2 2

A Method for Using Polyethylene Passive Samplers to Measure Polycyclic Aromatic Hydrocarbon Chemical Activity in Sediments

by

Loretta A. Fernandez

B.S. Civil Engineering
Northeastern University, Boston, MA 2002

B.A. International Relations
Tufts University, Medford, MA 1993

Submitted to the Department of Civil and Environmental Engineering in Partial Fulfillment of the Requirements of the Degree of

MASTER OF SCIENCE
IN CIVIL AND ENVIRONMENTAL ENGINEERING

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

September 2005

© 2005 Massachusetts Institute of Technology.
All rights reserved.

Signature of Author: _____
Department of Civil and Environmental Engineering
August 12, 2005

Certified by: _____
Philip M. Gschwend
Professor of Civil and Environmental Engineering
Thesis Supervisor

Accepted by: _____
Andrew J. Whittle
Chairman Departmental Committee on Graduate Students

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
SEP 15 2005
LIBRARIES

BARKER

A Method for Using Polyethylene Passive Samplers to Measure Polycyclic Aromatic Hydrocarbon Chemical Activity in Sediments

by

Loretta A. Fernandez

Submitted to the Department of Civil and Environmental Engineering
on August 12, 2005 in Partial Fulfillment of the
Requirements for the Degree of Master of Science in
Civil and Environmental Engineering

ABSTRACT

In order to aid in the determination of the hazards posed by hydrophobic organic compounds (HOCs) in sediment beds, a method for the use of polyethylene (PE) sheets as passive sampling devices for measuring chemical activities was explored. A model which depends on a concentration gradient and two mass transfer limiting zones in series was used. Internal tracer chemicals within the polyethylene devices (PEDs) were used to calibrate the mass transfer model which can have different mass transfer coefficients depending on the site and target chemicals being investigated. The model allowed for the measurement of HOC chemical activities by measuring the change of mass of tracer and target chemical within the PED, and knowing the PE-water partitioning coefficient, K_{PEW}, and the liquid solubility, $C_w^{sat}(L)$, of the target chemical.

The method was tested using PEDs impregnated with d10-phenanthrene and d10-pyrene. First, PEDs were used to measure known concentrations of phenanthrene and fluoranthene in stirred seawaters. Seeing that the PEDs performed well, returning results which were within 25% of the known chemical activities, PEDs were then tested for measuring phenanthrene, fluoranthene, and pyrene in Boston Harbor sediments. Porewaters of Boston Harbor sediments were extracted as a benchmark against which to assess the performance of three methods for measuring sediment chemical activities: (1) PEDs using impregnated tracers exposed for 52 and 92 days to simulated sediment beds, (2) sediment extractions and an equilibrium partitioning model as recommended by EPA for determining sediment benchmarks, and (3) PE samplers brought to equilibrium with sediment slurries. The results of this study showed that the two methods using PE passive samplers produced measurements which were within a factor of 2 of the porewater extraction results. The equilibrium partitioning model, however, produced results which were at least an order of magnitude different from the measurements of the other methods. Future work on PEDs is needed to develop faster response times and internal standards which will allow for the measurement of a more diverse set of HOCs.

Thesis Supervisor: Philip M. Gschwend
Title: Professor of Civil and Environmental Engineering

Acknowledgments

I would like to thank all of the people who have helped me to complete this work, especially my advisor, Philip Gschwend, our lab manager, John MacFarlane, and Xanat Flores for her help in operating the CHN analyzer. This material is based upon work supported under a National Science Foundation Graduate Research Fellowship. Any opinions, findings, conclusions or recommendations expressed in this publication are those of the author and do not necessarily reflect the views of the National Science Foundation. I would also like to thank the National Sea Grant College Program, NOAA under project number RC-87, and the MIT Sea Grant College Program under a federal grant number NA 16RG2255 for funding this work.

Table of Contents

List of Tables

List of Figures

Chapter 1: Introduction

Hydrophobic organic chemicals (HOCs) are present in varied aquatic environments and may have significant effects on the ecology of those environments. Understanding the fate and biological availability of HOCs in different environmental systems is important for predicting the effects of the chemicals on those systems. Among HOCs of environmental concern are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and dioxins. These largely anthropogenic compounds may enter water ways through runoff, atmospheric deposition, rainout, spills and direct dumping. HOCs accumulate in aquatic sediments due to their higher affinity for settling particles than the water phase. Even as HOC inputs are reduced to surface waters through recent efforts to limit their discharge, sediments may remain a source of contamination to overlying waters and continue to affect organisms living within and above them.

HOCs display various biological effects. Many compounds are known or suspected carcinogens and mutagens. In addition, all HOCs exhibit a baseline, or narcotic, toxicity by partitioning into an organism's membrane lipids and disrupting membrane functions.[1] HOCs may also be transferred up the food chain by accumulating in storage fats. As organisms higher up the food chain feed on contaminated prey, they may not be able to shed the HOCs as quickly as they consume more chemical exposing them to ever larger doses.[2] In addition to direct human contact, contaminated sediments may become a public health threat when contaminated fish and seafood are consumed.

Coastal zone managers have the difficult task of identifying highly toxic sediments and making decisions regarding their remediation or capping. These decisions are complicated by

the uncertainty involved in determining the level of toxicity of a particular sediment. The toxicity of HOC contaminated sediments is not only dependant on the level of contamination, but also on the presence of other materials which may strongly bind to the HOCs, making them less available to interact with organisms. The bioavailable fraction of a chemical in an environment is that which is not already more tightly bound to something else in the system than it would be to the organism. The freely dissolved fraction of the chemical is often used as an estimate of this bioavailable fraction.[3]

There are three widely used methods for determining the bioavailable fractions of HOCs in sediments, and each has its shortcomings in determining sediment toxicity. One of these methods is the direct extraction of sediment porewaters. Large volumes of sediments are required so that the pore waters may be squeezed out and then solvent extracted. This method may overestimate HOC concentration by including colloid- and particle-associated HOCs that could not be filtered or settled out of the sediments. The method is also limited by the large amounts of sediment required for testing. Other problems with this method include changing the chemistry of certain sediments through their handling. Anoxic sediments, for example, could be changed chemically and physically by moving them to an oxygenated environment and trying to squeeze the porewater out of them. These changes could effect the partitioning of HOCs within them.

A second method for determining bioavailable fractions of HOCs in sediments is to directly extract the sediments and apply an equilibrium partitioning model (EqP) to estimate the dissolved concentrations of HOCs. Equilibrium Partitioning Sediment Benchmarks (ESBs) proposed by the U.S. Environmental Protection Agency (EPA) use such a model in an attempt to

rank sediments based on how dangerous they are to benthic organisms.[3] This method is limited by the need to know partitioning coefficients for each compound measured between water and organic carbon (OC), K_{OC}, and water and black carbon (BC), K_{BC}. It is the OC and BC fractions of a sediment, f_{OC} and f_{BC} respectively, to which HOCs strongly sorb.[4-8] Measuring HOCs in sediments using this method involves a great deal of uncertainty due to the difficulty of measuring f_{OC} and f_{BC} accurately, and the amount of uncertainty in the K_{OC} and K_{BC} parameters. In addition, there may be other sorbents for HOCs which are not specifically considered such as clays and zeolites.[9, 10]

A third method which has been used to estimate the biologically available portion of HOCs in sediments has been the sampling of body tissues of benthic organisms.[11-13] Specifically, the concentrations in the lipid fractions (and sometimes the lipid and protein fractions) of organisms, where HOCs are believed to accumulate, are estimated based on PAH loads extracted from all organism tissues and attributed to accumulation in lipids (or lipids and proteins). Clams have been found to accumulate PAHs and PCBs from both the sediments and the water column, and their tissue concentrations fall somewhere in between what would be predicted due to equilibration with either medium.[12] Polychaete worms have also been used to estimate bioavailable concentrations of PAHs in sediments.[14] Recent studies have shown, however, that many polychaete worms are able to metabolize PAHs leading to an underestimation of PAH concentration.[15] Because many benthic organisms can move within sediments, the concentrations in their tissues reflect the effects of sorption from a large area of sediments. This limits their usefulness in measuring sediment concentrations in a specific location.

The many complications associated with each of the methods for estimating bioavailable fractions of HOCs mentioned above have led to research into devices which could be used as stand-ins for organisms.[16-20] These stand-ins, known as biomimetic or passive samplers, would not be affected by metabolism, mobility, or multiple-matrix complications (sediment/water column as for clams). By directly measuring concentrations in sediment porewaters, EqP model parameters for sediment/water systems are not necessary.

There are three types of passive sampling devices which have been most heavily researched. Semi-permeable membrane devices (SPMDs), triolein filled polyethylene bags, have long been used to measure HOC concentrations in aquatic environments.[16, 20] These devices could require deployment times of up to several months depending on the HOC of interest and the sediment, however, and often leak unknown amounts of triolein.[21] There are no published reports of their use directly in sediments.

Solid phase microextraction (SPME) has also been used to mimic uptake of HOCs by organisms and has the benefit of not requiring solvents for analysis.[18, 19, 22, 23] Also, because the fibers are inserted directly into the injection port of the analytical instrument, little mass of the analyte is lost, as occurs with solvent injection, allowing for detection limits in the nanogram per liter range for high molecular weight PAHs.[23] No subsequent re-analysis of a sample is possible however. While SPMEs have been used in aquatic environments, their thin fibers may be too fragile for *in situ* measurement of sediment porewaters.[22]

The research described in this thesis focuses on the use of a third type of passive sampler, polyethylene devices, or PEDs. Previous use of PEDs to measure sediment porewater concentrations has required the continual tumbling of PEDs and wet sediments in the laboratory until equilibrium partitioning between PEDs and sediments was reached. This was estimated to

take up to 60 days for a range of PAHs with molecular weights between 178 and 252 atomic mass units.[12, 17] This method does not allow for the *in situ* use of PEDs in sediment beds because equilibrations would require very long exposures and one would not know how close to equilibrium any given case would be.

To overcome this methodological difficulty, it was suggested that PEDs infused with tracer chemicals may be used to measure HOC concentrations in sediment porewaters without the need to continually mix the sediments, or for the PEDs and sediments to come to equilibrium. A method was proposed which would allow for the *in situ* measurement of the chemical activity of HOCs in sediments following exposure times which could be adjusted through sampler design. In order to test the proposed method, experiments were performed to compare the chemical activity measurements, acquired through the use of PEDs to (1) measurements acquired through direct sediment extraction and EqP models, and (2) observations using porewater extractions. The chemical activities of two PAHs, fluoranthene and pyrene, to which the method was tuned, were measured in samples of sediments collected from the Boston Harbor where significant levels of PAHs have been previously measured.[12, 24, 25]

In the future the PED method could be used to measure a range of HOCs by including additional internal standards within the PED and varying exposure times. Additional internal standards would be chosen which would have similar diffusivities and partitioning properties to HOCs we would like to measure. Exposure times would be chosen based on the thickness of the sampler and sizes of the chemicals of interest. The model could also be adjusted to allow for different sampler geometries and thicknesses, which could be adjusted to control exposure times for different sampling requirements.

The remainder of this thesis describes the physical model that is the basis of the PED method and the experiments that were performed to test it. Chapter 2 will describe a general measure of narcotic toxicity given by a cumulative HOC chemical activity (as opposed to chemical concentrations), and how a PED may be used to measure chemical activity in sediments. Chapter 3 describes experiments which were conducted to show that PEDs containing internal tracers could be used to accurately measure chemical activities of PAHs in a simple system containing only seawater. Chapter 4 describes the experiments which were conducted to compare measurements of chemical activities in the more complicated sediment/porewater bed systems using three methods, PEDs, sediment extraction, and porewater extraction. Chapter 5 discusses the results of the experiment, gives conclusions regarding the usefulness of the proposed PED method for sediment chemical activity measurement, and provides recommendations for how the PED method may be applied in the future.

References

1. Sikkema, J.; de Bont, J. A. M.; Poolman, B., Interactions of Cyclic Hydrocarbons with Biological Membranes. *The Journal of Biological Chemistry* **1994,** 269 (11), 8022-8028.

2. Watanabe, K. H.; Lin, H.-I.; Bart, H. L.; Martinat, P.; Means, J. C.; Kunas, M. L.; Grimm, D. A., Bayesian estimation of kinetic rate constants in a food-web model of polycyclic aromatic hydrocarbon bioaccumulation. *Ecological Modeling* **2005,** 181, 229-246.

3. Hansen, D. J.; DiToro, D. M.; McGrath, J. A.; Swartz, R. C.; Mount, D. R.; Spehar, R. L.; Burgess, R. M.; Ozretich, R. J.; Bell, H. E.; Reiley, M. C.; Linton, T. K., *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures.* In ed.; Office of Research and Development, U. S. E. P. A., 'Ed.'^'Eds.' Washington, DC, 2003; 'Vol.' p^pp.

4. Accardi-Dey, A.; Gschwend, P. M., Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science and Technology* **2002,** 36 (1), 21-29.

5. Accardi-Dey, A.; Gschwend, P. M., Reinterpreting liturature sorption data considering both absorption into organic carbon and adsorption onto black carbon. *Environmental Science and Technology* **2003,** 37 (1), 99-106.

6. Ghosh, U.; Zimmerman, J. R.; Luthy, R. G., PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environmental Science and Technology* **2003,** 37 (10), 2209-2217.

7. Cornelissen, G.; Kukulska, Z.; Kalaitzidis, S.; Christanis, K.; Gustafsson, O., Relations between environmental black carbon sorption and geochemical sorbent characteristics. *Environmental Science and Technology* **2004,** 38 (13), 3632-3640.

8. Thorsen, W. A.; Cope, W. G.; Shea, D., Bioavailability of PAHs: Effects of soot carbon and PAH source. *Environmental Science and Technology* **2004,** 38 (7), 2029-2037.

9. Zhu, D.; Herbert, B.; Schlautman, M.; Carraway, E.; Hur, J., Cation-pi bonding: A new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *Journal of Environmental Quality* **2004,** 33 (4), 1322-1330.

10. Nicholl, S. I.; Talley, J. W.; Silliman, S., Model verification of thermal programmed desorption-mass spectrometry for estimation of release energy values for polycyclic aromatic hydrocarbons on mineral sorbents. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2545-2550.

11. Farrington, J. W.; Goldberg, E. D.; Risebrough, R. W.; Martin, J. H.; Bowen, V. T., U.S. "Mussel Watch" 1976-1978: An overview of the trace-metal, DDE, PCB, hydrocarbon, and artificial radionuclide data. *Environmental Science and Technology* **1983,** 17 (8), 490-496.

