ESTCP
Cost and Performance Report

(ER-200624)

Demonstration and Evaluation of Solid Phase Microextraction for the Assessment of Bioavailability and Contaminant Mobility

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ESTCP

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COST & PERFORMANCE REPORT

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ACRONYMS AND ABBREVIATIONS

BAF	bioaccumulation factor
BCF	bioconcentration factor
BSAF	biota sediment accumulation factor
COV	coefficient of variable
ESB	Equilibrium Partitioning Sediment Benchmark
ESTCP	Environmental Security Technology Certification Program
GC	gas chromatography
GC-ECD	gas chromatography-electron capture detector
HOC	hydrophobic organic contaminant
HPLC	high-performance liquid chromatography
MDL	method detection limit
NASP	Naval Air Station Pensacola
NBSD	Naval Base San Diego
ng/L	nanograms per liter
NRWQC	National Recommended Water Quality Criteria (USEPA)
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PE	polyethylene
POM	polyoxymethylene
PRC	performance reference compounds
SERDP	Strategic Environmental Research and Development Program
SPME	solid phase microextraction
TOC	total organic carbon
USACE-ERDC	U.S. Army Corps of Engineers Engineer Research and Development Center
USEPA	U.S. Environmental Protection Agency
UT	University of Texas

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1.0 EXECUTIVE SUMMARY

1.1 OBJECTIVES OF THE DEMONSTRATION

The goal of the project was to develop and standardize a procedure using field deployable solid phase microextraction (SPME) for the measurement of freely dissolved porewater concentrations of hydrophobic organics and demonstrate the relationship of these measurements to contaminant flux, bioavailability, and bioaccumulation.

Specific objectives of the polydimethylsiloxane (PDMS) technology for hydrophobic organic compounds include:

- Determination of mobile and available contaminants in sediments
- Assessment of bioaccumulation potential in benthic organisms
- Assessment of vertical chemical profiles in surficial sediments and sediment caps.

The work was conducted in sediments both in laboratory and field testing. Laboratory testing allows sediments to be collected and tested in the laboratory, avoiding problematic field deployments where placement and retrieval is too difficult or costly. This testing also allows coupling of availability measurements with laboratory bioassays under controlled conditions avoiding the difficulties and variability of field bioassays. The field testing allows determination of availability and cap performance under conditions that might not be reproducible in the laboratory. All porewater measurements herein were measured in situ (i.e., in sediments whether field or lab) and require no porewater separation from the sediments prior to analysis.

1.2 TECHNOLOGY DESCRIPTION

In situ SPME is a passive sampling approach for measuring hydrophobic organic contaminants in porewater and involves the insertion of a polymer sorbent into the sediments for a specific period of time and measuring the contaminants sorbed to the polymer. The contaminant concentration on the polymer is directly proportional to the dissolved contaminant concentration in the porewater. The technology demonstrated here uses PDMS as a polymer sorbent as a thin coating on a glass core but is essentially equivalent to SPME using other sorbents such as polyoxymethylene (POM) and polyethylene (PE). The primary advantages of PDMS are cylindrical geometry (for ease of insertion into sediments), somewhat lower sorption capacity than POM and PE (which aids the rapid achievement of equilibrium), and commercial availability in a variety of sizes and polymer coating thicknesses. Simple approaches to shield the PDMS fiber and to segment and analyze the fiber were developed as part of the demonstration. Conventional analyses are employed that require no special processing or analytical techniques so any lab that can conduct polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyl (PCB) analyses can support the technology.

1.3 DEMONSTRATION RESULTS

Demonstration of the technology was conducted in several phases:

- *Laboratory demonstration of detection limits, accuracy, and reproducibility of PDMS-SPME for measurement of water concentrations*. The technology could measure hydrophobic organic contaminants (HOC) with accuracy and reproducibility equivalent to conventional techniques but with very low detection limits

- *Evaluation of kinetics of uptake of PDMS-SPME for water and porewater concentrations.* Models capable of describing PDMS-SPME uptake kinetics were developed and methods for field evaluation demonstrated.

- *Laboratory demonstration of the relationship between measured porewater concentrations and bioaccumulation in various benthic organisms*. The demonstration showed that the potential for bioaccumulation was approximately given by the product of the octanol-water partition coefficient, K_{ow}, of the compound and the measured porewater concentration.

- *Laboratory demonstration of cap performance assessment using measured porewater concentration profiles.* The demonstration showed that porewater concentrations in the biologically active zone of a sediment cap also indicated bioaccumulation in benthic organisms populating a cap. A cap that effectively reduced the porewater concentration to which benthic organisms were exposed was shown to be effective.

- *Field measurement of porewater concentration profiles in sediments*. The demonstration showed that vertical profiles in hydrophobic organic contaminants could be measured in situ, assisting in the evaluation of the mechanisms and rates of transport.

- *Field measurement of relationship between bioaccumulation in benthic organisms and measured porewater concentrations.* Field measurements of bioaccumulation in various benthic organisms and sediments were shown to correlate with measured porewater concentrations in the near surface sediments. Field measurements were complicated by the dynamics of uptake onto the sorbents, the dynamics of uptake in the organisms, and the presence of other stressors in the field.

1.4 IMPLEMENTATION ISSUES

The primary difficulties associated with the in situ PDMS measurement of porewater concentration is the time and cost of deployment and the complexities of interpretation of the results. Deployment may involve divers for both placement and retrieval (although sediment can also be retrieved by conventional means, e.g., coring, for laboratory testing) and long delay times between placement and retrieval (7-28 days). Expert knowledge is required to appropriately balance considerations such as achievable detection limit and rate of attainment of equilibrium. For more hydrophobic compounds, methods must be employed to assess attainment of equilibrium. The attainment of equilibrium is primarily controlled by site-specific processes and sediment properties. Failure to accurately assess polymer uptake kinetics and the degree of equilibration with a given exposure can significantly limit the applicability of the results.

2.0 INTRODUCTION

2.1 BACKGROUND

Soils and sediments acting as natural sorbents are the ultimate sink for many HOC. In stable sediment environments, however, only contaminants in the porewater, the interstitial space between sediment grains, will migrate through the sediment and be released to the overlying water. Even in sediments subject to resuspension, the partitioning of the contaminants from the solid to the water is critical to the fate of the contaminant. Moreover, much recent research suggests that what partitions to the porewater is most available and correlates well with the effects on benthic and higher organisms. Thus knowledge of the partitioning between phases or the amount of contaminant in the porewater is an important indicator of risk in the sediment environment.

The equilibrium distribution of HOC between sediments, water, and benthos has often been considered to be a linear and reversible partitioning process, which suggests that all of the sorbed contaminants are available to partitioning to porewater and biological receptors in the environment. This is the basis for the U.S. Environmental Protection Agency (USEPA) Equilibrium Partitioning Sediment Benchmarks (ESB) described in Hansen et al., 2003. Common adsorption/desorption behavior such as nonlinear isotherms, desorption hysteresis, and aging has been linked to reductions in the rate and extent of availability to organisms and is not described by the conventional linear partitioning model that is the basis for ESBs. The sequestration of contaminants into organic matter in sediments and soils has been ascribed to the effects of different soil or sediment organic matrices changing the rate or extent of contaminant sorption. The net effect, however, is a reduction in the rate or extent to which a contaminant may desorb into the adjacent porewater and accumulate in biota. Thus the risks of sediments are often overpredicted by conventional ESBs and the actual partitioning between sediment and water must be measured or predicted.

Because of the difficulty in predicting the actual partitioning between sediments and water, an alternative approach is to directly measure the porewater concentration. Studies by Lu et al. (2003, 2004, 2006) provided strong evidence that steady state bioaccumulation of a wide range of PAHs in benthic organisms is related to porewater concentration. Route of uptake and organism assimilation efficiency appears to influence only the dynamics of uptake and not the steady state accumulation (Lu et al., 2004). Evidence that porewater concentration is a reliable predictor of benthic bioaccumulation of hydrophobic organic compounds has also been provided by Kraaij et al. (2003) and Vinturella et al. (2004). In addition, Zimmerman et al. (2004) has shown reductions in bioaccumulation in clams due to the addition of activated carbon to sediments in approximate proportion to the reduction in porewater concentrations.

Despite these results, porewater concentrations are not routinely employed for the evaluation or assessment of bioavailability. Measurement of porewater concentrations by conventional methods are fraught with difficulties, including an inability to detect low concentrations in small sample volumes, geochemical changes in sediments upon collection and processing, and the difficulty of separating colloidally bound and truly dissolved contaminants from porewaters (Carr and Nipper, 2003). These effects complicate the analysis of porewater concentrations even in carefully controlled laboratory studies such as those conducted by Lu et al. (2003, 2004) and

make practical routine determination of porewater concentrations by conventional methods exceedingly difficult. Hawthorne et al. (2005) demonstrated an approach for the measurement of porewater concentration requiring only a small water volume under controlled laboratory conditions as long as the colloidal particles and associated contaminants could be separated from the sample. This method employs PDMS to extract and concentrate the sample (ex situ, i.e., after porewater separation) prior to analysis.

The goal of the project is to demonstrate that the porewater concentration can be measured with high resolution and accuracy without a priori separation of the porewater from sediments. The particular approach taken herein is to employ polydimethylsiloxane coated glass fibers to measure porewater concentration and porewater concentration profiles in sediments via an in situ (i.e., in whole sediments) SPME technique. The use of SPME has also been employed in laboratory evaluations of porewater concentrations in whole sediments, including by Mayer et al. (2000), Conder et al. (2003), Hawthorne et al. (2005), The focus herein is primarily to evaluate the applicability of the approach to in-sediment (i.e., in situ) conditions, particularly in the field. The testing evaluated the ability of SPME using a PDMS sorbent phase to provide direct measurements of mobile phase concentrations (i.e., porewater concentrations) and indicate the bioavailability of the contaminants as measured by bioaccumulation in various organisms. In so doing, the work seeks to strengthen the confidence and range of conditions under which porewater concentration of HOCs can be used as an indicator of the bioavailable fraction of contaminants as well as provide a tool capable of routine measurement of porewater concentrations.

2.2 OBJECTIVES OF THE DEMONSTRATION

The specific objectives of the project are listed below.

- Laboratory demonstration of detection limits and accuracy of PDMS-SPME for measurement of water and porewater concentrations
- Laboratory demonstration of kinetics of uptake of PDMS-SPME for water and porewater concentrations
- Laboratory demonstration of the relationship between measured porewater concentrations and bioaccumulation in selected benthic organisms
- Laboratory demonstration of cap performance assessment using measured porewater concentration profiles
- Field measurement of porewater concentration profiles in sediments
- Field measurement of relationship between bioaccumulation in benthic organisms and measured porewater concentrations.

2.3 REGULATORY DRIVERS

Screening levels and cleanup standards at contaminated sediment sites are generally based on bulk solid concentrations either on the basis of statistical inferences of effects (e.g., Long et al., 1995) or from water toxicity and the assumption of linear, reversible partitioning (Hansen et al.,

2003). The assumption of linear, reversible partitioning as used in sediment equilibrium partitioning benchmarks does not account for the reduced availability of contaminants sorbed to desorption-resistant phases and will generally lead to overly conservative estimates of levels of concern or cleanup levels. Statistical inferences of effects are based on data from a number of sites but do not take into account site-specific characteristics and may be either overly conservative or not conservative based on contaminant availability at the site. Appropriate and cost-effective prioritization of sites and remedial planning is dependent on the definition of appropriate cleanup levels that are neither overly conservative or lack any conservatism.

Site-specific bioassays could be used to help assess appropriate levels for a particular site, but chemical measures can generally be implemented with greater density and sensitivity. It is toward providing such a tool that the technology demonstrated herein is directed. The goal is demonstration of a tool that can provide an assessment of the bioavailable contaminants at a particular site and thus provide a tool that can help set cleanup levels that are neither overly conservative nor lead to unacceptable exposure and risks at a site.

In particular, the demonstration will evaluate whether in situ porewater measurements of chemical concentration by passive sampling with polymer sorbents can predict the outcome of bioaccumulation assays and therefore replace or complement those tests. Moreover, the demonstration will evaluate whether in situ porewater measurements of chemical concentration can provide a better indication of the performance of a sediment cap, including both chemical containment and reduction in bioaccumulation in cap-dwelling organisms. Conventional chemical measures such as bulk solids concentration are largely irrelevant to indications of cap performance since many sediment caps contain non-sorbing media that will generally show low bulk solid concentrations regardless of the contaminant transport rate through the cap.

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3.0 TECHNOLOGY

3.1 TECHNOLOGY DESCRIPTION

Solid-phase microextraction for hydrophobic organic contaminants involves the insertion of a polymer sorbent into the sediments, withdrawal after a period of time, preferably after achieving equilibrium or a known fraction of equilibrium, and measuring the contaminants sorbed to the polymer. Equilibrium is achievement of the steady state concentration in the sorbent-sediment-porewater system. The sorbent will initially deplete the porewater of an HOC and then the sediment will release more contaminant to restore equilibrium between all phases. The achievement of equilibrium allows the estimation of the equilibrium porewater concentration (the concentration in the porewater before introduction of the polymer sorbent into the matrix) with the ratio of the concentration in the sorbent, here as the concentration in a polymer-coated fiber, C_f, and a polymer sorbent-water partition coefficient, K_{fw}

$$C_w = \frac{C_f}{K_{fw}}$$

Non-equilibrium exposures must be corrected for the kinetics of uptake. In solid-phase microextraction, the amount sorbed to the polymer does not significantly modify equilibrium in the soil-water system due to the small mass absorbed. Despite this there is some depletion in the immediate vicinity of the polymer during a transient uptake period, and the rate of equilibration of the polymer sorbent is generally associated with transport processes in the sediment and not within the polymer. Polymer sorbents that are used typically include POM, PE, and PDMS. POM and PE are normally used in thin (25-100 µm) bulk layers while PDMS is coated in a thin layer (10-30 µm) on glass fibers. PE as a passive sampling tool has been developed by P. Gschwend (Gschwend, et al., 2011; Gschwend, 2010), while POM has been employed by a variety of researchers including R. Luthy (Ah, et. al, 2005; Jansen et. al, 2011), and S. Hawthorne (Gschwend, et. al, 2011). The term SPME has been most often applied to the use of PDMS but POM and PE are essentially equivalent extraction processes. PDMS is used here in that it is available as a thin coating (10-30 µm) of glass capillaries of various sizes (110-1000 µm). The capillary can be of arbitrary length and can be coiled in long, continuous lengths. The cylindrical shape is convenient for insertion into sediments, and the availability of thin layers with modest sorption capacity (compared to the slightly more sorbing POM and PE) speeds equilibration kinetics. The length can be segmented to achieve the desired vertical resolution or to provide sufficient sorbent volume to meet detection limit requirements. Costs of fabricating the PDMS-coated glass fibers range from approximately $1/m (for commercial available optical fibers) to $10-25/m (for specially fabricated coated fibers). Only 1-5 cm of this fiber is necessary for detection of HOC at sub-nanograms per liter (ng/L) concentrations, and therefore the cost of the PDMS is negligible compared to the chemical analysis. In addition, the analysis method demonstrated herein generally requires no special extraction or sample processing procedures, and the analysis cost is equal to or less than conventional water sample analysis costs.

For laboratory applications, the fiber can be placed directly into sediments. For smaller fiber sizes (<500 µm) they are easier to locate if inserted through a septum and then placed in the

sediments. For field applications, the fiber should be placed in a holder to protect from breakage. In coarse sediments (gravel, rocky, or filled with debris), the holder should be shielded by an external sheath. The holder used includes a 1-2 mm slot in a stainless steel rod. The PDMS fiber is fixed at each end within this slot using contaminant-free silicon (e.g., aquarium silicon). The holder can then be covered with a protective sheath (cylindrical tubing) with holes to allow water exchange (Figure 1a) or left unshielded for short lengths (up to 30 cm) in soft sediments (Figure 1b).

