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Table of Contents Entry

Colour graphic:

Text: A demonstration of solid phase microextraction techniques using polydimethylsiloxane fibers to assess in-situ contaminated sediment remedy performance at three sites.

Environmental Impact Statement

The manuscript contains new information about the practical application of passive sampling for remedy evaluation and includes analyses related to a variety of journal subject areas including: transport and fate of sediment contaminants, exposure and impacts to benthic organisms and novel analytical tools and measurement technologies. Specifically, the manuscript demonstrates that PDMS can be used to identify transport mechanisms and rates through the use of performance reference compounds for remedy performance assessment. Additionally, PDMS was shown to be applicable as a surrogate for direct biological assessment of reduction in bioavailability.

Remedy Performance Monitoring at Contaminated Sediment Sites Using Profiling Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Fibers

Courtney Thomas[1], David Lampert[1], and Danny Reible[2*]

[1]Department of Civil, Architectural and Environmental Engineering, University of Texas, Austin 78712

[2]Department of Civil and Environmental Engineering, Texas Tech University, Lubbock, TX 79409

*Corresponding Author

Abstract

Passive sampling using polydimethylsiloxane (PDMS) profilers were evaluated as a tool to assess the performance of in-situ sediment remedies at three locations, Chattanooga Creek (Chattanooga, TN), Eagle Harbor (Bainbridge Island, WA) and Hunter's Point (San Francisco, CA). The remedy at the first two locations was capping over PAH contaminated sediments while at Hunter's Point, the assessment was part of an in-situ treatment demonstration led by RG Luthy (Stanford University) using activated carbon mixed into PCB 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 the capping sites, the passive sampling approach was employed to measure intermixing during cap placement, contamination migration into the cap post-placement and recontamination over time. At the in-situ treatment demonstration site, reduction in porewater concentrations in treated versus untreated sediments were compared to measurements of bioaccumulation of PCBs in *Neanthes arenaceodentata.*

1. 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[1]. Often, in-situ sediment remedies of capping contaminated sediments with clean substrate with or without sorbing amendments[2-5] or in-situ treatment with sorbing amendments[6] 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[7]. 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[4]. In-situ treatment to reduce contaminant bioavailability is generally achieved by mixing activated carbon into the surficial sediments[6] due to its high sorbing capacity.

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[8-11]. 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[12]. 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.[13] 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.)[14]. 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[15-17]. They have been used less commonly for measurement of porewater concentration profiles in sediment[18].

This work seeks to explore the use of SPME PDMS fibers for determining the effectiveness of in-situ contaminated sediment remedies by application to both in-situ treatment and 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[19]. 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, and

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

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, and one in-situ treatment field site (Hunter's Point, San

Francisco, CA) contaminated with PCBs 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. Changes in porewater concentrations associated with activated carbon treatment were compared to changes in bioaccumulation in a marine polychaete deposit feeder, *Neanthes arenaceodentata*, at the in-situ treatment site and non-equilibrium corrections were estimated via measurements at two different fiber sizes with different intrinsic kinetics. The in-situ treatment demonstration was conducted by E. Janssen under the leadership of RG Luthy and methods and bioaccumulation measurements have been previously reported[15].

2. Materials and Methods

2.1 Chemicals, fibers, and samplers

For studies employing PRCs to evaluate fiber uptake kinetics (the two PAH contaminated capping sites), 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.[14] 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.

2.2 Sediment sampling sites

2.2.1 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[20], therefore the uptake kinetics were expected to be slow. Deployments were for a period of 14-16 days. For the second sampling event, uptake kinetics were determined using fibers with different 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.

2.2.2 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[21]. 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[21]. 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.

2.2.3 Hunter's Point, San Francisco, CA

Hunter's Point in San Francisco CA is a former US Navy shipyard and industrial facility. Sediments on and surrounding the site were contaminated by PCBs as a result of activities at the site. The studies here were porewater monitoring associated with a demonstration of activated carbon for bioavailability control at the site led by RG Luthy of Stanford University. Details of the demonstration procedures of which this work was a part have been reported elsewhere[15]. Information about the site has been documented by the USEPA[22] . SPME PDMS deployments were conducted in July 2009 using both the 230/210 μm and 1060/1000 μm fibers at 14 and 42 days in both treated and untreated sediment. The two deployment times and two fiber sizes were used in an attempt to determine the effects of kinetics on fiber uptake. The absorption of interfering compounds in the 42 day samples, however, led to a large variability among the triplicate samples and these were not usable in the analysis.