12. Lohmann, R.; Burgess, R. M.; Cantwell, M. G.; Ryba, S. A.; MacFarlane, J. K.; Gschwend, P. M., Dependency of plychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in *Mya Arenaria* on both water column and sediment bed chemical activities. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2551-2562.

13. Vinturella, A. E.; Burgess, R. M.; Coull, B. A.; Thompson, K. M.; Shine, J. P., Use of passive samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polycheates. *Environmental Science and Technology* **2004,** 38 (4), 1154-1160.

14. Vinturella, A. E.; Burgess, R. M.; Coull, B. A.; Thompson, K. M.; Shine, J. P., Importance of black carbon in distribution and bioaccumulation models of polycyclic aromatic hydrocarbons in contaminated marine sediments. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2578-2586.

15. Rust, A. J.; Burgess, R. M.; Brownawell, B. J.; McElroy, A. E., Relationship between metabolism and bioaccumulation of benzo[a]pyrene in benthic invertebrates. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2587-2593.

16. Huckins, J. N.; Manuweera, G. K.; Petty, J. D.; Mackay, D.; Lebo, J. A., Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environmental Science and Technology* **1993,** 27 (12), 2489-2496.

17. Booij, K.; Hoedemaker, J. R.; Bakker, J. F., Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environmental Science and Technology* **2003,** 37 (18), 4213-4220.

18. Oomen, A. G., Nonequilibrium solid-phase microextraction for determination of the freely dissolved concentration of hydrophobic organic compounds:Matrix effects and limitations. *Analytical Chemistry* **2000,** 72 (13), 2802-2808.

19. Leslie, H. A.; Oosthoek, A. J. P.; Busser, F. J. M.; Kraak, M. H. S.; Hermens, J. L. M., Biomimetic solid-phase microextraction to predict body residues and toxicity of chemicals that act by narcosis. *Environmental Toxicology and Chemistry* **2002,** 21 (2), 229-234.

20. Luellen, D. R.; Shea, D., Calibration and field verification of semipermeable membrand devices for measuring polycyclic aromatic hydrocarbons in water. *Environmental Science and Technology* **2002,** 36 (8), 1791-1797.

21. Adams, R. G. *Sediment-water exchange of polycyclic aromatic hydrocarbons in the lower Hudson Estuary.* Thesis S.M. --Massachusetts Institute of Technology Dept. of Civil and Environmental Engineering 2000., Massachusetts Institute of Technology, Cambridge, MA, 2000.

22. Leslie, H. A. *Biomimetic Solid-Phase Microextraction.* Universiteit Utrecht, Utrecht, the Netherlands, 2003.

23. Hawthorne, S. B.; Grabancki, C. B.; Miller, D. J.; Kreitinger, J. P., Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in mililiter sediment pore water samples and determination of Kdoc Values. *Environmental Science and Technology* **2005,** 39, 2795-2803.

24. McGroddy, S. E.; Farrington, J. W., Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts. *Environmental Science and Technology* **1995,** 29 (6), 1542-1550.

25. Wang, X.-C.; Zhang, Y.-X.; Chen, R. F., Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. *Marine Pollution Bulletin* **2001,** 42 (11), 1139-1149.

Chapter 2: Chemical activity as a measure of toxicity and how PEDs may be used to measure chemical activity in sediments

Introduction

While only certain hydrophobic organic chemicals (HOCs) are known to belong to specific toxic groups such as carcinogens, mutagens, or teratogens, all HOCs exhibit some narcotic, or baseline, toxicity due to their preferential partitioning into organism lipids.[1] While carcinogenic and mutagenic toxicity is due to the compound's binding to specific molecules necessary for a cell's health, narcotic toxicity is due only to the partitioning of the chemical into membrane lipids.[2] A compound's ability to partition into lipids, its lipophilicity, may be directly related to its hydrophobicity, a characteristic all HOCs share. Narcotic toxicity can be used as a measure of the minimum toxicity of an environmental medium due to HOCs.

A compound's octanol-water partition constant, K_{ow}, may be used as a gauge of the hydrophobicity of that compound, and this parameter has been directly related to lethal concentrations of that compound to different organisms. The maximum solubility of a chemical, *i*, in water is described by the saturated concentration of its liquid phase, $C_{iw}^{sat}(L)$. The lower $C_{iw}^{sat}(L)$ is, the more hydrophobic the compound is. Linear free energy relationships (LFERs) exist relating K_{iow} for many sets of compounds to $C_{iw}^{sat}(L)$. Schwarzenbach et al. (2003) give the following relationship for PAHs:

$$\log K_{iow} = -0.75 \log C_{iw}^{sat}(L) + 1.17 \qquad (2.1)$$

where K_{iow} is in (L_w/L_o) and

$C_{iw}^{sat}(L)$ is the saturated water concentration (mol/L_w) of the liquid chemical (a hypothetical liquid for those chemicals which are not liquids at the standard temperature of 25° C).[3]

Toxicity and hydrophobicity are linked through LFERs that relate K_{iow} to the dissolved concentration found to be lethal to fifty percent of a population of a particular organism, LC_{i50}. For fish with approximately 5% lipid content, this relationship has been described as: [4, 5]

$$\log(LC_{50}) \cong -\log(K_{ow}) + 1.7 \tag{2.2}$$

where LC_{50} is the dissolved concentration (mmol/L_w).

Toxicity and activity

As mentioned above, lipid bilayers are recognized to be the site of toxicity when considering narcosis effects.[1] It is the space that HOCs occupy within the membrane that disrupts critical membrane activities and effects cell functions.[3] HOC molar volumes have a range approximately between 0.013 and 0.004 mol/cm^3, while lipids may have molar volumes of approximately 0.004 mol/cm^3.[3] These values are similar enough that if one assumes similar molar volumes for HOCs and lipids, a critical volume fraction could be found that would lead to narcotic toxicity, and could be described as a mole fraction, x_{ilipid}^{toxic}, given as $\frac{mol\ HOC}{mol\ lipid}$.

$$\frac{vol\,HOC}{vol\,lipid} = \frac{\dfrac{mol\,HOC}{\sim 0.004 mol/cm^3}}{\dfrac{mol\,lipid}{\sim 0.004 mol/cm^3}} \approx \frac{mol\,HOC}{mol\,lipid} = x_{ilipid}^{toxic} \tag{2.3}$$

This critical mole fraction, x_{ilipid}^{toxic}, of HOCs in lipids can be measured using the concept of chemical activity. Since chemical activity in a system is independent of phase, assuming all phases are equilibrated, a critical chemical activity in sediments may be found.

Chemical activity

Because similar intermolecular forces control the solubility of a nonpolar HOC in a lipid, and the solubility of the HOC in its own pure liquid phase, an activity coefficient, γ_i, near 1 may be assumed for nonpolar HOCs in lipid.[3] This allows one to estimate an HOC's chemical activity, a_{ilipid}^{toxic}, as equivalent to concentration x_{ilipid}^{toxic} that would cause narcotic toxicity.

$$a_{ilipid}^{toxic} = \gamma_i x_{ilipid}^{toxic} \approx x_{ilipid}^{toxic} \tag{2.4}$$

Assuming chemical equilibrium between an organism and sediments, the toxic level of chemical activity in a sediment, a_{ised}^{toxic}, would also be equivalent to a_{ilipid}^{toxic}. Schwarzenbach et al. (2003) describe chemical activity using $C_{iw}^{sat}(L)$ as a reference point, this will also be the reference point for activities in this thesis. Chemical activity is defined as the ratio of the of the concentration of chemical in a given phase to the concentration that phase would have if equilibrated with water at $C_{iw}^{sat}(L)$:

$$a_{i\,sed} = \frac{C_{ised}}{K_{ised-w} C_{iw}^{sat}(L)} \tag{2.5}$$

$$a_{i\,lipid} = \frac{C_{ilipid}}{K_{ilipid-w} C_{iw}^{sat}(L)} \tag{2.6}$$

where $K_{ised-w} = \frac{C_{ised}}{C_{iw}}$ at equilibrium (L_w/kg dry wt), and

$K_{ilipid-w} = \frac{C_{ilipid}}{C_{iw}}$ at equilibrium (L_w/L_{lip}).

Equilibrium partitioning constants, $K_{i\,phase1\text{-}phase2}$ allow one to convert equilibrium concentrations from one phase to another. This also allows us to see that chemical activities in different phases are equivalent in systems that are at equilibrium.

$$a_{i\,sed} = \frac{C_{sed}}{K_{sed-w} C_{iw}^{sat}(L)}$$

$$C_{sed} = K_{sed-lipid} C_{lipid} \tag{2.7}$$

$$a_{i\,sed} = \frac{K_{sed-lipid} C_{lipid}}{K_{sed-w} C_{iw}^{sat}(L)} \tag{2.8}$$

$$a_{i\,sed} = \frac{\frac{C_{sed}}{C_{lipid}} C_{lipid}}{\frac{C_{sed}}{C_w} C_{iw}^{sat}(L)} \tag{2.9}$$

$$a_{i\,sed} = \frac{C_{lipid}}{K_{lipid-w} C_{iw}^{sat}(L)} = a_{i\,lipid} \tag{2.10}$$

If one can measure the chemical activity of any phase in a system that is at equilibrium, one will know the chemical activities in all the other phases.

Cummulative chemical activity

Studies have shown that the toxicities of narcotic chemicals are additive.[6, 7] This is consistent with the assumption that it is the cumulative space that the molecules occupy in the membranes that causes narcotic toxicity. If the sum of the volumes occupied by each chemical reaches the critical volume fraction, then narcotic toxicity would be observed. For this reason the toxicity of mixtures of HOCs must be considered to be the sum of the toxicities contributed by each HOC present. Based on the assumptions given above, a sediment, whose cumulative HOC chemical activity, $\Sigma a_{i\,sed}$, exceeds a_{lipid}^{toxic}, should be considered toxic.

A reliable and economical method of measuring $\Sigma a_{i\,sed}$ is desirable. This research examined whether a polyethylene sheet infused with tracer chemicals could allow for accurate measurement of HOC chemical activities without requiring that the device equilibrate with the sediments. Also, this approach would not require knowledge of specific sediment properties such as OC or BC fractions. HOCs measured with PEDs could then be summed to give a minimum approximation for $\Sigma a_{i\,sed}$.

Polyethylene sampler to measure chemical activity in sediments

The polyethylene devices (PEDs) to be used in this research are flat sheets of low density polyethylene (LDPE) with a thickness of 51 μm (2mil) and a density of 0.92 g/cm^3. The PEDs have been spiked with three tracer chemicals, d10-phenanthrene, d10-pyrene, and d12-chrysene. It is assumed that these tracers have the same diffusivities and partitioning constants as the target chemicals (phenanthrene, pyrene, fluoranthene, and chrysene) in polyethylene and sediments because of their nearly identical size, shape, and non-polarity.

Schwarzenbach et al. (2003) have described the flux of a chemical across a diffusive boundary between two different phases at a given time, *M(t)*, in mass per area, as follows:

$$M(t) = \left(\frac{t}{\pi}\right)^{1/2} \frac{C_{PE}^{o} - \frac{C_{SED}^{o}}{K_{SEDPE}}}{\frac{1}{D_{PE}^{1/2}} + \frac{1}{K_{SEDPE} D_{SED}^{1/2}}} \qquad (2.11)$$

where C_{PE}^{o} is the concentration in the PE at t=0 (mass/cm^3 PE),

C_{SED}^{o} is the concentration in the sediment at t=0 (mass/cm^3 sed),

D_{PE} is the diffusivity of the chemical in the polyethylene (cm^2/sec),

D_{SED} is the effective diffusivity of the chemical in the sediments (cm^2/sec), and

K_{SEDPE} is the equilibrium partitioning coefficient of chemical between the sediments and polyethylene (cm^3 PE/cm^3 sed)[3].

The numerator reflects the difference in equilibrium concentrations across the boundary, which is driving the flux of chemical, while the denominator represents the resistance of the media to the movement of molecules through them.

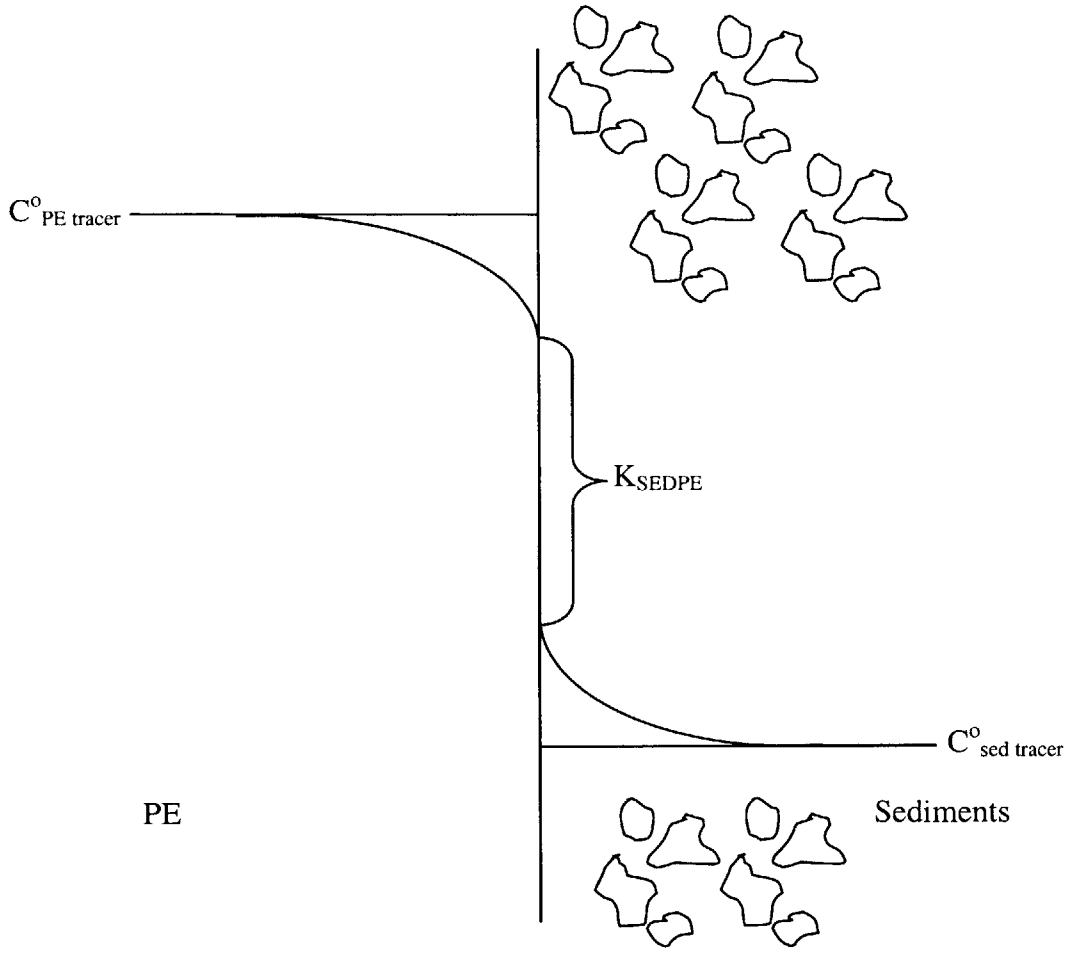

Figure 2.1 Diffusive boundary between PE and sediments for tracer chemical, present initially only in the PE.

