LABORATORY STUDY REPORT

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

ESTCP Project ER-0624

June 2008

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Environmental Security Technology Certification Program

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ACRONYM LIST

APW	Artificial pond water
BCF	Bioconcentration factors
BSAF	Biota-sediment accumulation
EPA	Environmental Protection Agency
GC	gas chromatography
HPLC	High performance liquid chromatography
PAH	poly cyclic aromatic hydrocarbon
PCB	poly chlorinated biphenyl
PDMS	poly dimethylsiloxane
SPME	Solid phase microextraction
TOC	Total organic carbon

1. LABORATORY DEMONSTRATION GOALS

The goal of the laboratory demonstration effort is to develop and standardize a procedure using field deployable solid phase micro extraction (SPME) for the measurement of freely-dissolved pore water concentrations and demonstrate the relationship of these measurements to contaminant flux, bioavailability and bioaccumulation. Pore water concentrations drive contaminant fluxes below the biologically active layer and in contaminated sediment caps a method for easily determining these levels provides a better means of evaluating contaminant migration and release. More importantly, direct measurement of that portion of the contaminant that is freely dissolved has been shown to be an effective tool for determining the bioavailable fraction and predicting bioaccumulation of simple partitioning contaminants. Even tissue concentrations of bioaccumulative contaminants can often be related to pore water concentrations. SPME has traditionally been used for the determination of aqueous phase concentrations but work in the laboratory has shown that it can be used for in situ determination of pore water concentrations if appropriately armored and strengthened and if sufficient time is provided for equilibration. The project is designed to determine and demonstrate the optimum approach to implementation of SPME for in situ determination of pore water concentrations and bioavailability of PAH and PCB in sediments. The goal is to move SPME from a laboratory approach to a routine field characterization tool.

The goals of the laboratory demonstration efforts are threefold:

1. Determine the limits of applicability of SPME by determination of method detection limits, reproducibility and accuracy for the measurement of pore water concentrations
2. Optimization of the field implementation approach for SPME including development of deployment approaches that maintain SPME integrity and maximize resolution in space and time of pore water concentrations
3. Demonstrate, under field-simulated conditions, the ability of SPME to predict accumulation in benthic organisms

The results of the laboratory efforts in each of these areas are presented in this report. Key results are identified and, where necessary, the need for follow up studies.

2. SUMMARY OF RESULTS

Laboratory studies have achieved their desired goal of defining the basic parameters of routine field deployment of SPME as a tool for the assessment of in-situ contaminant migration processes and bioavailability of PAH and PCB contaminants. This report summarizes the results of the laboratory studies. Field demonstrations are currently being planned based upon the results of these studies.

Studies of various extraction methods have demonstrated that desorption into solvents suitable for subsequent chemical analysis (into acetonitrile for HPLC analysis or hexane for GC analysis) is rapid and complete. Various sources of SPME fibers have been shown to be essentially equivalent with fiber water partition coefficients that are within approximately 0.16 log units (± 45%) for PAH and approximately 0.31 log units (±a factor of two) for PCB. It is unclear at this time whether this variability represents variations in fibers, or is simply due to the variability or uncertainty in estimated fiber-water partition coefficients available in the literature. This uncertainty defines the accuracy of quantitative concentration measurements with SPME fibers without conducting specific calibration. Greater accuracy could certainly be obtained by calibration of fiber-water partition coefficients for a given fiber.

The detection limit of the SPME fibers used in these studies was in the low ng/L level or less for the contaminants of concern using 1 cm of fiber. Detection limits were approximately inversely proportional to hydrophobicity (i.e. lower detection limits were observed for more hydrophobic compounds) since the sorption onto the fiber was approximately proportional to hydrophobicity.

Reproducibility of the SPME measurement was tested by comparison of independent replicates. Reproducibility was typically above 90% although occasional reproducibility were as low as 75%, typically associated with failure to achieve equilibrium. The characteristic time for achievement of steady state was less than a day for PAH in water, approximately a week for PAH with bare fiber in sediments but as long as a month for more hydrophobic PCB in sediments. The slow achievement of equilibrium for PCB may be the cause of the increased variability in reported fiber-water partition coefficients for PCB. Experimental results show that uptake kinetics are relatively insensitive to temperature. A model has been developed that will allow determination of equilibrium for any fiber geometry. The model parameters are currently being fit to the existing data and confirmation datasets will be collected with different fiber geometries.

A field deployable SPME system was developed with a protective sheath over a slotted rod containing the fiber. The dynamics of uptake on fiber within the field deployable system was essentially identical to that for the bare fiber. The model of chemical uptake will also be applied to define equilibrium times in the field deployable system. The existing data will be used to define the mass transfer resistance associated with the sheath layer. The vertical resolution of the field deployable system was assessed by evaluation of pore water concentration gradients in a layered system (sand over contaminated sediment). Sharp concentration gradients (approximately 1 cm resolution or better) were observed for all contaminants evaluated except

for the least hydrophobic, phenanthrene, presumably due to greater vertical spreading of this compound.

Retrieval of the field deployable SPME system may be subject to holding time limitations upon return to the laboratory. As a worse case analysis, SPME fibers were exposed to room temperature air and allowed to dry with monitoring of fiber concentration as a function of time. Volatile compounds such as phenanthrene showed almost complete loss within 24 hours while significant but more manageable losses were observed with less volatile species. This suggests that sample handling for SPME fibers should include many of the same precautions currently applied to liquid samples, i.e. tight seals and shipment on ice and storage at 4°C. Preliminary field experimentation has shown that these precautions can ensure that lab-processed fibers yield concentration measurements essentially identical to field measurements.

The final series of laboratory experiments were focused on comparison of fiber concentrations to measured bioaccumulation in freshwater and marine deposit feeding organisms. Bare fibers were exposed to the sediment during a 28 or 30-day bioaccumulation test using the selected organisms. The common deposit feeding oligochaetes and polychaetes used in these studies are ideal indicators of bioaccumulation due to the intensity of their interactions with sediment.

- In freshwater Anacostia River sediment populated with *Ilyodrilus templetoni,* lipid normalized accumulation was shown to correlate with absorbed fiber concentration (r^2>0.75), while organic carbon normalized bulk sediment concentration did not describe accumulation. The average lipid normalized PAH concentration in organism tissue was 1.6 times the measured fiber concentration while the lipid normalized PCB tissue concentration was approximately 5 times the measured fiber concentration. A model of biota-sediment accumulation factor (BSAF) based upon measured pore water concentration gave quantitative estimates of measured BSAF with a lipid/sediment organic carbon partition coefficient ratio of approximately 1.8.
- In marine New Bedford Harbor sediment sequentially diluted with freshwater sediment from Brown Lake, Mississippi, *Ilyodrilus templetoni* also accumulated PAH and PCB contaminants in amounts proportional to the fiber concentration. Both PAH and PCB concentrations in the organisms were significantly greater than expected from the experiments with Anacostia River sediments, however, with PCB accumulating to lipid normalized concentrations in the organism about 22 times that of the fiber. Correlation with biota-sediment accumulation factor was not attempted although an alternative model of accumulation using literature bioconcentration factors to estimate bioaccumulation was tested. Bioconcentration factors times measured pore water concentrations correlated well with lipid normalized tissue concentration.
- In marine sediment from Hunter's Point, California, *Neanthes arenaceodentata* also accumulated PCB in amounts proportional to fiber concentrations. In this case, average lipid normalized tissue concentrations reached 63 times the fiber concentration. Although the correlations were equivalent in all three bioaccumulation tests, the tissue to fiber concentration ratio appeared to depend upon ionic strength of the pore water. Pore water concentrations times bioconcentration factors were also correlated with observed accumulation in the organisms

The laboratory studies have shown the potential for SPME to correlate with and predict bioaccumulation in benthic organisms. The high resolution possible also suggests that the field deployable system may be effectively used to identify and evaluate in-bed transport processes. Field demonstration of these capabilities is currently underway.

3. LIMITS AND APPLICABILITY OF SPME

3.1 Fibers

Experiments were conducted with fiber (PM 170/110) from Poly Micro Industries located in Phoenix, Arizona that has a 110-µm core overlain with a 30-µm layer of polydimethylsiloxane (PDMS). That is the outer dimension of PM 170/110 is 170 µm. The fiber PDMS specific volume is 13.55 µL/m.

Some initial experiments were also conducted with a second fiber (FG 230/210) from Fiber Guide Industries located in Sterling, New Jersey. This fiber has dimensions of 230/210 (µm) (i.e. a 10-µm thick fiber layer on a 210-µm core). The fiber PDMS specific volume is 6.91 µL/m.

Fibers were exposed to an aqueous phase containing contaminants (either PAH or PCB) and due to the strong sorptive capacity of the fiber and the hydrophobicity of the contaminants of concern, would absorb contaminants at a high specific density. Analysis of this fiber then provides an estimate of contaminant mass that can be related back to the concentration of that contaminant in the aqueous phase. Thus, the fundamental measurement required for the analysis of PAH and PCB by SPME is the concentration of contaminant in the fiber. The pore water concentration can then be calculated by utilizing a partition coefficient between the SPME fiber and the aqueous phase (see Section 3.3).