Sediment preparation and bioaccumulation studies using *Neanthes arenaceodentata* were conducted by E. Janssen of Stanford University and are described elsewhere[15].

2.3 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.

Congener specific PCB analysis was conducted on an Agilent 6890 GC with a micro-ECD detector using the method described by Ghosh et al.[23] except no sample cleanup was performed for the PDMS extracts. This led to the accumulation of interfering compounds over time that led to a large variability among the triplicate 42 day samples and these were not employed in the analysis. Separation was achieved using a 60 m long, 250 μm diameter fused-silica model HP-5 capillary column from Agilent Technologies (Santa Clara, CA).

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. PCB standards were developed using a known PCB mixture from the EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, MI. The method simulates Aroclor 1242 using a 75:54:54 mixture of Aroclors 1232, 1248, and 1262, respectively. Standards ranging in

200 concentrations from 0.05 μg/L to 100 μg/L were used to determine each compound's response
201 factor. PCB 209 (decachlorobiphenyl) was used as an internal standard.

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

204 $$C_{PDMS} = \frac{A*RSF_{PAH}*V_{solvent}}{L_{fiber}*v_{fiber}*K_{pw}} \quad \text{Eq. 1}$$

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

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

211 $$C_{pw} = \frac{C_{PDMS}}{K_{pw} f_{ss}} \quad \text{Eq. 2}$$

212 K_{pw} is given by the correlations with octanol-water partition coefficient given by [19]

213 $$PAH: logK_{PDMS-W} = 0.725 logK_{ow} + 0.479 \quad (R^2 = 0.99) \quad \text{Eq. 3}$$

214 $$PCB: logK_{PDMS-W} = 0.947 logK_{ow} - 0.017 \quad (R^2 = 0.89) \quad \text{Eq. 4}$$

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

216 ### *2.4 Determination of Non-equilibrium*

217 Non-equilibrium corrections had to be made as the deployment time was not sufficient to
218 achieve equilibrium as indicated by measurable differences between the 230/210 μm and
219 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[24] 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[24, 25]:

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

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

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

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}[26]), 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/sec) and τ is a tortuosity factor which for a sediment with porosity 0.5 would be approximately 2.5[27].

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.

One could also employ a time series of measurements or even co-located samples at two different times on the same size fiber to estimate RD in a manner similar to that above. As indicated above, this was attempted only at Hunter's Point and the absorption of interfering compounds over time introduced significant uncertainty in the results.

3. Results & Discussion

3.1 Contaminant uptake kinetics

At the Chattanooga Creek site, two methods for determining the steady-state concentrations were employed. Figure 1 compares the RD estimated by using two fibers with different characteristic lengths and the RD estimated from PRCs. For the two-fiber 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 PRC. In addition, only compounds with concentrations exceeding the detection limits were included in this analysis. For the third monitoring event at the Chattanooga Creek site, seven mid-to-high range PAH compounds were compared between fibers to estimate RDs using the two-fiber 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, α = 0.05). The RD (m^2/d) values, calculated using both methods, for Chattanooga Creek were related by a linear relationship (r^2 = 0.95) to $logK_{ow}$:

$$RD = 4.6x10^{-7} * K_{ow} \quad \text{Eq. 7}$$

Only the PRC method was used at the Eagle Harbor site in November 2011. The observed RD values for the Eagle Harbor site were fit to a linear relationship with K_{ow} (slope = $1.6x10^{-6}$, r^2 = 0.99). At Hunter's Point, a similar approach yielded a slope of approximately $3x10^{-6}$ m^2/day and r^2=0.97. Note that all of these values are within approximately an order of magnitude of the diffusion only result. Also note that both Eagle Harbor and Hunter's Point are tidal systems and tidal flushing may account for the apparently higher transport rates.