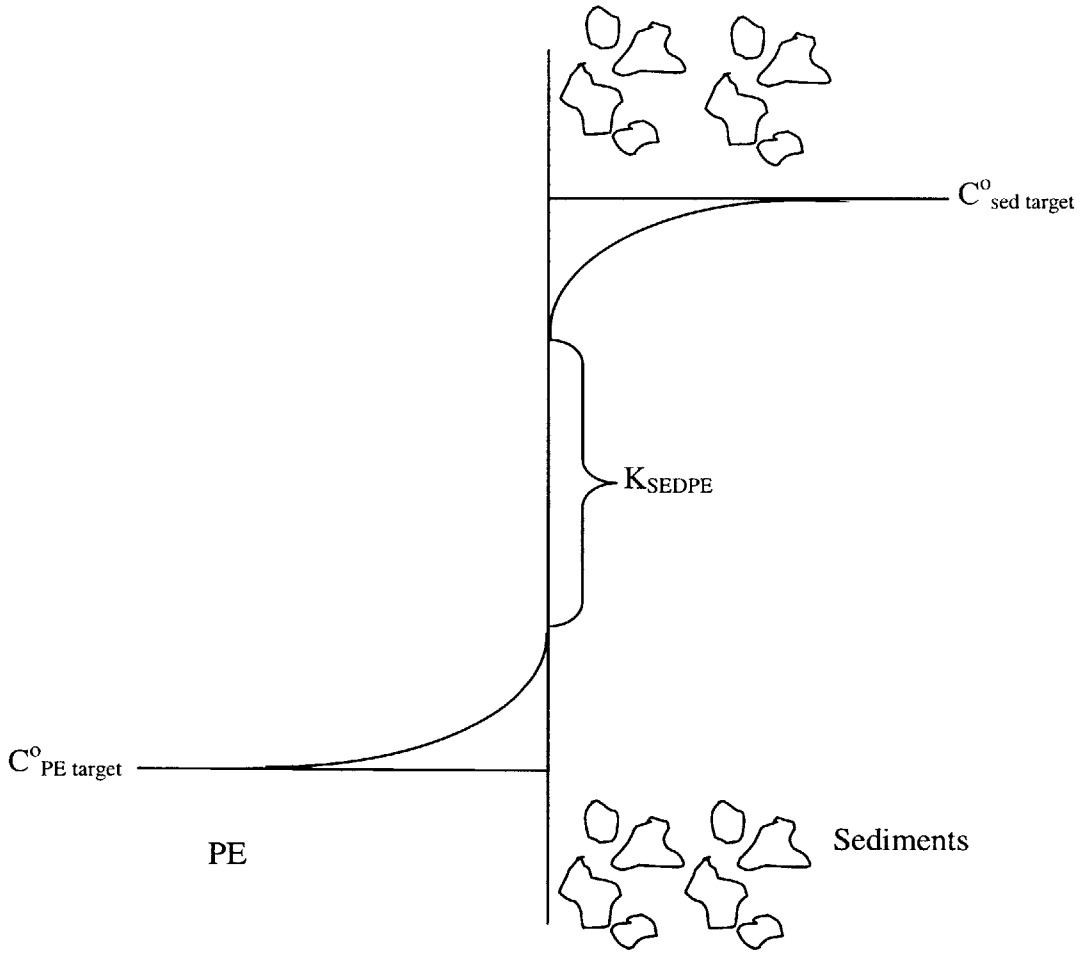

Figure 2.2 Diffusive boundary between PE and sediments for target chemical, present initially only in the sediments.

Two assumptions may be made about the concentrations of tracer chemicals and target chemicals in the two phases. First, deuterated compounds may be assumed to be non-existent in environmental samples, so C^o_{SED} for the tracer is zero (Figure 2.1). Second, the laboratory-prepared PED should be clean of any target chemicals, and so C^o_{PE} for the target may also be assumed to be zero (Figure 2.2). These assumptions allow us to simplify Equation 2.11 for tracer and target chemicals as follows:

$$M_{tracer}(t) = \left(\frac{t}{\pi}\right)^{1/2} \frac{C^{o}_{tracer\,PE}}{\frac{1}{D_{PE}^{\,1/2}} + \frac{1}{K_{SEDPE} D_{SED}^{\,1/2}}} \tag{2.12}$$

$$M_{target}(t) = \left(\frac{t}{\pi}\right)^{1/2} \frac{\frac{C^{o}_{target\,SED}}{K_{SEDPE}}}{\frac{1}{D_{PE}^{\,1/2}} + \frac{1}{K_{SEDPE} D_{SED}^{\,1/2}}} \tag{2.13}$$

If we allow

$$b = \left(\frac{t}{\pi}\right)^{1/2} \frac{1}{\frac{1}{D_{PE}^{\,1/2}} + \frac{1}{K_{SEDPE} D_{SED}^{\,1/2}}} \tag{2.14}$$

and substitute b into Equations 2.12 and 2.13, we get the following:

$$M_{tracer}(t) = b\, C^{o}_{tracer\,PE} \tag{2.15}$$

$$M_{target}(t) = b\, \frac{C^{o}_{target\,SED}}{K_{SEDPE}} \tag{2.16}$$

since we assume the parameters in b are the same for deuterated and non-deuterated compounds. Solving Equation 2.15 for b and plugging the result into Equation 2.16 allows us to solve for

$$\frac{C^{o}_{target\,SED}}{K_{SEDPE}}$$

$$\frac{C^{o}_{target\,SED}}{K_{SEDPE}} = \frac{M_{target}(t)}{M_{tracer}(t)}\; C^{o}_{tracer\,PE} \tag{2.17}$$

As described above, chemical activity is defined as the concentration in a given phase divided by a reference concentration, here taken to be $C_w^{sat}(L)$. Equation 2.17 may be converted to an expression of chemical activity by dividing both sides by $K_{PEW}\, C_w^{sat}(L)$

$$a_{target} = \frac{C^{o}_{target\,SED}}{K_{SEDPE}} \left(\frac{1}{K_{PEW} C^{sat}_{w}(L)} \right) \tag{2.18}$$

$$= \frac{M_{target}(t)}{M_{tracer}(t)} C^{o}_{tracer\,PE} \left(\frac{1}{K_{PEW} C^{sat}_{w}(L)} \right) \tag{2.19}$$

where K_{PEW} is the equilibrium partitioning coefficient of chemical between polyethylene and water (L_w/kg PE).

Because the PED areas are the same for $M_{target}(t)$ and $M_{tracer}(t)$, Equation 2.19 may be also be expressed as the following:

$$a_{target} = \frac{\Delta M_{target}}{\Delta M_{tracer}} C^{0}_{tracerPE} \left(\frac{1}{K_{PEW} C^{sat}_{w}(L)} \right) \tag{2.20}$$

where ΔM_{target} is the change in mass of pyrene in the PED, $M(t) * Area_{PE}$, and

ΔM_{tracer} is the change in mass of d10-pyrene in the PED, $M(t) * Area_{PE}$.

This allows one to find a_{target} by measureing only the changes in masses of tracer and target chemical in a PED, and the initial concentration of tracer in the PED, and knowing K_{PEW} and $C^{sat}_{w}(L)$.

PED design

This model suggests that chemical activity can be measured in porewaters and sediments using PE samplers without the need to know diffusivities in the different media or any partition constants beyond K_{PEW} and $C^{sat}_{w}(L)$. It assumes, however, that the concentration of tracer chemicals in the center of the PE strip does not change. This can be controlled by changing the thickness of the PED and the exposure times.

Models were developed to determine exposure times necessary to exchange measurable amounts of tracer chemical to the sediments without letting the diffusion front of chemical concentration reach the center of the PED thickness. A relationship between PE thickness and the exposure time required to lose 20% of the tracer mass from a PED was modeled using the following assumptions for a diffusive boundary between two phases as described by Equation 2.11:

(1) diffusivity of d10-pyrene in PE = $2x10^{-11}$ cm^2/s (as measured by Adams (2003) for pyrene), and

(2) effective diffusivity of d10-pyrene in the sediments = $4.3x10^{-10}$ cm^2/s (estimated using equations from Schwarzenbach et al. (2003) for effective diffusity in porous media, and solid water partitioning coefficient, K_d, measured in a PE tumbling experiment described later).[3, 8]

A loss of at least 20% of the tracer from the PED is desired so that the mass loss may be distinguished from the blank value considering the amount of uncertainty in gas chromatograph-mass spectrometer (GC/MS) analysis. Integration of a diffusing, chemical concentration front described by an error function shows that 29% of the mass may be lost before the concentration in the middle of the PED begins to change. An exposure time that would allow between 29% and 20% of a tracer chemical to diffuse from the PED is desired to satisfy the requirements for our ability to measure a change in concentration in the PED, and for a constant concentration to be held at the center of the PED. Based on the model (Figure 2.3), this implies that we want to expose 51 μm thick PE for about 50 days to reach 20% tracer loss.

The PEDs in this study were exposed for periods of 52 and 92 days. The first exposure period appears to be within the range which is modeled to allow for constant concentration of d10-pyrene and d12-chrysene at the center. It is expected that the concentrations of d10-phenanthrene at the center of the PEDs were reduced by >60%, and that the concentrations of d12-chrysene within the PEDs did not change enough to be accurately measured above the method's variability (i.e., <20% loss). The effects of these exposure times on our ability to measure chemical activities in the sediments will be discussed in the results section of this thesis.

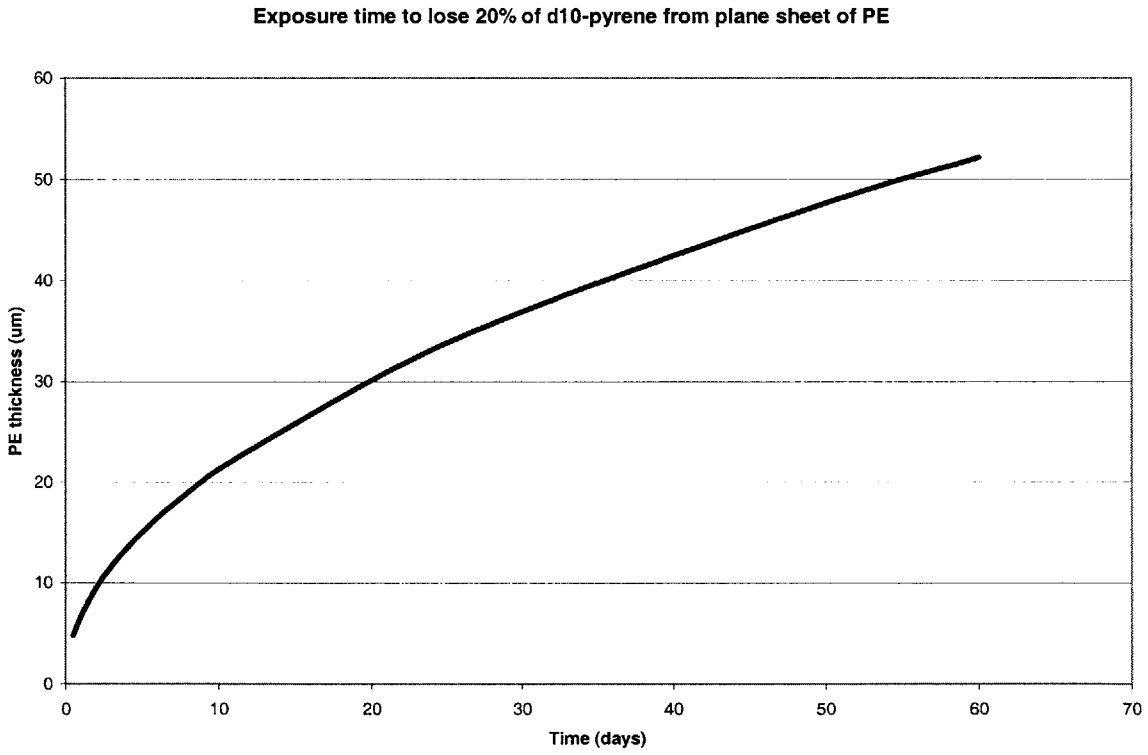

Figure 2.3 Model of the time required to lose 20% of d10-pyrene from a plane sheet PED vs. PED thickness

References

1. Sikkema, J.; de Bont, J. A. M.; Poolman, B., Interactions of Cyclic Hydrocarbons with Biological Membranes. *The Journal of Biological Chemistry* **1994,** 269 (11), 8022-8028.

2. Leslie, H. A. *Biomimetic Solid-Phase Microextraction.* Universiteit Utrecht, Utrecht, the Netherlands, 2003.

3. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental Organic Chemistry.* 2nd ed.; Wiley: Hoboken, N.J., 2003; 'Vol.' p xiii, 1313 p.

4. DiToro, D. M.; McGrath, J. A.; Hansen, D. J., Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue. *Environmental Toxicology and Chemistry* **2000,** 19 (8), 1951-1970.

5. McCarty, L. S.; Mackay, D.; Smith, A. D.; Ozburn, G. W.; Dixon, D. G., Interpreting aquatic toxicity QSARs: the significance of toxicant body residues at the pharmacologic endpoint. *The Science of the Total Environment* **1991,** 109/110, 515-525.

6. Hermens, J., Quantitative structure-activity relationships of environmental pollutants. In *Handbook of Environmental Chemistry*, ed.; Hutzinger, O., 'Ed.'^'Eds.' Springer-Verlag: Berlin, Germany, 1989; 'Vol.' 2E, p^pp 111-162.

7. Hansen, D. J.; DiToro, D. M.; McGrath, J. A.; Swartz, R. C.; Mount, D. R.; Spehar, R. L.; Burgess, R. M.; Ozretich, R. J.; Bell, H. E.; Reiley, M. C.; Linton, T. K., *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures.* In ed.; Office of Research and Development, U. S. E. P. A., 'Ed.'^'Eds.' Washington, DC, 2003; 'Vol.' p^pp.