After equilibrating a fiber with a desired water phase (e.g. pore water), the analysis proceeds by first desorbing the contaminant mass from the fiber into a phase suitable for analysis. For PAH analyses by high performance liquid chromatography (EPA 8310 with fluorescent detection using a Waters 2795 HPLC), acetonitrile is an appropriate solvent phase. For PCB analyses by gas chromatography (EPA 8082 with electron capture detection using an HP 6890), hexane is a suitable solvent. One hundred µL of solvent was used to extract the contaminants from the fiber (acetonitrile when analyzing PAH or hexane when analyzing PCB). The solvent is then analyzed for contaminant concentration based upon a conventional calibration curve for the instrument (Instrument response for a given solvent concentration). Calibration curves and basic QA/QC information for both PAH and PCB analysis can be found in Appendix D. The measured concentration of contaminant in the solvent can be converted to a fiber concentration:

$$fiber\ concentration(\mu g/L) = \frac{(concentration\ in\ solvent, \mu g/L) * (solvent\ volume, \mu L)}{(fiber\ sorbent\ density, \mu L/cm) * (fiber\ length, cm)} \qquad \textbf{Equation 1}$$

Typically, a fraction of the solvent used for extraction is injected into the analysis system. This is an inherent dilution of the sample that reduces ultimate detection limits (discussed in Section 3.4). The efficiency of desorption from the fiber into the solvent is evaluated in Section 3.5.

Thermal desorption can also be used for gas chromatographic analysis of fibers. In thermal desorption, the entire contents of the fiber sample can be injected for analysis and so there is no loss of sensitivity associated with solvent extraction. These initial experiments did not employ thermal desorption, however, in that this form of injection system is currently not routinely available in commercial laboratories. The potential benefits of thermal desorption is currently under investigation.

3.2 Extraction Efficiency and Alternative Extraction Methods

Three different processes of solvent extraction were evaluated to determine the most effective method for analyzing the SPME fiber. SPME fiber was exposed to a spiked PAH solution, allowed to equilibrate and then the fiber was extracted from the solution, cut, and placed in glass inserts. One hundred µL of solvent (acetonitrile) was added to each vial and placed in a 2 ml sampling vial. Samples were then either directly analyzed after solvent addition, heated for a specified amount of time, or placed on a shaker table. Figure 1 compares the contaminant concentrations for a range of PAH compounds after extraction by the three methods.

Two different desorption times were employed to evaluate the need for additional extraction time. For heating, samples were heated to a temperature of approximately 50°C and analyzed after 1 hr and 3 hrs of heating. Shaking of samples took place on a shaker table for 1 hr and 20 hrs. The samples were analyzed immediately after shaking. As shown by Figure 1, neither heating nor shaking significantly increased the contaminant extracted from the fiber. The direct injection samples were also subjected to a second extraction and no PAH were detected in the extract. Thus, simple direct extraction without heating or shaking was sufficient to achieve rapid extraction of PAH from a PDMS fiber. A table of analytical results for the PAH extraction can be found in Appendix A (Table A1).

A similar analysis was conducted with PCB as analytes and hexane as the solvent. Again, direct extraction was sufficient to fully remove the PCB from the fiber, as shown in Figure 2. Two samples of extracted fiber were subjected to a second extraction to further evaluate completeness of extraction. The fibers from direct injection sample at 0 hr and the heating sample at 3 hr were both re-extracted and analyzed. The first extraction removed 97+ percent of the analyte in both cases as shown in

Table 1: PCB Detected During Second Extraction of Fibers from Two Samples to Indicate Percent Remaining After a Single Extraction.

Second Extraction 0hr-d			
	Fiber Concentration (mg/L) - 1st extraction	Fiber Concentration (mg/L) - 2nd extraction	Percent Remaining %
PCB28	10.7	0.256	2.38
PCB52	20.5	0.590	2.88
PCB153	12.2	0.371	3.05
PCB138	11.9	0.306	2.58
PCB180	8.5	0.198	2.34
Second Extraction Sample 3hr- h			
	Fiber Concentration (mg/L) - 1st extraction	Fiber Concentration (mg/L) - 2nd extraction	Percent Remaining %
PCB28	11.6	0.255	2.20
PCB52	21.5	0.583	2.71
PCB153	10.9	0.398	3.65
PCB138	14.2	0.392	2.77
PCB180	7.3	0.242	3.30

Table **1** is a table containing results from PCB analysis can be found in Appendix A). (Table A2 as a result of these tests, desorption of contaminant was assumed essentially complete after a single direct extraction with essentially no holding or tumbling time being necessary. Thermal desorption can also be used for GC analysis but solvent extraction is within the capabilities of any commercial analytical laboratory.

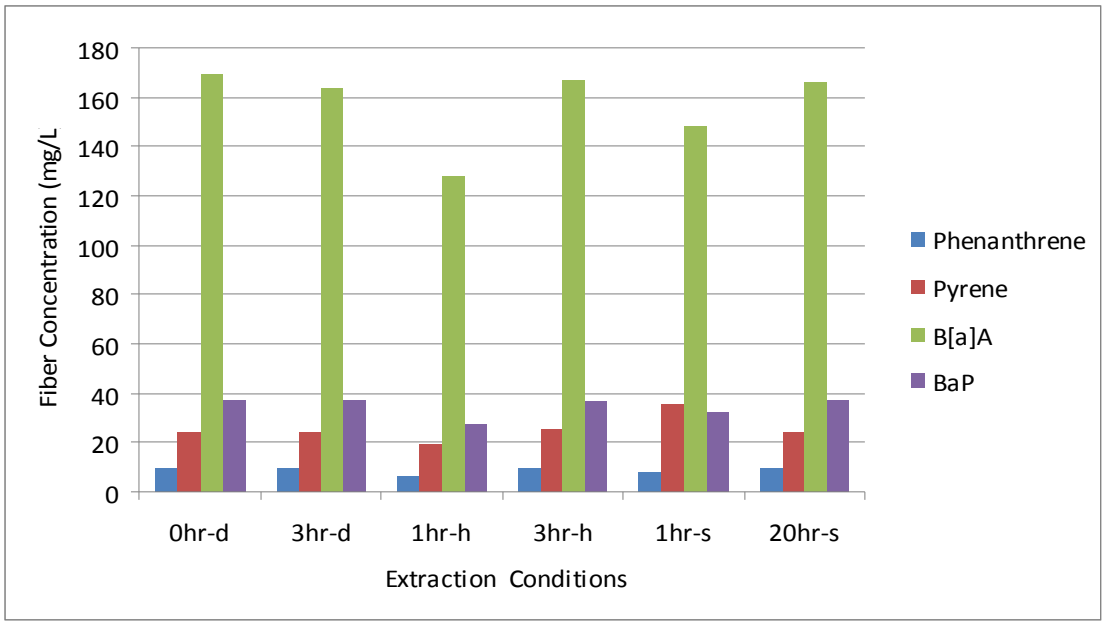

Figure 1: Comparison of Various Extraction Methods for PAH as Indicated by Fiber Concentration to Injected Extracts from Direct Injection (d)**, Heating** (h)**, Shaking** (s)**.**

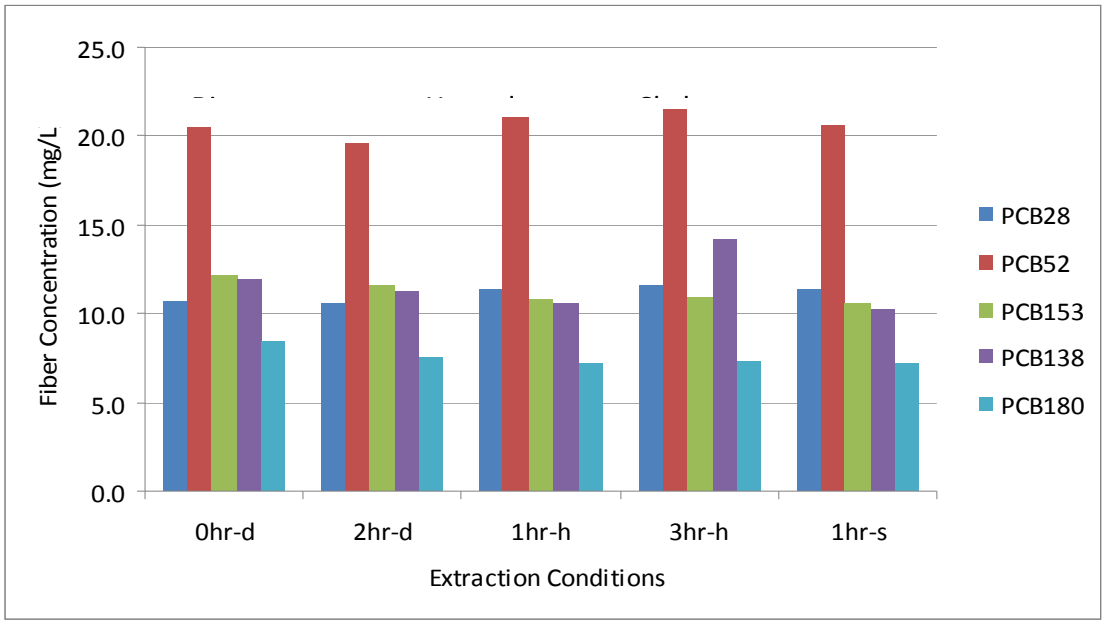

Figure 2: Comparison of Various Extraction Methods for PCB as Indicated by Fiber Concentration to Injected Extracts from Direct Injection (d)**, Heating** (h)**, Shaking** (s)**.**

3.3 Fiber-Water Partition Coefficients for Selected PAH and PCB

Fiber concentrations are converted to an interstitial water concentration through a fiber-water partition coefficient. It was expected that literature estimates of fiber-water partition coefficients could be used for routine analysis and that measurement of a fiber-water partition coefficient would only be necessary to provide higher accuracy measurements of concentration. As a check

of this ability and to estimate the uncertainty introduced in this manner, the fiber-water partition coefficients for PAH were determined for two different sources of SPME fibers and compared to literature values from other sources. In so doing, both the accuracy of pore water determination and the reproducibility with a variety of commercially available fibers and literature fiber-water partition coefficients could be assessed. Fiber-water partition coefficients for PCB were not measured in these initial experiments although the variability as seen in literature coefficients was evaluated. Experiments were conducted with a fiber (PM 170/110) from Poly Micro Industries located in Phoenix, Arizona that has a 110-µm core overlain with a 30-µm layer of poly dimethylsiloxane (PDMS). That is the outer dimension of PM 170/110 is 170 µm. The fiber PDMS specific volume is 13.55 µL/m. FG 230/210 is from Fiber Guide Industries located in Sterling, New Jersey, and has fiber dimensions of 230/210 (µm) (i.e. a 10-µm fiber layer on a 210-µm core). The fiber PDMS specific volume is 6.91 µL/m.

