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Passive Sampling to Evaluate Performance of *in situ* Sediment Remediation

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Passive Sampling to Evaluate Performance of *in situ* Sediment Remediation

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Dedication

To future women in science, technology, engineering, and mathematics fields.

Do not be afraid to trade in Barbie® for MATLAB® and a calculator. You can do it!

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Passive Sampling to Evaluate Performance of *in situ* Sediment Remediation

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In situ passive sampling is the use of a polymer sorbent to directly assess freely dissolved concentration (C_{free}) profiles within the environment. The primary focus herein is the use of passive sampling methods to detect and quantify persistent hydrophobic organic compounds (HOCs) in sediment porewater and surface water using solid phase microextraction (SPME) profilers with polydimethylsiloxane (PDMS) as the receiving phase sorbent.

Contaminated sediment sites pose a unique challenge in terms of remediation and monitoring for several reasons including: the large number of past and ongoing sources, sediment stability, and the extent of contamination. Capping with a clean layer of material, an accepted remediation approach, can reduce risk by stabilizing the underlying sediments, isolating the water column, and reducing contaminant flux. Evaluating cap performance is challenging due to the long time frames associated with migration of HOCs. Additionally, the non-sorbing nature of most caps limits the usefulness of bulk solid measurements. An alternative is the use of concentrations in the interstitial space or porewater to examine contaminant migration in the sediments and cap.

Traditionally, porewater concentrations are obtained through a conversion of bulk sediment concentrations using an assumed sediment-water partitioning coefficient. This assumption often leads to a misrepresentation of risk as not all organic carbon is created equal. An alternative is the use of passive sampling with polymer sorbents to estimate the freely available concentration, C_{free}. In this work the focus is on the use of solid phase microextraction with polydimethylsiloxane (SPME PDMS) as the sorbent. C_{free} is proportional to chemical activity; therefore an accurate measurement of C_{free} is necessary for risk assessment and determination of transport mechanisms and ultimately improved management of contaminated sediment sites.

A non-equilibrium correction protocol using performance reference compounds (PRCs) was developed to enhance the accuracy of the SPME PDMS method to assess C_{free}. The protocol was validated through laboratory experiments and field trials. Deployment times can be reduced without sacrificing accuracy when using the PRC protocol. Furthermore, it was shown that mathematical models of diffusive and advective flux can be fit using parameters determined from PRC desorption.

The SPME PDMS with PRCs method was used at three different remediated contaminated sediment sites, Chattanooga Creek, Eagle Harbor, and the West Branch of the Grand Calumet River, to illustrate its utility at evaluating performance of *in situ* remediation. Overall, the results from laboratory and field studies suggest that SPME PDMS is a valuable tool for evaluating performance of *in situ* sediment remediation.

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Chapter 1: Introduction

BACKGROUND AND PROBLEM STATEMENT

In situ passive sampling is the use of sorbents to directly measure contaminants from the environment without first collecting a sample and using laboratory extraction and processing to separate phases. A passive sampling material for organic contaminants is a polymeric material, often held on a support or holder, that can sorb and concentrate a contaminant of interest to measurable quantities directly from the adjacent water or porewater. Passive sampling methods were developed to address the need for a reliable, cost effective, and non-labor intensive technique for the monitoring of chemical fate and transport in the environment. Passive sampling methods for air, water, soil, and sediment are available.

Passive sampling methods are based upon the use of a sorbent to accumulate the target contaminant from the water, air, or sediment interstitial or porewater. The amount of target chemical that accumulates on the sorbent, at equilibrium, is related to the amount of the target chemical in the environment; for example, the relationship between a polymer sorbent and a sediment porewater would be described by the following:

$$C_p = K_{pw} C_w \qquad \text{Eq. 1}$$

where C_p is the concentration of the target compound on the sorbent, K_{pw} is the partition coefficient between the sorbent and the pore water, and C_w is the target compound's concentration in the porewater. The focus of this dissertation is the use of passive sampling methods to determine available and mobile concentrations of hydrophobic contaminants in sediment porewater or in the water column. The method allows for low detection limits by concentrating the contaminant of interest *in situ* and, because it is controlled by a thermodynamic partitioning process, measures only the freely dissolved contaminant concentration which can

partition into other phases such as biota. In the context of sediment pore water and the water column, passive sampling does not measure contaminants that are unable to partition into the water or porewater phase and therefore it does not measure the strongly sorbed and potentially biologically unavailable contaminants. The sorbents employed have very strong affinities for hydrophobic organic contaminants (HOCs) and only a small amount of sorbent is needed to concentrate the compounds of interest to a detectable level. Hundreds of mL of water may be required to achieve sub-ng/L detection limits of HOCs by conventional techniques, but only μL of polymer sorbent may be necessary to achieve the same detection limits by passive sampling (Greenwood et al., 2009). Achieving these low detection limits, however, may require leaving the passive sampler sorbent in place for days to weeks because of the slow uptake of contaminants onto the sorbent.

Passive sampling measurements have been shown to directly correlate with the interstitial water and water column concentrations of these compounds and they provide a measurement that is often not available by other means (Allan et al., 2013; Huckins et al., 2006; Alvarez et al., 2005). In particular, the method allows measurement of extremely low concentrations of hydrophobic contaminants with high spatial resolution in sediment porewater. It is not possible to measure porewater concentration with high spatial resolution by conventional techniques due to the requirements for large volumes of water to achieve detection limits. Passive sampling methods also overcome limitations and issues associated with the use of bulk solids to ascertain contaminant availability to benthic organisms (Lu et al., 2003; Kraaij et al., 2003; Verweij et al., 2004; Vinturella et al., 2004; Cornelissen et al., 2006; Lu et al., 2006; Janssen et al., 2011; Rosen et al., 2012) and evaluate contaminant mobility after remediation (Oen et al., 2011; Lampert et al., 2013). Passive sampling measured porewater concentrations are generally well correlated

with biological measures of effects such as bioaccumulation of hydrophobic organic contaminants (Friedman et al., 2009; Lu et al., 2011). This has been observed even in organisms whose route of exposure to the contaminants is expected to be via sediment ingestion. This observation is not seen because the porewater concentration is directly relevant to water exposure, but because it is a good indicator of the contaminant availability in the bulk solids (Lu et al., 2011). Passive sampling can be an effective sediment assessment tool as it is less subject to the site and sediment specific influences that relate bulk solid concentration to exposure and effects.

The ability of passive sampling to measure low concentrations *in situ* also enables the technique to evaluate contaminant availability and mobility after remedial approaches. *In situ* sediment management approaches such as capping and *in situ* treatment are not effectively assessed by bulk solid concentrations. For example, capping often involves a nonsorptive media, like sand, that does not accumulate contaminants and therefore migration through a cap is not normally detectable by bulk solid concentrations (Lampert et al., 2013). *In situ* treatment, which normally involves the addition of sorbents to sediments, does not change bulk-solid concentrations and therefore such measures are of little use in evaluating the performance of the treatment. In both cases, however, measurements of interstitial water concentrations by passive sampling can provide measure of contaminant availability and mobility and can be used to address remedial performance.

The primary focus here is on the use of passive sampling to detect and quantify persistent hydrophobic organic compounds (HOCs) like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediment porewater using solid phase micro-extraction (SPME) coated with polydimethylsiloxane (PDMS) fibers. SPME is a partition-based, solvent

free, negligible depletion technique that surpasses conventional porewater sampling techniques unreliability at quantifying the freely dissolved contaminant concentrations, which have been correlated to bioaccumulation potential and toxicity (Paine et al., 1996; Lu et al., 2011). PDMS is commercially available as a thin coating (10-35 μm) on glass capillaries of various sizes (110-1000 μm). The cylindrical shape is convenient for insertion into sediments and the availability of thin layers with modest sorption capacity speeds equilibrium kinetics when compared to similar thicknesses of the other commonly used sorbents like polyoxymethylene (POM) and polyethylene (PE) (Lampert et al., 2015).

This dissertation's work focuses on the implementation of the SPME PDMS approach in the field under a wide range of conditions to demonstrate its applicability and to resolve current difficulties and limitations in using the approach. The overall objective of this dissertation was to extend and overcome limitations of the SPME PDMS method and demonstrate its use in remedial performance assessment.

RESEARCH OBJECTIVES

In November 2012, the Society of Environmental Toxicology and Chemistry (SETAC) held a technical workshop "Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments" composed of forty-five passive sampling experts from academia, government, and industry with backgrounds in passive sampling development and use, as well as regulatory decision making. Six journal articles were published as part of a special edition of Integrated Environmental Assessment and Management entitled "Passive Sampling Methods for Contaminated Sediment." Included in their recommendations for future work was the need for further peer-reviewed publications of *in situ* passive sampling for evaluation of contaminated sites, as well as further development of methods to address field deployments of passive

sampling methods where the passive sampling method does not reach equilibrium with the surrounding porewater (Ghosh et al., 2014). The end objective of research in this field is to obtain regulatory acceptance of passive sampling methods. To complete this goal, a bridge between academic research and practical application must be achieved (Greenburg et al., 2013).

The proposed work for this dissertation seeks to address these needs along with development of QAQC strategies to correct for key interferences to facilitate confidence in the routine use of passive sampling devices as an *in situ* technology for evaluating remedial performance. The overall objective was to demonstrate the applicability of SPME PDMS fibers for evaluation of sediment remedial performance, including protectiveness in terms of contaminant concentrations and flux. A major focus of the effort is development of techniques for assessing deviation from equilibrium and on resolving concerns about volatile losses and other potential field sampling artifacts. To achieve the overall objective, several specific objectives were investigated including: (1) demonstration of the advantages of *in situ* PDMS fibers sampling methods over conventional techniques in terms of implementation and how the results can be used to evaluate remedy performance specifically in terms of contaminant flux and bioavailability, (2) evaluation of the most appropriate methods to evaluate the kinetics of uptake onto the SPME PDMS fiber and demonstrate those techniques under field conditions, and (3) quantification of the effects of key interferences in the technique including evaporation from the PDMS layer.

Several deployments of SPME PDMS fibers were conducted at contaminated sediment sites across the USA in different environments (marine and fresh water, river and bays or harbors), to assess the ability of the SPME PDMS method to measure the availability and mobility of sediment contamination, especially in the near surface (i.e. less than 10 cm from the

sediment-water interface), the mobility of the contamination, and the performance of remediation strategies like capping or *in situ* treatment. At these sites, grab samples, and cores were collected nearby the SPME PDMS sampler. These monitoring events included both direct sediment assessments, as well as an evaluation of remedy performance and quantification of contaminant flux. A discussion of the advantages and limitations is based upon a comparison between data found using the SPME PDMS method to results attained from conventional approaches (i.e. grab samples and sediment cores). A variety of approaches were used to evaluate kinetics of uptake and fractional approach steady state during these sampling events and the different methods were compared at a historically contaminated sediment site to determine if there is a significant difference between the methods and any severe limitations to implementing these methods in situ. The effects of field conditions on kinetics of uptake, as well as, compound and sorbent specific factors were evaluated. Models of kinetic uptake based upon internal and external resistance will be compared. Key potential interferences of the techniques, including evaporation were evaluated in laboratory experiments under controlled conditions.

This dissertation's findings will lead to improved confidence in the application and interpretation of the SPME PDMS techniques and advance the ability to effectively assess contaminant availability and mobility in sediments and the performance of remedial technologies.

DISSERTATION STRUCTURE

The dissertation is divided into the following chapters:

1. a literature review that will focus on the types of contaminants found in sediments, partitioning characteristics between contaminants and sediment porewater, and strategies for monitoring contaminated sediments, with an emphasis on passive sampling strategies.

2. the development of a methodology for assessing the kinetic uptake rates of compounds in SPME PDMS fibers using performance reference compounds and an external resistance model
3. an analysis of results from an experiment designed to quantify loss due to vaporization of compounds from the SPME PDMS fibers.
4. the derivation of diffusive and advective flux models to assess the importance of diffusive-like processes (i.e. diffusion, dispersion, and bioturbation) versus advection-like processes (i.e. groundwater upwelling and particle transport) how to fit these models using performance reference compound data and concentration profiles.
5. a discussion of results from field studies conducted at Chattanooga Creek (Chattanooga, TN) and Eagle Harbor (Bainbridge Island, WA) will be presented with a focus on interpretation of contaminant profiles, comparisons to bulk solid measurements, and near surface flux.
6. a discussion of results from a multi-year field study conducted along the West Branch of the Grand Calumet River (Hammond, IN) with a focus on contaminant profile changes from the sampled years, comparisons to bulk solid measurements, and estimation of flux for remedy performance monitoring.
7. a summary of research objectives and accomplishments will be presented along with any outstanding research needs that have arisen during the course of preparing this dissertation

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Chapter 2: Literature Review

The Importance of Freely Dissolved Concentrations

Sediments are a sink for hydrophobic organic contaminants due to their highly sorptive characteristics. With the introduction of more stringent environmental regulations, sources of these toxic and even carcinogenic compounds have been reduced or even ended, which causes the historically contaminated sediment to now act as a source to the surface waters. Contaminated sediments can have a degrading impact on environmental quality and for this reason there is a focus on remediation of these contaminated sediment sites by the EPA and USACE. Due to the sorbing nature of sediments, it is hard to assess a site's risk based upon bulk solid measurements (Greenburg et al., 2013) and therefore an accurate measurement method for the freely dissolved concentrations, which control transport processes and potentially exposure and risk, in the sediment porewater is needed.

The freely dissolved concentration in the sediment porewater (C_{free}) is the aqueous concentration of chemicals not bound to particulate matter, colloids, or dissolved organic carbon (Schwarzenbach, Gshwend, and Imboden, 2003). Only a tiny fraction of hydrophobic organic contaminants, such as PAHs, PCBs, and some pesticides and insecticides, in sediment are found as freely dissolved molecules, but this fraction controls several diffusive mass transfer processes including sorption and uptake by benthic organisms. Therefore development of methods and tools to directly assess the freely dissolved concentration of these contaminants is of value for the management of contaminated sediment sites, as the freely dissolved concentration can be used as a predictor for four key endpoints of conceptual site models: toxicity, bioaccumulation, flux, and exposure (Greenberg et al., 2013).

Relationship to Chemical Activity

The freely dissolved concentration of a compound normalized by its liquid solubility is equal to its chemical activity (Schwarzenbach, Gshwend, and Imboden, 2003):

$$\alpha = \frac{C_{free}}{S_L} \quad \text{Eq. 1}$$

where α is the chemical activity, C_{free} is the freely dissolved concentration, and S_L is the liquid solubility.

The chemical activity characterizes a compound's potential for diffusive transport and partitioning (Smedes et al., 2013, Mayer et al., 2014). Differences in chemical activity between the porewater and the surface water are the driving force for transport between them. The ability to estimate transport potential and rates of hazardous contaminants from deep sediment reservoirs to a layers populated by benthic organisms and the surface water is an important part of portraying the entire picture of risk at a contaminated sediment site.

Relationship to Bioavailability and Bioaccumulation Potential

The bioaccumulation factor (BAF) is a parameter used to relate the concentrations found in organism tissue to the concentrations measured in the surrounding media (Schwarzenbach, Gshwend, and Imboden, 2003):

$$BAF = \frac{C_{organism}}{C_{media}} \quad \text{Eq. 2}$$

There are several iterations of the BAF depending on the type of organism's mode of uptake. If the mode of uptake is from the dissolved phase only via sorption through tissue, or C_{media} equals C_{free}, the BAF is equal to a bioconcentration factor (BCF). If intake of sediment particles is considered to be an organism's main route of exposure to compounds in the environment, the BAF is related to the biota-sediment factor (BSAF) where C_{media} is equal to the

concentration in the particulate phase, typically normalized by organism lipids and sediment organic carbon. For organisms that are exposed to these compounds through their diet the BAF is equal to the biomagnification factor (BMF), where C_{media} is equal to the compound's concentration in their diet. The calculation of the BAF can be complicated as there can be more than one significant route of uptake. These factors are rarely normalized by activity and thus often show increases in concentration between organisms and media while activities may stay the same or decrease between organism and the media of exposure.

Multiple studies indicate that evaluating exposure to organisms through an estimate of a biota concentration from a freely-dissolved concentration multiplied by a BAF/BCF parameter is equal to concentrations found from direct tissue analysis (Kraaij et al., 2003, Lu et al., 2003, Cornelissen et al., 2006). Bioaccumulation is typically proportional to chemical activity and not total concentration in a media (e.g. in solids) and therefore an accurate method for quantifying the freely dissolved concentration within a sediment or surface water is necessary for accurate risk assessment.

PASSIVE SAMPLING METHODS FOR MONITORING FREELY DISSOLVED CONCENTRATIONS

Development of Passive Sampling Technology and Methods

The first applications of diffusion based passive samplers were for monitoring pollutants in the air for ambient air quality and personal monitoring in the workplace (Palmes et al., 1973). Over time the methods have been accepted officially as standard methods (e.g. ASTM, EPA, NIOSH, CEN, and ISO). Passive sampling methods for monitoring water and sediment have not seen the same acceptance from the regulatory agencies at the present time.

Passive sampling methods for monitoring contaminant concentrations in surface water and sediment porewater were introduced in the 1990s with the development of semi-permeable

membrane devices (SPMDs) (Huckins et al., 1990; Huckins et al., 2006). SPMDs mimic the ability of organisms, like fish or benthic organisms, to sequester contaminants into their tissues due to the device's design of an enclosed lipid layer in a non-porous membrane (Huckins et al., 1990). Huckins et al. (1990) discussed many of the problematic features of conventional sampling methods that are still valid today including the large amounts of water necessary to obtain the same detection limit compared to passive sampling methods and sampling/handling induced changes in sample concentration (e.g. sorption of contaminant onto sampling container's walls) (Greenwood et al., 2009). While extensive amounts of literature exist for SPMDs, they are not widely used to complete monitoring activities focused on sediments. Instead, techniques based on single-phase polymeric materials, determined to have the same affinity for hydrophobic compounds as SPMDs (Rusina et al., 2007), are more extensively used in the environmental monitoring of sediment due to the slow uptake kinetics and limited spatial resolution of SPMDs. Allan et al. (2009) found that any variability of reported concentrations between SPMD and single-phase sorbent techniques is likely due to the uncertainty associated with the sorbent-water partition coefficients and kinetic uptake rates.

During the 1990s, SPME techniques were developed based on the need for expeditious sample preparation in the laboratory setting. In 1989, the first paper describing the use of fused silica optical fibers coated with liquid and solid polymeric phases to measure analyte concentration or SPME was published by Belardi and Pawliszyn (1989). Arthur and Pawliszyn (1990) presented the first SPME device where the polymer-coated silica optical fibers were incorporated into a microsyringe for easy injection into a GC. Over the years, many different configurations of polymer extracting phases and solid supports (e.g optical fiber, tube, vessel walls, suspended particles, stir bar, disk/membrane) have been explored based upon the

analytes/contaminants of concern and the environmental matrix being sampled, but the basic principles of SPME remain (Lord et al., 2000). Mayer et al. (2000) suggested a matrix-SPME technology for environmental monitoring and the current thesis is focused on methods that developed from that approach. Building upon the foundation of Arthur and Pawliszyn (1990), matrix-SPME uses the entire surrounding sediment matrix as a reservoir for extraction. Passive sampling materials for organics including SPMDs, C18 extraction disks, POM, PE, and solid-phase microextraction fibers coated with PDMS have been applied and validated as techniques for different environmental sampling applications, but until the introduction of Mayer et al.'s (2000) matrix-SPME technique, the analysis of freely dissolved contaminants in dense heterogeneous environmental matrices (e.g. sediment and soil) remained a challenge.

The three most commonly used materials for matrix-SPME monitoring HOCs in sediment: polyethylene (PE) (Allan et al., 2012), polyoxymethylene (POM) (Cornelissen et al., 2008), and polydimethylsiloxane (PDMS) (Mayer et al., 2000) provide a measurement of pore water concentration equivalents based on their respective material-water partition coefficient. The materials mentioned above are all examples of SPME but differ in their sorptive capacities and detection limits. PE and POM have larger sorptive capacities and lower detection limits, but slower kinetics than PDMS (Jonker and Koelmans, 2001).

The methods that accompany the use of passive samplers for water or sediment porewater monitoring overcome many of the drawbacks of conventional monitoring techniques that rely on discrete grabs, spot or bottle samples, or deployment of biota, such as the large volume of water required to meet analytical detection limits, the uncertainties that accompany the analysis of biota tissue or lipid extracts, and the inability to capture concentrations that vary with time or episodic releases (Vrana et al., 2005). The contaminant that accumulates in the passive sampler's

sorbent is proportional to its dissolved or freely available concentration found in the porewater or water column. The dissolved concentration of the porewater or surface can be calculated from the accumulation of the sorbent and the sorbent-water partition coefficient. Non-equilibrium exposures of the passive sampler must be corrected for the uptake or fractional extent of equilibrium to obtain an accurate porewater or water column dissolved contaminant concentration. Note that passive sampling materials can be used in *ex situ* applications as well; predominately for determining partitioning ratios, toxicity testing, and bioaccumulation studies (Ghosh et al., 2014). *In situ* passive sampling methods have distinct advantages over *ex situ* when a study's goal is evaluating conditions in the field including development of depth discrete concentration profiles, ascertaining effects of site specific transport processes (i.e. groundwater intrusion, currents, and bioturbation), avoiding laboratory processing artifacts, and obtaining actual field exposures (Ghosh et al., 2014).

NON-EQUILIBRIUM PASSIVE SAMPLING

It is important to grasp the extent of equilibrium obtained between the target analytes concentration in the environment and the passive sampler sorbent since at equilibrium the concentration found from the passive sampler sorbent is directly related to the absolute porewater concentration though the compound's sorbent-water partition coefficient:

$$C_{free} = \frac{C_{polymer}}{K_{pw}} \qquad \text{Eq. 3}$$

Compounds reach their equilibrium between the passive sampler sorbent and porewater at different rates, depending on factors such as the compound's physiochemical properties and environmental factors, therefore methods of assessing the rate of uptake are necessary. The use of performance reference compounds (PRCs) is one such method. PRCs are compounds that are

inoculated in the passive sampler before use, not found in the environment, do not interfere with analysis, and have dissipation rates inversely related to the uptake rates of the target analytes. Thus the extent of release of the PRCs can be used to infer the extent of uptake of the target analytes. Huckins et al. (1993) provides a simple first order release theory behind the use of performance reference compounds (PRCs), to estimate the extent of equilibrium achieved during a field deployment for SPMDs. Huckins et al. (2002) built upon his theoretical work of PRCs with experimental work and found no hindrances to using PRC data to take into account environmental conditions (e.g. turbulence, biofouling, etc.) so that one can model the absorption of contaminants of concern by monitoring the desorption of similar analytes (i.e. deuterated or C-13 labeled homologs). Other authors (Booij et al., 2002; Fernandez et al., 2009) expanded on the use of PRCs to single phase polymeric materials (i.e. POM, PE, and PDMS).

For sediment applications, the passive sampler initially depletes the hydrophobic organic compounds (HOCs) from the porewater which is then replenished by desorption from the adjacent solids. The passive sampler can be left in place until the passive sampler sorbent and porewater are re-equilibrated with the solids or for a shorter period of time and then the equilibrium uptake would be estimated via PRCs or another method. Typically the total mass of HOC in the passive sampler sorbent and the porewater is negligible compared to the mass on the solids and thus the method is considered non-depletive and does not disturb the initial equilibrium in the sediment if exposed for a sufficient period of time to reach equilibrium. The negligible depletion criteria is important, for if substantial depletion does occur the estimated freely-dissolved concentrations will not reflect the original conditions in the sediment (Górecki and Pawliszyn, 1997, DiFilippo and Eganhouse, 2010, Mayer et al., 2014). A general rule of

thumb for ensuring the negligible depletion criterion is met is to use a polymer sorbent mass one hundred times lower than the organic carbon mass (Mayer et al., 2014).

Two model types were introduced with the advent of SPMDs to describe the exchange between the media being sampled and the passive sampling material for HOCs: chemical reaction kinetics (CRK) model and the mass transfer coefficient (MTC) model, which differ only by their rate constant definition (Huckins et al., 2006). The CRK model is based on bioconcentration models, where the exchange of HOCs between the material and the media is described as the net result of a reversible reaction that is first-order with respect to the HOC concentration. The MTC approach is based upon mass transfer coefficients and the first-order kinetic model of solute transport through successive transport resistances: the water boundary layer, biofilm, SPMD membrane, SPMD lipid layer (Huckins et al., 2006). The CRK and MTC models provided the starting point for assessing passive sampler kinetics but, as simple first order uptake models, do not explicit account for diffusion either within or outside of the passive sampler. As passive samplers have developed and their sorbent thicknesses have been reduced in an effort to decrease the exposure time necessary to reach equilibrium, the internal transport resistances associated with the sorbent less important relative to the external transport resistances associated with solute transport from the surrounding media to the passive sampler (Lampert et al., 2015). In addition, both resistances are likely controlled by diffusion, which external to the sorbent is retarded by sorption.

In work published by Fernandez et al. (2009), a mass transfer model was developed that accounted for the external transport resistances for diffusive transport of contaminants to a PE sheet and the internal transport resistances within the polymer sheet. Although this model is an improvement over others that only first order uptake, the inverse problem to assess uptake

kinetics is more complicated than is often needed since both internal and external mass transfer resistances are considered.

In thin layers of PDMS, internal transport resistances can usually be neglected (Lampert et al., 2015). Under such conditions, the model of Fernandez et al. (2009) can be replaced with an exact solution to the retarded diffusion process in the surrounding media that controls the rate of delivery of contaminant to the passive sampler. An exact solution for retarded diffusion of HOCs from the surrounding media to a SPME PDMS fiber was derived in rectangular coordinates for the PDMS coated fibers using Carslaw and Jaeger's (1986) analogous heat conduction problem (Lampert et al., 2015).

CURRENT USE OF PASSIVE SAMPLING METHODS

Key applications of passive sampling methods include water quality monitoring (Vrana et al., 2005; Adams et al., 2007; Allan et al., 2009; Ouyang et al., 2007; Ouyang and Pawliszyn, 2007), estimating the potential for bioaccumulation (Lu et al., 2003; Kraaij et al., 2003; Verweij et al., 2004; Vinturella et al., 2004; van der War et al., 2004; Cornelissen et al., 2006; Lu et al., 2006; Friedman et al., 2009; Janssen et al., 2011; Lu et al., 2011; Rosen et al., 2012), and assessment of performance of *in situ* remedial approaches (Lampert et al., 2011; USEPA, 2012).

Use of Passive Sampling Devices for Water Quality Monitoring of HOCs

Thirty-seven of the fifty-one examples of passive sampling field applications references by Vrana et al. (2005) are uses of SPMDs for aquatic monitoring. SPMDs are the most mature application of passive sampling of organics in the environment, but their use is mainly limited to water columns and ambient air as bulky cages are necessary for deployment and limit their applicability to sediment monitoring (Vrana et al., 2005).

Evolving from the use of LDPE as the membrane for SPMDs, single phase polymeric sorbents have been implemented as monitoring devices for aquatic environments. Adams et al. (2007) described the use of PE to measure dissolved HOC concentrations in aquatic environments and reported findings in the pg/L range. Ouyang et al. (2007) completed a study in Hamilton Harbor (Ontario, Canada) using PDMS fibers to measure six target PAHs that ranged in hydrophobicity. The fibers with preloaded standards were deployed at three different depths (1 m below the surface, 11 m below the surface, and 21 m below the surface). The standards showed greater dissipation at higher depths indicating an effect of turbulence and the importance of kinetic modeling using performance reference compounds when using passive samplers for environmental monitoring.

Passive Sampling Devices as a Surrogate for Bioaccumulation Measurements of HOCs

The ultimate usefulness of passive sampling depends upon the degree to which the water or porewater concentration provides a good indication of availability to biological organisms. The accumulation of contaminants in strongly sorbing carbon phases (e.g. black carbon) often limits the usefulness of bulk solids concentration as an indicator of exposure and effects (Ghosh et al., 2003; Beckingham and Ghosh, 2013). The route of exposure, particularly for deposit feeding benthic organisms, is likely through ingestion and assimilation of solids but if a significant portion of the HOC of interest is tied up largely in phases not readily accessible by normal metabolic processes, then effects such as bioaccumulation are unlikely to be directly indicated by the bulk solid concentration. Although the route of uptake and exposure is likely not through porewater for deposit feeding organisms it is possible that measurement of the porewater concentration in equilibrium with the labile fraction of contaminant on the solid phase is a better indicator of what organisms can actually access through normal ingestion processes. As shown

below, evidence from laboratory and field studies is heavily weighted towards the freely dissolved phase of HOCs as an indicator of bioavailability. Dissolved HOC concentrations are normally at low levels and can be confounded with contaminants associated with dissolved organic matter making measuring only the bioavailable fraction a unique challenge. The use of passive sampler sorbents as a surrogate for bioaccumulation measurements using live organisms overcomes several limitations associated with standardized bioaccumulation tests, such as maintenance of the organisms under laboratory conditions and complications associated with direct measurements of tissue residues (Vinturella et al., 2004).

Several laboratory studies have demonstrated the benefits of using passive sampling methods to assess the bioavailability and bioaccumulation over bulk solid measurements and conventional porewater techniques (Vinturella et al., 2004, Sun et al., 2009, Lu et al., 2011 and Gschwend et al., 2011). Vinturella et al. (2004) used polyethylene disks in a 60 day dual exposure study with marine polycheates, *Nereis virens*. A comparison between the PAH signatures in the polycheates and the PE disks determined that the relative amounts of PAHs were similar ($r^2 = 0.56$, $p = 0.012$) and therefore the polycheates and the PE disk were sensing the HOCs in a similar way.

Sun et al. (2009) showed that passive sampler sorbents could monitor the changes in bioavailability caused by the addition of activated carbon to contaminated sediment using the freshwater oligochaete, *Lumbriculus variegatus* and POM. A linear relationship between lipid-normalized PCB congeners and porewater concentrations in the treated (slope = 0.9375, r^2 = 0.7183) and untreated (slope = 1.280, r^2 = 0.6775) sediments was found for the tetrachlorobiphenyl congener; the use of passive sampling methods was able to predict changes in the bioavailable fraction through the use of activated carbon, which also signifies the ability of

passive samplers to be used for long term monitoring of amended and capped sediment sites (Sun et al., 2009).

In Lu et al. (2011), fibers were exposed to HOC contaminated sediment during a 21 to 28 day exposure using *Ilydrilus templetoni*, a common deposit feeding organism chosen for their intense interactions with the sediment as well as lack of metabolism of the HOCs. SPME PDMS fibers were placed in the microcosms along with the benthic organisms to measure porewater concentrations. When using Anacostia River sediment, bioaccumulation in the deposit feeders was well predicted by the product of the porewater concentration and the HOC's octanol-water partition coefficient (slope = 1.08, r^2 = 0.76) (Lu et al., 2011). Another study by Lu et al. (2011) diluted New Bedford Harbor sediment with sediment from Brown Lake (Vicksburg, MS). Bioaccumulation was well-predicted for these experiments as well by the product of the porewater concentration measured with PDMS SPME fibers and the HOCs octanol-water partition coefficient (slope = 1.24, r^2 = 0.76). A study completed by Gschwend et al. (2011) using Hunter's Point (CA) sediment and the marine polychaete, *Neanthes arenaceodentata*. Bioaccumulation of PCBs was well-predicted by the product of the porewater concentrations and the HOC's octanol-water partition coefficient (slope = 1.17-2.21, r^2 = 0.7-0.76) (Gschwend et al., 2011). The range of slopes stems from the uncertainty in the estimated fraction of steady state achieved in the fiber.

Use of Passive Sampling Devices for Assessing Effectiveness of Sediment Remediation

Sediment Screening

Sediment risk screening is often accomplished using equilibrium partitioning sediment benchmarks (ESBs). ESBs are often based upon porewater concentrations predicted from bulk solid measurements and assuming linear reversible partitioning to the sediments. Screening

levels based upon the EqP model may under predict or over predict the toxicity to benthos as it does not account for reduced availability of contaminants sorbed to desorption-resistant phases (Accardi-Dey and Gschwend, 2003). In addition, statistical inferences of effects are based upon 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 upon contaminant availability at the site. Appropriate and cost-effective prioritization of sites and remedial planning is dependent upon the definition of appropriate cleanup levels that are neither overly conservative or lack any conservatism.

Site-specific ESBs have been made possible by the technological advancements in passive sampling technologies. With passive sampling, the porewater concentrations can be directly measured instead of estimation through sediment concentrations and equilibrium partitioning theory therefore eliminating error associated with different types of organic carbon being present.

Contaminated Site Evaluation and Management

Capping is a widely used *in situ* remediation containment technique for sediment sites contaminated with HOCs. Sediment caps reduce the risk posed by the fate and transport of contaminants by stabilizing the underlying sediments, physically isolating the water column from sediment contaminants, and reducing contaminant flux to the benthic organisms and water column. Evaluating performance of a placed cap is challenging, however, due to the long time frames associated with migration of hydrophobic contaminants through a cap. In addition, the non-sorbing nature of most sediment caps limits the usefulness of bulk solid phase measurements of contamination. The use of passive sampling profilers results in lower detection limits and in the ability to construct vertical concentration profiles that assist in the determination of the

mechanisms and rates of transport within a sediment cap. This approach has been used at a variety of contaminated sediment sites using POM (Cornelissen et al., 2006; Cornelissen et al., 2008; Oen et al., 2011) and PE (Fernandez et al., 2009; Oen et al., 2011; Fernandez et al., 2012), but PDMS was not as commonly used in this way until recently (Lampert et al., 2013). The results discussed by Lampert et al. (2013) showed that SPME PDMS fibers were able to quantify pore water concentrations at the Anacostia River active capping demonstration and capture migration trends of HOCs through the cap that was not indicated by looking only at the bulk solid measurements.

SUMMARY

Passive sampling is an effective methodology for assessing the freely dissolved concentration of compounds within a sediment porewater or surface water. Due to the relationship between the freely dissolved concentration of a compound and its chemical activity, passive sampling methods are then transitively an effective methodology for addressing risk as interpreted through chemical transport and bioaccumulation.

The key limitation surrounding regulatory acceptance and universal use of passive sampling methods is the lack of confidence in them by regulators and other potential users not in the academic/developer set (Parkerton & Maruya, 2013, Greenberg et al., 2013). Several actions that would increase confidence in passive sampling methods include,

1. Practical application, in addition to detailed development literature, of non-equilibrium correction methods for the *in situ* and *ex situ* use of passive samplers (Ghosh et al., 2014).
2. Peer-reviewed case-studies of passive samplers at contaminated sediment sites accessible to regulators and potential users (Greenburg et al., 2013).

3. Detailed quality assurance/quality control strategies (Mayer et al., 2014). For example, potential desorption of more volatile compounds of interest from the passive sampler's sorbent during processing.

The subsequent chapters of this dissertation address these tasks and add to the body of work supporting the use of passive sampling methods with a focus on applying passive sampling methods to evaluate remediation efforts at contaminated sediment sites.

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Chapter 3: Evaluation of Methods to Evaluate Kinetics of Contaminant Uptake[1]

ABSTRACT

To quantify the freely dissolved concentrations of contaminants in sediment when using passive sampling methods, an accurate assessment of the kinetics of contaminant uptake onto the passive sampler's sorbent layer is necessary. Methods using performance reference compounds or colocation of passive sampling materials with varying sorbent thicknesses during *in situ* and *ex situ* studies can be used to fit the external resistance model and correct for non-steady state conditions between the sorbent and porewater. An *ex situ* comparison between the correction methods resulted in the same freely dissolved concentrations as those found using conventional equilibrium based methods. The use of performance reference compounds was found to be applicable for use at capped sediment sites to assess kinetic processes. The results of the *ex situ* and *in situ* studies suggest that these correction methods provide efficient and accurate means of determining the freely dissolved porewater concentrations. A graphical user interface was created based upon the use of these correction methods and the external resistance model. The ease of using the graphical user interface supports one of SETAC's passive sampling community initiatives of the mainstream use of performance reference compounds in static *in situ* environments.

[1] Portions of this chapter have been published: Lampert, D.J., Thomas, C., Reible, D.D., 2015. Internal and external transport significance for predicting contaminant uptake rates in passive samplers. Chemosphere 119, 910-916. D.J. Lampert provided the mathematical models. C.Thomas provided the experimental/field data. D.D. Reible was the supervising professor and is the corresponding author for the publication.

INTRODUCTION

It is important to grasp the extent of equilibrium obtained between the target analytes concentration in the environment and in the passive sampler since at equilibrium the concentration found using a passive sampling material is directly related to the absolute porewater concentration or freely dissolved concentration (C_{free}) though the compound's passive sampler material-water partition coefficients (K_{pw}). An accurate estimate of C_{free} is necessary for risk assessment (i.e. comparison to water quality criteria/sediment benchmarks or bioaccumulation potential/toxicity), and determination of fate and transport mechanisms. More accurate assessments of risk and transport could potentially lead to improved management of contaminated sediment sites (Mayer et al., 2014).

Compounds reach their equilibrium between the passive sampler material and the sediment porewater at different rates, depending on factors such as the compound's physiochemical properties and environmental factors, therefore methods of assessing the rate of uptake are necessary. The use of performance reference compounds (PRCs) is one such method. PRCs are not found in the environment, do not interfere with analysis, and have dissipation rates inversely related to the uptake rates of the target analytes. Deuterated PAHs or C13-labelled PCBs are examples of compounds used as hydrophobic organic compound (HOC) PRCs. Huckins et al. (1993) provided the theory behind the use of performance reference compounds (PRCs), to estimate the extent of equilibrium achieved during a field deployment for semipermeable membrane devices (SPMDs). Huckins et al. (2002) built upon his theoretical work of PRCs with experimental work and found no hindrances to using PRC data to take into account environmental conditions (e.g. turbulence, biofouling, etc.) so that one can model the adsorption of contaminants of concern by monitoring the desorption of similar analytes (e.g.

deuterated or C-13 labeled homologs). Other authors (Booij et al., 2002; Fernandez et al., 2009) expanded on the use of PRCs to single phase polymeric passive samplers (i.e. POM, PE, and PDMS). Burgess et al. (2013) demonstrated that PCB concentrations corrected to equilibrium using deuterated PAHs and C-13 labeled PCBs were not significantly different and therefore deuterated PAHs, the less expensive option for PRCs, can be used even when contaminants of concern are not PAHs.

For sediment applications, the passive sampler initially depletes the HOCs from the porewater, which are then replenished by desorption from the adjacent solids. The passive sampler can be left in place until the passive sampler sorbent and porewater are re-equilibrated with the solids or for a shorter period of time for which equilibrium uptake would be estimated via PRCs or another method. For *in situ* deployments of passive samplers, typically the total mass of HOC in the passive sampler and the porewater is negligible compared to the mass on the solids and thus the method is considered non-depletive and does not disturb the initial equilibrium in the sediment if exposed for a sufficient period of time to reach equilibrium. Uptake of HOCs to the passive sampler follows the trend presented in Figure 3-1. Ideally, desorption of the PRCs from the passive sampler is inversely related to the uptake of the compounds of interest as presented in Figure 3-1.

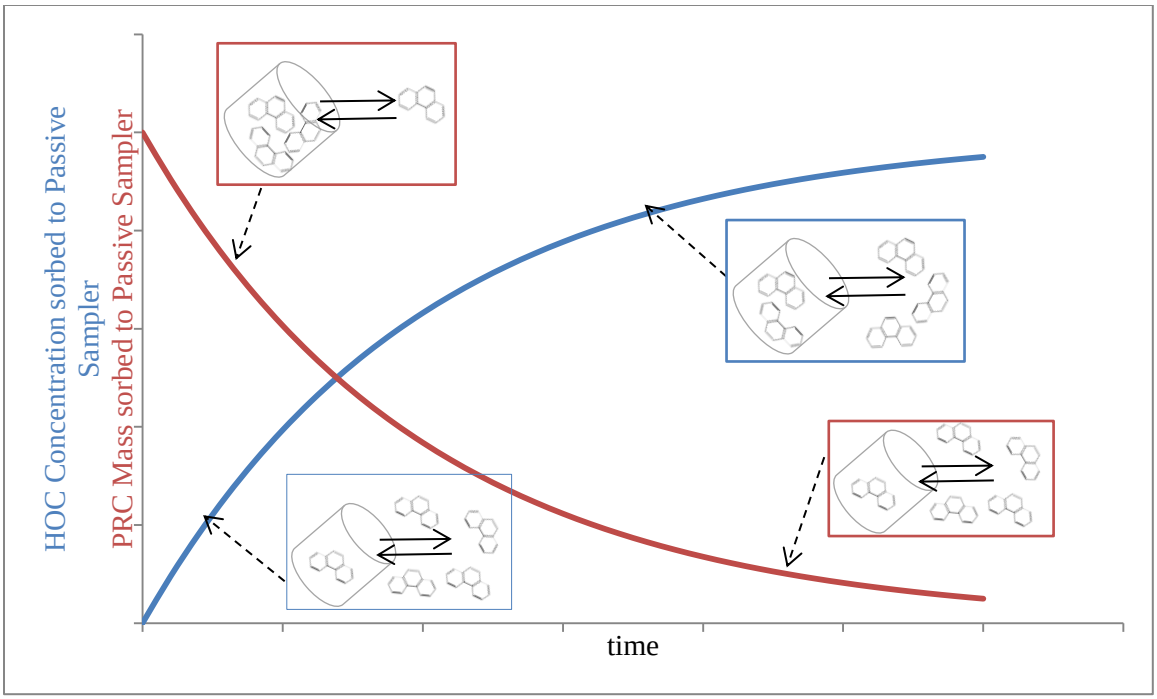


Figure 3-1. Uptake of a hydrophilic organic contaminant by a passive sampler over time.

Mathematical models of uptake

First Order Methods

Two first order model types were introduced with the advent of SPMDs to describe the exchange between the media being sampled and the passive sampling material for HOCs: chemical reaction kinetics (CRK) model and the mass transfer coefficient (MTC) model, which differ only by their rate constant definition (Huckins et al., 2006). The CRK model is based on bioconcentration models, where the exchange of HOCs between the passive sampler and the media is described as the net result of a reversible reaction that is first-order with respect to the HOC concentration. The exchange is mathematically represented as:

$$\frac{dC_p}{dt} = k_u C_w - k_e C_p \qquad \text{Eq. 1}$$

where C_w is the aqueous concentration, k_u is the rate constant for the forward or uptake process, k_e is the rate constant for the backward or release process, and C_p is the passive sampler concentration. Solving for C_p with the initial conditions of $C_p = 0$ at time zero results in the following:

$$C_p = K_{pw} C_w \left(1 - \exp\left(-k_e t\right)\right) \qquad \text{Eq. 2}$$

where K_{pw} is equal to k_u/k_e.

The MTC approach is based upon mass transfer coefficients and the first-order kinetic model of solute transport through successive transport resistances: the water boundary layer, biofilm, SPMD membrane, SPMD lipid layer (Huckins et al., 2006). Huckins et al. (2002, 2006) details the derivation of the following overall solute flux equation for SPMDs assuming the fluxes between the different transport resistance zones are linearly proportional to the concentration gradient through the zone and are all equal:

$$j = k_o \left(C_w - \frac{C_p}{K_{pw}} \right) \qquad \text{Eq. 3}$$

where C_p is the passive sampler concentration, K_{pw} is the passive sampler-water partition coefficient, and k_o is the overall mass transfer coefficient or overall conductivity. The concentration uptake in the passive sampler can be formulated as:

$$\frac{dC_w}{dt} = \frac{Aj}{V_s} = \frac{Ak_o}{V_s} \left(C_w - \frac{C_p}{K_{pw}} \right) \qquad \text{Eq. 4}$$

where A is the passive sampler's surface area and V_s is the passive sampler's volume. Solving for C_p with the initial condition of C_p equal to zero at time zero results in the same equation derived using the CRK Model (Equation 2). For the MTC Model,

$$k_e = \frac{Ak_o}{V_s K_{pw}}$$ Eq. 5

The MTC model, as developed in this manner, has the advantage of incorporating the physical dimensions of the passive sampler and therefore can be used to differentiate between two passive samplers of different dimensions (e.g. different surface area to volume ratios). The CRK and MTC Models both show that the concentration in the passive sampler gradually increases in time. When $k_e t >> 1$, the model reduces to $C_p = K_{pw} C_w$. If the passive sampler is exposed for only a short amount of time or is used for sampling highly hydrophobic contaminants, $k_e t << 1$ and the passive sampler's uptake is approximately equal to

$$C_p = K_{pw} C_w k_e t$$ Eq. 6

The amount of analyte found sorbed to the passive sampler can be defined as

$$M = V_p K_{pw} k_e C_w t$$ Eq. 7

where the apparent sampling rate of the passive sampler (R_p) is equal to the product of the passive sampler's volume (V_p), the partition coefficient (K_{pw}), and the rate constant describing release from the sampler (k_e). Defining the problem in terms of sampling rates provides a link between classical batch extraction techniques and passive sampling (Huckins et al., 2006). The amount of analyte absorbed after an exposure in terms of R_p is given by:

$$M = V_p K_{pw} C_w \left(1 - \exp\left(\frac{-R_p t}{V_p K_{pw}}\right)\right)$$ Eq. 8

From this equation the aqueous concentration can be determined. A convenient method to assessing k_e is to spike performance reference compounds, innocuous compounds not found or not in substantial quantities in the environment, into the passive sampler. Deuterated or C13-labelled compounds are widely used as PRCs (Booij et al., 2002; Fernandez et al., 2009; Ghosh et al., 2014). The dissipation of the PRCs is given by

$$N = N_0 \exp(-k_e t) \quad \text{Eq. 9}$$

If N_0, the initial mass of PRC sorbed to the material, and N, the remaining mass of PRC after exposure, are both known quantities, the equation can be solved for k_e. Several authors have shown the validity of using PRCs to assess kinetic uptake rates in materials (Huckins et. al, 2002; Booji et. al, 2002; Ellis et. al, 2008; Allen et. al, 2009; Allen et. al, 2010).