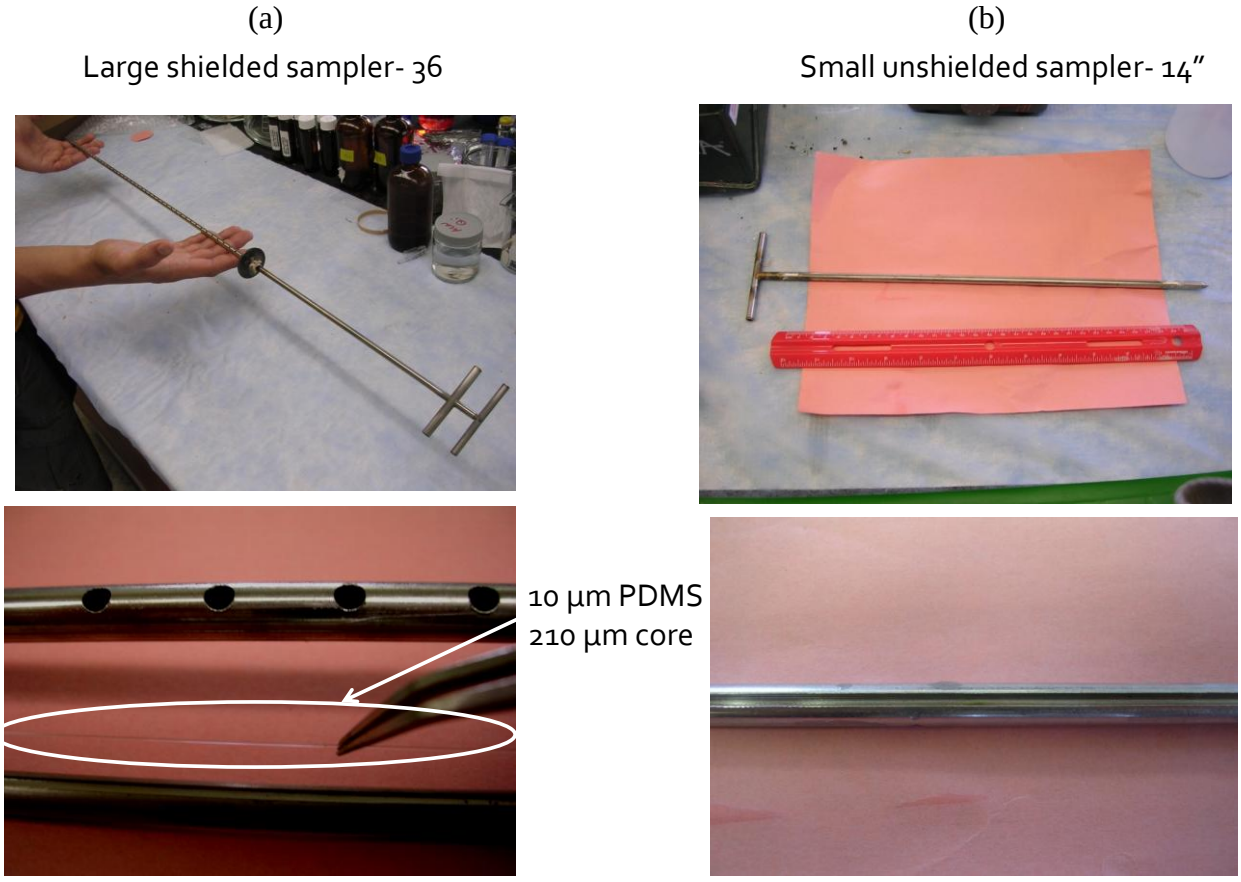

Figure 1. Shielded and unshielded holders for SPME fiber.
(a) Holder with shielding, a modified Henry's type sampler and (b) Unshielded holder

3.2 DEMONSTRATION RESULTS

The general results of the demonstration relative to each of the objectives are listed below. Detailed discussion of the results can be found in Section 6.

3.2.1 Laboratory Demonstration of Detection Limits and Accuracy of PDMS-SPME for Measurement of Water and Porewater Concentrations

The demonstration led to generalization of existing polymer-water partition coefficients and showed that the technology could measure HOC with accuracy and reproducibility equivalent to conventional techniques but with much lower detection limits.

3.2.2 Laboratory Demonstration of Kinetics of Uptake of PDMS-SPME for Water and Porewater Concentrations

The demonstration led to the development of models capable of describing PDMS-SPME uptake kinetics and to practical methods to evaluate uptake kinetics in field situations, including the simultaneous use of fibers of different sizes to infer kinetics as well as the use of performance reference compounds.

3.2.3 Laboratory Demonstration of the Relationship between Measured Porewater Concentrations and Bioaccumulation in Selected Benthic Organisms

The demonstration showed that the potential for bioaccumulation was proportional to measured porewater concentration for a variety of organisms and sediments. The bioconcentration factor between porewater concentration and organism bioaccumulation was approximately given by the octanol-water partition coefficient, K_{ow}, of the bioaccumulating compound.

3.2.4 Laboratory Demonstration of Cap Performance Assessment Using Measured Porewater Concentration Profiles

The demonstration showed that porewater concentrations in the biologically active zone of a sediment cap also indicated bioaccumulation in benthic organisms populating a cap. The *dilution* of bulk sediment concentration by inert nonsorbing sand was not effective at decreasing bioaccumulation in exposed organisms. The *separation* of benthic organisms from contaminated sediments by an inert nonsorbing sand layer, however, was effective as long as the depth of active bioturbation was less than the thickness of the sand layer.

3.2.5 Field Measurement of Porewater Concentration Profiles in Sediments

The demonstration showed that vertical profiles in hydrophobic organic contaminants could be measured in situ, assisting in the evaluation of the mechanisms and rates of transport. In general, multiple time series measurements are required to define contaminant dynamics.

3.2.6 Field Measurement of Relationship between Bioaccumulation in Benthic Organisms and Measured Porewater Concentrations

Field measurements of bioaccumulation in various benthic organisms and sediments were shown to correlate with measured porewater concentrations in the near surface sediments. Field measurements were complicated by the dynamics of uptake onto the sorbents, the dynamics of uptake in the organisms, and the presence of other stressors in the field. Measured bioaccumulation was generally 20-50% of that predicted by $K_{ow}C_{pw}$.

3.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The work described above has shown that passive sampling via PDMS has an excellent ability to describe the mobile and available fraction of hydrophobic organic contaminants such as PAHs and PCBs. The universal regulatory standard—solid phase concentration—has limited ability to define the risks and bioaccumulation potential from contaminated sediments because it cannot differentiate between bioavailable and nonbioavailable contaminants. Normalization of bulk

solid phase concentration with organic carbon can provide, in some instances, an improved ability to determine bioavailability and bioaccumulation potential for HOC. Theoretically, normalization of bulk solid phase concentration with organic carbon content should indicate bioavailability as long as the sediment and adjacent porewaters are in equilibrium and if the partitioning between these phases is linear and reversible. Unfortunately, this is rarely the case.

Passive sampling with PDMS to estimate porewater concentrations provides a more direct indication of the available fraction of contaminants. The truly dissolved porewater concentration that is measured by PDMS, appears to be directly related to bioaccumulation potential with a bio concentration factor given by approximately the octanol-water partition coefficient. This was demonstrated to be true for deposit feeders, even when the route of uptake is via sediment ingestion. In such cases, the porewater is not the source of contaminants to the organism but appears to be a good indicator because the sediment, organism, and adjacent porewater are in a state of quasi-equilibrium. Measurement of the porewater concentration provides a direct indicator of what can partition to other phases (either water or organism) from the solid phase. Ingestion of the sediment by a benthic organism may speed their approach to this equilibrium but does not change what can ultimately accumulate in the organism.

POM and PE could also be used as passive samplers with similar advantages and with similar results. The intrinsic kinetics of PDMS are somewhat faster than either POM or PE as a result of a lower sorbent-water partition coefficient (and therefore less depletion of the porewater adjacent to the sampler). PDMS can also be fabricated in a wide range of sizes on cylindrical glass cores, providing a convenient geometry for insertion directly into sediment for in situ measurement in the field or laboratory and allowing tailoring of detection limits (related to sorbent volume) and uptake kinetics (related to sorbent volume and surface area) to a particular situation. PDMS as well as POM and PE can also be used in the laboratory in tumbled sediments. In this scenario, the external mass transfer resistances are reduced and there are no significant advantages of PDMS over POM or PE.

Other means of porewater concentration measurement are generally unable to directly measure dissolved concentrations. Colloidal matter will typically be suspended in the porewaters and artificially increase the effective porewater concentration. Filtration and flocculation can reduce but not eliminate the effects of colloidal matter, the effect of which is more important for more hydrophobic compounds. Centrifugation is a means of generating large amounts of porewater relatively rapidly but holds the potential to artificially increase suspended HOC concentration by increasing the suspended colloidal and particulate matter.

A significant advantage of the in situ deployment of the passive sampler as developed herein is the ability to determine vertical profiles in concentration. This can be especially beneficial to evaluate the performance of sediment caps. A typical sediment cap with a nonsorbing media such as sand will not exhibit evidence of contaminant migration through bulk solid measurements. Porewater concentration profiles, however, will indicate whether contaminant migration is occurring, and by monitoring over time, the rate of migration can be estimated.

The primary limitation of passive sampling with PDMS or other sorbent is the difficulty of achieving equilibrium or accurately estimating the approach to equilibrium. Good results are

reported herein using both performance reference compounds or by using sorbents with two different characteristic dimensions (and therefore two different intrinsic kinetic behaviors). The ratio of the concentration between the two different size sorbents provides an indication of kinetics in any particular situation. It should be emphasized that the kinetics of uptake are controlled by the rate of equilibration of the surrounding media after local depletion of the porewater by the sorbent. In essentially all cases, the exterior mass transfer resistances control kinetics of uptake. Tidal or rapidly upwelling systems or systems with a large reservoir of contaminants (e.g., high organic carbon) will achieve equilibrium more rapidly than stagnant systems with a small contaminant reservoir. The fact that external processes control uptake means that passive sampling with PDMS, POM, or PE should include some means of estimating site-specific uptake kinetics, particular for highly hydrophobic PCBs.

Placement of the passive sampler may also be difficult in deep waters or in water where divers are not easily employed. In such cases conventional coring may be used to collect sediment samples and the passive sampler can be placed in the sediment in the laboratory. The only drawback of this approach is that it would not capture the effect of site-specific conditions that influence the in situ porewater concentrations. This could include rapid hyporheic exchange in the near surface sediments or rapid groundwater upwelling.

Another current limitation of the approach is that neither laboratories nor consulting firms have established the ability to conduct passive sampling successfully. The methods as developed herein, however, are transferrable and easily employed by laboratories or consulting firms should they wish to do so. We have begun work with additional laboratories and contaminants (e.g., Columbia Laboratories and dioxin contaminants) to demonstrate this capability.

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4.0 PERFORMANCE OBJECTIVES

The primary objectives of the demonstration program were to show that PDMS solid phase microextraction could be used in situ (in lab or field) for:

- The determination of mobile and available contaminants in sediments
- The assessment of bioaccumulation potential of hydrophobic contaminants in benthic organisms
- The assessment of vertical chemical profiles in surficial sediments and sediment caps.

A summary of the quantitative and qualitative performance objectives are shown in Table 1.

Table 1. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
High analytical accuracy and reproducibility under laboratory conditions	Measurement of fiber-water partition coefficients and replicate variability	% error of K_{fw} <20% coefficient of variation (COV) in replicates <20% Linearity of calibration curve r^2>0.9	Demonstrated for all PAH_{16} compounds except naphthalene due to weak sorption and subsequent loss of naphthalene. Linearity generally greater than 0.99 for PAHs except most hydrophobic due to difficulty in maintaining aqueous standards for highly hydrophobic compounds (also affects PCBs).
Low detection limits	Controlled measurement of detection limits	Detection limits of PAHs at least 10 times lower than comparison surface water quality criteria	Demonstrated for all PAH compounds except naphthalene due to weak sorption of naphthalene. Use of additional sorbent can improve naphthalene results. Demonstrated for PCBs based on literature and extrapolation of measured sorbent-water partition coefficients.
Estimation of PDMS uptake kinetics	Evaluate methods for kinetics estimation	Development of analytical model and methodology to fit to kinetics data from different approaches	External mass transfer resistance model transport model verified and applied under field and lab conditions to time series data, two different size sorbents data and performance reference compounds data.
Indicate cap performance	Evaluate profiles in sediments in lab and field	Demonstrate ability to determine porewater profiles with vertical resolution ~1 cm	Demonstrated in laboratory and field. Used to demonstrate cap performance in lab and field. Demonstrated substantial improvement over bulk solids measures.
Predict bioaccumulation potential in laboratory in situ tests	Simultaneous measurement of bioaccumulation and porewater concentration	Correlate PDMS and bioaccumulation with r^2>0.7. Measure biota-water concentration factor with precision of factor of 2	Demonstrated with variety of organisms and sediments. Measured steady state biota-water concentration factor 1.32 (±0.82)*K_{ow} with PAHs and PCBs, marine and freshwater systems, and a variety of deposit-feeding benthic organisms.

Table 1. Performance objectives (continued).

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives (continued)			
Predict bioaccumulation in field in situ tests	Simultaneous PDMS and bioaccumulation measurement in field	Correlate PDMS uptake and measured porewater concentration with bioaccumulation with r^2>0.7	Correlation r^2 typically >0.8. Biota-water accumulation factor more scattered than with laboratory tests and often lower, 0.2-0.5 K_{ow}, presumably due to influences of site stressors not found in laboratory tests.
Qualitative Performance Objectives			
Ease of application to laboratory in situ use	Evaluate ability to place and retrieve sorbent fibers from laboratory microcosms	Recovery and processing of fibers during laboratory experiments	Demonstrated. No significant losses, fiber integrity maintained during experiments, no losses due to organisms. Low molecular weight, volatile HOC such as naphthalene do exhibit significant losses with time.
Ease of field use	Evaluate ability to deploy and retrieve samplers in the field	Successful deployment and retrieval with divers	Demonstrated.
	Evaluate ability to process sorbent in the field and ship stabilized samples back to lab	Successful processing without sample loss	Demonstrated—Shipping of unprocessed sorbent success but substantial losses for low molecular weight compounds (e.g., naphthalene). Processing before shipment using prefilled autosampling vials eases field use and ensures sample stability.
Ease of analysis	Evaluate ability to directly analyze solvent in stabilized samples returned to lab	Analyses without further processing	Demonstrated—Some samples (Hunters Point) showed evidence of desirability of additional processing (sample cleanup). Desirable to remove fiber from sample vials for thicker 1060/1000 fibers prior to autosampling to avoid interference with sampling needle.

5.0 SITE DESCRIPTION

The demonstration employed sediments or conducted field studies at a variety of sites, as shown below.

Sediments (laboratory experiments/demonstrations)

- Anacostia River, Washington, DC
- Hunter's Point, San Francisco, CA
- New Bedford Harbor, MA
- Elizabeth River, VA

Field locations (in situ field deployments of the technology)

- Anacostia River, Washington, DC
- Hunter's Point, San Francisco, CA
- San Diego Harbor, San Diego, CA (in cooperation with ER-1550)
- Pensacola Harbor, Pensacola, FL (in cooperation with ER-1550)

The Anacostia River is a freshwater tidal estuary bordering the southern and eastern boundary of the District of Columbia.

The New Bedford Harbor – batch one (estuarine sediment). Sediment from the subtidal zone of New Bedford Harbor, New Bedford, MA, was collected in the spring of 2001. The total PCB concentration was 124 mg/kg. The concentration of 16 USEPA priority pollutant PAHs was 27 mg/kg.