Fiber-water partition coefficient measurement was conducted via static tests with 2 cm of PM 170/110 or 4 cm of FG 230/210 in 250 mL amber bottles. The longer length of FG 230/210 was to compensate for smaller PDMS volume per length of fiber. Fiber-water partition coefficients were calculated as uptake into fiber concentration divided by water concentration at equilibrium. Five replicates of both fibers were used but equipment failure led to the loss of three replicates of fiber B in these initial experiments. Both fiber and water concentrations were measured individually and used to calculate the fiber water partition coefficient. The initial water concentration of the created solutions was measured to determine the initial contaminant mass. The final mass is calculated from the concentration of SPME fiber and the water concentration measured during SPME fiber retrieval. At this fiber to water ratio, the sorption of the most hydrophobic compound analyzed, benzo[a]pyrene, caused a reduction in water concentration of about 15% and therefore was treated as essentially constant at its initial value.

2 L of de-ionized water was spiked with 100 µL of PAH stock solution (approximately 67 mg/L) containing a mixture of PAH dissolved in acetonitrile. Sodium azide was added to inhibit microbial degradation. The spiked solution was placed on the shaker table overnight to homogenize and then it was distributed to 250 mL amber bottles, filling as close to the top as possible to prevent any loss to the headspace. 2 cm of PM 170/110 or 4 cm of FG 230/210 fiber were introduced to the bottles. At the end of exposure, the fiber was analyzed by solvent extraction and the water concentration was analyzed by direct injection. The fiber-water partition coefficient is calculated as follow:

$$K_f = \frac{C_{fiber}}{C_{water}} \qquad \textbf{Equation 2}$$

Measurements were repeated with a range of concentrations to determine sorption isotherms (various dilutions of a stock solution) using 1 cm of PM 170/110 in 250 mL of water. Sorption isotherms so measured were linear although the best-fit slope (i.e. partition coefficient) was slightly lower than observed with the replicate single concentration partition coefficient measurements. The measured partition coefficients are shown in Table 2 with data via others methods reported in the literature. Specific underlying analytical data for the static test of single

concentration and isotherm fiber-water partition coefficient measurements can be found in Appendix A (Table A3, A4-8) along with an appropriate mass balance for each contaminant.

Fiber-water partition coefficients were also measured by the steady state concentration achieved during uptake kinetic experiments. The fiber-water ratio for these experiments was 1 cm fiber: 250 mL water for PM 170/110 and 2 cm fiber: 250 mL water for FG 230/210. 250 mL jars containing water spiked with mixture of PAH (~67 mg/L) at concentrations below solubility of the most hydrophobic compound were tumbled continuously with fibers removed at regular intervals for analysis of uptake. Both PM 170/110 and FG 230/210 fibers were used separately to compare the differences between the fiber uptake. The experiment was also conducted at three controlled temperatures (25°C, 12°C, and 4°C) to test the temperature effect on the fiber uptake. Once equilibrium was established between the fiber and the water concentration, the partition coefficient was estimated from the kinetics of uptake to the fiber by fitting the data to a two-parameter exponential rise equation (Equation 3) with non-linear regression.

$$C_{f/w} = C_{f/w,\infty}(1 - e^{(-k_e t)}) \qquad \textbf{Equation 3}$$

Where $C_{f/w}$ is the ratio of fiber concentration to water concentration, $C_{f/w,\infty}$ is the ultimate value for the ratio or the value at equilibrium, which is the fiber water partition coefficient as defined, and k_e is the elimination rate of contaminants from fiber.

Table 2 below displays the Log K_f values for both fibers at 25°C only. Discussion and comparison of results from the other studies completed at 12°C and 4°C can be found later in the kinetics section. Specific data pertaining to measured fiber and water concentrations for the kinetics studies can be found in Appendix A (Table A3-A12).

Table 2. Fiber-water Partition Coefficients (K_f, in logarithm form) **for PAH.**

Log K_f	This Study					Reference 1		Reference 2	Summary		
	Static - Single Concentration		Static Isotherm - Multi Concentration	Kinetic (25°C)		Static	Dynamic	Static	**Average**	**Std Dev**	Log K_{ow}
	PM 170/110	FG 230/210	PM 170/110	PM 170/110	FG 230/210						
Phenanthrene	3.71 (0.02)	3.83±0.03	3.77	3.74	3.79	4.01	3.98	3.83	3.83	0.11	4.57
Pyrene	4.26 (0.05)	4.43±0.09	4.17	4.27	4.27	4.62	4.63	4.32	4.37	0.17	5.18
Chrysene	4.76 (0.15)	4.64±0.06	4.63	4.61	4.62	4.84	4.92	4.69	4.71	0.12	5.86
B[a]A	4.75 (0.08)	4.78±0.04	4.61	4.66	4.65				4.69	0.07	5.91
B[b]F	4.92 (0.08)	5.21±0.02	4.75	5.00	4.99			5.23	5.02	0.18	6.00
B[k]F	4.96 (0.07)	5.31±0.03	4.80	4.62	4.83			5.23	4.96	0.23	6.00
B[a]P	5.14 (0.02)	5.30±0.07	4.86	4.64	4.79	4.90	5.19	5.24	5.01	0.24	6.04

Fibers used in this study (outer diameter/inner diameter)

PM 170/110 source: Poly Micro Industries (Phoenix, Arizona), fiber dimension: 170/110 (μm)

FG 230/210 source: Fiber guide industries (sterling New Jersey) fiber dimension: 230/210 (μm)

Ref1: Fiber was purchased from Supelco (Bellefonte, Pennsylvania), fiber dimension: 574/560 (μm) (Poerschmann J., et al. 2000)

Ref2: Fiber source: Poly Micro Industries (Phoenix, Arizona), fiber dimension: 170/110 (μm) (Ter Laak et al. 2006)

Table 2 displays fiber-water partition coefficients measured within the study compared to literature values measured by other investigators. Partition coefficients measured in this study completed with both PM 170/110 and FG 230/210 included static (single concentration, isotherm with multi-concentrations), and kinetic methods. The static experiments conducted with a single concentration were completed with both fiber types. The PM 170/110 fiber-water partition coefficients are given as an average with the standard deviation in parentheses. Static experiments completed with fiber FG 230/210 only contained two replicates due to problems with sampling, and the partition coefficients are given as an average and range. The results from the constant source experiment are consistent with other measured values and suggest that the fiber-water partition coefficient is effectively linear from low concentrations to saturation.

Literature reference one refers to partition coefficients measured by Poerschmann (et al 2000), who used both static and dynamic methods to measure fiber-water partition coefficients. In the dynamic method, a generator column packed with adsorbent spiked with objective compounds provides a source for constant dissolved aqueous concentration. Fiber-water partition coefficient was calculated as fiber concentration divided by the water concentration. The advantage of this method is to minimize the effect of loss of the compounds from water. Literature reference 2 is derived from studies completed by Ter Laak et al. (2000). Measurements determined by Ter Laak involved the static method; however, the water concentration was estimated assuming 100% mass balance in the system, which may be subject to error due to losses such as sorption to surfaces other than the fiber.

As shown by the second to last column of Table 2, the average error in the estimate of the partition coefficients of the various PAH compounds is approximately 0.16 log units or approximately 45%. Without specific testing with the particular fiber under study or additional studies to understand the source of the variability of the partition coefficient measurements, this would represent the standard of accuracy of the fiber water partition coefficients or the ability to estimate the pore water concentration from the measured fiber concentration.

As a check of the sensitivity to water concentration, fiber-water partition coefficients were also measured for phenanthrene and pyrene using a saturated solution with constant source of both contaminants. Both contaminants were placed in a solid form in 15 mL glass amber vials with five replicates. The solid used was calculated as over 10 times the solubility limit for phenanthrene and pyrene. De-ionized water was added to fill the vial. 3 cm of clean SPME fiber was inserted through the septa cap, 1 cm exposed to the air, 1 cm exposed to the water, and 1 cm in between water and cap. The vials were allowed to equilibrate for 10 days after which the fiber was removed and the bottom 1 cm was cut and placed in a High Performance Liquid Chromatography (HPLC) sample vial and diluted to 1 mL with acetonitrile. Since the water samples were highly concentrated with phenanthrene and pyrene, water samples were diluted before analysis. Both fiber and water were analyzed and the results were used to calculate fiber-water partition coefficients. The partition coefficients for phenanthrene and pyrene were within the expected ranges suggested by Table 2 despite the high concentration (Table 3). This suggests

that the fiber-water partition coefficient is effectively linear from low concentrations to saturation.

Table 3: Fiber-water Partition Coefficients (K_f, in logarithm form) **at Saturation Conditions.**

	C_{water} (µg/L)		C_{fiber} (µg/L)		Log K_f	
	Phen	Pyrene	Phen	Pyrene	Phen	Pyrene
1	664	13.2	3869459.98	225209	3.77	4.23
2	651	11.0	5785762	181005	3.95	4.22
3	528	9.3	3385294	131940	3.81	4.15
4	479	0	3211999	0	3.83	
5	8.9	12.7	60339	204951	3.83	4.21
				Average	3.84	4.20
				Std Dev	0.07	0.03
				Std err	0.031	0.017

PCB measurements were not undertaken in these initial studies due to the difficulty in acquiring suitable PCB standards and limited ability to maintain the integrity of those standards. An initial estimate of the ability to estimate pore water concentrations was undertaken by comparing literature fiber-water partition coefficients. Table 4 summarizes fiber-water partition coefficients of PCB from a variety of sources.