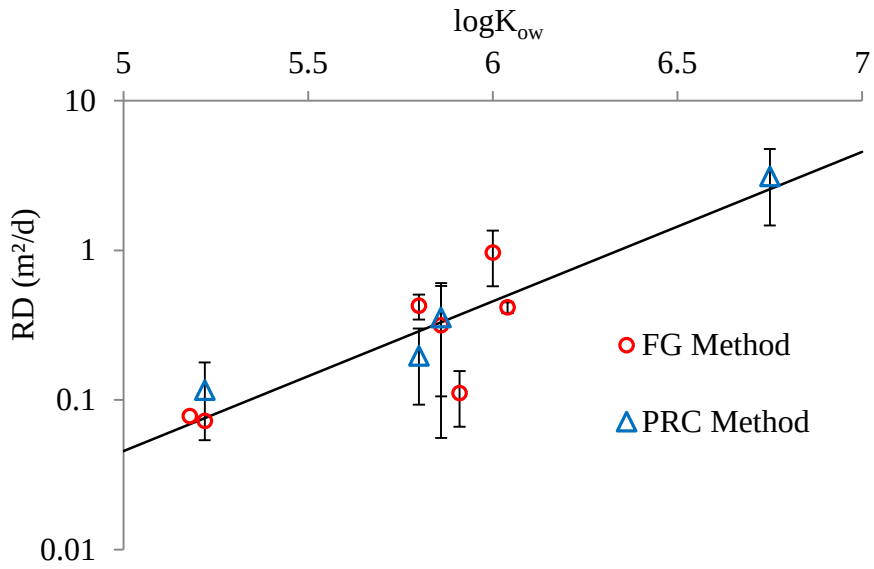


Figure 1. RD values found for PAHs based on the dissipation of PRCs (△) and comparison of PAH mass at time equal to 14 days of the 1060/1000 µm to the 230/210 µm fiber (○). Solid black line represents the line of best fit (RD = $4.6x10^{-7}$ *K_{ow}, r^2 = 0.95). All other compound RDs found using the comparison of PDMS thickness are based on two measurements. RD values found using the dissipation of PRCs are based on five measurements.

3.2 Assessment of remedy performance

3.2.1 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, and 3) low concentrations within the cap with high concentrations in the near surface due to recontamination from above.

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 2 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, the sampler was too short to complete penetrate through the cap. The caps at both the Eagle Harbor and Chattanooga Creeks sites were nominally 3-5 ft in thickness whereas only a 3 ft (~90 cm) long sampler was the maximum length used.

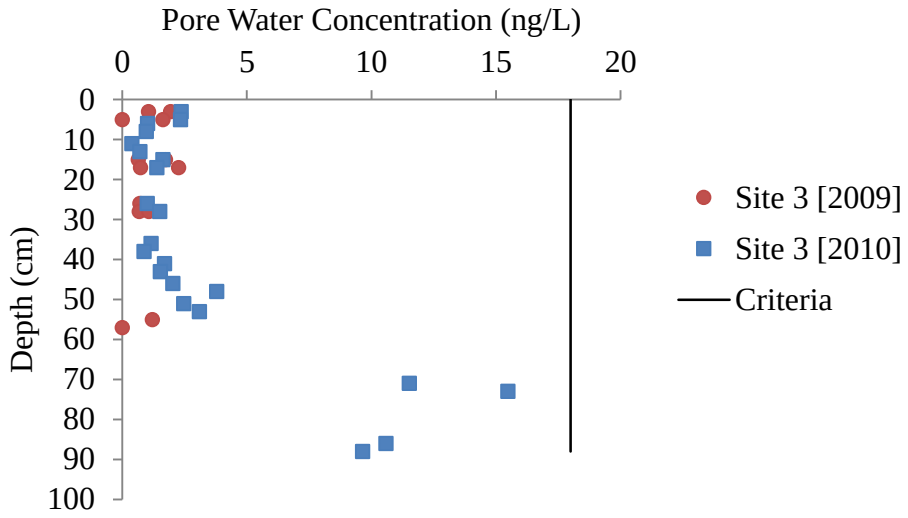
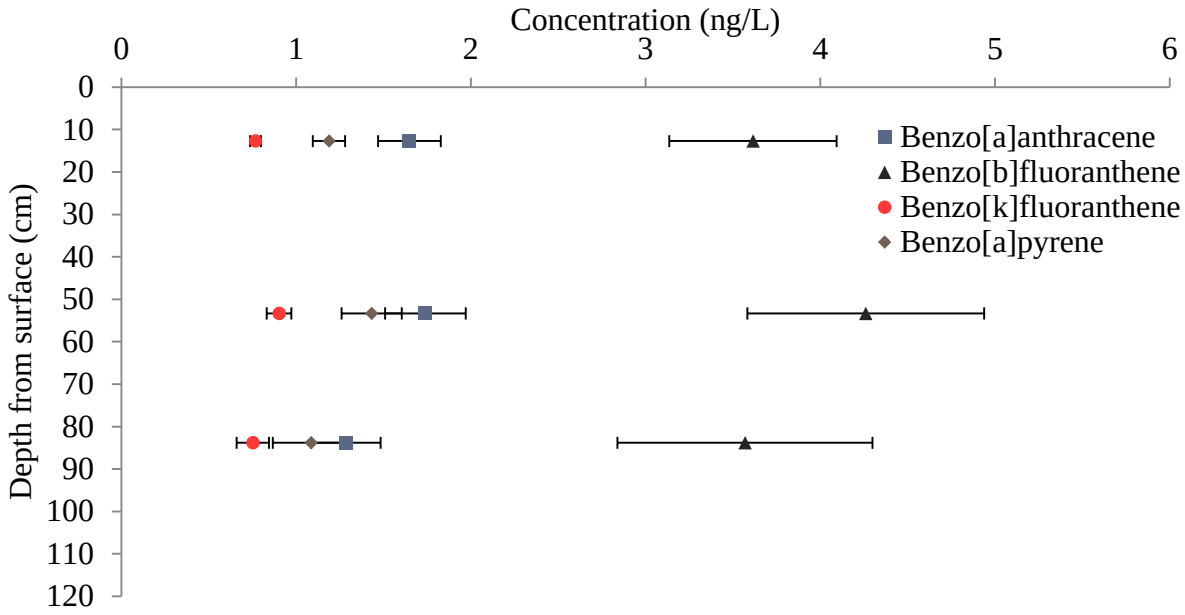


