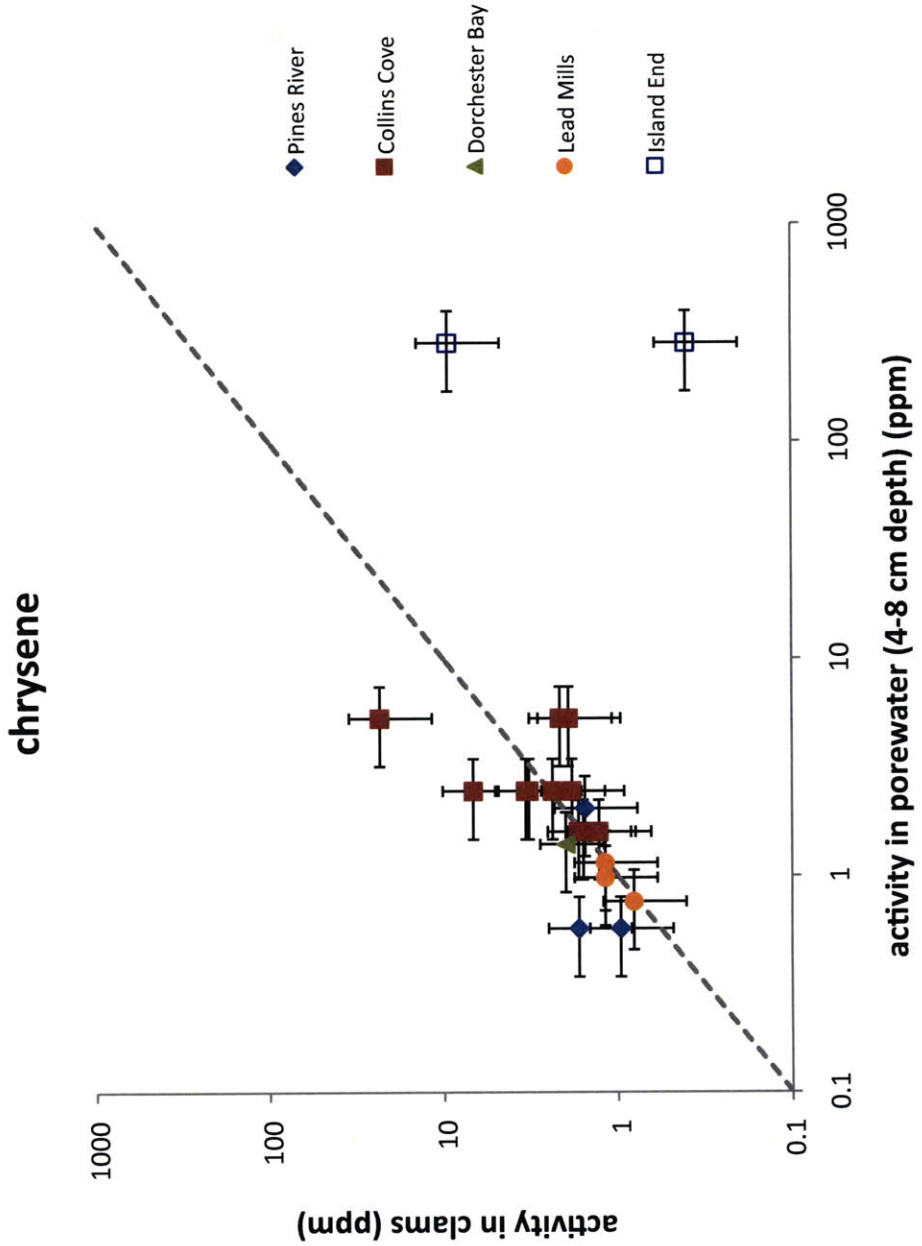

Figure 4.13. Chemical activities of chrysene measured in porewaters (4-8 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

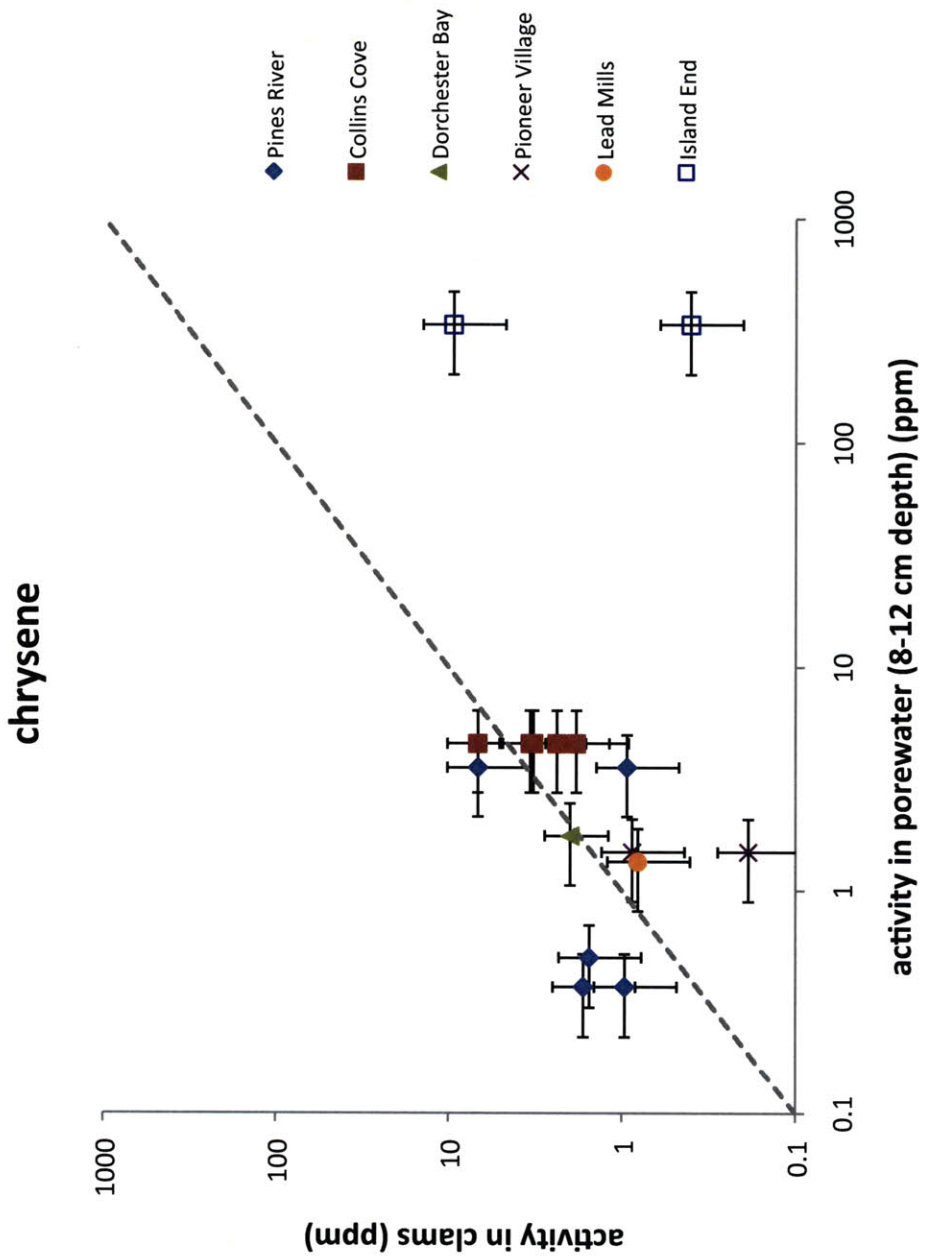

Figure 4.14. Chemical activities of chrysene measured in porewaters (8-12 cm depth) using PE passive sampler and in clam tissues at six sites near Boston, MA.

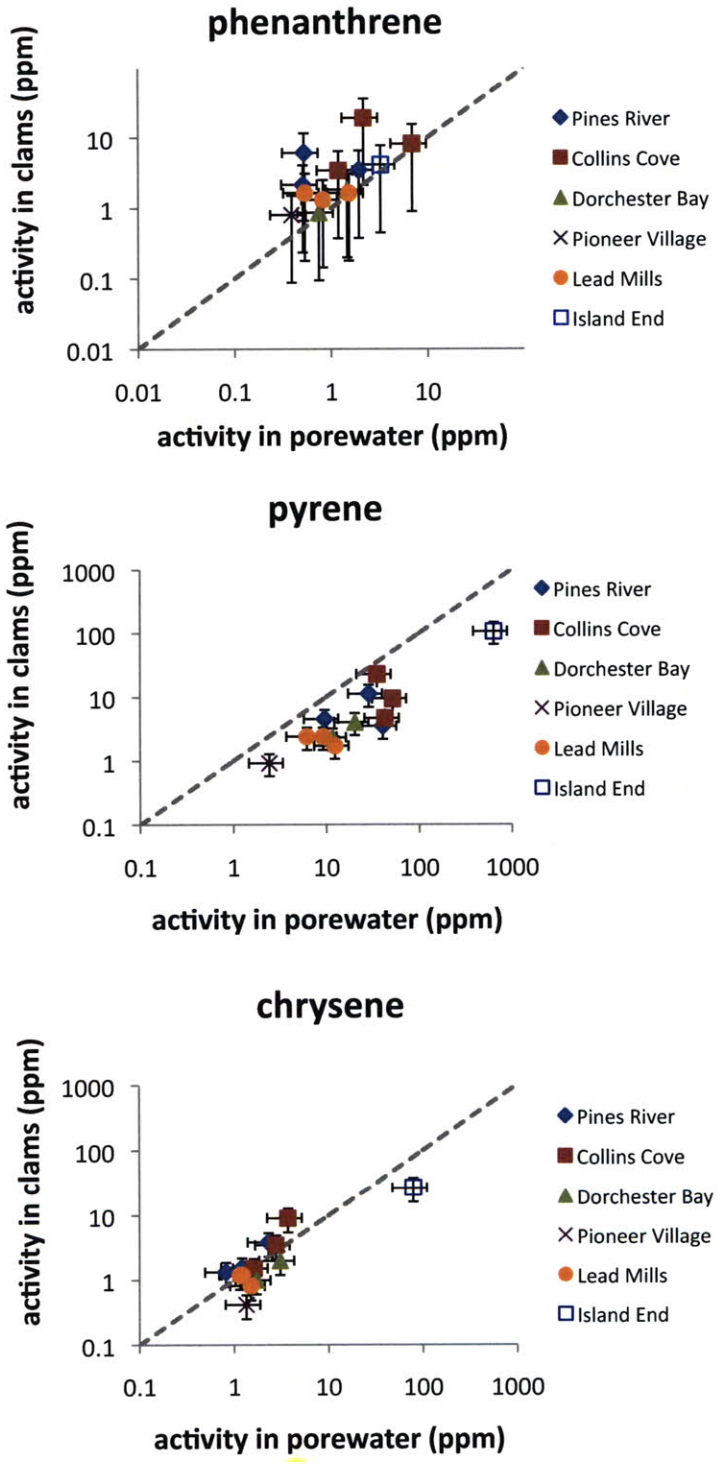

Figure 4.15. Chemical activities of three PAHs measured in porewaters (0-4 cm depth) using PE passive samplers and in clam tissues (averaged for each station) at six sites near Boston, MA.