The CRK and MTC models provided the starting point for assessing passive sampler kinetics, but as simple first order uptake models, they do not explicitly account for diffusion either within or outside of the passive sampler. As passive samplers have developed and their sorbent thicknesses have become thinner in an effort to decrease the exposure time necessary to reach equilibrium, the internal transport resistances associated with the sorbent have become less important relative to the external transport resistances associated with solute transport from the surrounding media to the PSM (Lampert et al., 2015). In addition, both resistances are likely controlled by diffusion, which external to the sorbent is retarded by sorption.

Dual Resistance Model

In the quasi-static conditions of sediments, a more appropriate model may be a diffusion based. In many cases, the desorption and diffusion or diffusion-like transport in the surrounding media controls (i.e. external mass transfer resistance) controls uptake into the passive sampler. In some cases, internal resistances (i.e. resistances within the polymer sorbent) may be important. In work published by Fernandez et al. (2009), a mass transfer model was developed that accounted for the external transport resistances for diffusive transport of contaminants to a PE sheet and the internal transport resistances within the polymer sheet. Although this model is an improvement over others that only include first order uptake, the dual resistance model (DRM)

that is extended to both internal and external mass transfer resistances to assess uptake kinetics is more complicated and requires more sophisticated evaluation than is often needed. On the other hand, it is representative of the most general condition of passive samplers in sediments likely to be encountered. The model considers diffusion for a system containing a finite passive sampler with a thickness 2L and a semi-infinite environmental matrix surrounding the passive sampler. The model is based upon Fick's second law:

$$\frac{\partial C_p}{\partial t} = \frac{D_p \partial^2 C_p}{\partial x^2} \qquad -L < x < L \qquad \text{Eq. 10}$$

$$\frac{\partial C_w}{\partial t} = \frac{D_s \partial^2 C_w}{\partial x^2} \qquad x < -L \; and \; x > L \qquad \text{Eq. 11}$$

where C_p and C_w are concentrations sorbed to the passive sampler and in the surrounding water, respectively, D_p and D_s are the diffusivities for the passive sampler and the surrounding environmental matrix (e.g sediment porewater), respectively. For completely saturated sediment, D_s describes molecular diffusion through the porewater retarded by sorption/desorption with the sediment bed particles. The sorption/desorption process from solids is assumed to be much faster than the diffusion through the sediment bed. At the passive sampler-environmental matrix interface, equilibrium partitioning theory is assumed valid,

$$\frac{C_p}{C_w} = K_{pw} \; at \; x = L \; and \; x = -L \; for \; t > 0 \qquad \text{Eq. 12}$$

and the flux into and out of the environmental matrix are set equal

$$D_p \frac{dC_p}{dx} = D_s \frac{dC_w}{dx} \quad at \; x = L \; and \; x = -L \qquad \text{Eq. 13}$$

The following boundary condition and initial conditions also apply for the compound,

$$\frac{dC_w}{dx} = 0 \; for \; x = \infty \; and \; x = -\infty \qquad \text{Eq. 14}$$

$$C_w(x, t=0) = C_{w,0} \text{ for } x > L \text{ and } x < -L \quad \text{Eq. 15}$$

$$C_p(x, t=0) = 0 \text{ for } -L < x < L \quad \text{Eq. 16}$$

If modeling the PRC desorption from the passive sampler, the following initial conditions are applied instead of the ones described above,

$$C_w(x, t=0) = 0 \text{ for } x > L \text{ and } x < -L. \quad \text{Eq. 17}$$

$$C_p(x, t=0) = C_{PRC,0} \text{ for } -L < x < L \quad \text{Eq. 18}$$

No closed form analytical solution exists for the finite thickness polymer sorbent. Fernandez et al. (2009) presented the following method for determining the fraction of equilibrium obtained over a defined period of time. The fraction of equilibrium obtained for the native contaminant accumulated in the polymer sheet and the PRC fraction remaining in the polymer sheet is described by integrating their Laplace domain concentrations over the polymer sheet:

$$M_C = \frac{\sqrt{\Psi}}{s^{\frac{3}{2}}(K_{pw} + \sqrt{\Psi}\coth(\sqrt{s}))} \quad \text{Eq. 19}$$

where M_C is the mass of the compound of interest in the porewater measured during a given deployment period normalized by the equilibrium mass of the compound within the Laplace domain, s is the dimensionless Laplace parameter based upon the dimensionless time variable ($T = \frac{tD_p}{L^2}$), and Ψ is equal to the ratio of the diffusion coefficients ($\Psi = \frac{D_s}{D_p}$).

$$\hat{M}_{PRC} = (\frac{1}{s} - \hat{M}_C) \quad \text{Eq. 20}$$

where $\hat{M}_{PRC}$ is the mass of the PRC remaining in the polymer after a given deployment period normalized by the initial PRC concentration spiked into the polymer. The Laplace domain solution can be transferred back into the time domain using the de Hoog numerical inversion algorithm (Hollenbeck et al., 1999). Ψ and K_{pw} are both functions of K_d, the sorption coefficient divided by the bulk density of the sediment, and can be reinterpreted as the following:

$$\Psi = \frac{D_s}{D_p} = \frac{D_w}{(1+r_{sw}K_d)\tau D_p} \quad \text{Eq. 21}$$

where D_w is the contaminant's diffusivity in water, r_{sw} is the volume ratio of whole sediment to water calculated by 1/n where n is the porosity of the sediment, τ is the tortuosity calculated by 1-ln(n^2). Using this model, a family of curves can be produced for values of K_d by solving this equation for various values of T. The appropriate K_d value for the PRCs used can be determined by locating the intersection of the fraction of PRC remaining in the polymer and the nondimensionalized time of the deployment (T). It is usually valid to assume a relationship between logK_d and logK_{ow} within a given compound class, therefore with at least two PRC K_d data points, we can estimate the remaining K_d values for the native contaminants under scrutiny. The K_d values for the native contaminants can be used to find the contaminant's Ψ and K_{pw} and subsequently M_C by inverting M_C. The porewater concentration is calculated by the following:

$$C_w = \frac{C_p}{K_{pw}M_C} \quad \text{Eq. 22}$$

External Resistance Only Model

An exact solution for diffusion of HOCs to passive sampling material assuming that transport external to the material controls uptake was derived by Lampert et al. (2015) using Carslaw and Jaeger's (1986) analogous heat conduction problem. Lampert et al. (2015) showed that at least for a thin layer of PDMS on a glass cylindrical core, external transport is most likely

to control uptake due to relatively high internal diffusion rates and the relatively high surface area to volume ratios, a thin thickness, normally used. For the derivation, the geometry of the passive sampler was assumed locally flat with symmetry conditions at x=0. For passive sampling materials with both sides exposed (e.g. a rectangular layer of POM), the x=0 point represents the centerplane of the sorbent layer. For a thin layer of PDMS on a cylindrical glass core, this assumption applies to the entire PDMS layer as long as the volume to area ratio of the fiber is approximately given by its thickness (thickness <<< diameter of the glass core). The following initial and boundary conditions apply:

$$K_{pw}L\frac{\partial C_p}{\partial t} = D\frac{\partial C_p}{\partial x} \; at \; x = 0 \qquad \text{Eq. 23}$$

$$\frac{\partial C_w}{\partial x} = 0 \; for \; x \to \infty \qquad \text{Eq. 24}$$

$$C_w(x, t = 0) = C_{w,0} \; for \; t = 0 \qquad \text{Eq. 25}$$

The exact solution is given by:

$$C(x,t) = K_{pw}C_{w,0}\left[1 - \exp\left(\frac{Rx}{K_{pw}L} + \frac{RDt}{L^2K_{pw}^2}\right)erfc\left(\frac{\sqrt{R}x}{\sqrt{4Dt}} + \frac{\sqrt{RDt}}{LK_{pw}}\right)\right] \qquad \text{Eq. 26}$$

and the mass adsorbed onto the PDMS fiber at x = 0 over time is given by:

$$M(t) = K_{pw}C_{w,0}L\left[1 - \exp\left(\frac{RDt}{L^2K_{pw}^2}\right)erfc\left(\frac{\sqrt{RDt}}{LK_{pw}}\right)\right] \qquad \text{Eq. 27}$$

Where C_p is the concentration measured using the passive sampler, L is the effective thickness of the passive sampler that is equal to the surface volume to area ratio and RD represents an effective transport parameter describing transport in the surrounding sediment. The entire bracketed term represents the extent of equilibrium, f_{ss}. The fraction of equilibrium can be

determined for specific compounds using either performance reference compounds or by using different sizes of passive sampling materials or difference exposure periods and then extrapolating to other compounds based upon a model. R is a retardation factor associate with sorption on the sediments and should be proportional to the hydrophobicity of the compound of interest, e.g. K_{ow}. D represents the diffusion coefficient in the sediment matrix which could be due to molecular diffusion in the porespace, or effective diffusion driven by a combination of advection and dispersion or tidal fluctuations or bioturbation. Since these processes are not normally known with precision, the product RD can be determined through the use of PRCs.

The use of this model to describe uptake kinetics onto a passive sampler using PRCs is described by Lampert et al. (2015). Assuming the control of uptake in a thin film surrounded by sediment with diffusion controlled transport is dominated by external mass transfer resistances, the fraction of PRC mass remaining after deployment is modeled by the following equation:

$$\frac{M(t)}{M_0} = \exp\left(\frac{RDt}{L^2 K_{pw}^2}\right) erfc\left(\frac{\sqrt{RDt}}{LK_{pw}}\right) \qquad \text{Eq. 28}$$

where M(t) is equal to the PRC mass remaining after a given time, M_0 is the initial PRC mass, R is the retardation factor, D is the effective diffusion coefficient, L is the effective thickness of the passive sampler that is equal to the surface volume to area ratio, and *erfc* represents the complementary error function, which is a tabulated function that can be found in mathematical reference texts and is also available function in Microsoft® Excel and other numerical languages. All other parameters have been previously defined. The only unknown parameter in the equation is the product of the retardation factor (R) and the effective diffusion coefficient (D).

Fitting of Model Parameters

Three approaches are available to estimate the RD parameter and ultimately each compound of interest's fraction of equilibrium achieved:

- retrieval of passive samplers in a time series to achieve sufficient samples to demonstrate equilibrium or to fit a model allowing an estimation of the extent of equilibrium,
- retrieval of two different types or thicknesses of passive samplers that have intrinsically different kinetics and use a model incorporating those differences to estimate the extent of equilibrium,
- use of performance reference compounds (PRCs) to estimate the extent of equilibrium

While a time series is possible in the laboratory, it is not normally convenient in the field and it is often unclear whether a time series is monitoring changing conditions, spatial variability, or a true approach to equilibrium. The use of two different types or thicknesses of passive samplers requires reliable measurements of the differences between the uptake of the different passive samplers and essentially doubles the amount of samples that must be analyzed. The use of PRCs when applied often represents the best estimate of uptake kinetics (Huckins et. al, 2002; Booji et. al, 2002; Ellis et. al, 2008; Allen et. al, 2009; Allen et. al, 2010). Its accuracy depends upon the degree to which the retarded diffusion of the selected PRC matches the retarded diffusion of the compound of interest within the sediment bed or capping layer (Apell and Gschwend, 2014). Deuterated or C13 labeled variants of the specific compound of interest are often best.

With the exception of direct evaluation of the approach to equilibrium with a time-series of samples, the interpretation of the extent of equilibrium depends upon the model of the uptake of the target compound. The most appropriate model for static sediment conditions where desorption and diffusion in the porespace likely control uptake on the passive sampler is a diffusion based model like those outlined by Fernandez et al. (2009) and Lampert et al. (2015). The Fernandez et al. (2009) approach is more rigorous than the Lampert et al. (2015) approach outlined above and involves more parameters than the single parameter estimation approach, but has the advantage that it can explicitly deal with internal mass transfer resistances. In general, the approach of Lampert et al. (2015) should provide satisfactory results since the transport parameter RD is fit to data and can implicitly incorporate the effects of internal mass transfer resistances and transient desorption in the surrounding sediments by estimating an "effective" transport parameter even if internal mass transfer resistances are not explicitly included in the model.

Calculation of the absolute porewater concentration

Accurate measurements of pore water concentrations are dependent on the ability to achieve equilibrium uptake in the passive sampling material or to extrapolate from the actual uptake to equilibrium using a known fractional extent of equilibrium achieved during a given deployment length. The time required to reach equilibrium is difficult to predict for field conditions and could be lengthy for highly hydrophobic contaminants. As discussed above, the kinetics of uptake are dependent upon the sediment and external transport processes and there are several different methods that can be applied to quantify the uptake kinetics and the fraction of equilibrium achieved. If the passive sampling sorbent has not reached equilibrium with the surrounding pore water, the absolute pore water concentration (C_w) is found using:

$$C_w = \frac{C_p}{f_{ss} K_{pw}} \quad \text{Eq. 29}$$

Where C_p is the concentration measured using the passive sampler and f_{ss} is the fraction of equilibrium achieved during deployment. The fraction of equilibrium can be determined for specific compounds using PRCs or by using different sizes of passive sampling materials or difference exposure periods and then extrapolating to other compounds based upon a model.

Using the dissipation of PRC mass from the passive sampling material, it is possible to estimate the uptake of the non-deuterated analogues. At equilibrium, the PRCs' concentrations on the material will approach zero and the remaining mass provides information regarding the extent of equilibrium achieved during the deployment period. Several difficulties associated with this method include: the cost and commercial availability of deuterated or C13 labelled compounds limits the number of PRCs that can be used for an exposure and the ability to identify compounds not present or in low concentrations in the sediment. In addition, both sorption and desorption must be linear, first order, reversible processes; this could be violated in sediments with high concentrations or containing strongly sorbing phases (e.g. activated carbon).

Applying the external resistance model described by Lampert et al. (2015), the fraction of PRC mass remaining sorbed to the PDMS layer, the passive sampling material of choice for our bench-scale experiments and *in situ* studies, after deployment is modeled by the following equation:

$$\frac{M(t)}{M_0} = \exp\left(\frac{RDt}{L^2 K_{PDMS-W}^2}\right) erfc\left(\frac{\sqrt{RDt}}{LK_{PDMS-W}}\right) \quad \text{Eq. 30}$$

where M(t) is equal to the PRC mass remaining after a given time, M_0 is the initial PRC mass on the fiber, R is the retardation factor, D is the effective diffusion coefficient, L is the effective

thickness of the PDMS layer that is equal to the surface volume to area ratio, and *erfc* represents the complementary error function, which is a tabulated function that can be found in mathematical reference texts and is also available function in Microsoft® Excel for Windows™ and other numerical languages. All other parameters have been previously defined. The only unknown parameter is the product RD. Knowing the fraction of PRC mass remaining, an RD consistent with the exposure time can be determined. The RD values for each PRC can be plotted against K_{ow}, an indicator of hydrophobicity:

$$\log RD = \alpha \log K_{ow} + \beta \qquad \text{Eq. 31}$$

Where α and β are site-specific parameters independent of compound. The retardation factor (R) is normally expected to be linearly dependent upon K_{ow}, while the effective diffusion coefficient is only weakly dependent upon a compound's hydrophobicity. A plot of logRD versus logK_{ow} is expected to be linear and the linear best fit curve can be used to estimate RD for compounds over the range of K_{ow}. Note that a linear relationship between logRD and logK_{ow} is not expected if the primary mechanism of contaminant transport is not diffusion, but rather particle-related transport (e.g. bioturbation). In cases such as these, RD would be expected to be independent of K_{ow} ($\alpha \approx 0$). The estimated RD values can be used in the following equation to determine the fraction of equilibrium achieved during a deployment period:

$$f_{ss} = 1 - \exp\left(\frac{RDt}{L^2 K_{PDMS-W}^2}\right) erfc\left(\frac{\sqrt{RDt}}{LK_{PDMS-W}}\right) \qquad \text{Eq. 32}$$

Additional methods for estimating the extent of equilibrium achieved during the deployment period include comparing fibers with the same PDMS thickness at two different times or the use of two collocated fibers with different PDMS thicknesses deployed for the same length of time (or multiple coating thickness (MCT) method). RD can be estimated using a

nonlinear root finding function or by trial and error knowing the ratio of the concentrations measured in the two different thicknesses of PDMS or at the two different times. The ratio of the mass measured in the two different fiber thicknesses is modeled by the following equation:

$$\frac{M(L_1,t)}{M(L_2,t)} = \frac{1-\exp\left(\frac{RDt}{L_1^2 K_{PDMS-W}^2}\right) erfc\left(\frac{\sqrt{RDt}}{L_1 K_{PDMS-W}}\right)}{1-\exp\left(\frac{RDt}{L_2^2 K_{PDMS-W}^2}\right) erfc\left(\frac{\sqrt{RDt}}{L_2 K_{PDMS-W}}\right)} \quad \text{Eq. 33}$$

The difference when using two different exposure times is that the thickness of the fiber, L, will be held constant and the exposure time will change. In contrast to PRC method, this approach has no additional analytical complexity and data from compounds over the entire range of hydrophobicity in question can calibrate the model.

This chapter summarizes the applicability of using the PRC method and the MCT method to evaluate the kinetic parameter RD that is needed to determine the fraction of steady state achieved during a deployment period. Results from an *ex situ* study regarding the applicability of using these correction methods to accurately quantify the freely dissolved porewater concentration are presented, along with an example of how these methods can be employed in the field. Details regarding the time necessary to achieve substantial depletion of PRCs from the spiking solution and the ideal ratio of the spiking solution solvents (methanol and water) to achieve uniform sorption are also included. Additionally, Appendix A contains the MATLAB graphical user interface (GUI) code that allows users of the GUI to implement the calculations for determining RD and f_{ss} for inputs of PDMS (or other PSM) thickness, length of deployment, and a set of PRCs.

MATERIALS & METHODS

Sorption of PRCs onto a thin layer of PDMS

The uptake of PRCs onto a 25 μm or 100 μm thick PDMS layer was assessed in a series of laboratory experiments regarding both time necessary to have sufficient uptake of PRCs from a spiking solution as well as the ideal makeup of the spiking solution solvent ratio to obtain uniform uptake of the PRCs. The SPME PDMS fibers were purchased from Polymicro Technologies (Phoenix, AZ). Sorption to the PDMS fibers was monitored over time in a series of experiments in sealed glass vials with Teflon-lined caps. The PDMS fibers tumbled in solutions based in 100/0, 80/20, 50/50, 20/80, or 0/100 v/v fractions of methanol to water spiked with 25 μL of a 100 mg/L deuterated PAH cocktail for 1, 4, 8, 14, 28 or 60 days. Samples of the spiking solution were taken at the time of spiking the fibers (day 0) and then at each time point when fibers were sampled. The cocktail purchased from Absolute Standards contained the following deuterated PAHs (dPAHs):

- Anthracene-d10
- Benzo(a)anthracene-d12
- Benzo(b)fluoranthene-d12
- Benzo(k)fluoranthene-d12
- Benzo(g,h,i)perylene-d12
- Benzo(a)pyrene-d12
- Chrysene-d12
- Dibenzo(a,h)anthracene-d14
- Fluoranthene-d10
- Indeno(1,2,3-cd)pyrene-d12

- Naphthalene-d8
- Phenanthrene-d10

After each time point was reached, the fibers were sectioned into five 2-cm segments and placed in 250 μL of acetonitrile for extraction. 25 μL of the extracts were analyzed using Agilent Technologies 1260 Infinity (Santa Clara, CA, USA) High Performance Liquid Chromatography (HPLC) with an ultraviolet-diode array (1260 DAD VL+) and fluorescence detector (1260 FLD Spectra) based upon EPA standard method 8310 in the SW846 series. The Phenomenex (Torrance, CA, USA) Luna 5μ C18 column (250 x 4.6 mm) used during the analysis was maintained 40°C. The HPLC is operated under isocratic conditions. The flow rate through the system is 1.0 mL/min at a water to acetonitrile ratio (v:v) of 3:7. For every ten samples analyzed, a 10 μg/L or 25 μg/L standard (Absolute Standards) containing dPAHs was analyzed to check proper running of the instrument. Standards ranging in concentrations from 0.1 μg/L to 250 μg/L were used to determine each compound's response factor.

Performance evaluation of PRC and MCT methods

The applicability of using PRC and MCT methods to evaluate the kinetic parameter, RD, needed to determine the fraction of steady state achieved during an experimental/deployment period, was tested by comparing the porewater concentrations found using PRC and MCT methods to those determined by using conventional equilibrium passive sampling techniques during an ex situ study. Both the PRC and MCT methods were also used during an *in situ* study at a capped contaminated sediment site to demonstrate the applicability of these two methods at assessing field conditions.

Fluoranthene-d10, chrysene-d12, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were selected as PRCs to cover a wide range of hydrophobicities. Stock solutions of fluoranthene-d10, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were purchased from Cambridge Isotope Laboratories. A stock solution of chrysene-12 was purchased from UltraScientific Analytical Solutions. The deuterated PAHs were selected as PRCs based on their lack of interference with their non-deuterated counterparts during analysis and their hydrophobicities mirrored the range of hydrophobicities in the target compounds, PAH_{16}. Fibers were placed in contact with a spiking solution containing the four PRCs and placed on an orbital shaker for ten days. Glass fibers with a core diameter measuring 500 μm coated with a 25 μm PDMS layer (Polymicro Technologies (Phoenix, AZ)) were used in addition to glass fibers with a core diameter measuring 210 μm coated with a 10 μm PDMS layer (Fiberguide (Stirling, NJ).

Three different sediments from the Netherlands were used: Sediment BB (f_{oc} = 4.29 ± 0.07), Sediment FD (f_{oc} = 2.31 ± 0.14), and Sediment SP (f_{oc} = 1.4 ± 0.1). Two 2 cm segments of each fiber dimension were placed in approximately 20 grams of sediment. The experiment was completed in replicate with five replicates per sediment. The vials containing the sediment and SPME PDMS fiber were placed on an orbital shaker (100 rpm) for the duration of the experiment. After 20 days, one segment of each 1060/1000 μm and 230/210 μm SPME PDMS fiber was removed and wiped with a DI water dampened lint free tissue to remove any particulate matter. After 42 days, the remaining segment of each fiber dimension was removed from their respective sediments and wiped with a DI water dampened lint free tissue to remove any particulate matter before extraction. Each 2 cm segment of the 550/500 μm fiber was placed in 250 μL of acetonitrile, while each 2 cm segment of the 230/210 μm fiber was placed in 150 μL of acetonitrile.

All extracts were analyzed using Agilent Technologies 1260 Infinity (Santa Clara, CA, USA) High Performance Liquid Chromatography (HPLC) with an ultraviolet-diode array (1260 DAD VL+) and fluorescence detector (1260 FLD Spectra) based upon EPA standard method 8310 in the SW846 series. The Phenomenex (Torrance, CA, USA) Luna 5µ C18 column (250 x 4.6 mm) used during the analysis was maintained 40°C. The HPLC is operated under isocratic conditions. The flow rate through the system is 1.0 mL/min at a water to acetonitrile ratio (v:v) of 3:7. For every ten samples analyzed, a 10 µg/L or 25 µg/L standard containing dPAHs was analyzed to check proper running of the instrument. Standards ranging in concentrations from 0.1 µg/L to 250 µg/L were used to determine each compound's response factor.

Applicability of PRC and MCT methods for *in situ* evaluation of capped sediments

Fluoranthene-d10, chrysene-d12, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were selected as PRCs to cover a wide range of hydrophobicities. Stock solutions of fluoranthene-d10, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were purchased from Cambridge Isotope Laboratories. A stock solution of chrysene-12 was purchased from UltraScientific Analytical Solutions. The deuterated PAHs were selected as PRCs based on their lack of interference with their non-deuterated counterparts during analysis and their hydrophobicities mirrored the range of hydrophobicities in the target compounds, PAH_{16}. Fibers were placed in contact with a spiking solution containing the four PRCs and placed on an orbital shaker for seven days. Glass fibers with a 10 µm or 25-30 µm PDMS coating used during this study were manufactured by Fiberguide (Stirling, NJ) or by Polymicro Technologies (Phoenix, AZ), respectively.

Before spiking (1060/1000 µm (outer/inner diameter)) or deployment (230/210 µm), the fibers were sequentially soaked in hexane, acetonitrile and Millipore water for cleaning. A

stainless steel rod with two 30 cm grooves was used to deploy the SPME PDMS fibers. One 1060/1000 μm fiber, pre-spiked with the four deuterated PRCs, was loaded in one of the rod's grooves and secured with silica sealant. Two 230/210 μm fibers were secured in the rod's other groove using silica sealant. The sampler rods were inserted perpendicular to the sediment surface at Chattanooga Creek. The samplers were deployed at a total of seven locations along a 2.5 mile stretch of the creek bed previously contaminated from a coal carbonization facility to explore the different sediment conditions of the site including uncapped, sand cap, and amended cap (AquaBlok®) portions of the creek. The deployment at Chattanooga Creek lasted for 14 days. After removal from the sediment, sediment particles were removed from the 1060/1000 μm and 230/210 μm fibers using a damp lint free tissue. The 1060/1000 μm fibers were then sectioned into 2-cm segments and placed in 250 μL of acetonitrile for extraction. The 230/210 μm fibers were sectioned into eight 1-cm segments and all eight segments were placed in 100 μL of acetonitrile for extraction.

All extracts from the *in situ* study were analyzed using Waters 2795 High Performance Liquid Chromatography (HPLC) according to EPA Method 8310. The column temperature was held at 40°C. Ultraviolet (UV) and fluorescence (FLD) detectors are used to quantify the EPA's 16 priority PAHs. The separation occurs using a 1.0 mL/min isocratic flow composed of 3:7 (v:v) water:acetonitrile. For every 10 samples analyzed, a 5 or 20 μg/L standard (UltraScientific) containing 16 PAHs and a 10 or 25 μg/L standard containing the four deuterated PAHs was analyzed to check proper running of the instrument. Standards ranging in concentrations from 0.05 μg/L to 100 μg/L were used to determine each compound's response factor.

RESULTS & DISCUSSION

Sorption of PRCs onto thin layer of PDMS

The amount of PRC sorbed to the PDMS increased over time for PDMS fibers tumbled in 50/50, 20/80, and 0/100 v/v methanol/water solutions. The PRC concentrations derived from PDMS fibers immersed in 100/0 and 80/20 v/v methanol/water solutions were non-detectable for all time points. The rate the PRCs were absorbed to the PDMS later depended on their hydrophobicity and indicated by their K_{ow}. For example, naphthalene-d8 ($logK_{ow}$ = 3.41) reached a steady state, indicated by negligible change in concentration at subsequent time points, between the PDMS layer and all the different solutions within 4 days. On the other hand, dibenz(a,h)anthracene-d14 ($logK_{ow}$ = 7.39) reached a steady state after 4, 8, and 14 days with the 50/50, 20/80, and 0/100 v/v methanol/water solution, respectively.

Figures 3-2 through 3-6 show the change in concentration over time for five dPAHs (naphthalene-d8 ($logK_{ow}$ = 3.41), anthracene-d10 ($logK_{ow}$ = 4.69), chrysene-d12 ($logK_{ow}$ = 5.9), benzo(k)fluoranthene-d12 ($logK_{ow}$ = 6.5), and dibenz(a,h)anthracene-d14 ($logK_{ow}$ = 7.39)) onto a PDMS layer (25 μm or 100 μm) to show how the differences in hydrophobicity of these compounds and the use of methanol in the spiking solution effects the amount of each PRC sorbing to the PDMS layer and the amount of time to reach a steady-state between the PDMS layer and the spiking solution.

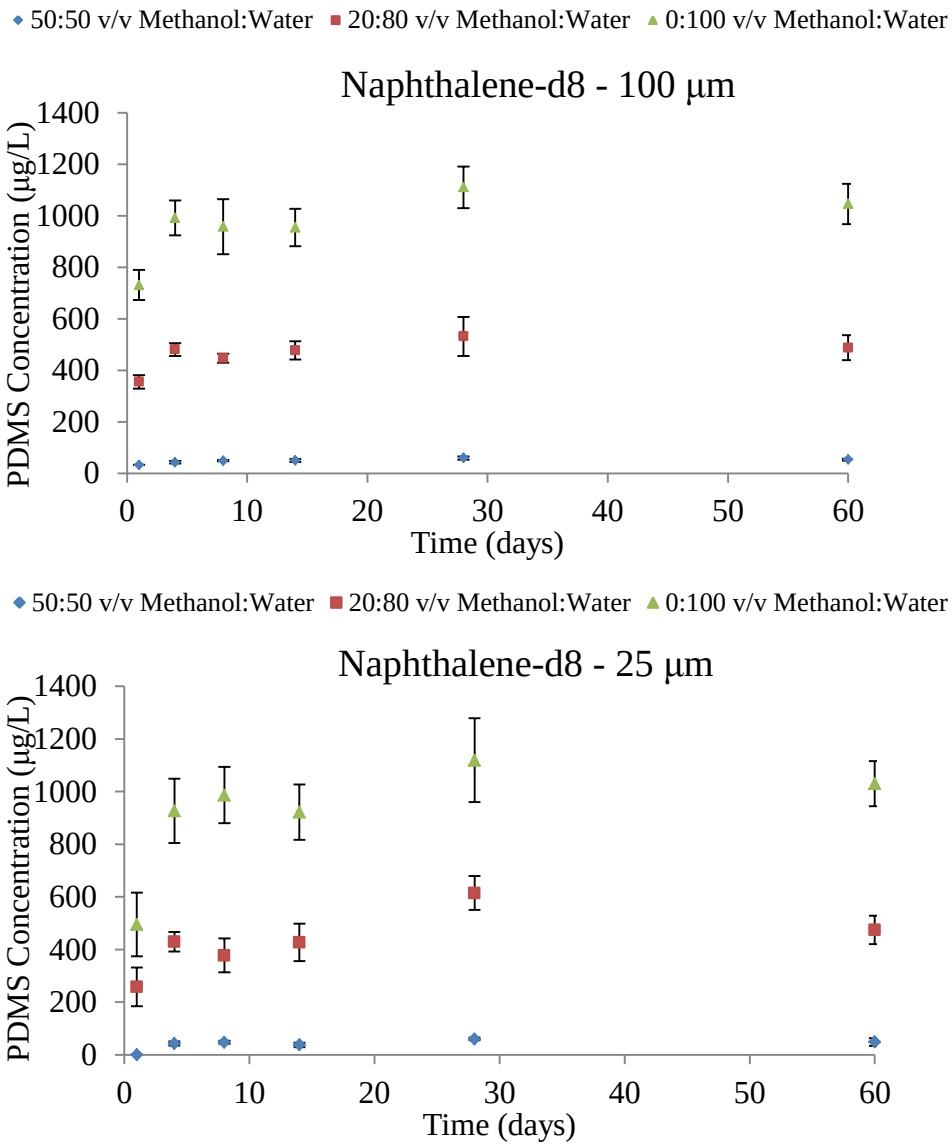


Figure 3-2. Naphthalene-d8 concentration sorbed to a 100 µm or 25 µm PDMS layer measured after different lengths of time in a spiking solution with either a 50/50, 20/80, or 0/100 methanol/water v/v makeup.

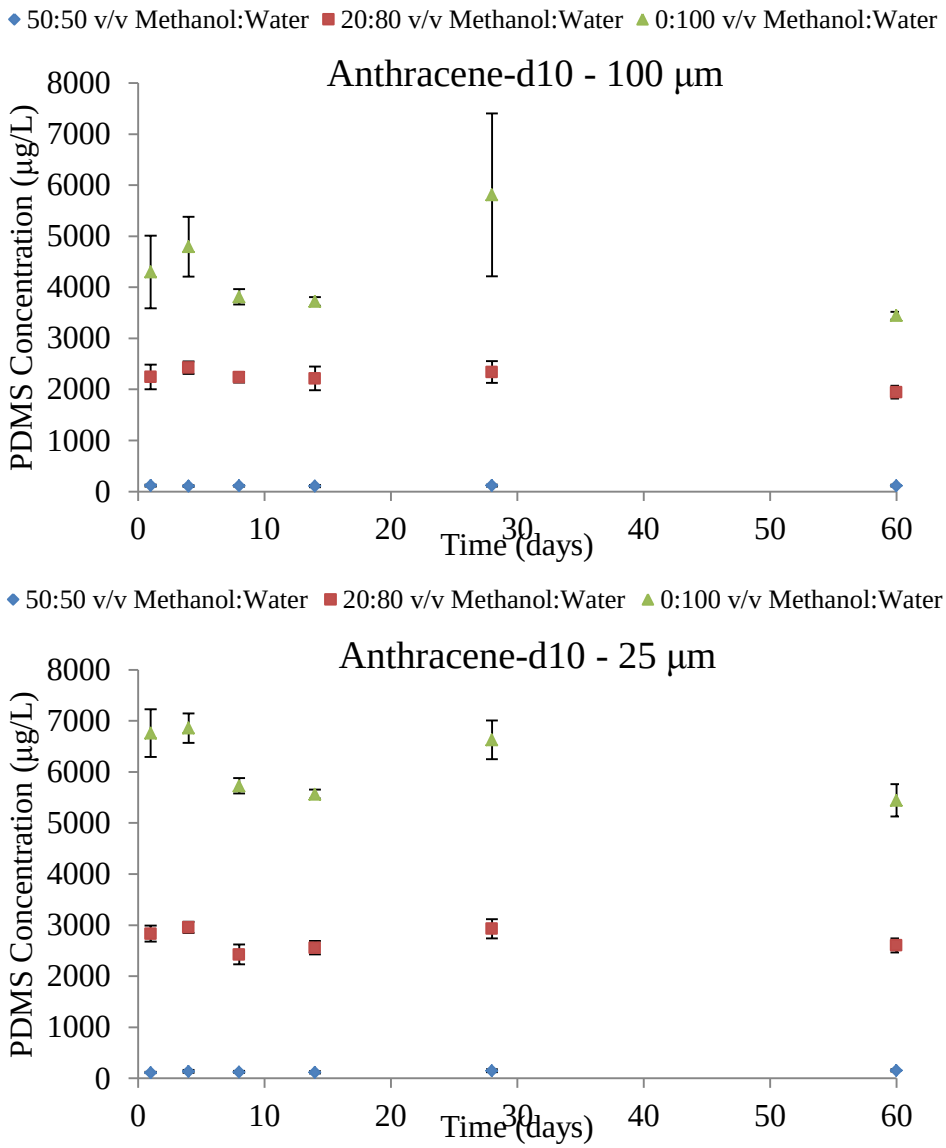


Figure 3-3. Anthracene-d10 concentration sorbed to a 100 µm or 25 µm PDMS layer measured after different lengths of time in a spiking solution with either a 50/50, 20/80, or 0/100 methanol/water v/v makeup.

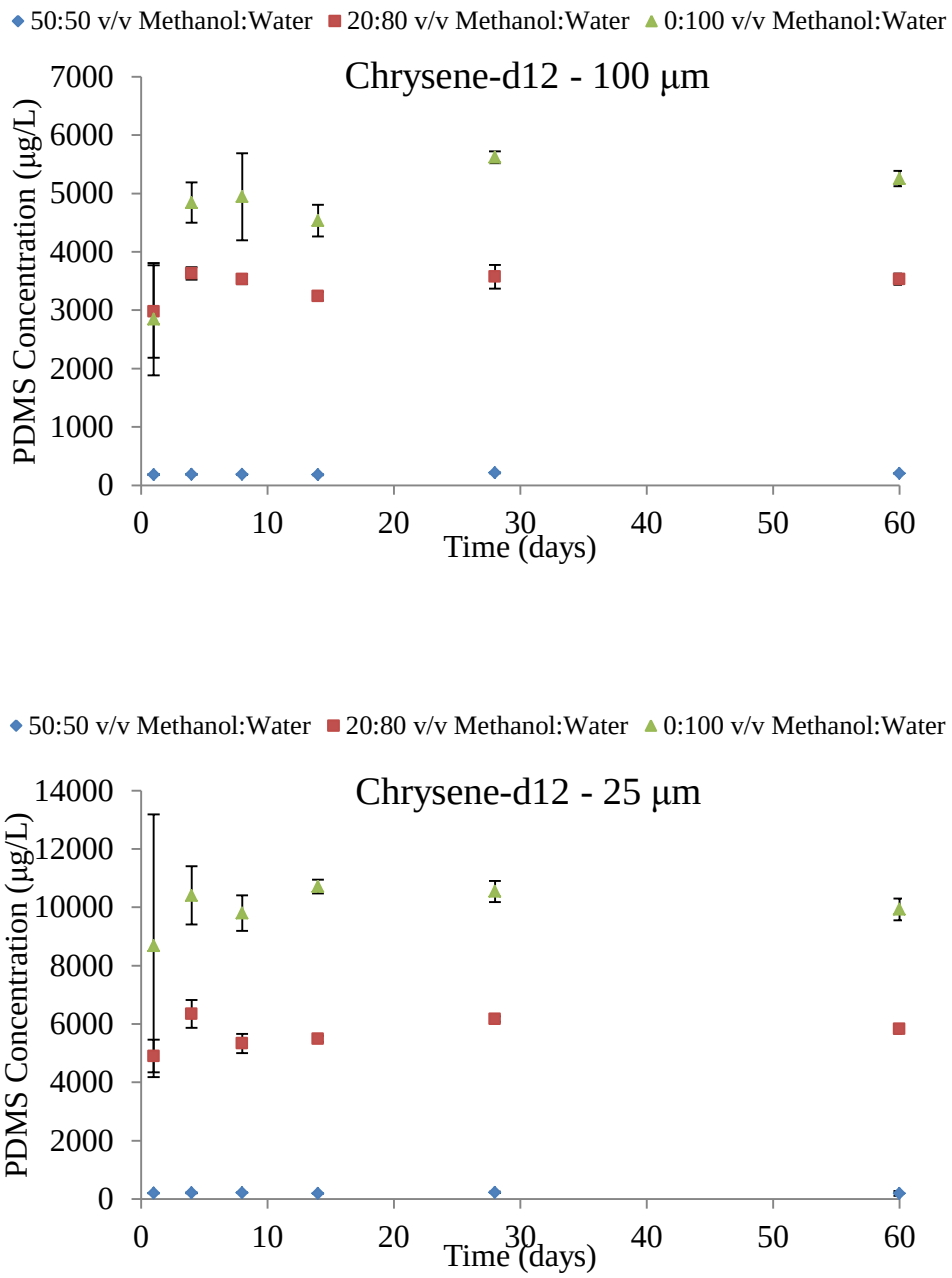
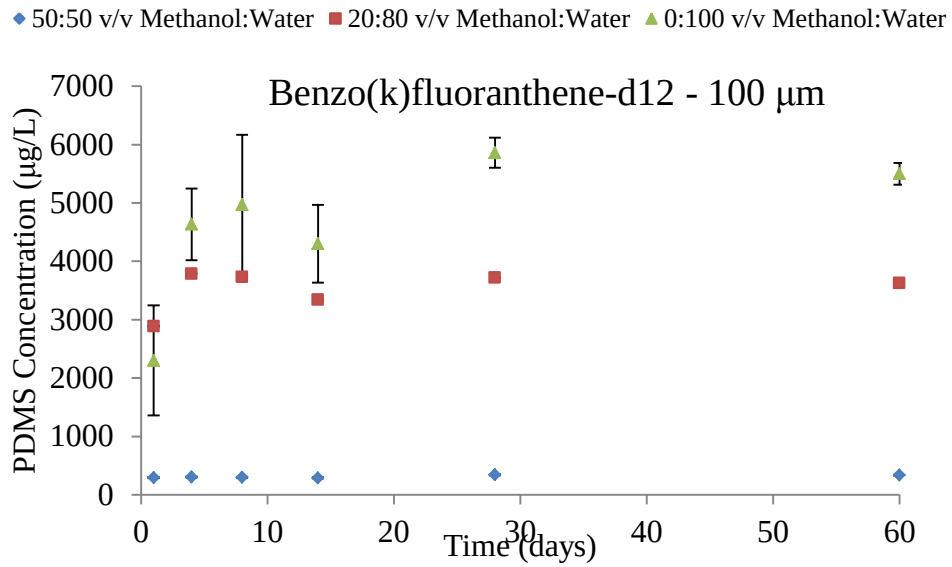


Figure 3-4. Chrysene-d12 concentration sorbed to a 100 µm or 25 µm PDMS layer measured after different lengths of time in a spiking solution with either a 50/50, 20/80, or 0/100 methanol/water v/v makeup.



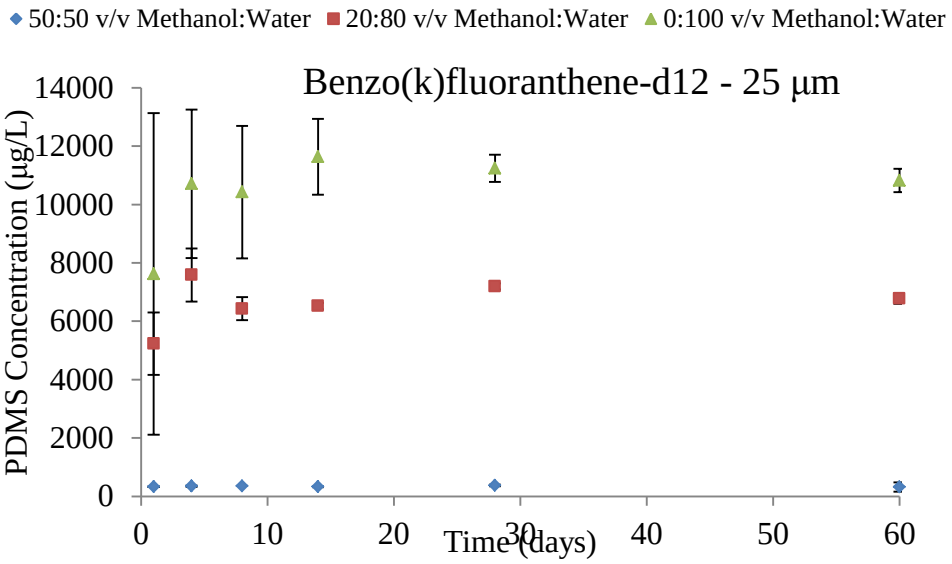


Figure 3-5. Benzo(k)fluoranthene-d12 concentration sorbed to a 100 µm or 25 µm PDMS layer measured after different lengths of time in a spiking solution with either a 50/50, 20/80, or 0/100 methanol/water v/v makeup.

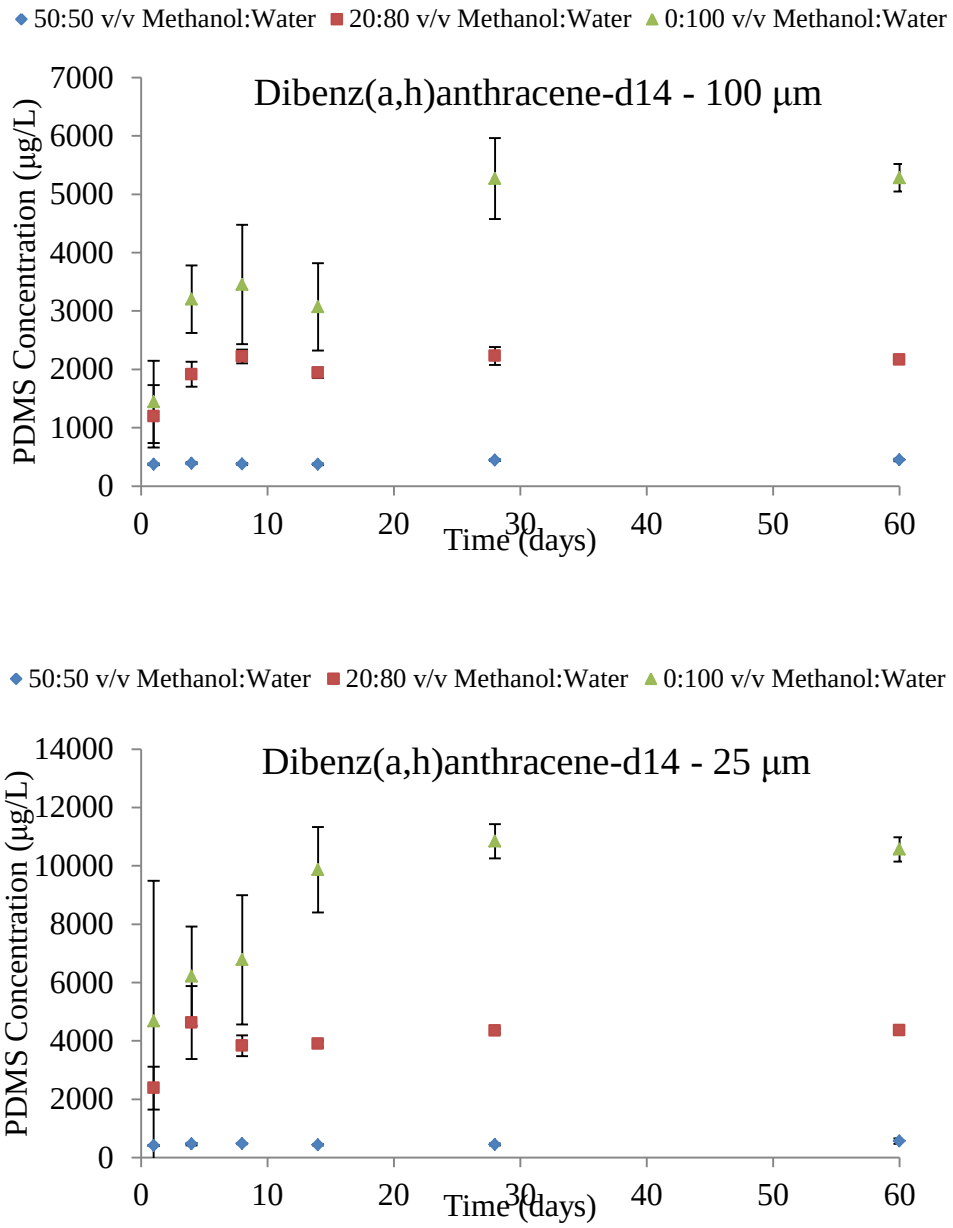


Figure 3-6. Dibenz(a,h)anthracene-d14 concentration sorbed to a 100 µm or 25 µm PDMS layer measured after different lengths of time in a spiking solution with either a 50/50, 20/80, or 0/100 methanol/water v/v makeup.