8. Adams, R. G. *Polyethylene devices and the effects of sediment resuspension on the cycling of PAHs and PCBs in the lower Hudson Estuary.* Thesis Ph. D. --Massachusetts Institute of Technology Dept. of Civil and Environmental Engineering 2003., Massachusetts Institute of Technology, Cambridge, MA, 2003.

Chapter 3: Measurement of chemical activities of phenanthrene and fluoranthene in spiked seawater samples using PEDs

Introduction

Before using PEDs to measure PAH chemical activities in sediments and porewaters, their use in the relatively more simple system of stirred seawater was tested. These tests were performed in order to determine the accuracy of measurements which could be obtained using tracer-infused PEDs and a similar diffusion model to that which would be used in the sediment/porewater system. The transfer of chemicals across the PED/water boundary is controlled, in this case, by the slow rate of diffusion through the PE and a thin boundary layer on the water side. Analysis of the effects of the water side boundary layer on the overall mass transfer rate indicate that the water side may be ignored and that the system may be modeled as a wall boundary.[1] The PED-water system experiments were performed in order to see if a similar wall boundary model to that described in the previous chapter, involving a single, rate limiting, diffusing layer, could be used to measure chemical activities of phenanthrene and fluoranthene in water samples using deuterated phenanthrene and pyrene as tracer chemicals in the PEDs.

The transfer of chemical mass, $M(t)_{in}$, across a wall boundary between different media is described by Schwarzenbach et al. (2003) as follows:

$$M(t) = \left(\frac{4}{\pi}\right)^{1/2} (D_{PE}\, t)^{1/2} \left(K_{PEW}\, C_w^o - C_{PE}^o\right) \qquad (3.1)$$

where C_w^o is the initial concentration of a chemical in the seawater (mol/cm$_w^3$),

C_{PE}^0 is the initial concentration of a chemical in the PE (mol/cm$_{PE}^3$), and

K_{PEW} is the polyethylene-water partition constant ((mol/cm$^3_{PE}$)/(mol/cm^3_w)).

Using tracer chemicals which do not occur in the natural environment allows one to assume that $C^o_{wtracer}$ is zero (Figure 3.1). For the tracer chemical, Equation 3.1 simplifies to:

$$M(t)_{tracer\,out} = \left(\frac{4}{\pi}\right)^{1/2} (D_{PE}t)^{1/2} \left(C^o_{PEtracer}\right) \tag{3.2}$$

as long as the tracer does not build up significantly in the water of a closed system (i.e., $C_W << C_{PE}/K_{PEW}$). Assuming that the mass of target chemical initially in the PED, $C^o_{PEtarget}$ is also zero (Figure 3.2), Equation 3.1 may be simplified as follows for the target chemical:

$$M(t)_{target\,in} = \left(\frac{4}{\pi}\right)^{1/2} (D_{PE}t)^{1/2} \left(K_{PEW}\, C^o_{wtarget}\right) \tag{3.3}$$

If we assume that the diffusivities in the PE are the same for both the tracer and target chemicals, and we allow $c = \left(\frac{4}{\pi}\right)^{1/2} (D_{PE}t)^{1/2}$, then

$$M(t)_{tracer\,out} = c\, C^o_{PEtracer} \tag{3.4}$$

and

$$M(t)_{target\,in} = c\, K_{PEW}\, C^o_{wtarget} \tag{3.5}$$

We could use Equation 3.4 to solve for c, in any particular deployment, then use this c to calculate the target concentration using Equation 3.5. Alternatively, solving Equation 3.4 for c and plugging the result into Equation 3.5 allows one to solve for $C^o_{wtarget}$ as follows:

$$C^o_{wtarget} = \frac{M(t)_{target\,in}\, C^o_{PEtracer}}{M(t)_{tracer\,out}\, K_{PEW}} \tag{3.6}$$

Since the area of the PEDs is the same for $M(t)_{target\,in}$ and $M(t)_{tracer\,out}$, Equation 3.6 may also be expressed as:

$$C^{o}_{wtarget} = \frac{\Delta M_{targetin} C^{o}_{PEtracer}}{\Delta M_{traceout} K_{PEW}} \tag{3.7}$$

In this form, we may now use more traditional units for concentration and the partition constant:

$C^{o}_{wtarget}$ is the initial concentration of target chemical in the water (mol/L_w),

$C^{o}_{PEtracer}$ is the initial concentration of tracer chemical in the water (mol/kg PE), and

K_{PEW} is the partition constant for polyethylene and water ((mol/kg_{PE})/(mol/L_w)).

Also, it is not necessary to know the area of the PED.

Using the solubility of the hypothetical liquid compound, $C^{sat}_{w}(L)$, at the temperature and salinity conditions of interest, the initial chemical activity of the target compound in the seawater may be calculated.

$$a_{target} = \frac{C^{o}_{wtarget}}{C^{sat}_{w}(L)} \tag{3.8}$$

The model described above allows one to use a PED to measure concentration or chemical activity of a target chemical in water without having to allow the PED and water to come to equilibrium.

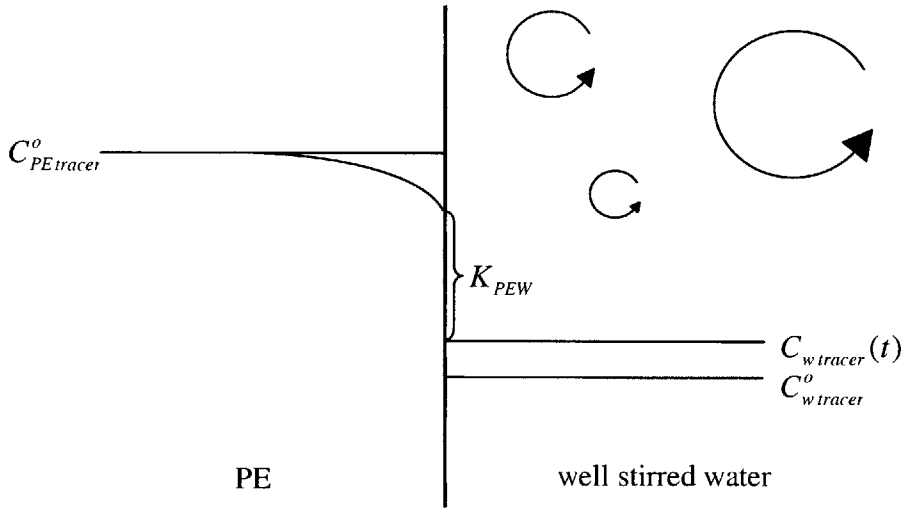

Figure 3.1 Diffusive wall boundary between PE sheet and well mixed seawater showing assumed concentration flux of tracer from PE to water. In closed laboratory system, tracer concentration in the water may change with time; this would not occur in real world setting.

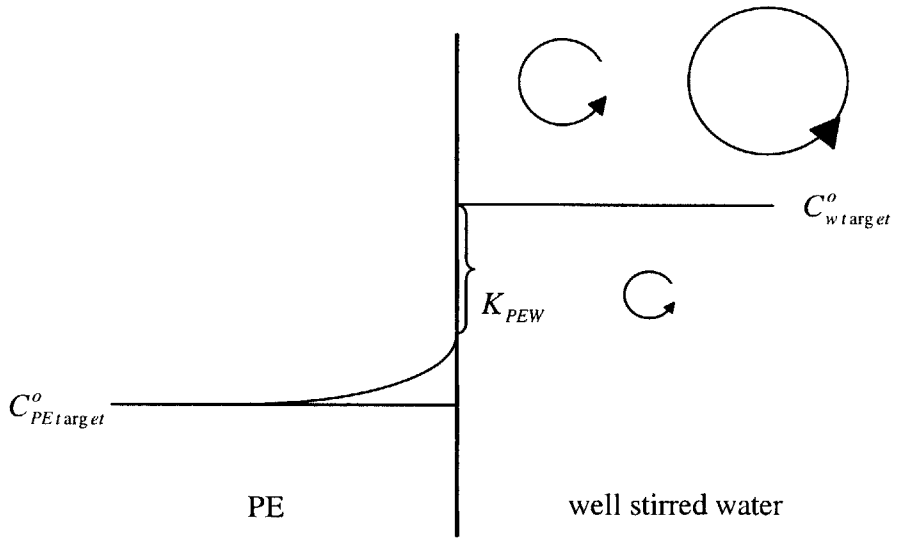

Figure 3.2 Diffusive wall boundary between PE sheet and well mixed seawater showing concentration gradient driving transfer of target chemical from water to PE. In the case of an infinite bath (i.e., as would likely be the case at a field site), $C^0_{w\,target}$ will not change.

Experiment

An experiment was designed to test a PE-based method that uses the model described above to measure the chemical activities of two representative PAHs, phenanthrene and fluoranthene, in well mixed seawater. PEDs were exposed to seawaters in such a way that a large seawater volume-to-PED mass ratio was maintained (>1.5 x 10^5 L_w/kg_{PE}), ensuring that the activity of the target chemical in the water did not change very much during the course of the experiment. Target chemicals were spiked into collected water samples at concentrations which were approximately 100 times greater than dissolved concentration of these chemicals which have been measured in Boston Harbor before in order to eliminate the effects of background target chemical concentrations on measurements.[2]

Methods

Materials

All solvents used for rinsing, standards, and extractions were JT Baker Ultra-resi-analyzed (Phillipsburg, NJ). All low-density polyethylene (PE) sheeting, used for sampling devices was 51 ± 3 μm thick, and manufactured by Carlisle Plastics, Inc., Minneapolis, MN. Fluoranthene and chrysene used in the winter experiment were purchased as the solid phase (Aldrich Chemical Co., Milwaukee, WI). All other chemicals were solvent dissolved Ultra Scientific, North Kingston, RI, except sodium azide which was manufactured by Fluka Chemie AG, Buchs, Switzerland. Clean water used was reverse osmosis pretreated and run through an ion-exchange and activated carbon filter system (Aries Vaponics, Rockland, MA) until a resistance of 18 MOhm was achieved.

Preparation of Polyethylene Devices (PEDs)

PE was soaked in a jar of dichloromethane (DCM) for 48 hours, followed by methanol (MeOH) for 48 hours, and finally rinsed three times and allowed to soak in clean water for 48 hr. Approximately 16 g PE were then allowed to equilibrate with approximately 1-L of an aqueous solution of d10-phenanthrene, d10-pyrene, and d12-chrysene, each at a concentration of 250 μg/L, for at least three months.

Seawater collection

All seawater samples were collected from near shore on the eastern side of Dorchester Bay, Massachusetts (42°17.90'N, 71°01.02'W) (Figure 3.3). Water was collected in 20-L glass carboys that had previously been cleaned by soaking in a 5% by volume Extran 1000 biodegradable detergent-water solution for 1 week. The carboy was then rinsed three times in reverse osmosis filtered water, and finally rinsed three times in Aries filtered water (see above).

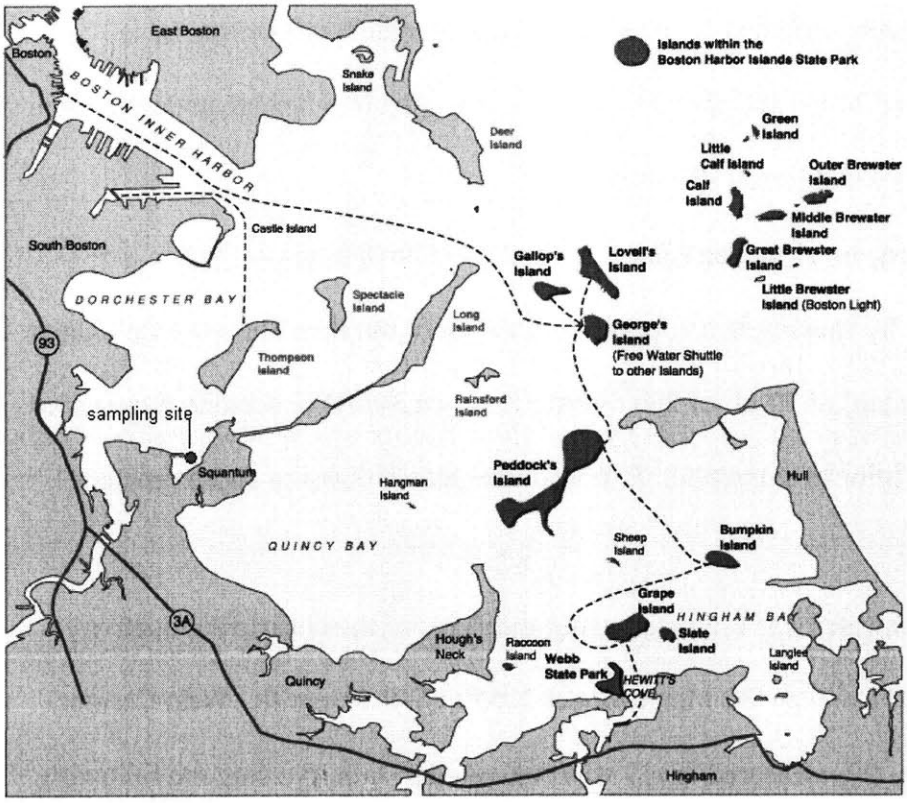

Figure 3.3 Seawater and sediment sampling site, at end of sand bar, east of Squantum Marina, Dorchester Bay (Boston Harbor, MA)[3]

Winter seawater sample

Water for the winter experiment was collected December 14, 2003 and stored for one month at 4° C before being brought to room temperature (18.5° C) on the lab bench. The seawater was then siphoned through solvent rinsed copper tubing into a clean 20-L carboy to remove settled material. The carboy was darkened with aluminum foil to avoid photodegradation of chemicals, and 325 μL of 6.0 μg/mL phenanthrene in methanol, 150 μL of 132 μg/mL fluoranthene in acetone, and 250 μL of 870 μg/mL chrysene in acetone were added to the water and stirred with a glass-covered stir bar for 24 hr. Six pieces of PE totaling 43.7 mg were then suspended in the water from a 24 gauge copper wire (National Manufacturing Co., Sterling, IL), for 24 hr. After the PE was removed, 25 μL of 266 ng/mL d14-*p*-terphenyl in

hexane were added as a recovery standard, and each piece was extracted three times in approximately 4 mL DCM for 24 hr. DCM extracts were exchanged into hexane under nitrogen (4.8 grade nitrogen, BOC Gasses, Murray Hill, NJ).

Three 100 mL subsamples of the seawater were extracted three times each in approximately 4 mL hexane by shaking in a volumetric flask for 5 min then allowing the phases to separate. A recovery standard of 50 μL of 266 ng/mL d14-*p*-terphenyl in acetone were added to each seawater subsample prior to extraction. Extracts were blown down to approximately 1 mL under nitrogen.