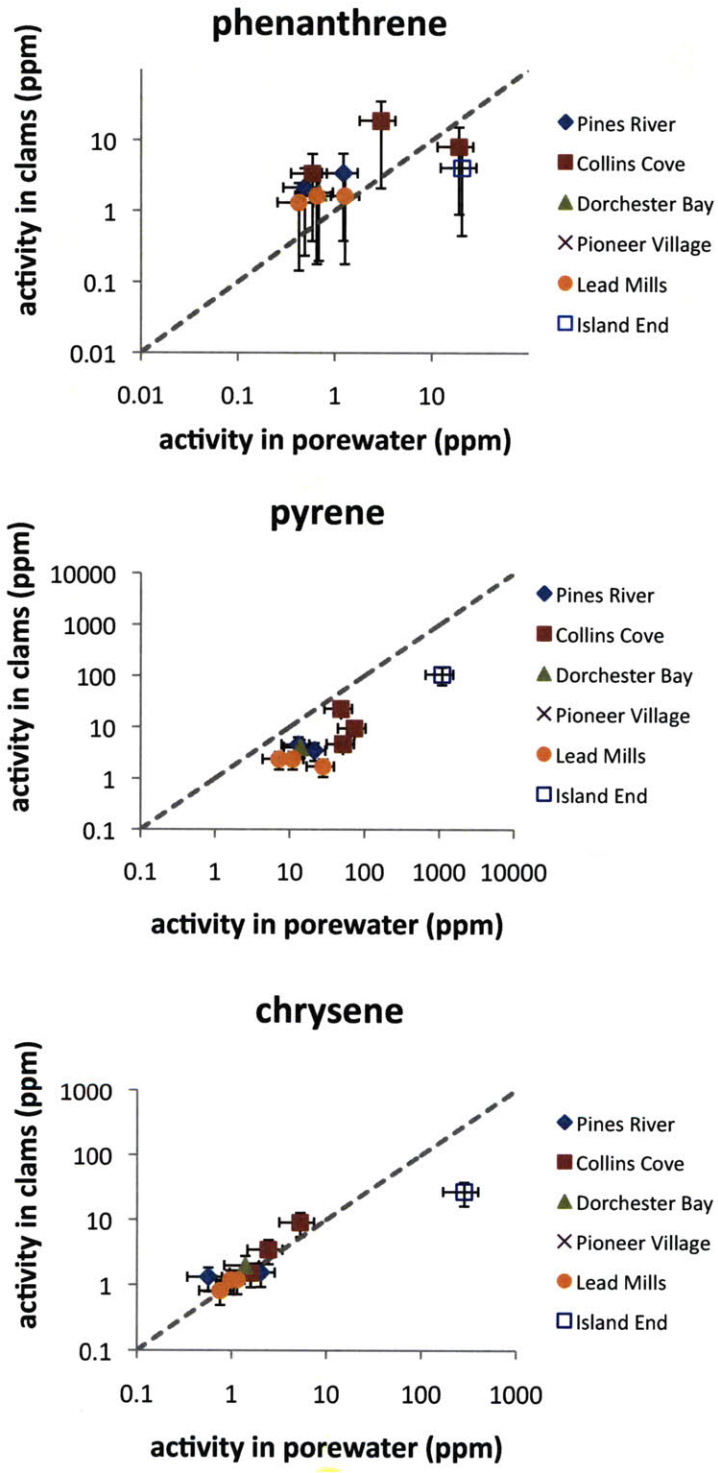

Figure 4.16. Chemical activities of three PAHs measured in porewaters (4-8 cm depth) using PE passive samplers and in clam tissues (averaged for each station) at six sites near Boston, MA.

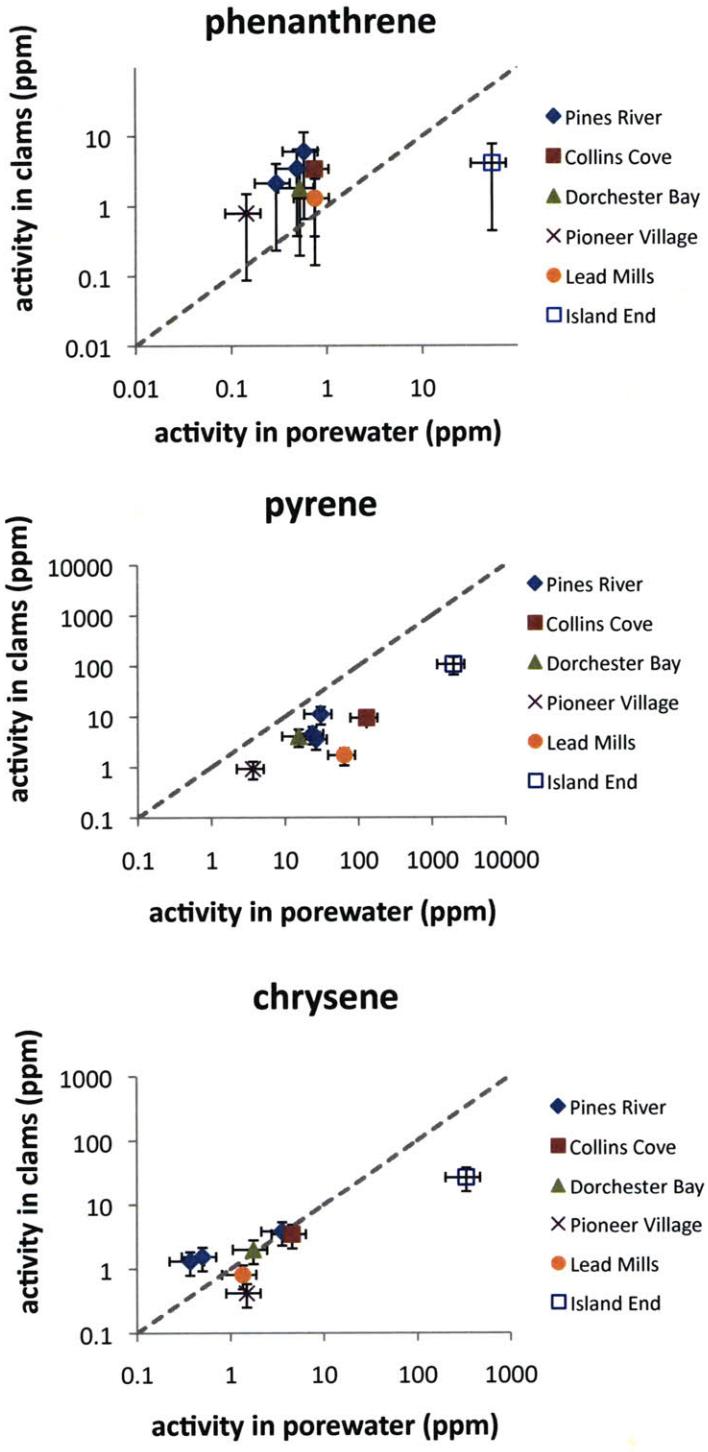

Figure 4.17. Chemical activities of three PAHs measured in porewaters (8-12 cm depth) using PE passive samplers and in clam tissues (averaged for each station) at six sites near Boston, MA.

Chapter 5: Conclusions

The primary goal of this research was to develop a method for measuring porewater concentrations and chemical activities of hydrophobic organic chemicals, such as PAHs, in sediment beds. Of the three methods used to measure or deduce C_{PW} in Chapters 1 and 2 (TOC-corrected C_{PW}, airbridge-measured C_W, and PE-deduced C_{PW}), the PE-PRC method was the easiest to perform. Direct extraction of porewaters from field-collected sediment samples requires careful handling to ensure that porewaters are not drained or exchanged with the water column. Once in the laboratory, additional care (e.g., redox protective) and time consuming handling are required to prevent changes in partitioning between phases. In addition, centrifuging 0.4 L of sediments from the submerged Boston Harbor field site described in Chapter 1 produced only 62 mL of porewaters that could be solvent extracted and measured for TOC content. The airbridge measurement technique required very careful handling of the apparatus and long experiment duration (months) with multiple subsamples in order to confirm that equilibrium was reached. As PE-deduced concentrations typically match those measured using other methods within about a factor of two, and risk-assessment models use even larger safety factors, the PE-PRC method can be a useful tool for measuring porewater concentrations of PAHs in intact sediment beds without the labor and time required by other methods.

A second goal of this research, using chemical activities measured in sediments to predict tissue concentrations in benthic organisms, was examined in Chapter 4. Again, using correlations of chemical activities in PE and clam tissues, PE-deduced chemical activities were able to predict chemical activities of pyrene and chrysene in clam tissues to within a factor of 3.

The simplicity of measuring chemical activities using the PE-PRC method would make it possible to take more measurements of any given site. Deployment, recovery, extraction and analysis of PE samplers are significantly easier than the collection and extraction of clams or sediments. PE extractions can be accomplished by simply soaking PE strips in solvent; no further separation steps are required. This simplicity saves time. While the extraction of all the PE samples in this study (n= 32) were completed over a period of just 3 days, corresponding clam and sediment extractions required many weeks to complete. Without separations and solvent transfers, smaller volumes of solvents are necessary. While 100's of mL of different solvents were required in the extraction, exchanges, and separations of clam and sediment extracts, PE samples required less than 100 mL of a single solvent (in this work PE extracts were exchanged into hexane for consistency with tissue and sediment extracts). Thus, many more stations could be sampled for the same effort and material costs as would be expended on sediment or organism samples. While other passive sampling techniques do not require any solvents (e.g. solid phase micro-extraction with direct desorption on a GC column) (Arthur and Pawliszyn 1990; Mayer et al. 2000; Hawthorne et al. 2005), by extracting PE samplers into a solvent, multiple analyses of the extracts can be made.