Table 4: Fiber-water Partition Coefficients (*K_f*, in logarithm form) of PCB.

Congener	Ref 1 dynamic	Ref 2 static	Ref 3 kinetics	Ref 4 kinetics	**Average**	**Standard Deviation**	**Log Kow**
PCB1	4.03				**4.03**		**4.51**
PCB15	4.65				**4.65**		**5.22**
PCB18			4.96		**4.96**		**5.35**
PCB17			4.85		**4.85**		**5.35**
PCB28	5.04	4.8	5.04		**4.96**		**5.55**
PCB44			5.27		**5.27**		**5.79**
PCB49			5.28		**5.28**		**5.89**
PCB52	5.55	5.38	5.37	5.7	**5.49**	**0.17**	**5.86**
PCB65		5.32			**5.32**		**5.71**
PCB70			5.32		**5.32**		**6.00**
PCB74			5.3		**5.3**		**6.01**
PCB101		5.65	5.3		**5.48**	**0.25**	**6.33**
PCB105		5.79			**5.79**		**6.39**
PCB110			5.31		**5.31**		**6.25**
PCB112		5.64			**5.64**		**6.22**
PCB118	5.97	5.78	5.0	5.8	**5.64**	**0.43**	**6.46**
PCB138		6.20			**6.20**		**6.71**
PCB153	6.05	6.15		5.3	**5.84**	**0.47**	**6.79**
PCB154		6.17			**6.17**		**6.65**
PCB155		6.03			**6.03**		**6.35**

PCB156		6.28			**6.28**		**6.84**
PCB180	6.24	6.4		5.9	**6.18**	**0.26**	**7.17**

Fibers used in this study (outer diameter/inner diameter)

Ref1: Fiber was purchased from Supelco (Bellefonte, PA), fiber dimension: 574/560 (μm) (Poerschmann J., et al. 2000)

Ref2: Fiber guide industries (Sterling, New Jersey) fiber dimension: 230/200 (μm) (Mayer P. 2000)

Ref3: Fiber guide industries (Sterling, New Jersey) fiber dimension: 230/210 (μm) (Schneider et al., 2006)

Ref4: Fiber was purchased from Supelco (Bellefonte, Pennsylvania), fiber dimension: 574/560 (μm) (Oomen et al., 2000)

Log K_{ow} values estimated from Hanson et al. (1999)

The lack of duplicate measures for most congeners makes it difficult to estimate the uncertainty in evaluating pore water concentration of PCB but the few common measurements suggest a greater uncertainty than with PAH. The average error is of the order of 0.31 log units or an uncertainty of a factor of two in predicting pore water concentration without specific measurements of the fiber-water partition coefficient in use. While measurement of the fiber-water partition coefficient could always be undertaken for a particular fiber and or sample matrix to reduce uncertainty, the difficulty in such a determination suggests that a literature value may often be relied upon. Based upon the available measurements this suggests an average uncertainty of a factor of two for PCB measurements (compared to the uncertainty of approximately ±45% with PAH).

The fiber-water partition coefficients should correlate with the hydrophobicity of the compounds. Figure 3 shows a correlation of the average fiber-water partition coefficients in Table 3 and Table 4 versus the octanol-water partition coefficients. The octanol-water partition coefficients for the PCB were estimated as per Hanson et al. (1999)

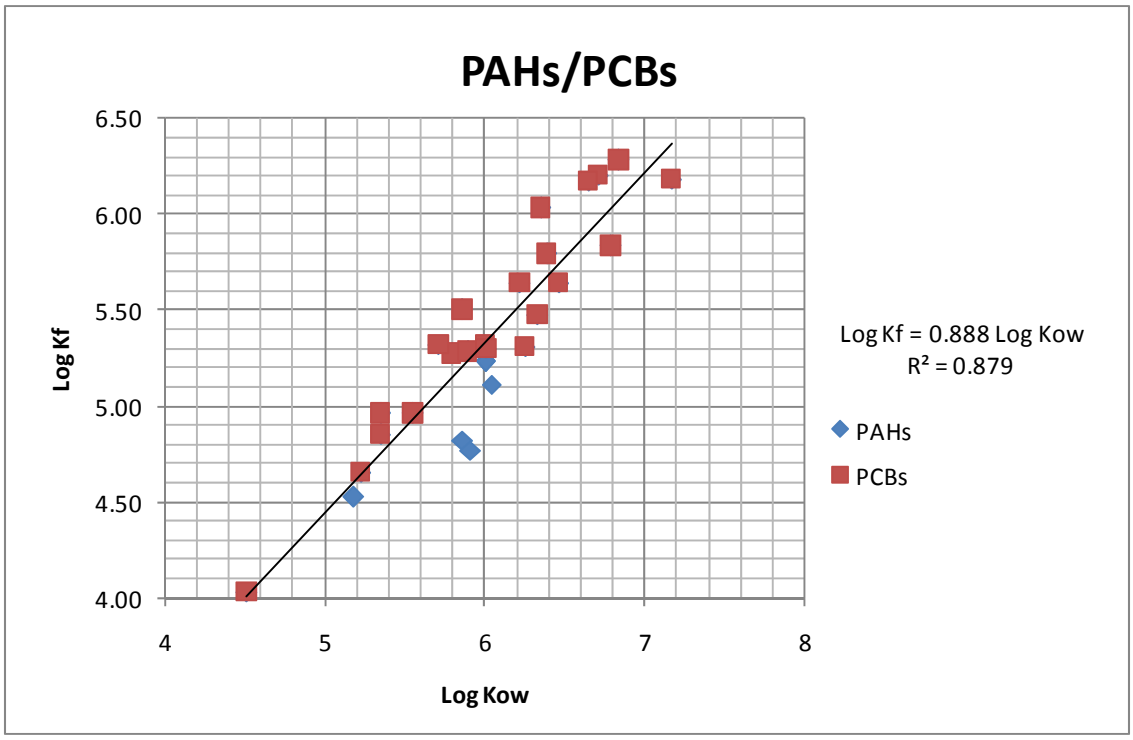

Figure 3: Log K_{ow} Plotted Against Log K_f for Average K_f From Tables 2 and 4.

Similar correlations were generated from the PAH partition coefficients measured in this study. For example, the isotherms generated from multiple different concentrations give a partition coefficient that correlates with octanol-water partition coefficient as shown in Figure 4. For this figure, the fiber-water partition coefficients (in logarithm form) for each of the seven PAH measured from the isotherm experiment is plotted against its corresponding Log K_{ow}.

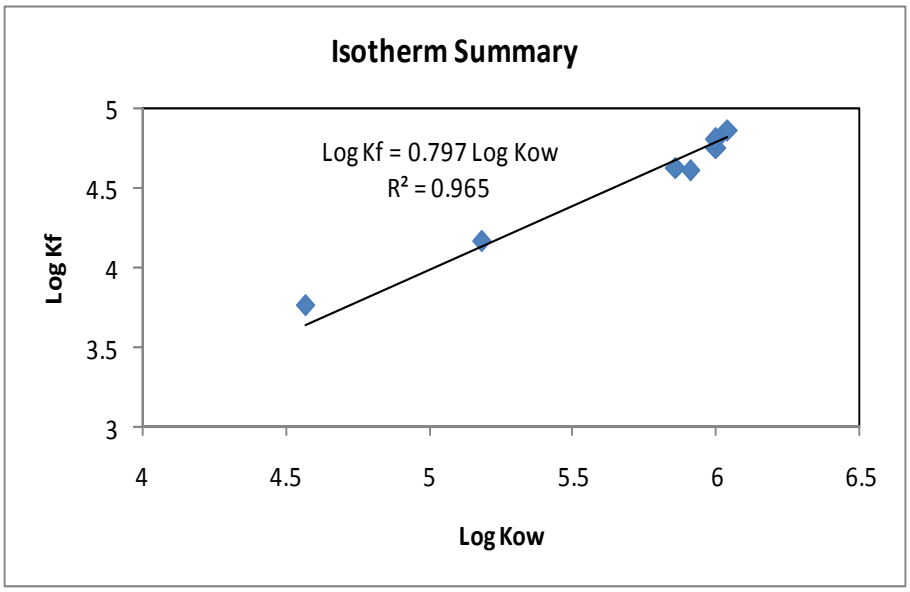

Figure 4: Log K_{ow} Plotted Against Log K_f Generated From Isotherms With Multiple Water Concentration for All Seven PAH.

Partition coefficient measurement with the two different SPME fibers (PM 170/110 and FG 230/210) were conducted at three different temperature conditions (25°C, 12°C, and 4°C) in order to determine differences in fiber-water partition coefficients with variations in surrounding temperature. These measurements were based on steady state values achieved during fiber uptake kinetic tests (see details in Section 3.3). The results are outlined in Table 5. For fiber FG 230/210, multiple problems with sampling at 4°C (unrelated to temperature) complicated the determination of a consistent fiber-water partition coefficient; therefore, data of 4 °C for this fiber were not listed.