New Bedford Harbor – batch two (estuarine sediment). Sediment from the subtidal zone of New Bedford Harbor, New Bedford, MA, was collected in the fall of 2008. The total PCB concentration was 137 mg/kg. The concentration of 16 USEPA priority pollutant PAHs was 17 mg/kg. The total organic carbon (TOC) content was 4.1%.

Elizabeth River (estuarine sediment). Sediment from the subtidal zone of the Elizabeth River was collected in the spring of 2003. The concentration of 16 USEPA priority pollutant PAHs was 27 mg/kg. The TOC was 3.4 %. The sediment was predominantly sandy.

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6.0 TEST DESIGN AND RESULTS

6.1 TREATABILITY OR LABORATORY STUDY RESULTS

6.1.1 Laboratory Demonstration of Detection Limits, Accuracy, and Kinetics of PDMS-SPME for Measurement of Water Concentrations

Laboratory studies have achieved their desired goal of defining the basic parameters of routine field deployment of SPME as a tool for the assessment of water concentration to indicate in situ contaminant migration processes and bioavailability of PAH and PCB contaminants. In the current study, PDMS-coated fibers from two different sources and three different sizes were employed. Table 2 summarizes the fibers used in these studies.

Chemical analysis involved exposure of the fiber to a contaminant in water or sediments and then extraction into a solvent which is subsequently analyzed by chromatography. Studies of various extraction methods demonstrated that desorption into solvents suitable for subsequent chemical analysis (into acetonitrile for high-performance liquid chromatography [HPLC] analysis or hexane for gas chromatography [GC] analysis) is rapid and complete. In this work, PAHs were analyzed by Waters 2795 HPLC with fluorescent detection (USEPA Method 8310) and PCBs were analyzed by Hewlett Packard 6890 GC with electron capture detection (Method 8082).

Table 2. PDMS-coated fibers used in this demonstration (dimensions and source).
Polymicro Industries (Phoenix, AZ) and Fiberguide (Sterling, NJ)

Fiber Designation	Inside dia. µm	Outside dia. µm	PDMS Volume (V) µL/m	PDMS L=V/Area (A) µm	Source
170/110	110	170	24.7	13.2	Polymicro
230/210	210	230	9.6	6.9	Fiberguide
1060/1000	1000	1060	29.2	97.1	Polymicro

The ability to detect HOC with PDMS depends upon having an accurate estimate of the PDMS-coated fiber-water partition coefficient, K_{fw}, to relate the accumulated uptake on the fiber to a water concentration. No differences in fiber-water partition coefficient were noted among the three fibers used in this study despite their fabrication at different times from different manufacturers. The fiber-water partition coefficient should correlate with the hydrophobicity of the compound and thus can be correlated with K_{ow}. A potential source of error is uncertainty in the values of the K_{ow} with values from different sources often differing by a factor of 2 (0.3 log units). Thus the source of K_{ow} should be defined when developing a correlation. In the present study, fiber-water partition coefficients of PCBs and PAHs as measured by Mayer et al. (2000) were employed to correlate with a consistent set of K_{ow} values, Mackay et al. (1992) for PAHs and Hawker and Connell (1988) for PCBs. Mayer et al. (2000) employed K_{ow} values based only on PCB chlorine number and thus the correlation as given was inconsistent with the Hawker and Connell K_{ow} values. Since only two PAHs, phenanthrene and fluoranthene, were measured by Mayer et al. (2000), we measured PDMS-water partition coefficients of seven medium to high

molecular weight PAHs to supplement Mayer's data. The resulting correlation and confidence intervals, applicable to high molecular weight PAHs and PCBs, are given by:

$$LogK_{fw} = 1.06(\pm 0.058)LogK_{ow} - 1.16(\pm 0.35) \quad R^2 = 0.94 \quad HPAHs - PCBs \quad (2.1)$$

This correlation included compounds with Log K_{ow} up to 7.36 but only a single compound with a K_{ow}<5. Experimental measurements of PDMS-water partition coefficients for low to medium molecular weight PAHs were measured and combined with the seven PAHs identified above to develop an alternative correlation for PAHs only

$$LogK_{fw} = 0.839(\pm 0.048)LogK_{ow} + 0.117(\pm 0.21) \quad R^2 = 0.97 \quad PAHs \quad (2.2)$$

This correlation gives similar values to Equation (2.1) for the K_{ow} range of mid to high molecular weight PAHs but is more consistent with observations for low K_{ow} PAHs. Table 3 compares the observed PAH PDMS-water partition coefficients with that predicted by both relationships. Note that other factors such as temperature and salinity may influence fiber-water partition coefficients but measurements showed no significant trend with either, suggesting that the effects of these factors are within the accuracy of the correlations (approximately $\pm$ a factor of two based upon the uncertainty in values of K_{ow}).

Table 3. Comparison of measured and observed PDMS-coated fiber-water partition coefficients (in log units).

PAHs	Log K_{ow}	Measured	Predicted		Predicted	
		Log K_{fw}	Log K_{fw}[a]	% error	Log K_{fw}[b]	% error
Naphthalene	3.37	1.89	2.94	55.8	3.06	62.1
Dibenzofuran	4.30	3.60	3.72	3.85	3.77	4.7
2-Methylnaphthalene	3.90	3.41	3.39	-0.6	3.47	1.6
Fluorene	4.18	3.63	3.62	-0.2	3.68	1.3
Acenaphthene	3.92	3.56	3.41	-4.3	3.48	-2.2
Phenanthrene	4.57	4.04	3.95	-2.2	3.97	-1.7
Anthracene	4.54	4.03	3.93	-2.6	3.95	-2.0
Fluoranthene	5.22	4.48	4.50	0.4	4.46	-0.3
Pyrene	5.18	4.55	4.46	-1.9	4.43	-2.5
Chrysene	5.86	4.72	5.03	6.6	4.95	4.9
Benzo[a]anthracene	5.91	4.93	5.08	3.0	4.99	1.2
Benzo[b]fluoranthene	5.80	5.08	4.98	-1.9	4.90	-3.5
Benzo[k]fluoranthene	6.00	5.08	5.15	1.4	5.06	-0.5
Benzo[a]pyrene	6.04	5.09	5.18	1.9	5.09	-0.1
Dibenz[a,h]anthracene	6.75	5.15	5.78	12.2	5.62	9.2
Benzo[g,h,i]perylene+indenopyrene	6.50	5.21	5.57	6.9	5.43	4.3

[a]predicted by Equation (2.2)
[b]predicted by Equation (2.1)
Values shown in red are subject to large uncertainty due to coefficients of variation >20% in calibration measurements.

POM and PE sorbents behave similarly to PDMS but are slightly more sorbing. As reported in Gschwend et al. (2011), the polymer water partition coefficient for PE is given by log $K_{PE\text{-}water}$ (L_{water}/kg_{PE})=1.00(±0.05)*log K_{ow} – 0.287(±0.335) (r^2=0.96) and log $K_{POM\text{-}water}$=0.791*log K_{ow} + 1.018 (r^2=0.947) for POM. The estimated partition coefficients are typically two to five times

larger for POM and PE than PDMS. This gives rise to lower detection limits for a given volume of sorbent but longer uptake kinetics, as is discussed in Section 7.

The hydrophobicity of a compound largely defines detection limits, with the more hydrophobic, high molecular weight compounds being detected more sensitively. Low molecular weight PAHs are also difficult to measure due to volatility from both solutions and from PDMS fibers. A combination of these factors leads to relatively high uncertainty in the measurement of naphthalene. High molecular weight compound standards are also difficult to prepare and maintain, leading to relatively high uncertainty in measurements of these compounds. In both cases, the correlation of fiber-water partition coefficient with octanol-water partition coefficient is expected to more accurately indicate partitioning to the PDMS than the measurements.

Detection limits are summarized in Table 4 for PDMS-coated fibers for selected PAHs using USEPA Method 8310 and fluorescent detection on a Waters 2795 HPLC. The detection limits are based on 1 cm of a fiber coated with 6.9 µL/m (10 µm layer of PDMS on 210 µm glass core). The fiber sorption and the detection limits are proportional to PDMS volume. Thus the detection limit using 10 cm of fiber is 10 times lower and the detection limit using 1 cm of the 30 µm thick PDMS layer on a 1 mm core fiber is 14 times lower than the listed value. In addition, Table 4 shows the coefficient of variation at a specific low concentration and the correlation coefficient indicating linearity of the fiber response to concentration as well as a comparison of the fiber detection limit to that by direct injection. The concentration level selected for the coefficient of variation measurements was chosen to be a concentration well below surface water quality criteria (National Recommended Water Quality Criteria) that is often used as a comparison for surface water and porewater concentration measurements. The coefficient of variation provides an indication of the accuracy of the concentration measurements.

Table 4. Comparison of detection limits by direct water injection versus SPME with PDMS and coefficient of variation and correlation coefficient for SPME.
Analysis by HPLC with USEPA 8310 with fluorescent detection

PAHs	Log K_{ow}	Surface Water Quality Criteria µg/L[a]	Water MDL* µg/L Direct Injection	SPME MDL µg/L[b]	Low Conc. µg/L	COV % Lowest Conc.	Linearity SPME r^2
Naphthalene	3.37	9.58	0.07	0.3332	2.35	88.8	0.1547
Dibenzofuran	4.30		0.14	0.0123	1.64	10.0	0.985
2-Methylnaphthalene	3.90		0.19	0.0268	3.73	70.2	0.9817
Fluorene	4.18	3460	0.81	0.0697	0.503	5.6	0.9984
Acenaphthene	3.92	640	0.32	0.0315	0.526	14.1	0.9996
Phenanthrene	4.57		0.23	0.0076	0.362	1.3	0.9973
Anthracene	4.54	26400	0.222	0.0075	0.018	18.1	0.998
Fluoranthene	5.22	90	0.210	0.0025	0.101	9.9	0.9985
Pyrene	5.18	2590	0.209	0.0021	0.055	8.1	0.9987

*MDL = method detection limit

Table 4. Comparison of detection limits by direct water injection versus SPME with PDMS and coefficient of variation and correlation coefficient for SPME (continued).

Analysis by HPLC with USEPA 8310 with fluorescent detection

PAHs	Log K_{ow}	Surface Water Quality Criteria µg/L[a]	Water MDL µg/L Direct Injection	SPME MDL µg/L[b]	Low Conc. µg/L	COV % Lowest Conc.	Linearity SPME r^2
Chrysene	5.86	0.018	0.0698	0.00048	0.0012	19.1	0.9967
Benzo[a]anthracene	5.91	0.018	0.0266	0.00011	0.0048	3.9	0.9978
Benzo[b]fluoranthene	5.80	0.018	0.03650	0.00011	0.00089	11.6	0.9945
Benzo[k]fluoranthene	6.00	0.018	0.00650	0.00002	0.00039	8.0	0.9781
Benzo[a]pyrene	6.04	0.018	0.01830	0.00005	0.0021	5.8	0.9755
Dibenz[a,h]anthracene	6.75	0.018	0.02630	0.00007	0.009	5.5	0.9241
Benzo[g,h,i]perylene+indenopyrene	6.50	0.018	0.04540	0.00010	0.0234	7.0	0.9179

[a]USEPA's National Recommended Water Quality Criteria (NRWQC) are given for comparison to detection limits.
[b]PDMS volume for SPME is 0.069 µL (1 cm length of 230/210 fiber).

6.1.2 Evaluation of Kinetics of Uptake of PDMS-SPME for Water and Porewater Concentrations

The accurate measurement of water and porewater concentration depends upon the ability to achieve equilibrium uptake in the PDMS fiber. Equilibrium is relatively rapid in stirred water (hours to days) and can be easily established by measurement of a time sequence. In sediments, equilibrium can take far longer and may be more difficult to establish, particularly in the field, due to uncertain transport processes, heterogeneity, and time requirements.

Laboratory measurements of uptake kinetics can be accomplished directly by examining a time series of measurements in homogenized sediments. Figure 2 depicts the approach to steady state of several PAH and PCB compounds in static laboratory experiments with Anacostia River sediments.

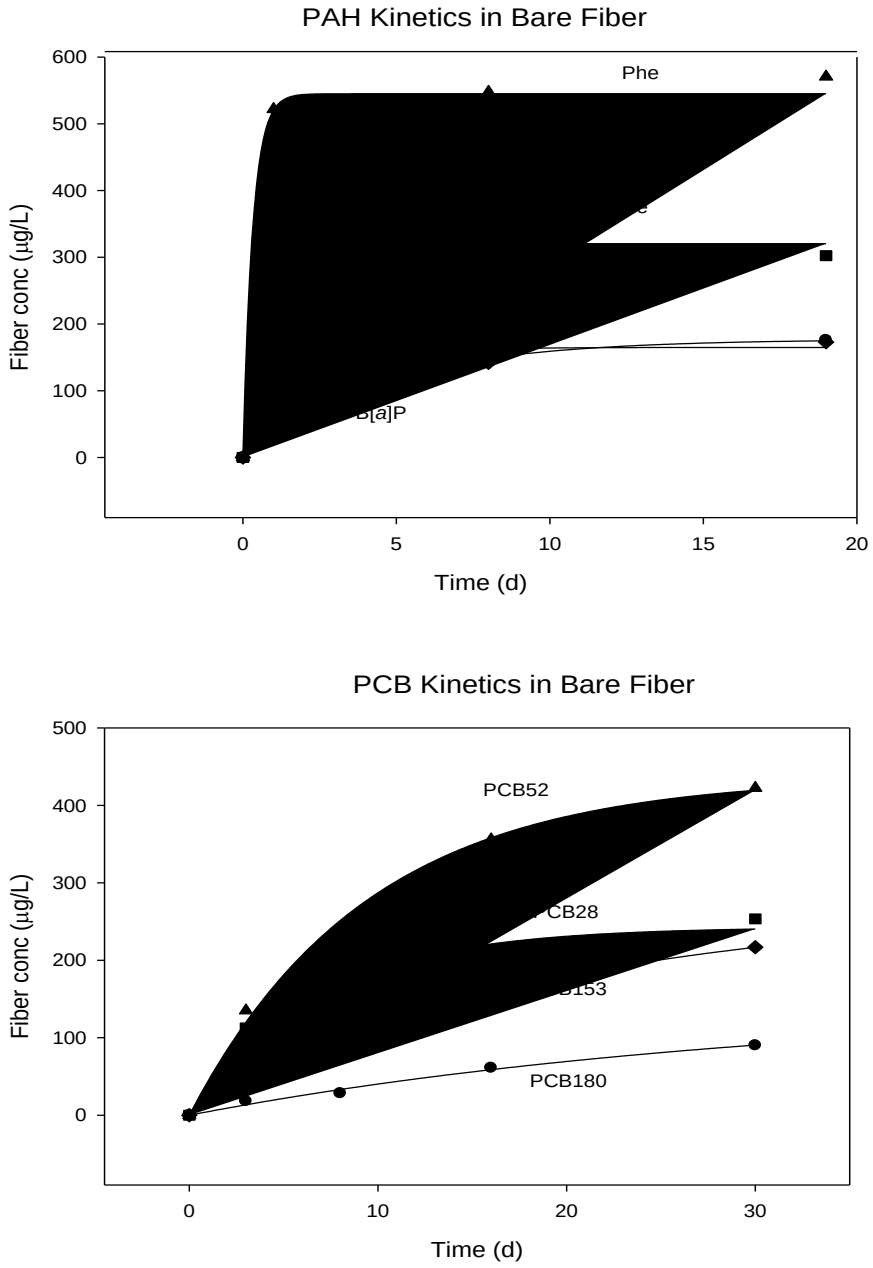

Figure 2. Kinetics of uptake of selected PAHs and PCBs from Anacostia River sediments onto 30 µm PDMS fiber on 110 µm glass core.