PE samplers for directly measuring porewater chemical activities may be more useful for predicting the risk to benthic organisms posed by PAH contamination in sediments, than measurement of the organisms themselves. While in this work samples were all collected at the same time, organism concentrations have been observed to vary temporally even when water and sediment concentrations did not (Piccardo et al. 2001). Even at a single station, clam concentrations in this work were observed to vary by up to an order of magnitude, while PE samplers gave consistent results. PE samplers would be especially useful at the most polluted

sites, where organisms may be very difficult, if at all possible, to find. Unlike organism concentration, porewater chemical activity is a reproducible measure that can be taken in any sedimentary system regardless of which, if any, organisms are present.

PE samplers could be applied in other ways to the problem of assessing the environmental risk associated with contaminated sediments. Samplers could be used instead of costly 28-day organism exposure studies in the assessment of dredged materials for open-water disposal (U.S.EPA 1998). PE-deduced chemical activities could also be combined with existing methods for determining Equilibrium Partitioning Sediment Benchmarks (ESBs) to determine the potential toxicity of a given sediment to organisms for which narcotic toxicity data have been compiled. Although Chapter 4 presented data for only three PAHs, if the diffusivities of the PAHs in PE at 10°C were known or could be estimated, chemical activities for additional compounds (including the 34 PAHs recommended for measurement in determining ESBs) could be calculated by applying the methods described in Chapter 3. Using PE instead of EqP models, which include sorption only to f_{OC} as described in the EPA's guidance document, would improve ESBs by going straight to porewater concentrations and avoiding K_d calculation.

Finally, PE samplers could reduce the labor and expense involved in measuring porewater concentration or chemical activity gradients with depth into sediment, as was described for a submerged Boston Harbor site in Chapter 1. Porewater measurement at the field site required divers to collect and cap a core before bringing it to the surface. Once in the laboratory, the sediment core, again, required careful handling. Subsequent sectioning and porewater separation yielded very small (10s of mL) porewater volumes making extract analysis a challenge. PE samplers, however, were deployed and retrieved from the side of a boat by a single person. Although the field site was strewn with cobbles, divers confirmed that the frames

(Figure 2.1) penetrated the sediments and strips were intact when the sampler was recovered. The strips could then be sectioned into finer intervals than the sediment core because obtaining an extractable porewater volume was not a concern. By deploying the strip across the bed-water interface, one could easily assess the gradients driving bed-to-water column transfers. Such an application would be useful in determining the efficacy of in-place capping of contaminated sediments.

Future work

There are many areas were additional research would improve the applicability of passive sampling using PE.

- In order to apply the mass-transfer model outlined in Chapter 3 to additional chemicals, and in place sediments, PE diffusivities for those chemicals at environmentally relevant temperatures and pressures must be measured.
- As HOCs of many other classes contaminate sediments, the PE-PRC method could be tested for measuring porewater concentrations and chemical activities of chemicals of these other classes (e.g. PCBs, pesticides, dioxins).
- The PE-PRC method could also be tested for measuring chemical activities of chemicals in soils, where the effective diffusivity term for the porous media, used in the mass-transfer model, would include the possibility of diffusion through air-filled pores.

References

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Piccardo, M. T., Coradeghini, R. and Valerio, F. Polycyclic aromatic hydrocarbon pollution in native and caged mussels. *Marine Pollution Bulletin* **2001**, 42, 951-956.

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Appendix A: Matlab code for modeling PE-sediment mass transfer

HOC diffusion was considered to occur in a system consisting of two media, a finite PE strip of thickness $2l$ and semi-infinite sediment on both sides, and to follow Fick's second law:

$$\partial C/\partial t = D\,\partial^2 C/\partial x^2 \qquad \text{(A.1)}$$

where C is concentration in g/cm^3, t is time in s, and D is diffusivity in cm^2/s. The region $-l < x < l$ was of one substance (here PE) in which the diffusion coefficient was D_{PE}, and the two regions $x < -l$ and $x > l$ were of another substance (here sediments) in which the diffusion coefficient was D_{SED}. Initially, the concentration in the region $-l < x < l$ was C^0_{PE}, while the concentration in the regions $x < -l$ and $x > l$ are C^0_{SED}. Boundary conditions at the interfaces were as follows:

$$C_{SED}/C_{PE} = K_{SEDPE} \text{ at } x = l \text{ and } x = -l \quad \text{for } t > 0 \qquad \text{(A.2)}$$

and

$$D_{PE}\,\partial C_{PE}/\partial x = D_{SED}\,\partial C_{SED}/\partial x \text{ at } \quad x = l \text{ and } x = -l \qquad \text{(A.3)}$$

As no analytical solution could be found for this problem, a finite-difference numerical approach was used to model mass transfers in the system. The numerical model was tested against analytical solutions for two cases: (1) where diffusion coefficients are the same in the two materials, and the partition coefficient is equal to one, and (2) where the region $0 < x < l$ is so long that the system behaves as two semi-infinite layers with different diffusion coefficients and

a partition coefficient not equal to one. Results of the numerical model matched those of the analytical solution.

The following Matlab code was used to numerically model diffusion between PE and sedimentary porous medium. Parameters in the code below simulate an HOC such as pyrene in sediments such as those from Dorchester Bay assuming 70% porosity.

```
% explicit finite-difference approximation to 1-D diffusion in 1
direction %
% with a no flux boundary on PE side of a PE-sediment composite
material %

clear all;

runtime=75; %time in hours
Ksedpe=0.13; %cm^3(PE)/cm^3(sed)
Kpesed=1/Ksedpe;

CoinPE=1; %Co in the PE (ug/cm^3 PE)
CoinSED=0; %Co in the Sediments (ug/cm^3)

Dpe=2*10^-11; %(cm^2/s)
Dsed=2.23*10^-10; %Dsed (cm^2/s)

dt=1; % (sec)
r=0.05;

dxpe=((Dpe*dt)/r)^0.5; % (cm)
dxsed=((Dsed*dt)/r)^0.5; % (cm)

pesections=12.7*10^-4/dxpe; % for 25.4 um thick PE
PE=round(pesections);

% setting up initial conditions, t=0
    % setting the PE section equal to Co in PE

for i=1:PE
   C(i)=CoinPE;
end;

    % setting seds equal to Co in seds

sedsections=1500*10^-4/dxsed;
SED=round(sedsections);
```

```
for i=PE+1:PE+SED
   C(i)=CoinSED;
end;

time=0;
Coboundary=CoinPE;
for j=1:(runtime*3600);
    time=time+1;

    %no flux boundary

    Coboundary=Coboundary+2*r*(C(1)-Coboundary);

    C(1)=C(1)+r*(Coboundary-2*C(1)+C(2)); %first pe point

    for i=2:PE-1
        C(i)=C(i)+r*(C(i-1)-2*C(i)+C(i+1)); % pe points
    end;

    % wall boundary

    C(PE)=(((C(PE+1)*Dsed*dxpe)+(C(PE-
1)*Dpe*dxsed))*Kpesed)/((Dsed*dxpe)+(Dpe*dxsed*Kpesed)); %last PE
point
    C(PE+1)=C(PE+1)+r*((C(PE)/Kpesed)-2*C(PE+1)+C(PE+2)); %first SED
point

    for i=PE+2:PE+SED-1
        C(i)=C(i)+r*(C(i-1)-2*C(i)+C(i+1)); % rest of sed points
    end

    C(PE+SED)=CoinSED; % boundary condition

end;

% calibrating x axis (position in cm)
totallength=(SED*dxsed)+(PE*dxpe);
for i=1:PE
    x(i)=(i*dxpe);
end
PElength=PE*dxpe;
for i=PE:PE+SED
    x(i)=(PElength+((i-PE)*dxsed));
end

plot(x,C,'-')
xlabel('position (cm)')
ylabel('concentration (ug/cm^3)')
```

Appendix B: Analyses of possible loss of PAH from PE during solvent swabbing or exposure to air

Solvent swab tests

Due to the presence of coal tar at one of the sites sampled in this work, a test of swabbing techniques for removing material from the surface of the polyethylene (PE) and the possible affects swabbing might have on concentrations of PAHs measured in the PE was conducted. First, three strips of 25 μm thick PE (21 to 32 mg) were tumbled with sediments and water from Island End, Chelsea, MA in three round bottomed flasks for 56 d. Upon removal from sediment slurry, each PE strip was sectioned in to 3 subsamples. Each subsample was rinsed in laboratory water, dried with a kim-wipe, and swabbed with a hexane soaked kim-wipe. One subsample from each flask was then wiped using a second hexane soaked kim-wipe, while another subsample from each flask was wiped using a second hexane soaked kim-wipe and a dichloromethane soaked kim-wipe. All subsamples were then extracted three times in dichloromethane and analyzed using a gas chromatograph/mass spectrometer. No significant differences between PE concentrations in the three groups of subsamples were observed for any of the six PAHs measured (Table B.1). We conclude from this test that a single hexane swab was sufficient to remove any coal tar residue adhering to the surface of the PE without changing the adsorbed PAH concentration.

Table B.1. PAH concentrations (μg/g PE) in PE subsamples from three PE-sediment slurry tumbling tests (phen=phenanthrene, anth=anthracene, fluo=fluoranthene, pyr=pyrene, b(a)a=benz(a)anthracene, chry=chrysene).