Figure 2. Depiction of benzo[a]pyrene profiles in cap material (Site 3) at Chattanooga Creek, TN in 2009 (●) and 2010 (■). Also shown is a comparative criteria, the EPA surface water quality standard of 18 ng/L

A second scenario 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 3 from a location in Eagle Harbor. Due to the strongly sorbing nature of high molecular weight PAHs, 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[21]. Note that the concentrations are quite low, well below EPA surface water quality standards indicating that this degree of intermixing may have minimal consequences.



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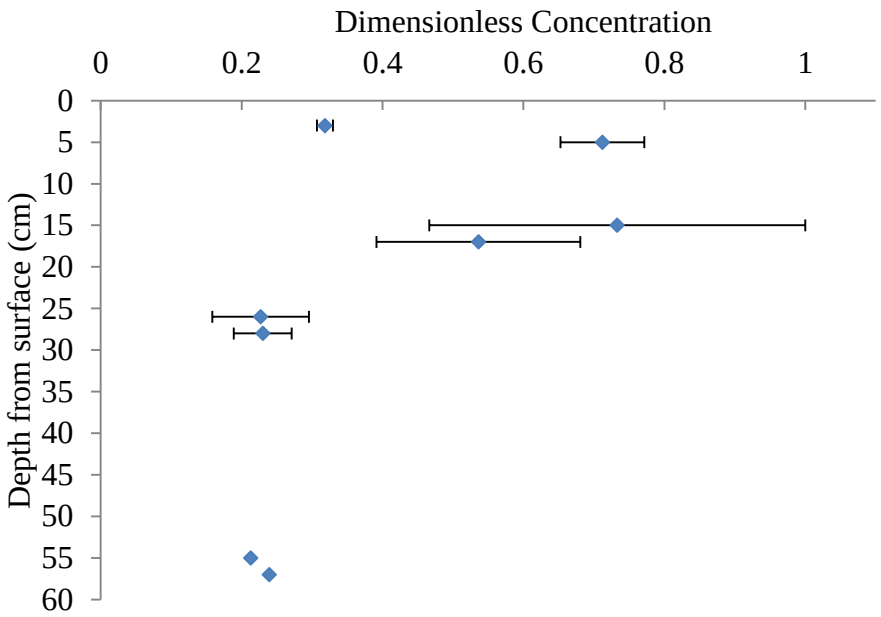
335 Figure 3. Concentration profiles of four HPAHs at the Wyckoff/Eagle Harbor Site in the 120 cm
336 thick capping layer. Error bars represent the range of the mean porewater concentration (n=2). The
337 EPA surface water quality criteria (not shown) for all compounds depicted is 18 ng/L.

338 A final scenario encountered is where ongoing contaminant sources re-contaminated the
339 surficial sediments. Such a profile is depicted in Figure 4, where low concentrations are measured
340 within and below the cap and high concentrations are measured in the near surface region.
341 Concentrations were normalized to the highest observed concentration in the cap simply to
342 emphasize that the highest concentrations are now near the surface and not associated with
343 migration from below. Profiling porewater concentrations are one of the clearest ways to show
344 that the near surface concentration is not connected to migration from the capping layer below.