The salinity of the seawater was estimated using measures of the electric conductivity. Conductivity was determined using an EC Meter Model 2052 (VWR Scientific, West Chester, PA). The 25° C conductivity (K) measured in mS was converted to salinity using the following polynomial[4]:

$$\text{Salinity (g/L)} = 4.98 \times 10^{-1} K + 9.54 \times 10^{-3} K^2 - 3.941 \times 10^{-4} K^3 + 1.092 \times 10^{-5} K^4 - 1.559 \times 10^{-7} K^5 + 8.789 \times 10^{-10} K^6 \quad (3.9)$$

Molar concentrations of salinity were calculated assuming 1 mole of sea salts weighs 68.4 g.

Spring seawater sample

Water for the spring 2004 experiment was collected March 27, 2004 and stored for 2 weeks at 4° C before being brought to room temperature (22.5° C) on the lab bench and siphoned into a 19-L carboy. Again, the carboy was darkened using aluminum foil and this time spiked with 400 μL of a spiking solution containing 21.1 ± 2.4 μg/ml phenanthrene, 23.7 ± 2.9 μg/ml fluoranthene, and 2.1 ± 0.4 μg/ml chrysene in methanol. The seawater was stirred with a glass-covered stir bar for 24 hr before six pieces of PE totaling 21.5 mg were suspended in the water

using copper wire as described above. The PE was removed 48 hr later and extracted in DCM as described above.

Four 500 mL subsamples of the seawater were extracted three times each in approximately 10 mL of hexane, as above, using a recovery standard of 100 μL 500 ng/mL *p*-terphenyl in acetone. A larger extraction volume was used in order to measure the d10-pyrene concentration in the seawater after exposure to spiked PED. A smaller PED mass-to-water volume ratio more closely approximated the infinite bath case. Salinity was estimated as described above.

Summer seawater sample

Water for the summer 2004 experiment was collected June 25, 2004 and used immediately. Solids were allowed to settle before the water was siphoned into a clean, darkened 19-L carboy and sodium azide (NaN_3) was added as a biocide to an approximate concentration of 10 mM. The water was stirred with a glass-covered stir bar for 5 hr before being spiked with 400 μL of a solution containing 21.1 ± 2.4 μg/ml phenanthrene, 23.7 ± 2.9 μg/ml fluoranthene and 2.1 ± 0.4 μg/ml chrysene in methanol. The seawater was stirred for 23 hr before six pieces of PE totaling 16.9 mg were suspended in the water using copper wire as described above. The PE was removed 50 hr later and extracted in DCM as described above.

Four 500 mL subsamples of the seawater were extracted three times each in approximately 10 mL of hexane, as described above, using a recovery standard of 100 μL 475 ng/mL *p*-terphenyl in acetone. Salinity was estimated as described for the winter experiment.

GC/MS Analysis

All extracts were analyzed on a GC/MS (Hewlett Packard 6890 Series; JOEL MS-GCMate). Splitless 1-μL injections were made onto a 30 m Phenomenex Zebron ZB-5 capillary column (0.25 mm internal diameter with a 0.50 μm film thickness). The injection port temperature was 280° 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 at 4° C/min until a temperature of 300° C was reached and remained there for 9.5 min. The MS was operated in selected ion monitoring (SIM) mode at a resolution of 500 in EI+ mode.

Measurements were calibrated using a standard containing 34 aromatic compounds ranging in molecular weights from 128 atomic mass units (naphthalene) to 300 atomic mass units (coronene). This standard included each of the tracer and target chemicals used in this study, as well as those used as recovery and injection standards, each at 50 ng/ml. The standard was run between every 3 to 5 sample measurements to monitor instrument stability, and was used to determine a response factor (integrated peak area/unit mass) for each compound measured.

M-terphenyl added to each extract was used to calculate the total mass of target, tracer, or recovery standard (compound of interest) in an extract. A ratio of the mass of a compound of interest to the mass of *m*-terphenyl was calculated as the quotient of the integrated peak of the compound of interest divided by its response factor, over the integrated peak of m-terphenyl divided by its response factor. This ratio was then multiplied by the known mass of *m*-terphenyl added to each extract, resulting in the total mass of compound of interest present in an extract. This method eliminates the need to know exact volumes of extracts or injections.

Repeated measurements of the calibration standard were also used to calculate the measurement uncertainty for the instrument. This uncertainty was calculated to be approximately ± 15% for d10-phenanthrene and d10-pyrene in the calibration standard.

Organic Carbon Analysis

Total organic carbon (TOC) measurements were taken for the seawater used in the spring and summer experiments. Approximately 500 ml of seawater were filtered through glass fiber filters (Whatman GF/F, Whatman International Ltd., Brentford, UK) Particulate organic carbon (POC) was measured using a loss-on-ignition approach. Briefly, the weight of the filters was determined after drying overnight in a 90° C oven and again after combustion at 375° C under oxygen for 24 hr. Dissolved organic carbon (DOC) was measured in the filtered water, after acidification with phosphoric acid (Phosphoric Acid GR, EM Science, Gibbstown, NJ) to a pH of 1, and sparging with TOC-grade air (BOC Gasses, Murray Hill, NJ), until TOC measurements stabilized as determined using a Shimadzu 5000 TOC (Shimadzu Scientific Instruments, Columbia, MD). POC and DOC were combined and reported as TOC.

Results

Chemical activities for phenanthrene and fluoranthene were determined using the PED method for each of the three trials (Table 3.1). Although chrysene had also been spiked into the seawaters, 1 and 2 day exposures were not long enough for significant amounts of the deuterated chrysene tracer to diffuse from the PEDs (differences in masses before and after these incubations were within the uncertainty of the measurement). For this reason, chrysene chemical

activity was not determined. The large uncertainties reported for chemical activities in Table 3.1 are due to the propagation of measurement uncertainties through the calculations.

Table 3.1 Known and measured seawater chemical activities

Test date		Known Initial Activity[b] (ppm)	Measured Initial Activity[c] (ppm)	Mass Balance[d]
Winter				
	phananthrene	44	16 ± 6	0.97
	fluoranthene	1800	1600 ± 2300	0.60
Spring				
	phananthrene	160	150 ± 40	1.15
	fluoranthene	690	680 ± 630	1.10
Summer				
	phananthrene	160	140 ± 100	1.18
	fluoranthene	770	980 ± 780	1.28

[b]Known initial activity based on spike added to seawater sample, not corrected for partitioning to DOC.
[c]Measured initial activity based on exposed PEDs and application of model. Uncertainty based on propagation of uncertainty in measurements through model calculations.
[d]Mass recovered from seawater and PED divided by mass added to water.

Chemical activities were calculated using K_{PEW} and $C_w^{sat}(L)$ which had been corrected for temperature and salinity.[1, 5, 6]

$$\ln K_{PEW\,(tempcorrected)} = -\frac{\Delta H_s^e}{RT} + C_1 \tag{3.10}$$

$$\ln\ C_w^{sat}(L) = -\frac{\Delta H_s^e}{RT} + C_2 \tag{3.11}$$

where ΔH_s^e is the excess enthalpy of solution in water (kJ/mol),

R is the gas constant (KJ/mol K),

T is the absolute temperature (K), and

C_1 and C_2 are constants.

and

$$K_{PEW(saltcorrected)} = K_{PEW(tempcorrected)} \cdot 10^{K^S \cdot [salt]} \tag{3.12}$$

$$C^{sat}_{w(saltcorrected)}(L) = C^{sat}_{w(tempcorrected)}(L) \cdot 10^{K^S \cdot [salt]} \tag{3.13}$$

where K^S is the Setschenow constant (1/M), and

[salt] is the salt concentration (M).

An analysis was also performed to determine if the particulate and dissolved organic carbon present in the seawater samples could significantly affect chemical activity measurements. The freely dissolved fraction of the chemical of concern, considering the sum of dissolved and particulate organic carbon (TOC), may be estimated from the measured TOC concentration and organic carbon/water partition constants, K_{OC} (Table 3.2). [1]

$$f_{iw} = \frac{1}{1 + [TOC] \cdot K_{iOC}} \tag{3.14}$$

TOC measurements of 2.5 and 7.5 (mg/L) for the spring and summer trials, respectively, would not have had significant effects on the activities of phenanthrene and fluoranthene in these waters. TOC concentration was not measured for the winter trial. The largest effect of organic carbon in the seawater would have been seen in the summer experiment for the more strongly sorbing fluoranthene. In this case 68% of the compound would be estimated to be freely dissolved if one uses [TOC] and K_{OC}. However, as almost 90% of the TOC was present as DOC (Table 3.3), the fraction in the water should be estimated using K_{DOC}, which for fluoranthene is

approximated as 10^4.[1] Estimated in this way approximately 89% of the compound would be freely dissolved. This analysis neglects the possible effects of black carbon on the system.

Table 3.2 Chemical properties used in the calculation of activities of phenanthrene and fluoranthene

	log K_{PEW} [a]	ΔH^e_s [a]	K^s [b]	log K_{OC} [c]	log $C_w^{sat}(L)$ [d]
phananthrene/ d10-phenanthrene	4.3	18	0.3	4.2	5.9
fluoranthene/ d10-pyrene	5	29	0.3	4.8	7.0

[a] K_{PEW} and ΔH^e_s values from Adams (2003) in (mol/kg PE)/(mol/L_w) for 23 deg C and (kJ/mol), respectively.

[b] K^s values from Schwarzenbach et al. (2003).

[c] K_{OC} calculated using K_{OW} values from Schwarzenbach et al. (2003) and log K_{OC} = 0.989 log K_{OW} - 0.346 from Karickhoff (1981) (for 25ºC).

[d] $C_w^{sat}(L)$ values calculated from $C_w^{sat}(s)$ values from de Maagd et al. (1998) and using $C_w^{sat}(L) = C_w^{sat}(s)\, e^{\Delta fusG/RT}$ as given in Schwarzenbach et al. (2003) (for 25ºC) (in mol/L).

Table 3.3 Seawater sample properties

Collection Date	Temperature during PED incubation (deg C)	Salinity (M)	DOC (mg/L)	POC (mg/L)
December 14, 2003	17.5	0.29		
March 27, 2004	22.5	0.40	1.3	1.2
June 25, 2004	17-21	0.43	6.6	0.9

Conclusions

The wall boundary model for PEDs in well-mixed seawater worked best in determining chemical activities of phenanthrene and fluoranthene after exposures of at least 2 days in our 20-L carboy systems. Except for the phenanthrene measurement in the winter test, which gave approximately 35% of the known activity, all measurements came within 25% of the known initial activities. Mass balance calculations performed showed that the mass of target chemical added to the system was recovered using the PED and seawater extractions (adjusted to include entire seawater volume), indicating that losses to volatilization, biodegradation, or photodegradation were negligible (Table 3.1).

The experiments helped us gain confidence in the use of tracer chemicals to provide information on mass transfer rates across matrix boundaries. As long as the diffusivity of the tracer and target compounds in PE may be assumed to be similar, diffusivity does not need to be known in order to determine the mass transferred across the matrix interface.

References

1. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental Organic Chemistry*. 2nd ed.; Wiley: Hoboken, N.J., 2003; 'Vol.' p xiii, 1313 p.

2. Lohmann, R.; Burgess, R. M.; Cantwell, M. G.; Ryba, S. A.; MacFarlane, J. K.; Gschwend, P. M., Dependency of plychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in *Mya Arenaria* on both water column and sediment bed chemical activities. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2551-2562.

3. Massachusetts Department of Conservation and Recreation Boston Harbor Islands. http://www.mass.gov/dcr/parks/metroboston/harbor.htm (August 3, 2005),

4. Webster, I. The salinity of coastal waterways. http://www.ozestuaries.org/indicators/In_Salinity_f.html (August 9, 2005),

5. Adams, R. G. *Polyethylene devices and the effects of sediment resuspension on the cycling of PAHs and PCBs in the lower Hudson Estuary.* Thesis Ph. D. --Massachusetts Institute

of Technology Dept. of Civil and Environmental Engineering 2003., Massachusetts Institute of Technology, Cambridge, MA, 2003.

6. May, W. E.; Wasik, S. P., Determination of the Solubility Behavior of Some Polycyclic Aromatic Hydrocarbons in Water. *Analytical Chemistry* **1978,** 50 (7), 997-1000.

7. Karickhoff, S. W., Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* **1981,** 10 (8), 833-846.

Chapter 4: Measurement of PAH chemical activities in Boston Harbor Sediments

Introduction

Having seen that a wall boundary model may be used with a tracer infused PED in order to measure chemical activities of PAHs in water, it is now desired to extend the model and test the PEDs in sediment beds. This system requires us to expand the mass transfer model to include a second layer through which the chemicals must diffuse, the sediments. This model was described in Chapter 2.

Experiments were conducted to check if the PED method could be used to measure the chemical activities of phenanthrene, pyrene, fluoranthene, and chrysene in Boston Harbor sediments. These PAHs are assumed to have similar chemical properties to those which were used as tracers, d10-phenanthrene, d10-pyrene, and d12-chrysene. By assuming similar chemical properties, such as partitioning constants and diffusivities in and between different media, we may apply the model for mass transfer between the PEDs and sediments described earlier in this thesis. Boston Harbor was chosen as a sampling site because these PAHs have been measured in the sediments in the past.[1-3]

Four methods for measuring chemical activities in sediments and porewaters were followed. These methods include:

(1) incubating PED samplers with stagnant sediments on the benchtop for 52 and 92 days,

(2) solvent extracting sediments and applying an equilibrium partitioning model using a partitioning constant calculated from both OC and BC fractions in sediment,

(3) tumbling of PE, sediment, and water, until equilibrium partitioning of chemicals between the three media is reached, then using a polyethylene-water partitioning constant, K_{PEW}, to determine chemical activity, and

(4) extracting porewaters centrifuged from sediment sample.

The partitioning coefficients needed for use of each of the methods just mentioned are available in the literature (Table 4.1).

Table 4.1 Equilibrium partitioning constants for phenanthrene, pyrene, fluoranthene, and chrysene

	log K_{PEW}[a]	log $C_w^{sat}(L)$[b]	log K_{OC}[c]	log K_{BC}
phenanthrene	4.3	-4.7	4.2	5.9[d]
fluoranthene	4.9	-5.3	4.8	7.0[d]
pyrene	5.0	-5.2	4.6	6.4[e]
chrysene	5.7	-6.1	5.4	7.9[d]

[a] K_{PEW} values from Adams (2003) in $(mol/kg_{PE})/(mol/L_w)$ for 23ºC.