Tumbled PE Flask	Section			phen	anth	fluo	pyr	b(a)a	chry
1	A	wiped with hexane (2X) and DCM		4.0	25	122	107	39	36
1	B	wiped with hexane (2X)		6.2	40	173	151	54	49
1	C	wiped with hexane (1X)		3.8	24	111	97	36	33
2	A	wiped with hexane (2X) and DCM		8.0	41	184	158	56	50
2	B	wiped with hexane (2X)		8.8	46	185	163	61	57
2	C	wiped with hexane (1X)		8.4	44	186	158	56	51
3	A	wiped with hexane (2X) and DCM		3.4	17	86	77	29	27
3	B	wiped with hexane (2X)		6.8	35	149	128	47	43
3	C	wiped with hexane (1X)		7.3	37	163	140	52	48
		wiped with hexane (2X) and DCM	average	5.2	28	131	114	41	38
			SD	2.5	12	49	41	13	12
			CV	0.49	0.44	0.38	0.36	0.32	0.31
		wiped with hexane (2X)	average	7.3	40	169	147	54	50
			SD	1.4	6	18	18	7	7
			CV	0.19	0.14	0.11	0.12	0.13	0.15
		wiped with hexane (1X)	average	6.5	35	153	132	48	44
			SD	2.4	10	38	31	11	9
			CV	0.37	0.30	0.25	0.24	0.23	0.21

Modeled loss/gain of PAH to/from air during sampler handling

The possibility of losing significant amounts of PRC or gaining significant amounts of target chemical to or from the air during sampler handling was modeled using Eqn 2.10. Calculations were made for the most volatile PRC/target chemical used in this work, phenanthrene. Assuming a 1 hr air exposure, diffusivity of phenanthrene in air of 0.05 cm^2/s, and an air-water partition coefficiant, K_{aw}, of $10^{-2.9}$, less than 0.2% of the d10-phenanthrene PRC would be lost. Correspondingly, PE would have become less than 0.2% equilibrated with air concentrations of phenanthrene. As the other compounds measured in this work have lower K_{aw} than phenanthrene, their losses/gains are expected to be even lower over the same exposure time. PE samplers used in this work were exposed to the air for times shorter than one hour.

Appendix C: Derivation of Laplace solution for diffusion model

The following is the derivation of the Laplace space expression for the fractional PRC mass lost from a polymer film to an infinite bed of sediment porous medium. First we expressed concentrations, distance and time in non-dimensional terms.

$$\hat{C}_{PE} = \frac{C_{PE}}{C_{PE,init}} \tag{C.1}$$

$$\hat{C}_{SED} = \frac{C_{SED}\, K_{PESED}}{C_{PE,init}} \tag{C.2}$$

$$\hat{x} = \frac{x}{l} \tag{C.3}$$

$$T = \frac{t\, D_{PE}}{l^2} \tag{C.4}$$

At the boundary of the polymer film and the sediment ($\hat{x} = 1$), $\hat{C}_{PE} = \hat{C}_{SED}$ for all t > 0, and Eqn. 3.5 may be expressed as

$$\frac{\partial \hat{C}_{PE}}{\partial \hat{x}} = \frac{\psi}{K_{PESED}} \frac{\partial \hat{C}_{SED}}{\partial \hat{x}} \qquad \text{at } \hat{x} = 1 \tag{C.5}$$

where $\psi = D_{SED}/D_{PE}$ and K_{PESED} is the polymer-sediment partition coefficient (cm^3 sediment/cm^3 polymer) .

Fick's 2nd Law for diffusion in the polymer and in the sediment may also now be expressed in non-dimensional terms

$$\frac{\partial^2 \hat{C}_{PE}}{\partial \hat{x}^2} = \frac{\partial \hat{C}_{PE}}{\partial T} \qquad \hat{x} < 1 \tag{C.6}$$

$$\frac{\partial^2 \hat{C}_{SED}}{\partial \hat{x}^2} = \frac{1}{\psi} \frac{\partial \hat{C}_{SED}}{\partial T} \qquad \hat{x} > 1 \tag{C.7}$$

By symmetry, a zero-flux boundary may be placed in the center of the sampler:

$$\frac{d\hat{C}_{PE}}{d\hat{x}} = 0 \qquad \text{at } \hat{x} = 0$$

The remote boundary in the sediment is:

$$\frac{d\hat{C}_{SED}}{d\hat{x}} = 0\ , \qquad \text{at } \hat{x} = \text{infinity}$$

The initial condition is:

$$\hat{C}_{PE,init} = 1 \text{ and } \hat{C}_{sed,init} = 0, \qquad \text{at T} = 0$$

Taking the Laplace transform, the diffusion expressions become:

$$\frac{\partial \bar{\hat{C}}_{PE}}{\partial \hat{x}} = \frac{\psi}{K_{PESED}} \frac{\partial \bar{\hat{C}}_{SED}}{\partial \hat{x}}, \qquad \hat{x}=1 \qquad \text{(C.8)}$$

$$\frac{d^2 \bar{\hat{C}}_{PE}}{d\hat{x}^2} = s\bar{\hat{C}}_{PE} - 1, \qquad \hat{x}<1 \qquad \text{(C.9)}$$

$$\frac{d^2 \bar{\hat{C}}_{SED}}{d\hat{x}^2} = \frac{s}{\psi} \bar{\hat{C}}_{SED}, \qquad \hat{x}>1 \qquad \text{(C.10)}$$

and the boundary conditions become:

$$\frac{d\bar{\hat{C}}_{PE}}{d\hat{x}} = 0, \qquad \text{at } \hat{x} = 0$$

$$\frac{d\bar{\hat{C}}_{SED}}{d\hat{x}} = 0, \qquad \text{at } \hat{x} = \text{infinity}$$

The following expressions for $\bar{\hat{C}}_{PE}$ and $\bar{\hat{C}}_{SED}$ satisfy Equations B.8, B.9 and B.10, and the boundary and initial conditions:

$$\overline{\overline{C}}_{PE} = A\cosh(\hat{x}\sqrt{s}) + \frac{1}{s} \tag{C.11}$$

$$\overline{\overline{C}}_{SED} = Be^{-\sqrt{\frac{s}{\psi}}\hat{x}} \tag{C.12}$$

where

$$A = -\left(s(\cosh(\sqrt{s}) + \frac{\sinh(\sqrt{s})K_{PESED}}{\sqrt{\psi}}\right)^{-1} \tag{C.13}$$

and

$$B = \frac{-A\sinh(\sqrt{s})K_{PESED}e^{\sqrt{\frac{s}{\psi}}}}{\sqrt{\psi}} \tag{C.14}$$

Integrating $\overline{\overline{C}}_{PE}$ from $\hat{x} = 0$ to $\hat{x} = 1$ gives the Laplace-domain mass of PRC in the polymer section:

$$\overline{\overline{M}}_{PRC} = \left(\frac{1}{s} - \frac{\sqrt{\psi}}{s^{3/2}\left(K_{PESED} + \sqrt{\psi}\coth\left(\sqrt{s}\right)\right)}\right) \tag{C.15}$$

By integrating over half the thickness of the film, $\overline{\overline{M}}_{PRC}$ gives the fraction of initial mass remaining in the sampler, as $\overline{\overline{M}}_{PRC,init} = 1$, and the two halves are mirror images or each other.

A similar derivation was followed for the case where target chemical is present only in the porous medium initially and diffuses into the polymer section. In this case Eqns. B.9 and B.10 become

$$\frac{d^2\overline{\overline{C}}_{PE}}{d\hat{x}^2} = s\overline{\overline{C}}_{PE}, \qquad \hat{x} < 1 \tag{C.16}$$

$$\frac{d^2\overline{\hat{C}}_{SED}}{d\hat{x}^2} = \frac{s}{\psi}\overline{\hat{C}}_{SED} - \frac{1}{\psi}, \qquad \hat{x}>1 \tag{C.17}$$

Eqns. B.11 and B.12 become

$$\overline{\hat{C}}_{PE} = D\cosh(\hat{x}\sqrt{s}) \tag{C.18}$$

$$\overline{\hat{C}}_{SED} = Be^{-\sqrt{\frac{s}{\psi}}\hat{x}} + \frac{1}{s} \tag{C.19}$$

where

$$D = \left(s(\cosh(\sqrt{s}) + \frac{\sinh(\sqrt{s})K_{PESED}}{\sqrt{\psi}} \right)^{-1} \tag{C.20}$$

Now integrating $\overline{\hat{C}}_{PE}$ from $\hat{x} = 0$ to $\hat{x} = 1$ gives the Laplace-domain mass of target chemical in the polymer section (Eqn. 3.7):

$$\overline{\hat{M}}_{target} = \frac{\sqrt{\psi}}{s^{3/2}\left(K_{PESED} + \sqrt{\psi}\coth\left(\sqrt{s}\right)\right)} \tag{C.21}$$

Again, this is the fraction of the equilibrium mass of target chemical in the section, as $\overline{\hat{M}}_{target,inf} = 1$, and the two halves are mirror images of each other. Equation B.15 for the PRC contains the result above for the target, so it may be written:

$$\overline{\hat{M}}_{PRC} = \left(\frac{1}{s} - \overline{\hat{M}}_{target}\right) \tag{C.22}$$

Appendix D: Matlab functions and scripts for numerically inverting Eqns. 3.7 and 3.8 to real-space values

A. Mass_in.m

```
% Laplace-domain expression for the mass of target chemical taken up by
% polymer from porous medium
%   K12 ((mass/volume phase 1)/(mass/volume phase 2))is partitioning
%     coefficient between phase 1 (polymer) and phase 2 (porous medium)
%   Y is ratio of diffusivities (D(porous medium)/D(polymer))
%   s is the Laplace parameter

function F = Mass_in(s,Y,K12);
global K12;
global Y;
F = (Y.^0.5)./((s.^1.5).*(K12+(Y.^0.5).*coth(sqrt(s))));
```

B. Mass_out.m

```
% Laplace-space expression for the mass of PRC transfered from
% polymer to porous medium
%   K12 is partitioning coefficient between phase 1 (polymer) and phase 2
%   (porous medium)
%   Y is ratio of diffusivities (D(porous medium)/D(polymer))
%   s is the Laplace parameter


function F = Mass_out(s,Y,K12);
global K12;
global Y;
F = (1./s)-((sqrt(Y))./(s.^(3/2).*(K12+sqrt(Y).*coth(sqrt(s)))));
```

C. Deffective.m

```
% calculates effective diffusivity, Deff
% given MW, porosity, and tortuosity for Kd input in units of vol water/vol
% sediment

function F=Deffective(Kd);

%clear all

MW=276; % MW=molar mass (g/mol)
Dw=(2.7*10^-4)/(MW^0.71); % Dw=diffusivity in water (cm^2/s)
phi=0.6;  % porosity
rsf=1/phi;   % ratio of sediments to fluid
f=1/(1+rsf*Kd);   %fraction in fluid assuming Kd in (Lw/Lsed)
tau=3;   % tortuosity
```

```
Dpm=Dw/tau;  % diffusivity in porous medium
F=f*Dpm; %(cm^2/sec)
```