345



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347 Figure 4. Dimensionless concentration (C/C_{max}) of pyrene during the November 2009 sampling
348 event at the downstream edge of the capped region of the Chattanooga Creek site. Error bars
349 represent the range of the dimensionless porewater concentration (n = 2). The range is not shown
350 for depths greater than 30 cm as only one measurement was made during the first sampling event.

351 A comparison of PDMS porewater concentrations to grab samples at Eagle Harbor was
352 completed to determine if regulatory decisions would have been different if SPME results had
353 been available at the time. The grab samples were collected by United States Army Corps of
354 Engineers- Seattle District. Ten of the sediment grab locations overlapped with SPME deployment
355 locations. PDMS samplers measure the bioavailable fraction of the contaminant, while grab
356 samples provide a bulk solid concentration. An effective organic carbon partition coefficient was
357 calculated using the following relationship between the porewater and bulk solids concentrations:

358 $$K_{oc} = \frac{W_s}{C_{pw}^{SPME} f_{oc}}$$ Eq. 8

359

This comparison assumes equilibrium partitioning between the solids and adjacent porewaters. W_s is the concentration measured from the grab samples (ug/kg), C_{pw}^{SPME} is the porewater concentration measured via PDMS SPME fibers (ug/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 $logK_{oc}$-$logK_{ow}$ relationship is approximately 0.25 log units or 1.8 times higher than the $logK_{oc}$ values reported by Baker et al.[28] using the relationship: $LogK_{oc} = 0.903LogK_{ow} + 0.094$ indicating that solid phase concentrations over predicted porewater concentration compared to measured SPME values. This is normally the result of sorption onto strongly sorbing phases such as "black" carbon[29]. 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.