[b] $C_w^{sat}(L)$ values calculated from $C_w^{sat}(s)$ values from de Maagd et al. (1998) and using $C_w^{sat}(L) = C_w^{sat}(s)\, e^{\Delta fusG/RT}$ as given in Schwarzenbach et al. (2003) (for 25ºC) (in mol/L).

[c] K_{OC} calculated using K_{OW} values from Schwarzenbach et al. (2003) and log K_{OC} = 0.989 log K_{OW} - 0.346 from Karickhoff (1981) (for 25ºC).

[d] calculated from Schwarzenbach et al. (2003) (for 25ºC).

[e] from Accardi-Dey and Gschwend (2002) (for 25ºC).

Except for the PED method to be tested, each of the methods listed above has been used to measure PAH concentration in Boston Harbor sediments in the past.[1, 3-5] The second method, using an equilibrium partitioning model and OC fractions in the sediments, but ignoring BC fractions, is the method suggested by the EPA for determining how dangerous sediments are to benthic organisms.[6] Long-term tumbling of PE, sediments and water (to equilibrium) has been used to measure PAH concentrations in Boston Harbor, and in Delfzijl Harbor, Netherlands.[1, 7]

Extraction of porewater is the most direct method to determine porewater chemical activities, but is complicated by the need for large amounts of sediment, and the need to consider colloid and dissolved organic matter to which the chemicals of interest may extensively bind.[3, 8]

The PEDs were exposed to sediments on the benchtop, instead of in the field, so that sediment heterogeneities on the scale of the PED dimensions could be eliminated by mixing sediments and removing large shells and rocks. This would allow us to improve the likelihood that chemical activities in different sediment sub-samples were the same.

Field Sampling

The sampling location was selected based on previous measurement of significant PAH concentrations in Dorchester Bay, Boston Harbor.[1, 5] Sediments were collected in October 2004, from Dorchester Bay, east of Squantum Marina, along the tip of a sand bar that is sheltered from waves on one side (42°17.90'N, 71°01.02'W) (Figure 4.1). Approximately 30 L of sediments were collected from the top 20 cm of the sediment bed, just below the water level at low tide. Sediment temperature was measured at 21° C at time of sampling. A sieve with openings of approximately 1 cm was used to separate sediments from large shells and rocks in the field. The sediments were brought back to the lab and sifted through a 2 mm sieve to remove gravel and shells and then thoroughly mixed with gloved hands and large metal spoons. Sediments were stored in amber glass jars, at room temperature (approximately 21° C) until after PED exposure, when they were refrigerated at 7° C.

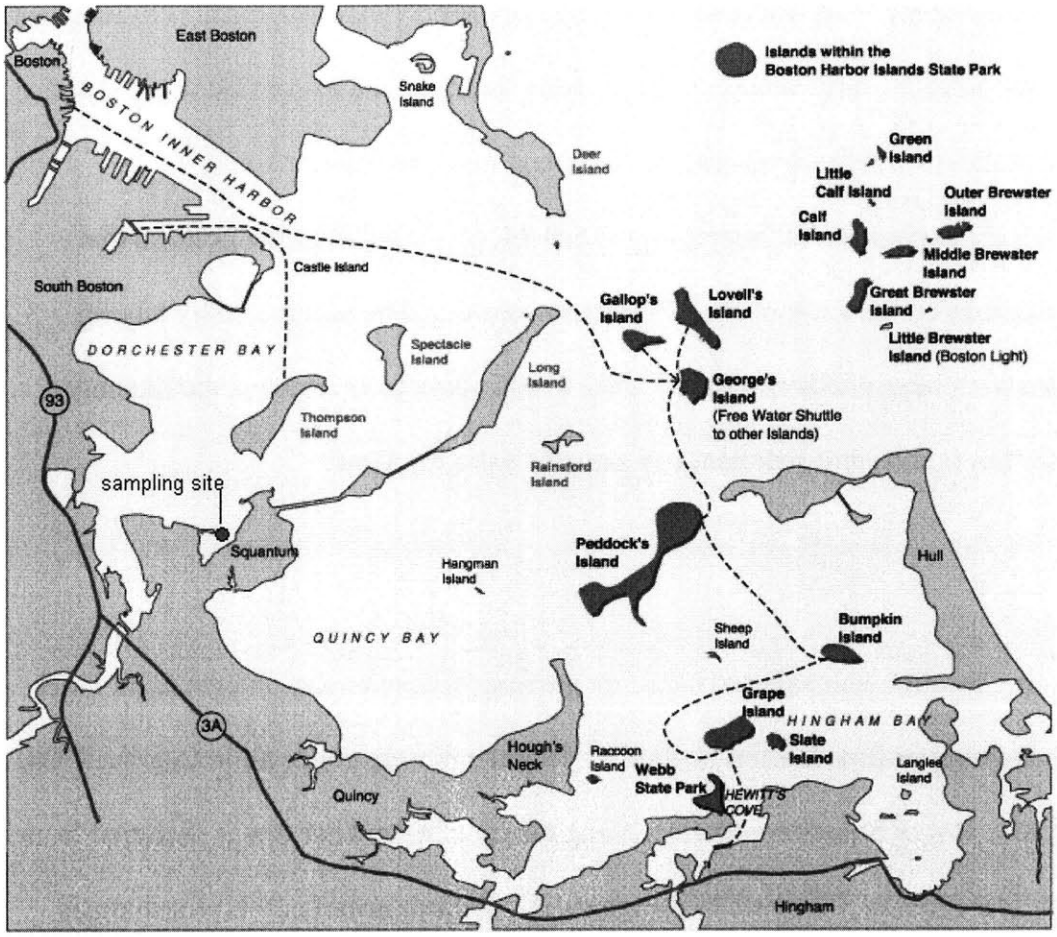

Figure 4.1 Sediment sampling site, at end of sand bar, east of Squantum Marina, Dorchester Bay (Boston Harbor, MA)[9]

Materials

All solvents used for rinsing, standards, and extractions were JT Baker Ultra-resi- analyzed (Phillipsburg, NJ). All low-density polyethylene (PE) sheeting, used for sampling devices, was 51 ± 3 μm thick manufactured by Carlisle Plastics, Inc., Minneapolis, MN. All tracer chemicals and standards were solvent dissolved Ultra Scientific (North Kingston, RI). Clean water used was reverse osmosis pretreated and run through an ion-exchange and activated carbon filter system (Aries Vaponics, Rockland, MA) until a resistance of 18 Mohm was

achieved. All glassware was solvent rinsed. Jar and vial caps were all lined with solvent-rinsed aluminum foil.

PED Experiment

Preparation of PEDs

PE was soaked in a jar of dichloromethane (DCM) for 48 hours, followed by methanol (MeOH) for 48 hr, and finally rinsed three times and allowed to soak in clean water for 48 hr. Approximately 16 g PE were then allowed to equilibrate with approximately 1-L of an aqueous solution of d10-phenanthrene, d10-pyrene, and d12-chrysene, each at a concentration of 250 μg/L, for 12 mo.

Sediment-PED exposures

Portions of the mixed sediment sample were transferred to amber glass jars ranging in diameter from 2 to 10 cm and 10 cm tall. Small strips of PE material (approximately 40 mg) were pushed through the center of each sediment sub-sample until the PE extended from the bottom of the jar to the top of the sediments (Figure 4.2). The jars were tapped on the bench to remove air pockets, topped off with seawater to limit head space, and capped. Six PEDs were removed from the sub-sample jars after 52 days, briefly rinsed in clean water to remove sediments, and lightly wiped with a Kim-wipe (Kimberly-Clark Corp., Roswell, Georgia). *P*-terphenyl in hexane (10 μL at 30 μg/ml) was dripped onto the PED as a recovery standard before extracting three times in 15 mL of DCM. The combined extracts were then exchanged into hexane under a gentle stream of high-purity nitrogen, and reduced to approximately 1 mL. *M*-

terphenyl (50 μL at 1.2 μg/ml) was then added to the extracts as an injection standard before gas chromatograph-mass spectrometer (GC/MS) analysis.

Three more sediment sub-samples were allowed to incubate with PEDs for 92 days. The PEDs were then removed from the jars and prepared as described above for GC/MS analysis, except that the recovery standard was added to the PED during the first DCM extraction to avoid volatilization of *p*-terphenyl during transfer. The sensitivity of the GC/MS instrument was observed to be low at the time of analysis, so extracts were blown down under nitrogen to approximately 100 μL and re-analyzed.

Figure 4.2 Amber glass jar (10 cm diameter x 10 cm tall) containing sediment sub-sample and PED. Shown after 52 day incubation.

Solvent extraction of sediments

Approximately 12 g of sediment (dry wt.) from each of the nine PED-exposed sub-samples were placed into 50-mL, foil covered, ground glass stoppered test tubes. Each sub-

sample was tumbled for 1 hr with 20 mL chloroform, 10 mL methanol, and 10 μL of *p*-terphenyl as a recovery standard (at 30 μg/ml), then allowed to settle for 24 hr. The solvents were removed and the sediments were extracted two more times in 30 mL of chloroform as described above. The combined extracts were reduced under a gentle stream of nitrogen, and anhydrous sodium sulfate ($NaSO_4$) was added to each sample to remove residual water before being transferred to hexane. Finally, extracts were run through columns containing elemental copper and $NaSO_4$ to remove elemental sulfur and water before being blown down to approximately 1 mL. *M*-terphenyl injection standard (50 μL at 1.2 μg/ml) was added to extracts before GC/MS analysis.

BC and OC 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 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.[1, 10] Both OC and BC samples were acidified with 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 used in the 52 day exposure test (18 samples total) were performed for each of the two measurements (BC and OC). Acetanilide (Elemental Microanalysis Limited, Okehampton, UK) was used as a calibration standard for the analytical method. Blanks were run between every three samples. Blanks were always less than 4.6×10^{-4} % C.

Tumbling of PE, sediments and water

Six sub-samples of the sieved, mixed sediment, approximately 43 g dry wt. each, were placed in 250 mL round bottom flasks along with approximately 0.4 g of PE and 200 mL of water. Three flasks were then tumbled continuously for 21 days, while three more flasks were tumbled continuously for 42 days. PED concentrations from the two exposure times were compared to determine if the sediment/water/PE system had come to equilibrium. As sub-samples were removed from the tumbling apparatus, portions of the PE were extracted and prepared for GC/MS analysis as described above.

Porewater extraction

Although the sieved, mixed sediment sample was stored in a tightly sealed jar, the sample had partially dried during storage. In order to collect enough porewater from the sample to allow for solvent extraction, additional seawater, collected at the time of sediment sampling, was added to the sediment. The wetted sediments were stored on the lab bench for 7 days to allow for equilibration between sediments and seawater. The sample was then divided between four 200 ml centrifuge tubes, containing approximately 300 g of wet sediments each, and centrifuged at 1500 g for 20 min. The porewaters were glass pipetted from the surface of the centrifuged sediments and this 30 mL water sample was centrifuged again at 1500 g for 20 min to further separate solids from the liquid portion. *P*-terphenyl in acetone (10 µl at 0.3 µg/mL) was added to the resulting supernatant as a recovery standard. The water sample was extracted three times in a foil darkened separation funnel with approximately 15 mL of DCM. The water sample and DCM were shaken for 5 min and allowed to separate for 10 min with each extraction. The combined DCM extract was then run through a column containing anhydrous $NaSO_4$ to remove

residual water before being exchanged to hexane under a gentle stream of nitrogen. The extract was blown down to approximately 100 μL and *m*-terphenyl (10 μL at 1.2 μg/mL) was added as an injection standard. GC/MS analysis was finally performed.

GC/MS Analysis

All extracts were analyzed on a GC/MS (Hewlett Packard 6890 Series; JOEL MS-GCMate). Splitless 1-μL injections were made using an autoinjector onto a 30 m Phenomenex Zebron ZB-5 capillary column (0.25 mm internal diameter with a 0.50 μm film thickness). The injection port temperature was 280° 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 at 4° C/min until a temperature of 300° C was reached and remained there for 9.5 min. The MS was operated in selected ion monitoring (SIM) mode at a resolution of 500 in EI+ mode.

Measurements were calibrated using a standard containing 34 aromatic compounds ranging in molecular weights from 128 atomic mass units (naphthalene) to 300 atomic mass units (coronene). This standard included each of the tracer and target chemicals used in this study, as well as those used as recovery and injection standards, each at 50 ng/ml. The standard was run between every 3 to 5 sample measurements to monitor instrument stability, and was used to determine a response factor (integrated peak area/unit mass) for each compound measured.

M-terphenyl added to each extract was used to calculate the total mass of target, tracer, or recovery standard (compound of interest) in an extract. A ratio of the mass of a compound of interest to the mass of *m*-terphenyl was calculated as the quotient of the integrated peak of the compound of interest divided by its response factor, over the integrated peak of m-terphenyl divided by its response factor. This ratio was then multiplied by the known mass of *m*-terphenyl

added to each extract, resulting in the total mass of compound of interest present in an extract. This method eliminates the need to know exact volumes of extracts or injections.

Repeated measurements of the calibration standard were also used to calculate the measurement uncertainty for the instrument. This uncertainty was calculated to be approximately ± 15% (± 1 σ) for d10-phenanthrene and d10-pyrene in the calibration standard.

QA/QC

The recovered mass of *p*-terphenyl was used to estimate how much of the target and tracer chemicals were recovered by the extraction process. PE extractions yielded recoveries of 90% ± 14% (n = 12). For sediment extractions recovery of *p*-terphenyl averaged 53% ± 7% (n = 9). And, for porewater the recovery of *p*-terphenyl was 80% ± 2% (n=1, measured 3 times).

Results

Porewater extraction method

Porewaters centrifuged from the sediments were solvent extracted to determine $C_{porewater}$ (mol/L_w) which could then be divided by C_w^{sat} to obtain chemical activity. The average of three measurements of the porewater extract, $C_{porewater}$, was used to calculate the porewater activity (Table 4.2).

$$a_{porewater} = \frac{C_{porewater}}{C_w^{sat}} \qquad (4.1)$$

$C_{porewater}$ for phenanthrene measured in this study was higher than that which had previously been measured in porewaters at other sites within Boston Harbor (42 ng/L, compared to <10 ng/L measured by McGroddy and Farrington (1995)) (Appendix D). Porewater concentrations

of pyrene, however, are much lower than those previously measured in the same study (8 ng/L this study vs. 10 – 100 ng/L by McGroddy and Farrington (1995)). Only fluoranthene concentrations, measured at 10 ng/L, were within the range of those previously measured.