D. Script for creating plots of fractional PRC loss vs. T

```
% Script used to create plots of fractional PRC loss vs. T for various Kd

hold on
clear all;
T=1:1:150;
global Y;
global K12;
for n=1:9
    Kpew=10^4.3*0.92; %polymer-water partition coefficient for PRC
(cm^3/cm^3)
    Kd=10^(0.5+n*0.5);
    K12=Kpew/Kd;
    Dsed=Deffective(Kd);
    Dpe=5.3*10^-10;   %diffusivity of PRC in polymer (cm^2/s)
    Y=Dsed/Dpe;
for i=1:150
   M(i)=invlap('Mass_out', [T(i)]); % invlap.m (Hollenbeck 1998; Hollenbeck
et al. 1999)
   Data(i,n)=M(i);
end
plot(T,M,'r')
xlabel('non-dimentional time,(t*D1/L^2)')
ylabel('M(t)/Minit')

end
hold off
```

E. Script for finding fractional equilibration of target chemical in polymer sampler

```
% Script used to find the fraction equilibration of target chemical in
polymer
% exposed to porous medium for a given non-dimensional time, T

clear all;
T=1.62;  % non-dimensional time of deployment

global Y;
global K12;

   Kpew=10^6.7*0.92; % Kpew for target chemical (Lw/Lpe)
    Kd=10^6.8;  %Kd of porous medium (Lw/Lpm)
    K12=Kpew/Kd;
    Dsed=Deffective(Kd);
    Dpe=1.22*10^-11;    %diffusivity of target chemical in polymer (cm^2/s)
    Y=Dsed/Dpe;

   M=invlap('Mass_in', [T]); % invlap.m (2,3)
   fraction_equilibrated=M
```

References

Hollenbeck, K. J. (1998). "INVLAP.M: A matlab function for numerical inversion of Laplace transforms by the de Hoog algorithm." from cambridge.org/us/engineering/author/nellisandklein/downloads/invlap.m.

Hollenbeck, K. J., Harvey, C. F., Haggerty, R. and Werth, C. J. A method for estimating distributions of mass transfer rate coefficients with application to purging and batch experiments. *Journal of Contaminant Hydrology* **1999**, 37, 367-388.

Appendix E: Curves describing target chemical uptake to sampler for various ψ and K_{PESED}

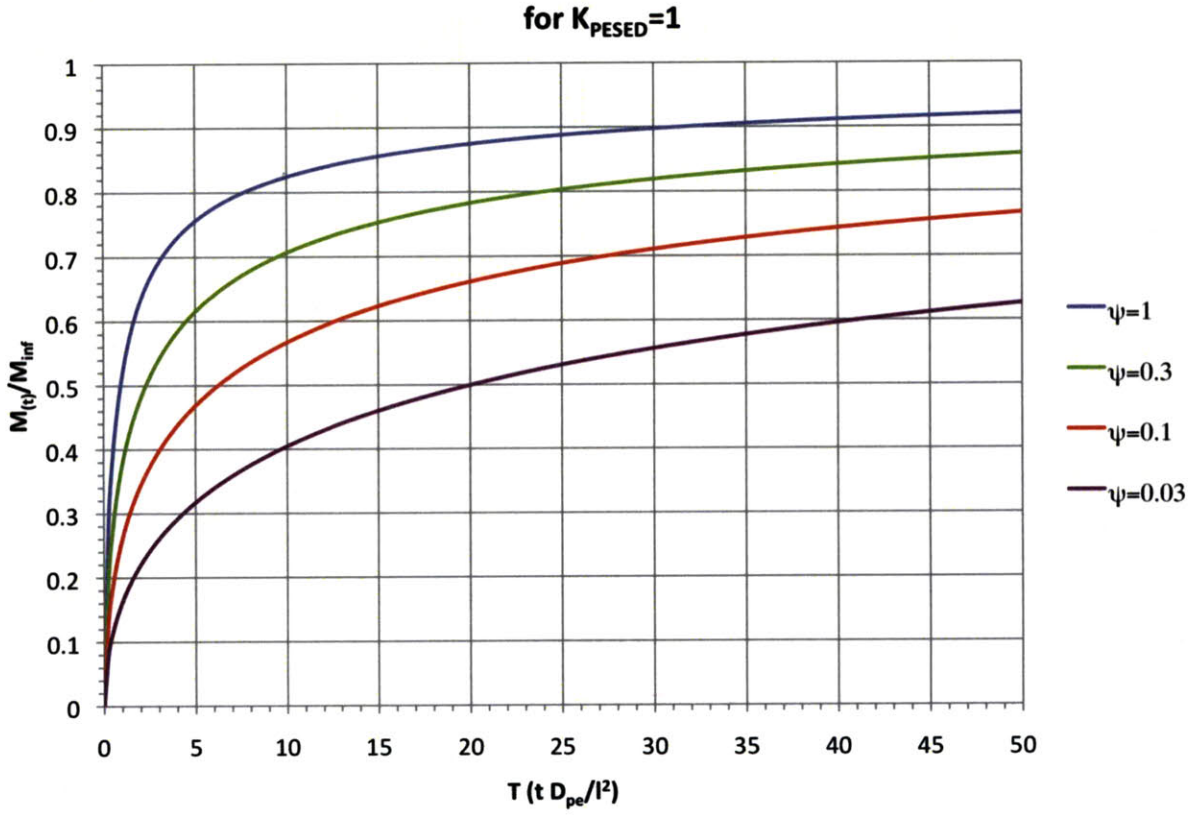

Figure E.1. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 1 and ψ from 0.03 to 1.

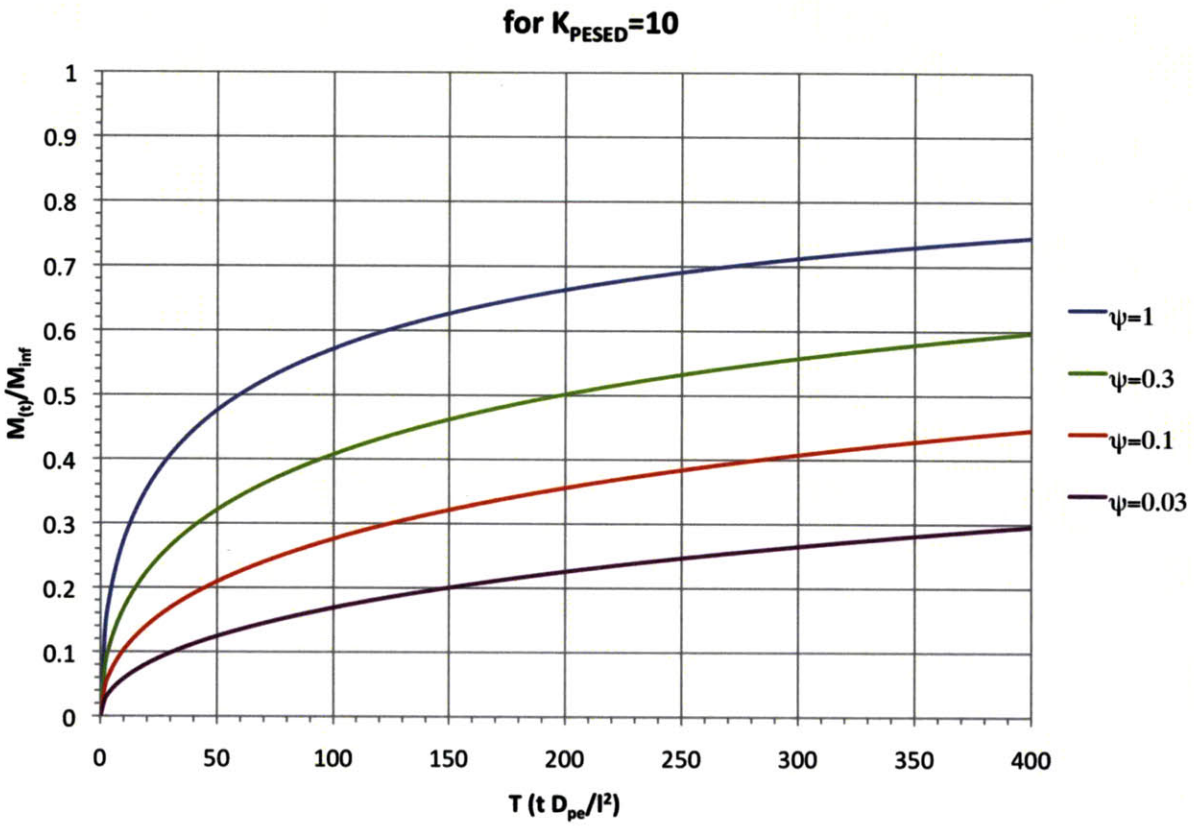

Figure E.2. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 10 and ψ from 0.03 to 1.