There is a tradeoff between the amount of PRC sorbed to the PDMS layer and the variation in the amount of PRC sorbed to the PDMS layer for the different compositions of the spiking solutions. The least amount of PRC mass found sorbed to the PDMS layer occurred when using a 50/50 v/v methanol/water solution. The highest amount of PRC mass is found

sorbed to the PDMS layer when spiking of the dPAHs is completed using a 0/100 v/v methanol/water solution, but it also has the highest covariance associated with the three spiking solutions. The coefficient of variation associated with naphthalene-d8, the least hydrophobic compound in this study, and dibenz(a,h)anthracene-d14, the most hydrophobic compound in this study, for the different methanol/water solution makeups are presented in Table 3-1. While the coefficient of variation remains consistent for naphthalene and other lower molecular weight PRCs at approximately 10% for the discussed spiking solutions, the coefficient of variation decreases up to an order of magnitude when using methanol as part of the spiking solution for dibenz(a,h)anthracene and the more hydrophobic PRCs. The importance of using methanol in the makeup of the spiking solution becomes less significant when tumbling of the passive sampling material for 28 days or longer as the coefficient of variation for all compounds and all spiking solutions is approximately 10% or lower.

Table 3-1. Coefficient of variation associated with naphthalene-d8 and dibenz(a,h)anthracene-d14 detected on a thin layer of PDMS after being tumbled in spiking solutions with different methanol and water volume fractions.

	Coefficient of Variation - 1 day		
Naphthalene-d8	***50/50 v/v $MeOH/H_2O$***	***20/80 v/v $MeOH/H_2O$***	***0/100 v/v $MeOH/H_2O$***
550/500 µm	-	0.29	0.24
500/300 µm	-	0.07	0.08
Dibenz(a,h)anthracene-d14			
550/500 µm	0.04	0.31	1.03
500/300 µm	0.03	0.45	0.49
Compound	***Coefficient of Variation - 4 days***		
Naphthalene-d8	***50/50 v/v $MeOH/H_2O$***	***20/80 v/v $MeOH/H_2O$***	***0/100 v/v $MeOH/H_2O$***
550/500 µm	0.19	0.09	0.13
500/300 µm	0.11	0.05	0.07
Dibenz(a,h)anthracene-d14			
550/500 µm	0.09	0.27	0.27
500/300 µm	0.04	0.11	0.18
Compound	***Coefficient of Variation- 8 days***		
Naphthalene-d8	***50/50 v/v $MeOH/H_2O$***	***20/80 v/v $MeOH/H_2O$***	***0/100 v/v $MeOH/H_2O$***
550/500 µm	0.11	0.17	0.11
500/300 µm	0.04	0.04	0.11
Dibenz(a,h)anthracene-d14			
550/500 µm	0.03	0.09	0.33
500/300 µm	0.04	0.05	0.30
Compound	***Coefficient of Variation- 14 days***		
Naphthalene-d8	***50/50 v/v $MeOH/H_2O$***	***20/80 v/v $MeOH/H_2O$***	***0/100 v/v $MeOH/H_2O$***
550/500 µm	0.23	0.17	0.11
500/300 µm	0.11	0.07	0.08
Dibenz(a,h)anthracene-d14			
550/500 µm	0.05	0.03	0.15
500/300 µm	0.04	0.05	0.24
Compound	***Coefficient of Variation - 28 days***		
Naphthalene-d8	***50/50 v/v $MeOH/H_2O$***	***20/80 v/v $MeOH/H_2O$***	***0/100 v/v $MeOH/H_2O$***
550/500 µm	0.09	0.10	0.14
500/300 µm	0.11	0.14	0.07
Dibenz(a,h)anthracene-d14			
550/500 µm	0.08	0.02	0.05
500/300 µm	0.03	0.07	0.13
Compound	***Coefficient of Variation - 60 days***		
Naphthalene-d8	***50/50 v/v $MeOH/H_2O$***	***20/80 v/v $MeOH/H_2O$***	***0/100 v/v $MeOH/H_2O$***
550/500 µm	0.31	0.11	0.08
500/300 µm	0.07	0.10	0.08
Dibenz(a,h)anthracene-d14			
550/500 µm	0.55	0.03	0.04
500/300 µm	0.05	0.03	0.04

Of the three spiking solution compositions, the 20/80 v/v methanol/water solution is the most ideal for facilitating sorption of dPAHs onto a PDMS layer. While the PRC concentrations found sorbed to the PDMS layer are not the highest, they are the most consistent. Additionally, the time required to reach a steady state between the PDMS layer and the spiking solution is reduced when using the 20/80 v/v methanol/water solution versus the 0/100 v/v methanol/water solution.

Performance evaluation of PRC and MCT methods

The ERM relationship between logRD and $\log K_{ow}$ was fit with the PRC and MCT method data for the fibers in contact with the different sediments for 20 days. For the 230/210 μm SPME PDMS fiber, all concentrations of the four PRCs were below detection limits and therefore the porewater concentrations derived from this fiber are assumed to be at equilibrium. However, there were quantifiable amounts of the four PRCs sorbed to the 550/500 μm SPME PDMS fiber and therefore the concentrations derived using these fibers would have to be corrected. The α parameter values for the three sediments were approximately unity. The logβ parameter values for the three different sediments and two methods are found in Table 3-2. The α values being near unity and the β parameter values being on the order of molecular diffusion ($\sim 10^{-6}$ m^2/d) for all three sediments is expected since diffusion is the dominant transport mechanism during an *ex situ* study. The MCT and PRC methods were found to be interchangeable as their slopes (logβ) were statistically identical.

Table 3-2. logβ and correlation coefficient (r^2) values for the three different sediments (BB, SP, and FD) and the two different kinetic uptake correction methods (PRC and MCT).

	BB - PRC	BB - MCT	SP - PRC	SP - MCT	FD - PRC	FD - MCT
logβ	-6.2 ± 0.1	-6.4 ± 0.1	-5.9 ± 0.06	-7.3 ± 0.17	-6.3 ± 0.14	-6.1 ± 0.09
r^2	0.64	0.98	0.82	0.71	0.8	0.65

A comparison between the porewater concentrations derived using the equilibrium, PRC, and MCT methods indicated that using methods based on kinetic corrections for non-steady state conditions produced concentrations that were in general not significantly different from concentrations produced following the equilibrium method (Figure 3-7). For example, the freely dissolved concentration of fluorene, a lower hydrophobicity PAH, for the FD sediment was found to be 60 ± 4 ng/L using the EQ method, 58 ± 7 ng/L using the PRC method, and 56 ± 7 ng/L using the MCT method. The same level of reproducibility and accuracy for the MCT and PRC methods at correcting to equilibrium concentrations was also found for concentrations in the BB and SP sediments;. Chrysene, a medium level hydrophobic PAH, concentrations in the BB sediment were determined to be 10 ± 1 ng/L vs 7 ± 0.9 vs. 8 ± 1 for EQ, PRC, and MCT methods, respectively. The results indicate that the three methods result in accurate and reproducible freely dissolved porewater concentrations.

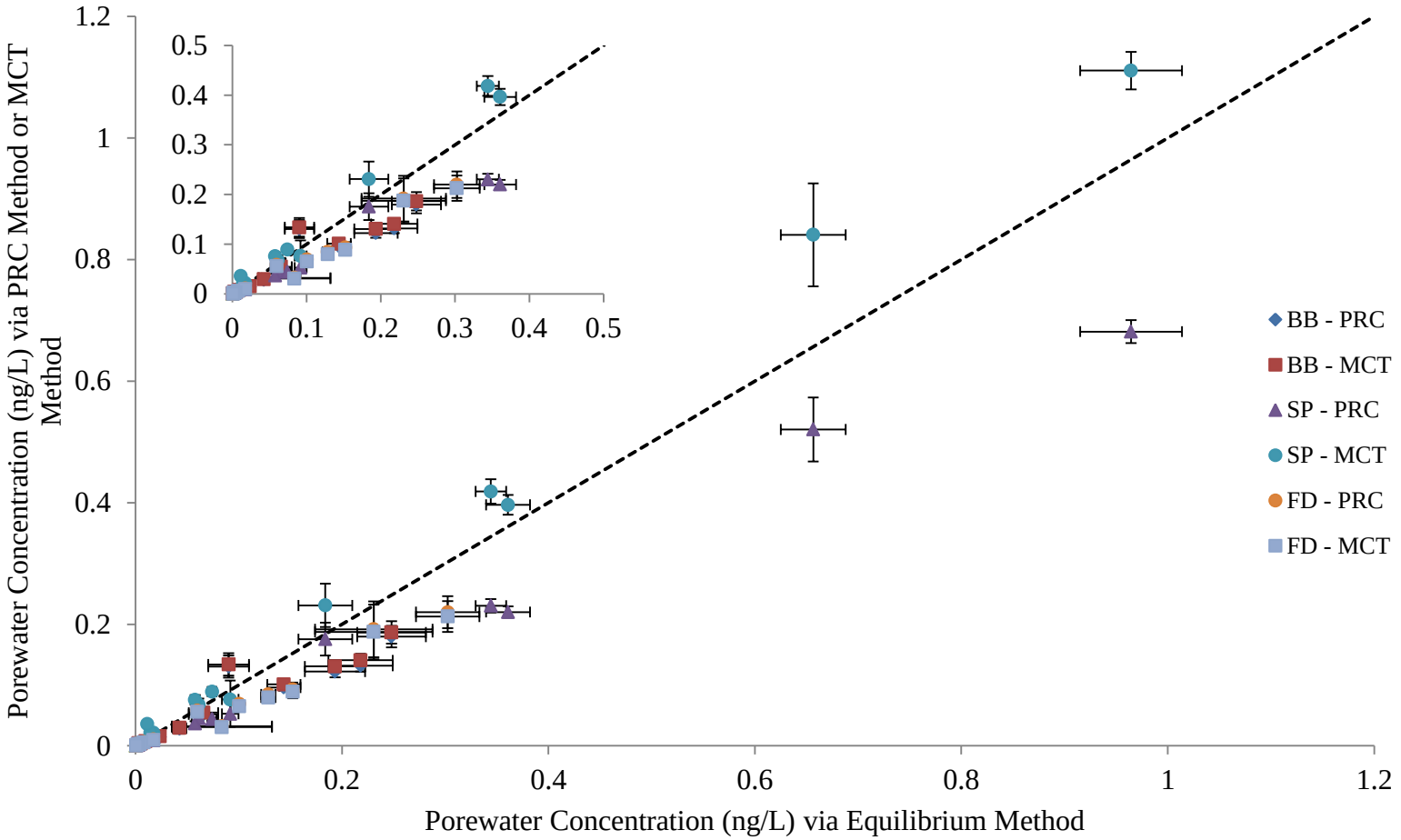


Figure 3-7. Porewater concentrations (ng/L) derived using the equilibrium method (tumbled for 42 days), the PRC method (tumbled for 20 days), and the MCT method (tumbled for 20 days). The broken line represents a 1:1 relationship. The horizontal error bars represent the standard deviation associated with the equilibrium method measurements (n = 4 for BB sediment treatment and n= 5 for SP and FD sediment treatments). The vertical error bars represent the standard deviation associated with either the PRC method or the MCT method (n = 4 for BB sediment treatment and n = 5 for SP and FD sediment treatments). The inset provides a zoomed in view to the bulk of the data.

Application of External Resistance Model to Field Data

The values of L for the two fibers for the MCT approach used at the Chattanooga Creek site were 9.56 μm and 29.15 μm for the 230/210 and the 1060/1000, respectively. The primary contaminants of concern at the Chattanooga Creek site were PAHs, therefore when using the MCT method the ERM model was fit using mass ratios of the sixteen common parent PAHs found sorbed to the two fibers. Additionally, the ERM model (Equation 27) was fit with the four PRCs previously mentioned. For this deployment and the compounds of interest, the minimum value of σ was greater than 90,000, implying that the ERM was appropriate for the data.

The values of RD calculated using the PRC Method and the MCT Method for the 14 day deployment at Chattanooga Creek (Chattanooga, TN) are presented in Figure 3-8. As there was found to be no significant difference (p-value = 0.15, $\alpha = 0.05$) between the RD estimates found using the different methods, all of the data were used to fit the values of α and β, which were determined to be 1 +/- 0.1 and -7.1 +/- 0.7, respectively, with an $r^2 = 0.63$.

Note that when using the MCT method, estimates of RD for each compound on interest can be determined as long as the compound's concentration is above its analytical detection limit. This is not the case when using the PRC method. Once the relationship between RD and K_{ow} is determined, the resulting relationship can be used to estimate the fraction of steady state for any sorbent fiber dimension (L), compound (K_{pw}), and time of exposure (t). The estimate of the fraction of steady state is then used as a correction factor to determine the freely dissolved concentration (Equation 29).

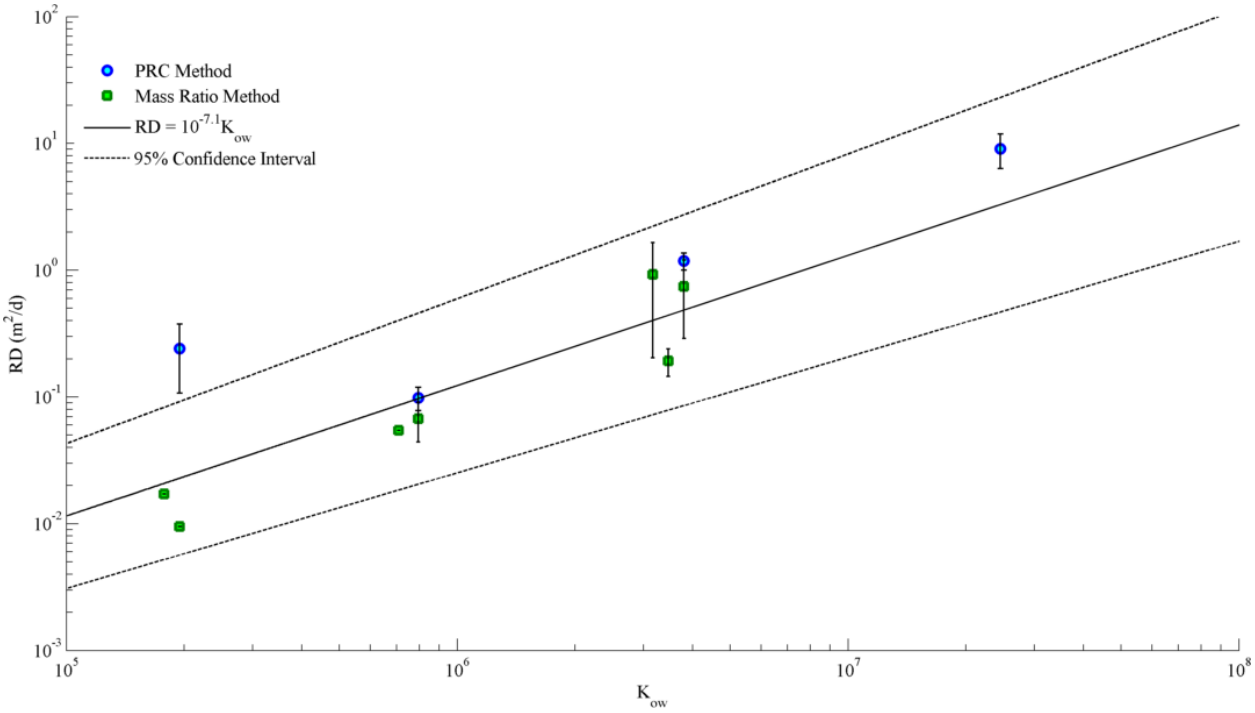


Figure 3-8. Estimated values of RD (average +/- standard deviation) from fitting the ERM with using the PRC and MCT methods.

Results from the studies presented in this chapter show that the MCT and PRC methods can be used for ex situ and in situ studies using passive sampling techniques to decrease the experiment or field deployment length, while still maintaining the measurement accuracy of the freely dissolved porewater concentrations. As shown for deuterated PAHs, a mixture of 80% water and 20% methanol for the spiking of these compounds onto the PDMS layer for the PRC method increased the consistence of sorption to the PDMS layer. It is important to have a low error or high level of consistency as any error (i.e. a highly variable initial PRC concentration) will propagate through the calculations for fitting the ERM. The use of PRCs is beneficial for in situ studies. For example, benzo(a)pyrene, benzo(g,h,i)perylene, and dibenz(a,h)anthracene, the most hydrophobic compounds at Chattanooga Creek, would take on the order of months to reach an equilibrium between the porewater and PDMS sorbent. By using the PRC or MCT method, the experimental time in the lab or in the field can be reduced to the order of days or weeks without sacrificing accuracy.

SIGNIFICANCE & IMPLICATIONS

One of the recommendations for future work that came from the November 2012 SETAC technical workshop previously mentioned was the further development of in situ non-equilibrium passive sampling methodologies where PRCs would be used to correct to equilibrium concentrations (Ghosh et al., 2014). This work provides validation of PRCs as a method to correct for non-equilibrium conditions and provide guidance on how to use PRCs when monitoring at contaminated sites. Additionally, the source code

for a standalone application is presented in Appendix A. This aim of this standalone application is to streamline the calculation process for a targeted audience of government agencies and engineering consulting agencies that do not perform their own analytical work.

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Chapter 4: Volatile Loss of Compounds from SPME PDMS fibers

ABSTRACT

A model was developed of volatile losses of compounds between the time of retrieval and processing of a sorbent layer used as a passive sampler. The model focused on initial losses when external mass transfer resistances control evaporative losses and conditions of sample processing in generally stagnant air, e.g. processing in a sheltered location. The results suggest that thicker sorbent layers should be used and the samplers should be processed rapidly onsite or kept at low temperatures after retrieval enroute to an off-site facility for processing to ensure retention of more volatile compounds. For example, to retain 90% of naphthalene for a 24 hour exposure to ambient air (20°C) a PDMS sorbent thickness of 1.4 cm would have to be used. The model developed can also be applied to other passive sampling sorbents to estimate initial desorption rates and sampling times necessary to achieve a specific level of compound retention. The model suggests that passive samplers routinely used to monitor hydrophobic organic compounds may not provide quantitative measurement of naphthalenes or other volatile compounds without special efforts to reduce losses of these compounds.

INTRODUCTION

The emerging technology of passive sampling for sediment has many benefits over conventional sampling techniques. Passive sampling methods are more cost effective and efficient than conventional sampling techniques for water and sediment sampling. For example, conventional sampling techniques for water samples can require

up to thousands of liters of water to reach detection limits and even then can be impacted by small sediment particles, colloids, and DOM that negate the representativeness of the sample (Burgess, 2012, Greenberg et al., 2013). Additionally, conventional solvent extraction techniques for sediment samples strip the majority of the compounds from the sediment; this method is useful for gaining a measure of the total compound mass within the sediment, but does not provide useful information about the fraction of the compound that is bioavailable and controls fate and transport mechanisms within the sediment porewater (Burgess, 2012).

Even with these documented benefits (Booij et al., 2003, Vrana et al., 2005, Gschwend et al., 2011, Janssen et al., 2011, Lu et al., 2011, Lampert et al., 2013, Ghosh et al., 2014, Mayer et al., 2014), passive sampling has seen limited acceptance by regulatory agencies for sediment management decisions in part due to the lack of robust quality assurance and control (QA/QC) strategies (Ghosh et al., 2014, Mayer et al., 2014, Parkerton and Maruya, 2014). Of particular concern for volatile analytes is the loss of the target compound during passive sampling processing and handling. Any loss would lead to an underestimation of the concentration of the volatile target analyte and, in the case of performance reference compounds (PRCs), an overestimation of the extent of steady state. These losses are possible during the period of passive sampler processing between retrieval and extraction into a stable solvent. Underestimation of toxicity units when evaluating narcosis toxicity is an example of how underestimations of the freely dissolved concentrations can cause issues for risk assessment and management. Narcosis can be heavily dominated by low molecular weight compounds (USEPA, 2003), which

are also the compounds that exhibit the greatest volatile losses from the sorbent layer). The lower molecular weight and less hydrophobic compounds will be associated less with the solids than their more hydrophobic counterparts and therefore their contribution to the calculation of toxicity units could be higher.

This paper seeks to develop a model of the volatile losses as a function of processing time for *in situ* solid phase microextraction (SPME) polydimethylsiloxane (PDMS) passive samplers. In addition, the model will be used to infer the potential for volatile losses from the other two most commonly used passive sampling sorbents for hydrophobic organic contaminants: polyoxymethylene (POM) and polyethylene (PE).

Equation 1 represents the mass balance on a PDMS layer with an initial concentration of a volatile compound resulting from exposure to a sediment porewater or surface water that is exposed to the air during processing before extraction.

$$V_f \frac{dC_f}{dt} = k_d A(C_{g,bulk} - \frac{C_f H}{K_f}) \qquad \text{Eq. 1}$$

where V_f is the volume (m^3) of the passive sampler sorbent layer, $C_{g,bulk}$ is the concentration of the compound in the ambient air ($\mu g/m^3$), A is the surface area of the passive sampler layer (m^2), H is the Henry's Law Constant (dimensionless), k_d is the desorption rate coefficient (m/day), and C_f is the concentration sorbed to the passive sampler sorbent layer ($\mu g/m^3$). The model assumes that the primary resistance to evaporation is external to the passive sampler which is appropriate to assess the initial rate of evaporative losses during sample processing. The model predicts the air-fiber partition coefficient by conceptualizing a thin layer of water (the samplers are withdrawn

wetted by the pore or surface water) in equilibrium with the surface of the passive sampler. The concentration of the contaminant of concern in the air at the interface of the passive sampler is then given by $C_f \frac{H}{K_{fw}}$. $C_{g,bulk}$ in the sample processing area is assumed approximately equal to zero therefore Equation 1 can be rewritten as

$$\frac{dC_f}{dt} = -k_d \left(\frac{H}{LK_{fw}} \right) C_f \qquad \text{Eq. 2}$$

which when solved using the following initial condition,

$$C_f \left(t = 0 \right) = C_o \qquad \text{Eq. 3}$$

leads to Equation 4.

$$C_f = C_{f,o} e^{\frac{-k_d H}{LK_{fw}} t} \qquad \text{Eq. 4}$$

Equation 4 is an exponential decay function and therefore the half-life of the compound on the PDMS layer is equal to

$$t_{1/2} = \frac{ln2}{k_d H / LK_{fw}} \qquad \text{Eq. 5}$$

Experiments were conducted to assess desorption rates of compounds from a thin layer of PDMS during normal processing in ambient air in a protected area (i.e. relatively stagnant air). Normal processing of SPME PDMS involves retrieval of the PDMS from the medium of exposure, sectioning into individual samples and placement in an extraction solvent that would effectively eliminate any further volatile losses. In the laboratory this can be done quickly (seconds to minutes) but in the field, time may be

required to transport the sample to a stable work location or to transport back to the laboratory. Experiments evaluating volatile losses over periods of up to 48 hours were conducted. The results were used to fit a model based upon the Henry's Law Coefficient, the polymer-water partitioning coefficient, and the thickness of the polymer to investigate the effects of PDMS thickness and ambient air temperature on the desorption rate.

METHODOLOGY

During this study, 60 mL vials were filled with an aqueous solution containing naphthalene, fluorene, acenapthene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene. These compounds were selected as they are common contaminants of concern at capped sediment sites due to their highly sorptive nature in sediment systems and therefore could pose a potential source of recontamination after other sources of contamination have ceased. Twenty centimeters of SPME PDMS fiber with approximate outer/inner diameter dimensions of 230/210 μm (10 μm PDMS thickness), 559/486 μm (34 μm PDMS thickness) and 1060/1000 μm (30 μm PDMS thickness) were placed into the vials containing the aqueous solution and tumbled for a minimum of fourteen days. The vials were transferred into temperature controlled environmental chambers set at 4°C, 20°C, and 25°C. Three replicates are used for each material and temperature treatment. A blank containing only deionized water and 20 cm of a specific thickness SPME PDMS fiber for each temperature treatment was included to monitor for any

interferences such as sorption of compounds from the environmental chamber's atmosphere. The fibers were removed from the aqueous solution and segmented into 1 cm pieces and placed in 150 μL of acetonitrile after exposure to the ambient air for the following pre-determined times: 0 minute, 0.5 minute, 1 minute, 1.5 minutes, 2 minutes, 3 minutes, 4 minutes, 5 minutes, 7 minutes, 10 minutes, 15 minutes, 20 minutes, 30 minutes, 1 hour, 2 hours, 6 hours, 8 hours, 12 hours, 24 hours, and 48 hours. The fiber segments remained in the acetonitrile aliquot overnight for extraction.

The extracts were analyzed using an Agilent Technologies 1260 Infinity (Santa Clara, CA, USA) High Performance Liquid Chromatography (HPLC) with a ultraviolet-diode array (1260 DAD VL+) and fluorescence detector (1260 FLD Spectra) based upon EPA standard method 8310 in the SW846 series. The column used was a Phenomenex (Torrance, CA, USA) Luna 5μ C18 column (250 x 4.6 mm) maintained at 40°C. The HPLC was operated under isocratic conditions with a flow rate through the system of 1.0 mL/min with a water to acetonitrile ratio (v:v) of 3:7.

RESULTS AND DISCUSSION

Analysis of the concentration gradients over time revealed that the more hydrophobic compounds had very little to no desorption from the PDMS layer. For the 559/486 μm SPME PDMS fiber, no substantial desorption was observed for compounds with a $\log K_{ow}$ of 4.7 or higher, 5.29 or higher, 6.58 or higher, for ambient temperatures of 4°C, 20°C, and 25°C, respectively. For the 1060/1000 μm SPME PDMS, no substantial desorption was observed for compound with a $\log K_{ow}$ of 4.7 or higher and 5.9 or higher

for ambient temperatures of 4°C and 20°C. At 25°C, all compounds of interest exhibited some loss from the PDMS layer when exposed to ambient temperature conditions of 25°C. For the 230/210 μm SPME PDMS fiber, there was substantial change from the initial concentration sorbed to the PDMS layer over the duration of the experiment for all three temperature treatments. Generally, the PAHs of most concern for substantial loss are naphthalene ($\log K_{ow}$ = 3.41), acenaphthene ($\log K_{ow}$ = 4.06), fluorene ($\log K_{ow}$ = 4.2), anthracene ($\log K_{ow}$ = 4.69), and phenanthrene ($\log K_{ow}$ = 4.74). Figures 4-1 through 4-9 depict the concentration versus time for compounds that showed the most change in concentration. The general behavior shown in Figures 4-1 through 4-9 is a relatively rapid (exponential) loss initially followed by a slowing of evaporation at long time, likely associated with increasing importance of internal mass transfer resistances on evaporation. Our goal is to model the initial losses to ensure that any such losses are small (e.g. less than 10%) during sample processing.

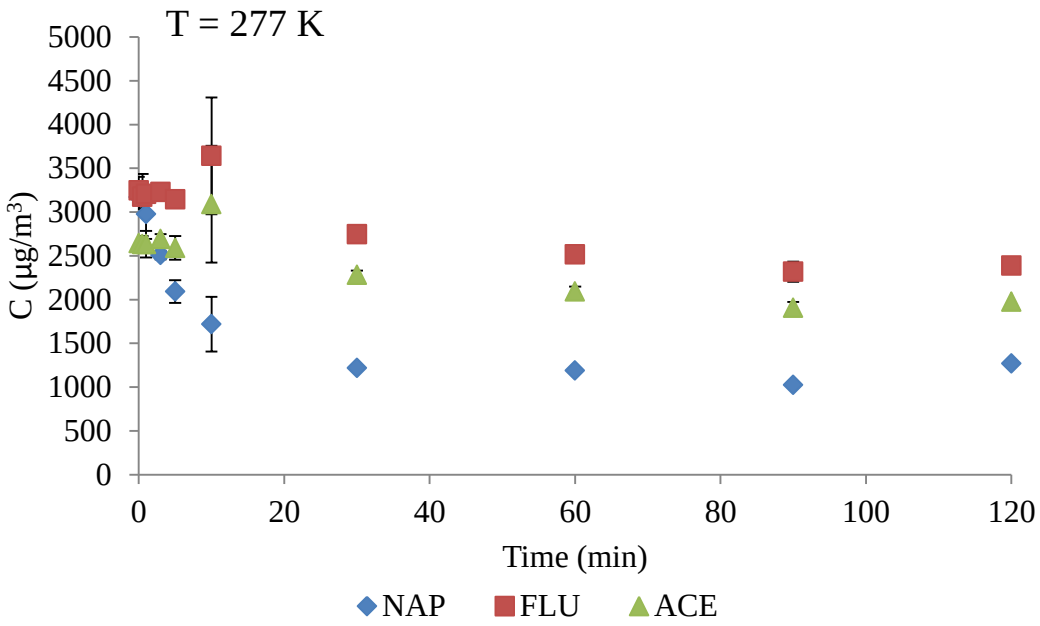

Figure 4-1. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 277 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 559/486 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), and acenaphthalene (ACE).

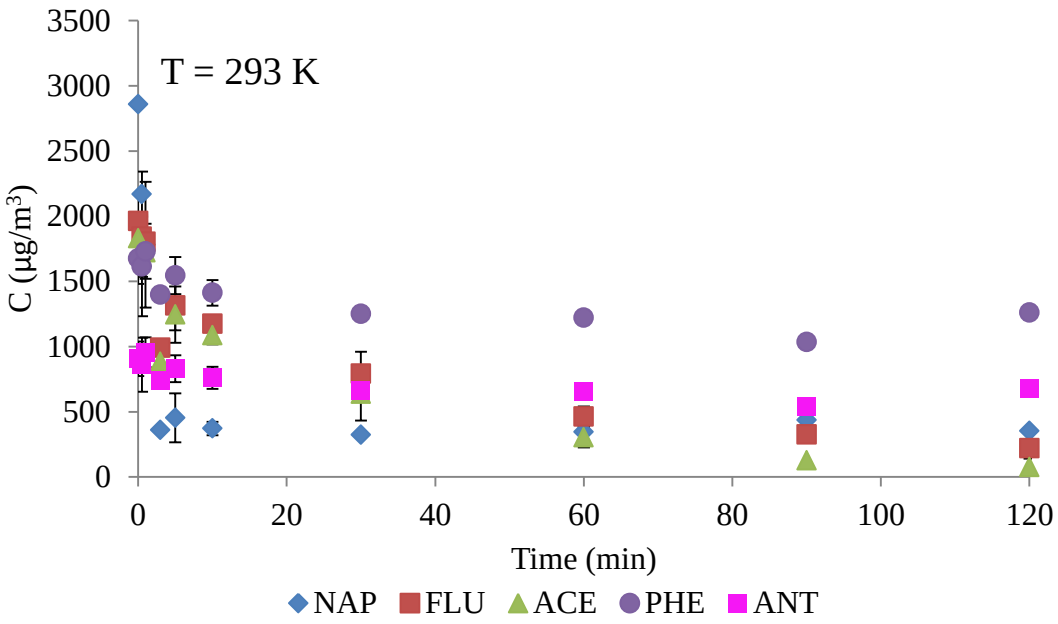

Figure 4-2. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 293 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 559/486 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), phenanthrene (PHE), and anthracene (ANT).

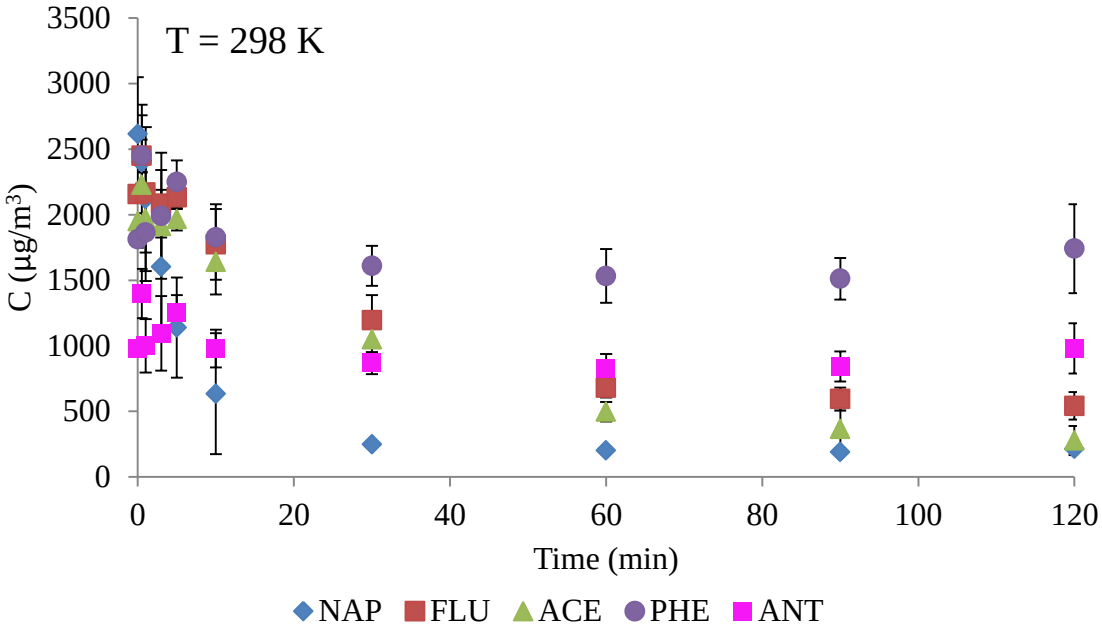

Figure 4-3. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 298 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 559/486 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), phenanthrene (PHE), and anthracene (ANT).

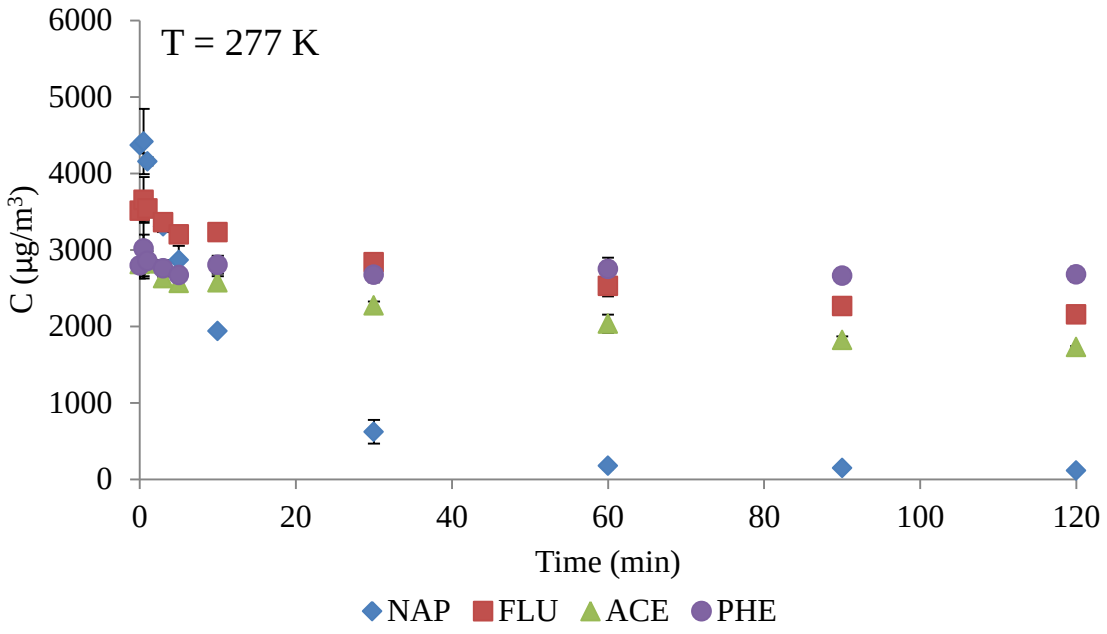

Figure 4-4. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 277 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 1060/1000 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), and phenanthrene (PHE).

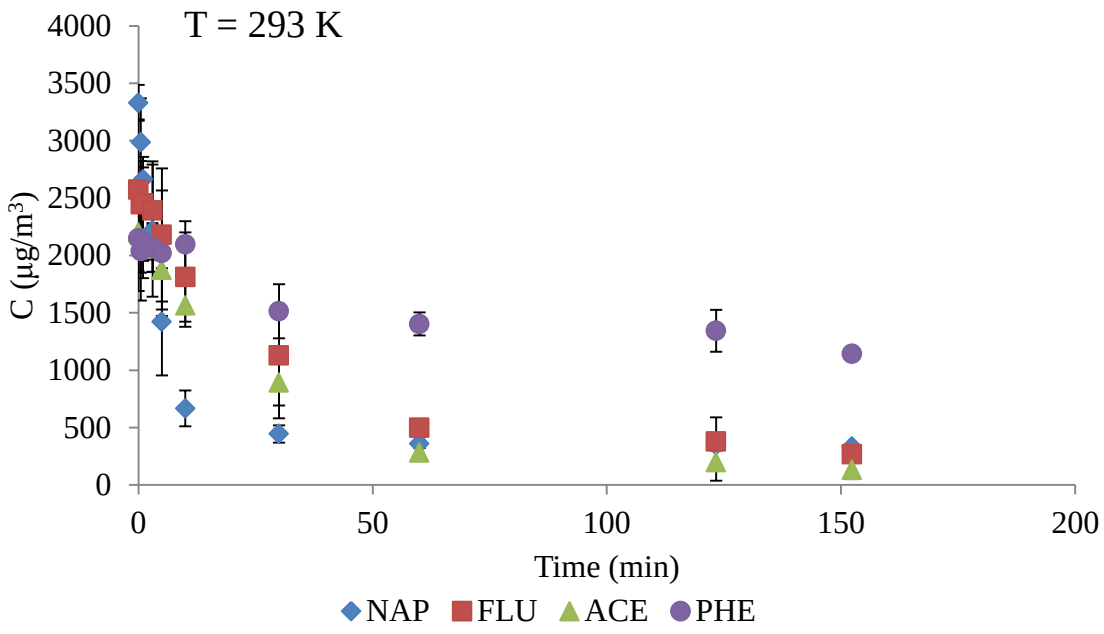

Figure 4-5. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 293 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 1060/1000 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), and phenanthrene (PHE).

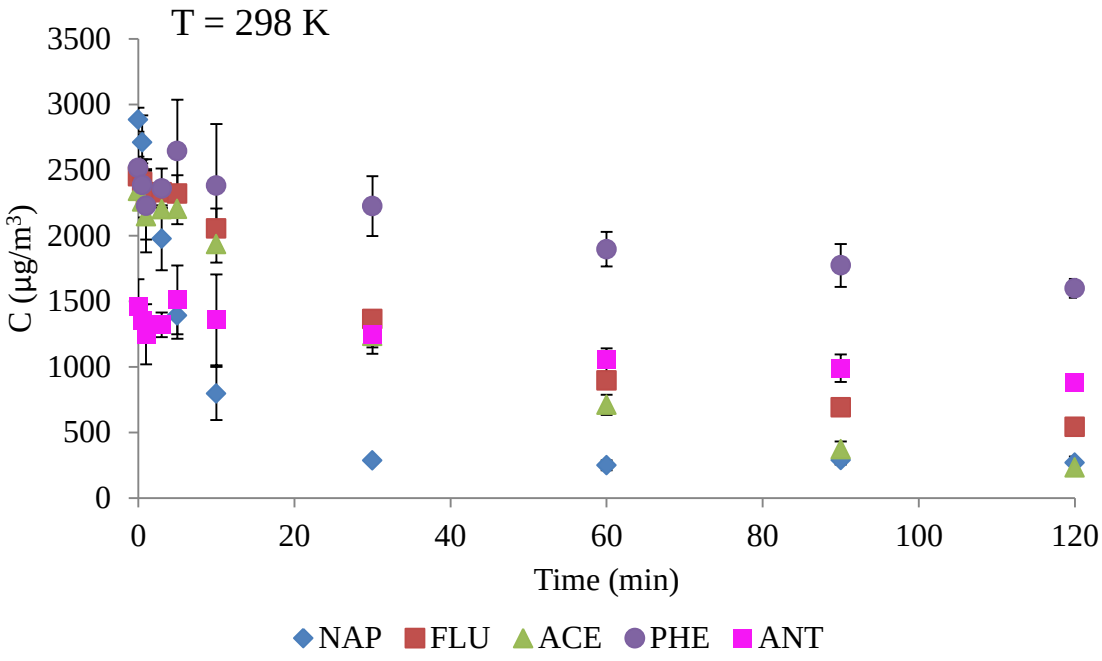

Figure 4-6. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 298 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 1060/1000 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), phenanthrene (PHE), and anthracene (ANT).

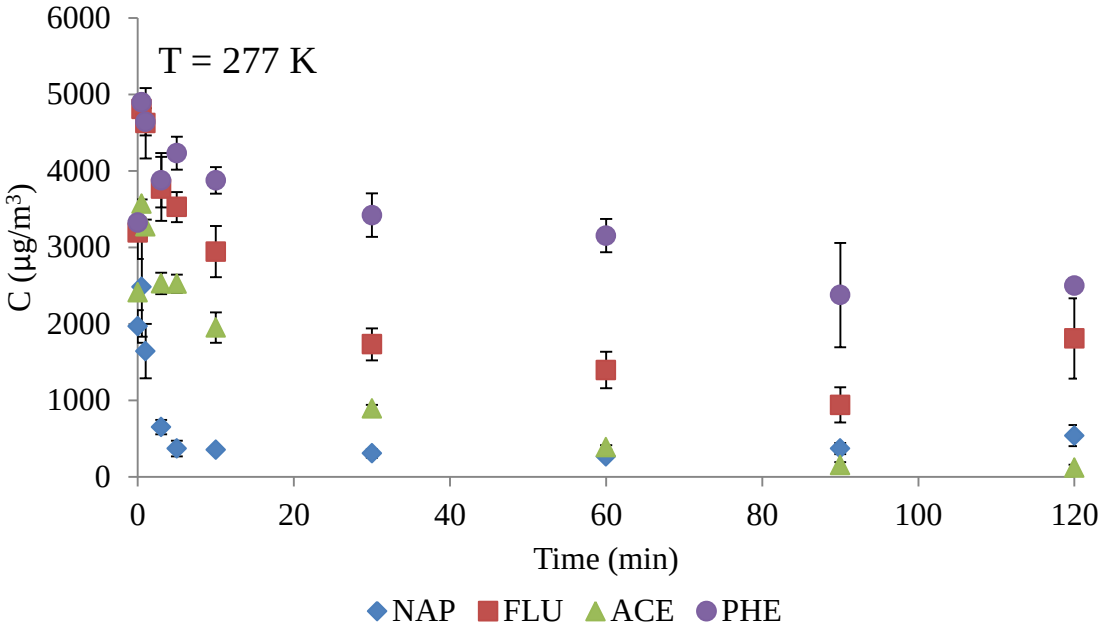

Figure 4-7. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 277 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 230/210 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), and phenanthrene (PHE).