The kinetics of uptake are dependent upon the sediment and external transport processes and are difficult to define under field conditions. A practical means of estimating the kinetics or estimating equilibrium uptake by extrapolating from limited data is required for field evaluation. Huckins et al. (2002) described the use of impregnated performance reference compounds (PRC) during field deployments to estimate the extent of equilibrium attained within the device. The passive sampling device is initially equilibrated with an innocuous species that is not native to the sediment. The mass of the PRC is then measured after the deployment in an effort to

determine the extent of equilibrium. Difficulties with this approach include appropriate identification of a compound not present or present in very low concentrations that can be used as a PRC. In addition, the hydrophobicities (and therefore kinetics of uptake) of the PRCs should be similar to the compounds of interest and equilibrium must be achieved during preequilibration prior to use of the passive sampler. To measure porewater concentrations of compounds with a range of hydrophobicities, more than one PRC would typically be required to assess the variation of uptake with hydrophobicity. Finally sorption and desorption must be linear, first order, and reversible processes (generally valid at low concentrations but may not be valid at high concentrations or in the presence of strongly sorbing phases such as activated carbon). Radio labeled compounds (^{3}H or ^{14}C labeled compounds) are convenient for this purpose but may require a separate chemical analysis for the PRC. Deuterated compounds are not radioactive and are detectable by the same analytical techniques as the compounds of interest. Here, selected deuterated PAHs (d12-Fluoranthene, d12-chrysene, d12-benzo[b]fluoranthene and d14-dibenz[a]anthracene) were used as PRCs for other PAHs because they eluted from a HPLC chromatographic separation at different times than the parent compound and still allowed fluorescence detection. The fractional loss of these compounds provides an estimate of the fractional approach to steady state after a period of exposure. That is, a 75% reduction in the PRC corresponds to 75% of the achievement of steady state conditions for that compound. By fitting the fractional approach to steady state for these deuterated PAHs to a model of sorption onto the passive sampler (as described below), the fractional approach to steady state for any compound could be estimated.

Alternative approaches were also developed and demonstrated herein that could be used to complement performance reference compounds using

- Sorbent fibers of two different sizes (which exhibit different uptake kinetics)
- Sorbent fibers of the same size collected at two different times.

These measurements were fit to a model of sorbent uptake (described below) and used to estimate deviation from equilibrium. One advantage of the sorbent exposure for two different times or two different size fibers is that there is no additional analytical complexity. In addition, if the compounds of interest represent a wide range of hydrophobicities such as PAH_{16}, PAH_{34} or PCB congeners, data from all compounds over the entire range of hydrophobicities can be used to calibrate the model and yield higher accuracy estimates of the required nonequilibrium corrections. The approach can be applied to any passive sampling device using PDMS, POM, PE, or SPMDs, e.g.

The uptake kinetics model used to calibrate the data is described in Lampert (2010). Because the PDMS layer on the fiber is thin, the time to achieve steady state in passive sediment porewater sampling is normally controlled by external mass transfer resistances. A small zone around the polymer sorbent is depleted during the transient process, and the achievement of steady state is controlled by how fast this zone is replenished by the surrounding media. In a static system, this occurs via diffusion but it can occur much more rapidly by groundwater upwelling or downwelling, tidal pumping, bioturbation or hyporheic exchange; hence the requirement for site specific calibration of fiber uptake kinetics. An analysis of uptake into a thin film from a static

sediment (in which diffusion is the only operative process) suggests that the external mass transfer controls as long as the following relationship holds

$$\sigma \gg 1 \; where \; \sigma = \frac{t_{external}}{t_{internal}} = \frac{36 D_s K_{fw}^2}{RD} \qquad 2.3$$

where D_s is the diffusivity in the sorbent, K_{fw} is the sorbent polymer-water partition coefficient and RD is the product of the retardation factor and effective diffusivity in the surrounding sediment. Assuming the diffusivity of the sorbent is less than or equal to 1/36 of the diffusivity in the surround medium, the value of σ is approximately given by the ratio of $K_{fw}^2/\rho_b K_{sw}$ where ρ_b is the bulk density of the sediments and K_{sw} is the sediment water partition coefficient for the compound of interest. Since $K_{fw} \sim K_{sw}$ the value of σ is typically of the order of K_{fw} and much greater than 1 and therefore external mass transfer resistances dominate, at least under diffusion controlled conditions. This is also typically true of other polymer sorbents such as POM and PE.

Assuming external mass transfer resistances control uptake in a thin film (locally two dimensional) surrounding by a static sediment (diffusion controlled transport), the mass uptake into a sorbent fiber is given by

$$M(t) = K_{fw} C_{pw} L \left[1 - exp\left(\frac{RDt}{L^2 K_{fw}^2}\right) erfc\left(\frac{\sqrt{RDt}}{LK_{fw}}\right)\right] \text{ for uptake of contaminants}$$

$$M(t) = C_0 \left[exp\left(\frac{RDt}{L^2 K_{fw}^2}\right) erfc\left(\frac{\sqrt{RDt}}{LK_{fw}}\right)\right] \text{ for desorption of PRCs} \qquad (2.4)$$

where L is the surface volume to area ratio of the fiber (the thickness if a rectangular film) and the other parameters are as defined previously.

The bracketed term is the fractional approach to steady state or equilibrium for uptake of compounds. Key simplifications that lead to this solution are locally flat coordinates (which is a good approximation even for the small cylindrical fibers used herein due to the thin layer of PDMS) and control by external mass transfer resistances. When performance reference compounds are used, the bracketed term (fractional approach to equilibrium) is measured directly and a value of RD can be determined for each performance reference compound. When measures at two different times or two different size fibers are used, the ratio of the observed concentration determines a value of RD for each compound measured A correlation between these measured values of RD and a measure of hydrophobicity, K_{ow}, can then be developed to allow predictions of RD for any other compound K_{ow}. The retardation factor, R, is normally expected to be linearly dependent upon K_{ow}, while the effective diffusivity, D, is only a weak function of compound and therefore RD is normally expected to be linearly dependent upon K_{ow}. This is shown in Figure 3 in which measurements of RD estimated by two different size fibers and RD estimated from performance reference compounds are compared in a field experiment conducted in Chattanooga Creek, TN. This system represents a nontidal, low-permeability, and low-sorbing sediment system where uptake is expected to be very slow. The blue symbols represent estimated values of RD from the ratio of two different size fibers (230/210 and 1060/1000 in Table 2) while the red symbols indicate the values from four

deuterated performance reference compounds (d10-fluoranthene, d12-chrysene, d12-benzo[b]fluoranthene, and d14-dibenz[a]anthracene). Both give essentially the same result, shown by the linear fitted line in blue. Note that the thick versus thin fiber data provides estimates of RD for each compound present above detection limits, in this case, seven mid-to high-range PAH compounds. The performance reference compound approach provides estimates for only the four reference compounds. In this case RD is given by the best fit relationship $RD = 5x10^{-7}K_{ow}m^2/day$, which can be substituted into Equation (2.4) to estimate the fraction of steady state for any sorbent fiber dimension (L), compound (K_{fw}) and time of exposure (t). Note also that a linear relationship between RD and K_{ow} is not expected if particle-related transport such as bioturbation is the primary mechanism of contaminant transport in the zone of interest. In such cases, RD would be expected to be essentially independent of K_{ow}.

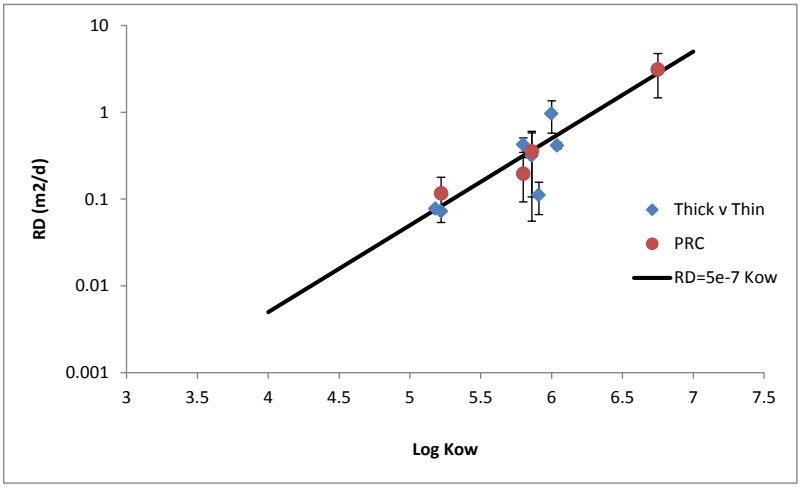

Figure 3. Experimentally determined external transport factor (RD) relationship to K_{ow} (with standard error) to estimate PDMS uptake kinetics (Chattanooga Creek, TN)

The kinetics of uptake of different compounds (pyrene and benzo[a]pyrene) on different size PDMS fibers (230/210 and 1060/1000) are illustrated by example in Figure 4. In this example, a 14-day exposure of the sorbent fiber in this relatively stagnant system led to uptake of approximately 41% and 74% of steady state for benzo[a]pyrene in the 1060/1000 and 230/210 fiber, respectively. The predictions of deviation from steady state are relatively insensitive to error in the estimated value of RD. If the ratio of RD to K_{ow} is in error by a factor of 2 there is a 22% error in the predicted fractional approach to steady state for benzo[a]pyrene (32 versus 41%) and even less for less hydrophobic compounds. The sensitivity to estimation error can be substantially greater far from steady state and therefore it is desirable to design sediment exposures to achieve as close to steady state as possible. The PDMS update rates are also compared to POM (76 µm thick, half thickness 38 µm) and PE (25 µm thick, half thickness of 12.7 µm) in Figure 4. The latter two materials tend to be slower due to their greater sorption capacity although that can be offset by the use of thin sorbent layers.

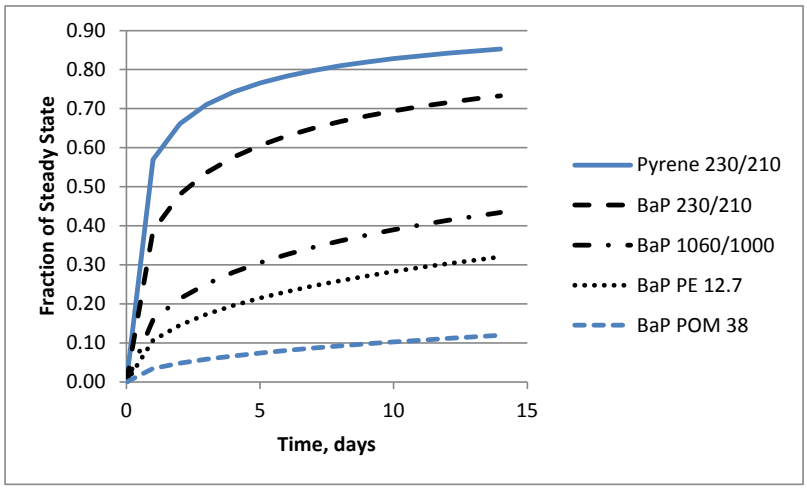

Figure 4. Approach to steady state of various polymer sorbents and contaminants (based on Figure 3).
(PDMS outer and inner thickness in μm; PE, POM half thickness in μm)

The model of transient uptake could also be used directly to estimate the fractional approach to equilibrium by using predictive estimates of retardation factor and effective diffusivity. In static environments in which active mixing processes are expected to be minimal, the diffusivity and retardation can be estimated by

$$D \sim \mathfrak{D}_w \phi^{4/3} \text{ granular media} \qquad D \sim \frac{\phi \mathfrak{D}_w}{1 - \ln \phi} \text{ consolidated sediment}$$
$$R \sim \phi + \rho_b K_{sw} \tag{2.5}$$

The estimate of effective diffusivity in granular media is from Millington and Quirk (1961) while that for consolidated sediment is from Boudreau (1997). In both cases, $\mathfrak{D}_w$ is the molecular diffusivity of the compound in water and ϕ is the void fraction or porosity of the sediment. In situations where linear reversible sorption is expected to apply, $K_{sw} \sim f_{oc} K_{oc}$ where f_{oc} is the fraction organic carbon and K_{oc} is the organic carbon-based partition coefficient (e.g., related to the octanol-water partition coefficient, K_{ow} in a relationship such as $Log\ K_{oc} = 0.903\ Log\ K_{ow} + 0.094$ [Baker et al., 1996]).

Active mixing of porewaters by tidal mixing, groundwater upwelling, bioturbation or hyporheic exchange will speed transport and can be incorporated into Equation (2.4) by considering an effective diffusion coefficient. In general, however, this is difficult to estimate a priori in field sediments and the use of performance reference compounds (e.g., deuterated compounds), time series measurements, or two different size sorbent fibers is recommended to fit uptake kinetics model to observations as outlined above.

6.1.3 Laboratory Demonstration of the Relationship between Measured Porewater Concentrations and Bioaccumulation in Selected Benthic Organisms

A series of laboratory experiments was conducted focused on comparison of fiber concentrations to measured bioaccumulation in freshwater and marine deposit feeding organisms. Bare fibers were exposed to PAH and/or PCB contaminated sediment during a 21- or 28-day bioaccumulation test using the selected organisms. The common deposit feeding organisms used in these studies are ideal indicators of steady state bioaccumulation due to the intensity of their interactions with sediment and lack of significant metabolism of the contaminants of interest.

- In Anacostia River (DC) sediments, the bioaccumulation in a freshwater oligochaete, *Ilyodrilus templetoni*, was well-predicted by the product of pore-water concentration and compound octanol-water partition coefficient (slope=1.08, r^2=0.76), as reported in Lu et al. (2011). No corrections were required for steady state uptake in the 28-day tests based on static experiments in the same sediment. A similar relationship between bioaccumulation and porewater concentrations in Anacostia river sediment was also observed in a previous study, in which the porewater concentrations were measured by conventional liquid-liquid extraction (Lu et al., 2003). The bioaccumulation in the *Ilyodrilus* can also be characterized with a bioconcentration factor of 1.08 defined by the ratio of the lipid normalized tissue concentration to the porewater concentration.
- In a sediment from New Bedford Harbor (New Bedford, MA) diluted with a fresh-water sediment from Brown Lake (Vicksburg, MS), the bioaccumulation of PAHs and PCBs in the freshwater oligochaete, *Ilyodrilus templetoni*, was also well-predicted by the product of porewater concentration and compound octanol-water partition coefficient (slope=1.24, r^2=0.76) as reported in Lu et al. (2011). Corrections for unsteady bioaccumulation were made via a model (Lampert, 2010), and the fractional approach to equilibrium ranged from 0.43-0.97 for PAHs (benzo[a]pyrene to phenanthrene, respectively) and 0.04-0.60 for PCBs (PCB 180-28, respectively). The use of the sequentially diluted sediment allowed evaluation of a much larger range of sediment and porewater concentration than could be evaluated using the fresh sediment. In addition, the dilution with freshwater sediment allowed use of the freshwater oligochaete in the bioaccumulation testing. The large estimated corrections for steady state in the more hydrophobic compounds subjected their porewater concentration and bioconcentration factor estimates to greater uncertainty.
- In sediment from Hunter's Point, CA, the bioaccumulation of PCBs in the marine polychaete, *Neanthes arenaceodentata*, was also well-predicted by the product of porewater concentration and the compound's octanol-water partition coefficient (slope=1.17-2.21, r^2=0.7-0.76), as reported in Gschwend et al. (2011). The range of slopes reflects uncertainty in estimation of the correction for nonequilibrium accumulation in the fiber. The estimated fractional approach to steady state was 0.73-0.83 for PCB 31, the least hydrophobic PCB measured, and 0.08-0.16 for PCB 180, the most hydrophobic.

All these preliminary studies exhibited lipid normalized bioaccumulation proportional to the product of the porewater concentration and octanol-water partition coefficient with a slope of approximately unity. This suggests that the lipid normalized bioaccumulation in organisms (C_b/f_l) at steady state appears to be well represented by the relationship

$$\frac{C_b}{f_l K_{ow} C_{pw}} \sim 1 \qquad (2.6)$$

or alternatively that the effective bioaccumulation factor is approximately the octanol-water partition coefficient.