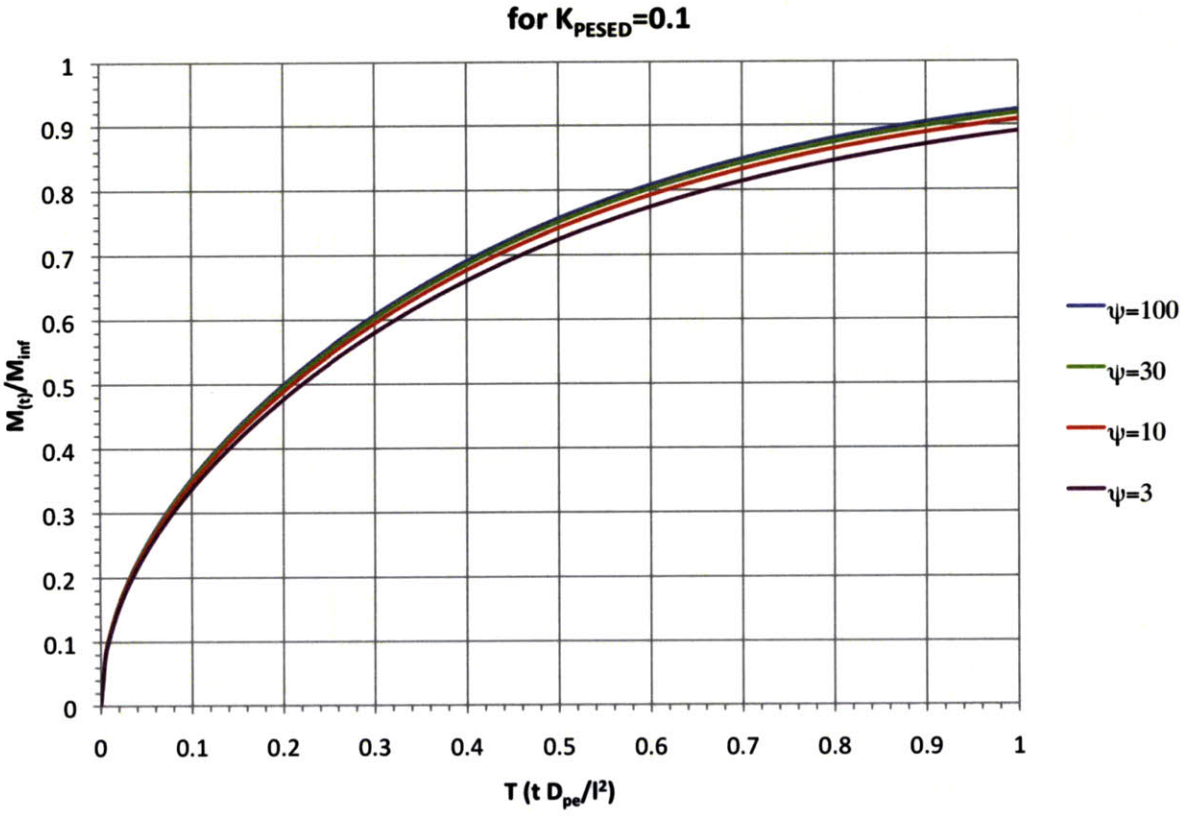

Figure E.3. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 0.1 and ψ from 3 to 100.

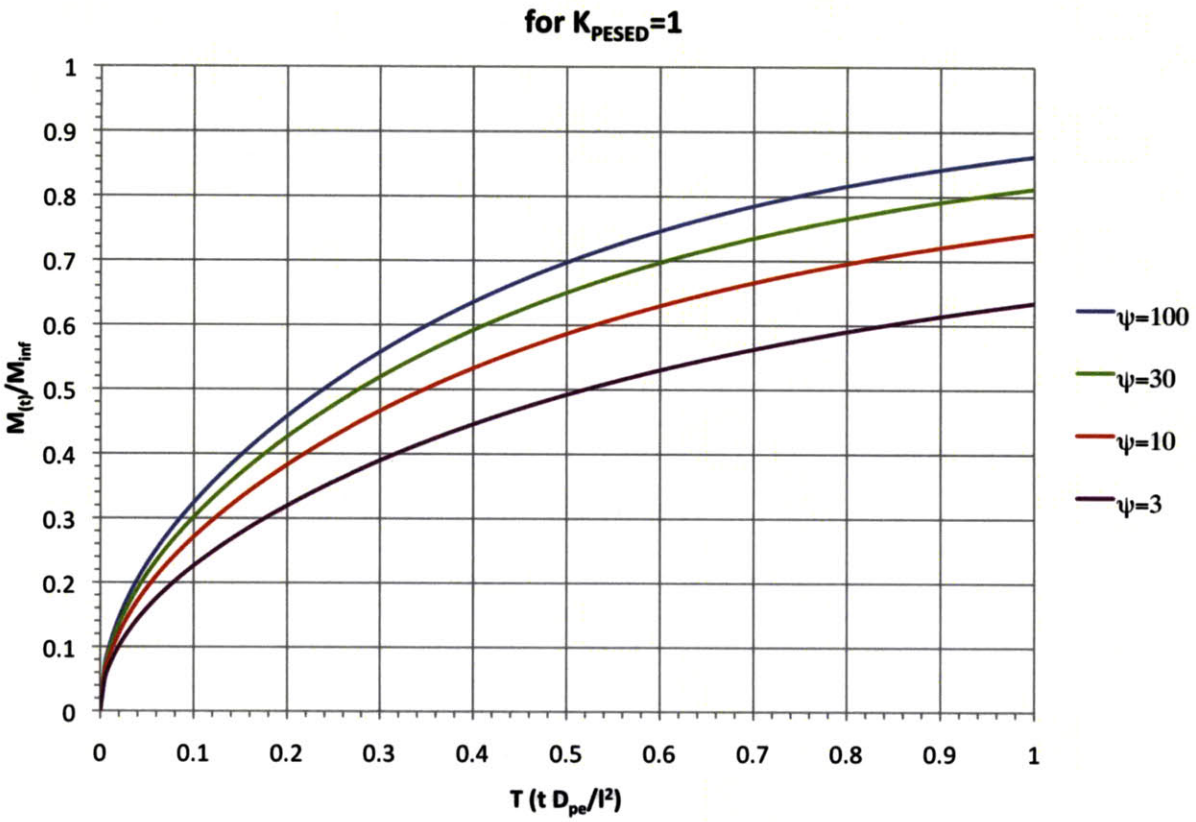

Figure E.4. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 1 and ψ from 3 to 100.

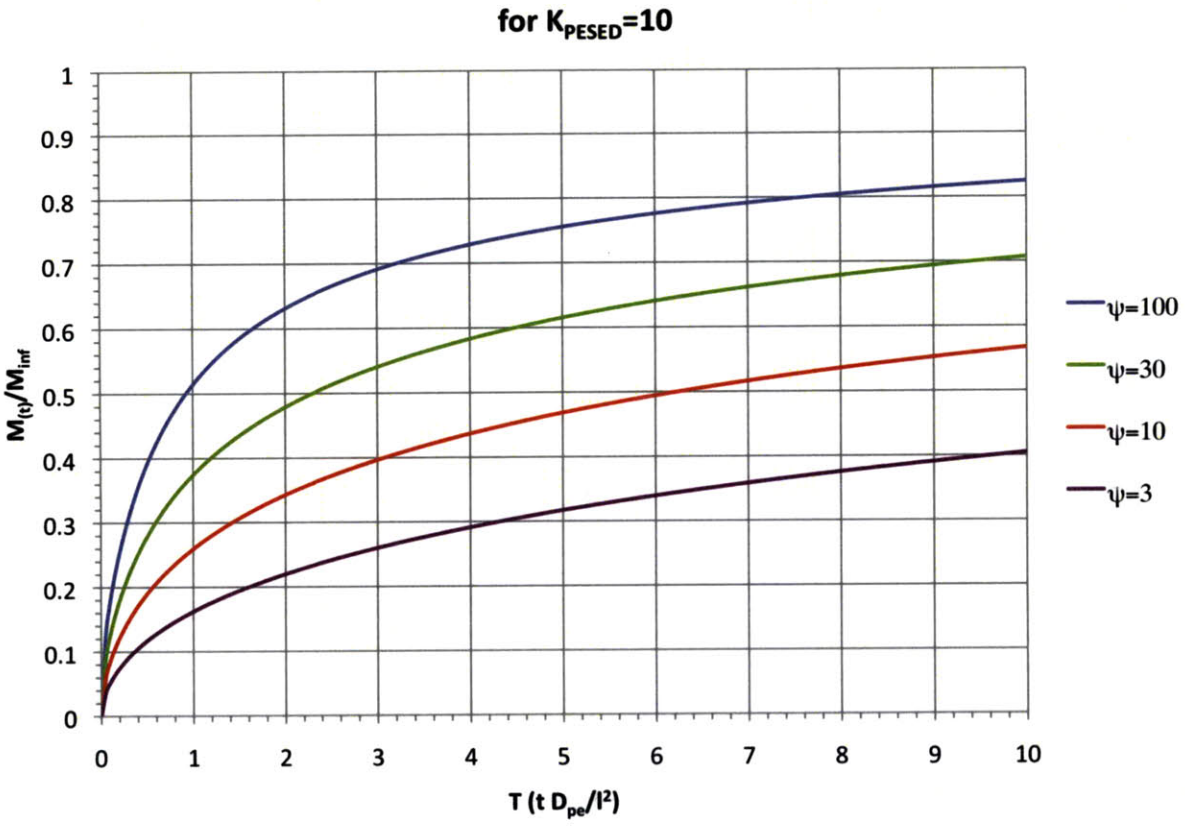

Figure E.5. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 10 and ψ from 3 to 100.

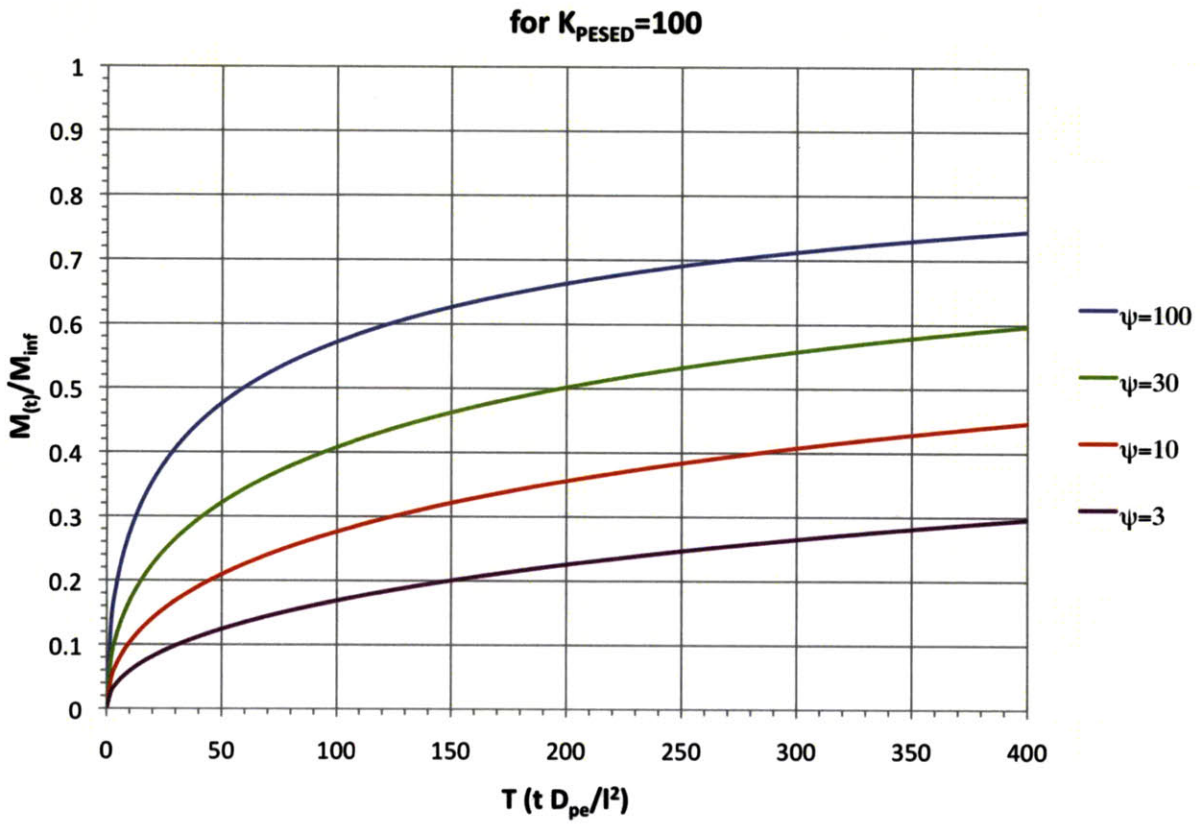

Figure E.6. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 100 and ψ from 3 to 100.