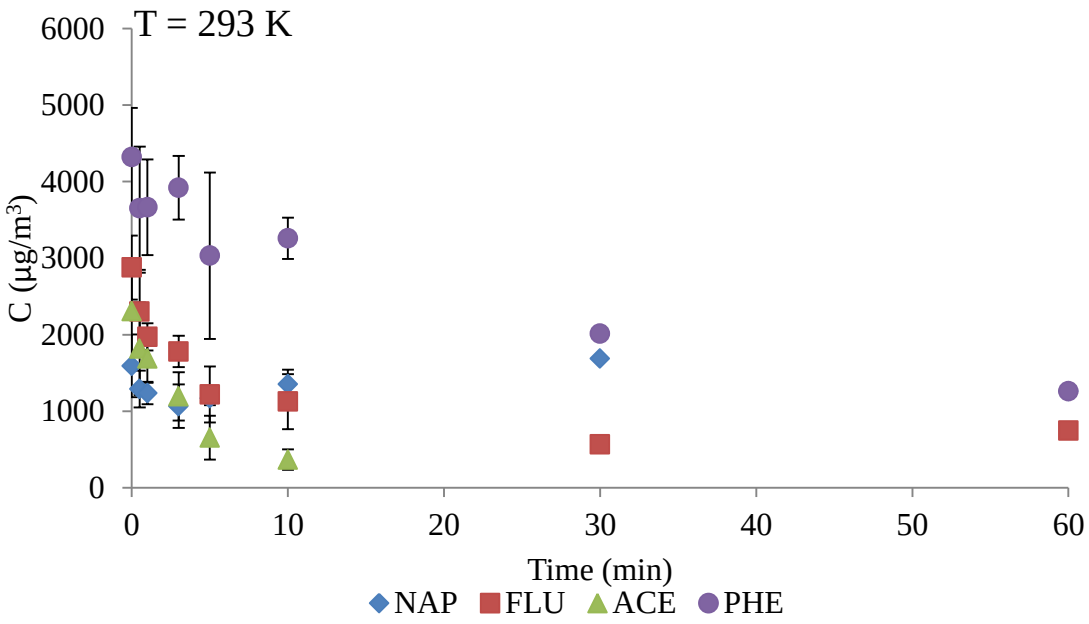

Figure 4-8. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 293 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 230/210 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), and phenanthrene (PHE).

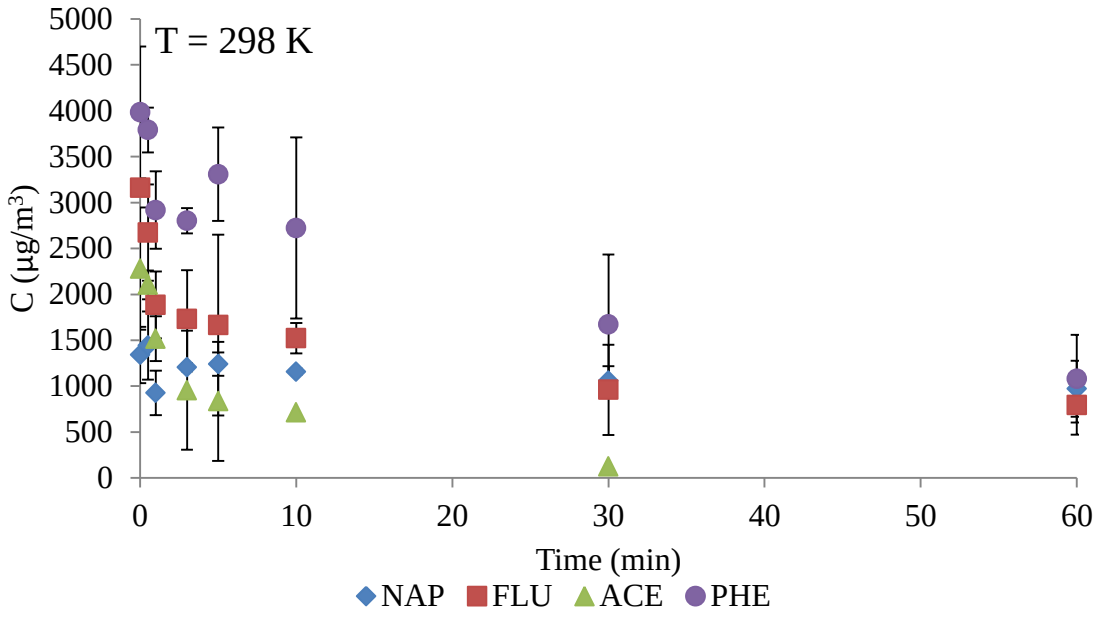

Figure 4-9. Concentration (µg/m^3) versus time (min) of exposure to ambient air at a temperature of 298 K for compounds sorbed to SPME PDMS fiber with outer diameter/inner diameter dimensions of 230/210 µm. Changes in concentration were only noted for naphthalene (NAP), fluorene (FLU), acenaphthalene (ACE), and phenanthrene (PHE).

A compound's vapor pressure (P_v) governs the exchange rate between the compound and the substrate to which it is sorbed (DelleSite, 1997). Vapor pressure, Henry's Law coefficient, and temperature relationships were available for the PAHs of most concern in this study and dimensionless Henry's Law Coefficients for them at ambient temperatures of 277 K, 293 K, and 298 K are found in Table 4-1. k_d is proportional to the diffusion coefficient within the PDMS layer divided by the boundary layer thickness. The diffusivity within the PDMS layer for the compounds exhibiting the highest rate of loss from the PDMS layer is approximately $10^{-10\pm0.15}$ (m^2/s) (Rusina et al.,

2010) and therefore k_d is expected to be relatively constant (see Figure 4-10). $\log k_d$ is approximately equal to 2 ± 1.1 (average ± 95% confidence interval). Naphthalene k_d values were lower than the other four compounds and this variation is due to the high degree of uncertainty for naphthalene measurements as any change in air flow conditions or exposure time will impact naphthalene the greatest.

If we look at k_d^*, which is equal to $\frac{k_d H}{L K_{fw}}$, there is a positive linear relationship between $\log(k_d^*)$ and log(H) indicating that compounds with smaller values of H/K_{fw} will desorb at a slower rate (see Figure 4-11). The slope of $\log(k_d^*)$ and log(H) is approximately one, which leads support to the model. Therefore to maintain the integrity of the sampler, they should be wrapped to prevent cross-contamination and stored at low temperatures to reduce H. The variability seen in Figure 4-10 and Figure 4-11 could be attributed to the different air flow conditions of the temperature controlled environmental chambers used for each different temperature treatment.

As indicated by the relationship between $\log(k_d^*)$ and log(H), the dimension of the SPME PDMS fiber, or any polymer sorbent layer, has an effect on the half-life of the compound. There was found to be little difference in half-lives between the 1060/1000 μm and 559/486 μm SPME PDMS fibers for the three temperatures of this study due to their PDMS thicknesses being of similar magnitude. In general, there is a decrease in the desorption half-life of the compounds for all temperatures when using the 230/210 μm SPME PDMS fiber versus the 1060/1000 μm and 559/486 μm SPME PDMS fiber. For

example, naphthalene, the most volatile PAH in this study, has a half-life of 0.2 hours when initially sorbed to a 1060/1000 μm or 559/486 μm SPME PDMS fiber and exposed to an ambient air temperature of 25°C compared to a half-life of 0.02 hours when sorbed to a 230/210 μm SPME PDMS fiber at the same temperature. As previously mentioned, keeping the samplers at a lower temperature and thereby reducing the vapor pressure as a driving force for desorption from the SPME PDMS fiber is also encouraged. For example, the half-life of naphthalene on a 230/210 μm SPME PDMS fiber can be increased to 0.2 hours by storing the sampler at 4°C. Figure 4-12 compares the half-life values for the different SPME PDMS thicknesses observed versus half-life values predicted from the linear relationship between $\log(k_d^*)$ and logH.

The half-life results suggest that when using SPME PDMS fibers with dimensions of 559/486 μm or 1060/1000 μm, both with an approximate PDMS thickness of 30 μm, compounds with $\frac{H}{K_{fw}} > 10^{-5}$ are stable ($C/C_o \geq 0.9$) for 20 minute exposure periods at an ambient air temperatures of 25°C. Compounds with $\frac{H}{K_{fw}} > 10^{-6}$ are stable for 20 minute exposure periods sorbed to a 230/210 μm SPME PDMS fiber, with an approximate 10 μm thickness of PDMS, and exposed to an ambient air temperatures of 25°C. In general, the results suggest that thicker sorbent layers should be used and the samplers should be kept at low temperatures between retrieval and processing to ensure the most accurate set of data is captured at a field site. Figure 4-12 depicts the predicted versus observed half-life times in days for the different SPME PDMS fiber thicknesses. The predicted values

were calculated from the relationship between logH and $\log k_d^*$. The observed values for the 230/210 μm SPME PDMS fiber were consistently lower than predicted. This could be caused by the increased difficulty of processing the 230/210 μm SPME PDMS fibers that are more brittle than their thicker counterparts. The variation seen for the observed values is potentially caused by the changing air flow dynamics in the environmental chambers.

The model (Equation 4) can be used to infer losses of these contaminants from other passive sampling materials like polyoxymethylene (POM) and polyethylene (PE). Estimates of k_d^* values for POM and PE can be determined from multiplying the experimentally determined k_d constant by the ratio of the Henry's Law Constant of the compound of interest to either the POM or PE-water partition coefficient (K_{POM} or K_{PE}). Relationships between K_{ow} and the polymer-water partition coefficients (K_{fw}) are found in Ghosh et al. (2014). Figure 4-13 shows the modelled C/C_o versus time curves for a 10 μm or 30 μm sorbent layer thickness of PDMS, POM, and PE, the most common passive sampling sorbent materials for sampling hydrophobic organic contaminants, exposed to air at 4°C or 20°C. Note that the predictions are limited to initial losses when air-side mass transfer resistances control and therefore may be used to define a conservative processing criteria for such materials (i.e. one that may overestimate volatile losses) The desorption rates are much slower for POM compared to PDMS for high volatility PAHs due to higher K_{fw} in POM. For example, naphthalene's $\log K_{fw}$ is equal to 2.9 for PDMS and 3.2 for POM. The impact of K_{fw} lessens as H decreases, therefore if volatile hydrophobic compounds, like naphthalene for narcosis measurements, are the compounds

of most interest, it would be beneficial to use POM versus PDMS or PE to minimize volatile losses between retrieval of the samplers and extraction. Note that the deployment time to reach equilibrium between the porewater and sorbent when using POM or PE samplers is longer than those of PDMS, so there is a tradeoff to be mindful of when sampling for a wide range of hydrophobicities.

Table 4-2 provides estimates of the sampling time required to ensure 90% concentration retention of naphthalene using PDMS, POM, and PE passive sampling sorbents of various thicknesses at 20°C and 4°C, respectively. If samplers are retrieved and immediately stored at low temperatures, there is an increase in the time required to achieve 90% concentration retention. For example, when using a 30 μm PDMS sorbent layer, the sampling time required to achieve 90% concentration retention increases from approximately 2 minutes to 7 minutes. Using thicker sorbent layers is an option for increasing the retention time of the compounds sorbed to the polymer, but using thicker sorbent layers also increases the time necessary to reach equilibrium between the polymer and the sediment porewater or surface water. For example, a 1.4 cm thickness of PDMS would retain 90% of naphthalene sorbed to it for a twenty-four hour period exposed to ambient air at 293K, but it would take over 2,500 years to reach 90% of equilibrium in a capped system like the Eagle Harbor site described in Chapter 5. If less volatile hydrophobic organic contaminants are the contaminants of concern for a site, then it would be more efficient to use thinner sorbent layers to decrease the deployment time of the samplers.

Table 4-1. $logK_{fw,}$ logH, and $logH/K_{fw}$ values for select PAHs at the temperatures of interest.

	$logK_{fw}$ [1]	logH @ 277K	$logH/K_{fw}$ @ 277K	logH @ 293K	$logH/K_{fw}$ @ 293K	logH @ 298K	$logH/K_{fw}$ @ 298K
Naphthalene	2.95	-2.38[2]	-5.3	-1.86[3]	-4.8	-1.76[3]	-4.7
Acenaphthene	3.42	-2.81[4]	-6.2	-2.35[4]	-5.8	-2.28[4]	-5.7
Fluorene	3.52	-3.05[4]	-6.6	-2.61[4]	-6.1	-2.39[4]	-5.9
Anthracene	3.77	-3.26[4]	-7.1	-2.84[4]	-6.7	-2.63[4]	-6.5
Phenanthrene	3.79	-3.39[4]	-7.3	-2.96[4]	-6.9	-2.75[4]	-6.7

[1] K_{fw} values from Ghosh et al. (2014)
[2] Henry's Law Constant values ($Pa*m^3/mol$) from Alaee et al., (1996) converted to dimensionless form by dividing by R, the universal gas constant (8.314 $Pa*m^3mol^{-1}K^{-1}$), and T, the absolute temperature (K)
[3] Henry's Law Constant values ($Pa*m^3/mol$) from Bamford et al. (1999) converted to dimensionless form by dividing by R, the universal gas constant (8.314 $Pa*m^3mol^{-1}K^{-1}$), and T, the absolute temperature (K)

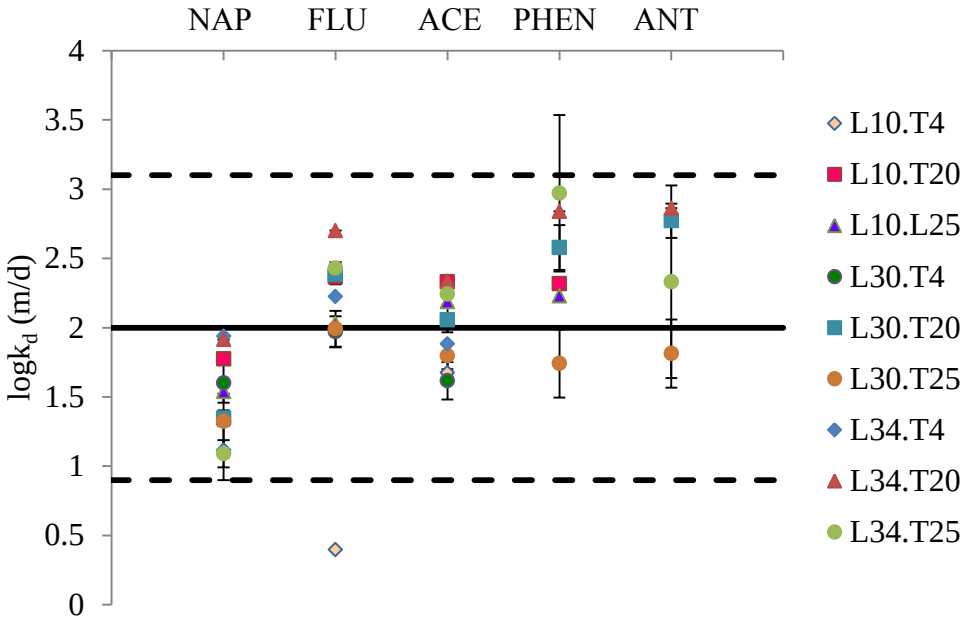

Figure 4-10. log(k_d) for the compounds that showed the most rapid desorption for all treatments. There is no correlation between the two variables. $logk_d$ is a constant equal to 2±1.1 (average ± 95% confidence interval, n = 31). Solid line represents average and broken lines represent average ± 95% confidence interval bounds.

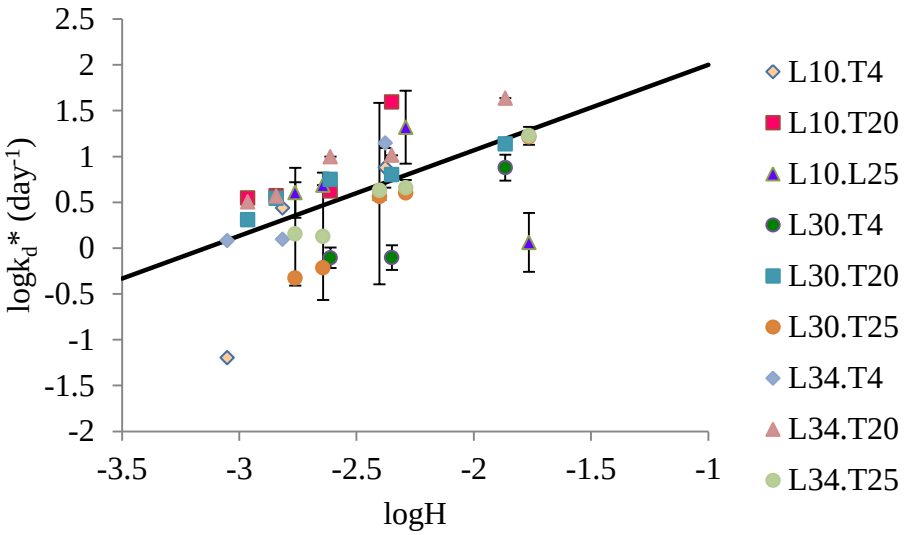

Figure 4-11. logH (H is dimensionless) verus $logk_d^*$ for all SPME PDMS dimensions and temperatures. The solid black line represents the relationship between logH and $logk_d^*$ where $logk_d^* = 0.93(\pm0.2)logH + 3(\pm0.5)$, $r^2 = 0.39$.

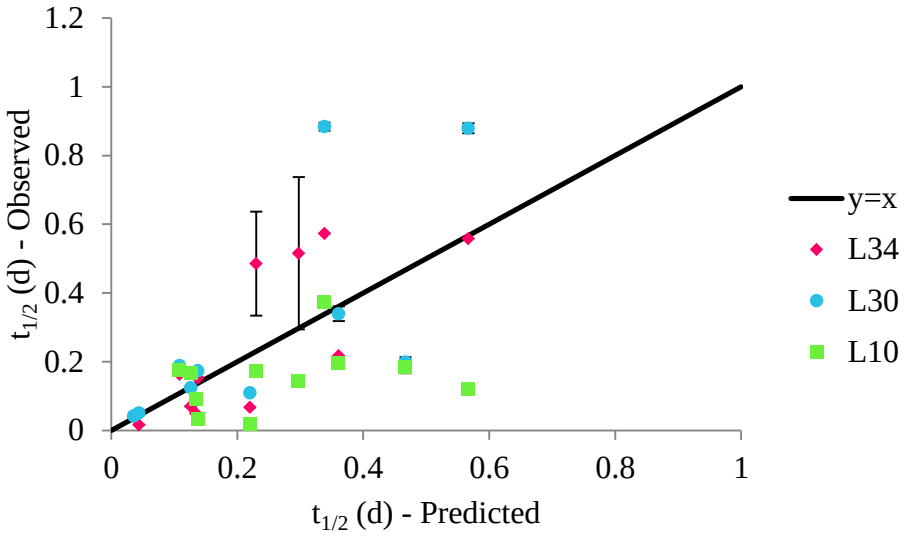

Figure 4-12. Observed half-life values versus predicted half-life values for naphthalene, fluorene, acenaphthene, phenanthrene, and anthracene desorption from SPME PDMS fibers using the relationship determined between log(k_d^*) and logH. The black solid line represents a one-to-one relationship.

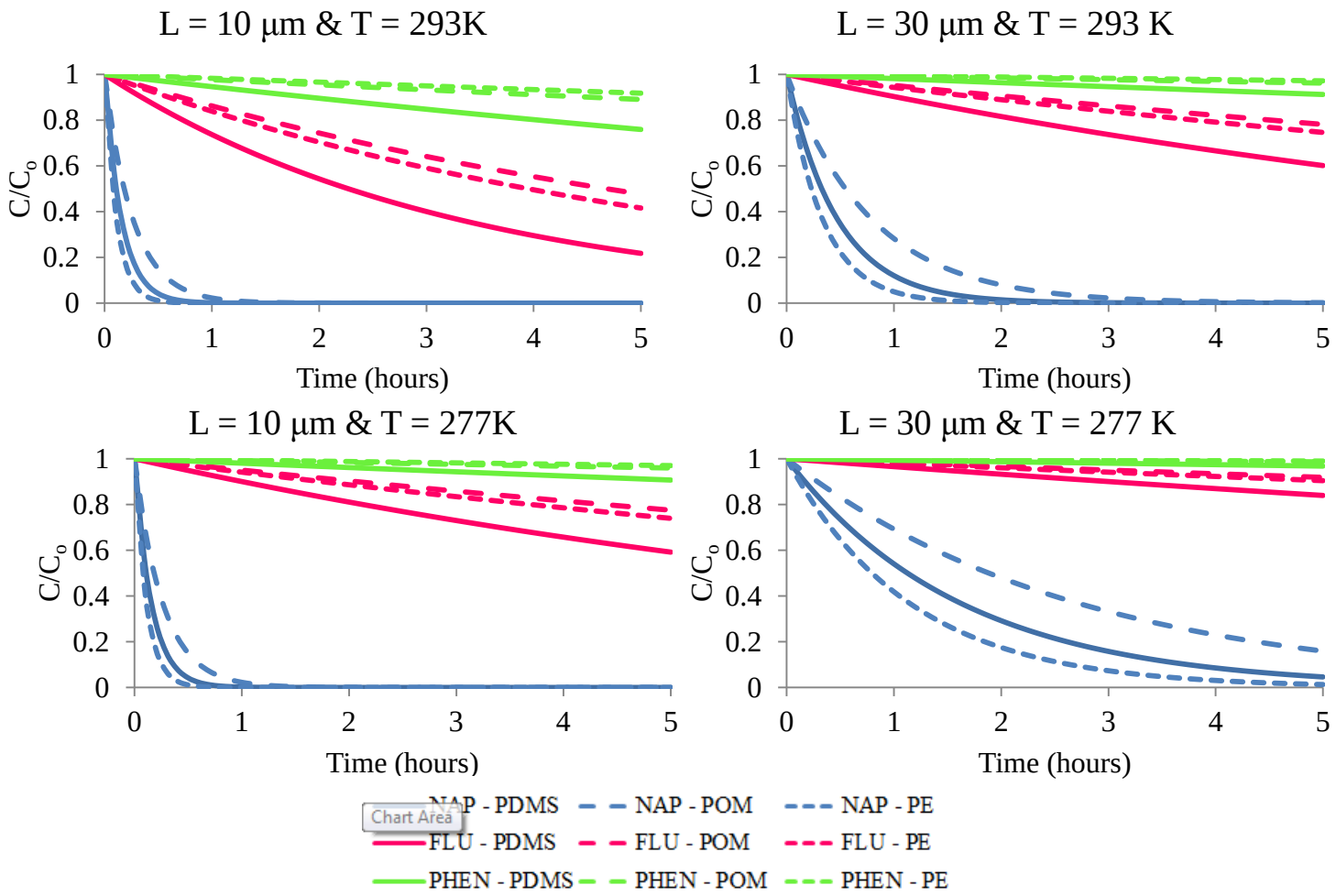

Figure 4-13. Modeled C/C_o values for 10 µm and 30 µm thick PDMS, POM, and PE passive sampling materials for naphthalene (NAP), fluorene (FLU), and phenanthrene (PHEN) exposed to ambient air at 4°C (277 K) and 20°C (293K).

Table 4-2. Estimates of the time (min) at which $C/C_o = 0.9$ for naphthalene (NAP) for different thicknesses of passive sampling sorbents: PDMS, POM, and PE exposed at 277K and 293K using model parameters tabulated above. Estimates based on k_d model fit of 10^2 m/d.

	NAP C/Co = 0.9 at Time (min)	
	T = 277 K	T = 293K
PDMS		
10 um	3	1
30 um	10	3
100 um	34	10
POM		
10 um	6	1.7
30 um	17	5
100 um	57	17
PE		
10 um	2	0.7
30 um	7	2.1
100 um	24	7

SIGNIFICANCE & IMPLICATION

One of the concerns when completing field sampling events with passive sampling methods is the accuracy of the reported concentrations especially for the low molecular weight compounds that are more volatile. The experiments, using SPME PDMS fibers of different thicknesses exposed to various ambient air temperatures, provided a fit to a model that incorporates the compound's Henry Law Coefficient and sorbent-water partitioning coefficient to estimate a compound's desorption rate. The model can be expanded to different sorbent materials commonly used to monitor hydrophobic organic contaminants in sediment porewater and surface water through the use of the sorbent specific partitioning coefficient. Estimates for the sampling time necessary to ensure 90% concentration retention on the polymer sorbent layer, indicated POM would be the most appropriate material, of the three modeled, for the monitoring

applications of the most volatile compounds. POM is not optimum for *in situ* field measurement of the most hydrophobic compounds, however, due to the long equilibration times necessary (Thomas et al., 2014). In general, passive samplers that provide the best performance (rapid uptake) for highly hydrophobic compounds are not optimum for monitoring less hydrophobic, more volatile compounds, and vice versa. The selection of a passive sampler must be based upon the sampling objectives and the selection of the optimum sampler thickness, material, and exposure and processing conditions to achieve the desired uptake and ensure sample integrity during processing.

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Chapter 5: Interpretation of Porewater Concentration Profiles Measured Using Profiling Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers[2]

ABSTRACT

Passive sampling using polydimethylsiloxane (PDMS) profilers were evaluated as a tool to assess the performance of in-situ sediment remedies at two locations, Chattanooga Creek (Chattanooga, TN), and Eagle Harbor (Bainbridge Island, WA). The remedy at these locations was capping over PAH contaminated sediments. The implementation and results at these contaminated sediment sites were used to illustrate the utility and usefulness of the passive sampling approach. Two different approaches were employed to evaluate kinetics of uptake onto the sorbent fibers. At these capped sites, the passive sampling approach was employed to measure intermixing during cap placement, contamination migration into the cap post-placement and recontamination over time.

INTRODUCTION

Contaminated sediment sites pose a unique challenge in terms of remediation for a variety of reasons including: the large number of past and ongoing sources than can be contributing factors, sediment movement based on natural and anthropogenic events, the sheer scale of contamination at many sites, the presence of endangered species or other ecologically valuable resources, and the diversity of concerns and opinions of the affected communities (EPA, 2005). Often, *in situ* sediment remedies of capping contaminated sediments with clean substrate

[2] A condensed version of this chapter has been published Thomas, C., Lampert, D., Reible, D., 2014. Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. Environmental Science: Processes & Impacts 16, 445-452. D.Lampert provided the mathematical models. D. Reible is the corresponding author.

with or without sorbing amendments (Wang et al., 1991, Thoma et al., 1993, Palermo et al., 1998, Reible et al., 2006) or *in situ* treatment with sorbing amendments (Ghosh et al., 2011) provide preferred options because they are relatively low cost and minimally invasive compared to removal options. Sediment caps reduce the risk posed by the fate and transport of contaminants by stabilizing the underlying sediment and physically isolating and reducing the flux to the water column and benthic communities (Lampert and Reible, 2009). The layer can consist of clean sediment, sand, gravel, and other borrow materials or can utilize more advanced designs utilizing geotextiles, sorbents, and other chemical and biological facets (Palermo et al., 1998). *In situ* treatment to reduce contaminant bioavailability is generally achieved by mixing activated carbon into the surficial sediments due to its high sorbing capacity (Ghosh et al., 2011).

The fact that contaminants are not removed or destroyed by these *in situ* options puts greater emphasis on monitoring remedy performance over time. Traditional measures such as bulk solids concentrations are not generally useful since the contaminant concentration does not change and, in the case of capping with non-sorbing materials such as sand, migration of contaminant through the cap will not lead to significant increases in the cap layer solids concentration.

An alternative monitoring approach is passive sampling of the interstitial waters in treated sediments or in the cap layer. Porewater sampling directly indicates the mobile phase contaminant and the use of a partitioning equilibrium sampler provides a measure of the freely dissolved portion of contaminant that has been shown to be a better indicator of bioaccumulation in benthic organisms even when the route of uptake is through ingestion (Kraaij et al., 2003, Lu et al., 2003, Lu et al., 2011, Mayer et al., 2013). Passive sampling is often implemented through the use of sorbents like polyethylene (PE), polyoxymethylene (POM), and polydimethysiloxane

(PDMS) to concentrate contaminants from water or porewater, that is, solid phase microextaction (SPME). Each of the sorbents behaves similarly although the term SPME is often applied only to the use of PDMS. The primary differences between the sorbents are the geometry of the commercially available forms and small differences in the sorptive characteristics. The volume to area ratio of the sorbent as defined by the geometry is a key factor in defining the kinetics of uptake and time to equilibrium. Passive sampling methods overcome problems associated with conventional sampling methods including the large amounts of water necessary to obtain the detection limits, and sampling or handling induced changes in sample concentration for example from sorption of contaminant onto sampling container's walls (Allan et al., 2009). The primary focus here is on the use of passive sampling via SPME PDMS fibers to measure reductions on porewater concentration after in-situ sediment treatment with activated carbon as an indicator of reduction in bioavailability and the measurement of vertical porewater concentration profiles in sediment caps to evaluate cap performance, including contaminant migration and fluxes as well as the mechanisms of cap contamination. PDMS is employed here because it is slightly less sorbing than POM or PE, and available as thin coatings on cylindrical glass fibers which aids in relatively rapid equilibration with porewater.

A laboratory study conducted by Lampert et al. (2011) demonstrated SPME PDMS fibers as a method to quantify sediment concentration in sediment caps. Passive sampling of the porewater concentrations in the microcosms using SPME PDMS enabled quantification of high resolution vertical concentration profiles that were used to infer contaminant migration rates and mechanisms. The in-situ use of SPME PDMS fibers was demonstrated in the field at an active capping demonstration at the Anacostia River (Washington D.C.) (Lampert et al., 2014). Findings highlighted the advantages of using passive sampling methods over conventional

methods based on solid-phase concentrations especially for limited sorption capacity capping materials like sand. POM and PE have also been used in the field for the assessment of in-situ sediment treatment technologies (Janssen et al., 2011, Beckingham and Ghosh, 2013, Fernandez et al., 2009). They have been used less commonly for measurement of porewater concentration profiles in sediment (Oen et al., 2011).

This work seeks to explore the use of SPME PDMS fibers for determining the effectiveness of in-situ contaminated sediment remedies by application of capping at several sites. The emphasis is on development of practical field approaches for the routine use of profiling PDMS passive samplers for remedy evaluation. PDMS coated fibers have the advantage of convenient cylindrical geometry for insertion into sediments, the ability to fabricate fibers with widely varying sorbent thicknesses, and, the PDMS provides relatively fast uptake kinetics compared to similarly dimensioned PE or POM (Ghosh et al., 2013). The detection limits of PDMS are not as low with similarly dimensioned POM or PE, but that is rarely a problem in contaminated sediments. The objectives of this study were to

1) Evaluate approaches for evaluation of kinetics of uptake and correction for non-equilibrium uptake in the field,

2) Interpret target compound concentration profiles to evaluate the effectiveness of the in-situ sediment remedies, and

3) Compare freely dissolved porewater concentrations determined via SPME PDMS passive sampling techniques and conventional techniques that utilize the transformation of a bulk solid concentration into a porewater concentration through a sediment-water portioning coefficient, K_d.

In order to address these objectives, results from the two unique capping field sites (Chattanooga Creek, Chattanooga, TN and Eagle Harbor, Bainbridge Island, WA) contaminated with a range of PAH compounds are presented. Vertical profiles in terms of concentration were used at the capping sites to assess mechanisms and rates of cap contamination and non-equilibrium corrections were estimated via performance reference compounds (PRCs) and use of two different size fibers with different kinetic uptake rates.

MATERIALS AND METHODS

Chemicals, fibers, and samplers

For studies employing PRCs to evaluate fiber uptake kinetics, four deuterated PAHs covering a range of hydrophobicities were employed. Stock solutions of fluoranthene-d10, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were purchased from Cambridge Isotope Laboratories. A stock solution of chrysene-d12 was purchased from Ultra Scientific Analytical Solutions. The deuterated PAHs were selected as performance reference compounds (PRCs) based on their lack of interference with their non-deuterated counterparts during analysis and their hydrophobicities mirrored the range of hydrophobicities in the target compounds, the PAH_{16} priority pollutants. Fibers were placed in contact with a spiking solution with final aqueous concentrations of 30 μg/L fluoranthene-d10, 80 μg/L chrysene-d12, 50 μg/L benzo(b)fluoranthene-d12, and 25 μg/L dibenz(a,h)anthracene-d14 for seven days. Calculations and previous measurements had shown that seven days was sufficient for PRC depletion from the spiking solution and sorption onto the fiber to occur.

The glass fibers used during this study were manufactured by Fiberguide (Stirling, NJ) or by Polymicro Technologies (Phoenix, AZ). Three different sizes of fibers were used for these

studies: glass fibers with a core diameter measuring 1000 μm were coated with either a 30 μm or 35.5 μm layer of PDMS, and the other set consisted of 210 μm cores coated with a 10 μm PDMS layer. The coating concentration is approximately 115 μL PDMS per meter of fiber, 97.1 μL PDMS per meter of fiber, 6.91 μL PDMS per meter of fiber for the 1071/1000 μm (outer/inner diameter) fiber, the 1060/1000 μm fiber, and the 230/210 μm fiber, respectively. Before each use, fibers were soaked sequentially in hexane, acetonitrile, and deionized water. No interfering peaks were detected in the fibers after cleaning.

For ease of insertion and protection from sand and gravel in the sediments, the fibers were secured in modified Henry samplers (M.H.E Products) using a waterproof caulk. The devices are similar to those described in Lampert et al. (2011) with slight differences. Modifications included 4 mm diameter perforations in the outer sheath, a 2 mm groove in the inner rod of the sampler, and the attachment of a washer that rests at the sediment-water interface during deployments. The groove length of the inner rod dictates the sampling length of the sampler. The outer sheath facilitates fiber-porewater contact while protecting the fiber. The inner rod secures the fiber from movement during deployment and retrieval. The samplers were washed with hot water and detergent, soaked sequentially in hexane and acetonitrile, flushed with deionized water, and dried at 180°C overnight.

Sediment sampling sites

Chattanooga Creek (Chattanooga, Tennessee)

Three different sampling events were completed in November 2009, November 2010, and June 2011, along a 2.5 mile stretch of Chattanooga Creek (Chattanooga, TN) near a former coal carbonization facility. A total of seven locations were selected for sampler deployment to

explore the different sediment conditions of the site including uncapped, fresh sand/sediment capped, capped with amendments (AquaBlok®), upstream and downstream locations. For each sampling event, at least four sampling locations were within the capped portion of the creek and two sampling locations were placed outside of the capped region. Chattanooga Creek can be described as a non-tidal system containing low permeability and low sorbing sediment (EPA 2011), therefore the uptake kinetics were expected to be slow. Deployments were for a period of 14-16 days. No kinetic correction data was collected for the November 2009 study. For the November 2010 sampling event, uptake kinetics were determined using fibers with different PDMS coating thicknesses (230/210 μm vs. 1060/1000 μm). For the final sampling event, uptake kinetics were determined using fibers with different thicknesses (230/210 μm vs. 1060/1000 μm) and using the previously mentioned four deuterated PAHs as PRCs.

Eagle Harbor (Bainbridge Island, Washington)

The Wyckoff-Eagle Harbor Superfund site is located off the east side of Bainbridge Island, Washington. Operation of a former wood-treating facility and a former shipyard left the area contaminated with creosote, pentachlorophenol, various polycyclic aromatic hydrocarbons, and heavy metals (USACE, 2012). In a partnership between the EPA and the U.S. Army Corps of Engineers approximately 70 acres of the site were capped with clean sediments (USACE, 2012). The sediment cap undergoes monitoring to ensure buried contaminants are not leaching into the surface water. Samplers were deployed into the capped sediments and into the overlying water column in November 2011 for a period of 7 days. The fibers used during the deployments were manufactured by Polymicro Technologies (Phoenix, AZ) and were composed of a 35.5 μm PDMS coating on a 1000 μm diameter core (1071/1000), or a 30 μm PDMS coating on a 1000 μm diameter core (1060/1000) PDMS fibers spiked with deuterated PAHs were used to

determine uptake kinetics. The data collected using PDMS complements other monitoring activities like cores and grab samples performed by the U.S. Army Corp of Engineers and USEPA.

Chemical analysis

Upon removal from the sediment or water column, the PDMS fibers were wiped with a lint free tissue to remove any particulate matter. All fibers except the 230/210 μm fibers were sectioned into 2 cm pieces and placed in a 2 mL autosampler vial containing a 250 μL insert containing 250 μL of acetonitrile for extraction. The 230/210 μm fibers were sectioned into 8 2-cm segments; the top four segments were placed in a 2 mL autosampler vial containing a 250 μL insert containing 100 μL of acetonitrile. The same procedure was followed for the bottom four fiber segments.

The PDMS solvent extracts were analyzed using Waters 2795 High Performance Liquid Chromatography (HPLC) with ultraviolet-diode array (UV) and fluorescence (FLD) detectors according to EPA Method 8310 for PAH_{16} analysis. The Phenomenex Luna 5μ C18 column (250×4.6 mm) temperature was held at 40°C. The separation occurred using a 1.0 mL/min isocratic flow composed of 3:7 (v:v) of water: acetonitrile.

Check standards and blanks were used with every sample set to ensure performance. For PAHs, a 5 or 20 μg/L standard (Ultra Scientific) containing 16 PAHs was analyzed. Standards ranging in concentrations from 0.05 μg/L to 100 μg/L were used to determine each compound's response factor.

On the basis of the chemical analysis of the extract, the concentrations associated with the fiber were calculated as follows:

$$C_{PDMS} = \frac{A*RSF_{PAH}*V_{solvent}}{L_{fiber}*v_{fiber}*K_{pw}} \quad \text{Eq. 1}$$

Where A is the HPLC response integration area, RSF_{PAH} is response factor from a standard curve unique to each PAH, $V_{solvent}$ is the volume of solvent used to extract fiber, L_{fiber} is the length of fiber sample, v_{fiber} is the specific volume of fiber (volume per unit length), and K_{pw} is the fiber-water partition coefficient unique to each PAH.

The porewater concentrations are then determined through the sorbent-water partition coefficient:

$$C_{pw} = \frac{C_{PDMS}}{K_{pw} f_{ss}} \quad \text{Eq. 2}$$

K_{pw} is given by the correlations with octanol-water partition coefficient given by (Ghosh et al., 2014),

$$PAH: logK_{PDMS-W} = 0.725 logK_{ow} + 0.479 \quad (R^2 = 0.99) \quad \text{Eq. 3}$$

$$PCB: logK_{PDMS-W} = 0.947 logK_{ow} - 0.017 \quad (R^2 = 0.89) \quad \text{Eq. 4}$$

and f_{ss} is the degree of non-equilibrium, estimated by the methods below.

Determination of Non-equilibrium

Non-equilibrium corrections had to be made as the deployment time was not sufficient to achieve equilibrium as indicated by measurable differences between the 230/210 μm and 1060/1000 μm (or 1071/1000 μm) fibers and substantial amounts of PRC in the fibers after deployment. Corrections were made on the basis of a model of uptake into the fiber that assumes external mass transfer resistances control uptake and that the uptake is effectively one-dimensional. These assumptions are generally valid for PDMS and the fiber geometries used

here (Lampert et al., 2015) and may be valid under most conditions for other low volume to surface area passive sampler materials as well.

The external mass transfer processes are modeled as a retarded diffusion process with retardation associated with sorption and desorption onto the stationary solid phase in sediment media. The mass absorbed by the fiber over time is equal to (Lampert et al., 2015, Lu et al., 2014):

$$M(t) = K_{pw} C_0 L_{fiber} v_{fiber} \left[1 - \exp\left(\frac{RDt}{\ell^2 K_{pw}^2} \right) erfc\left(\frac{\sqrt{RDt}}{\ell K_{pw}} \right) \right] = K_{pw} C_0 L_{fiber} v_{fiber} f_{ss} \qquad \text{Eq. 5}$$

M(t) is the mass absorbed on the fiber in time, t, K_{pw} is the sorbent polymer-water partition coefficient, C_0 is the porewater concentration, ℓ is the volume to area ratio of the polymer coating on the fiber, and R·D is the product of the sorption related retardation factor in the sediment surrounding the fiber and effective diffusivity, and f_{ss} is the fraction of equilibrium achieved. The desorption of the PRCs from the sorbent follow the same model except that the bracketed term (f_{ss}) is positive and contains only the second term in the equation above. D is only slightly compound dependent, generally much less than a factor of two within a group of homologs, while R is expected to be proportional to the hydrophobicity of the compound. If the octanol-water partition coefficient, K_{ow}, is employed as an indicator of hydrophobicity, the factor RD is expected to increase linearly with K_{ow}. In the case of diffusion only in the sediment media, with retardation largely controlled by the rapidly exchangeable, linear sorbing sediment organic carbon ($K_d \sim K_{oc} f_{oc}$), the order of RD would be expected to be

$$RD \sim \rho_b K_{oc} f_{oc} \frac{\phi \mathscr{D}_w}{\tau} \sim \left(1 \frac{kg}{L} \right) (0.35 K_{ow})(0.05) \frac{0.5\left(5x10^{-6} \frac{cm^2}{\sec} \right)}{2.5} \sim 1.6(10^{-7}) \frac{m^2}{day} K_{ow} \qquad \text{Eq. 6}$$

where ρ_b is the bulk (dry) density of the sediment (assumed ~1 kg/L), K_{oc} is the organic carbon partition coefficient (approximately 0.35 K_{ow}) (Arnot and Gobas, 2003), f_{oc} is the fraction organic carbon (assumed 5%) ϕ is the sediment void fraction (assumed 50%), $\mathscr{D}_w$ is the molecular diffusivity of the contaminant in water (assumed 5 x10^{-6} cm^2/s) and τ is a tortuosity factor which for a sediment with porosity 0.5 would be approximately 2.5 (Boudreau, 1996).

Under conditions influenced by advection, which are also subject to retardation, a similar behavior would be expected although the effective diffusivity in that case would not be closely related to the molecular diffusivity of the compound and the factor would likely be greater than 1x10^{-7} m^2/day. In a situation where particle movement is important, for example during bioturbation, the model may still be applicable but a linear correlation with hydrophobicity would not be expected since there would be no retardation in a stationary sorbing phase.

In a given system characterized by a particular representative value of RD, the fractional approach to steady state depends only upon time, the hydrophobicity of the compound through the sorbent-water partition coefficient, and the volume to area ratio of the fiber in use. The state of non-equilibrium can be assessed through estimation of RD. This can be accomplished through either PRCs or by using fibers with different measurements of ℓ.

Knowing the initial PRC mass and the mass after a deployment of time t we can assess the degree of non-equilibrium for the PRC ($f_{ss} = M(t)/M_0$). With a known fiber and sorbent water partition coefficient, RD can be determined and fitted to a correlation with K_{ow}. Once such a relationship is found, K_{ow} of other compounds of interest can be used to estimate f_{ss}. Twelve 2-cm fiber replicates of PRC spiked fibers, taken before both deployments, were used to estimate the mean initial concentration for each PRC at time zero. Losses during transport to the site for deployment were found to be negligible (<10%).

A second method for estimating contaminant uptake kinetics is to utilize the differences of PDMS fiber geometries. The value of RD can be estimated by comparing the ratio of the mass of a particular contaminant on one fiber to another with a different volume to area ratio deployed for the same length of time. The ratio is only a function of known quantities and the unknown RD. Samplers were deployed into the sediments containing one 1071/1000 μm fiber (ℓ = 34.3 μm), 1060/1000 μm fiber (ℓ = 29.2 μm) or 230/210 μm fibers (ℓ = 9.6μm). This approach requires that the co-located fibers are exposed in identical environments.

RESULTS & DISCUSSION

Contaminant uptake kinetics

At the Chattanooga Creek site, two methods for determining the steady-state concentrations were employed. For the MCT method, only the concentrations of PAHs with a $\log K_{ow}$ greater than 5.22 were employed due to apparent evaporative losses of the less sorbing PAHs as described in Chapter 4. In addition, only compounds with concentrations exceeding the detection limits were included in this analysis. For the monitoring event at the Chattanooga Creek site, seven mid-to-high range PAH compounds were compared between fibers to estimate RDs using the MCT method and four PRCs were used to estimate RDs using the PRC method. The estimated values of RD from the two methods are not significantly different (p-value = 0.15, $\alpha = 0.05$). The logRD (m^2/d) values, calculated using both methods, for Chattanooga Creek were related by a linear relationship ($\log RD = \alpha \log K_{ow} + \log\beta$) ($\alpha = 1 \pm 0.1$, $\beta = -7.1 \pm 0.7$, n = 57, $r^2 = 0.63$) to $\log K_{ow}$. The fraction of steady state achieved during the 14 day deployment was estimated to range from 21 ± 18% for dibenz(a,h)anthracene ($\log K_{ow}$ = 7.39), the most

hydrophobic compound monitored at this site, to 71 ± 15% for naphthalene ($logK_{ow}$ = 3.41), the least hydrophobic of the compounds monitored at this site.

Only the PRC method was used at the Eagle Harbor site in November 2011. The observed logRD values for the Eagle Harbor site were fit to a linear relationship with $logK_{ow}$ ($\alpha = 1 \pm 0.2$, $\beta = -6 \pm 0.1$, n = 20, $r^2 = 0.41$). The fraction of steady state achieved during the 14 day deployment was estimated to range from 50 ± 3% for dibenz(a,h)anthracene ($logK_{ow}$ = 7.39), the most hydrophobic compound monitored at this site, to 90 ± 1% for naphthalene ($logK_{ow}$ = 3.41), the least hydrophobic of the compounds monitored at this site. Note that the RD values for compounds of interest at both sites of these values are within approximately an order of magnitude of the diffusion only result.

Assessment of remedy performance

Porewater Profile Measurements in Sediment Caps

Several different scenarios of contaminant behavior within the cap and sediment were identified including: 1) low concentrations within the cap with a sharp increase in concentration in the underlying contaminated sediment, 2) a low uniform contamination profile within the cap layer due to intermixing with the contaminated sediment, presumably during placement of the cap, 3) high concentrations of less sorbing contaminants within the near surface with uniform low concentrations of more sorbing contaminants throughout the cap indicative of surface recontamination, and 4) uniform low concentrations of less sorbing contaminants within the near surface while concentrations of more sorbing contaminants increase with depth, which could be indicative of depletion or vertical migration.