Table 4.2 Calculated chemical activities (in ppm) using four measurment methods[a]

	Method				
	PED		Sediment extraction	PE tumbled with sediments and water[b]	Porewater extraction
	52 day exposure	92 day exposure			
$a_{phenanthrene}$	0.48 ± 0.15		0.14 ± 0.20	1.1 ± 0.9	10.8 ± 0.5
a_{pyrene}	4.5 ± 1.6	3.4 ± 1.2	0.45 ± 0.42	2.5 ± 1.5	6.2 ± 0.3
$a_{fluoranthene}$	7.4 ± 2.6	2.7 ± 0.9	0.05 ± 0.06	2.9 ± 1.4	9.0 ± 0.5
$a_{chrysene}$			0.0023 ± 0.0042	1.4 ± 1.5	

[a]uncertainties estimated from propagation of measurement errors
[b]results of 42 day tumbling exposure

Extracts of sediment porewaters included PAHs that were associated with colloids and dissolved organic carbon (DOC). This may have resulted in higher PAH levels in the extracts than those which would be due to the truly dissolved PAHs. The effects of the colloids and DOC may have been quantified if a TOC analysis had been performed on the water sample prior to extraction. This analysis was not performed, however.

PED in sediment bed method

Measurement of PED concentrations of pyrene, fluoranthene, and d10-pyrene provided data necessary to calculate chemical activities of pyrene and fluoranthene in Dorchester Bay sediments (Table 4.2). Because pyrene and fluoranthene have the same molecular weights, and are both apolar, it is expected that the two compounds will have similar molecular diffusion rates in different media.[11] For this reason it is believe that the tracer chemical d10-pyrene may be used as a reference chemical for both compounds. Using Equation 2.20 to calculate the chemical activities of pyrene and fluoranthene in sediments requires K_{PEW} and C_{wat}^{sat} values for each chemical (Table 4.1). The initial concentration of d10-pyrene in the PED, $C_{tracerPE}^{0}$, was taken to be the average of the measurements of d10-pyrene in six blank PEDs (9.7 ±1.4 μg/g PE). The standard deviation of the concentrations of the six blank PEDs was within the uncertainty for the instrument.

Although tracer chemicals were included in the PEDs for their use in measuring phenanthrene and chrysene activities in the sediments, difficulties were encountered in collecting data necessary to make the measurement calculations. The concentrations of phenanthrene in the unexposed (blank) PEDs exceeded the concentrations measured in the exposed PEDs. This is likely due to the contamination of the blank PED during storage and the transfer of phenanthrene to the sediments during exposure. Since one of the assumptions used in developing the PED-sediment model was that $C_{target PE}^{o}$ was zero, phenanthrene was not calculated for the sediments using the model described in Chapter 2. Instead, the deuterated phenanthrene tracer was used to determine how close to equilibrated the PED and sediments were. The phenanthrene concentration in the PED could then be used to solve for chemical activity in the system.

After 52 and 92 days of exposure, the d10-phenanthrene concentration in the PEDs had dropped by 81% and 99% respectively. As the PEDs are exchanging masses of tracer and target chemicals with the sediments at the same rates, we may assume that the PEDs and sediments are as equilibrated in their exchange of phenanthrene as well. While the PEDs and sediments may not be perfectly equilibrated (at which point we would expect to see undetectable concentrations of tracer chemical in the PED) they are close enough that an approximation of sediment activity may be made. An estimate of the mass transfer coefficient, k, which may be used for both deuterated and non-deuterated phananthrene, may be made using the following equation:

$$\ln(C_{PE}(t) - C_{PE}^{eq}) = \ln(C_{PE}^{o} - C_{PE}^{eq}) - kt \qquad (4.2)$$

For d10-phenanthrene C_{PE}^{eq} will be zero and Equation 4.2 becomes

$$\ln C_{PE}(t) = \ln C_{PE}^{o} - kt \qquad (4.3)$$

Using Equation 4.3, the mass transfer coefficient for this experiment was ~ 0.042 d^{-1} (average of k's calculated for 52 and 92 day exposures). Equation 4.2 may now be used to calculate what the equilibrium concentration of phenanthrene in the PED would be. The results of the calculation indicate that the concentration in the PE after 52 day incubations (averaging 34 ng/g PE) are the concentrations which would appear in the PEDs at equilibrium. This gives an activity for phenanthrene in the sediments of 0.48 ppm. Data on phenanthrene in the PE for the 92 day exposure was not available due to low instrument sensitivity at the time of analysis.

Chrysene chemical activity could not be calculated because not enough tracer chemical, d12-chrysene, was transferred across the PE/sediment interface in the given exposure time. Also, no chrysene was detected in PED extracts (Appendix B). This result was expected when the exposure time was selected to ensure enough d10-pyrene crossed the interface without depleting the d10-pyrene concentration in the center of the PED. Because d12-chrysene is larger

than d10-pyrene, it is expected to diffuse more slowly through PE and sediments. Loss of a measurable amount of tracer chemical would therefore require a longer exposure time than that required for d10-pyrene.

Sediment extraction method

The concentrations and chemical activities of phenanthrene, pyrene, fluoranthene and chrysene were measured in the sediments through solvent extraction. Reported C_{sed} (mol/kg dry sed) measurements are the averages of the extractions of nine sediment sub-samples (Appendix C). Chemical activity was calculated by estimating a partitioning constant, K_d, based on f_{OC} and f_{BC} measurements, and K_{OC} and K_{BC} estimates (Tables 4.1 and 4.3). The f_{OC} and f_{BC} values measured in this study were similar to those measured at the same site by Lohmann et al. (2004) (0.64% and 0.13% respectively). The difference between the fractions measured in this study and those measured previously may be due to spatial variations in OC and BC content at the sampling site and the way the samples were collected. Sediments from a large area were combined and mixed in this study, while Lohmann et al. took four separate smaller samples from a site nearby. The sieving of the sediment sample in this study may have also affected f_{OC} and f_{BC}.

The following equations for calculating sediment chemical activity are given by Schwarzenbach et al. (2003) and Accardi-Dey and Gschwend (2002):

$$a_{sed} = \frac{C_{sed}}{K_d C_w^{sat}} \tag{4.4}$$

$$K_d = f_{OC} K_{OC} + f_{BC} K_{BC} C_w^{n-1} \tag{4.5}$$

$$K_d = \frac{C_{sed}}{C_w} \tag{4.6}$$

The K_d used in Equation 4.4 was a value found by iteration using Equations 4.5 and 4.6. Values for C_w were plugged into the Equations 4.5 and 4.6, using measured values for C_{sed}, f_{OC} and f_{BC}, and reported values for K_{OC} and K_{BC} (Table 4.1), until a K_d was found which would satisfy both equations. The Freundlich coefficient, n, was assumed to be 0.7 following Lohmann et al. (2004) although values ranging from 0.6 to 0.8 have been reported.[1, 4, 5, 12] Once an internally consistent value for C_w ($=C_{sed}/K_d$) was determined, the corresponding chemical activity was found by dividing it by $C_w^{sat}(L)$.

Table 4.3 Measured sediment PAH concentrations (ng/gdw) and OC and BC fractions

	Mean	Minimum	Maximum
$C_{sed\ phen}$	11.9 ± 6.3[a]	3.5	25.8
$C_{sed\ pyr}$	26.4 ± 8.8[a]	12.3	39.1
$C_{sed\ fluo}$	25.7 ± 5.8[a]	13.7	30.9
$C_{sed\ chry}$	29.2 ± 20.5[a]	10.2	68.5
f_{OC}	0.3 ± 0.1%[b]	0.2%	0.7%
f_{BC}	0.3 ± 0.1%[c]	0.2%	0.5%

[a] n = 9
[b] n=17
[c] n=16

In order to calculate chemical activity using the method described above, accurate K_{OC} and K_{BC} values are required and an accurate measure of f_{BC} is needed. Because of the higher

affinity of BC than OC for PAHs, and the significant amount of BC present in the sediments, the $f_{BC}K_{BC}$ term dominates and makes the accuracy of K_{BC} more important for measurement of chemical activity. Current EPA guidance does not include BC influence on K_d, making chemical activity estimates using this method even worse.

Tumbling of PE, sediments, and water method

The third method used to measure chemical activity in the sediments required the tumbling of PE, sediments and water until equilibrium partitioning within the system was achieved. The following equation could then be applied to measure chemical activity:

$$a = \frac{C_{PE}}{K_{PEW} C_w^{sat}(L)} \tag{4.7}$$

where C_{PE} is the concentration of chemical in the tumbled PE (mol/kg PE), K_{PEW} is in (L/kg PE), and $C_w^{sat}(L)$ is in (mol/L). Due to the large amount of PE added to the sediment slurries, the initial chemical activity of the sediments may have been reduced. An analysis of how much of the target chemical originally on the sediments ended up in the PE showed, however, that the mass lost to PE was always < 10%. This amount of loss is not expected to significantly affect the chemical activities measured using this method. Average PE concentrations for the three PEDs tumbled for 21 days were greater than one standard deviation different from the PE concentrations for the PEDs tumbled for 42 days (Table 4.4). For this reason it is not possible to definitively say that the system had come to equilibrium before the end of the 42 day tumbling period. The 42 day exposures were used in Equation 4.6 to calculate chemical activities with the assumption that these values were close to the equilibrium values.

Table 4.4 PAH concentrations in the tumbled PEDs[a]

	after 21 days of tumbling (ng/g PE)	after 42 days of tumbling (ng/g PE)
C_{PE} *phen*	27 ± 11	77 ± 3
C_{PE} *pyr*	274 ± 40	314 ± 39
C_{PE} *fluo*	182 ± 31	234 ± 17
C_{PE} *chry*	120 ± 15	131 ± 41

[a]n=3

Comparison of chemical activity measurement methods

The chemical activities measured using the PED method at a 52 day exposure gave chemical activities which were closest to those given using the porewater extraction method (Table 4.2). The sediment extraction method using an EqP model to calculate chemical activity gave results that were one to two orders of magnitude lower than the other methods. The high uncertainties associated with the calculated activities are due to the propagation of both measurement errors and uncertainties in the partitioning constants carried through the activity calculations.

In addition, because the activities measured were intended more for inter- comparison between the measurement methods, K_{PEW} and $C_w^{sat}(L)$ were not corrected for temperature and salinity as they would have been if accurate measurements were sought. The salinity and temperatures for the sediments and porewaters for each method were the same except for the porewater extraction method which may have had increased salinity due to addition of seawater

after sediments had partially dried. Higher salinity would have had the affect of raising the relative activity of PAHs in the porewaters.

References

1. Lohmann, R.; Burgess, R. M.; Cantwell, M. G.; Ryba, S. A.; MacFarlane, J. K.; Gschwend, P. M., Dependency of plychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in *Mya Arenaria* on both water column and sediment bed chemical activities. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2551-2562.

2. Wang, X.-C.; Zhang, Y.-X.; Chen, R. F., Distribution and partitioning of polycyclic aromatic hydrocarbons (PAHs) in different size fractions in sediments from Boston Harbor, United States. *Marine Pollution Bulletin* **2001,** 42 (11), 1139-1149.

3. McGroddy, S. E.; Farrington, J. W., Sediment porewater partitioning of polycyclic aromatic hydrocarbons in three cores from Boston Harbor, Massachusetts. *Environmental Science and Technology* **1995,** 29 (6), 1542-1550.

4. Accardi-Dey, A.; Gschwend, P. M., Reinterpreting liturature sorption data considering both absorption into organic carbon and adsorption onto black carbon. *Environmental Science and Technology* **2003,** 37 (1), 99-106.

5. Accardi-Dey, A.; Gschwend, P. M., Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science and Technology* **2002,** 36 (1), 21-29.

6. Hansen, D. J.; DiToro, D. M.; McGrath, J. A.; Swartz, R. C.; Mount, D. R.; Spehar, R. L.; Burgess, R. M.; Ozretich, R. J.; Bell, H. E.; Reiley, M. C.; Linton, T. K., *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures.* In ed.; Office of Research and Development, U. S. E. P. A., 'Ed.'^'Eds.' Washington, DC, 2003; 'Vol.' p^pp.

7. Booij, K.; Hoedemaker, J. R.; Bakker, J. F., Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. *Environmental Science and Technology* **2003,** 37 (18), 4213-4220.

8. Hawthorne, S. B.; Grabancki, C. B.; Miller, D. J.; Kreitinger, J. P., Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in mililiter sediment pore water samples and determination of Kdoc Values. *Environmental Science and Technology* **2005,** 39, 2795-2803.

9. Massachusetts Department of Conservation and Recreation Boston Harbor Islands. http://www.mass.gov/dcr/parks/metroboston/harbor.htm (August 3, 2005),

10. Gustafsson, O.; Haghseta, F.; MacFarlane, J.; Gschwend, P. M., Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environmental Science and Technology* **1997,** 31 (1), 203-209.

11. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M., *Environmental organic chemistry*. 2nd ed.; Wiley: Hoboken, N.J., 2003; 'Vol.' p xiii, 1313 p.

12. Kleineidam, S.; Rugner, H.; Ligouis, B.; Grathwohl, P., Organic Matter Facies and Equilibrium Sorption of Phenanthrene. *Environmental Science and Technology* **1999,** 33 (10), 1637-1644.

Chapter 5: Discussion and Conclusions

Discussion

This study compared a new method for the assessment of PAHs in sediments with other approaches that have been used in the past. The experiments were not intended to produce accurate measurements of chemical activities in the Dorchester Bay sediment bed due to manipulation of the sediments (sieving, mixing, and benchtop storage), but rather to allow for comparison between measurement methods.

Many of the results of this study compare favorably with previous measurements in Dorchester Bay. Lohmann et al. (2004) measured $C_{\text{sed pyr}}$ to be 40 ng/gdw in samples collected in October 2001 (compared to 26 ng/gdw in this experiment). Their results for f_{OC} and f_{BC} were also similar to those in this study at 0.64% and 0.13%, respectively (compared to 0.3% and 0.3% in this experiment). Accardi-Dey and Gschwend (2002) measured a fluoranthene/pyrene ratio of 1 in this area with f_{OC} and f_{BC} of 1.2% and 0.26%, respectively. The fluoranthene/pyrene ratio measured in this experiment was also 1.