Table 5: Fiber-water Partition Coefficients (in logarithm form) **Measured at Varying Temperatures with Two Different PDMS Fibers.**

Log K_f	PM 170/110			FG 230/210		**Average**	**Std Dev**
	25°C	12°C	4°C	20°C	12°C		
Phenanthrene	3.74	3.86	3.92	3.79	3.84	3.83	0.07
Pyrene	4.27	4.34	4.48	4.27	4.31	4.33	0.09
Chrysene	4.61	4.67	4.60	4.69	4.69	4.65	0.05
B[a]A	4.66	4.81	4.80	4.78	4.76	4.76	0.06
B[b]F	5.00	5.07	4.87	5.13	5.02	5.02	0.10
B[k]F	4.62	4.83	4.50	4.79	4.75	4.70	0.13
B[a]P	4.64	4.91	4.70	4.89	4.78	4.78	0.12

Figure 5 visually displays the variation between the two SPME fibers and the temperature at which the experiments were conducted. The variation between fiber-water partition coefficients is greater for the more hydrophobic PAH such as B[k]F and B[a]P. No correlation has been observed between temperature changes and changes in the fiber-water partition coefficient. Therefore, any effect of temperature is small relative to variability from other sources. See tables in Appendix A (Table A9-A13) for complete underlying analytical data.

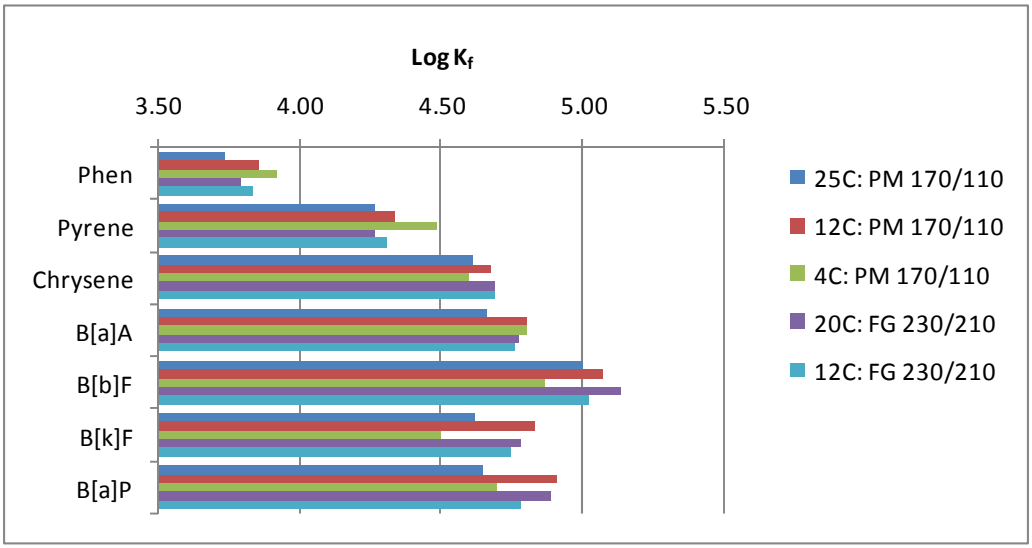

Figure 5: Variations in Fiber-water Partition Coefficients in Both SPME Fiber Types and in Different Temperatures.

3.4 Length of SPME Fiber to Achieve Specific Detection Limits

The fiber-water partition coefficient is an indication of the sensitivity per unit volume of fiber for measuring pore water concentrations. The length of fiber defines the total volume of sorbent for a given fiber geometry. The following table displays the fiber water partition coefficients, equipment detection limits, and the pore water detection limits for both 1 and 5 cm lengths of SPME PM 170/110 (fiber volume of 13.55 µL/m). Since the detection of pore water is based on the volume of fiber used, the greater the volume, the lower the detection limit will be for all measured analytes. Alternatively, the detection limit can define the potential resolution of the pore water sampling by defining how much fiber is needed to effectively measure the observed concentrations. The water detection by the fiber was calculated based on the following equation.

$$C_{\text{det water}} = \frac{C_{\text{det SPME}}}{K_f} = \frac{MDL * V_{solvent}}{V_{PDMS} * K_f} \qquad \textbf{Equation 4}$$

In the above equation, MDL is the measured method detection limit as measured by the concentration of analyte in the injected phase (25 µL HPLC, 1µL GC) as determined from the standard deviation of 7 analyses of a sample near the detection limit multiplied by the student-t value associated with 99% confidence of detection of a non-zero concentration (3.143). $V_{solvent}$ is the volume of solvent used to extract contaminants from the SPME fiber, 100 µL was used during this study. V_{PDMS} is the volume of polymer coating on the SPME fiber (13.55 µL/m for fiber PM 170/110 and 6.91 µL/m for fiber FG 230/210). K_f is the fiber-water partition coefficient determined specifically for each PAH or PCB contaminant.

Table 6: Detection Limits for 1 cm and 5 cm SPME Fiber (PM 170/110) for Various Compounds. For FG 230/210 (with ½ of the PDMS volume per length of fiber) **the Detection Limits are Approximately Double Those Shown.**

Compound	Log $K_{fiber,\ water}$ (static experiments)	Method detection limit (ng/L)	$C_{det,water}$ (1 cm fiber) (ng/L)	$C_{det,water}$ (5 cm fiber) (ng/L)
Phenanthrene	3.71	33	4.76	0.95
Pyrene	4.23	65	2.8	0.56
Chrysene	4.76	117	1.5	0.31
B[a]A	4.75	44	0.57	0.11
B[b]F	4.92	61	0.54	0.11
B[k]F	4.96	18	0.15	0.029
Benzo[a]pyrene	5.15	23	0.12	0.024
PCB 28	4.80	23	0.27	0.053
PCB 52	5.38	25	0.077	0.016
PCB 153	6.15	18	0.096	0.0019
PCB 138	6.2	20	0.0095	0.0019
PCB 180	6.4	35	0.01	0.002

The detection limit is approximately inversely proportional to hydrophobicity of the compound since the mass sorbed onto the fiber is roughly proportional to the hydrophobicity. Figure 6 shows the correlation between detection limit (1 cm fiber from

Table 6) and octanol-water partition coefficient.

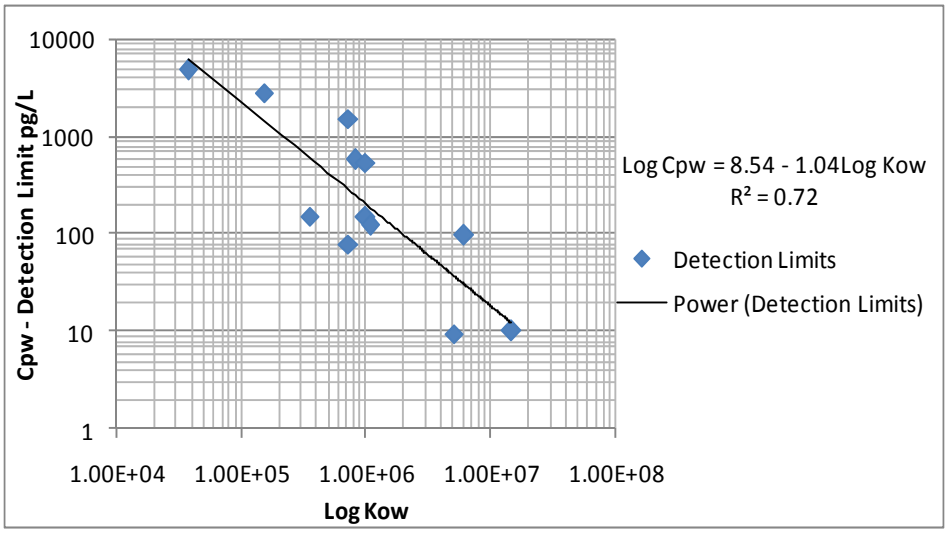

Figure 6: Detection Limit versus Log K_{ow} for 1 cm of PM 170/110. Detection Limits can be Lowered by Use of More Fiber or a Fiber with More sorbent Per Unit Volume.

3.5 Pore Water Concentration after Spiking Clean Sediment

The ability of the SPME fiber to measure pore water concentrations was first established by measuring the pore water concentration in spiked sediment. 200 g of clean sediment was spiked with phenanthrene and pyrene and allowed to tumble for 2 weeks. After tumbling, the sediment was analyzed for contaminant concentrations. Three samples were taken for bulk sediment analysis. The results are shown in Table 7 below. The third replicate for phenanthrene has been left out of this analysis due to problems with the analysis.

Table 7: Spiked Sediment Concentration (bulk sediment concentration)**.**

Sediment Concentration mg/kg		
	Phen	Pyrene
	64.30	11.18
	61.32	11.35
		11.68
Average	62.81	11.40
STD	2.11	0.25
Std err	1.22	0.15

For pore water measurements, five replicate fibers, each 1 cm in length were inserted into a spiked sediment within sealed bottle. The fibers were left to equilibrate for 1 week before analyzing. Once the 1 cm fibers were extracted, they were flushed with distilled water to remove excess sediment and placed in the bottom of a 100 µL glass insert within a sampling vial. To the

vial, 100 µL of acetonitrile was added and screw cap securely tightened. The vial was shaken by hand for approximately 30 seconds to complete desorption. Each sample was analyzed using HPLC (70% acetonitrile, 30% water). Pore water concentrations are determined from the fiber concentration and the fiber-water partition coefficient. The results for the pore water concentrations are shown in Table 8.

Table 8: Measured Pore Water Concentration by SPME for Spiked Sediment of Table 7.