The first scenario is that of a concentration profile with very low concentrations within the cap and sharp increase in concentration at the interface with the underlying sediment. This is typically the desired scenario for a cap. Figure 5-1 shows just such a profile during sampling in November 2010 at Chattanooga Creek, TN. Also shown are samples at the same location in November 2009 showing good agreement in the near surface concentrations between the two years. In 2009, samplers were too short to penetrate the cap and were lengthened for 2010. The sampler in 2010 showed slightly elevated concentrations but they remain below the comparative criteria, the EPA surface water quality standard. It is likely that the porewater concentrations at the bottom of the sampler were slightly elevated, but the sampler used in 2009 was too short to complete penetrate through the cap. The caps at both the Eagle Harbor and Chattanooga Creek sites were nominally 3-5 ft in thickness whereas only a 3 ft (~90 cm) long sampler was the maximum length used.

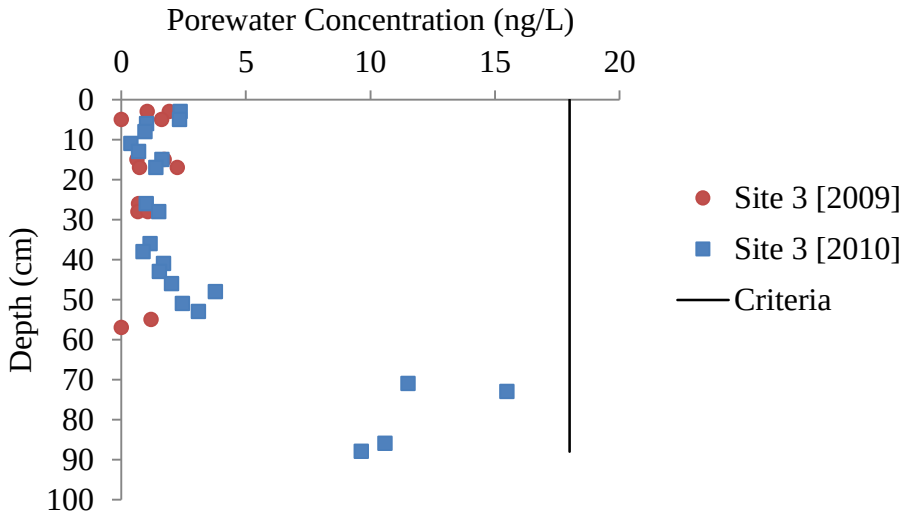

Figure 5-1. Depiction of benzo(a)pyrene profiles in cap material at Chattanooga Creek, TN in 2009 (●) and 2010 (■). Also shown is a comparative criteria, the EPA surface water quality standard of 18 ng/L

A second common scenario observed at capped contaminated sediment sites is when there exists intermixing of contaminated native material with the clean capping material, likely during the placement of the cap. This may result in a nearly uniform concentration profile as seen in Figure 5-2 from a location in Eagle Harbor. Due to the strongly sorbing nature of HPAHs, they generally serve as a tracer of particle movement rather than porewater migration. The cap at this location had been in place since 1994 and is approximately 120 cm thick (USACE, 2012). Note that the concentrations are quite low, well below EPA surface water quality standards indicating that this degree of intermixing may have minimal consequences.

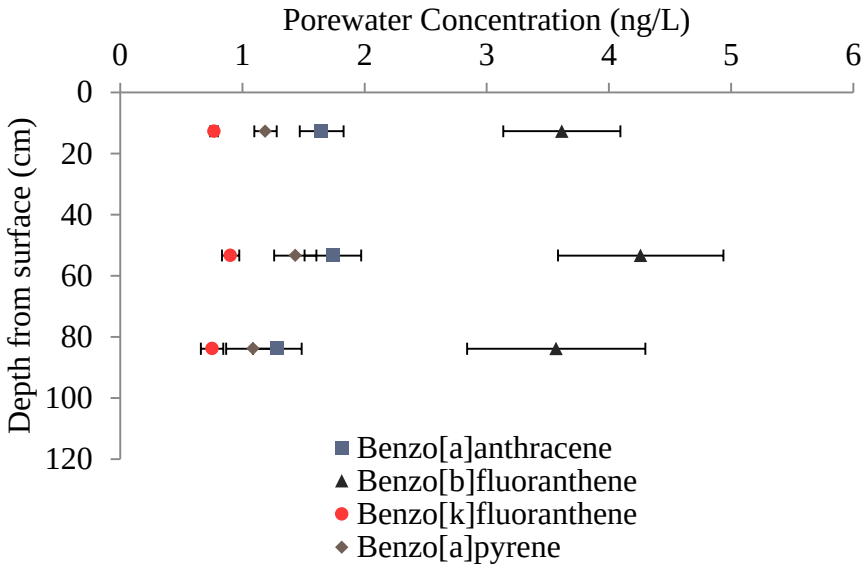

Figure 5-2. Concentration profiles of four HPAHs at the Wyckoff/Eagle Harbor Site in the 120 cm thick capping layer. Error bars represent the range of the mean porewater concentration (n=2). The EPA surface water quality criteria (not shown) for all compounds depicted is 18 ng/L.

Another scenario commonly encountered is where ongoing contaminant sources re-contaminated the surficial sediments. The goal of cap monitoring is to prove that the cap is effectively sequestering the contaminants from the overlying water column and benthic communities. Evidence that is consistent with migration through a cap found using SPME PDMS

fibers would cause a location to be reexamined and may ultimately lead to further remediation efforts. Sampling locations at both sites were indicative of migration. Such profiles are depicted in Figure 5-3 and in Figure 5-4. At Chattanooga Creek (Figure 5-3), low concentrations are measured within and below the cap and high concentrations are measured in the near surface region. Concentrations were normalized to the highest observed concentration in the cap simply to emphasize that the highest concentrations are now near the surface and not associated with migration from below.

At Eagle Harbor, Location G-8 had the highest LPAH concentrations measured relative to all other sampling locations, but these substantial quantities of LPAHs in the near-surface were not coupled with high concentrations of HPAHs at depth (see Figure 5-4). LPAHs weather or deplete at a faster rate than HPAHs, therefore observing high concentrations of LPAHs not coupled with high concentrations of HPAHs is inconsistent with migration into the cap. Location G-8 is one of the easternmost sampling locations at this site near private marinas, the low levels of contamination are most likely caused by a recent contamination by off-site suspended sediment moving into the sampled area. The same trend was also seen at Location H-10.5 at the Eagle Harbor site, although with more modest concentrations of LPAHs than at Location G-8.

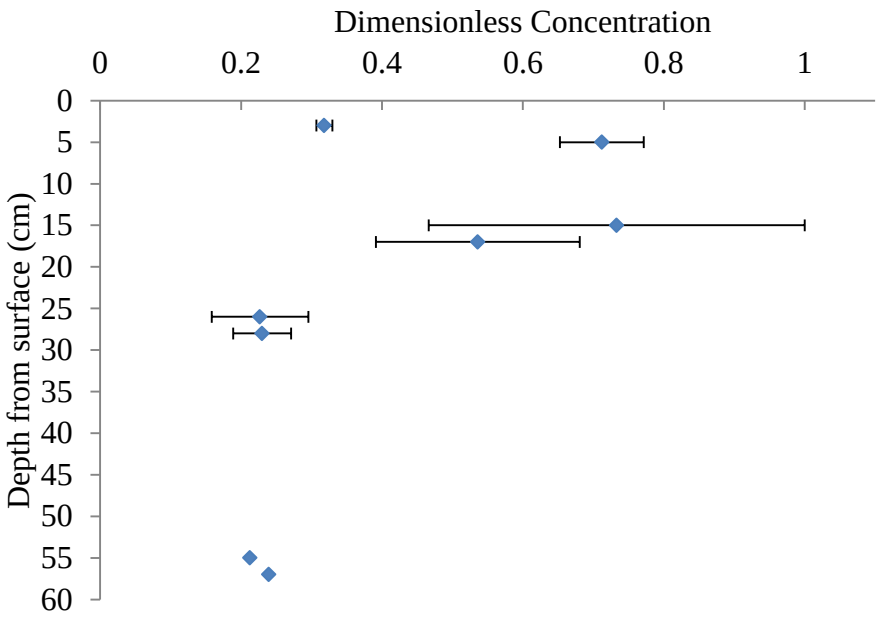

Figure 5-3. Dimensionless concentration (C/C_{max}) of pyrene during the November 2009 sampling event at the downstream edge of the capped region of Chattanooga Creek. Error bars represent the range of the dimensionless porewater concentration (n = 2). The range is not shown for depths greater than 30 cm as only one measurement was made during the first sampling event.

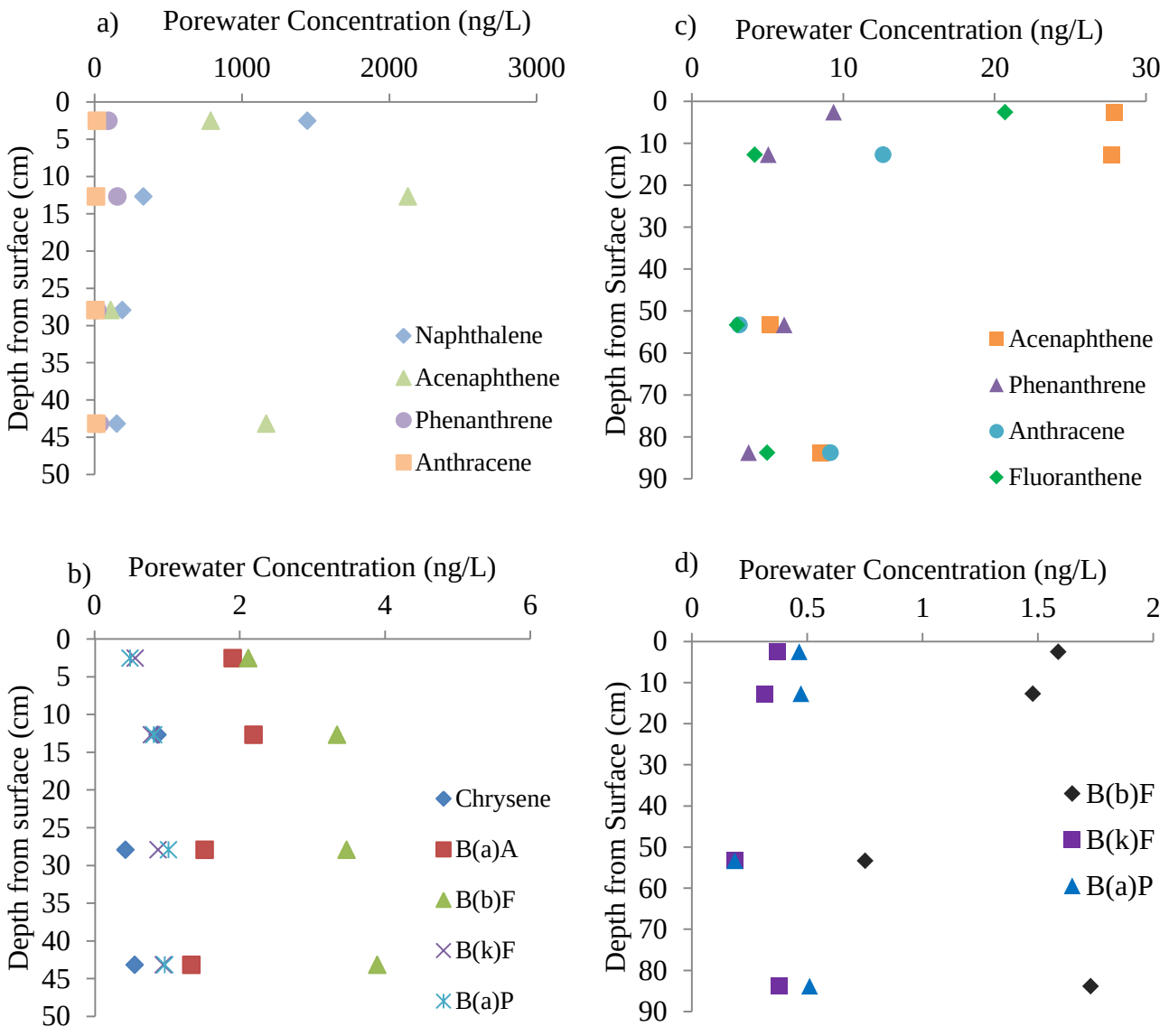

Figure 5-4. (a) LPAH and (b) HPAH concentration profiles for Location G-8 at the Eagle Harbor site. (c) LPAH and (d) HPAH concentration profiles for Location H-10.5.

Like the previously mentioned examples, concentration profiles for Location J-9 at the Eagle Harbor site suggested migration, but this location's observations pointed towards vertical migration. At this location the LPAHs were relatively uniform in concentration, while HPAH concentrations increased with depth (see Figure 5-5). These profiles are consistent with vertical migration through a cap, but after further review of previous five-year review (USACE, 2007), it

was hypothesized that depletion rather than migration was the cause of these profiles as the site may have never been capped or the cap was very thin.

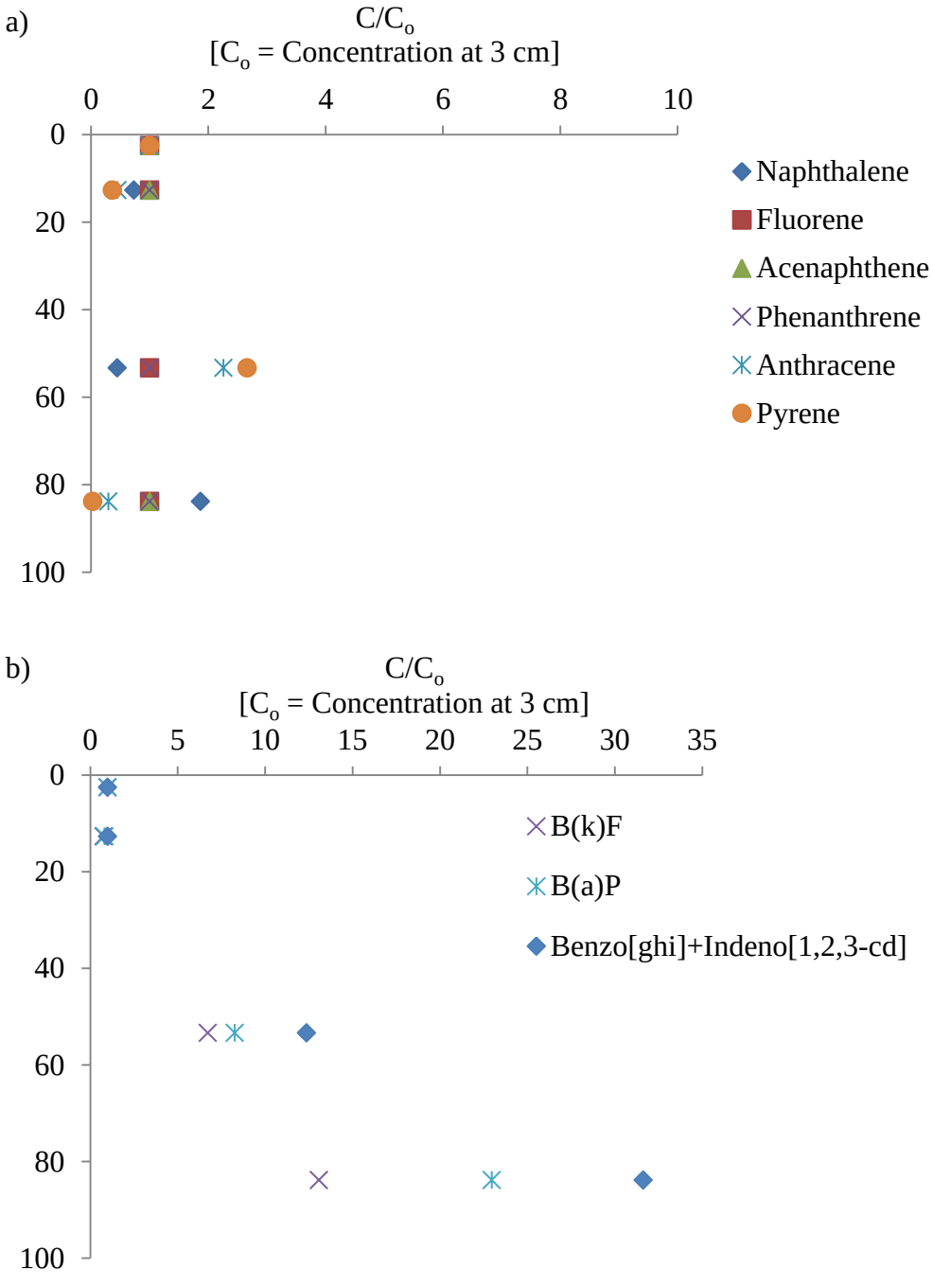

Figure 5-5. (a) LPAH and (b) HPAH C/C_o values for depths where C_o is the concentration measured near the surface of the cap.

Comparing SPME PDMS and bulk solid derived porewater concentrations

Currently, sediment quality guidelines derived using equilibrium partitioning theory are not based on directly measured freely dissolved concentrations, but rather on freely dissolved concentrations derived from a bulk solid concentration and a sediment-water partition coefficient found in literature (Mayer et al., 2014). This could lead to a misrepresentation of risk as contaminants sorbed to particulate matter are not bioavaliable. To determine the level of misrepresentation, porewater concentrations from SPME-PDMS profilers and bulk solid concentrations from grab samplers were utilized. The grab samples were collected by United States Army Corps of Engineers- Seattle District. Ten of the sediment grab locations corresponded with SPME deployment locations. PDMS samplers measure the bioavailable fraction of the contaminant, while grab samples provide a bulk solid concentration. An effective organic carbon partition coefficient was calculated using the following relationship between the porewater and bulk solids concentrations:

$$K_{oc} = \frac{W_s}{C_{pw}^{SPME} f_{oc}} \qquad \text{Eq. 7}$$

This comparison assumes equilibrium partitioning between the solids and adjacent porewaters. W_s is the concentration measured from the grab samples (μg/kg), C_{pw}^{SPME} is the porewater concentration measured via PDMS fibers (μg/L), and f_{oc} is the organic carbon fraction of the sediment. A plot of the effective organic carbon partition coefficients calculated using the bulk solid and SPME PDMS data in the upper 10 cm of the cap is presented in Figure 5. The best fit of the observed $\log K_{oc}$-$\log K_{ow}$ relationship is approximately 0.25 log units or 1.8 times higher than the $\log K_{oc}$ values reported by Baker et al. (1997) using the relationship: $LogK_{oc} = 0.903 LogK_{ow} + 0.094$ indicating that solid phase concentrations over predicted

porewater concentration compared to measured SPME PDMS values. This is normally the result of sorption onto strongly sorbing phases such as "black" carbon (Accardi-Dey and Gschwend, 2003). Because sorption onto these strongly sorbing phases is typically quite slow, the deviation between measured and bulk-solid predictions of porewater concentrations is consistent with aged contaminants and strongly solid-associated contaminants. That is, the data suggest that much of the observed contamination is associated with past contamination and possible migration of contaminated sediment particles from source areas. If the sediment was contaminated by recent migration in the porewater, a smaller deviation would be expected between measured and bulk-solid predicted porewater concentrations. The greater mobility and potentially more recent contamination by LPAHs may be reflected in the smaller deviation at low $logK_{ow}$ in Figure 5-6.

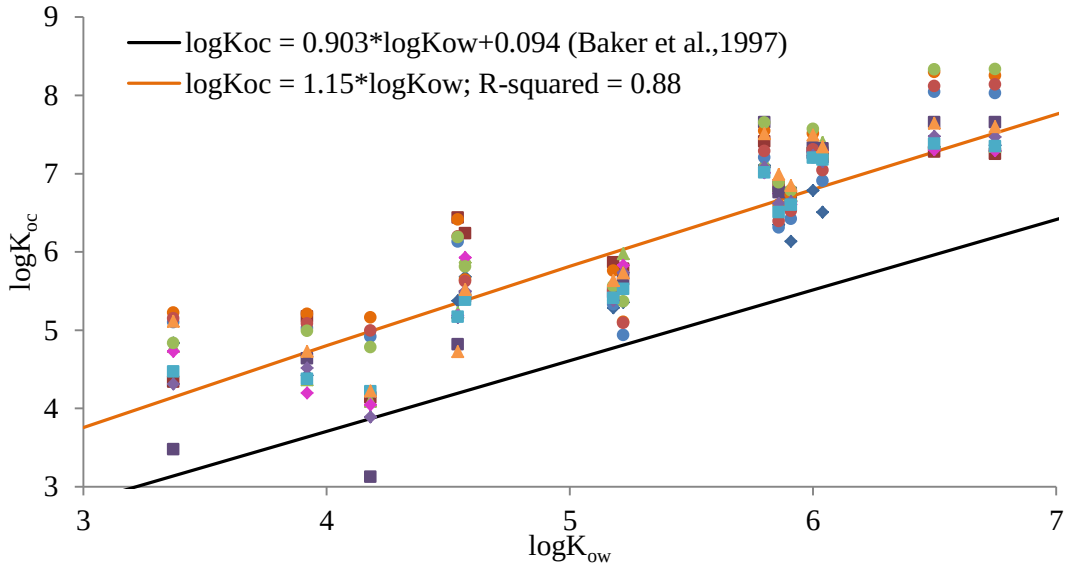

Figure 5-6. $LogK_{oc}$-$LogK_{ow}$ relationship determined from the upper 10 cm of twelve sampling locations at Eagle Harbor where grab samples and SPME samples overlapped. The orange solid line represents the best fit relationship of the field data (slope = 1.15, r^2 = 0.88). The black solid line represents the relationship determined by Baker et al. (1997) between $logK_{oc}$ and $logK_{ow}$.

SIGNIFICANCE & IMPACT

The results from the field deployments demonstrated that PRCs are a viable option to measure the state of non-equilibrium between a passive sampling material and the surrounding environment, but that other options can also be used although with generally greater uncertainty. The sampling in sediment caps showed that SPME PDMS methods can be quite helpful in identifying transport mechanisms and rates and separating placement intermixing and recontamination from contaminant migration through a cap. The conclusions drawn from the porewater sampling, however, may differ quantitatively from the conclusions that would be found from bulk solids and are more representative of risk. The field examples show that passive sampling can provide useful tools for remedy assessment.

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Chapter 6: Monitoring Contaminant Flux and Intermixing within Sediment Caps using in situ Solid Phase Microextraction Techniques

ABSTRACT

The freely dissolved concentration in porewater provides an indication of mobile contaminants in sediment beds. Solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fiber measurements have been shown to directly correlate with the interstitial porewater and water column concentrations of hydrophobic organic contaminants (HOCs). Moreover, the rate of equilibration of PDMS passive samplers is typically controlled by the rate of the interstitial mixing external to the passive sampler. Thus the combination of the measured concentration gradient or difference between sediment and overlying water and the rate of equilibration of the passive sampler provides an indication of the flux of bioavailable contaminants.

In this work, the rate of equilibration of contaminant uptake in the passive sampler is estimated via pre-equilibrated performance reference compound (PRCs). A simple model of the release of these PRCs is used to predict interstitial mixing in the sediment surrounding the passive sampler and to aid in the estimation of the steady state uptake of sediment contaminants. The foundations of the model will be discussed and its results are used to predict fluxes from the sediment at several contaminated sediment sites including Chattanooga Creek, TN, and Eagle Harbor, WA to illustrate the utility and usefulness of the SPME PDMS approach at evaluating contaminant flux and to indicate the magnitude of the effective interstitial mixing rates in these different environments.

INTRODUCTION

Remediation strategies that include capping sediments have been utilized since the 1970s by the US Army Corps of Engineers (Palermo et al., 1998) as a tool to eliminate resuspension of contaminated sediment into surface waters, stymie contaminant diffusive and advective migration, and isolate benthic communities from contaminated material (Reible, 2014). Various materials are used for capping depending on the contaminants of concern and environmental conditions. For example, a clean sand cap could be appropriate for sites with contaminants of concern like strongly solid associated hydrophobic organic contaminants, without tidal pumping or vertical upwelling, as in this case a simple diffusive barrier is likely required (Thibodeaux et al., 1991). In a case where vertical upwelling or tidal pumping mechanisms are at play, a cap amended with clays or sorbents such as activated carbon and organophilic clays would be a superior option over a clean sand cap (Reible, 2014). Amended caps with activated carbon or organophilic clays are also options when dealing with high concentrations of strongly solid associated contaminants or with NAPLs, respectively.

Monitoring after completion of remediation activities is a crucial part of the remediation process and there are both long-term and short-term reduction goals that need to be addressed when monitoring for remediation effectiveness (Apitz et al., 2004). For both long-term and short-term monitoring goals, it is critical to understand contaminant behavior in terms of direction and magnitude of flux (Liu et al., 2013). A compound's chemical activity determines its partitioning behavior and differences between chemical activities in different phases determines their fate and transport. Freely-dissolved concentrations can be used to approximate chemical activity if normalized by compound specific solubilities (Reichenberg and Mayer, 2009). SPME PDMS and other passive sampling materials measure the freely-dissolved aqueous concentrations in

sediment or overlying water columns and therefore measures chemical activity of HOCs (Mayer et al., 2014). The gradient between the porewater concentrations and the water column concentrations drives the flux of bioavailable contaminants. A handful of studies have been completed utilizing passive sampling materials to discern diffusive flux, including SPMDs in a laboratory study to evaluate the effects of installation of a cap proposed as a remediation strategy in an Oslo harbor, Norway (Schaanning, 2006), LDPE attached to horizontal and vertical plates of novel passive sampling support developed by Lui et al. (2013) and testing in urbanized areas of Hailing Bay, and POM in a field assessment of an activated carbon amendment cap pilot study in the Grasse River (Beckingham and Ghosh, 2013). These diffusive flux estimates relied upon measured concentration gradients or the rate of uptake in a passive sampler covering the surface. The latter system could artificially eliminate any advective flow while the other analyses would underestimate the flux if processes other than diffusion are operative.

Here we propose using SPME PDMS fibers spiked with performance reference compounds (PRCs) *in situ* to determine both a concentration gradient and diffusive/advective transport rates. The ability to estimate flux is an advantage of passive sampling methods over conventional sediment monitoring techniques especially for recently remediated systems. Flux measurements can be used to estimate the breakthrough time of contaminants through the cap and be used as an indicator of remediation technique effectiveness.

Fluxes are estimated based upon *in situ* SPME PDMS passive sampling techniques. Applications to two capped contaminated sediment sites; a river (Chattanooga Creek, Chattanooga, TN) and a tidal harbor (Eagle Harbor, Bainbridge Island, WA) show the ability of the SPME PDMS passive sampling technique to measure flux from sediment to water column

through a sediment cap. PAH concentration profiles into the sediment, cap, and overlying water column will be presented for each of the sites along with flux calculations.

THEORETICAL CONSIDERATIONS

A SPME PDMS fiber with cylindrical geometry placed in a saturated sediment bed is subject to diffusive and advective mass transport processes external to the PDMS sorbent layer as shown in Figure 6-1. Diffusive processes include not only molecular diffusion in the pore space but could also include diffusive-like processes such as dispersion associated with tidal fluctuations, hyporheic exchange or bioturbation, the mixing processes associated with the normal life cycle activities of benthic organisms. Advection is primarily the result of groundwater upwelling, but also leads to dispersion in the media.

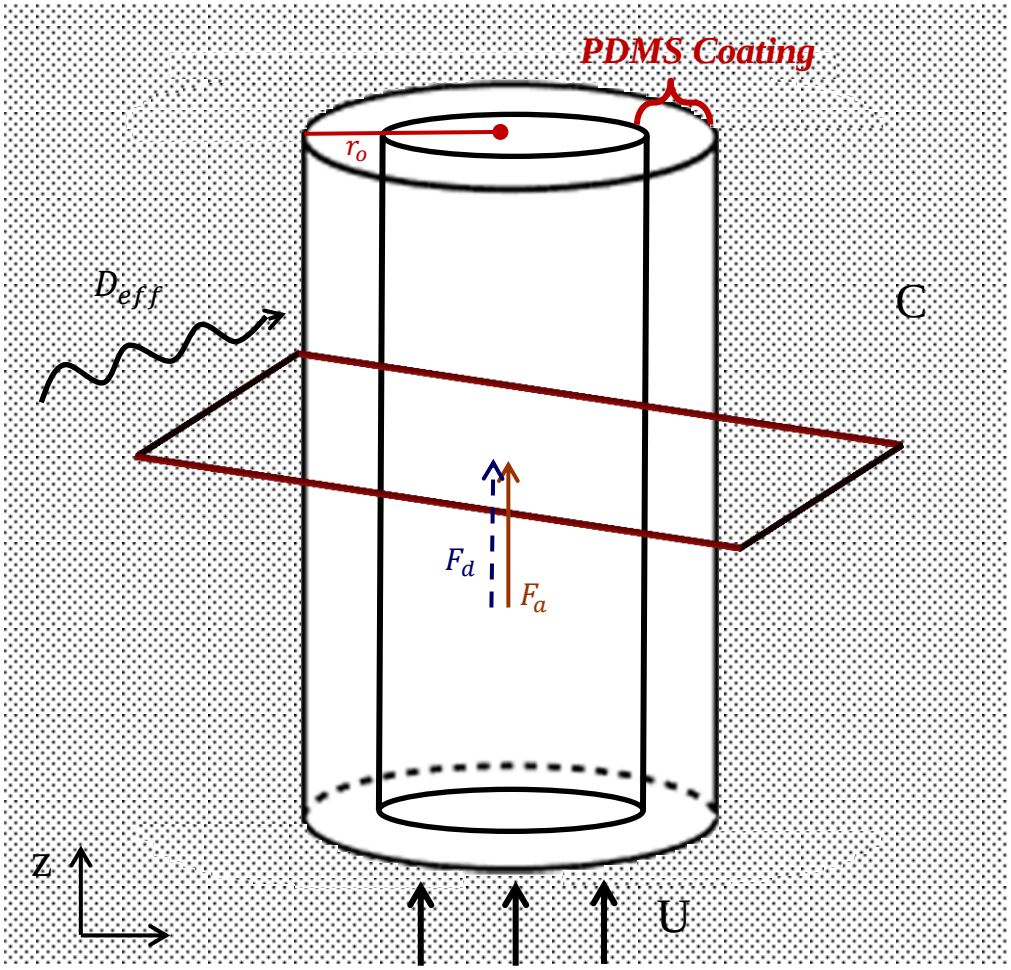

Figure 6-1. SPME-PDMS fiber placed in porous sediment bed subject to advective and diffusive fluxes.

The general transport equation for a non-reactive contaminant subject to diffusive and advective transport in a porous media is given by the equation (Choy and Reible, 2000),

$$R_f \frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - U\frac{\partial C}{\partial z} \qquad \text{Eq. 1}$$

where R_f is the retardation factor defined as the ratio of the total concentration in the sediment to the freely dissolved concentration in the porewater, C is the freely dissolved porewater

concentration, D is the diffusivity of the contaminant, U is the porewater's velocity, and z is longitudinal axis perpendicular to an x-y plane representing the sediment, cap, or surface water layer.

Integrating Equation 1 over the z-coordinate results in the one dimensional advective-diffusive flux equation (Thibodeaux and Mackay, 2011),

$$F = -D\frac{dC}{dz} + UC \qquad \text{Eq. 2}$$

The relative magnitude of advective to diffusive mass transfer processes can be determined through the Peclet number. Utilizing SPME PDMS methods and PRC methods, the variables describing diffusive and advective flux perpendicular to the SPME PDMS fiber can be estimated. The following sections presents a method for determining a site specific Peclet number as well as models evaluating the flux assuming diffusion-like processes and purely advective processes.

Effective Diffusion in a Porous Media

Contaminant transport in porous media is due to advection, diffusion/dispersion, decay, and bioturbation. Contaminant transport due to diffusive processes could be based on just molecular and Brownian diffusion (Thibodeaux and Mackay, 2011) or include other transport processes, like bioturbation and other mechanisms of particle transport, that can be modeled like diffusion. Diffusive flux occurs in capped systems when there is a concentration gradient between the cap layer porewater and the remaining native sediment porewater or surface water (Palermo et al., 1998). Diffusion can be the main process promoting contaminant transport in low permeability capped systems and when hydraulic gradients are not conducive to advective transport (Choy and Reible, 2000). The net steady state molecular diffusion flux of a

contaminant can be described by Fick's Law coupled with corrections for the tortuosity and porosity of the fully saturated porous media (Millington and Quirk, 1961),

$$F_d = -\varphi^{4/3} D_w \frac{dC}{dz} \qquad \text{Eq. 3}$$

where $\varphi^{4/3} D_w$ is the matrix molecular diffusivity of the contaminant in the porewater. φ is the sediment bed's porosity. For a more consolidated sediment, instead of the $\varphi^{4/3}$ multiplier from assuming the Millington and Quirk model (1961), D_w should be multiplied by $\varphi/(1-\ln\varphi^2)$ (Boudreau, 1996). Note that a variety of processes might be modeled as diffusion–like processes. Bioturbation and tidal pumping both give rise to long-term concentration profiles that are diffusive in nature. In addition, the combination of advection and diffusion/dispersion might be approximately modeled as an effective diffusion coefficient when the ratio of $UL_z \big/ \left(\varphi^{4/3} D_w + D_{dispersion}\right)$ is of order unity or less. In such cases, Equation 2 becomes

$$F_d = -D_{eff} \frac{dC}{dz} \qquad \text{Eq. 4}$$

Where D_{eff} is the matrix molecular diffusivity for diffusion only or an effective coefficient that captures the mixing by the diffusive-like processes also occurring.

Determination of D_{eff}

As discussed in Thomas et al. (2014) and Lampert et al. (2014), a fit of $R_f D_{eff}$ can be found from coupling PRC desorption measurements with the external mass transfer resistance model, where the fraction of PRC mass remaining after a certain deployment period is modeled as:

$$\frac{M(t)}{M_0} = \exp\left(\frac{R_f D_{eff} t}{L^2 K_{PDMS}^2}\right) erfc\left(\frac{\sqrt{R_f D_{eff} t}}{L K_{PDMS}}\right) = 1 - f_{ss} \quad \text{Eq. 5}$$

where M(t) is equal to the PRC mass remaining after the deployment period, M_0 is the initial PRC mass absorbed to the fiber, R_f is the retardation factor, D_{eff} is the effective diffusion coefficient, L is the effective thickness of the PDMS fiber that is equal to the surface volume to area ratio, K_{PDMS} is the PDMS polymer partition coefficient given in Ghosh et al. (2014), and f_{ss} is the fraction of steady state achieved during the deployment period. The system dependent value of $R_f D_{eff}$, the lumped parameter of the sorption related retardation factor in the sediment and the effective diffusivity, is the only unknown in the above equation. The site-specific R_f can be estimated based on the organic carbon partition coefficient (K_{oc}) or from field measurements of sediment-water distribution coefficient (K_d) that can be calculated from bulk solid data and porewater data and therefore D_{eff} can be isolated.

Concentration gradients between the sediment porewater and surface water can be measured by the profiling SPME PDMS fibers. Using the PRC method to characterize the extent of equilibrium achieved during a deployment, two site specific parameters, R_f and D_{eff}, are estimated. Equation 4 can be reinterpreted using these parameters into

$$F_d = -\frac{R_f D_{eff}}{\rho_b f_{oc} K_{oc}} \frac{dC}{dz} \quad \text{Eq. 6}$$

or for highly hydrophobic compounds, where accumulation on mobile colloidal organic carbon results in an additional flux

$$F_d = -\frac{R_f D_{eff}}{\rho_b f_{oc} K_{oc}} (1 + C_{DOC} K_{DOC}) \frac{dC}{dz} \quad \text{Eq. 7}$$

where ρ_b is the bulk density, f_{oc} is the organic carbon fraction, K_{oc} is the organic-carbon partition coefficient, C_{DOC} is the dissolved organic carbon concentration, and K_{DOC} is the dissolved organic-carbon.

Advective Flux & Porewater Velocity

For some sediment/cap layers, diffusion/dispersion is not the main transport process in effect and an advective model of the transport processes may be more appropriate.. Advection is due to differences in groundwater hydraulic gradients and could cause porewater movement in the upwards or downwards vertical direction (Reible, 2014). The steady state flux due to advection (F_a) is the product of the fluid velocity (U) and the porewater concentration (C),

$$F_a = UC \qquad \text{Eq. 8}$$

or for highly hydrophobic compounds, where accumulation on mobile colloidal organic carbon results in an additional flux

$$F_a = U(C + C_{DOC}K_{DOC}) \qquad \text{Eq. 9}$$

Determining Site-Specific Peclet Number

By modeling the mass transfer between the SPME PDMS segments and the porewater as that of a flowing fluid around a sphere buried in a packed bed (Guedes de Carvalho et al., 2004), the site specific Peclet number (Pe) and ultimately the longitudinal porewater velocity can be estimated from deployments of SPME PDMS fibers utilizing the PRC method. SPME PDMS fibers are deployed in cylindrical housings that are approximately 0.63 cm in diameter. If the SPME PDMS cylindrical fibers and cylindrical housing are modeled as spheres with the same PDMS volume (see Figure 6-2), the equations developed to describe fluid flow around a sphere

buried in a bed of particles by Guedes de Carvalho et al. (2014) can be used to estimate transport parameters of contaminants in a porous media.

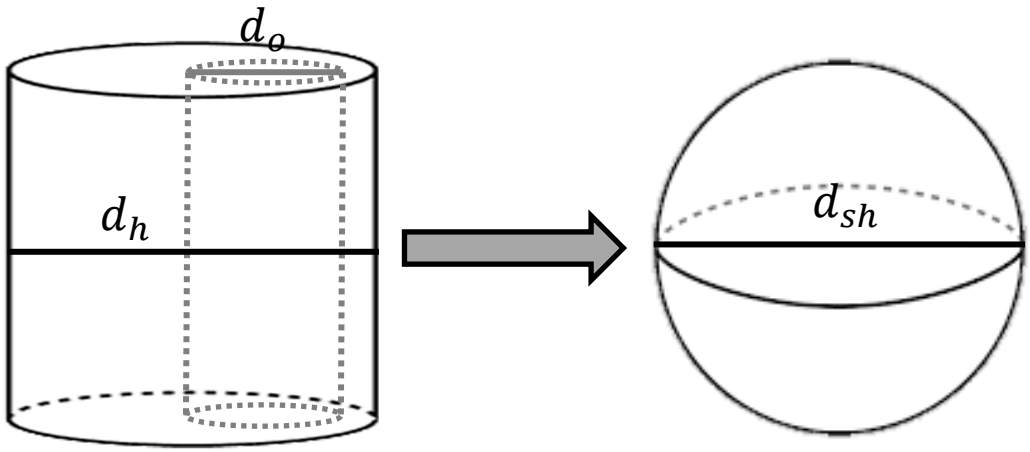

Figure 6-2. Cylindrical SPME PDMS fiber with diameter d_o placed in a cylindrical metal holder with diameter d_h translated into a spherical solid with a diameter d_{sh} to conserve PDMS volume. The boundary of the inner rod that holds the SPME PDMS fiber is not shown, but the SPME PDMS fiber is offset in the above figure to account for the inner rod.

Here the modeled sphere releasing the PRC is a sphere surrounding the housing. If a SPME PDMS fiber with an outer diameter of d_o was encased in the cylindrical housing with a diameter (d_h) for deployment into the sediment, the distance from the SPME PDMS layer to the porous media would be equal to $\frac{d_h}{2} - d_o$. This is taken as the radius and length of the cylindrical volume from which PRCs are releasing. The area of the release zone outside of the cylindrical housing is defined as $A_h = \pi d_h l$, where l is the distance from the SPME PDMS layer to the porous media. The volume of the release zone can be defined as $V_h = \pi \frac{d_h^2}{4} l$. The equivalent

diameter of a sphere for the cylindrical housing is equal to $d_{sh} = \left(\frac{6}{\pi} V_h\right)^{1/3}$. The cylindrical housings with a diameter of 0.63 cm define the distance from the SPME PDMS fiber to the porous media. The SPME PDMS fibers commonly used have diameters ranging from 200 μm to over 1000 μm.

A PDMS layer is coated onto a glass cylindrical core with a diameter, d_i. The addition of the PDMS coating creates a cylinder or fiber with a diameter, d_o The SPME PDMS fiber's area is defined as $A_f = \pi d_o l$. The SPME PDMS fiber's PDMS volume is defined by $V_f = \pi\left(\frac{d_o^2 - d_i^2}{4}\right) l$

The equivalent sphere's diameter is equal to $d_{sf} = \sqrt[3]{\frac{3}{2} d_o^2 l}$. The spherical representation of the SPME PDMS fiber housing is placed in a packed bed representing a porous media with sediment grains of diameter (d_m) and porosity (φ). The PRC data can be used to estimate the mass transfer coefficient, k, from the surface of the effective sphere and thus the Sherwood number ($Sh = \frac{k d_{sh}}{D_w / \tau}$).

Guedes de Carvalho et al. (2004) proposed equations relating the Sherwood number (Sh) and Peclet number (Pe) for Schmidt numbers (Sc) less than or greater than 550. Based upon the solutes (PAHs) under consideration in this paper, Sc > 550 for temperatures up to 313K (Table 6-1) and therefore the following equation can be used to determine Pe as the porosity and Sherwood number, as described below, are known:

$$\frac{Sh}{\varphi} = \left[4 + \frac{4}{5}(Pe)^{2/3} + \frac{4}{\pi} Pe\right]^{1/2} \left[1 + \frac{Pe}{9}\frac{d_m}{d_h} - 1.16x10^{-2}\left(Pe\frac{d_m}{d_h}\right)^{1.268}\right]^{1/2} \quad \text{Eq. 10}$$

The Peclet number determined using Equation 10 is based upon the interstitial velocity (u_o) at great distance from the sphere, $Pe = \frac{u_o d_{sh}}{D_w / \tau}$. D_w is the molecular diffusion coefficient and τ is the sediment's tortuosity.

Table 6-1. Schmidt number for compounds on interest. For the temperatures typically of concern in the sediments, Sc > 550 for PAHs.

	Properties of Water		NAP	FLU	ACE	PHEN	ANT	FLA	PYR	CHR	BAA	BAP	BBF	DBA
T (K)	μ (Pa*s)	ρ (kg/m³)	Sc											
273	0.001794	999.3	2086	2508	2378	2636	2636	2884	2884	3143	3143	3374	3374	3617
293	0.000993	998.2	1063	1278	1212	1343	1343	1470	1470	1601	1601	1719	1719	1843
313	0.000658	992.2	665	800	758	840	840	919	919	1002	1002	1075	1075	1153

All of the Sherwood number variables ($Sh = \frac{kd_{sh}}{D_w/\tau}$), as defined by (Guedes de Carvalho et al., 2004) are known when using the SPME PDMS with PRC method. The mass transfer coefficient (k) is determined from the loss of PRCs from the PDMS layer using

$$F_{PRC} = V_f \frac{dC_{PRC,pdms}}{dt} = kA_h (C_{PRC,pw}\Big|_{z\to\infty} - C_{PRC,pw}\Big|_{z=0}) \quad \text{Eq. 11}$$

$C_{PRC,pw}$ at distance ($z\to\infty$) is the PRC concentration in the porewater and $C_{PRC,pw}$ at the PDMS-porewater interface (z = 0). $C_{PRC,pw}$ at distances away from the SPME PDMS sphere is effectively zero. Written in terms of PDMS concentrations, Equation 11 transforms into

$$\frac{dC_{PRC,pdms}}{dt} = \frac{kA_h}{V_f}(-\frac{C_{PRC,pdms}}{K_{pdms}}) \quad \text{Eq. 12}$$

where K_{pdms} is the PDMS-water partition coefficient.

Solving for k from Equation 12 yields the following,

$$k = -\left\{\ln(\frac{C_{PRC,t}}{C_{PRC,0}})\right\}\left(\frac{K_{pdms}V_f}{A_h t}\right) \quad \text{Eq. 13}$$

where $C_{PRC,t}$ is the PRC remaining sorbed to the polymer layer after an exposure time t and $C_{PRC,0}$ is the initial concentration of PRC spiked to the polymer sorbent layer.

Using k, the Sherwood number and Peclet number can be determined. The Peclet number provides an indication of the relative importance of advective processes to

diffusive processes. The advective velocity can augment or attenuate the chemical flux. If the advective velocity is in the same direction as the concentration gradient, the mass transport will be enhanced (Thibodeaux and Mackay, 2011). If the porewater's advective velocity is in opposition of the concentration gradient, the mass transfer will be diminished (Thibodeaux and Mackay, 2011).

MATERIALS & METHODS

Description of Sediment Sites

Eagle Harbor (Bainbridge Island, Washington)

The Wyckoff-Eagle Harbor Superfund site is located off the east side of Bainbridge Island, Washington. Due to operation of the former Wyckoff wood-treating facility and a former shipyard, the area was added to the EPA's Superfund National Priority List (NPL) in 1987. The site is contaminated with creosote, pentachlorophenol, various PAHs, and heavy metals. In a partnership between the EPA and the USACE, approximately 70 acres of the site were capped with clean sediments. The sediment cap is monitored to ensure buried toxins are not leaching into the surface water. A monitoring study conducted in November 2011 complemented other monitoring activities, including bulk solid and flux chamber measurements, conducted by the EPA and USACE and provided porewater concentrations of PAH contaminants as a function of depth within the sediment cap using 1060/1000 μm SPME PDMS fibers manufactured by Polymicro Technologies (Phoenix, AZ). Seventeen locations were sampled along three transects in Eagle Harbor.