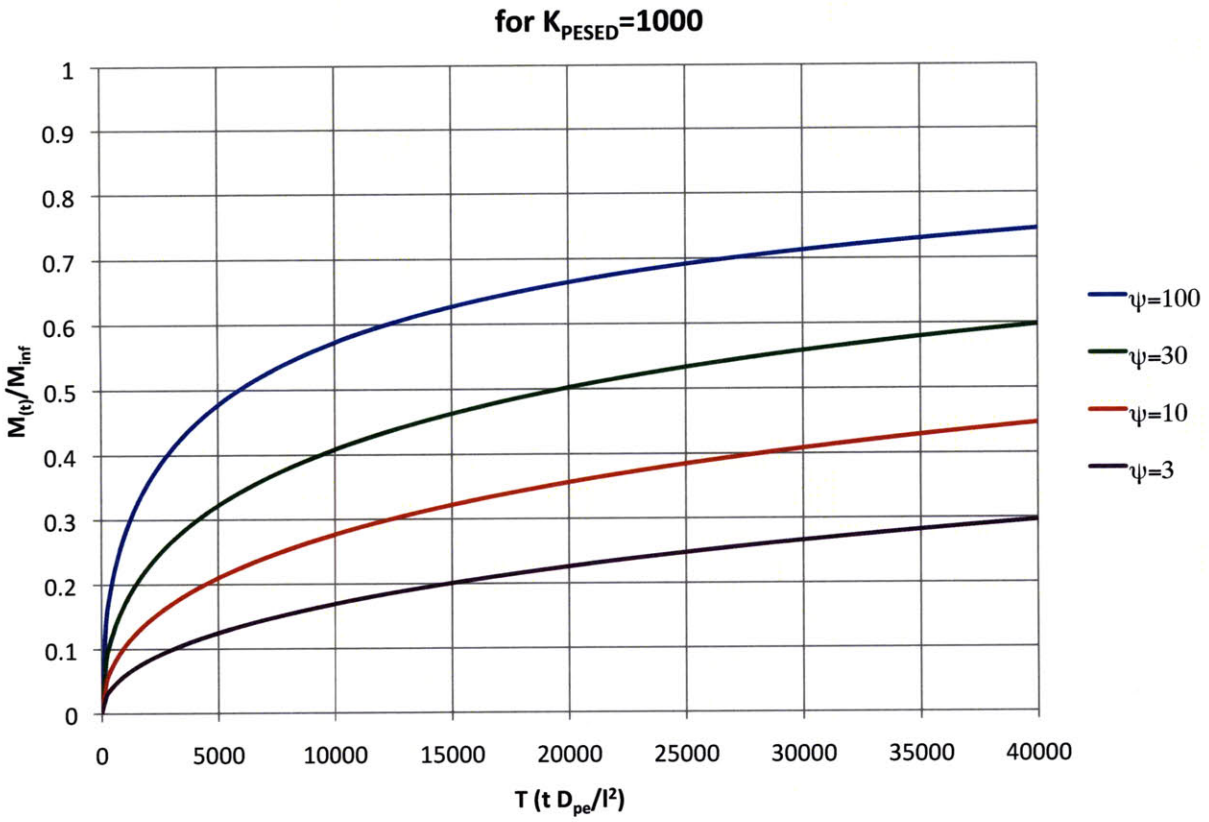

Figure E.7. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 1000 and ψ from 3 to 100.

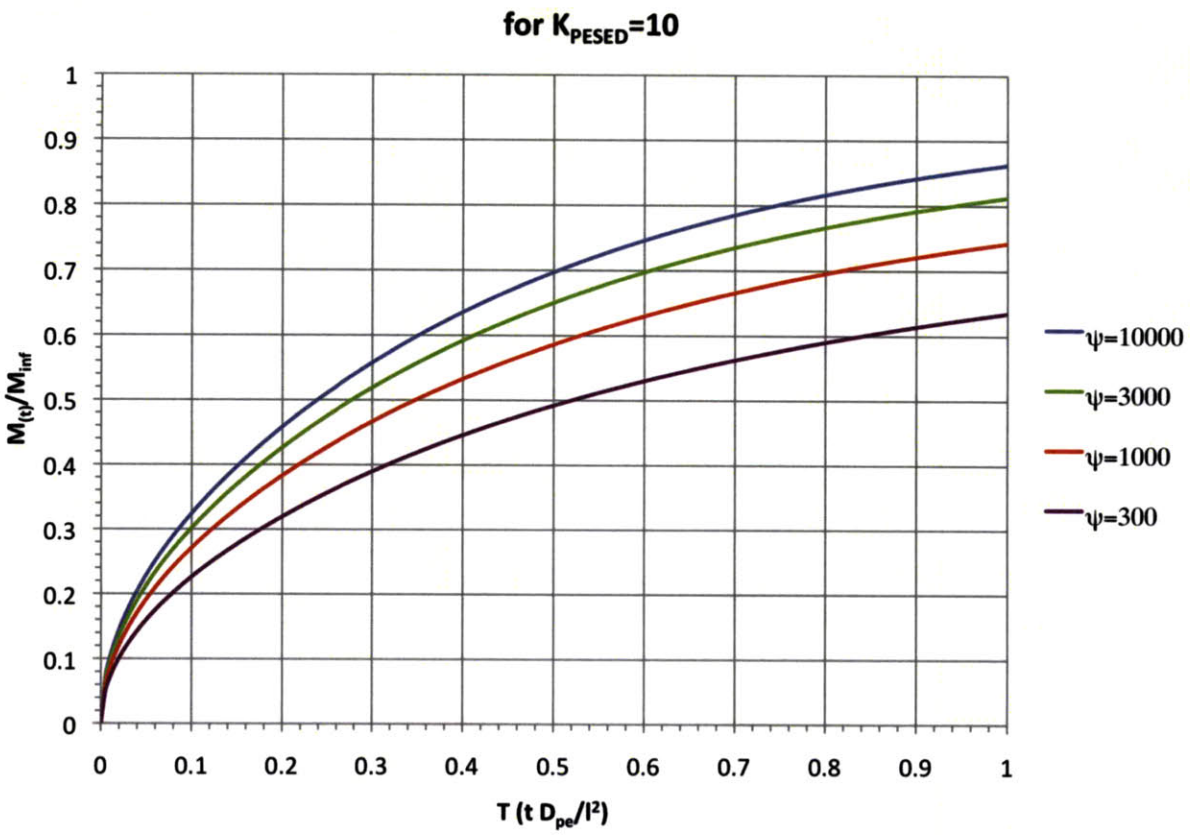

Figure E.8. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 10 and ψ from 300 to 10,000.

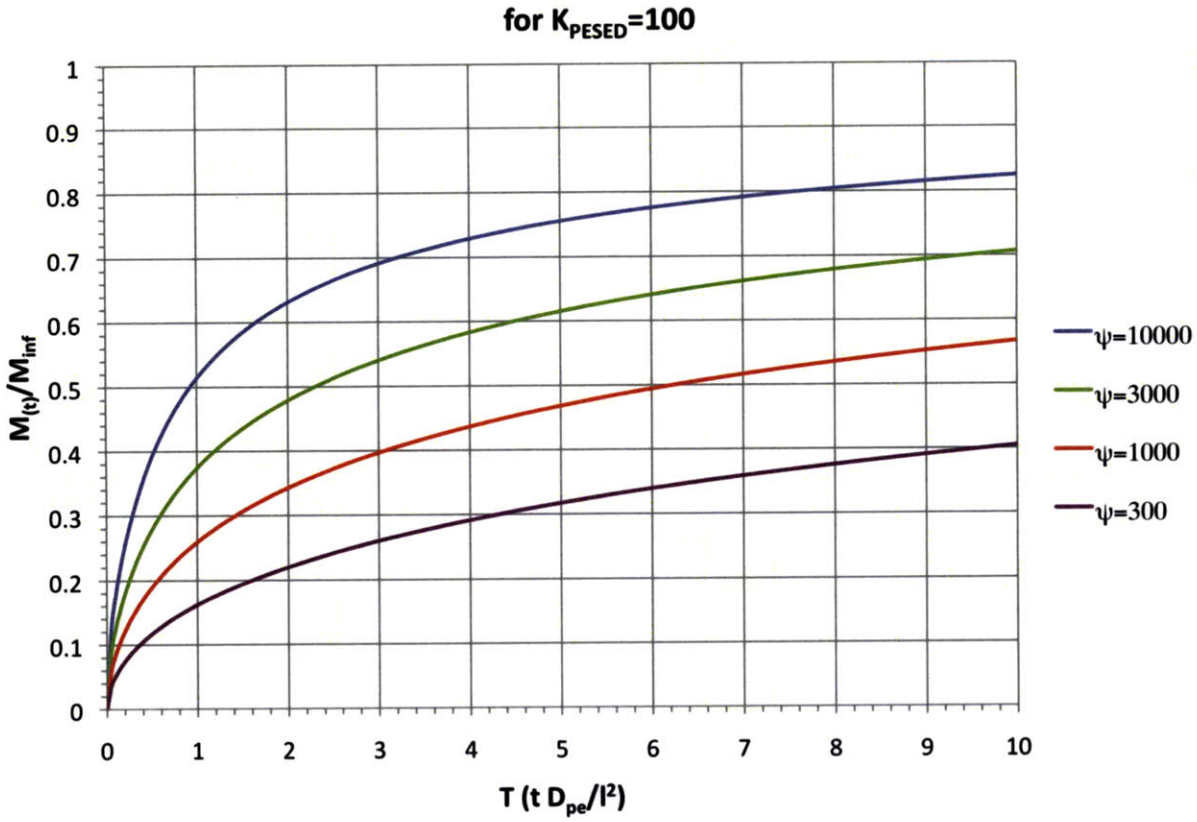

Figure E.9. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 100 and ψ from 300 to 10,000.