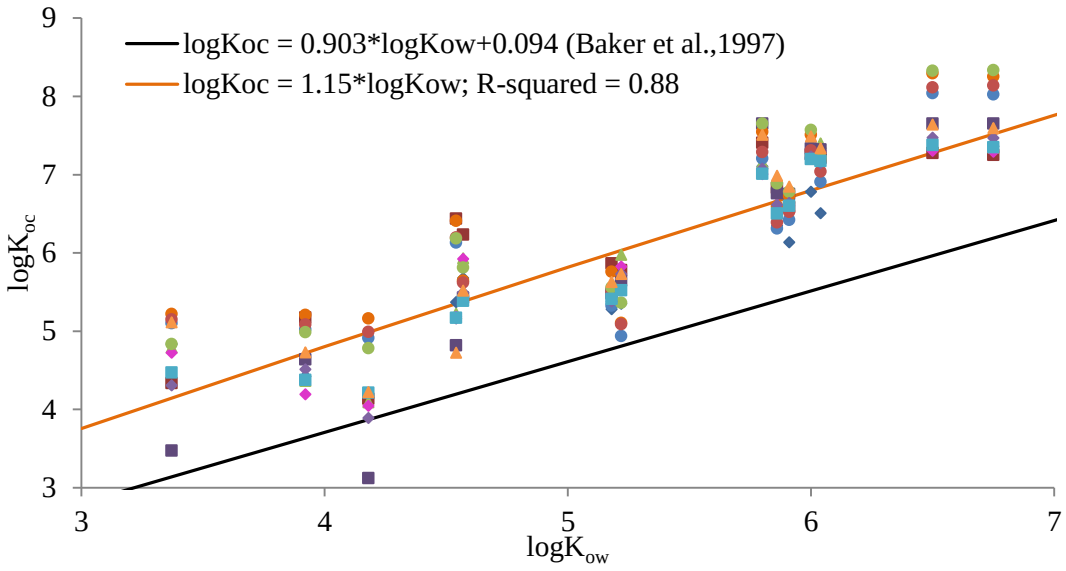


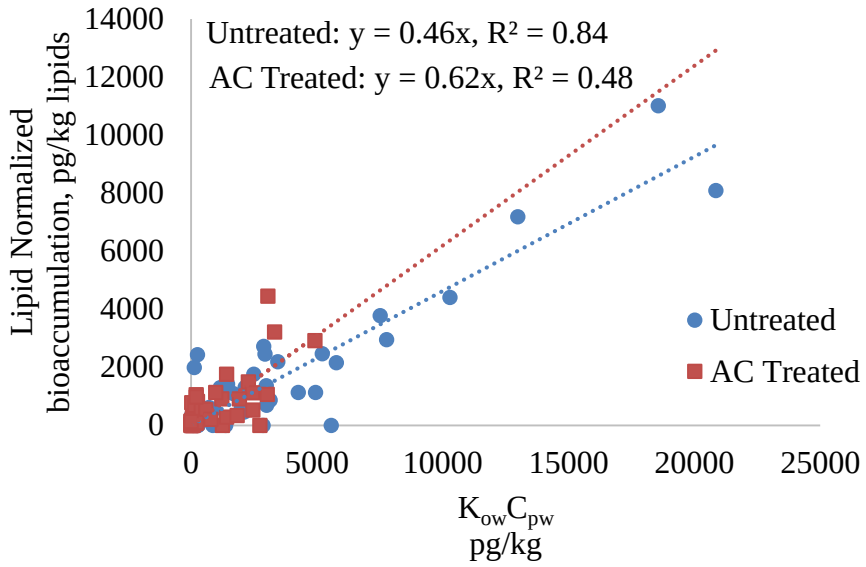
Figure 5. $LogK_{oc}$-$LogK_{ow}$ relationship determined from the upper 10 cm of twelve sampling locations at Eagle Harbor where grab samples and SPME samples overlapped. The orange solid line represents the best fit relationship of the field data (slope = 1.15, r^2 = 0.88). The black solid line represents the relationship determined by Baker et al.[28] between $logK_{oc}$ and $logK_{ow}$.

3.2.2 Assessment of Bioavailability Reduction with AC Treatment

The primary goal of the PDMS monitoring in support of the activated carbon treatment demonstration at Hunter's Point was to evaluate the ability of PDMS to predict the reduction in bioavailability due to the sequestration of PCBs by the activated carbon. The effort also employed POM[15] although the slow equilibration of the POM made its in-situ use problematic. The relatively fast uptake kinetics of the PDMS made it possible to predict porewater concentrations from short-time exposures with less substantial, and presumably less uncertain, corrections for non-equilibrium. The total porewater PCBs, as measured by the sum of the 47 individual congeners that were quantified was 23.4 ng/L in the untreated sediment and 3.7 ng/L in the AC treated, for an overall reduction of 84%. The total PCBs in the *Neanthes arenaceodentata* was 71.9 ng/kg lipid in the untreated sediments and 29.7 ng/kg in the treated, for a 59% reduction.

Although both the porewater concentration and the bioaccumulation of PCBs in the test organism were reduced, the reductions in the *Neanthes arenaceodentata* were not as great as the porewater changes. This might be explained by the efficiency of bioaccumulation in the organisms. Figure 6 shows the bioaccumulation by individual congener compared to the product of porewater concentration and octanol-water partition coefficient for untreated and treated sediments. We have previously shown that this product is a good indicator of potential bioaccumulation of PAHs and PCBs in a deposit feeding organism[10]. Note, however, in Figure 6 that the actual bioaccumulation for both the untreated and treated sediments is only about half that suggested by the $K_{ow}C_{pw}$ product. The lower bioaccumulation may be the result of other stressors in the field environment. There was also a slightly lower lipid content in the untreated sediments (2.4 vs 3.2%) perhaps due directly to stress associated with the higher contaminant load. There is more scatter in the treated case, possibly as a result of the relatively low, near detection limit, concentrations of individual congeners in the treated sediments.

In conclusion, the passive samplers were able to show dramatic reductions in bioavailability as reflected by reductions in interstitial water concentration and this reduction was approximately consistent with the reduced bioaccumulation in bioassays.



410

411 Figure 6. Lipid normalized bioaccumulation vs $K_{ow}C_{pw}$ in untreated and AC treated sediments at

412 Hunter's Point (San Francisco, CA).

413 ## 4. Summary and Conclusions

414 The results from the field deployments demonstrated that PRCs are a viable option to

415 measure the state of non-equilibrium between a passive sampling material and the surrounding

416 environment but that other options can also be used although with generally greater uncertainty.

417 The sampling in sediment caps showed that PDMS can be quite helpful in identifying transport

418 mechanisms and rates and separating placement intermixing and recontamination from

419 contaminant migration through a cap. The sampling in an in-situ treatment plot showed that

420 porewater concentrations can be a useful surrogate for direct biological assessment of

421 bioavailability reduction. The conclusions drawn from the porewater sampling, however, may

422 differ quantitatively from the conclusions that would be found in a bioassay. All three examples

423 show that passive sampling can provide useful tools for remedy assessment.

424

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