The ratio represented by Equation 2.6 was tested in eight additional laboratory bioaccumulation tests with two different sediments (New Bedford Harbor and Elizabeth River) and four different organisms. The organisms included

- *Leptocheirus plumulosus*, a borrowing amphipod that lives in close physical contact with the sediment (USEPA, 2000). It builds semipermanent tubes and is capable of surface deposit feeding (by ingestion of sediment, detritus, phytodetritus, and benthic microalgae).
- *Neanthes arenaceodentata*, an infaunal marine polychaete widely distributed throughout the world occurring primarily in estuarine intertidal sand or muddy sand beaches. This species constructs nonpermanent mucoid tubes and deposit feeds on small particles, including course sediment particles.
- *Macoma nasuta*, a free-burrowing bivalve that deposit feeds by siphoning the top 1-2 millimeter layer of the sediment surface.
- *Lumbriculus variegatus*, a freshwater infaunal oligochaete widely distributed in North America and Europe. These species burrow in the sediment and ingest sediment particles below the sediment surface.

New Bedford Harbor sediments were employed in PCB bioaccumulation tests for each organism. Elizabeth River sediments were employed in PAH bioaccumulation tests with the *Leptocheirus* and *Neanthes* organisms. The measured lipid-normalized bioaccumulation of each PCB congener and PAH were divided by the product of the octanol-water partition coefficient and the measured porewater concentration. The results are depicted in Table 5.

Table 5. Measured normalized bioaccumulation in laboratory studies of various organisms.

Site/#	Organism	$\frac{C_b}{f_l K_{ow} C_{pw}}$	Standard Deviation	N
New Bedford Harbor #1	Leptocheirus plumulosus	1.257	0.868	247
	Neanthes arenaceodentata	0.841	1.08	213
	Lumbriculus variegatus	1.66	0.81	322
New Bedford Harbor #2	Leptocheirus plumulosus	1.45	0.82	318
	Macoma nasuta	1.18	0.45	144
Elizabeth River #1	Leptocheirus plumulosus	1.2	0.7	10
	Neanthes arenaceodentata	0.9	0.79	11
Elizabeth River #2	Leptocheirus plumulosus	0.617	0.503	18
Averages		**1.32**	**0.82**	**1283**

This data shows that bioaccumulation is well estimated by an effective bioconcentration factor (BCF) of approximately 1. While the best estimate is 1.32, it is not significantly different from unity.

Bioaccumulation cannot normally be estimated by bulk solid concentration as a result of variations in chemical availability. Porewater concentrations as measured by PDMS SPME, however, have shown a high ability to predict bioaccumulation in a variety of organisms and sediments under steady conditions. Porewater concentrations appear to be a direct indicator of availability and provide a measure of the labile contaminant that is equilibrating between sediment, organism, and porewater. Because the organisms typical accumulate contaminants as a result of ingestion rather than directly from the porewater, the validity of the porewater approach depends upon the equilibration of all three phases. While this is a reasonable assumption in the relatively static sediments, there may be conditions in which it is not applicable.

6.1.4 Laboratory Demonstration of Cap Performance Assessment Using Measured Porewater Concentration Profiles

The final laboratory experiments were designed to demonstrate the effectiveness of PDMS fibers for the measurement of contaminant concentration profiles in sediments and to use the profile measurements to demonstrate the ability to monitor effectiveness of a sediment cap. Specifically, the effectiveness of thin-layer sand capping was explored through experiments with laboratory-scale microcosms populated with the deposit-feeding oligochaete, *Ilyodilus templetoni*. Passive sampling of porewater concentrations in the microcosms using PDMS-coated fibers enabled quantification of high resolution vertical concentration profiles that were used to infer contaminant migration rates and mechanisms.

A series of laboratory microcosms of PAH-contaminated sediments with sand caps of varying thicknesses were set up and analyzed. In addition, a control cell without a cap was monitored throughout the study. The experiments were conducted in small plexiglass microcosms 27 cm long by 8 cm wide with a total depth of 15 cm. The microcosms consisted of an underlying contaminated sediment layer overlain with a clean sand layer of varying thicknesses (2, 4, 6, and 10 cm) overlain with 0.5 cm of clean (uncontaminated) sediment. Thus microcosms with cap thicknesses of 0 (control), 2.5, 4.5, 6.5, and 10.5 cm were monitored in this study. Artificial river water consisting of 0.5 mM NaCl, 0.2 mM $NaHCO_3$, 0.05 mM KCl, and 0.4 mM $CaCl_2$ dissolved in deionized water was passed over the microcosms at a velocity of approximately 10 cm/hr. The flow of the overlying water was employed to maintain effectively zero PAH concentrations and high dissolved oxygen concentrations at the sediment-water interface throughout the experiments. Redeposition of sediments is likely necessary for recolonization of a sand cap by deposit feeders and the 0.5 cm of clean sediment simulated that condition. To encourage colonization of the surface sediments, 250 organisms (~26,000 #/m^2) of a freshwater deposit-feeding oligochaete Ilyodrilus templetoni were placed into this microcosm. Adult worms varied in length from 2-5 cm and had an average wet weight of approximately 3 mg. The depth of interaction in the sediments was approximately equal to the organism length. The dry weight to wet weight ratio of the test organisms was roughly 0.2 to 1 and the lipid contents on a dry weight basis was 8.8±3.1%. PDMS fibers were placed into the microcosms, then sampled and analyzed in triplicate at 28 days to determine concentration profiles at 1-cm resolution.

Organisms were collected at 28 days in all microcosms. Additionally, a microcosm with a 4 cm sand cap was maintained for 56 days to investigate longer-term behavior. Details of the experimental procedures and results can be found in Lampert et al. (2011).

The PDMS fibers successfully measured porewater migration through the cap as a result of organism activity and molecular diffusion. Pyrene concentration profiles illustrate the observed behavior and are shown in Figure 5. Also shown is the correlation between lipid normalized organism bioaccumulation versus that predicted by porewater concentration.

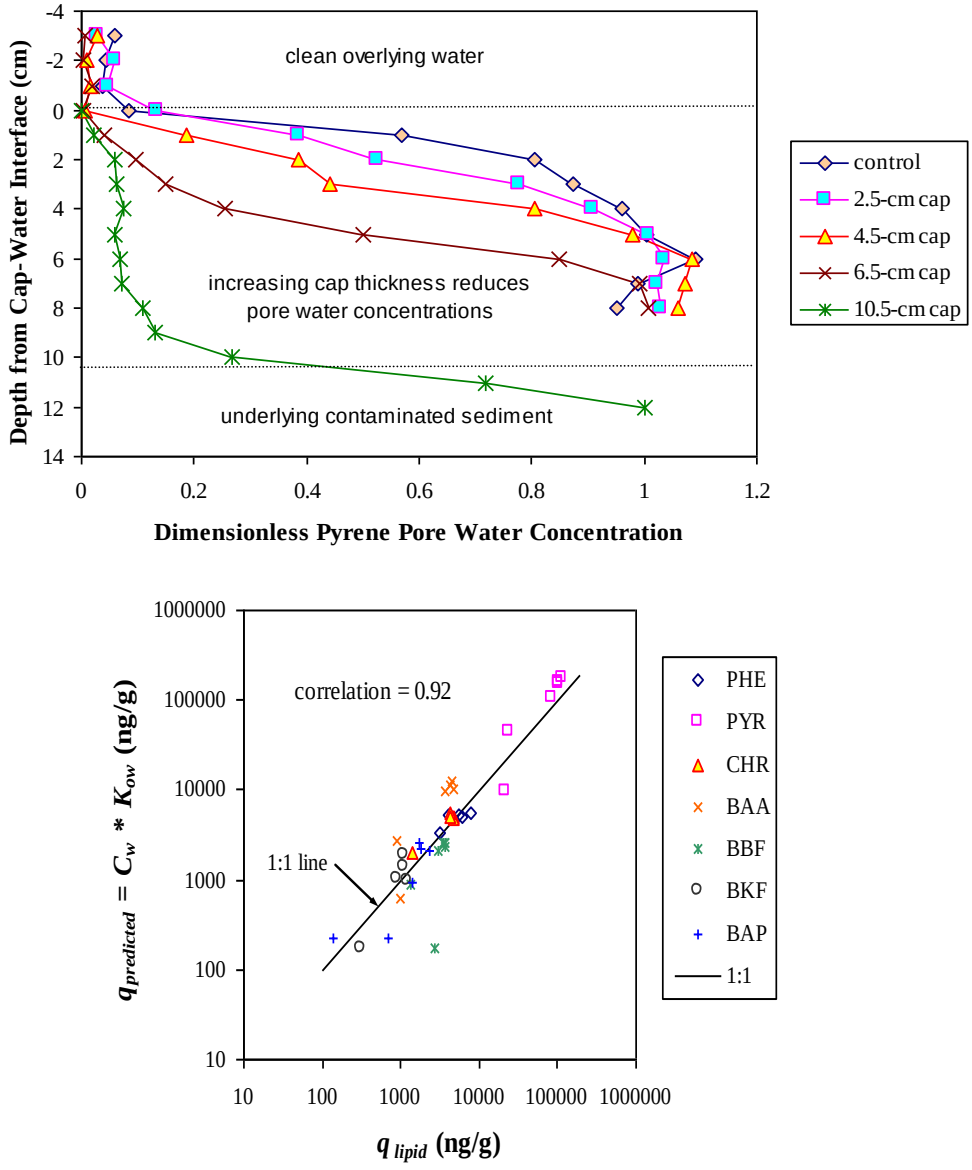

Figure 5. Observed pyrene concentration profiles as a function of cap thickness, illustrating rapid mixing of contaminants in a thin layer cap when depth of organism interaction is greater than cap thickness.
Also shown is the correlation between lipid normalized bioaccumulation and bioaccumulation predicted by $K_{ow}C_{pw}$ where C_{pw} is measured by PDMS fibers averaged over 0-5 cm.

Observed concentration profiles were consistent with models that combine traditional contaminant transport processes (sorption-retarded diffusion) with bioturbation. Predictions of bioaccumulation based on contaminant porewater concentrations within the surface layer of the cap correlated well with observed bioaccumulation in the benthic organism (correlation coefficient of 0.92). The results of this study show that thin-layer sand caps of contaminated sediments can be effective at reducing the bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in benthic organisms as long as the thickness of the cap layer exceeds the depth of organism interaction with the sediments and transport in the underlying sediment is dominated by diffusion. Advective conditions were not tested but may result in contaminant migration into the biologically active zone without organism interactions.

6.2 FIELD TESTING

6.2.1 Field Measurement of Porewater Concentration Profiles in Sediments

The field deployable SPME system was developed with a protective sheath over a slotted rod containing the fiber as previously shown in Figure 1. To demonstrate the applicability of the system to the field, the tools were deployed in the Anacostia River, Washington. The Anacostia River is a freshwater tidal system that drains an urban watershed encompassing 176 square miles in Maryland and DC. The river suffers from overall poor water quality caused by numerous pollutants, including suspended solids, excess nutrients, toxics, trash, and debris. Contaminants in sediments in this area are controlled by deposition from dispersed sources, and the bulk solid concentrations of contaminants are relatively uniform and show little change with time. An active capping project was conducted in the river to demonstrate the ability to place cap amendments in sediments for purposes of remediation. The demonstration was implemented by a team led by Danny Reible and the Hazardous Substance Research Center/South and Southwest with the support and assistance of a number of other organizations. Amendments placed included Aquablok® (a permeability control agent), coke in a reactive core mat (to demonstrate the ability to place high value sorbents in a thin layer in sediments), apatite (as a phosphate-based metals control agent) and sand (as a control). Details of the cap's placement and analysis of aspects of cap behavior can be found in Reible et al. (2006), McDonough et al. (2007) and Barth et al. (2008). The sand cap was nominally 1 ft (30 cm) thick. The coke in the reactive core mat was approximately 1 cm thick and was overlain by 6 inches (15 cm) of sand. The AquaBlok layer was approximately 4-6 inches thick (10-15 cm) and overlain by approximately 6 inches (15 cm) of sand. These nominal thicknesses could be as much as 10 cm thicker in some locations and intermixing with the underlying sediment may have contributed to an even greater apparent thickness.

Because sources were not controlled in the vicinity of the demonstration, the surficial sediments ultimately trended toward contamination concentrations similar to pre demonstration levels. Thus the bulk sediment profile observed post demonstration cap placement was a layer of contaminated sediment at the surface, a relatively clean capping layer and then contaminated underlying sediment. An analysis of diffusive migration from the sediment through the cap layers suggests that contaminants in the underlying sediment should penetrate entirely through the relatively nonsorbing sand layer of 6-12 inches within 15-36 months. Tidally induced motion, particularly in the high permeability sand layer would be expected to speed that migration and lead to relatively uniform concentrations in the sand cap layer. The presence of

contamination at the surface would also be expected to lead to rapid contamination and relatively uniform concentration profiles with depth.

The use of non-sorbing cap materials (e.g., sand, which was used in the surface layer of all caps), however, limited the ability of bulk solid measures to indicate contaminant migration through the cap. This is illustrated in Figure 6a which shows bulk solid concentrations as a percentage of their concentration in the underlying sediment in a high resolution core collected 30 months after the construction of the caps in the Anacostia active capping demonstration area. Also shown is the percentage of fines in each sediment interval indicating the fraction of sediment (as opposed to sand) in that interval. The bulk solid concentrations are consistent with the presence of sediment in a sample and do not provide any indication of contaminant migration within the cap.

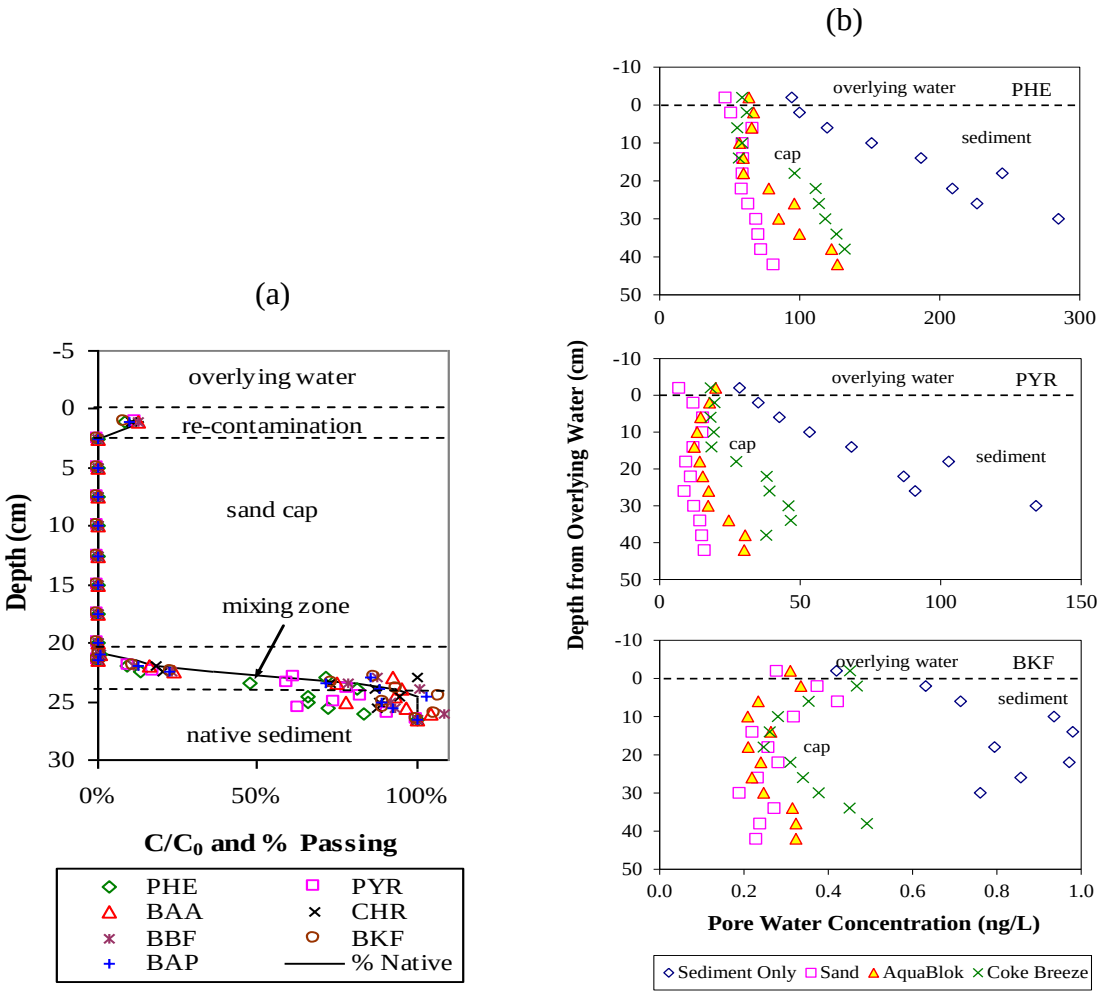

Figure 6. (a) Bulk solid concentrations of selected PAHs in the sand cap, (b) Porewater concentration of three PAHs in the sediment and in a sand, sand and AquaBlok, and sand and coke breeze layer caps.