The chemical activities were measured in this study using four methods. Of the four methods, the porewater extraction method is the most direct route to a measure of chemical activity. Comparing the results of the other methods to the results of the porewater extraction method gives one an idea of the accuracy of the measurement method. Both of the PE methods (insertion in a bed for 2 to 3 mos or tumbling in a sediment slurry for 3 to 6 weeks) and the sediment extraction method produced chemical activity values for phenanthrene which were significantly smaller than that measured using the porewater extraction method. This may have been due to contamination of porewater extract. Having more than one porewater sample may

have provided a clearer picture of caused the difference in measured activities. The chemical activities measured using the porewater extraction method may be higher than those measured using other methods due to the PAHs associated with the dissolved organic material and colloids which remained in the water sample after centrifuging. Additional testing of the porewaters, including DOC and POC analysis, would have provided information which would have allowed for the adjustment of the dissolved concentrations due to PAH partitioning to these OC fractions. Larger sediment volumes should be centrifuged in the future to allow for these analyses. Chemical activity results for both of the PED methods were quite similar for pyrene and fluoranthene. Here the 52-day PED exposure produced measurements which were within a factor of two of the porewater extraction method. The tumbled PED method produced chemical activity measurements within a factor of 3 of those measured using the porewater extraction method.

The most surprising results of the experiment were the very low activities calculated by using an equilibrium partitioning model and accounting for OC and BC fractions in calculating a K_d. These results were at least an order of magnitude lower than those that were calculated using the other methods. It is this method, however, which is recommended by the EPA for ranking sediments based on their PAH toxicity.[3] The discrepancies between the EqP model determined activities and those determined using the other methods may be due to the difficulties in measuring the OC and BC fractions in sediments, and the variability in the partitioning behavior of different types of OC and BC which are not differentiated in our analysis. Other materials may also be present in the sediment which are not included in the EqP model, but which also sorb PAHs. HOCs are known to sorb to clay and zeolite minerals, for example.[4, 5]

PED method for measuring activity in sediments

It appears that method of inserting tracer-infused PEDs into sediment beds described in this thesis for measuring chemical activity porewaters produces results which are consistent with results produced by other methods which have been used to measure chemical activity in sediments in the past. A field trial will help to determine the feasibility of the method for general use in determining cumulative PAH activities. Field trials should include PEDs of different thicknesses and different exposure times to measure a range of PAHs and optimize deployment times. The shortest deployment times which produce measurable results are desired to improve sampling efficiency and increase chances of successful sampling campaigns.

There would be many benefits to using the PED method described in this study to measure chemical activities in sediment beds over the current methods used. This method could provide an efficient means of measuring a depth profile of sediment activities. PEDs could be inserted into a sediment bed then sliced after exposure at known intervals. There would be no need to take a sediment core and analyze sediment sections separately. Also, PE is an inexpensive material which is easily handled in the field and the laboratory. PE extracts may be stored for long periods of time for reanalysis if needed.

An inexpensive method of measuring sediment activities, such as the PED method, would be helpful in environmental decision making. The method would allow for more sites of concern to be investigated, helping to focus remediation resources on those which are the greatest toxic threats to organisms and public health.

References

1. Lohmann, R.; Burgess, R. M.; Cantwell, M. G.; Ryba, S. A.; MacFarlane, J. K.; Gschwend, P. M., Dependency of plychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in *Mya Arenaria* on both water column and sediment bed chemical activities. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2551-2562.

2. Accardi-Dey, A.; Gschwend, P. M., Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science and Technology* **2002,** 36 (1), 21-29.

3. Hansen, D. J.; DiToro, D. M.; McGrath, J. A.; Swartz, R. C.; Mount, D. R.; Spehar, R. L.; Burgess, R. M.; Ozretich, R. J.; Bell, H. E.; Reiley, M. C.; Linton, T. K., *Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures.* In ed.; Office of Research and Development, U. S. E. P. A., 'Ed.'^'Eds.' Washington, DC, 2003; 'Vol.' p^pp.

4. Nicholl, S. I.; Talley, J. W.; Silliman, S., Model verification of thermal programmed desorption-mass spectrometry for estimation of release energy values for polycyclic aromatic hydrocarbons on mineral sorbents. *Environmental Toxicology and Chemistry* **2004,** 23 (11), 2545-2550.

5. Zhu, D.; Herbert, B.; Schlautman, M.; Carraway, E.; Hur, J., Cation-pi bonding: A new perspective on the sorption of polycyclic aromatic hydrocarbons to mineral surfaces. *Journal of Environmental Quality* **2004,** 33 (4), 1322-1330.

Appendices

Appendix A

Data for PE in stirred seawater experiments

Winter seawater sample

Calculated spike levels

phenanthrene	(mol/L)	$0.67 \times 10^{-9} \pm 0.02 \times 10^{-9}$
fluoranthene	(mol/L)	$5.9 \times 10^{-9} \pm 0.2 \times 10^{-9}$
Temp. during incubation	(deg C)	17.5
Conductivity	mS	32.2
Salinity	(M)	0.29
DOC	(mg/L)	no data
POC	(mg/L)	no data
Total water vol.	(L)	16.4

	PE concentration				PE mass
	phenanthrene (ng/g PE)	d10-phenanthrene (ng/g PE)	fluoranthene (ng/g PE)	d10-pyrene (ng/g PE)	(g)
Blank PED 1	529	11553	<30	25015	0.0114
Blank PED 2	370	9929	<30	17662	0.0098
Blank PED 3	296	11079	<30	26030	0.0127
Blank PED 4	267	11851	<30	26940	0.0134
Blank PED 5	294	11172	<30	29642	0.0115
Blank PED 6	391	11920	<30	32940	0.0105
Exposed PED 1	827	2708	21424	17231	0.0070
Exposed PED 2	699	2580	18825	11477	0.0077
Exposed PED 3	1098	3819	21318	27466	0.0081
Exposed PED 4	1161	2994	22913	20521	0.0082
Exposed PED 5	1148	2830	21678	26903	0.0061
Exposed PED 6	1094	2873	20170	20555	0.0066

	water concentration			
	phenanthrene (ng/L)	d10-phenanthrene (ng/L)	fluoranthene (ng/L)	d10-pyrene (ng/L)
Seawater 1	86.6	<20	1368	<20
Seawater 2	61.7	21.0	1020	<20
Seawater 3	60.8	<20	1062	<20

Spring seawater sample

Calculated spike levels

phenanthrene	(mol/L)	$2.5 \times 10^{-9} \pm 0.3 \times 10^{-9}$
fluoranthene	(mol/L)	$2.5 \times 10^{-9} \pm 0.3 \times 10^{-9}$
Temp. during incubation	(deg C)	22.5
Conductivity	(mS)	42.9
Salinity (M)	(M)	0.40
DOC	(mg/L)	1.3
POC	(mg/L)	1.2
Total water vol.	(L)	19

	PE concentration				PE mass
	phenanthrene (ng/g PE)	d10-phenanthrene (ng/g PE)	fluoranthene (ng/g PE)	d10-pyrene (ng/g PE)	(g)
Blank PED 1	454	9363	<30	15241	0.0122
Blank PED 2	589	10652	<30	10259	0.0067
Blank PED 3	741	9734	<30	11734	0.0083
Blank PED 4	no data	no data	no data	no data	0.0083
Blank PED 5	no data	no data	no data	no data	0.0144
Blank PED 6	no data	no data	no data	no data	0.0117
Exposed PED 1	7325	884	12560	11488	0.0045
Exposed PED 2	10624	1523	18658	9924	0.0029
Exposed PED 3	10116	1859	17569	6060	0.0037
Exposed PED 4	8934	629	19251	7732	0.0032
Exposed PED 5	10494	1836	16731	8041	0.0031
Exposed PED 6	8939	853	19910	9105	0.0041

	water concentration			
	phenanthrene (ng/L)	d10-phenanthrene (ng/L)	fluoranthene (ng/L)	d10-pyrene (ng/L)
Seawater 1	619	9.32	711	<4
Seawater 2	372	7.03	391	<4
Seawater 3	491	10.28	588	<4
Seawater 4	475	6.60	559	<4

Summer seawater sample

Calculated spike levels

phenanthrene	(mol/L)	$2.5 \times 10^{-9} \pm 0.3 \times 10^{-9}$
fluoranthene	(mol/L)	$2.5 \times 10^{-9} \pm 0.3 \times 10^{-9}$
Temp. during incubation	(deg C)	17-21
Conductivity	(mS)	45.8
Salinity (M)	(M)	0.43
DOC	(mg/L)	6.6
POC	(mg/L)	0.9
Total water vol.	(L)	19

	PE concentration				PE mass
	phenanthrene (ng/g PE)	d10-phenanthrene (ng/g PE)	fluoranthene (ng/g PE)	d10-pyrene (ng/g PE)	(g)
Blank PED 1	116	8604	<30	7408	0.0212
Blank PED 2	78.6	7035	<30	4987	0.0206
Blank PED 3	131	7732	<30	5025	0.0226
Blank PED 4	32.9	2859	<30	5393	0.0270
Blank PED 5	78.2	3572	<30	3993	0.0282
Blank PED 6	147	7890	<30	5333	0.0277
Exposed PED 1	5642	241	19808	3519	0.0034
Exposed PED 2	3390	214	12838	3248	0.0039
Exposed PED 3	10324	604	22531	3567	0.0026
Exposed PED 4	9091	210	22255	3637	0.0029
Exposed PED 5	9734	236	27414	3683	0.0021
Exposed PED 6	10977	203	32720	4254	0.0020

	water concentration			
	phenanthrene (ng/L)	d10-phenanthrene (ng/L)	fluoranthene (ng/L)	d10-pyrene (ng/L)
Seawater 1	526	7.36	517	2.36
Seawater 2	447	5.95	446	1.71
Seawater 3	453	6.36	468	2.62
Seawater 4	468	5.74	468	1.55

Appendix B

Data for PEDs inserted in simulated sediment beds

	PE concentrations						PE mass	Jar
	phenanthrene (ng/g PE)	d10-phenanthrene (ng/g PE)	fluoranthene (ng/g PE)	pyrene (ng/g PE)	d10-pyrene (ng/g PE)	% recovery of p-terph	(g)	diameter (cm)
Blank PED 1	44.58	5839	<30	<30	9763		0.0234	
Blank PED 2	100.8	7161	<30	<30	8136		0.0106	
Blank PED 3	36.78	5508	<30	<30	7468		0.0267	
Blank PED 4	58.99	6331	<30	<30	9466		0.0192	
Blank PED 5	77.29	7595	<30	<30	7618		0.0127	
Blank PED 6	88.38	8806	<30	<30	10941		0.0266	
Blank PED 7	44.95	7163	<30	<30	10655		0.0225	
Blank PED 8	86.02	8851	<30	<30	11373		0.0120	
Blank PED 9	60.79	7043	<30	<30	9933		0.0245	
Blank PED 10	86.01	4200	<30	<30	11788		0.0113	
Blank PED 11	58.75	5163	<30	<30	9891		0.0178	
52 day exposure								
Sample 1	15.30	678.4	94.93	129.5	5597		0.0563	10
Sample 2	43.13	1112	214.6	154.2	6342		0.0347	2
Sample 3	40.77	1446	207.7	222.9	6481		0.0507	2
Sample 4	36.53	1682	164.1	172.9	7792		0.0457	10
Sample 5	32.36	732.4	244.6	219.0	6493		0.0268	2
Sample 6	33.49	1844	192.5	204.0	7032		0.0476	2
92 day exposure								
Sample 7	<5	50.77	93.39	253.4	4068	102%	0.0437	10
Sample 8	<5	93.68	206.1	298.2	2621	93%	0.0261	2
Sample 9	12.07	24.63	106.0	220.6	2496	63%	0.0379	2

	Sediment concentrations						
	phenanthrene (ng/gdw)	d10-phenanthrene (ng/gdw)	fluoranthene (ng/gdw)	pyrene (ng/gdw)	d10-pyrene (ng/gdw)	chrysene (ng/gdw)	% recovery of p-terph
Sample 1	6.383	0.000	13.44	14.41	0.296	13.07	44%
Sample 2	5.831	0.084	16.21	13.75	0.839	12.07	54%
Sample 3	5.215	0.056	12.27	10.09	0.346	8.290	48%
Sample 4	11.91	0.060	13.91	17.86	0.601	29.60	46%
Sample 5	5.749	0.068	13.38	13.48	0.662	10.17	46%
Sample 6	4.087	0.164	12.85	12.11	0.000	8.970	64%
Sample 7	2.205	0.000	8.735	7.860	0.661	6.539	64%
Sample 8	9.067	0.073	16.94	21.43	0.592	37.52	55%
Sample 9	3.209	0.000	11.30	10.62	2.291	7.947	53%

	OC fractions	
	$f_{OC} + f_{BC}$ (% C)	f_{BC} (% C)
Sample 1	0.3931	0.358915
	0.4773	0.226773
	0.5323	0.260594
Sample 2	0.3730	0.203735
	0.3896	0.181465
	0.6465	0.317015
Sample 3	0.5643	0.155945
	0.6171	0.194332
	0.3630	0.310085
Sample 4	0.7323	0.242605
	0.7853	0.250659
	1.0075	0.474231
Sample 5	0.4603	0.174715
	0.4372	no data
	no data	0.254631

	OC fractions	
	$f_{OC} + f_{BC}$ (% C)	f_{BC} (% C)
Sample 6	0.6555	0.278687
	0.7400	0.324933
	0.6003	no data

Appendix C

Data for PE tumbled with sediment slurries

	PE concentrations							PE mass added to	PE mass
	phenanthrene (ng/g PE)	d10-phenanthrene (ng/g PE)	fluoranthene (ng/g PE)	pyrene (ng/g PE)	d10-pyrene (ng/g PE)	chrysene (ng/g PE)	% recovery of p-terph	slurries (g)	extracted (g)
tumbled for 21 days									
Slurry 1	43.13	1466	226.5	297.5	6718	142.0	no data	0.3400	0.0627
Slurry 2	21.69	2101	166.7	222.6	5124	110.0	no data	0.4600	0.0822
Slurry 3	16.71	1559	154.5	218.4	5210	109.2	no data	0.4754	0.0640
tumbled for 42 days									
Slurry 4	61.69	2860	238.2	281.5	4232	170.0	76%	0.4345	0.0463
Slurry 5	69.72	3203	252.6	274.8	5619	148.2	95%	0.4328	0.0588
Slurry 6	70.09	4289	211.5	255.9	5867	74.60	90%	0.4072	0.0636

Blank concentrations for d10-phenanthrene and d10-pyrene same as those shown in Appendix B

Appendix D

Data for porewater extractions

Volume porewater extracted: 30 mL

3 analyses of same extract

	Porewater concentrations					
	phenanthrene (ng/L)	d10-phenanthrene (ng/L)	fluoranthene (ng/L)	pyrene (ng/L)	d10-pyrene (ng/L)	% recovery of p-terph
1	34.23	<5	7.953	6.614	<5	78%
2	33.13	<5	8.133	6.652	<5	81%
3	33.82	<5	7.926	6.980	<5	81%