Chattanooga Creek (Chattanooga, Tennessee)

The watershed of Chattanooga Creek encompasses seventy-five square miles and was historically home to foundries, coal carbonization, wood preserving, and chemical plants that lead to high levels of coal tar contaminants in the creek's sediments. Initial cleanup of a 2.5 mile stretch of Chattanooga Creek included removal of sediment and placement of a protective isolation barrier composed of either native material or Aquablok® topped with native material in areas were upwelling of NAPL was observed. A monitoring study was conducted in June 2011 using 1060/1000 μm SPME PDMS fibers manufactured by Polymicro Technologies (Phoenix, AZ) and 230/210 μm SPME PDMS fibers manufactured by Fiberguide (Sterling, NJ). Seven locations were sampled along Chattanooga Creek within the capped region as well as downstream of the cap.

The west branch of the Grand Calumet River

Over 100 years of industrial use and pollution from a variety of industries including petrochemical refining and storage, steel mills, automobile and consumer appliance fabrication, and chemical manufacturing has impacted the Grand Calumet River (Cohen et al., 2002). Currently over 90% of the river's flow is from effluent discharges of industries and waste water treatment plants that surround the 13 miles of river that originates in Gary, IN and flow into Lake Michigan (Cohen et al., 2002).

Remediation of the Grand Calumet River began recently under the Roxanna Marsh Great Lakes Legacy Act Project. The area was divided into five zones (EPA, 2013). In 2012, remediation of Zone A that included the west branch of the Grand

Calumet River was completed. The remaining four zones are in progress or still remain in the investigation stage (EPA, 2009). Although the west branch of the Grand Calumet River only spans a one mile stretch, it is located in one of the most industrial areas in the USA and includes Roxana Marsh, a habitat for a diverse population of plant and animals (EPA, 2008). While pollutant discharge has been reduced in the Great Lakes over the last 20 years, sediment in tributaries like the Grand Calumet River remains heavily contaminates with PCBs, PAHs, heavy metals, and pesticides (EPA, 2008).

Remediation activities at the west branch of the Grand Calumet River included removal of approximately 150,000 yd^3 of sediment from the top 2 ft layer of sediment in the Roxana Marsh area and an additional 235,000 yd^3 dredged from the west branch stretch and subsequent placement of a cap to isolate the remaining contaminated sediment from the overlying water column (EPA, 2013). The cap design called for six inches of organoclay covered by an additional twelve inches of sand and was designed to cover 345,000 yd^3 of contaminated sediment (EPA, 2013).

SPME PDMS fibers, sampling devices, and PRCs

The fibers used during these studies were manufactured by Polymicro Technologies (Phoenix, AZ). For the Eagle Harbor and Chattanooga Creek field studies, the core diameter of the glass fibers measured 1000 μm and the PDMS coating was approximately 30 μm thick. At the west branch of the Grand Calumet River, the core diameter of the glass fibers measured approximately 486 μm and the PDMS coating was

approximately 36 μm. The fibers were soaked sequentially in hexane, acetonitrile, and deionized water before use and checked for any interfering analytes after cleaning.

During the field studies, the fibers were secured in modified Henry samplers, as previously described in Thomas et al. (2014), for ease of insertion and protection of the delicate fibers, while maintaining fiber-porewater contact. The samplers have working lengths of 30 cm, 60 cm, or 90 cm, and are driven perpendicular into the sediment surface. When monitoring the water column, samplers with a 30 cm working length are secured to the top of a 60 cm or 90 cm working length sampler that is driven into the sediment surface. The samplers were washed with hot water and detergent, soaked sequentially in hexane and acetonitrile, flushed with deionized water, and dried at 180°C overnight before use. The sampler was also checked to ensure that the cleaning process removed any residual analytes from previous field studies.

All field studies employed PRCs to evaluate fiber uptake kinetics. As the target compounds were PAHs at both sites, four deuterated PAHs covering a range in hydrophobicities were employed. Stock solutions of fluoranthene-d10, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were purchased from Cambridge Isotope Laboratories. A stock solution of chrysene-d12 was purchased from Ultra Scientific Analytical Solutions. Fibers were tumbled in a spiking solution with aqueous concentrations of 30 μg/L fluoranthene-d10, 80 μg/L chrysene-d12, 50 μg/L benzo(b)fluoranthene-d12, and 25 μg/L dibenz(a,h)anthracene-d14 for seven days before being secured in the sampling devices for deployment.

Analytical Methods

After the specified deployment period is complete, the samplers are removed from the sediment or water column and processed. The SPME PDMS fiber is cut into segments using a ceramic cutter based upon the objectives of a given project. For example, sampling within the biologically active zone (e.g. 0-10 cm) may be a priority to complete a comparison between benthic criteria or priority may be given to deeper segments (e.g. 10-20 cm, 20-30 cm, etc.) to evaluate deeper contamination and sources of potential migration into the biologically active zone. The segments are placed directly in an extracting solvent to await analysis in the laboratory. For all field studies, the SPME PDMS fibers were sectioned into 2 cm segments and placed in a 2 mL autosampler vial containing an insert filled with 250 μL of acetonitrile.

All PDMS solvent extracts are analyzed using Waters 2795 High Performance Liquid Chromatography (HPLC) with ultraviolet-diode array (UV) and fluorescence (FLD) detectors according to EPA Method 8310 for PAH_{16} analysis. The Phenomenex Luna 5m C18 column (250 x 4.6 mm) temperature was held at 40°C. The separation occurred using a 1.0 mL/min isocratic flow composed of 3:7 (v/v) water-acetonitrile. For every 10 field samples analyzed, a 5 or 20 μg/L check standard (UltraScientific) containing 16 PAHs was analyzed to check proper running of the instrument. Standards ranging in concentrations from 0.05 μg/L to 100 μg/L are used to determine each compound's response factor.

RESULTS

Calculation of Site Specific Effective Diffusivities from PRC desorption

Lampert et al. (2014) discussed an approach for extrapolating the external kinetic model based upon measured kinetic parameters (e.g. R_fD_{eff}) and K_{ow} to other compounds within a given class using a power fit:

$$R_f D_{eff} = 10^{\beta} K_{ow}^{\alpha} \quad \text{Eq. 15}$$

For all of the sampling events, PRCs were utilized to estimate the site specific and compound independent parameters α and β. The fit of R_fD_{eff} (m^2/d) versus K_{ow} for the four deuterated PAHs used as PRCs at the Eagle Harbor site was α = 1.08 ± 0.28, β = -6.7 ± 1.7, r^2 = 0.6. The model parameters for the Chattanooga Creek site were estimated following the same procedure. For Chattanooga Creek, Lampert et al. (2014) reported the model parameters, α, β, and r^2 as 1.0 ± 0.1, -7.1 ± 0.7, and 0.63, respectively. Model parameters, α, β, and r^2 for the west branch of the Grand Calumet River, the focus of Chapter 7, are estimated as 1.1 ± 0.03, -7.3±0.2, and r^2=0.62, respectively. The transport kinetics at Eagle Harbor, a tidal system, are more rapid than at the other sites that are both part of river systems; although, only slightly elevated than transport kinetics of the west branch of the Grand Calumet River. The difference seen between Chattanooga Creek and the west branch of the Grand Calumet River is most likely due to greater retardation in the Grand Calumet sediment due to an organophilic clay enriched cap layer versus the sand cap at Chattanooga Creek.

If diffusive transport processes are dominant in the sediment media, with retardation largely controlled by rapidly exchangeable, linear sorbing sediment organic carbon ($K_d \sim K_{oc} f_{oc}$), the order of $R_f D_{eff}$ would be expected to be $R_f D_{eff} \sim \rho_b K_{oc} f_{oc} \frac{\varphi D_w}{\tau}$. The estimates of R_f from $R_f \sim K_{oc} f_{oc} \rho_b \sim K_d \rho_b$ for Eagle Harbor and the west branch of the Grand Calumet River are based upon $K_{oc}f_{oc}$ estimates from comparing bulk solid measurements to porewater measurements. In the cap layer at Eagle Harbor, the relationship between $\log K_d$ and $\log K_{ow}$ was found to be equal to $\log K_d = 1.03(\pm 0.03)\log K_{ow} - 1.04(\pm 0.18)$, $r^2=0.87$. The relationship for the cap layer at the west branch of the Grand Calumet River was found to be equal to $\log K_d = 1.04(\pm 0.1)\log K_{ow} - 2.1(\pm 0.6)$, $r^2=0.45$.The tortuosity (τ) can be approximated using either the Millington and Quirk (1961) or the Boudreau (1996) approximations for tortuosity described above. If one assumes a bulk density (ρ_b) of 1 kg L^{-1}, an approximate molecular diffusivity (D_w) of $5x10^{-6}$ cm^2/s, porosities of 0.5 for all sites, uses the K_d estimates found from the bulk solid data and porewater data at the Eagle Harbor or west branch of the Grand Calumet River, and estimates tortuosity using either the Millington and Quirk approximation or the Boudreau approximation, the order of $R_f D_{eff}$ can be approximated (see Table 6-2). An approximation of K_{oc} by $0.35K_{ow}$ (Arnot and Gobas, 2003) and an assumption of an f_{oc} of 0.05 can be used for Chattanooga Creek to estimate R_f as no bulk solid measurements were taken at this site (see Table 6-2). Figure 6-3 shows the best-fit relationships determined from PRC desorption in the field for the three discussed field sites. Figures 6-4 and 6-5 show the PRC derived $R_f D_{eff}$-K_{ow} relationship along with $R_f D_{eff}$-K_{ow}

relationships derived from approximations based upon the molecular diffusion coefficient described above for Eagle Harbor and the west branch of the Grand Calumet River, respectively. As one can see from the comparisons between the different estimates of $R_f D_{eff}$, site specific estimates of this parameter are necessary for accurate fate and transport modeling. At Eagle Harbor, the use of these approximations would overestimate the transport of lower molecular weight compounds; while at the west branch of the Grand Calumet, the use of these approximations would underestimate transport of high molecular weight compounds. The impact of retardation and diffusive-like processes is best captured by direct assessment using the PRC method, rather than estimations found in literature as all sediment sites are unique.

Table 6-2. Estimates of $R_f D_{eff}$ (m^2/d) for Eagle Harbor, Chattanooga Creek, and the west branch of the Grand Calumet River using (1) $R_f = K_{oc} f_{oc} \rho_b$ and $D_{eff} = D_w \frac{\varphi}{\tau}$ where $\frac{\varphi}{\tau}$ can be approximated using either the Millington and Quirk (MQ) correction or the Boudreau (B) correction, (2) the site-specific R_f as determined from K_d and $D_{eff} = D_w \frac{\varphi}{\tau}$ where $\frac{\varphi}{\tau}$ can be approximated using either the Millington and Quirk (MQ) correction or the Boudreau (B) correction, or (3) $R_f D_{eff}$ as measured from PRC desorption data

Site	(1) $K_{oc} f_{oc} \rho_b D_w \frac{\varphi}{\tau}$	(2) $R_f D_w \frac{\varphi}{\tau}$	(3) $R_f D_{eff}$ (*measured*)
Eagle Harbor (EH)	$10^{-6.4} K_{ow}$ (MQ) $10^{-6.7} K_{ow}$ (B)	$10^{-5.7} K_{ow}$ (MQ) $10^{-6} K_{ow}$ (B)	$10^{-6.7 \pm 1.7} K_{ow}^{1.1 \pm 0.28}, r^2 = 0.6$
Chattanooga Creek (CC)	$10^{-6.4} K_{ow}$ (MQ) $10^{-6.7} K_{ow}$ (B)	-	$10^{-7.1 \pm 0.7} K_{ow}^{1 \pm 0.1}, r^2 = 0.63$
West Branch of the Grand Calumet (WBGCR)	$10^{-6.4} K_{ow}$ (MQ) $10^{-6.7} K_{ow}$ (B)	$10^{-6.8} K_{ow}$ (MQ) $10^{-7.1} K_{ow}$ (B)	$10^{-7.3 \pm 0.2} K_{ow}^{1.1 \pm 0.03}, r^2 = 0.62$

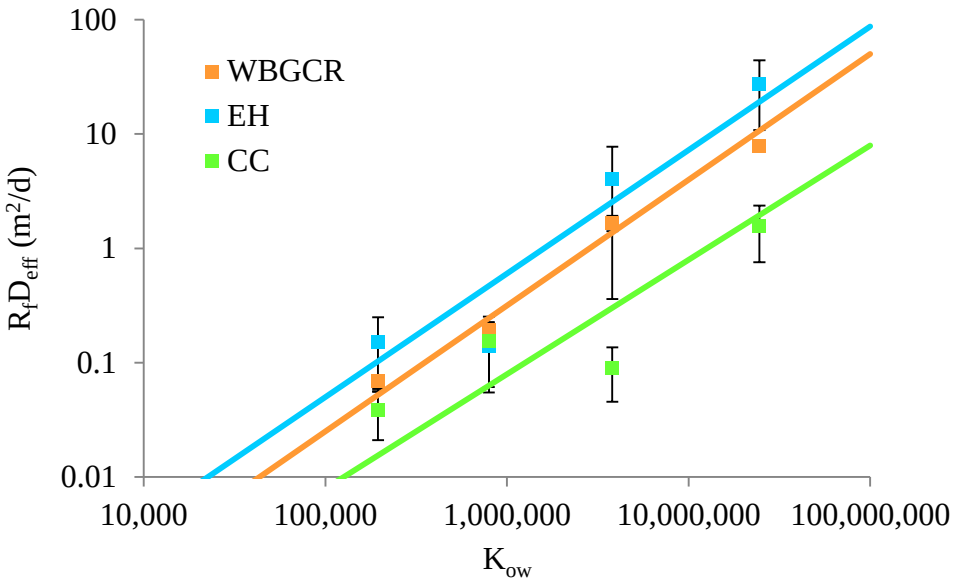

Figure 6-3. R_fD_{eff} versus K_{ow} as measured using PRC method at three contaminated sediment sites: west branch of the Grand Calumet River (WBGCR), Eagle Harbor (EH), and Chattanooga Creek (CC).

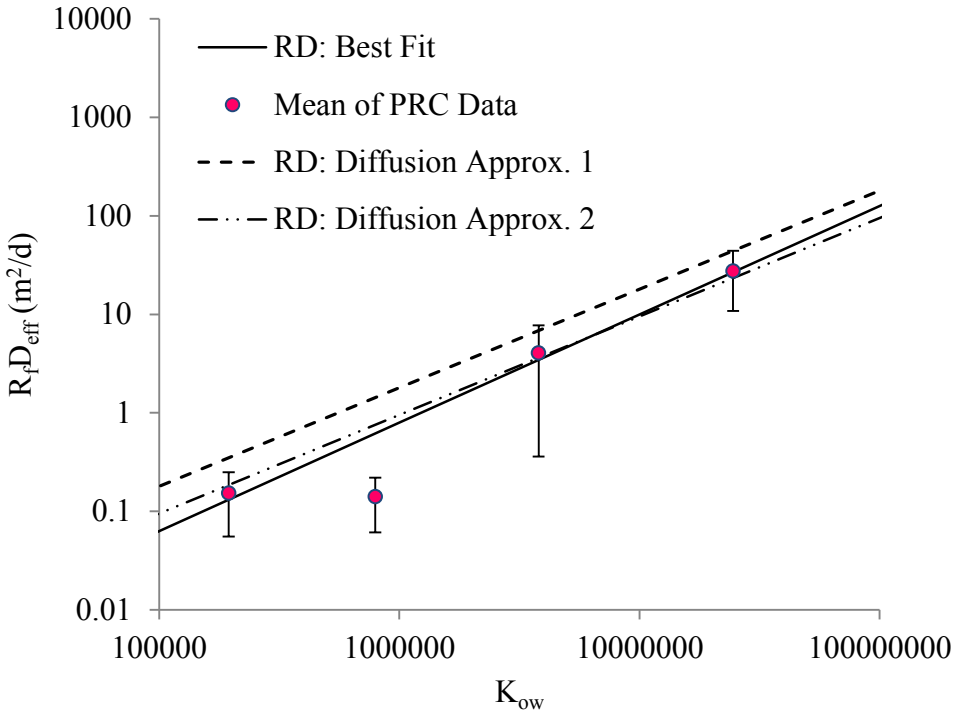

Figure 6-4. R_fD_{eff} versus K_{ow} for Eagle Harbor sediment. The black line represents the line of best fit for R_fD_{eff} calculated using the PRC method: $R_f D_{eff} \sim 10^{-6.7\pm1.7} K_{ow}^{1.08\pm0.28}$, $r^2 = 0.6$. The broken lines indicate the estimated of R_fD_{eff} using approximations based upon molecular diffusion, $R_f D_{eff} \sim 10^{-5.7} K_{ow}$ using the Millington and Quirk approximation (RD: Diffusion Approx. 1) and $R_f D_{eff} \sim 10^{-6} K_{ow}$ using the Boudreau approximation (RD: Diffusion Approx. 2).

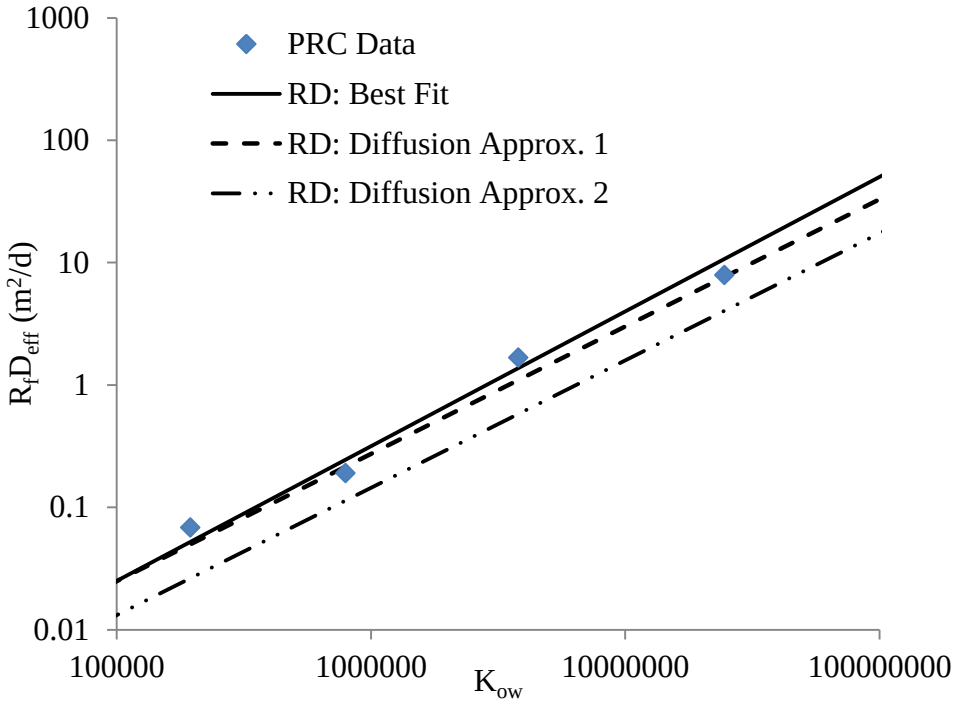

Figure 6-5. R_fD_{eff} versus K_{ow} for the west branch of the Grand Calumet River sediment. The black line represents the line of best fit for R_fD_{eff} calculated using the PRC method: $R_f D_{eff} \sim 10^{-7\pm0.2} K_{ow}^{1.1\pm0.03}$, $r^2 = 0.62$. The broken lines indicate the estimated of R_fD_{eff} using approximations based upon molecular diffusion, $R_f D_{eff} \sim 10^{-6.8} K_{ow}$ using the Millington and Quirk approximation (RD: Diffusion Approx. 1) and $R_f D_{eff} \sim 10^{-7.1} K_{ow}$ using the Boudreau approximation (RD: Diffusion Approx. 2).

Calculation of Effective Velocity from PRC Desorption

In this section, we apply the alternative model assuming the enhanced transport and PRC release (releative to molecular diffusion) is advective. Each site will be treated separately.

Eagle Harbor

Concentrations measured at the Eagle Harbor site were generally low and did not present significant trends except sampling locations G-8 and J-9, which showed potential

trends of migration. Figure 6-6 shows the summation of the low molecular weight PAHs (LPAHs) and the carcinogenic, or very hydrophobic and an indicator of particle transport, (CPAH) concentrations for all of the sediment sampling locations monitored during the 2011 study. Sampling location G-8 was the outermost sampling location along Transect 2 and exhibited elevated concentrations of LPAHs in near the sediment-water interface, compared to the other Eagle Harbor sampling locations, and relatively concentrations of CPAHs. Typically, LPAHs weather more rapidly and therefore the relative high concentrations at sampling location G-8 suggest a more recent exposure of a source-like material or recent lateral movement of LPAHs from a nearby source. Sampling location J-9's concentration profile is indicative of vertical migration as LPAH concentrations were relatively uniform with depth while CPAH concentrations were high at depth and decreased towards the sediment-water interface.

As discussed in Chapter 5, an effective organic carbon partition coefficient was calculated using the relationship between the porewater and bulk solids concentrations, $K_{oc} = \frac{W_s}{C_{pw}^{SPME} f_{oc}}$. This comparison assumes equilibrium partitioning between the solids and adjacent porewaters. W_s is the concentration measured from the grab samples (µg/kg), C_{pw}^{SPME} is the porewater concentration measured via PDMS fibers (µg/L), and f_{oc} is the organic carbon fraction of the sediment. The grab sample/bulk solid data was provided by the USACE District 10. The $\log K_{oc} f_{oc}$ relationship to $\log K_{ow}$ for Location J-9 is $\log K_{oc} f_{oc} = 1(\pm 0.06) \log K_{ow} - 0.75(\pm 0.3)$.

The 1060/1000 μm SPME PDMS fiber was deployed in cylindrical housings with a diameter of 0.63 cm. Table 6-3 contains the spherical dimensions used to approximate the SPME PDMS fiber/housing system. The mass transfer coefficient determined from PRC desorption data was equal to $1.2x10^{-5} \pm 6x10^{-6}$ cm/s. Equation 8 was used to determine the site-specific Pe number of 0.9, which indicates that advective transport should not be ignored when completing chemodynamic models of contaminant transport within a cap or sediment layer. The model provides a porewater velocity estimate of 0.92 cm/d.

Table 6-3. Spherical dimensions used to approximate the cylindrical 1060/ 1000 μm SPME PDMS fiber and housing for modeling the mass transfer between the porewater fluid and a spherical solid mass in a porous media.

Cylindrical Dimensions		
Housing Diameter (d_h)	0.64	cm
Release Zone Surface Area (A_h)	0.42	cm^2
Release Zone Volume (V_h)	0.067	cm^3
Distance to Media (l)	0.21	cm
PDMS Volume (V_f)	2.05E-04	cm^3
Spherical Dimensions		
Housing Diameter (d_{sh})	0.50	cm
Sediment Diameter (d_m)	0.05	cm

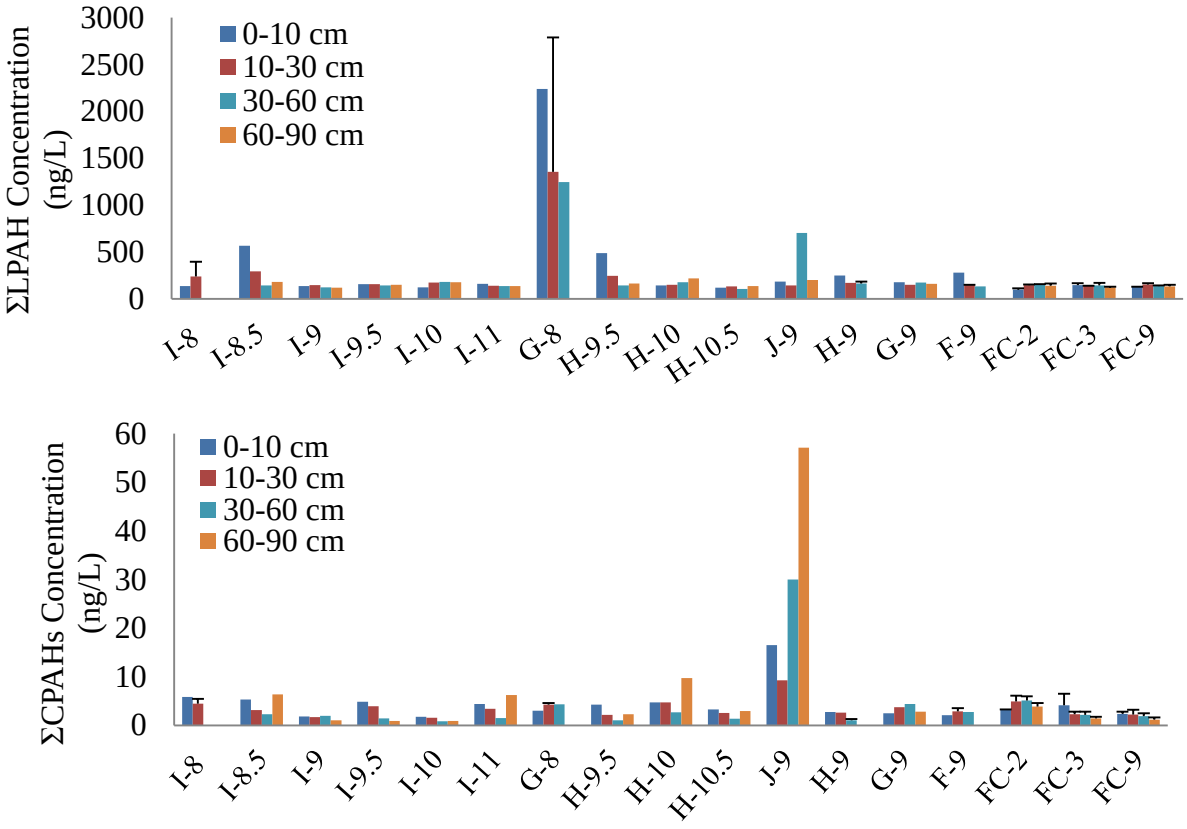

Figure 6-6. Depth-discreet summation of lower molecular weight PAHs (LPAHs) and carcinogenic PAHs (CPAHs) for each sampling location at Eagle Harbor. Sampling locations G-8 and J-9 showed distinctive profiles compared to all other sampling locations at the Eagle Harbor site.

Chattanooga Creek

Sampling location 5 at the Chattanooga Creek site was located within an oxbow of the creek. During remediation efforts, upwelling of NAPL was seen in the oxbow and the concentrations measured using SPME PDMS at these locations are the highest of the locations sampled. Figure 6-7 shows fluoranthene concentrations sampled for at the Chattanooga Creek site #5. The cap layer is approximately 45 cm of sand, clean sediment, and AquaBlok®. The same cylindrical housing and fiber geometry was used

for the Chattanooga Creek deployment as for the Eagle Harbor deployment (see Table 6-2). As bulk solid data was not available for the Chattanooga Creek sampling locations, R_f was estimated using $0.35K_{ow}f_{oc}\rho_b$, where f_{oc} was assumed to be 0.05 and ρ_b was assumed to be 1 kg/L. Without an accurate estimate of R_f and an accurate estimation of the cap layer boundaries, the analysis of D_{eff} and U flux is at best an approximation. k was determined to be $1.1x10^{-5}\pm2.3x10^{-6}$ cm^2/s for Chattanooga Creek sediment. Pe was estimated to be 0.5 and the effective velocity estimated to be 0.5 cm/d.

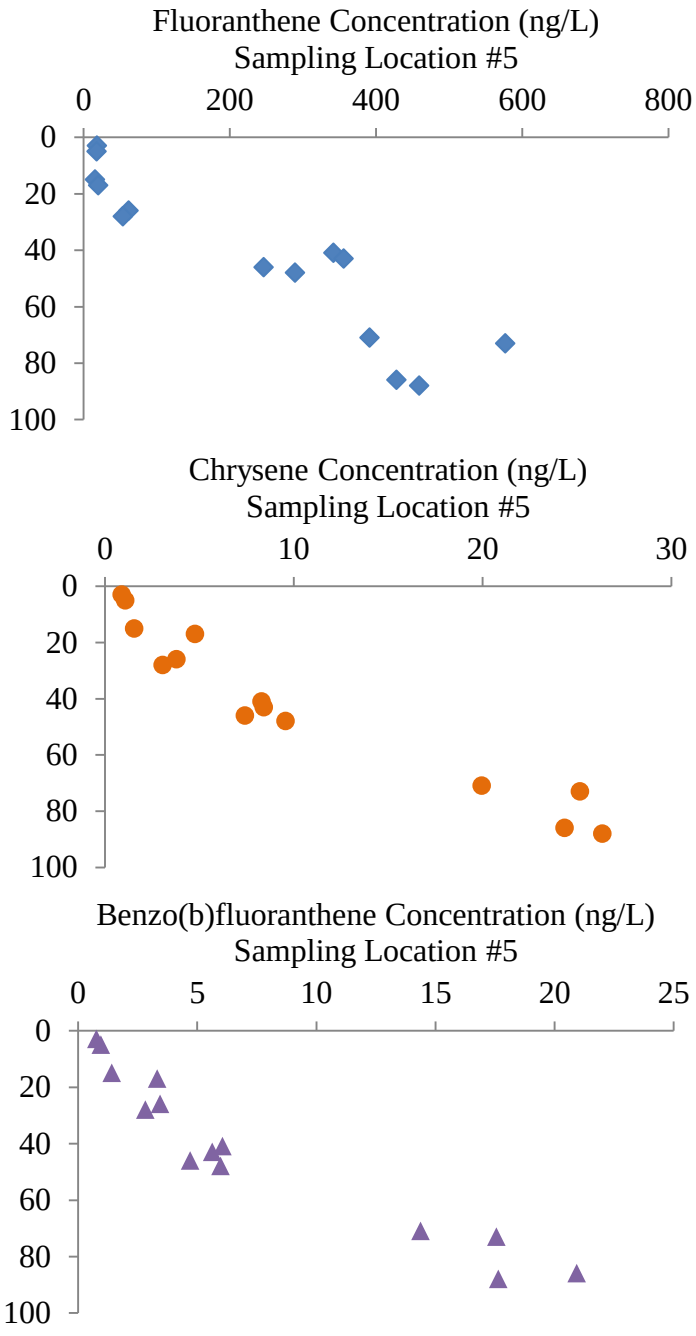

Figure 6-7. Concentration profiles of fluoranthene, chrysene, and benzo(b)fluoranthene at sampling location #5 within the oxbow region of Chattanooga Creek where upwelling was noted during remediation activities.

The west branch of the Grand Calumet River

Location 13 at the west branch of the Grand Calumet River exhibited the highest concentrations seen at the site. The gravel layer depth at this site is 25.9 cm. Only a nominal amount (~5.3 cm) of the sand and organophilic clay was placed at this location, which has caused the upper cap layer to become recontaminated as there was no substantial barrier to retard contaminant migration. Three 90-cm working length SPME PDMS samplers were deployed within a 1-m triangle of one another at this site. While these measurements cannot be considered replicates, they do give an indication as to spatial differences at a sampling location. For the 21 day deployment, the value of k was determined to be $3.2x10^{-5}\pm2x10^{-5}$ cm^2/s. Using the model described above, the fluid velocity was determined to be 0.3±0.15 cm/d. The parameters used to calculate the equivalent sphere for the cylindrical sampler holder are found in Table 6-4. Instead of the 1060/1000 μm SPME PDMS fibers used at Eagle Harbor and Chattanooga Creek, a 558.8/486 μm SPME PDMS fiber was used at the west branch of the Grand Calumet River.

Location 13

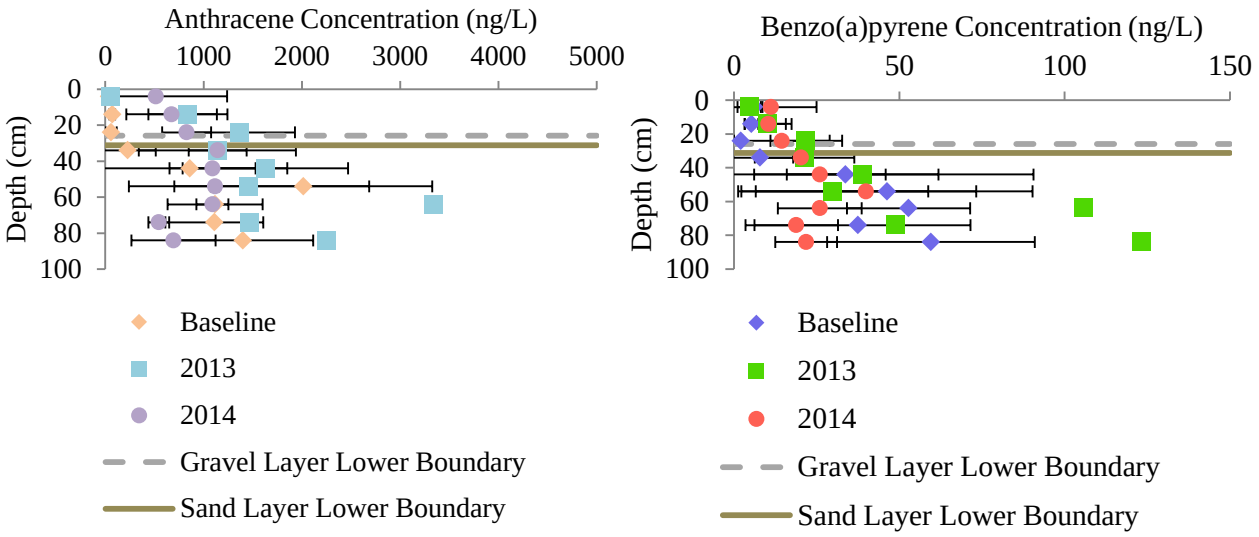

Figure 6-8. Concentration profiles of anthracene, a representative LPAH, benzo(a)pyrene, a representative HPAH, for the baseline monitoring event in 2012, and the subsequent 2013 and 2014 monitoring event for sampling location 13.

Table 6-4. Spherical dimensions used to approximate the cylindrical 558/486 µm SPME PDMS fiber and housing for modeling the mass transfer between the porewater fluid and a spherical solid mass in a porous media.

Cylindrical Dimensions		
Housing Diameter (d_h)	0.64	cm
Release Zone Surface Area (A_h)	0.52	cm^2
Release Zone Volume (V_h)	0.083	cm^3
Distance to Media (l)	0.26	cm
PDMS Volume (V_f)	1.54E-04	cm^3
Spherical Dimensions		
Housing Diameter (d_{sh})	0.50	cm
Sediment Diameter (d_m)	0.05	cm

Calculation of Contaminant Flux

Table 6-6 contains estimates of near-surface flux for fluoranthene if diffusion is modelled as effective diffusion or as an effective velocity for Eagle Harbor (EH)

sampling location J-9, Chattanooga Creek (CC) sampling location 5, and the west branch of the Grand Calumet River (WBGCR) sampling location 13 using parameters described in Table 6-5. The estimates of the near-surface flux are similar for the two methods of estimation. The benefit of calculating flux using the effective velocity is it is only dependent on a concentration at a particular depth and not a gradient like the effective diffusivity flux. In principle, fluxes could be estimated on the basis of a single near-surface concentration. This may also be useful to estimate an upwelling velocity in that measuring a velocity of less than 1 cm/day is very difficulty using traditional methods. The estimated velocities should be viewed as values consistent with the mass transfer analysis however, rather than actual velocities, until detailed comparisons with measured upwelling rates can be conducted. Calculating the effective velocity from this method is also a benefit as well, as determining effective velocities, especially at low rates can be difficult for the current technology.

Table 6-5. Fluoranthene's concentrations in the near surface (~ 3 cm below cap interface), retardation factor within the cap layer, effective diffusivity within the cap layer, and effective velocity within the cap layer for Eagle Harbor (EH) sampling location J-9, Chattanooga Creek (CC) sampling location 5, and the west branch of the Grand Calumet River (WBGCR) sampling location 13.

Parameter	EH (J-9)	CC (L5)	WBGCR (L13)
$C_{o\,near\,surface}$ (ng/L)	44	73	500
Cap: R_f (-)	34,700	3,400	1,500
Cap: D_{eff} (cm^2/yr)	11	17	7.5
U (cm/d)	0.9	0.5	0.3

Table 6-6. Magnitude of flux for fluoranthene within the near surface of the cap layer at Eagle Harbor (EH) sampling location J-9, Chattanooga Creek (CC) sampling location 5, and the west branch of the Grand Calumet River (WBGCR) sampling location 13.

Flux ng/cm2/yr	EH (J-9)	CC (L5)	WBGCR (L13)
$D_{eff}\frac{\Delta C}{\Delta z}$	7	12	60
UC	15	13	55

SIGNIFICANCE & IMPLICATIONS

The ability to estimate flux is another example of an advantage of passive sampling methods over conventional sediment monitoring techniques especially for recently remediated systems. Flux measurements can be used to estimate the breakthrough time of contaminants through the cap and be used as an indicator of remediation technique effectiveness.

In this chapter, estimates of site-specific Pe numbers were determined, which indicate the relative important of diffusive-like versus advection-like transport processes for chemical fate and transport within the sedment. It was shown that the effective diffusivity was approximately an order of magnitude larger than the molecular diffusivity, indicating that diffusive-like mechanisms are augmenting molecular diffusion. Future work should verify the accuracy of estimating the effective velocity using PRC desorption with column experiments at set porewater velocities.

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Chapter 7: Characterization of PAH fate and transport utilizing SPME PDMS to address cap effectiveness at the West Branch of the Grand Calumet River

ABSTRACT

In May 2012, placement of a layered cap composed of organoclay, sand, and gravel was completed in the West Branch of the Grand Calumet River (WBGCR) near Hammond, Indiana. During the month following cap placement, passive sampling using *in situ* solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers was conducted to ascertain the baseline concentration profiles at twenty-one locations along the length of the WBGCR. In October/November 2013 and September/October 2014, the twenty-one locations were sampled again using the SPME PDMS fibers. Additionally sediment cores were taken adjacent to the deployment locations of the SPME PDMS fibers.

For the WBGCR cap, trends of high concentrations within the underlying sediment and low concentrations within the capped and near surface region or relatively low concentrations at both depth and the near surface, both indicative of effective containment, were seen at most locations for both the baseline (2012), 2013, and 2014 studies. Several locations exhibited trends of intermixing and observances of concentrations greater than surface water quality criteria were noted in the near surface (0-15 cm). This paper presents the results from the three sampling events at the WBGCR and provides quantitative support of the remedy's effectiveness from the use of passive sampling techniques supplemented with bulk solid data and observations from cores.

The chapter highlights the ability to collect and interpret trends from passive

sampler profiles collected at the same locations, within the accuracy of differential GPS, over time. Profiles showing similar trends year to year provide an indication of the intrinsic variability between samples while samples showing substantially different profiles provide an indication of system changes or greater small-scale variability. Small-scale variability appeared to be the primary cause of substantial variations in NAPL impacted locations due to the heterogeneity associated with NAPL residual. Discussion related to predicting contaminant fate and transport behavior over time is also included.

INTRODUCTION

Over 100 years of industrial use and pollution from a variety of industries including petrochemical refining and storage, steel mills, automobile and consumer appliance fabrication, and chemical manufacturing has impacted the Grand Calumet River (Cohen et al., 2002). Currently over 90% of the river's flow is from effluent discharges of industries and waste water treatment plants that surround the 13 miles of river that originates in Gary, IN and flow into Lake Michigan (Cohen et al., 2002).

Remediation of the Grand Calumet River began recently under the Roxanna Marsh Great Lakes Legacy Act Project. The area was divided into five zones (EPA, 2013). In 2012, remediation of Zone A that included the west branch of the Grand Calumet River was completed. The remaining four zones are in progress or still remain in the investigation stage (EPA, 2009). Although the west branch of the Grand Calumet River only spans a one mile stretch, it is located in one of the most industrial areas in the USA and includes Roxana Marsh, a habitat for a diverse population of plant and animals

(EPA, 2008). While pollutant discharge has been reduced in the Great Lakes over the last 20 years, sediment in tributaries like the Grand Calumet River remains heavily contaminates with PCBs, PAHs, heavy metals, and pesticides (EPA, 2008).

Remediation activities at the west branch of the Grand Calumet River included removal of approximately 150,000 yd^3 of sediment from the top 2 ft layer of sediment in the Roxana Marsh area and an additional 235,000 yd^3 dredged from the west branch stretch and subsequent placement of a cap to isolate the remaining contaminated sediment from the overlying water column (EPA, 2013). The cap design called for six inches of organoclay covered by an additional twelve inches of sand and was designed to cover 345,000 yd^3 of contaminated sediment (EPA, 2013).

Sediment caps reduce the risk posed by the fate and transport of contaminants by stabilizing the underlying sediments, physically isolating the water column from sediment contaminants, and reducing contaminant flux to the benthic organisms and water column. When evaluating a sediment cap's performance, focus is placed on the interstitial water contaminant concentrations and contaminant flux reductions. Conventional sediment and porewater measurement techniques measure both the dissolved and particulate-associated fractions; this is a hindrance as only the dissolved fraction defines several of the system's mass transfer processes and is key to modeling a contaminant's fate, transport, and toxicity (Mayer et al., 2014). The freely-dissolved contaminant concentrations can be measured using solid phase microextraction (SPME) profilers with polydimethylsiloxane (PDMS) as the receiving phase sorbent. Additionally, the use SPME PDMS profilers results in lower detection limits and in the

ability to construct vertical concentration profiles that assist in the determination of the mechanisms and rates of transport within a sediment cap when coupled with equilibrium correction methods like performance reference compounds (PRCs) that allow for estimation of a site specific retardation factor and effective diffusivity (Lampert et al., 2013, Thomas et al., 2014).

This work sees to explore the use of SPME PDMS fibers as a long term evaluation tool for remediated sediment sites. Three SPME PDMS sampling events occurred in conjunction with USEPA/USACE monitoring activities. A baseline sampling event conducted in May/June 2011 occurred during the same month as cap placement ended at the west branch of the Grand Calumet River. The goal of the baseline sampling event was to evaluate the initial concentration conditions of the cap with the following data quality objectives (DQOs): determination of any near-surface (0-20 cm) cap porewater concentration exceedances of any PAHs' surface water quality criteria (SWQC), and investigation into the degree of intermixing of contaminants within the cap as a baseline for future cap performance monitoring.

Additional sampling events occurred in October/November 2013 and in September/October 2014. Twenty-one locations were sampled each year. Similar DQOs were addressed and comparisons between the three data sets to determine the effectiveness of the cap approximately a year or two years after placement in terms of migration trends, flux, and exceedances of surface water quality criteria.

MATERIALS AND METHODS

Chemicals, fibers, and samplers

Four deuterated PAHs covering a range of hydrophobicities were employed as performance reference compounds (PRCs). Stock solutions of fluoranthene-d10, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14 were purchased from Cambridge Isotope Laboratories. A stock solution of chrysene-d12 was purchased from Ultra Scientific Analytical Solutions. The deuterated PAHs were selected as performance reference compounds (PRCs) based on their lack of interference with their non-deuterated counterparts during analysis and their hydrophobicities mirrored the range of hydrophobicities in the target compounds, the PAH_{16} priority pollutants. Fibers were placed in contact with a 80/20 v/v water/methanol spiking solution with concentrations of 30 μg/L fluoranthene-d10, 80 μg/L chrysene-d12, 50 μg/L benzo(b)fluoranthene-d12, and 25 μg/L dibenz(a,h)anthracene-d14 for twenty-eight days. Calculations and previous measurements had shown that seven days was sufficient for PRC depletion from an 80/20 v/v water/methanol spiking solution and sorption onto the fiber to occur.

The glass fibers used during this study were manufactured by Polymicro Technologies (Phoenix, AZ). Each sampler contained a 486 μm glass core fiber coated with a 36.4 μm PDMS layer. Before each use, fibers were soaked sequentially in hexane, acetonitrile, and deionized water. No interfering peaks were detected in the fibers after cleaning.

For ease of insertion and protection from sand and gravel in the sediments, the fibers were secured in modified Henry samplers (M.H.E Products) using a waterproof

caulk. The devices are similar to those described in Lampert et al. (2011) with slight differences. Modifications included 4 mm diameter perforations in the outer sheath, a 2 mm groove in the inner rod of the sampler, and the attachment of a washer that rests at the sediment-water interface during deployments. The groove length of the inner rod dictates the sampling length of the sampler.

For the May/June 2012 and October/November 2013 deployments, twenty-five samplers with working lengths of 60 cm or 90 cm were deployed into the sediment and three samplers with 30 cm working lengths were deployed into the surface water at twenty-one predetermined locations (see Figure 7-1). For the September/October 2014 deployment, twenty-five samplers with working length of 90 cm were deployed into the sediment and three samplers with working lengths of 30 cm were deployed into the surface water. The outer sheath facilitates fiber-porewater contact while protecting the fiber. Samplers with working lengths of 30 cm do not have outer sheaths. The inner rod secures the fiber from movement during deployment and retrieval. Before use the samplers were washed with hot water and detergent, soaked sequentially in hexane and acetonitrile, flushed with deionized water, and dried at 180°C overnight.