Unlike bulk solid measures, PDMS porewater analyses showed significant contaminant migration within the sandy surface layer. Figure 6b shows the results of the PDMS porewater analysis of three PAHs (phenanthrene, pyrene, and benzo[k]fluoranthene, representative of a

low, medium and high molecular weight PAH, respectively) in the Anacostia caps 44 months after placement. Unlike the bulk solid measures, the porewater profiles show extensive mixing throughout the cap. The relatively uniform vertical profiles of all compounds in the sand layers (upper 25-30 cm in sand and AquaBlok and 15 cm in coke breeze) suggests that the tidal mixing was an important mixing process in the more permeable surface layers. Less evidence of tidal induced mixing is seen in the lower permeability sediment which exhibit a distinct decrease close to the surface. The most hydrophobic compound, BkF, also shows more limited mixing in that the concentration is highest in the near surface, presumably associated with recontamination of the surface by deposition as shown in Figure 6. BkF would be expected to be more retarded by sorption than either of the other two compounds shown, presumably leading to the less uniform concentration distribution. The detection of the contaminants throughout the cap layer demonstrates that the porewater profiling system is a more sensitive indicator of contaminant migration into a sediment cap than a bulk solid measurement.

The porewater concentrations in the cap layers are substantially lower than the porewater concentration in the sediment suggesting that the caps are more protective than the exposed sediment. The relatively low concentrations despite significant mixing throughout the cap may be the result of mixing related dilution or limited migration of contaminants from below.

A second deployment of PDMS fibers in the Anacostia River was conducted in October of 2008. This test was intended to evaluate bioaccumulation in organisms but organism recovery was poor. Porewater concentration profiles in capped layers were again relatively uniform as indicated by the prior testing. The samples collected were, however, useful to evaluate the ability of a commercial laboratory to analyze the PDMS samples as well as a check of interlab variability. Randomly selected samples were processed by placing PDMS fibers into solvent and then analyzed both at the University of Texas and at TestAmerica, Pittsburgh, PA. As shown in Figure 5, the interlaboratory comparison suggests that the samples could be analyzed by a commercial laboratory with similar analytical results. There was a consistent variation between the University of Texas (UT) and TestAmerica measurement of pyrene (although within a factor of two) suggesting a difference in calibration between the two laboratories. The variability in benzo[a]pyrene was also substantial between the two laboratories, particularly at low concentrations, although the average deviation was less than 10%. The conclusions of this test was that a commercial laboratory could provide chemical analysis for the processed PDMS samples and achieve concentration and detection limits similar to that achieved in the research laboratory.

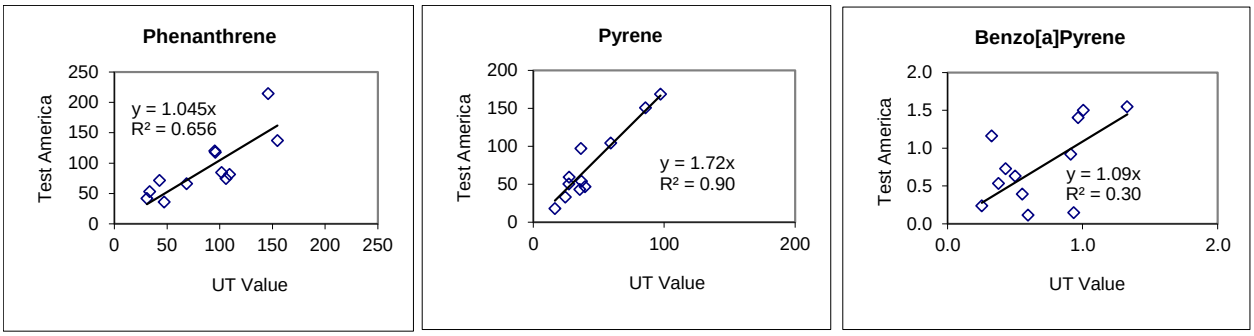

Figure 7. Comparison of Test America and UT PDMS samples.
(All porewater concentrations in ng/L)

The methodology presented here for evaluation of porewater profiles as a function of depth for the evaluation of cap performance has also been applied to the following sites as part of separate programs:

- McCormick and Baxter, Portland OR (in cooperation with Oregon Department of Environmental Quality)
- Pacific Sound Resources, Seattle, WA (in cooperation with U.S. Army Corps of Engineers)
- Chattanooga Creek, TN (in cooperation with USEPA)

These studies have served to provide wider use and dissemination of the technology and will lead to greater acceptance and use of the technology.

6.2.2 Field Measurement of Relationship between Bioaccumulation in Benthic Organisms and Measured Porewater Concentrations

The final focus of the demonstration program was demonstration of the relationship between bioaccumulation in benthic organisms and PDMS-measured porewater concentrations under field conditions. This is inherently more difficult than in the laboratory due to variability in organisms and their behavior as well as an inability to control environmental conditions. These studies were undertaken at four locations as part of the core program and in extensions of the core program in support of activities under SERDP Project ER-1550.

- Anacostia River, Washington, DC
- Hunter's Point, San Francisco, CA
- San Diego Harbor, San Diego, CA (in cooperation with ER-1550)
- Pensacola Harbor, Pensacola, FL (in cooperation with ER-1550)

6.2.2.1 Anacostia River

Field bioaccumulation experiments were conducted in the area of the Anacostia active capping demonstration in June 2007, 38 months after cap placement, using caged organisms following the procedures outlined by Burton et al. (2005). As indicated previously, organism deployments were planned at other times but organism recovery was poor. Organism recovery in the AquaBlok® capped area was also low during this deployment so bioaccumulation results are based on organism bioaccumulation in the uncapped sediment control area, a sand cap, and a coke breeze/sand cap designed to effectively contain hydrophobic organics. The standard in situ chamber was a cylinder constructed of transparent core tubing of cellulose acetate butyrate with a 6.67 cm inner diameter, 6.98 cm outer diameter, 0.16 cm wall thickness, and cut to a length of 12.7 cm. Polyethylene closures were used to cap each end. Two 4×8 cm rectangular windows were cut on each core tube opposite each other and covered with nylon mesh to allow water movement in and out of the chambers. The test organisms used in the experiments was *Lumbriculus variegates*, a tubificid oligochaete that is a deposit- (sediment-) feeding organism that achieves equilibrium bioaccumulation uptake rapidly due to large rates of sediment processing and does not significantly metabolize PAHs. The test organisms were placed into the cages by divers along with a sample of the surficial sediment/cap material at each location. The

organisms were allowed to accumulate PAHs for 28 days, then the chambers were removed by divers. The worm tissues were then analyzed for PAH concentrations and lipid content.

PDMS porewater profilers were placed in the sediment adjacent to the cages to allow comparison of porewater concentrations to measured bioaccumulaton. The profilers were deployed and retrieved by divers at the same time as the organism cages, that is, after 28 days. The PDMS fibers, 170/110 fibers in Table 2, were assumed to be at equilibrium since static experiments with Anacostia River sediments suggested all PAHs up to benzo[a]pyrene would achieve equilibrium within approximately 10 days using this fiber (Figure 2). More rapid equilibrium would be expected in the field due to tidal motion and groundwater movement, but equilibrium would be expected in this case even in the absence of such motion.

Both bulk solid and measurement porewater concentration were evaluated as a predictor of bioaccumulation. The average of the 0-10 cm PDMS measurements using 170/110 fibers were employed to estimate porewater concentration over the depth of bioturbation. Based on the laboratory experiments described previously, the measured lipid normalized bioaccumulation was compared to the predictor of the product of the octanol water partition coefficient and the measured porewater concentration, that is,

$$C_b/f_l = K_{ow}C_{ow} \tag{2.7}$$

As indicated in the preceding sections, this presumes that bioaccumulation in the water, sediment, and biota system can be described by equilibrium in the biota, water, and sediment system and that the octanol-water partition coefficient characterizes the partitioning to the biota lipids.

Cores were not collected at the same time as the deployment of the cages, but cores in each of the cap materials and the adjacent sediment control were available from 30 months after cap placement. The average concentration of contaminants in the upper 10 cm of these cores were compared to the biota sediment accumulation factor (BSAF) as a predictor of organism uptake, that is,

$$C_b/f_l = C_s/f_{oc} \tag{2.8}$$

The latter is equivalent to a BSAF of 1. As noted by Burkhard (2006), a BSAF of 1-2 should be applicable for equilibrium of nonmetabolizing contaminants in benthic organisms. Commonly, however, a substantial fraction of the contaminants may be in a nonbioavailable form and BSAF less than unity may be observed, even in systems in apparent equilibrium. The advantage of the PDMS technology is that the porewater concentration provides an indication of the available amount of contaminant and may avoid the conservative assumption of 100% bioavailability that is inherent in an assumption of a BSAF~1. This was previously demonstrated in laboratory bioaccumulation tests, but in this section the applicability of the paradigm to field conditions will be evaluated.

Figure 8 compares the observed and predicted bioaccumulation for all measured PAHs (phenanthrene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene,

benzo(k)fluoranthene, and benzo(a)pyrene). Equation (2.8), the bulk solid estimator, significantly overpredicted the bioaccumulation in the organism, illustrating that many of the contaminants were not bioavailable. The BSAF value that would be consistent with the observed bioaccumulation would be 0.068. The porewater concentration, however, correlated well with bioaccumulation (r^2=0.81 versus 0.51) and Equation (2.7) predicted bioaccumulation more accurately that Equation (2.8) (factor of 2 versus a factor of about 15). The average prediction assuming a lipid water partition coefficient is K_{ow} was approximately half the observed bioaccumulation on average, suggesting an observed water-lipid partition coefficient or water-lipid bioaccumulation factor (BAF) of ~2 K_{ow}. Lu et al. (2011) observed a lipid water partition coefficient of 1.08 K_{ow} in laboratory studies of bioaccumulation from Anacostia River sediments with a different tubificid oligochaete. The difference may be due to experimental variability or failure to appropriately estimate equilibrium either in the fiber or organism or both.

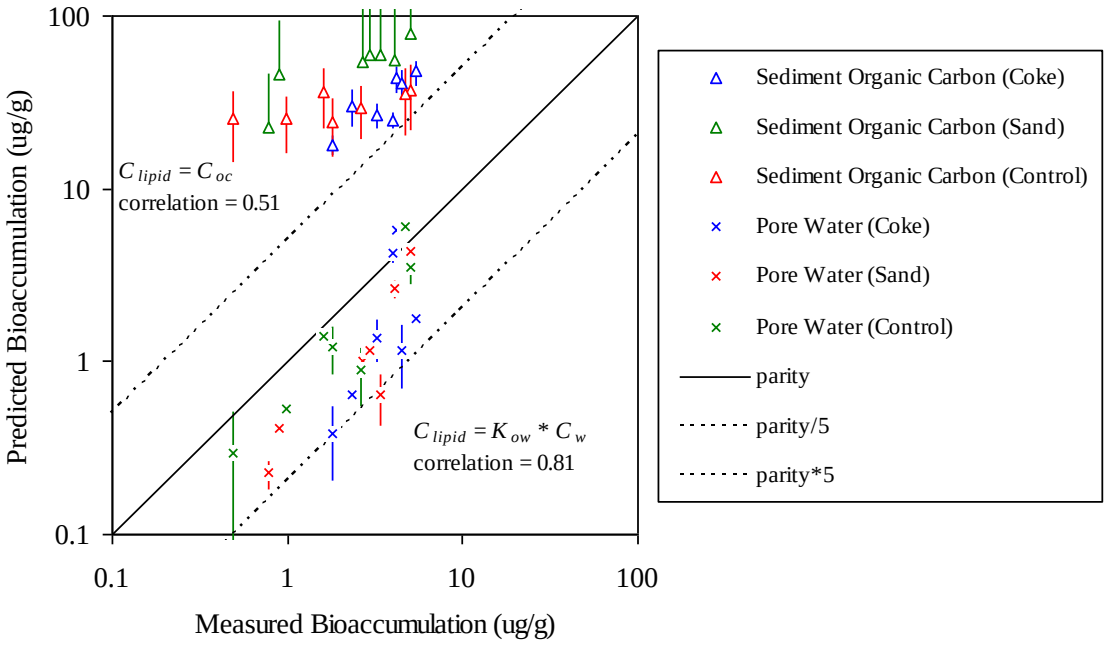

Figure 8. Correlation of predicted and observed lipid normalized bioaccumulation assuming BSAF=1 (using solid concentration as predictor) or BAF=K_{ow} (using porewater concentration as predictor) for all measured PAH compounds (phenanthrene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene).

A similar difference between observed and porewater predicted bioaccumulation was noted in the second demonstration with PCBs at Hunter's Point, San Francisco, CA. This bioaccumulation test was conducted with *Neanthes arenaceodentata* in cooperation with R.G. Luthy and E. Janssen of Stanford University. The organisms were placed in an intertidal zone in cages similar to those used in the Anacostia and exposed to Hunter's Point sediment containing total PCBs of approximately 1 mg/kg (0.966 mg/kg). Both untreated cells and cells treated with activated carbon (3.4% activated carbon by dry weight) were deployed. The organisms were exposed for 14 days and then their lipid content and PCB body burden were measured by

Stanford personnel using gas chromatograph-electron capture detector (GC-ECD). Both 230/210 and 1060/1000 PDMS was placed in the sediment-populated cages for two time periods (14 or 42 days) and retrieved and analyzed at the UT, also by GC-ECD. The analysis parameters were identical except that the Stanford analysis required sample extraction with solvent and cleanup with silica gel. The extraction of the PDMS fibers in the UT analysis was placed directly into injection solvent without further sample cleanup. Three replicates were collected of all samples. The 42-day data showed a substantial increase in coefficient of variation among replicates compared to the 14-day data (57% versus 26%). The increased variability was believed to be associated with an increased sorption of compounds that interfered with the PCB analysis since no sample cleanup was attempted. Only the 14-day PDMS data was compared to bioaccumulation data due to the larger variability of the 42-day data. Steady state uptake onto the PDMS was predicted from the 14-day measurements based on a model assuming diffusion controlled transport in the pore space of the sediment. The corrections are shown in Figure 9a. The validity of the assumed diffusion was tested by comparison of the predicted equilibrium in the thin (230/210) and thick (1060/1000) fiber. This is shown in Figure 9b. The slope of near unity suggests that the steady state uptake corrections are valid.