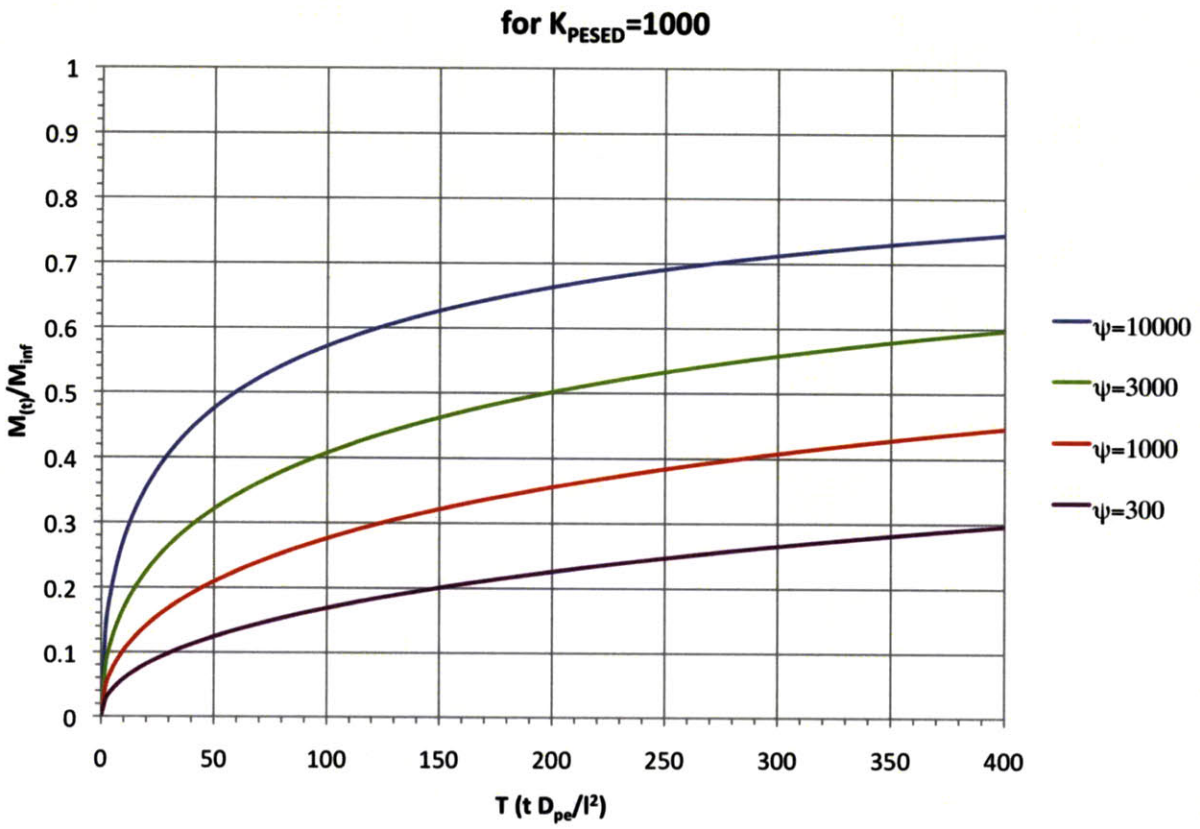

Figure E.10. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 1,000 and ψ from 300 to 10,000.

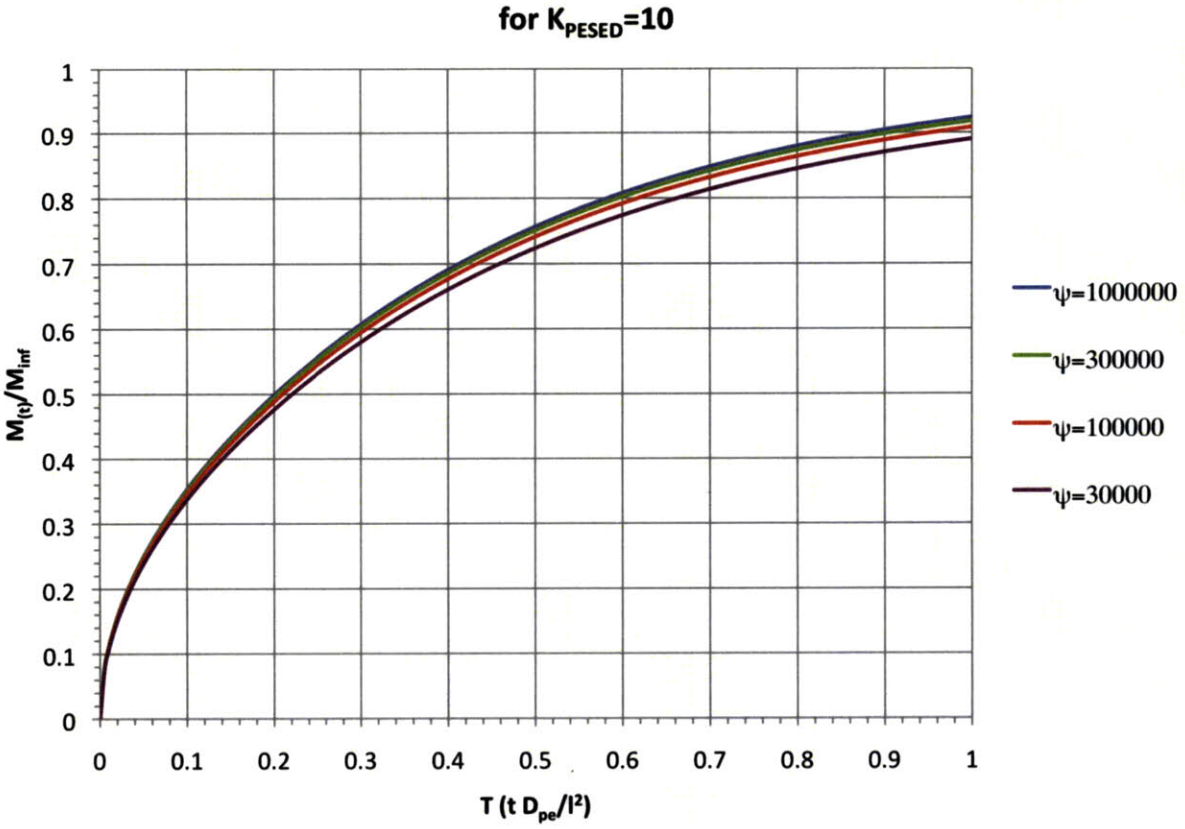

Figure E.111. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 10 and ψ from 30,000 to 1,000,000.

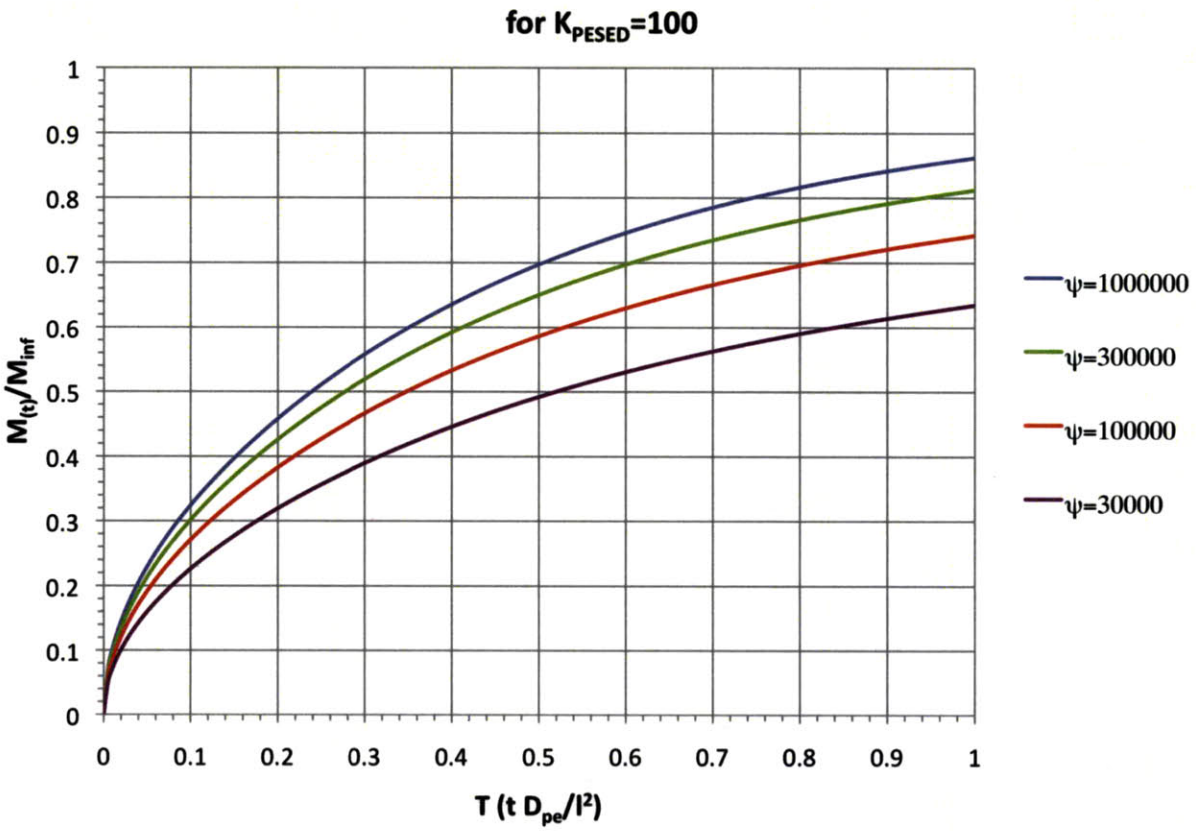

Figure E.12. Curve describing target chemical uptake to sampler from porous medium vs. non-dimensional exposure time for K_{PESED} = 100 and ψ from 30,000 to 1,000,000.