Figure 7-1. SPME PDMS sampling locations along the West Branch of the Grand Calumet River.

SPME PDMS Processing

Upon removal from the sediment or water column, the PDMS fibers were wiped with a deionized water dampened lint free tissue to remove any particulate matter. All fibers were sectioned into 2 cm pieces and placed in a 2 mL autosampler vial containing a 250 µL insert containing 250 µL of acetonitrile for extraction. The SPME PDMS fibers deployed into the sediment were then sectioned into adjacent 2-cm fiber segments from each target depth. Target depths for the 90 cm working length sediment samplers included: 3-5 cm, 5-7 cm, 13-15 cm, 15-17 cm, 23-25 cm, 25-27 cm, 33-35 cm, 35-37

cm, 43-45 cm, 45-47 cm, 53-55 cm, 55-57 cm, 63-65 cm, 65-67 cm, 73-75 cm, 75-77 cm, 85-87 cm, 87-89 cm. The target depths for the 60 cm working length sediment samplers followed the same plan as for the 90 cm working length sediment samples with the last 2-cm segment being at a depth of 55-57 cm below the sediment-water interface. The SPME PDMS fibers deployed in the surface water were sectioned into adjacent 2-cm fiber segments from the following target depths: 3-5 cm, 5-7 cm, 13-15 cm, 15-17 cm, 23-25 cm, 25-27 cm.

Several deviations from the above sampling plan were noted for sampling locations 2, 3, 4, 5, 6, 11, 12, 15, 18, and 20. At these locations at least one segment was not recoverable due to severe breakage caused by small stones entering the sampler housing. Every other segment length was analyzed, for example 3-5 cm, 13-15 cm, 23-25 cm etc and the other segments were saved as duplicates.

Chemical analysis

The solvent extracts were analyzed using Waters 2795 High Performance Liquid Chromatography (HPLC) with ultraviolet-diode array (UV) and fluorescence (FLD) detectors or using an Agilent Technologies 1260 Infinity (Santa Clara, CA, USA) High Performance Liquid Chromatography (HPLC) with an ultraviolet-diode array (1260 DAD VL+) and fluorescence detector (1260 FLD Spectra) according to EPA Method 8310 for PAH_{16} analysis. The Phenomenex Luna 5µ C18 column (250 × 4.6 mm) temperature was held at 40°C. The separation occurred using a 1.0 mL/min isocratic flow composed of 3:7 (v:v) of water: acetonitrile.

Check standards and blanks were used with every sample set to ensure performance. For PAHs, a 5 or 20 µg/L standard (Ultra Scientific) containing 16 PAHs was analyzed. Standards ranging in concentrations from 0.05 µg/L to 200 µg/L were used to determine each compound's response factor.

RESULTS & DISCUSSION

Determination of Non-equilibrium

As discussed in Chapter 3, the corrections for non-equilibrium in sediment can be ascertained by coupling in-situ PRC desorption measurements with the external mass transfer resistance model, where the fraction of PRC mass remaining after a certain deployment period is modeled as:

$$\frac{M(t)}{M_0} = \exp\left(\frac{RDt}{L^2 K_{PDMS}^2}\right) erfc\left(\frac{\sqrt{RDt}}{LK_{PDMS}}\right) = 1 - f_{ss} \qquad \text{Eq. 1}$$

where M(t) is equal to the PRC mass remaining after the deployment period, M_0 is the initial PRC mass absorbed to the fiber, R is the retardation factor, D is the effective diffusion coefficient, L is the effective thickness of the PDMS fiber that is equal to the surface volume to area ratio, K_{PDMS} is the PDMS polymer partition coefficient given in Ghosh et al. (2014), and f_{ss} is the fraction of steady state achieved during the deployment period. The system dependent value of RD, the lumped parameter of the sorption related retardation factor in the sediment and the effective diffusivity, is the only unknown in the above equation.

Non-equilibrium correction factors were determined utilizing four deuterated PAHs (fluoranthene-d10, chrysene-d12, benzo(b)fluoranthene-d12, and dibenz(a,h)anthracene-d14) as PRCs for each of the sampling events at the WBGCR site. For the May/June 2012 study, ten 2-cm fiber replicates of the SPME PDMS PRC spiked fibers, taken before deployment, were used to estimate the mean initial concentration for each PRC sorbed to the SPME PDMS fiber. PRC spiked SPME PDMS fibers were deployed at four locations throughout the WBGCR sampling area. After the twenty day deployment, the mass remaining sorbed to the SPME PDMS was compare to the initial mass and used to fit the ERM model parameter RD to estimate the fraction of steady state achieved. A linear relationship between $\log K_{ow}$ and logRD was found to have a slope of 1.1 ± 0.09 and an intercept of -7 ± 0.6 with a r^2 of 0.59. The fraction of steady state achieved during the 20 day deployment ranged from 47% for dibenz(a,h)anthracene ($\log K_{ow}$ = 7.39) to 84% for naphthalene ($\log K_{ow}$ = 3.41).

For the October/November 2013 study, six 2-cm fiber replicates of the SPME PDMS PRC spiked fibers were used to estimate the mean initial concentration for each of the PRCs sorbed to the SPME PDMS fiber. PRC spiked SPME PDMS fibers were deployed at all twenty-one sampling locations for the WBCGR sampling area. Due to high levels of variability in the PRC concentrations found after exposure, the fraction of steady state values determined in the May/June 2012 were used as correction factors.

For the September/October 2014 study, 10 2-cm fiber replicates of the SPME PDMS PRC spiked fibers were taken in the lab before traveling to the WBGCR site. An additional 10 2-cm fiber segment replicates were taken on the day of deployment in the field to ensure that the most accurate estimate of the initial PRC concentration was used to calculate RD and subsequently f_{ss}. PRC spiked SPME PDMS fibers were deployed at all 21 locations sampled throughout the WBGCR sampling area in the sediment and also in the surface water. For the twenty-one day deployment period, a linear relationship between $\log K_{ow}$ and logRD was determined to have a slope 1 ± 0.03 of which an intercept of -7.3 ± 0.2 and an r^2 of 0.62 for the SPME PDMS samplers deployed into the sediment.

Unlike the first two deployments, the more hydrophobic PRCs were still sorbed to the PDMS for the SPME PDMS fibers deployed in the surface water. A mass transfer coefficient for the PRC loss from the PDMS layer is obtained by solving the following mass balance:

$$V_{pdms}\frac{dC_{prc,pdms}}{dt} = -k_l A_{pdms}\left(\frac{C_{prc,pdms}}{K_{pdms-w}}\right) \quad \text{Eq. 2}$$

with the initial condition,

$$C_{prc,\,pdms}(t = 0) = C_{prc,o} \quad \text{Eq. 3}$$

where V_{pdms} is the PDMS volume (m^3), k_l is the mass transfer coefficient for the loss of PRC mass from the PDMS layer (m/d), A_{pdms} is the surface area of the PDMS coating, and $K_{pdms\text{-}w}$ is the PDMS-water partition coefficient. The desorption rate coefficient can

be determined from the the mass/concentration fraction of PRC ($C_{prc,t}/C_{prc,o}$) remaining after a deployment time (t).

$$k_l = -\frac{\ln\left(\frac{C_{prc,t}}{C_{prc,o}}\right) L_{pdms} K_{pdms-w}}{t} \qquad \text{Eq. 4}$$

The fraction of steady state (f_{ss}) achieved for a given contamianant and a given exposure time in the surface water can be determined using the desorption rate coefficient,

$$f_{ss} = 1 - \exp\left(-\frac{k_l t}{K_{pdms-w} L_{pdms}}\right) \qquad \text{Eq. 5}$$

For the twenty-one day deployment period, a linear relationship between $\log K_{ow}$ and $\log k_l$ was determined to have a slope of -0.28 with an intercept of -3.8 and an r^2 of 0.49. This relationship can be used to determine k_l and f_{ss} for all of the contamaints of interest and the equilibrium concentration in the surface water can be determined similarly to the equilibrium concentration calculations in sediment,

$$C_{sw}^{eq} = \frac{C_{pdms}}{K_{pdms} f_{ss}} \qquad \text{Eq. 6}$$

Contaminants with a $\log K_{ow}$ values ≤ 5.3 were found to be at equilibrium. The fraction of steady state achieved during the deployment for the most hydrophobic contaminant of interest, dibenz(a,h)anthracene ($\log K_{ow} = 7.39$), was 0.53.

Sediment Concentration Profiles

Vertical profiles of PAH concentrations were obtained for depths up to 90 cm from the sediment-water interface. Surface water column measurements were obtained

using fibers deployed above the sediment-water interface. Generally, agreement between the baseline (2012), 2013, and 2014 data was excellent with differences typically substantially less than a factor of two in the near surface region although at depth, some differences were noted. Those inter-year differences are likely due to local variations in cap depth and/or levels of contamination at exact sampler location, which can vary between years.

Results from the 2012 baseline monitoring event highlighted several areas where relatively high PAHs levels were found in the near surface compared to a surface water quality criteria (SWQC) (sampling locations 2, 6, 8, 13, 18, 19, 20, and 21), where NAPL residue was found on the SPME-PDMS fiber during retrieval (sampling locations 4, 13, and 18), and where more extensive intermixing was noted (sampling locations 12, 13, 17, 19, and 20). Comparisons to SWQC for sediment porewater are conservative comparisons as porewater concentrations are more concentrated. In 2013, porewater concentrations in excess of the SWQCs were noted at sampling locations 2, 3, 4, 7A, 8, 9, 10, 11, 12, 13, 14, 17, 18, 19, 20A, and 21. Relatively high concentrations of PAHs were observed in the near surface (0-15 cm below the sediment-water interface) at sampling locations 12A, 13, 15, 18, and 19. Sampling locations were more extensive intermixing between the native sediment layer and capping layer was observed from its vertical concentration profile included sampling locations 12, 17, 19, and 20. From the 2014 monitoring event, PAH concentrations above SWQC in the near surface were noted at sampling locations 8, 13, 14, and 18 ; exceedances of SWQC for sampling depths greater than 10-15 cm were also noted at sampling locations 3, 4, 6, 8, 9, 10, 11, 12, 13, 14, 16,

18, 19, 20, and 21 for depths below 15 cm beneath the sediment-water interface. Intermixing was noted at sampling locations 12, 13, 17, 19, and 20.

The observations made based upon the data collected during the 2013 and 2014 monitoring trips are consistent with observations made during the baseline study. There were no exceedances of SWQC noted in the surface water for all three monitoring events and the exceedances within the sediment porewater were for high molecular PAHs (i.e, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(a)pyrene), although there were rare measurements of naphthalene at depth that exceeded naphthalene's SWQC.

Figures 7-2 through 7-5 compare 2012, 2013, and 2014 total PAH ($\sum PAH$) and high molecular weight PAH ($\sum HPAH$) profiles at stations that exhibited intermixing in 2012. Similar trends were seen in subsequent monitoring events. Figure 6 compares 2012, 2013, and 2014 total PAH ($\sum PAH$) and high molecular weight PAH ($\sum HPAH$) profiles at two stations that indicate an effective cap layer. The broken and solid horizontal lines indicate where the gravel cap layer ends and where the sand/organophilic clay layer ends. The cap was designed to have 15 cm (6") of an organophilic clay layer coved by 30 cm (12") of sand and a top gravel layer for protection. The cap layer thickness is inconsistent over the site. Some of the locations like location 13 and 17 have a nominal or no sand/organiphilic clay layer. These are the sites where the most extensive intermixing is seen with the SPME PDMS samplers.

Location 12

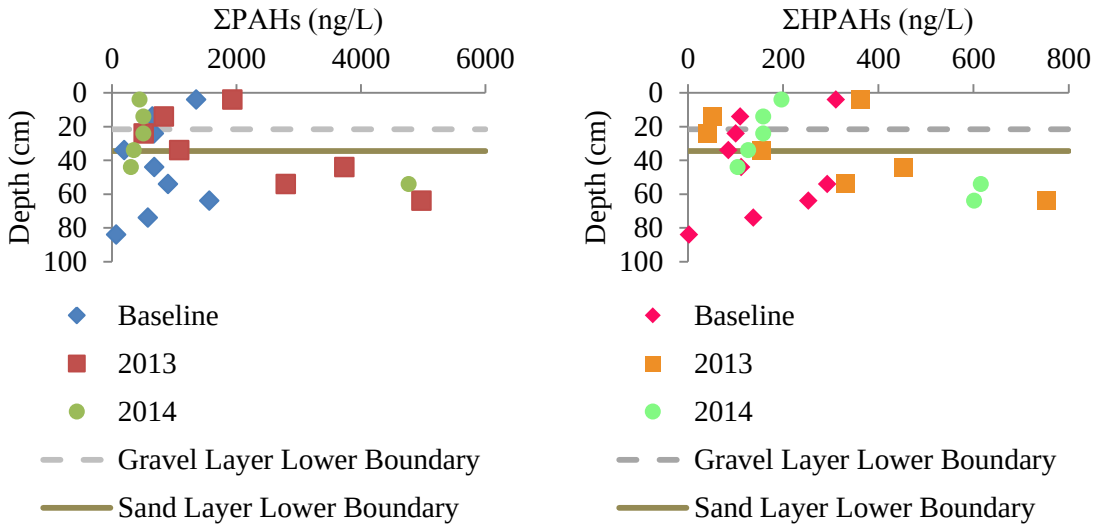

Figure 7-2. Concentration profiles of total PAHs (ΣPAHs) and high molecular weight PAHs (ΣHPAHs) for the baseline monitoring event in 2012, and the subsequent 2013 and 2014 monitoring events for sampling location 12. Exceedances of surface water quality criteria and observations of intermixing were observed. The broken horizontal line represents the depth of the gravel layer and the solid horizontal line represents the depth of the sand/clay layer.

Location 17

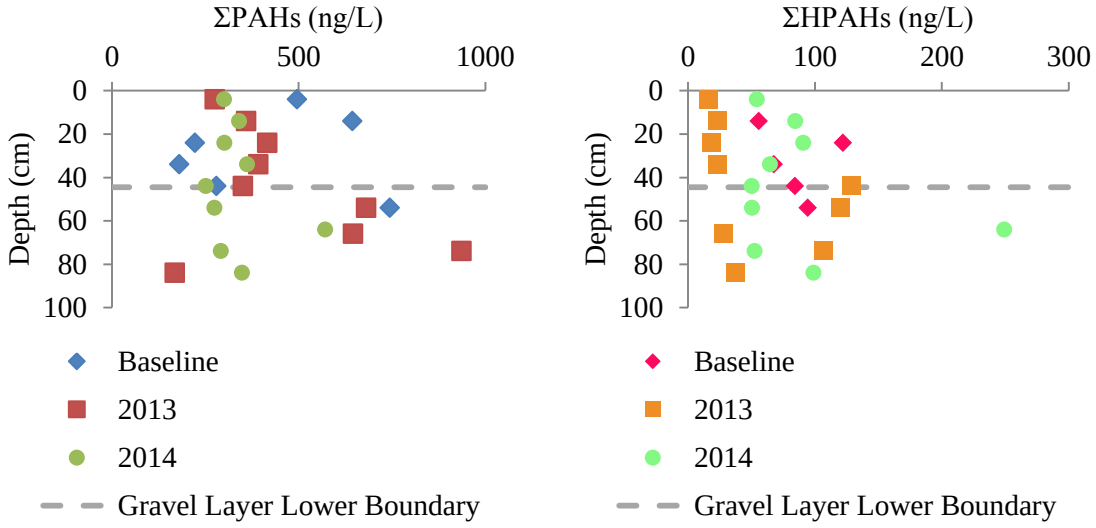

Figure 7-3. Concentration profiles of total PAHs (ΣPAHs) and high molecular weight PAHs (ΣHPAHs) for the baseline monitoring event in 2012, and the subsequent 2013 and 2014 monitoring events for sampling location 17. Observations of intermixing were observed. The broken horizontal line represents the depth of the gravel layer. There was no indication of a sand/organophilic clay cap layer at this location.

Location 18

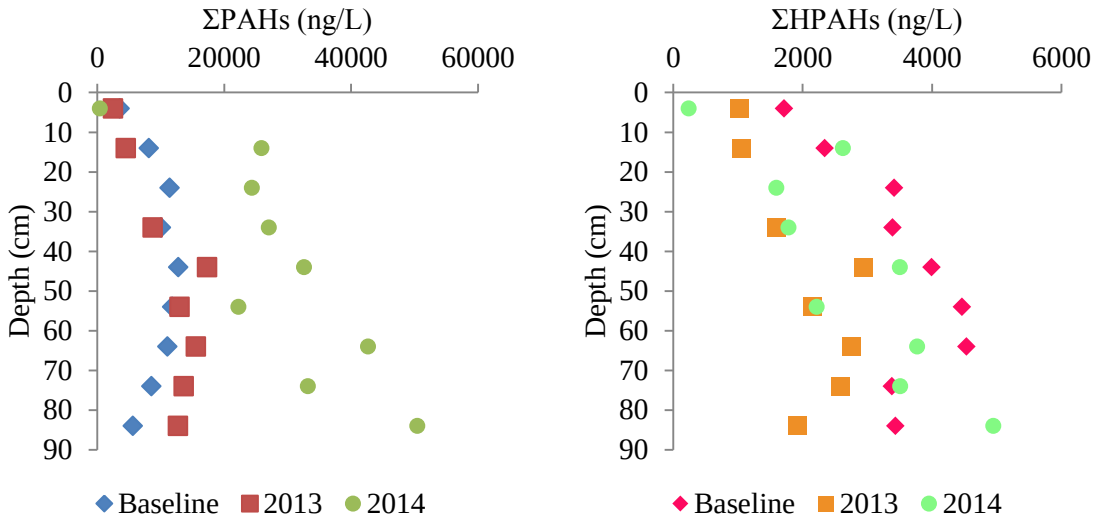

Figure 7-4. Concentration profiles of total PAHs (ΣPAHs) and high molecular weight PAHs (ΣHPAHs) for the baseline monitoring event in 2012, and the subsequent 2013 and 2014 monitoring events for sampling location 18. Exceedances of surface water quality criteria, observations of intermixing, and NAPL residue on the SPME PDMS fiber were observed. No cap was placed at location 18 as it is located in a utility corridor.

Location 19

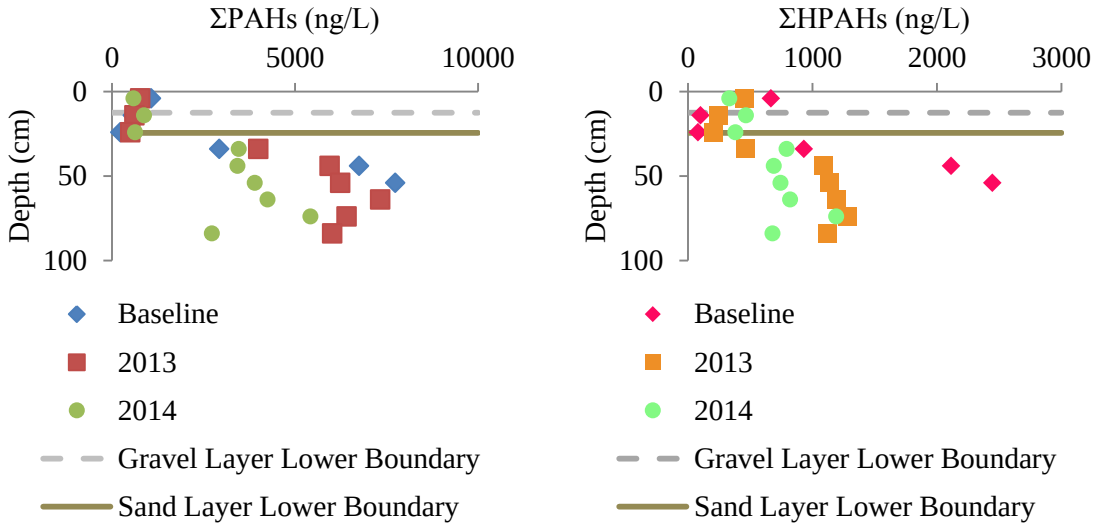

Figure 7-5. Concentration profiles of total PAHs (ΣPAHs) and high molecular weight PAHs (ΣHPAHs) for the baseline monitoring event in 2012, and the subsequent 2013 and 2014 monitoring events for sampling location 19. Exceedances of surface water quality criteria and observations of intermixing were observed. The broken horizontal line represents the depth of the gravel layer and the solid horizontal line represents the depth of the sand/clay layer.

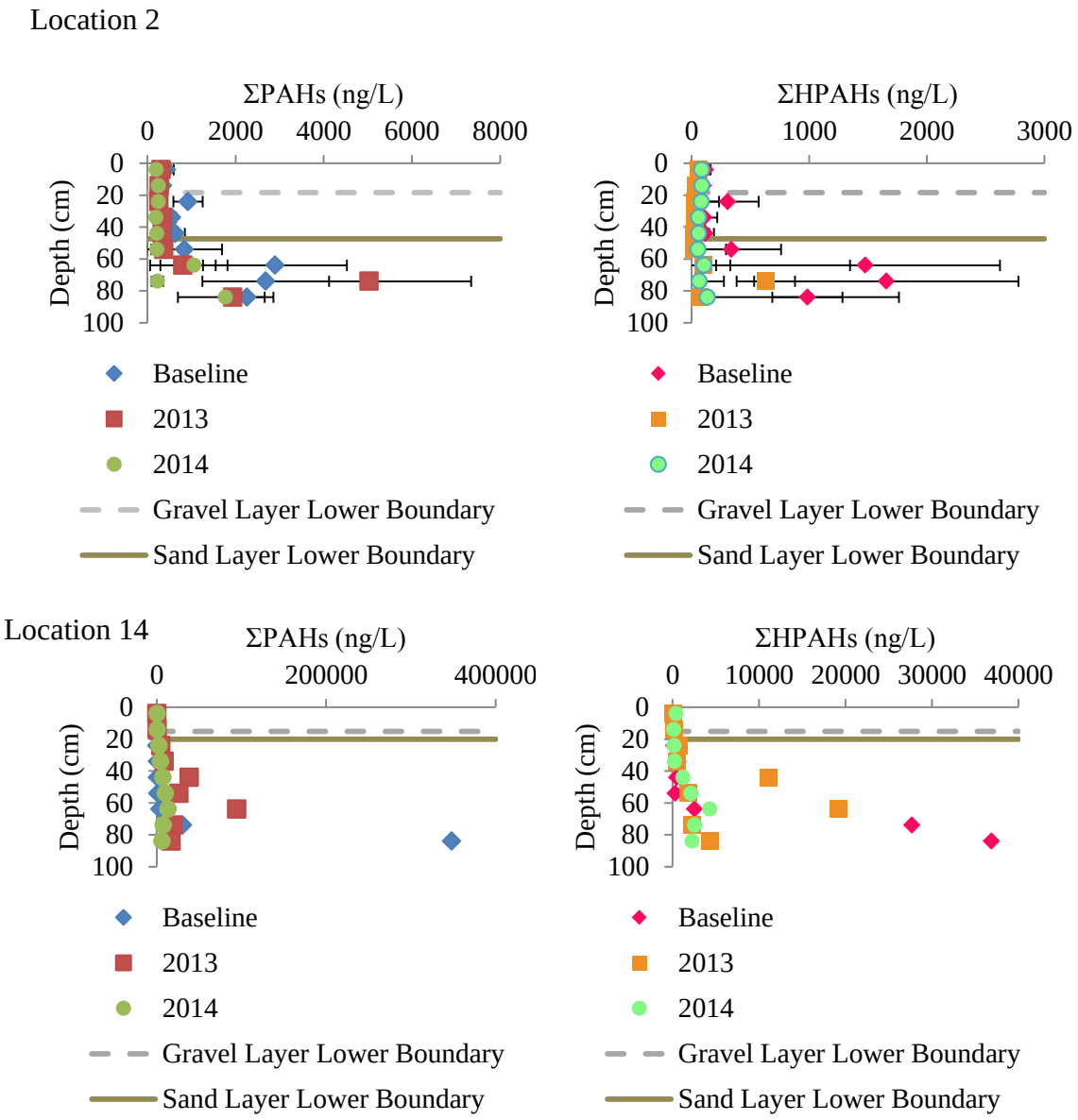

Figure 7-6. Concentration profiles of total PAHs (ΣPAHs) and high molecular weight PAHs (ΣHPAHs) for the baseline monitoring event in 2012 and the 2013 sampling event for sampling locations 2 and 14. These concentration profiles observed at these two sampling locations are examples of an effective cap layer. The broken horizontal line represents the depth of the gravel layer and the solid horizontal line represents the depth of the sand/clay layer.

Comparison to bulk solids

The monitoring events at the west branch of the Grand Calumet River were joint efforts with the EPA and USACE. Sediment cores were taken at the sampling locations where the SPME PDMS samplers were deployed. Currently, one way of obtaining sediment porewater concentrations, approved by regulatory agencies, is to use equilibrium partitioning (EqP). For this method, porewater concentrations are calculated from bulk solid concentrations from cores and grab samples divided by the product of the organic carbon fraction (f_{oc}) and tabulated values of the contaminant's organic carbon partition coefficient (K_{oc}).

Bulk solid concentrations were determined for the upper cap layer and the lower cap/native sediment layer using Soxhlet extraction procedures completed by the Energy and Environmental Research Center GC/MS Lab. Using the bulk solid concentrations (W_s, μg/g) and the SPME PDMS porewater concentrations (C_{pw}, μg/L), a sediment-water partition coefficient was calculated for the compounds of interest, PAHs, at all the sampling locations,

$$K_d = K_{oc} f_{oc} = \frac{W_s}{C_{pw}} \qquad \text{Eq. 7}$$

Baker et al. (1997) provides a relationship between $\log K_{oc}$ and $\log K_{ow}$,

$$logK_{oc} = 0.903 logK_{ow} + 0.094 \qquad \text{Eq. 8}$$

Using f_{oc} values typical for a sand/gravel cap layer (0.01) and organophilic clay/native sediment layer (0.1), Eq. 8 was converted into a cap or native sediment specific $\log K_d$-$\log K_{ow}$ relationship. Figures 7-7 and 7-8 show the $\log K_d$-$\log K_{ow}$

relationship determined for PAHs at WBGCR in the cap and in the native sediment, respectively. For the cap layer (Figure 7-7), the majority of the observed $\log K_d$ values are less than the predicted $\log K_d$ values indicating that using bulk solid concentrations to estimate porewater concentrations would under predict the actual porewater concentrations. This is expected as the upper cap layer consists primarily of sand and gravel, non-highly sorptive materials. Conversely, the majority of $\log K_d$ values measured from the native sediment layer are above the predicted $\log K_d$ values from Baker et al. (1997) $\log K_{oc}$ values. This observation indicates that porewater concentrations derived through EqP would be overestimated. If bulk solid concentrations from the cores collected at the sampling locations were the only means to assess porewater concentrations, the regulatory decisions could be very different as the cap layer and native sediment layer would be viewed as less or more contaminated than in reality, respectively. These discrepancies could also lead to miscalculation in flux potential.

When evaluating in situ remediation effectiveness, specifically capping, it is important to have the most accurate collection of data significant to transport and risk. The freely dissolved or porewater concentration is the driver for fate and transport in capped systems and is also a more reliable indicator of risk to benthic organism (Kraaij et al., 2003, Lu et al., 2003, Cornelissen et al., 2006). The results from the comparison of observed versus predicted $\log K_d$ values within the cap layer and the native sediment layer highlight the need to accurately assess the freely-dissolved concentration as seen through the failure of EqP theory at this site. Sediment and cap systems are heterogeneous and the detail required to successfully implement EqP theory based on organic carbon content of

the system is insurmountable. Passive sampling directly assesses the freely-dissolved concentration and has no dependence on organic carbon, which can vary highly with depth for capped sediments. Table 7-1 holds the average $logK_d$ values determined within the cap layer, native sediment layer, and both layers together.

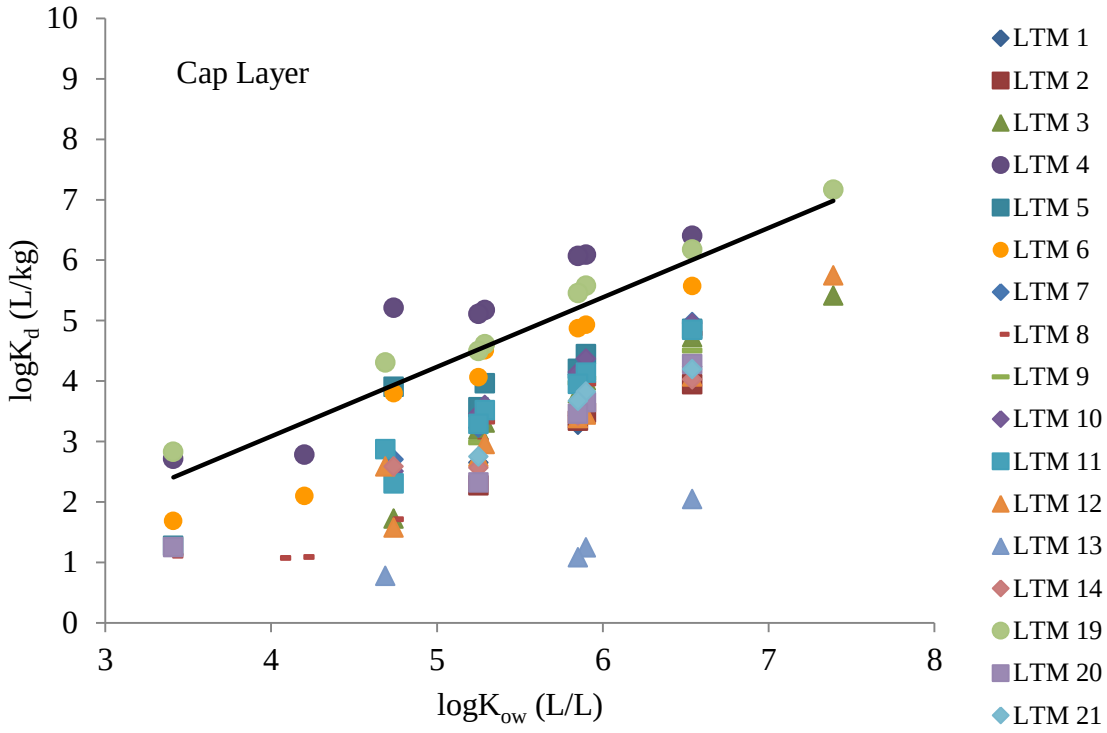

Figure 7-7. $LogK_d$ determined within the cap layer at WBGCR sampling locations from core samples and SPME PDMS samples. The black solid line represents $logK_d$ determined using the Baker et al. (1997) relationship between $logK_{oc}$ and $logK_{ow}$ and a typical porosity of a sand cap of 0.01.

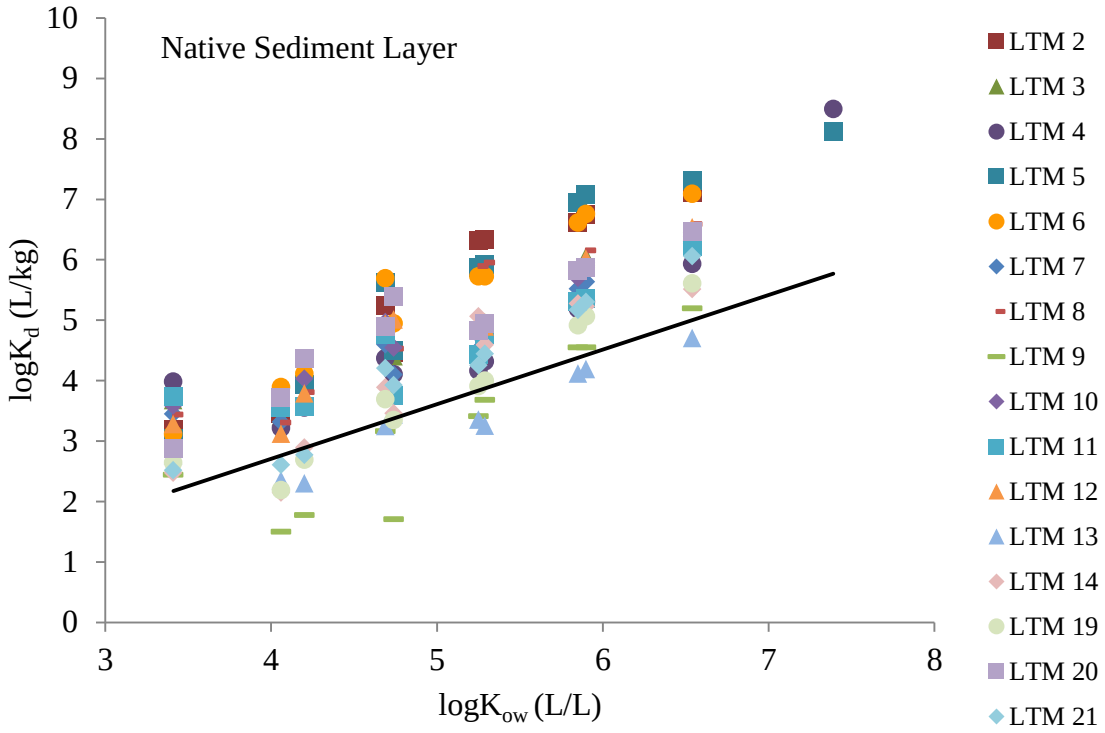

Figure 7-8. LogK_d determined within the native sediment layer at WBGCR sampling locations from core samples and SPME PDMS samples. The black solid line represents logK_d determined using the Baker et al. (1997) relationship between logK_{oc} and logK_{ow} and a porosity typical for organoclay/sediment of 0.1.

Table 7-1 $\log K_d$ (average ± standard deviation) determined within the cap layer, native sediment layer, and the both layers taken together.

	NAP	FLU	ACEN	PHEN	ANTHRA	FLUOR	PYR	CHRY	BAA	BAP	DBA
	$\log K_d$ (L/kg) (average ± standard deviation)										
Upper Cap Layer											
Average	1.8	2.0	1.1	2.8	2.6	3.8	3.2	4.1	3.9	4.6	6.1
Standard Deviation	0.8	0.9	-	1.2	1.3	0.7	0.8	1.1	1.1	1.0	0.9
Lower Cap & Native Sediment Layer											
Average	3.1	3.4	3.1	4.1	4.6	4.8	4.8	5.7	5.6	6.2	8.3
Standard Deviation	0.5	0.7	0.7	0.9	0.8	0.8	0.9	0.8	0.8	0.7	0.3
Cap & Native Sediment Layer											
Average	2.8	3.2	2.9	3.6	4.1	4.5	4	4.9	4.7	5.4	7
Standard Deviation	0.8	0.9	0.8	1.2	1.2	0.9	1.1	1.2	1.2	1.2	1.4

Contaminant Transport

Using the method described in Chapter 6, the PRC C/C_o values at sampling location 13, sampling location 17, and sampling location 18 led to Peclet numbers near unity and therefore simple models of effective diffusion in a semi-infinite system capped by a finite layer can be used to model the concentration profiles at this site (Choy and Reible, 2000).

The unsteady-state chemodynamic diffusive transport model of a semi-infinite region with a uniform initial concentration ($C_{sediment}$) capped by a finite layer with a different uniform initial concentration (C_{cap}) and zero concentration at the surface is defined by the following boundary conditions (Choy and Reible, 2000):

$$\frac{\partial C}{\partial t} = \left(\frac{D_{eff}}{R_f} \right) \frac{\partial^2 C}{\partial z^2} \qquad \text{for } z \in [0, \infty) \qquad \text{Eq. 9}$$

$$C(z,t)\big|_{z=0} = 0 \qquad \text{for } t > 0 \qquad \text{Eq. 10}$$

$$C(z,t)\big|_{z \to \infty} = C_{sediment} \quad \text{for } t > 0 \qquad \text{Eq. 11}$$

$$C(z,t)\big|_{t=0} = \begin{cases} C_{cap} & z \in [0, z_{cap}) \\ C_{sediment} & z \in [z_{cap}, \infty) \end{cases} \qquad \text{Eq. 12}$$

The concentration profile of this system is given by,

$$C(z,t) = C_{sediment} + \left(\frac{C_{cap} - C_{sediment}}{2} \right) \left\{ erfc\left[\frac{R_f (z - z_{cap})}{\sqrt{4 D_{eff} R_f t}} \right] + erfc\left[\frac{R_f (z + z_{cap})}{\sqrt{4 D_{eff} R_f t}} \right] \right\} - C_{cap} erfc\left[\frac{R_f z}{\sqrt{4 D_{eff} R_f t}} \right]$$

$z \in [0,\infty)$, $t > 0$

Eq. 13

and the surface flux is given by,

$$F(t)\big|_{z=0} = \sqrt{\frac{D_{eff} R_f}{\pi t}} \left[\left(\frac{C_{cap} - C_{sediment}}{2} \right) \left\{ \exp\left[-\frac{R_f z_{cap}^2}{4 D_{eff} t} \right] + \exp\left[\frac{R_f z_{cap}^2}{4 D_{eff} t} \right] \right\} + C_{cap} \right] \qquad \text{for } t > 0$$

Eq. 14

Porewater concentrations at sampling location 13 have been consistently the highest, and at some depths are tenfold the compound specific SWQC. Due to the elevated concentrations, triplicate SPME PDMS samplers have been deployed into the sediment during the monitoring events; additionally, surface water samplers have been deployed at this sampling location. Sampling location 13 has a nominal sand/organophilic clay layer of approximately 5.3 cm. Other sampling locations that showed intermixing included sampling location 17, where no indication of a sand/organophilic clay layer was found from the cores. Sampling location 18 was not capped and can act as a reference for comparing fluxes from capped layers.

For the purposes of contaminant modeling at the WBGCR, the value of C_o is the concentration at the cap-sediment interface and the effective diffusivity can be determined with the use of PRCs. Figure 7-9 presents concentration profiles over the three years of monitoring for anthracene, a representative low molecular weight PAH

(LPAH), and benzo(a)pyrene, a representative high molecular weight PAH (HPAH) at sampling locations 13.

Using the initial concentrations found in the cap layer and the native sediment layer and the contaminant specific parameters, R_f and D_{eff} (see Table 7-2), Equation 13 can be used to model the baseline year and also subsequent years to predict cap concentration levels. Figures 7-10 and 7-11 are parity plots of the predicted anthracene concentrations found using Equation 13 and the baseline concentrations measured in the cap and native sediment porewater and the measured concentrations found in the porewater at sampling location 13 for the 2013 (Year 1) and 2014 (Year 2) monitoring events. The measured and predicted values were mostly within a factor of two of one another.

Figures 7-12 and 7-13 depict the predicted and actual concentration profiles for anthracene and benzo(a)pyrene for the baseline (2012), 2013 (Year 1), and 2014 (Year 2) as well as predicted concentration profiles 10 years after finished remediation efforts using effective diffusivity models. Due to the large retardation factor for the bottom cap layer/native sediment, there was little change in concentration at depth. The models support what is seen during sampling events: changes in concentration for less hydrophobic PAHs, with minimal changes in concentrations for more hydrophobic compounds. Less hydrophobic compounds like anthracene are going to deplete faster, while depletion is slower for more hydrophobic compounds like benzo(a)pyrene.

Location 13

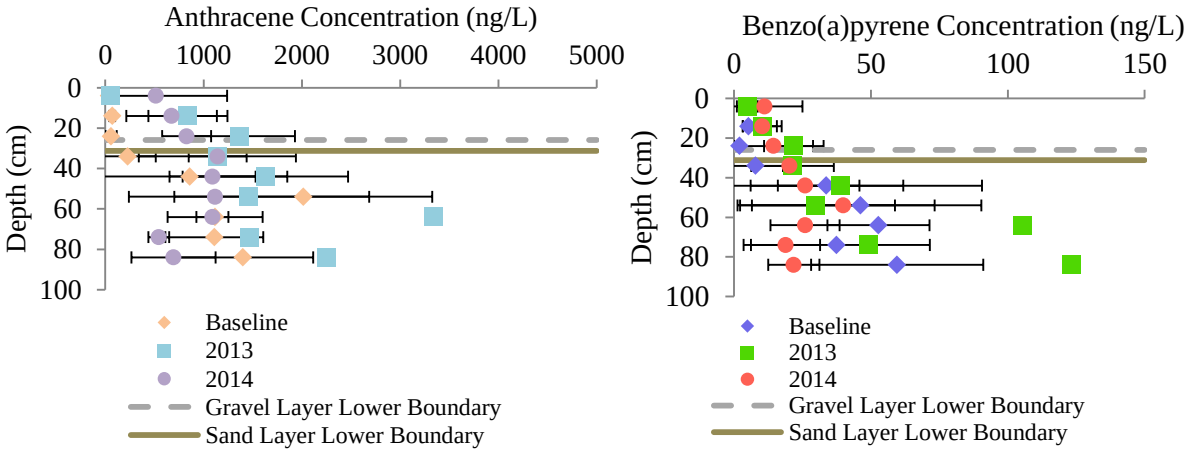

Figure 7-9. Concentration profiles of anthracene, a representative LPAH, benzo(a)pyrene, a representative HPAH, for the baseline monitoring event in 2012, and the subsequent 2013 and 2014 monitoring event for sampling locations 13 and 18.

Table 7-2. Mass transport parameters for anthracene and benzo(a)pyrene at sampling location 13 of WBGCR.

	Sampling Location 13	
Parameter	ANT	BAP
$C_{o,cap}$ (ng/L)	800	10
$C_{o,sediment}$ (ng/L)	1600	60
z_{cap} (cm)	31	
Upper Cap: R_f (-)	20	61
Upper Cap: D_{eff} (cm^2/yr)	2,630	46,700
Lower Cap/Sed: R_f (-)	1,400	33,700
Lower Cap/Sed: D_{eff} (cm^2/yr)	37	85

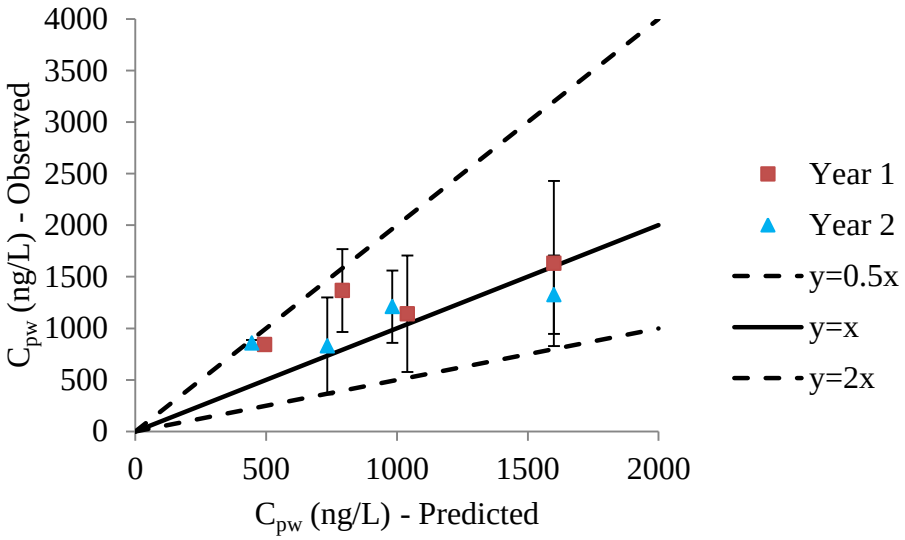

Figure 7-10. Anthracene porewater concentrations measured at within the cap layer at sampling location 13 versus porewater concentrations predicted from Equation 13 with inputs of $C_{o,\ cap}$ = 800 ng/L. $C_{o.sediment}$ = 1600 ng/L, z_{cap} = 31 cm, R_f = 20, and D_{eff} = 2,630 cm^2/yr. The majority of the observed porewater concentrations are within a factor of 2 from the predicted porewater concentrations.

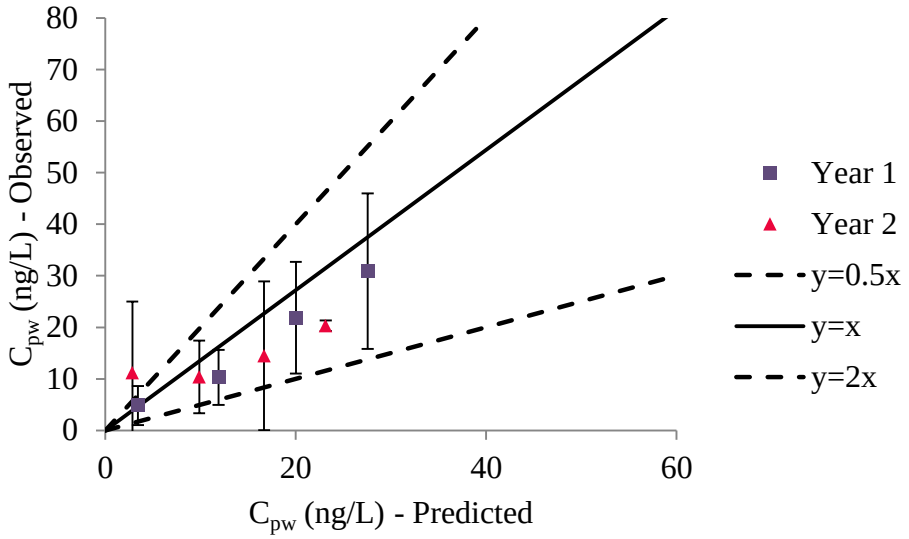

Figure 7-11. Benzo(a)pyrene porewater concentrations measured at within the cap layer at sampling location 13 versus porewater concentrations predicted from Equation 13 with inputs of $C_{o,\ cap}$ = 10 ng/L. $C_{o.sediment}$ = 60 ng/L, z_{cap} = 31 cm, R_f = 61, and D_{eff} = 46,700 cm^2/yr. The majority of the observed porewater concentrations are within a factor of 2 from the predicted porewater concentrations.