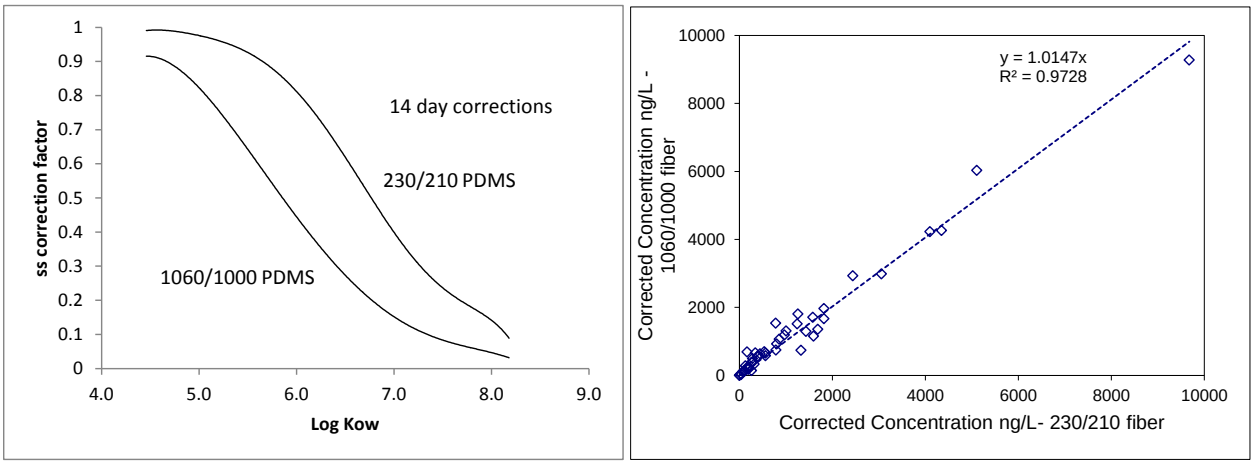

Figure 9. Hunters Point 14-day corrections for steady state PDMS uptake and comparison of correction porewater concentrations (ng/L).
(all measured PCB congeners)

The relationship between body burden (lipid normalized) and PDMS measured porewater concentration is shown in Figure 10 for both untreated and activated carbon treated microcosms.

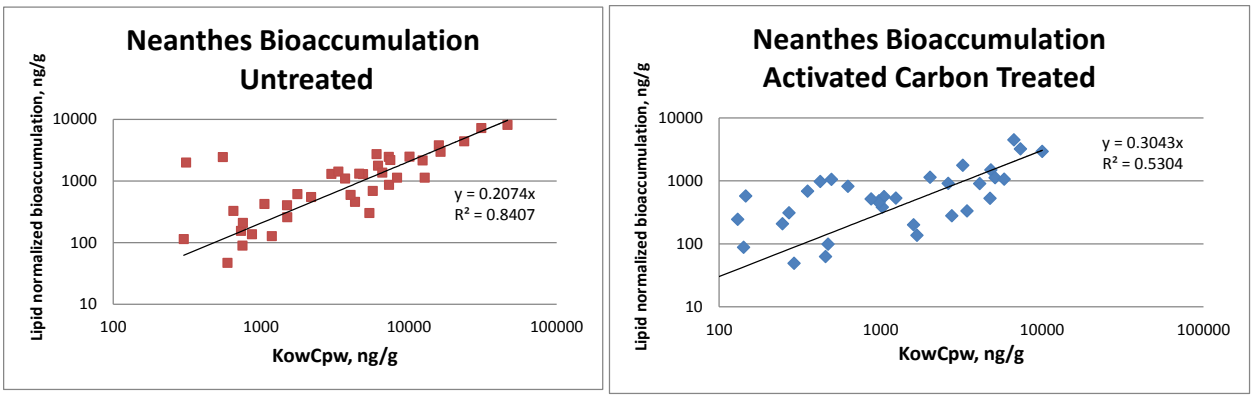

Figure 10. Bioaccumulation as a function of PDMS-measured porewater concentration for both untreated (left) and activated carbon treated (right) microcosms
(all measured PCB congeners)

The untreated microcosms show a good agreement with measured porewater concentration although the apparent BCF is about 0.21 K_{ow}, less than the approximately unity found in laboratory studies and less than the 0.5 K_{ow} found in the Anacostia studies. The apparent BCF in activated carbon treated cells is about 0.3 K_{ow}. The scatter in the activated carbon treated cells may reflect substantial concentration uncertainty in porewater concentration due to the low concentration in the activated carbon treatment cells. The coefficient of variation of replicates in the activated carbon treated measurements was about 60% relative to the 26% in the untreated cells. The lipid-normalized bioaccumulation was reduced by 59% between untreated and activated carbon treatments while the measured porewater concentrations were reduced by 83%. The reason for the relatively low value of BCF relative to laboratory studies and the difference between reductions in porewater concentrations and reductions in bioaccumulation may be due to stressors common to both cells in the field or perhaps due to the fact that the PDMS was buried within the sediment layer, and organisms are exposed at the sediment water interface and may reflect a more complex exposure scenario than sediment alone.

In this field demonstration, sediment concentrations also correlate with organism bioaccumulation. Figure 11 indicates the relationship between sediment concentration (organic carbon normalized) and organism bioaccumulation (lipid-normalized). The slope of the best-fit line is consistent with an effective BSAF of 0.757, close to the accepted equilibrium value of 1-2. This suggests that much of the PCB may be bioavailable and reversibly sorbed if both porewater concentration and organic carbon normalized bulk solid concentration correlate with bioaccumulation.

The bulk solid concentration cannot describe changes in uptake due to the addition of activated carbon since the solid concentration does not change significantly with treatment. Although the total sediment concentration does not change with the addition of activated carbon, the carbon normalized sediment concentration does change. In this case, 3.4% of activated carbon was mixed into the sediments making a total carbon content of 3.4+1%~4.4%. Figure 11 also shows the carbon normalized sediment concentration in the activated carbon treated microcosms and uses that as a predictor of post-treatment bioaccumulation. This indicator works well in this case although it suggests that the activated carbon and the sediment organic carbon are approximately equally effective at absorbing the PCBs whereas it is expected to be much more sorbing than

sediment organic carbon. The ability of carbon normalized sediment concentration to predict bioaccumulation is not general and depends on the contaminant being bioavailable and reversibly sorbed to solids.

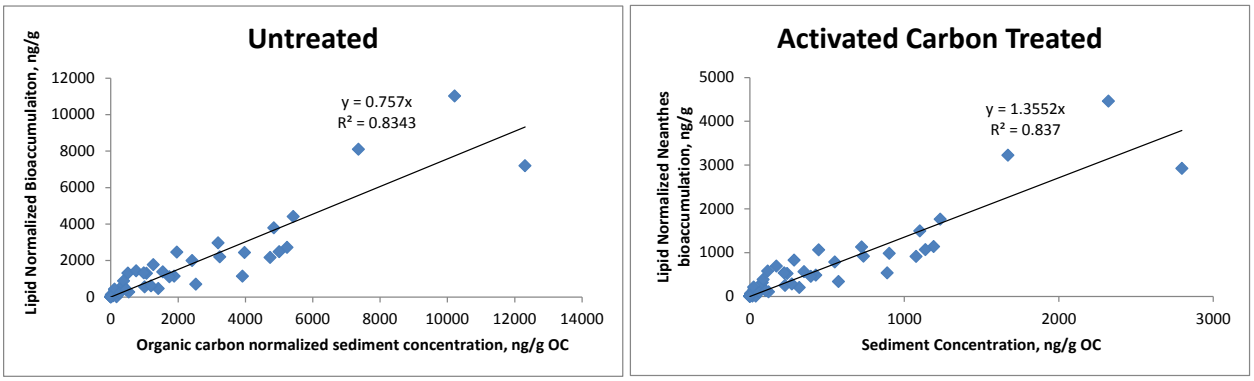

Figure 11. Relationship between lipid normalized bioaccumulation and sediment concentration
(all measured PCB congeners)

6.2.2.2 ER-1550 Field Locations (San Diego and Pensacola Naval Bases)

Two additional field demonstrations of PDMS measurement of porewater concentrations were conducted in cooperation with ER-1550, a project devoted to the development of a sediment ecotoxicity assessment ring, SEA Ring. The SEA Ring employs a variety of organism exposure modules coupled with chemical assessment modules to provide an indication of ecotoxicity of contaminated sediments. Details of the system and its deployment and interpretation can be found in the ER-1550 reports. Only a summary relevant to the PDMS samplers is included here. The PDMS samplers were deployed twice as part of regular deployments of the SEA Ring, in San Diego, CA, and in Pensacola, FL.

Naval Base San Diego (NBSD) is the largest Navy base on the West Coast of the United States, encompassing 13 different piers, and is the principal home port of 54 ships. Located on San Diego Bay, CA, several pier areas at NBSD have been listed as potentially at risk for aquatic life impacts (SWRCB, 2005). A transect of three contaminated sites between piers at NBSD (5 and 6) was selected for evaluation. In addition, a reference site was selected with low levels of contamination. Bioaccumulation was measured in a 21-day laboratory exposure of the mussel *Muscalista*. A short term (2-day exposure) in the field yielded inconsistent bioaccumulation data due to a substantial number of non-detects. Chemical measures included porewater measured by PDMS exposed for 2 and 21 days, porewater measured with centrifuged sediment, and bulk solid concentration (normalized by organic carbon). PDMS measurements were analyzed at UT. Centrifuged sediment porewater and tissue bioaccumulation was measured by U.S. Army Corps of Engineers Engineer Research and Development Center (USACE-ERDC).

The PDMS fibers used in this study were 230/210 fibers with a 10 µm PDMS coating on a 210 µm diameter glass core. The fibers were housed in the sheath systems shown in Figure 1. For the in situ assessment, they were deployed in tandem with the SEA Rings, positioned around perimeter within close (~1-2 inches) proximity to the bioaccumulation exposure chambers. SPME deployment periods were 2 and 21 days. Upon retrieval, the PDMS fibers were immediately cleaned, processed into solvent in 5 cm intervals, and analyzed for PAHs. Figure 12

shows the ability of the various measures of porewater concentration to predict the observed bioaccumulation. Because the indicators included in Figure 12 represent different exposure periods, three PAHs of similar hydrophobicity were evaluated—benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[a]pyrene. This eliminates the variability associated with different rates of uptake of compounds of different hydrophobicity.

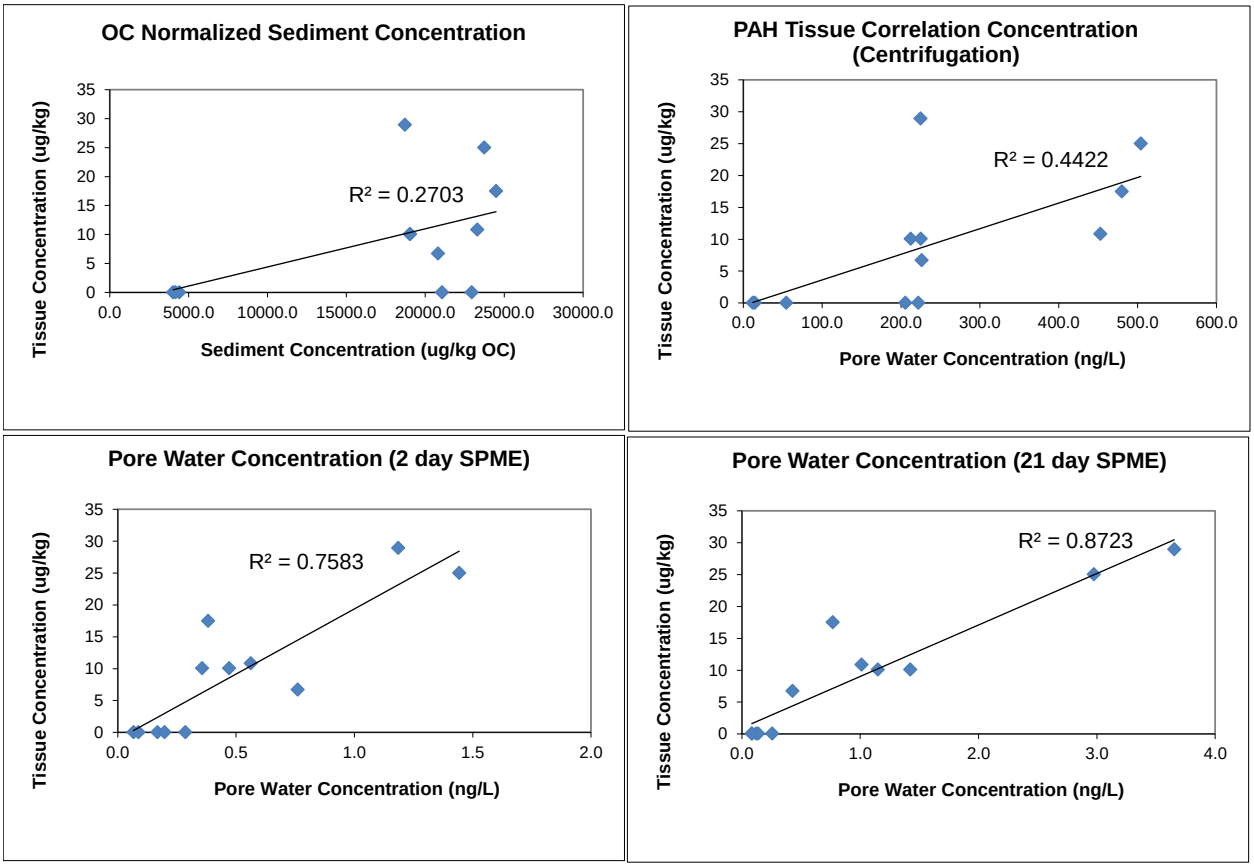

Figure 12. Correlation of bioaccumulation of benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene with various indicators of availability

As shown by Figure 12, the best correlation with tissue bioaccumulation was the in situ measures of porewater concentration by SPME with PDMS. The 21-day PDMS exposure was somewhat better than 2-day exposure as a result of differences between uptake kinetics of organisms and the PDMS. Organic carbon normalized sediment concentration did not correlate with tissue bioaccumulation. Porewater concentration, as measured by centrifugation, was weakly correlated with tissue bioaccumulation. In addition, the concentration measured in centrifuged sediment porewater was a factor of 100 higher than that measured by passive sampling. This indicates that centrifugation led to resuspension of solids and colloidal material and artificially higher porewater concentrations due to colloidally bound PAHs. The results indicate again the importance of defining availability by measuring porewater concentration but doing so in a way that does not artificially distort the porewater concentration as apparently occurs by centrifugation.

The final site was the Naval Air Station Pensacola (NASP) Yacht Basin, located at the mouth of Bayou Grande, adjacent to Pensacola Bay, Pensacola, FL. The site is contaminated by a variety

of contaminants including PAHs, and the SEA Ring was deployed at three test locations (designated NASP 6, 11, and 25 and a reference station, NASP 9). Figure 13 summarizes the correlation observed between organic carbon normalized sediment concentration and PDMS measured porewater concentration in both lab and field measurements of short-term (96-hour) bioaccumulation in *Leptocheirus plumulosus*. The SEA Ring is designed for short deployments although this means that steady state bioaccumulation will not be achieved. Thus only a correlation with measured porewater concentration (or sediment concentration) is sought to define a site-specific indicator of relative bioaccumulation. The measured fiber concentration is corrected for disequilibrium to predict the porewater concentration.

The organic carbon normalized sediment concentration provided only a weak correlation suggesting that bioavailability is limited by factors other than simply the amount of organic carbon present. Porewater concentrations, however, appeared to capture the relative bioavailability in that a good correlation was observed between bioaccumulation and that metric. The significance of the nonzero intercept in the correlation may be the presence of PAH elimination mechanisms in the *Leptocheirus plumulosus* or simply a reflection of detection limits in body burden measurements. Note the substantially higher bioaccumulation amounts in the laboratory studies reflecting the presence of other stressors in the field studies that limited organism uptake. This again suggests that laboratory studies will generally be conservative and often are indicators of potential uptake and bioaccumulation rather than actual bioaccumulation that would be measured in the field.