Porewater (µg/L)		
	Phen	Pyr
	149.16	3.39
	161.33	4.18
	191.20	4.07
	167.14	4.83
	151.12	3.69
Average	163.99	4.03
STD	16.91	0.55
Std err	7.56	0.24

After analyzing the samples, the fiber in each glass insert was removed, wiped dry, and placed in a new glass insert. One hundred µL of fresh acetonitrile was added to the glass insert and the sample was then reanalyzed to determine if any residual concentrations were previously left on the fiber. Phenanthrene was the only concentration detected, below 0.3 µg/L. Predicted pore water concentrations were calculated from the bulk sediment concentrations and sediment water partition coefficient.

$$K_{sw} = \frac{C_{sediment}}{C_{porewater}} \qquad \textbf{Equation 5}$$

$$K_{sw} = K_{oc} f_{oc} \qquad \textbf{Equation 6}$$

$$C_{porewater} = \frac{C_{sediment}}{K_{oc} f_{oc}} \qquad \textbf{Equation 7}$$

Table 9: Comparison of Predicted and Measured Pore Water Concentrations (spiked sediment)**.**

	Phen	Pyr
log Koc	4.36	4.97
foc	1.25	1.25
Average Sediment conc (µg/g)	63	11
Predicted porewater conc (µg/L)	219	9.8
Measured porewater conc (µg/L)	164	4

The pore water concentration measured by the SPME fiber is lower than the concentration predicted by the bulk sediment concentration. This may be a reflection of slight desorption resistant phenomena even in this freshly spiked sediment or failure to reach equilibrium

(discussed in Section 4). Regardless, this experiment accomplished its goal of demonstrating the ability to measure the spiked compounds in the pore water sediment.

3.6 SPME Reproducibility for PAH and PCB

In order to test fiber reproducibility, pore water concentrations were measured in the Anacostia sediment by inserting the SPME fiber into the sediment for 30 d. Four replicates were placed in four 15 mL amber glass vials. The reproducibility of the replicates was calculated using the percent absolute error in replicate measurements. In the relationship below, C_i is the SPME pore water measurement; C_{SPME} is the average of SPME measurements.

$$\text{Reproducibility} = 100 - \frac{100\sqrt{\frac{1}{(n-1)}\sum_{i=1}^{n}(C_i - \overline{C_{Fiber}})^2}}{\overline{C_{Fiber}}} \qquad \textbf{Equation 8}$$

PAH reproducibility was tested with a bare fiber inserted into a 15 mL vial filled with Anacostia sediment and allowed to equilibrate for 30 days. Four replicates were used and the fiber calculation was based on 6 cm of fiber.

Table 10: Reproducibility of Bare Fiber PAH Analyses by SPME.

	Porewater Concentration (ng/L)				Average	Reproducibility
Phen	225	211	237	240	228	94.26
Pyrene	1057	1017	1074	1017	1041	97.25
B[a]A	6.01	6.74	6.21	7.10	6.52	92.36
B[b]F	1.49	1.25	1.61	1.64	1.50	88.32
B[k]F	1.02	0.78	0.83	0.68	0.83	82.92
B[a]P	1.55	1.06	0.90	1.02	1.13	74.84

PCB reproducibility was tested similarly to that of PAH with a bare fiber inserted into a 15 mL vial with Anacostia sediment. The fiber was inserted into the sediment for 35 days and fiber concentration was calculated based on 6 cm of fiber.

Table 11: Reproducibility of PCB.

	Porewater Concentration (ng/L)				Average	Reproducibility
PCB 28	0.656	0.615	0.548	0.611	0.61	92.61
PCB 52	0.486	0.490	0.458	0.449	0.47	95.67
PCB 153	0.041	0.045	0.047	0.046	0.04	94.54
PCB 138	0.034	0.034	0.035	0.036	0.03	96.60
PCB 180	0.006	0.006	0.007	0.007	0.01	91.10

Evaluation of PAH and PCB reproducibility was repeated with fiber placed within a field deployable sampling device created for this project in Anacostia sediment. The field deployable sampling device is essentially a shielded rod containing the fiber. The external shield is slotted to allow water passage from the sediment to the fiber. Analyses for reproducibility are based on 1 cm of fiber for PAH and 2 cm of fiber for PCB. Even though the fiber lengths differ between the various experiments, this will not affect the calculated reproducibility since the fiber concentration is normalized by the fiber length. See fiber concentration calculation equation in

Section 3.1 (Equation 1). Reproducibility of both PAH and PCB in the field deployable system is shown in Table 12 below.

Table 12: Reproducibility of PAH and PCB in Field Deployable Sampling Device.

	Porewater Concentration (ng/L)				Average	Reproducibility
Phen	71.6	73.1	70.4	63.5	69.68	92.86
Pyrene	50.6	57.0	49.5	45.9	50.74	99.31
Chrysene	2.79	3.97	2.33	1.57	2.67	98.95
B[a]A	2.33	3.41	2.82	1.97	2.63	98.19
B[b]F	1.17	1.79	1.57	1.59	1.53	96.04
B[k]F	0.47	0.60	0.35	0.30	0.43	95.51
B[a]P	0.58	0.70	0.46	0.46	0.55	96.41
PCB 28	0.473	0.445	0.382	0.415	0.43	90.84
PCB 52	0.352	0.277	0.247	0.261	0.28	83.52
PCB 153	0.036	0.029	0.028	0.027	0.03	85.11
PCB 138	0.035	0.026	0.026	0.026	0.03	83.84
PCB 180	0.007	0.005	0.004	0.004	0.005	76.64

The reproducibility data showed above measures the pore water concentration after 30 days of exposure to the sediment. Prior to equilibrium, the fiber concentrations can vary significantly between replicates. Compounds that come to equilibrium quickly such as phenanthrene do not show a large variability while others, such as the high molecular weight PCB, show greater variability between the replicates. Inadequate time for the achievement of complete equilibrium is likely the cause of the slightly higher but still modest variability in the high molecular weight PCB. This is explored in more detail in Section 4. The lower concentrations observed in the field deployable sampling device experiments is simply a reflection that different sediments were employed in those experiments and do not indicate that the field deployable sediments were biased low relative to the bare fiber measurements.

4. OPTIMIZATION OF SPME FIELD SAMPLING DEVICES

4.1 Design of Field Deployable Sampling Devices

The purpose of the field deployable sampling devices is to physically protect the SPME fiber during sampling while allowing free water movement between the sediments and the fiber surface. A simple device that accomplishes these goals is shown in Figure 7 and pictured in Figure 8. The system employs a slotted rod protected by an outer sheath that is slotted to allow water movement back and forth.

Deployment of the system is expected to be:

- In-situ when sediment cannot be removed without compromising pore water integrity
- In-situ when pore water chemical gradients must be retained (e.g. when identifying fate and transport processes in near surface sediments)
- In-situ to assess migration under field conditions (e.g. conceptual model development or remedial demonstration, full-scale implementation)
- Ex-situ (e.g. in a box core removed to the laboratory) when appropriate cores can be collected and maintained or when field deployment is hazardous (e.g. divers in chemically or physically hazardous environments)

The system is expected to complement ex-situ pore water centrifugation and analysis approaches and offer opportunities (e.g. in-situ profile monitoring) that cannot be accomplished by such approaches.

Successful implementation of the system requires an understanding of its limitations and optimization of the field deployment approach. Specific concerns are equilibration time, spatial resolution and sample integrity and these characteristics will be explored in this section.

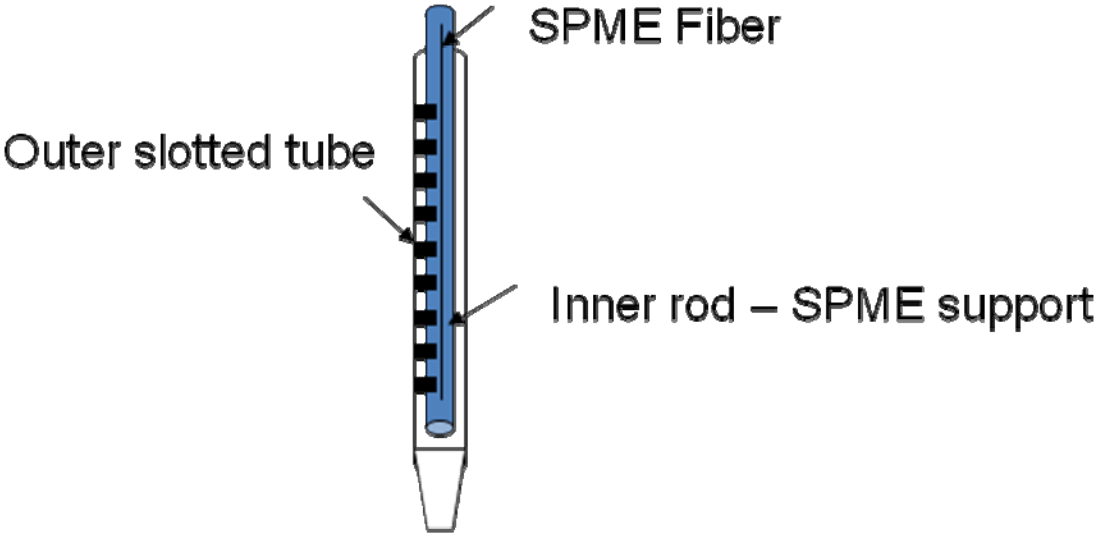

Figure 7: Schematic of Field Deployable SPME Sampling Device.

Figure 8: Picture of Field Deployable SPME Sampling Device.