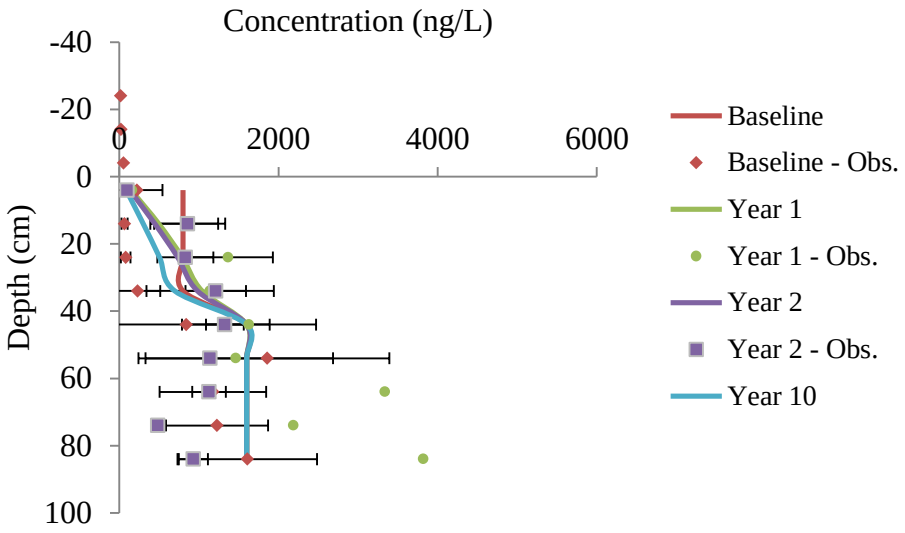

Figure 7-12. Anthracene porewater concentrations measured at sampling location 13 versus porewater concentrations predicted from Equation 13 for the Baseline (2012), Year 1 (2013), and Year (2014) monitoring events. Predictions for concentration profiles 10 years after cap placement with transport processes modeled as lumped diffusion are also shown.

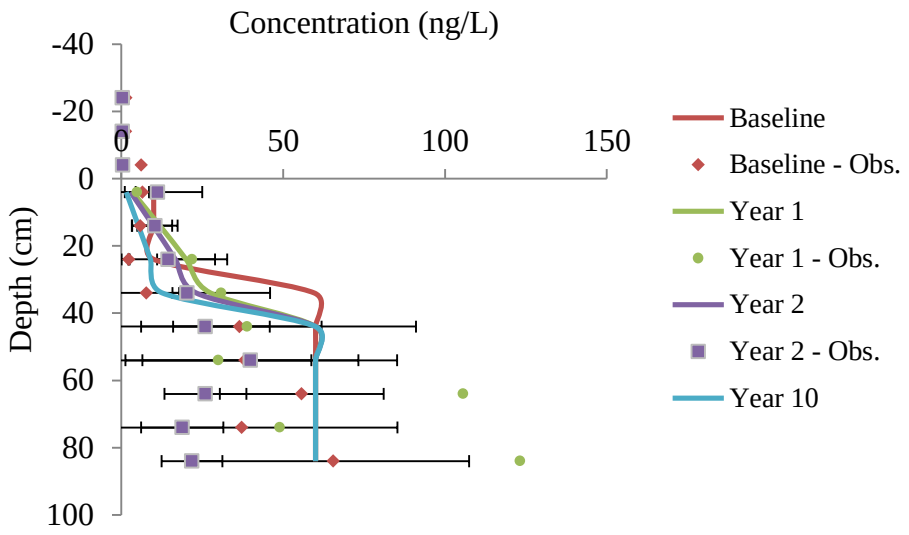

Figure 7-13. Benzo(a)pyrene porewater concentrations measured at sampling location 13 versus porewater concentrations predicted from Equation 13 for the Baseline (2012), Year 1 (2013), and Year (2014) monitoring events. Predictions for concentration profiles 10 years after cap placement with transport processes modeled as lumped diffusion are also shown

SIGNIFICANCE & IMPLICATIONS

Due to the current state of the science for *in situ* remediation efforts, there is a need for long-term monitoring of contaminated sediment sites to ensure that remediation efforts are effective years after remediation is completed. The freely dissolved concentration of a contaminant is the driver of its fate and transport within a system. Passive sampling technology is a tool that efficiently and accurately measures freely dissolved concentrations within the sediment or surface water. When coupled with PRC methods for non-equilibrium corrections, the use of passive samplers can also provide information about the magnitude of diffusive or advective transport processes. The site specific parameters obtained using passive sampling methods can be used to calibrate

diffusive and advection site specific models, which are an important part of sediment risk assessment and management. More accurate calibration of these models will lead to more accurate representation of risk and a fuller understanding of management activities that need to occur.

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Chapter 8: Summary & Recommendations for Future Work

RESEARCH OBJECTIVES

The research completed for this dissertation overall demonstrates the applicability of SPME PDMS fibers for evaluation of remediated sediment sites in terms of hydrophobic organic compounds (HOCs) concentrations and flux. Passive sampling techniques, of which SPME PDMS fibers are an example, provide an accurate measurement of the freely-dissolved concentration in the sediment and surface water at these contaminated sediment sites. The freely-dissolved concentration has been shown to be a better indicator of toxity, bioaccumulation potential, and transport potential.

This dissertation had the following umbrella objectives to build upon the current level of knowledge regarding passive sampling methods and aid in reaching the goal of regulatory acceptance of passive sampling methods:

1. demonstration of the advantages of *in situ* PDMS fibers sampling methods over conventional techniques in terms of implementation and how the results can be used to evaluate remedy performance specifically in terms of contaminant flux and bioavailability,
2. evaluation of the most appropriate methods to evaluate the kinetics of uptake onto the SPME PDMS fiber and demonstrate those techniques under field conditions, and
3. quantification of the effects of key interferences in the technique including evaporation from the PDMS layer.

These objectives were achieved through laboratory experiments, thought experiments, and field demonstrations at remediated contaminated sediment sites that included Chattanooga Creek (Chattanooga, TN), Eagle Harbor (Bainbridge, WA), and the west branch of the Grand Calumet River (Hammond, IN).

RESEARCH CONCLUSIONS

Chapter 3: Evaluation of Methods to Evaluate Kinetics of Contaminants Uptake

One of the recommendations for future work that came from the November 2012 SETAC technical workshop previously mentioned was the further development of in situ non-equilibrium passive sampling methodologies where PRCs would be used to correct to equilibrium concentrations (Ghosh et al., 2014). This work provides validation of PRCs as a method to correct for non-equilibrium conditions and provide guidance on how to use PRCs when monitoring at contaminated sites.

Methods using performance reference compounds or colocation of passive sampling materials with varying sorbent thicknesses during *in situ* and *ex situ* studies can be used to fit the external resistance model and correct for non-steady state conditions between the sorbent and porewater. An *ex situ* comparison between the correction methods resulted in the same freely dissolved concentrations as those found using conventional equilibrium based methods. The use of performance reference compounds was found to be applicable for use at capped sediment sites to assess kinetic processes. The results of the *ex situ* and *in situ* studies suggest that these correction methods provide efficient and accurate means of determining the freely dissolved porewater

concentrations. A graphical user interface was compiled from MATLAB® source code based upon the use of the PRC correction method and the external resistance model. The source code for a standalone application is presented in Appendix A. This aim of this standalone application is to streamline the calculation process for a targeted audience of government agencies and engineering consulting agencies that do not perform their own analytical work.

Chapter 4: Volatile Loss of Compounds from Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers

One of the concerns when completing field sampling events with passive sampling methods is the accuracy of the reported concentrations especially for the low molecular weight compounds that are more volatile. This chapter addresses one of the remaining QAQC methods that needs to be addressed before passive sampling techniques can be accepted as a standard method. The experiments, using SPME PDMS fibers of different thicknesses exposed to various ambient air temperatures, provided a fit to a model that incorporates the compound's Henry Law coefficient and sorbent-water partitioning coefficient to estimate a compound's desorption rate. In general, compounds of interest with a $\log K_{ow} \geq 5$ are stable for approximately one day when using SPME PDMS fibers.

The model can be expanded to different sorbent matierials commonly used to monitor hydrophobic organic contaminants in sediment porewater and surface water through the use of the sorbent specific partitioning coefficient. Estimates for the sampling time necessary to achieve 90% concentration retention on the polymer sorbent layer,

indicated POM would be the most appropriate material, of PDMS, POM, and PE, for the monitoring applications of the most volatile compounds. There is little difference between the three sorbent materials when monitoring more hydrophobic compounds in terms of compound retention. Although, there is a difference in the deployment time in the sediment or surface water to achieve equilibrium as discussed in Chapter 2 and Chapter 3 for the compounds, and therefore the selection of the most appropriate polymer sorbent and sorbent thickness must be made based upon factors including the volatility of the compounds of interest and the security of the site, which impacts the deployment time length.

The results suggest, regardless of sorbent material type, that thicker sorbent layers should be used and the samplers should be kept at low temperatures between retrieval and processing either on site or enroute to an off-site facility for processing to ensure the most accurate set of data is captured.

Chapter 5: Interpretation of Porewater Concentration Profiles Measured Using Profiling Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers

The results from the field deployments at Chattanooga Creek and the west branch of the Grand Calumet River demonstrated that PRCs are a viable option to measure the state of non-equilibrium between a passive sampling material and the surrounding environment, but that other options, like collocated sorbent materials of different geometries, can also be used although with generally greater uncertainty. The sampling in sediment caps showed that SPME PDMS methods can be quite helpful in identifying transport mechanisms and rates and separating placement intermixing and

recontamination from contaminant migration through a cap. The conclusions drawn from the porewater sampling, however, may differ quantitatively from the conclusions that would be found from bulk solids and are more representative of risk. The field examples show that passive sampling can provide useful tools for remedy assessment.

Chapter 6: Monitoring Contaminant Flux and Intermixing within Sediment Caps using *in situ* Solid Phase Microextraction Techniques

The Pe number for a sediment system can be determined using SPME PDMS techniques coupled with PRC methods to indicate if mass transport can be modelled using a lumped diffusive-like parameter or if advective processes need to be modelled explicitly. A simple model of the release of these PRCs is used to predict interstitial mixing and to aid in the estimation of the steady state uptake of sediment contaminants.

Additionally, D_{eff} can be determined from the release of PRCs and the site specific R_f, determined from comparisons between bulk solid data and porewater data. If D_{eff} is greater than D_w, as it was for both Chattanooga Creek and the west branch of the Grand Calumet River, then mass transport processes that can be modelled like diffusion are augmenting molecular diffusion processes.

The Pe number found at sampling locations along Chattanooga Creek (Chattanooga, TN), Eagle Harbor (Bainbridge Island, WA), and the west branch of the Grand Calumet River (WBGCR) indicated that mass transport could be modeled using a lumped parameter for diffusive-like processes, as transport due to advection was not substaintial comparatively.

Estimations of flux are important when evaluating sediment caps. They are a direct indicator of the effectiveness of a cap layer as caps are designed to reduce contaminant flux. The parameters that can be estimated using the discussed model (U, D_{eff}, and R_f) can be used to estimate the breakthrough time of the cap, which can lead to an improvement of the risk assessment and could aid in decision-making actions regarding further remediation operations at a site.

Chapter 7: Characterization of PAH Fate and Transport Utilizing Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers to Address Cap Effectiveness at the West Branch of the Grand Calumet River

The chapter highlights the ability to collect and interpret trends from passive sampler profiles collected at the same locations, within the accuracy of differential GPS, over time and is a culmination of the topics discussed in the previous chapters. Profiles showing similar trends year to year provide an indication of the intrinsic variability between samples while samples showing substantially different profiles provide an indication of system changes or greater small-scale variability. Using the model described in Chapter 6, estimates of the relative importance of diffusive-like versus advective transport were calculated.

This chapter also fulfills the need for one of the SETAC technical workshop's future work items. The analysis of concentration profiles over several years using PRCs is not usually seen for contaminanted sediment sites. This work can be used as a guide for the implementation of passive sampling techniques over the life of a sediment cap.

RECOMMENDATIONS FOR FUTURE WORK

The use of passive sampling methods for evaluation of bioavailability and remedial evaluations is becoming less taboo, but passive sampling methods have not seen regulatory acceptance. To achieve this goal, several outstanding issues that were not addressed in this dissertation are discussed below.

Comprehensive list of target compound and demonstration of ability to quantify

The most common compounds sampled for using passive sampling specific for hydrophobic organic contaminants are PCBs and PAHs. These classes of compounds are very prevalent in contaminated sediment, but development of passive sampling methods for other compounds receiving regulatory attention like dioxins, chlorobenzene, and EPA contaminants of emerging concern including polybrominated diphenyl ethers, perfluorinated compounds, pharmaceuticals, and personal care products. Partitioning coefficients and detection limits would have to be quantified in addition to field demonstrations.

Use and modelling of performance reference compounds in amended caps

One of the key assumptions when using performance reference compounds is that sorption is linear. However, if the sorption and desorption of the compound from the passive sampler or surrounding medium are concentration dependent (i.e. nonlinear sorption), the PRC desorption cannot reliably describe the uptake of the compound of interest. Passive samplers exhibit linear sorption to a high degree, but nonlinear sorption may prevail in the surrounding medium (e.g. with activated carbon treated sediments). *Ex situ* experiments could be developed to test the effect of activated carbon and other

highly sorptive materials on the desorption of PRCs. If the use of PRCs is still applicable for amended systems, this would rid a current limitation of the method.

Appendix A: MATLAB Source Code for Evaluating the Fraction of Steady State Achieved between a Thin Layer of Polymer Sorbent & Sediment Porewater Assuming External Mass Transfer Resistances are Dominant

In this appendix, the source code a standalone application compiled from MATLAB that calculates α and β of the logRD-logK_{ow} relationship, assuming the validity of the ERM for the compounds of interest, is presented. The user inputs include the thickness of the PSM, the time length of deployment, and the PRC ratios (fraction of the PRC mass remaining sorbed to the PSM sorbent layer) for a given site. The user can enter the PRC ratios directly if there is only one ratio for each PRC used. The source code and an example of using the application begins on the next page. If there are multiple ratios for each PRC, the user can import a .csv file containing the ratios. Interested parties are encouraged to contact the author for more information and instructions for using the standalone application.

```
function varargout = PRC_PDMS_GUI(varargin)
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%The GUI interface was created by Courtney L. Thomas and is based upon the
%external resistance model discussed in Lampert et al. (2015). The purpose
%of this GUI is to calculate the fraction of steady state achieved between
%the porewater and a specific passive sampling sorbent,
%polydimethylsiloxane, for monitoring of hydrophobic organic compounds. The
%fraction of steady state acts as a correction factor to determine the
%freely-dissolved concentration, an indicator of fate/transport and
%bioaccumulation potential, from the concentration found sorbed to the
%polymer sorbent.
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
gui_Singleton = 1;
gui_State = struct('gui_Name',       mfilename, ...
                   'gui_Singleton',  gui_Singleton, ...
                   'gui_OpeningFcn', @PRC_PDMS_GUI_OpeningFcn, ...
                   'gui_OutputFcn',  @PRC_PDMS_GUI_OutputFcn, ...
                   'gui_LayoutFcn',  [] , ...
                   'gui_Callback',   []);
if nargin && ischar(varargin{1})
    gui_State.gui_Callback = str2func(varargin{1});
end

if nargout
    [varargout{1:nargout}] = gui_mainfcn(gui_State, varargin{:});
else
    gui_mainfcn(gui_State, varargin{:});
end
% End initialization code - DO NOT EDIT

% --- Executes just before PRC_PDMS_GUI is made visible.
function PRC_PDMS_GUI_OpeningFcn(hObject, eventdata, handles, varargin)
% This function has no output args, see OutputFcn.
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
% varargin   command line arguments to PRC_PDMS_GUI (see VARARGIN)

% Choose default command line output for PRC_PDMS_GUI
handles.output = hObject;
```

```
% Update handles structure
guidata(hObject, handles);

% --- Outputs from this function are returned to the command line.
function varargout = PRC_PDMS_GUI_OutputFcn(hObject, eventdata, handles)
% varargout  cell array for returning output args (see VARARGOUT);
% hObject    handle to figure
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Get default command line output from handles structure
varargout{1} = handles.output;



function thick_PRC_Callback(hObject, eventdata, handles)
% hObject    handle to thick_PRC (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of thick_PRC as text
%        str2double(get(hObject,'String')) returns contents of thick_PRC as a double

% --- Executes during object creation, after setting all properties.
function thick_PRC_CreateFcn(hObject, eventdata, handles)
% hObject    handle to thick_PRC (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function time_PRC_Callback(hObject, eventdata, handles)
% hObject    handle to time_PRC (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of time_PRC as text
%        str2double(get(hObject,'String')) returns contents of time_PRC as a double
```

```
% --- Executes during object creation, after setting all properties.
function time_PRC_CreateFcn(hObject, eventdata, handles)
% hObject    handle to time_PRC (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
   set(hObject,'BackgroundColor','white');
end

% --- Executes on button press in PAH.
function PAH_Callback(hObject, eventdata, handles)
% hObject    handle to PAH (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hint: get(hObject,'Value') returns toggle state of PAH


% --- Executes on button press in PCB.
function PCB_Callback(hObject, eventdata, handles)
% hObject    handle to PCB (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hint: get(hObject,'Value') returns toggle state of PCB

% --- Executes on button press in Reset.
function Reset_Callback(~, eventdata, handles)
% hObject    handle to Reset (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA

close(gcbf)
PRC_PDMS_GUI

% --- Executes on selection change in About.
function About_Callback(~, eventdata, handles)
% hObject    handle to About (see GCBO)
```

```
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: contents = cellstr(get(hObject,'String')) returns About contents as cell array
%        contents{get(hObject,'Value')} returns selected item from About

A = get(handles.About,'Value'); %get currently selected option from menu
if A == 2
   reset(handles.Info);
   set(handles.Info,'BackgroundColor','white');
   set(handles.Info,'Title','Additional
Information','TitlePosition','centertop','FontSize',11,'FontWeight','bold');
   set(handles.BackgroundInfo,'Visible','on')

   set(handles.Instructions,'Visible','off');
   set(handles.Import,'Visible','off');
   set(handles.CalcMulti,'Visible','off');
   set(handles.References,'Visible','off');
   set(handles.CmpdProp,'Visible','off');
   set(handles.ImportCmpdProp,'Visible','off');
   set(handles.InstrucAddCmpd,'Visible','off');

elseif A == 3
    reset(handles.Info);
    set(handles.Info,'BackgroundColor','white');
    set(handles.Info,'Title','Additional
Information','TitlePosition','centertop','FontSize',11,'FontWeight','bold');
    set(handles.CmpdProp,'Visible','on');
    set(handles.ImportCmpdProp,'Visible','on');
    set(handles.InstrucAddCmpd,'Visible','on');

   set(handles.Instructions,'Visible','off');
   set(handles.Import,'Visible','off');
   set(handles.CalcMulti,'Visible','off');
   set(handles.References,'Visible','off');
   set(handles.BackgroundInfo,'Visible','off');

elseif A == 4
       reset(handles.Info);
       set(handles.Info,'BackgroundColor','white');
       set(handles.Info,'Title','Additional
Information','TitlePosition','centertop','FontSize',11,'FontWeight','bold');
```

```
        set(handles.Instructions,'Visible','on');
        set(handles.Import,'Visible','on');
        set(handles.CalcMulti,'Visible','on');


            set(handles.References,'Visible','off');
            set(handles.BackgroundInfo,'Visible','off');
        set(handles.CmpdProp,'Visible','off');
        set(handles.ImportCmpdProp,'Visible','off');
            set(handles.InstrucAddCmpd,'Visible','off');


elseif A == 5
          reset(handles.Info);
          set(handles.Info,'BackgroundColor','white');
          set(handles.Info,'Title','Additional
Information','TitlePosition','centertop','FontSize',11,'FontWeight','bold');
          set(handles.References,'Visible','on');

          set(handles.Instructions,'Visible','off');
          set(handles.Import,'Visible','off');
          set(handles.CalcMulti,'Visible','off');
          set(handles.BackgroundInfo,'Visible','off');
          set(handles.CmpdProp,'Visible','off');
          set(handles.ImportCmpdProp,'Visible','off');
                    set(handles.InstrucAddCmpd,'Visible','off');


end

% --- Executes during object creation, after setting all properties.
function About_CreateFcn(hObject, eventdata, handles)
% hObject    handle to About (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: popupmenu controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
   set(hObject,'BackgroundColor','white');
end
```

```
% --- Executes on button press in Save.
function Save_Callback(hObject, eventdata, handles)
% hObject    handle to Save (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
[filename, pathname] = uiputfile({'*.m';'*.slx';'*.mat';'*.*'},'Save as');

% --- Executes on button press in Open.
function Open_Callback(hObject, eventdata, handles)
% hObject    handle to Open (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
[FileName,PathName] = uigetfile('*.m','Select the MATLAB code file');

% % --- Executes on button press in Instructions.
function InstrucAddCmpd_Callback(hObject, eventdata, handles)
% % hObject    handle to Instructions (see GCBO)
% % eventdata  reserved - to be defined in a future version of MATLAB
% % handles    structure with handles and user data (see GUIDATA)
Instruct_fig = figure;
set(Instruct_fig,'MenuBar','none','Name','Excel Worksheet Setup for Importing
Compounds & Properties Not Found in Preprogrammed List','NumberTitle','off');
imageArray =imread('InstrucAddCmpd.jpg');
imshow(imageArray);

% --- Executes on button press in ImportCmpdProp.
function ImportCmpdProp_Callback(hObject, eventdata, handles)
% hObject    handle to ImportCmpdProp (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: contents = cellstr(get(hObject,'String')) returns ImportCmpdProp contents as
cell array
%        contents{get(hObject,'Value')} returns selected item from
%        ImportCmpdProp


global CmpdProp
set(handles.Other,'Visible','on');
[filename, pathname]=uigetfile;
Path=strcat(pathname,filename);
[ndata, headertext] = xlsread(Path);
```

```
Col1 = headertext(:,1);
Col2 = Col1(2:length(Col1),1);
Col2 = cellstr(Col2);
ndata1 = (num2cell(ndata(:,1)));
ndata2 = (num2cell(ndata(:,2)));
CmpdProp = [Col2, ndata1, ndata2];
set(handles.CompoundProperties,'Data',CmpdProp);
set(handles.CmpdList,'String',Col2);

% --- Executes on selection change in CmpdList.
function CmpdList_Callback(hObject, eventdata, handles)
% hObject    handle to CmpdList (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: contents = cellstr(get(hObject,'String')) returns CmpdList contents as cell array
%        contents{get(hObject,'Value')} returns selected item from CmpdList


% --- Executes during object creation, after setting all properties.
function CmpdList_CreateFcn(hObject, eventdata, handles)
% hObject    handle to CmpdList (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: listbox controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
   set(hObject,'BackgroundColor','white');
end


% --- Executes on button press in PopulateTable.
function PopulateTable_Callback(hObject, eventdata, handles)
% hObject    handle to PopulateTable (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

SelectedPRCs = get(handles.CmpdList,{'string','value'});
SelectedPRCs = (SelectedPRCs{1}(SelectedPRCs{2}));

%Creation of table containing selected compounds, their ratios, and label
```

```
columnname = {'Compound','Ratio','Label?'};
columnformat = {'char','numeric',{'d8','d9','d10','d12','d13','d14','13C-3','13C-4','13C-
6','13C-8','13C-12','no label'}};
columneditable = [true true true];
z = zeros(length(SelectedPRCs),1);
j = num2str(z,1);
dat(:,1) = SelectedPRCs;
dat(:,2) = {j(1)};
dat(:,3) = {j(1)};

RatioTable2 = uitable;
set(RatioTable2,'Parent',handles.Input,'Units','normalized','Position',[0.375 0.662 0.569
0.303]);
set(RatioTable2,'Data',dat,'ColumnName',columnname,'ColumnFormat',columnformat,'C
olumnEditable',columneditable,'RowName',[]);
set(RatioTable2,'CellEditCallBack',@GetPRCRatios_EditCallback);

 function GetPRCRatios_EditCallback(o,e)
 global PRCRatios
 tabledata = get(o,'data');
 tabledata = tabledata(:,2);
 tabledata = str2double(tabledata);
 PRCRatios = tabledata;


% --- Executes on button press in Calculate.
function Calculate_Callback(hObject, eventdata, handles)

% hObject    handle to Calculate (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

global PRCRatios
%Calling L & t
L = str2num(get(handles.thick_PRC,'string'))*10^-6; %thickness of PDMS (m)
t = str2num(get(handles.time_PRC, 'string')); %time of exposure (d)


%Calling Kf
K1 = get(handles.CmpdList,{'string','value'});
K1 = (K1{1}(K1{2}));
K1 = cellstr(K1);
n = length(K1);
```

```
Kf_matrix = zeros(n,1);
P = get(handles.CompoundProperties,'data');
for i = 1:n
Kf(i) = vlookup2(P,K1(i,1),3,1);
Kow(i) = vlookup2(P,K1(i,1),2,1);
end
Kf_matrix = cell2mat((transpose(Kf)));

Kow_matrix = cell2mat((transpose(Kow)));

% Call Lookup table & use C/Co values to get x from lookup table
LUT = get(handles.XLookupTable,'data');


k = length(PRCRatios);
for j = 1:k
x(j) = fcm(LUT,PRCRatios(j));
end
x_matrix = transpose(x);
size(Kf_matrix)
size(x_matrix)
% Converting x into RD
RD_matrix = x_matrix.*L.^2.*(10.^Kf_matrix).^2./t;
%Plot
RD_Kow_Plot = axes;
set(RD_Kow_Plot,'Parent',handles.Results,'Units','normalized','Position',[0.179 0.54
0.735 0.389]);
hold on
loglog(Kow_matrix,log10(RD_matrix),'o'); %plot data points
%determine fit
Alpha1 = get(handles.forcealpha,'value');
if Alpha1 == 0
[p,S] = polyfit(Kow_matrix,log10(RD_matrix),1);
rsquared = corrcoef(Kow_matrix,log10(RD_matrix));
rsquared = rsquared(1,2);
xfit = (min(Kow_matrix)-.5):(max(Kow_matrix)+0.5);
yfit = polyval(p,xfit);
hfit = loglog(xfit,yfit);
xlabel('logK_o_w');
ylabel('logRD (m^2/d)');
hold off
eqn = ['logRD = ' sprintf('%2.2flogKow + %2f',[p(1),p(2)])];
eqn = eqn(1:end-3);
```

```
eqn2 = ['r^2 = ' sprintf('%2f',[rsquared])];
eqn2 = eqn2(1:end-3);
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.225 0.931 0.579
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn)
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.227 0.9 0.570
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn2)
end

if Alpha1 == 1
[p,S] = polyfitZero(10.^Kow_matrix,RD_matrix,1)
rsquared = corrcoef(10.^Kow_matrix,(RD_matrix));
rsquared = rsquared(1,2);
xmin = min(Kow_matrix-1);
xmax = max(Kow_matrix+1);
xfit = 10.^xmin:10.^(xmin-2):10.^xmax;
yfit = polyval(p,xfit);
hfit = plot(log10(xfit),log10(yfit));
xlabel('logK_o_w');
ylabel('logRD (m^2/d)');
hold off
eqn = ['logRD = ' sprintf('logKow + %2.4f',[log10(p(1))])];
eqn = eqn(1:end-3);
eqn2 = ['r^2 = ' sprintf('%2f',[rsquared])];
eqn2 = eqn2(1:end-3);
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.225 0.931 0.579
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn)
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.227 0.9 0.570
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn2)
end

% table with fss values
PAH_CB = get(handles.PAH,'value'); %callback from Compounds of Interest - (1)
interested in PAHs (0) not interested in PAHs
PCB_CB = get(handles.PCB,'value'); %callback from Compounds of Interest - (1)
interested in PCBs (0) not interested in PCBs
Other_CB = get(handles.Other,'value');

if PAH_CB == 0 && PCB_CB == 0 && Other_CB == 0
   msgbox('Must Select Compounds of Interest.','Error','error');
```

```
end
if Other_CB == 1
    P = get(handles.CompoundProperties,'data');
    s = num2cell(transpose(1:length(P)));
    CC = [s P];
    for i = 1:length(P)
    Kow2(i) = vlookup2(CC,i,3,1);
    CmpdPAH(i) = vlookup2(CC,i,2,1);
    Kpdms(i) = vlookup2(CC,i,4,1);
    end
    Kow2 = transpose(Kow2);
    Kow2 = cell2mat(Kow2);
    Kpdms = transpose(Kpdms);
    Kpdms = cell2mat(Kpdms);
    CmpdPAH = transpose(CmpdPAH);
    RD_PAH = 10.^(polyval(p,Kow2));
    fss_PAHs = 1-
exp(RD_PAH.*t./(10.^Kpdms).^2./L.^2).*erfc(sqrt(RD_PAH.*t./(10.^Kpdms).^2./L.^2))
;
    fss_PAHs = num2cell(fss_PAHs);
    fss_PAHs(cellfun(@isnan,fss_PAHs))= {[1]};
    fss_data = [CmpdPAH fss_PAHs];

    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.476
0.165]);

set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);

end
if PAH_CB == 1
    P = get(handles.CompoundProperties,'data');
    s = num2cell(transpose(1:length(P)));
    CC = [s P];
    for i = 1:16
    Kow2(i) = vlookup2(CC,i,3,1);
    CmpdPAH(i) = vlookup2(CC,i,2,1);
    Kpdms(i) = vlookup2(CC,i,4,1);
```

```
    end
    Kow2 = transpose(Kow2);
    Kow2 = cell2mat(Kow2);
    Kpdms = transpose(Kpdms);
    Kpdms = cell2mat(Kpdms);
    CmpdPAH = transpose(CmpdPAH);
    RD_PAH = 10.^(polyval(p,Kow2));
    fss_PAHs = 1-
exp(RD_PAH.*t./(10.^Kpdms).^2./L.^2).*erfc(sqrt(RD_PAH.*t./(10.^Kpdms).^2./L.^2))
;
    fss_PAHs = num2cell(fss_PAHs);
    fss_PAHs(cellfun(@isnan,fss_PAHs))= {[1]};
    fss_data = [CmpdPAH fss_PAHs];

    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.476
0.165]);

set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);

end
if PCB_CB == 1
    P = get(handles.CompoundProperties,'data');
    s = num2cell(transpose(1:length(P)));
    CC = [s P];
    for i = 1:209
    count(i) = i+16;
    Kow3(i) = vlookup2(CC,count(i),3,1);
    CmpdPCB(i) = vlookup(CC,count(i),2,1);
    Kpdms2(i) = vlookup(CC,count(i),4,1);
    end
    Kow3 = transpose(Kow3);
    Kow3 = cell2mat(Kow3) ;
    Kpdms2 = transpose(Kpdms2);
    Kpdms2 = cell2mat(Kpdms2);
    CmpdPCB = transpose(CmpdPCB);
    RD_PCB = 10.^(polyval(p,Kow3));
```

```
    fss_PCBs = 1-
exp(RD_PCB.*t./(10.^Kpdms2).^2./L.^2).*erfc(sqrt(RD_PCB.*t./(10.^Kpdms2).^2./L.^2
));
    fss_PCBs = num2cell(fss_PCBs);
    fss_PCBs(cellfun(@isnan,fss_PCBs))= {[1]};
    fss_data = [CmpdPCB fss_PCBs];
    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.476
0.165]);

set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);

end
if PAH_CB && PCB_CB == 1
    P = get(handles.CompoundProperties,'data');
    s = num2cell(transpose(1:length(P)));
    CC = [s P];
    for i = 1:225
    Kow4(i) = vlookup2(CC,i,3,1);
    CmpdALL(i) = vlookup(CC,i,2,1);
    end
    Kow4 = transpose(Kow4);
    Kow4 = cell2mat(Kow4) ;
    CmpdALL = transpose(CmpdALL);
    RD_ALL = 10.^(polyval(p,Kow4));
    fss_ALL = 1-
exp(RD_ALL.*t./(10.^Kow4).^2./L.^2).*erfc(sqrt(RD_ALL.*t./(10.^Kow4).^2./L.^2));
    fss_ALL = num2cell(fss_ALL);
    fss_ALL(cellfun(@isnan,fss_ALL))= {[1]};
    fss_data = [CmpdALL fss_ALL];
    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.476
0.165]);
```

```
set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);
end


% --- Executes on button press in Import.
function Import_Callback(hObject, eventdata, handles)
% hObject    handle to Import (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
global CL2
global PRCmultidata
[filename, pathname]=uigetfile;
Path=strcat(pathname,filename);
[ndata, headertext] = xlsread(Path);
CL1 = headertext(:,1);
CL2 = CL1(2:length(CL1),1);
PRCmultidata = ndata;

% --- Executes on button press in CalcMulti.
function CalcMulti_Callback(hObject, eventdata, handles)
% hObject    handle to CalcMulti (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
global CL2
global PRCmultidata
%Calling L & t
L = str2num(get(handles.thick_PRC,'string'))*10^-6; %thickness of PDMS (m)
t = str2num(get(handles.time_PRC, 'string')); %time of exposure (d)
%Calling Kf
CL2 = cellstr(CL2);
n = length(CL2);
Kf_matrix = zeros(n,1);
P = get(handles.CompoundProperties,'data');
for i = 1:n
Kf(i) = vlookup2(P,CL2(i),3,1);
Kow(i) = vlookup2(P,CL2(i),2,1);
end
Kf_matrix = cell2mat((transpose(Kf)));
Kow_matrix = cell2mat((transpose(Kow)));

% Call Lookup table & use C/Co values to get x from lookup table
```

```
LUT = get(handles.XLookupTable,'data');
[row, col] = size(PRCmultidata);
for rr = 1:row
   for cc = 1:col
      x(rr,cc) = fcm(LUT,PRCmultidata(rr,cc));
   end
end
x_matrix = x;
%Converting x into RD
for i = 1:n
Lmat(i) = L;
tmat(i) = t;
end
Lmat = ((transpose(Lmat)));
tmat = ((transpose(tmat)));
A = Lmat.^2.*(10.^Kf_matrix).^2./tmat;
for rr = 1:row
   for cc = 1:col
      A(rr,cc) = A(rr);
      Kow_matrix(rr,cc) = Kow_matrix(rr);
   end
end
RD_matrix = x_matrix.*A;
%Plot
RD_Kow_Plot = axes;
set(RD_Kow_Plot,'Parent',handles.Results,'Units','normalized','Position',[0.179 0.54
0.735 0.389]);
hold on
loglog(Kow_matrix,log10(RD_matrix),'o'); %plot data points
%determine fit
Alpha1 = get(handles.forcealpha,'value');
if Alpha1 == 0
[p,S] = polyfit(Kow_matrix,log10(RD_matrix),1);
MeanMat = mean(log10(RD_matrix),2);
loglog(Kow_matrix(:,1),MeanMat,'s')
for rr = 1:row
   RDmatrow(rr,:) = log10(RD_matrix(rr,:));
   STD(rr) = std(RDmatrow(rr,:));
end
STD = transpose(STD);
ploterr((Kow_matrix(:,1)),MeanMat,[],STD,'s','logxy','hhy',.3)
for rr = 1:row
   for cc = 1:col
```

```
      MeanMat(rr,cc) = MeanMat(rr);
   end
end
rsquared = corrcoef(Kow_matrix,log10(RD_matrix));
rsquared = rsquared(1,2);

xfit = (min(Kow_matrix)-.5):(max(Kow_matrix)+0.5);
yfit = polyval(p,xfit);
hfit = loglog(xfit,yfit);
xlabel('logK_o_w');
ylabel('logRD (m^2/d)');
%hold off
eqn = ['logRD = ' sprintf('%2.2flogKow + %2f',[p(1),p(2)])];
eqn = eqn(1:end-3);
eqn2 = ['r^2 = ' sprintf('%2f',[rsquared])];
eqn2 = eqn2(1:end-3);
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.225 0.931 0.579
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn)
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.227 0.9 0.570
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn2)
end
if Alpha1 == 1
   KowColumn = Kow_matrix(:);
   RDColumn = RD_matrix(:);
[p,S] = polyfitZero(10.^KowColumn,RDColumn,1);
MeanMat = mean((RD_matrix),2);
plot(Kow_matrix(:,1),log10(MeanMat),'s')
for rr = 1:row
   RDmatrow(rr,:) = log10(RD_matrix(rr,:));
   STD(rr) = std(RDmatrow(rr,:));
end
STD = transpose(STD);
ploterr(((Kow_matrix(:,1))),log10(MeanMat),[],STD,'s','hhy',.3)

for rr = 1:row
   for cc = 1:col
      MeanMat(rr,cc) = MeanMat(rr);
   end
end
rsquared = corrcoef(10.^Kow_matrix,(RD_matrix));
rsquared = rsquared(1,2);
```

```
xmin = min(Kow_matrix-1);
xmax = max(Kow_matrix+1);
xfit = 10.^xmin:10.^(xmin-2):10.^xmax;
yfit = polyval(p,xfit);
hfit = plot(log10(xfit),log10(yfit));
xlabel('logK_o_w');
ylabel('logRD (m^2/d)');
%hold off
eqn = ['logRD = ' sprintf('logKow + %.2g',[log10(p(1))])];
eqn2 = ['r^2 = ' sprintf('%2f',[rsquared])];
eqn2 = eqn2(1:end-3);
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.225 0.931 0.579
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn)
uicontrol('Parent',handles.Results,'Style','text','Units','normalized','Visible','on','Position',[
0.227 0.9 0.570
0.07],'BackgroundColor','White','FontSize',10,'FontWeight','bold','String',eqn2)
end

% table with fss values
PAH_CB = get(handles.PAH,'value'); %callback from Compounds of Interest - (1)
interested in PAHs (0) not interested in PAHs
PCB_CB = get(handles.PCB,'value'); %callback from Compounds of Interest - (1)
interested in PCBs (0) not interested in PCBs
Other_CB = get(handles.Other,'value');
if PAH_CB == 0 && PCB_CB == 0 && Other_CB == 0
    msgbox('Must Select Compounds of Interest.','Error','error');
end
if Other_CB == 1
   P = get(handles.CompoundProperties,'data');
   s = num2cell(transpose(1:length(P)));
   CC = [s P];
   for i = 1:length(P)
   Kow2(i) = vlookup2(CC,i,3,1);
   CmpdPAH(i) = vlookup2(CC,i,2,1);
   Kpdms(i) = vlookup2(CC,i,4,1);
   end
   Kow2 = transpose(Kow2);
   Kow2 = cell2mat(Kow2);
   Kpdms = transpose(Kpdms);
   Kpdms = cell2mat(Kpdms);
   CmpdPAH = transpose(CmpdPAH);
   RD_PAH = 10.^(polyval(p,Kow2));
```

```
    fss_PAHs = 1-
exp(RD_PAH.*t./(10.^Kpdms).^2./L.^2).*erfc(sqrt(RD_PAH.*t./(10.^Kpdms).^2./L.^2))
;
    fss_PAHs = num2cell(fss_PAHs);
    fss_PAHs(cellfun(@isnan,fss_PAHs))= {[1]};
    fss_data = [CmpdPAH fss_PAHs];

    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.476
0.165]);

set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);
end
if PAH_CB == 1
    P = get(handles.CompoundProperties,'data');
    s = num2cell(transpose(1:length(P)));
    CC = [s P];
    for i = 1:16
    Kow2(i) = vlookup2(CC,i,3,1);
    CmpdPAH(i) = vlookup2(CC,i,2,1);
    Kpdms(i) = vlookup2(CC,i,4,1);
    end
    Kow2 = transpose(Kow2);
    Kow2 = cell2mat(Kow2);
    Kpdms = transpose(Kpdms);
    Kpdms = cell2mat(Kpdms);
    CmpdPAH = transpose(CmpdPAH);
    RD_PAH = 10.^(polyval(p,Kow2));
    fss_PAHs = 1-
exp(RD_PAH.*t./(10.^Kpdms).^2./L.^2).*erfc(sqrt(RD_PAH.*t./(10.^Kpdms).^2./L.^2))
;
    fss_PAHs = num2cell(fss_PAHs);
    fss_PAHs(cellfun(@isnan,fss_PAHs))= {[1]};
    fss_data = [CmpdPAH fss_PAHs];
    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
```

```
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.576
0.165]);

set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);

end
if PCB_CB == 1
    P = get(handles.CompoundProperties,'data');
    s = num2cell(transpose(1:length(P)));
    CC = [s P];
    for i = 17:225
    Kow3(i) = vlookup2(CC,i,3,1);
    CmpdPCB(i) = vlookup(CC,i,2,1);
    Kpdms2(i) = vlookup(CC,i,4,1);
    end
    Kow3 = transpose(Kow3);
    Kow3 = cell2mat(Kow3) ;
    Kpdms2 = transpose(Kpdms2);
    Kpdms2 = cell2mat(Kpdms2);
    CmpdPCB = transpose(CmpdPCB);
    RD_PCB = 10.^(polyval(p,Kow3));
    fss_PCBs = 1-
exp(RD_PCB.*t./(10.^Kpdms2).^2./L.^2).*erfc(sqrt(RD_PCB.*t./(10.^Kpdms2).^2./L.^2
));
    fss_PCBs = num2cell(fss_PCBs);
    fss_PCBs(cellfun(@isnan,fss_PCBs))= {[1]};
    fss_data = [CmpdPCB fss_PCBs];
    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.576
0.165]);

set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);

end
if PAH_CB && PCB_CB == 1
    P = get(handles.CompoundProperties,'data');
```

```
    s = num2cell(transpose(1:length(P)));
    CC = [s P];
    for i = 1:225
    Kow4(i) = vlookup2(CC,i,3,1);
    CmpdALL(i) = vlookup(CC,i,2,1);
    end
    Kow4 = transpose(Kow4);
    Kow4 = cell2mat(Kow4) ;
    CmpdALL = transpose(CmpdALL);
    RD_ALL = 10.^(polyval(p,Kow4));
    fss_ALL = 1-
exp(RD_ALL.*t./(10.^Kow4).^2./L.^2).*erfc(sqrt(RD_ALL.*t./(10.^Kow4).^2./L.^2));
    fss_ALL = num2cell(fss_ALL);
    fss_ALL(cellfun(@isnan,fss_ALL))= {[1]};
    fss_data = [CmpdALL fss_ALL];
    %create table containing fss values for Compounds of Interest
    fss_table = uitable;
    colname = {'Compound','fss'};
    colform = {'char','numeric'};
    coledit = [false false];
    set(fss_table,'Parent',handles.Results,'Units','normalized','Position',[0.231 0.239 0.576
0.165]);

set(fss_table,'Data',fss_data,'ColumnName',colname,'ColumnFormat',colform,'ColumnEd
itable',coledit,'RowName',[]);
end

% % --- Executes on button press in Instructions.
function Instructions_Callback(hObject, eventdata, handles)
% % hObject    handle to Instructions (see GCBO)
% % eventdata  reserved - to be defined in a future version of MATLAB
% % handles    structure with handles and user data (see GUIDATA)
Instruct_fig = figure;
set(Instruct_fig,'MenuBar','none','Name','Excel Worksheet Setup for Muliple PRC Ratio
Entries','NumberTitle','off');
imageArray =imread('ImportExcelDatatoGUI.jpg');
imshow(imageArray);

function References_Callback(hObject, eventdata, handles)
% hObject    handle to References (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)
```

```
% Hints: get(hObject,'String') returns contents of References as text
%        str2double(get(hObject,'String')) returns contents of References as a double

% --- Executes during object creation, after setting all properties.
function References_CreateFcn(hObject, eventdata, handles)
% hObject    handle to References (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end

function CmpdProp_Callback(hObject, eventdata, handles)
% hObject    handle to CmpdProp (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    structure with handles and user data (see GUIDATA)

% Hints: get(hObject,'String') returns contents of CmpdProp as text
%        str2double(get(hObject,'String')) returns contents of CmpdProp as a double

% --- Executes during object creation, after setting all properties.
function CmpdProp_CreateFcn(hObject, eventdata, handles)
% hObject    handle to CmpdProp (see GCBO)
% eventdata  reserved - to be defined in a future version of MATLAB
% handles    empty - handles not created until after all CreateFcns called

% Hint: edit controls usually have a white background on Windows.
%       See ISPC and COMPUTER.
if ispc && isequal(get(hObject,'BackgroundColor'),
get(0,'defaultUicontrolBackgroundColor'))
    set(hObject,'BackgroundColor','white');
end
```

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Vita

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