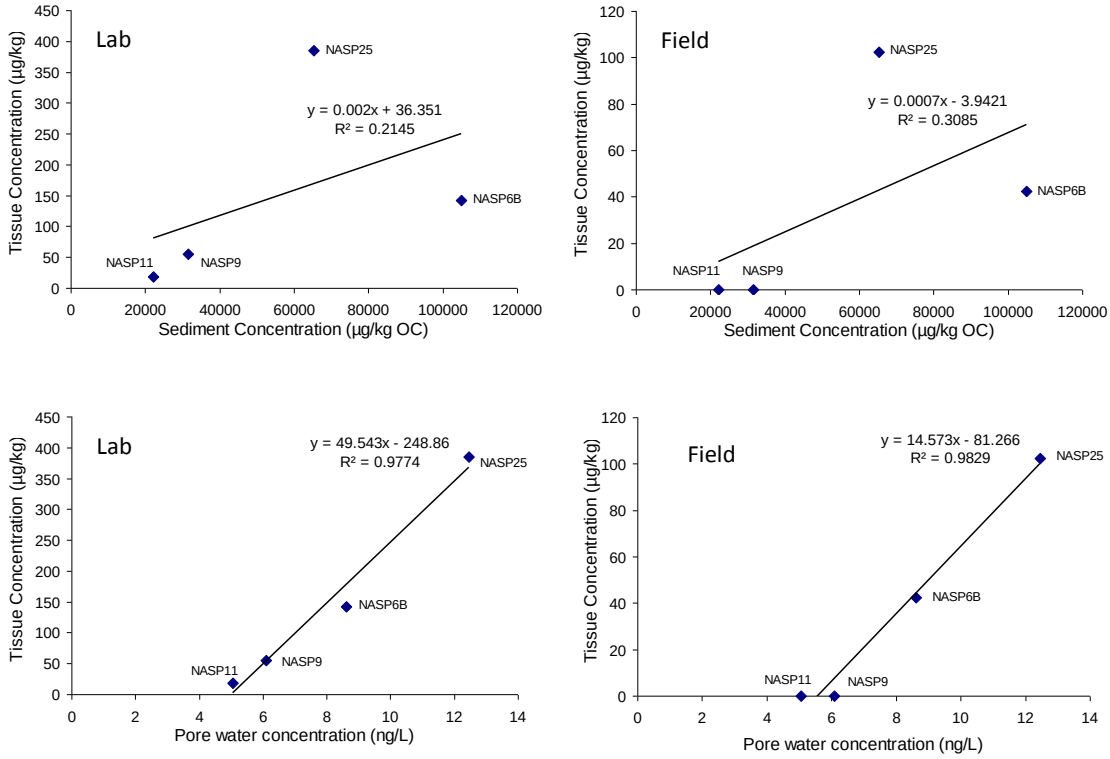

Figure 13. Uptake of PAHs from 96 h exposures with the amphipod Leptocheirus plumulosus in both lab (left) and in situ (right).

Top figures show comparisons of organism uptake with organic carbon normalized sediment concentrations. Bottom figures show organism uptake relative to SPME-derived porewater concentrations. For simplicity, each data point represents the sum of pyrene, B[a]a, B[b]f, B[k], and B[a]P from each of the four stations.

7.0 PERFORMANCE ASSESSMENT

As outlined in the preceding section, the detailed performance objectives included:

- High analytical accuracy and reproducibility under laboratory conditions
- Low detection limits
- Estimation of PDMS uptake kinetics
- Indicate cap performance
- Predict bioaccumulation potential in laboratory in situ tests
- Predict bioaccumulation in field in situ tests
- Ease of application to laboratory in situ use
- Ease of field use
- Ease of analysis

A discussion of each of these follows.

7.1 HIGH ANALYTICAL ACCURACY AND REPRODUCIBILITY UNDER LABORATORY CONDITIONS

This performance objective was met by conducting a calibration of the PDMS fiber in prepared water standards using PAHs. Linearity of the resulting calibration for mid-range HOCs was very high with r^2>0.99. High molecular weight compounds are also expected to meet this standard although this could not be demonstrated due to the difficulty of preparing and maintaining aqueous standards for very hydrophobic compounds. Coefficients of variation from the resulting linear curve were less than 20% for all PAH compounds except naphthalene. Naphthalene is not concentrated significantly on the PDMS fiber and losses to air are rapid, making it difficult to measure naphthalene via PDMS without increasing PDMS layer volume/thickness. Coefficients of variation by conventional extraction methods were also between 10 and 20% suggesting that the accuracy of the PDMS methods were essentially identical to that expected by conventional methods. PCB calibrations were not attempted but instead correlations of fiber sorption with hydrophobicity defined in the literature were employed. The literature correlations for PCB sorption versus hydrophobicity as measured by K_{ow} were consistent with extrapolations of such correlations with PAHs. All predictions of fiber-water partition coefficients were found to be within the accuracy of the estimates of Kow (typically 0.2-0.3 log units or a factor of 1.5-2). The effects of salinity and temperature (over 10-25°C) were also within this standard of accuracy and corrections for these effects were not attempted.

7.2 LOW DETECTION LIMITS

Measured detection limits were well below concentrations typically achievable by conventional analytical methods. Measured method detection limits by fluorescence HPLC ranged from 0.07 µg/L for fluorene to 0.05 ng/L (0.00005 µg/L) for benzo[a]pyrene using only 1 cm of 230/210 PDMS fiber. One cm of 1060/1000 fiber would yield detection limits more than 10 times lower. Reductions in detection limits could also be achieved by increasing the length of fiber employed in the measurement. Detection limits for direct injection via fluorescence HPLC ranged from 0.81 to 0.018 µg/L for the same compounds. Thus an extraction/concentration step

would require a concentration enhancement of 12 to 1400 to achieve the same detection limits as the PDMS. The direct extraction PDMS method as employed here also achieves detection limits well below comparative low level quality criteria (surface water quality standards).

Detection limits are not significantly lower than that achievable by conventional standards, however, for naphthalene and alkylated naphthalenes. In addition, the strong dependence of detection limit on compound hydrophobicity suggests that this in situ method may not be appropriate for measurement of sum of PAHs or for analysis of PAH_{34} which includes many of the compounds that are not effectively measured by an in situ passive sampling method.

7.3 ESTIMATION OF PDMS UPTAKE KINETICS

A complication of the in situ passive sampling method is the need for correction for any deviations from equilibrium. The ability to predict bioaccumulation is dependent upon a state of quasi-equilibrium between sorbent, porewater, solid, and biota. The sorbent sampler should be deployed for a time sufficient to achieve equilibrium with the adjacent porewater or corrected to estimate the equilibrium uptake. For PDMS and, under most conditions POM and PE, the achievement of equilibrium is dependent upon external mass transfer resistances or the time required to reequilibrate the solids and porewater around the passive sampler. In this work, the use of performance reference compounds such as deuterated PAHs was demonstrated as was an alternative, based on using sorbents with two different surface area to volume ratios (and therefore two different rates of uptake). The ratio of the two was related to the external transport resistances through a simple model and used to estimate or test models of uptake kinetics. The kinetics of uptake of the PDMS is typically more rapid than either POM or PE, which may provide advantages in some applications. The accuracy of the kinetic correction decreases as the magnitude of the correction increases. That is a factor of two correction, as was typically observed for a hydrophobic PAH such as benzo[a]pyrene that after exposures of 1-2 weeks is potentially much more accurate than a factor of 5-10 that might be required to correct a hydrophobic PCB concentration after a similar period of exposure.

7.4 INDICATE CAP PERFORMANCE

A major advantage of an in situ approach is the determination of porewater concentration profiles in the in situ sediments. Due to the low detection limits of the method, it is possible to measure porewater concentration profiles with high resolution (1 cm). This can be used to evaluate contaminant migration within a cap. In addition, since the method does not depend on the sorption characteristics of the cap layer, the method can monitor contaminant migration in nonsorbing materials such as sand. This was demonstrated in both laboratory and field measurements at resolutions as low as 1 cm.

7.5 PREDICT BIOACCUMULATION POTENTIAL IN LABORATORY IN SITU TESTS

The primary goal of the demonstration was to show that the measured PDMS uptake porewater concentrations can be related to bioaccumulation in benthic organisms and therefore be used as an indicator of bioavailability. In a variety of laboratory tests with different organisms, sediments and PAH and PCB contaminants, the ratio of bioaccumulation to equilibrium uptake

in the PDMS was given by K_{ow} within a factor of about 2. The use of porewater concentration to predict bioaccumulation provided a more reliable indicator than solid phase concentration even for deposit feeding organisms where the route of uptake was expected to be through sediment ingestion.

7.6 PREDICT BIOACCUMULATION IN FIELD IN SITU TESTS

The use of PDMS to predict bioaccumulation was also extended to field tests. In field tests, caged organisms were used to control exposures although a variety of stressors are encountered in the field that may not be reproduced in laboratory experiments. In field tests, the ratio of bioaccumulation to PDMS measured equilibrium porewater concentration was lower than in laboratory measurements and typically of the order of 0.2-0.5 K_{ow}. Good correlations were observed between field measured porewater concentrations and bioaccumulation in caged organisms but the apparent complication of additional field stressors reduced the absolute magnitude of the bioaccumulation. The PDMS measured porewater concentration, however, is typically a better indicator of bioaccumulation than bulk solid concentration or porewater concentration by active means (e.g., centrifugation), which may be in error by orders of magnitude at some sites.

7.7 EASE OF APPLICATION TO LABORATORY IN SITU USE

The evaluation of the previous performance indicators suggests that PDMS measured porewater concentrations can be an effective means of indicating contaminant migration in caps and predicting potential bioaccumulation. The final qualitative performance indicators are designed to evaluate whether they can be used simply and easily.

Application in the laboratory by the developed method is easily accomplished. The PDMS fibers can be placed in situ into sediments without shielding and withdrawn and analyzed at any time. Their size (<1 mm diameter) suggest that this can be accomplished with minimal disturbance to the surrounding sediment. Very small fibers may need to be inserted into a septum to aid location and withdrawal. The developed method of segmenting the PDMS fiber, then placing directly into an autosampling vial with insert and 100 200 µL of solvent followed by direct injection into an analyzer (GC or HPLC) was demonstrated to be simple and effective. The lack of additional processing steps is a major advantage of the method, avoiding time, cost, and potential contaminant losses due to sample cleanup or extraction steps.

7.8 EASE OF FIELD USE

In the field, PDMS fiber use is more complicated. Sediments can be brought from the subsurface via coring and analyzed on ship or in the laboratory. Placement in situ in the field, however, would typically require divers and shielded fibers to protect them during placement. The developed system was found to be easy to deploy in all but the most difficult of subsurface environments (e.g., sediments armored by rock). Deployment remotely from the surface is possible but this was not fully developed or tested by the demonstration. The primary difficulty is ensuring proper vertical placement, particularly in soft sediments where the lack of resistance of the sediment makes it difficult to define the sediment-water interface. Retrieval by divers or remotely by simply withdrawing an attached line was demonstrated and proved easy to

implement in all environments. Processing of PDMS fibers onshore by sectioning and placing into autosampling vials with inserts prefilled with 100-200 µL of solvent proved to be an effective processing method. These stabilized samples could then be shipped back to the laboratory for analysis without concerns for a sample degradation during transit.

7.9 EASE OF ANALYSIS

As indicated above, a major advantage of the PDMS passive sampling approach for measurement of porewater is the lack of additional sample processing. The sectioned PDMS fibers inserted into solvent filled autosampling vials can be analyzed directly. This was found to be sufficient at all sites except for 42-day samples deployed at Hunter's Point. High variability in these samples may have been due to the sorption of other compounds, in this case sulfur compounds that interfered with PCB analysis. One possible approach may have been to add a small amount of activated copper to the sample vials in this case to eliminate these compounds, but this was not attempted. In general, however, the direct extraction onto the PDMS fiber followed by extraction into injection solvent was sufficient to eliminate other interfering compounds.

8.0 COST ASSESSMENT

8.1 COST MODEL

In situ sediment monitoring with PDMS.

Table 6. Cost model.
(Basis=1 m of PDMS unless noted)

Cost Element	Cost Items	Estimated Costs	
Fabrication of PDMS	Cost of third party fabrication	250 m length 500 m length	$26.80/m $17.40/m
Fabrication of shielding system	Cost of Henry's style probes Machining modifications	Probe cost Machining – 2 hrs/m	$200/m $100/m
Predeployment processing of PDMS	PDMS length cleaning Loading in shielded system Shipment to site	Lab technician- 1 hr/m Shipment	$50/m $100
Deployment	Divers and field support	Diving team – 1 day/site Field support – 2 person-days/site	$2000 $2000
Retrieval	Divers (optional) Field support team Autosampling vials with solvent	Field support team- 2 person-days/site Consumables Shipment	$2000 $100/m $100
Lab Analysis	Commercial laboratory costs	$100/sample, 10 samples/m	$1000/m
Interpretation	Kinetics and analysis	Senior analyst, 80 hrs/site Associate analyst 80 hrs/site	$8000 $4000
TOTAL	Per site - 20 PDMS profilers deployed 10 PDMS profiles, 5 samples/m	Assume 1 m/sample	 $47,736 $28,236

8.2 COST DRIVERS AND ANALYSIS

The cost is largely driven by the costs of chemical analysis and interpretation and interpretation (kinetics evaluation) of the resulting chemical data. The chemical analysis is equal to or less than the cost of conventional analysis due to the lack of requirements for sample processing during analysis. Interpretation, however, includes interpretation of the deviation from steady state and this may require some additional chemical analyses (e.g., deuterated compounds) or additional samples (to evaluate multiple sorbent fibers at a particular location). Neither requirement adds appreciably to the chemical analysis requirements per sample since performance reference compounds are chosen to avoid interference with chemical analysis (e.g., deuterated PAHs can be quantified in the same analyses as conventional PAHs).

Additional costs are associated with divers for placement of samplers. This would not be a cost associated with samples retrieved in conventional or box cores and monitored in the laboratory by PDMS. In situ field placement, however, is best conducted using divers to ensure good control over location and depth of placement.

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9.0 IMPLEMENTATION ISSUES

The primary difficulties associated with the technology are the time and cost of deployment and the complexities of interpretation of the results. Deployment may involve divers for both placement and retrieval (although alternative approaches exist with some limits in attainable objectives) and long delay times between placement and retrieval (7-28 days). Expert knowledge is required to appropriately balance considerations such as achievable detection limit and rate of attainment of equilibrium. Failure to accurately assess polymer uptake kinetics and the degree of equilibration with a given exposure can significantly limit the applicability of the results.

At the current time, fabrication of appropriate PDMS fibers (selection of PDMS layer thickness and core thickness) requires expert knowledge to optimize for detection limits and kinetics of uptake. Although commercial fabricators can manufacture the fiber, there are no off-the-shelf fibers available for typical sediment bioavailability testing. There are also no commercial laboratories or consultants that can be hired to accomplish a turnkey sampling operation.

There is, however, growing recognition of the value of the collected porewater data and there is increasing requests for such analyses. Currently such analyses are being conducted by the developers of the technology in cooperation with these groups. Although no regulatory standards currently exist for porewater information, surface water quality standards are being increasingly used as a comparative standard for the collected porewater concentration data. While conservative, the application of surface water quality standards to porewater is likely to be protective of environmental and human health. Increasing availability of both porewater data and a framework for its use and evaluation ensures that the technology will grow and that laboratories and consultants will ultimately be able to provide this service in lieu of the technology developers.

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