4.2 Equilibration Time

The time required for equilibration of the SPME fibers with hydrophobic PAH and PCB contaminants were assessed in a series of laboratory experiments. The primary focus of these experiments was on assessing the kinetics of uptake of the more hydrophobic contaminants (which were expected to be slower). Thus sampling sufficient to achieve precise estimates of contaminants taken up rapidly was not conducted. The initial experiments focused on fiber PM 170/110 and room temperature (22°C). Subsequent experiments expanded on these studies with different fiber (FG 230/210) and different temperatures (4°C and 12°C). Anacostia river sediment was used in all kinetics measurements. The initial kinetics measurement was conducted in 15 ml amber vials. 10 cm fibers were inserted into the sediment with the help of a syringe piercing through the septa of the caps. Two fibers were inserted in one vial, one for PAH analysis and one for PCB analysis. At specific times, fibers were withdrawn from the sediment, cleaned by wet tissue paper. The bottom 6 cm fibers that were immersed in sediments were cut

and extracted for PAH and PCB analysis. To test the difference in uptake and whether or not the field-sampling device creates significance in equilibration time, uptake kinetics in the sampling device were also measured. This experiment was conducted in one-liter glass bottles. The field deployable sampling devices were loaded with 10 cm of fiber (two 2.5 cm replicates for PAH and one 5 cm sample for PCB). The devices were inserted into the consolidated sediment and allowed to equilibrate for various time periods, removed, cut and analyzed. The bottle was loosely covered by aluminum foil. In the subsequent experiments with different fibers and different temperatures, fibers were exposed directly to the sediment through 1cm diameter Teflon disks (septa of 2ml auto-sampling vials). Four 2.5 cm fibers were inserted per one disk, all fibers were exposed to one bottle and the bottle was fully sealed with screw cap. At specific times, one septa disk was retrieved from the sediment; the four 2.5 cm fibers were removed from the septa, cleaned and cut for analysis. (Two for PAH analysis and Two for PCB analysis).

Comparative studies were also conducted with bare fiber SPME in water. 250 mL jars containing water spiked with PAH were tumbled continuously with fibers removed at regular intervals for analysis of uptake. The external mass transfer resistances during these studies were expected to be negligible and thus these studies allow estimation of the effective diffusion coefficient of the compound in the fiber. The studies with exposed and sheathed fibers then provide an indication of the extent to which these sediment monitoring approaches will slow the achievement of equilibrium.

The results are summarized in Table 13. Figure 10 through Figure 11 indicate the approach to steady state for selected PAH compounds at different exposure conditions and Figure 14 through Figure 1 indicate the approach to steady state for PCB compounds. PCB seem to require significantly longer time to achieve steady state in the PDMS matrix. In the following figures, the concentrations are displayed as fiber concentrations (µg/L) instead of pore water concentrations. The goal is to observe the kinetics of uptake from water (either spiked water or sediment pore water) to the fiber. Before equilibrium is reached, converting fiber concentration to pore water concentration is not desirable. The uptake data were fit to a two-parameter exponential rise equation by non-linear regression.

$$C_{fiber} = C_{fiber,\infty}(1 - e^{-k_e t}) \qquad \textbf{Equation 9}$$

In the above equation, the $C_{fiber,\infty}$ concentration is the ultimate compound concentration that can be absorbed into the fiber coating and k_e is elimination rate, which was used to calculate the time to steady state. (e.g. time to 95% steady state was calculated as):

$$t_{95} = \frac{3}{k_e} \qquad \textbf{Equation 10}$$

Results for uptake kinetics from spiked water and sediment are listed in Table 13 and Table 15. Further data concerning the following figures can be found in Appendix A (Tables A15-A22) and Appendix B (Tables B1-B4).

Table 13: Time (days) to Achieve 95% of Equilibrium for PAH Compounds. These Represent Exponential Models Fit to Measurements of Fiber Uptake at Least 5 Individual Times.

PAH Time to 95% of Steady State (d)									
Condition	Fiber Type	Temp	Phen	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
Fiber in Water	PM 170/110	25°C	0.24	1.09	1.79	2.27	3.86	1.44	2.17
		12°C	0.33	0.79	0.63	0.82	0.87	0.81	0.98
		4°C	1.21	2.64	3.56	5.34	5.41	2.28	5.19
	FG 230/210	20°C	0.16	0.42	1.06	0.95	1.71	1.31	1.52
		12°C	0.56	0.41	0.61	0.19	0.71	0.57	0.16
Fiber in Sediment	PM 170/110	25°C	0.97		3.63		5.74		13.15
		12°C	1.09	2.34	5.81	8.02	11.93	12.65	12.52
		4°C	2.19	3.39	3.84	20.17	12.72	13.04	24.27
	FG 230/210	12°C	0.55	0.92	2.60	3.59	4.80	4.21	5.19
		4°C	0.35	1.10	2.55	3.31	4.57	3.66	3.57
Fiber in Rod in Sediment	PM 170/110	25°C	1.55		2.83		11.39		16.07

Overall, fiber PM 170/110 displays consistently longer kinetics than fiber FG 230/210. With regard to temperature, the time to steady state is similar between 12°C and 4°C conditions for fibers exposed to sediment. When comparing times to steady state, specifically at 12°C, fiber PM 170/110 is approximately 2 times slower compared to fiber FG 230/210 consistently when considering all PAH compounds. This is consistent with a model of fiber uptake kinetics (discussed later) that suggests that uptake rate is proportional to the surface area to volume ratio when external mass transfer resistances control uptake. Fiber FG 230/210 reaches 95% of steady state for all compounds, including the especially hydrophobic ones, within 10 days. For all conditions with each SPME fiber, 30 days is a sufficient equilibration time. The standard error in estimated times to 95% of steady state can be found in the Table 14.

Standard error in the time to reach steady state (tss) calculated from standard error in estimated k values for the uptake equation as follows:

$$C_f = C_{f,\infty}(1 - e^{-kt})$$ **Equation 11**

Using a procedure for relating errors in measured quantities to error in calculated quantity the following equations were applied:

$$t_{ss} = 3/k$$ **Equation 12**

$$\Delta t_{ss} = \frac{\partial(t_{ss})}{\partial k}\Delta k$$ **Equation 13**

$$\Delta t_{ss} = \left(3/k^2\right)\Delta k$$ **Equation 14**

Where Δk is the standard error in the estimated rate of uptake k

To estimate the uncertainty in percentage of steady state achieved during a 30-day equilibration period, the following equations were used:

$$\%_{ss} = 1 - e^{-kt}$$ **Equation 15**

$$\Delta\%_{ss} = \frac{\partial(\%_{ss})}{\partial k}\Delta k$$ **Equation 16**

$$\%_{ss} = 30e^{-k(30)}\Delta k$$ **Equation 17**

Table 14: Standard Error in Tme to 95% of Steady State Estimates for PAH, in Days.

Standard Error in Time to 95% Steady State									
Condition	Fiber Type	Temp	Phen	Pyrene	Chrysene	B[a] A	B[b] F	B[k] F	B[a] P
Fiber in Water	PM 170/110	25°C	0.02	0.12	0.53	0.49	1.01	0.56	0.68
		12°C	0.11	0.22	0.32	0.32	0.41	0.33	0.35
		4°C	0.32	0.67	1.04	1.47	2.25	1.16	1.96
	FG 230/210	20°C	0.04	0.11	0.44	0.23	0.67	0.51	0.60
		12°C	0.08	0.13	0.29	0.12	0.31	0.31	0.14
Fiber in Sediment	PM 170/110	25°C	0.24		1.09		1.47		1.04
		12°C	0.18	0.55	1.85	2.53	4.75	5.92	1.48
		4°C	1.20	0.54	1.95	9.94	4.93	7.55	9.96
	FG 230/210	12°C	0.51	0.35	1.08	1.02	1.47	1.71	1.68
		4°C	0.36	0.45	1.04	0.79	1.03	1.78	2.26
Fiber in Rod in Sediment	PM 170/110	25°C	0.66		1.51		4.91		5.63

For most conditions, a low standard error is observed, however, experiments conducted within water display lower standard error than those completed within sediment.

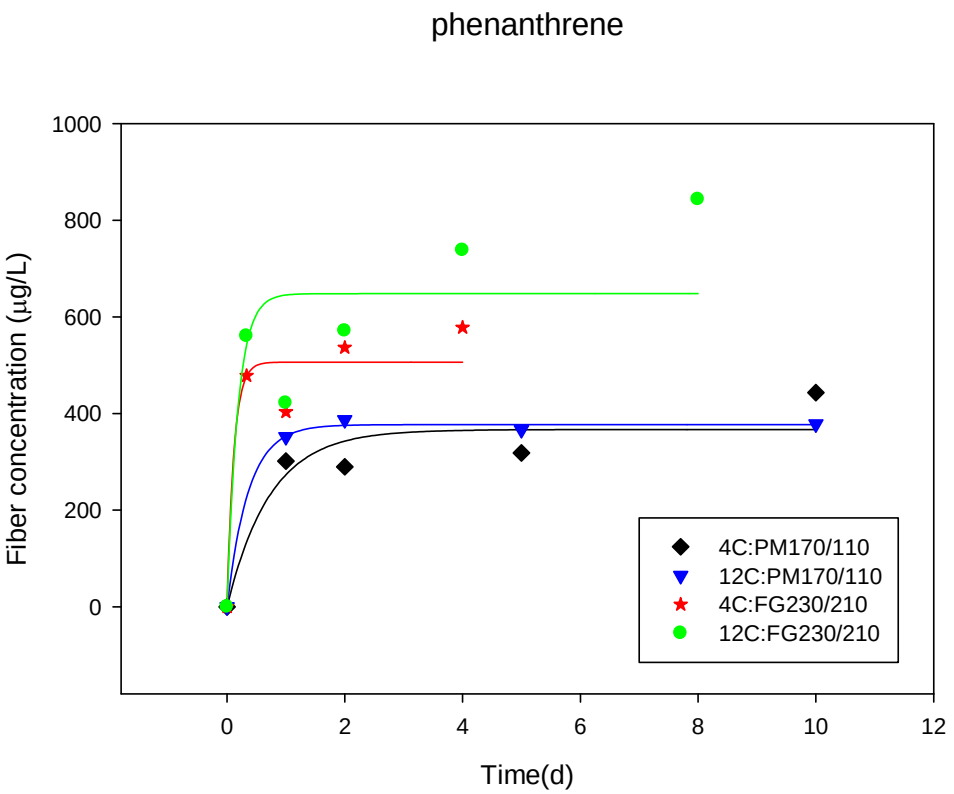

Figure 9: Uptake of Phenanthrene in Sediment to SPME Fiber at 4 Different Conditions with 2 Types of SPME Fiber and 2 Constant Temperatures (4° C and 12°C)**.**

Of all PAH, phenanthrene is the fastest of the compounds evaluated to reach equilibrium and is the least hydrophobic of the test compounds. Figure 10 and 11 display the uptake kinetics for the more hydrophobic pyrene and B[a]P, respectively. The differences between fibers (thickness and surface area) appear to be most significant factor controlling uptake after compound hydrophobicity. FG 230/210 has a thinner polymer coating and therefore reaches a steady state concentration in less time than PM 170/110. Also shown in these figures is the effect of temperature on the time to reach steady state. Overall, temperature effects are not substantial but differences are observed in uptake between the two SPME fibers despite the fact that the equilibrium uptake is not significantly affected by temperature (as shown in Section 3).

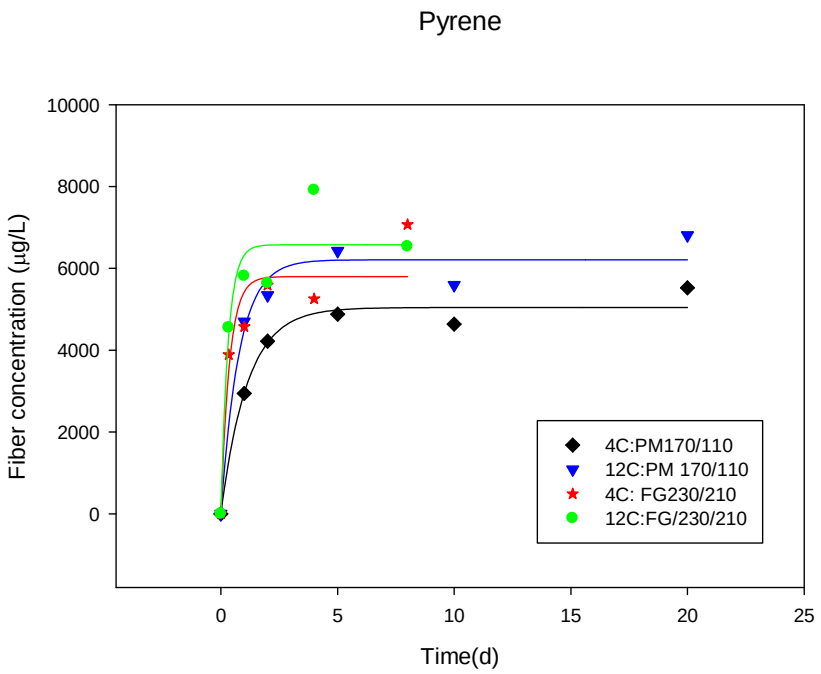

Figure 10: Uptake of Pyrene in Sediment to SPME Fiber at 4 Different Conditions with 2 Types of SPME Fiber and 2 Constant Temperatures (4°C and 12°C)**.**

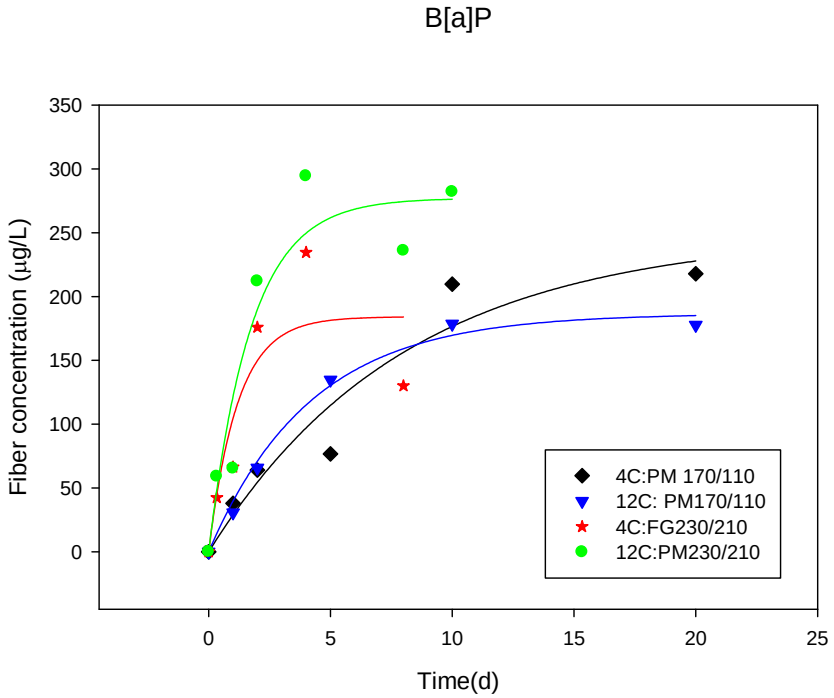

Figure 9: Uptake of B[a]P in Sediment to SPME Fiber at 4 Different Conditions with 2 Types of SPME Fiber and 2 Constant Temperatures (4°C and 12°C)**.**

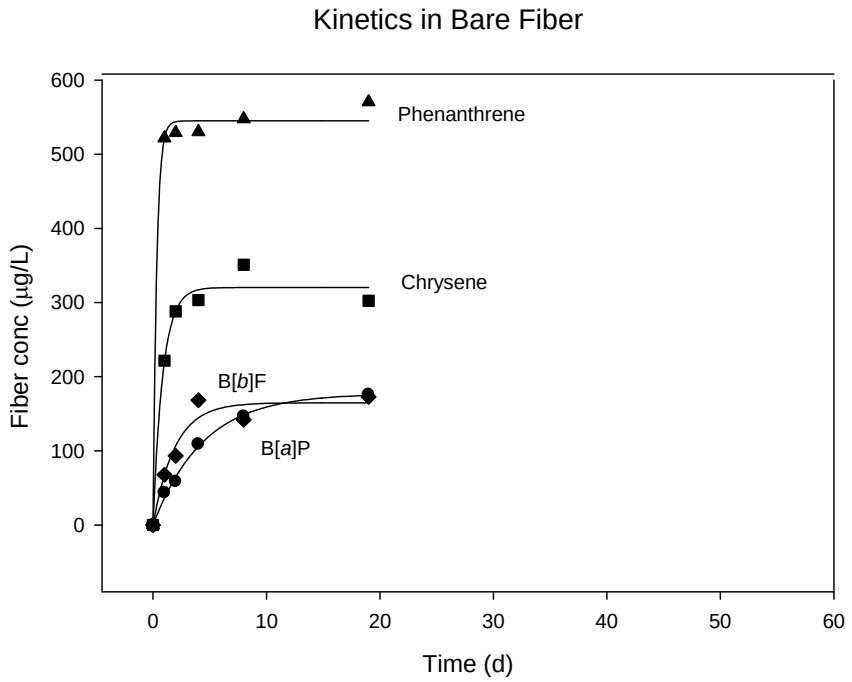

Figure 10: Uptake Kinetics of PAH in Bare Fiber at 25°C with PM 170/110.

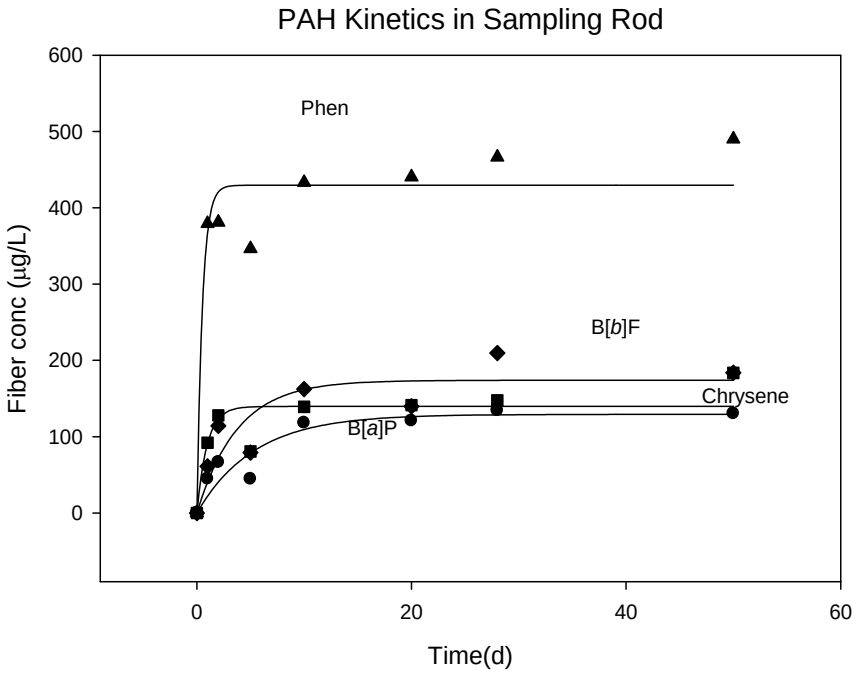

Figure 11: Uptake Kinetics of PAH in Sampling Rod at 25°C with PM 170/110.

Similarly, PCB compounds were also analyzed to determine the differences in kinetic uptake between the two fiber types and the effect of temperature as well as comparisons to bare fiber and fiber in an SPME sampling device. The following figures display data from two PCB congeners, 52 and 138. Times to steady state as estimated by the exponential rise fit are shown in the following table for the data for select congeners analyzed.

Table 15: Time (day) **to Achieve 95% of Equilibrium for PCB Compounds. These Represent Exponential Models Fit to Measurements of Fiber Uptake at Least Five Individual Times.**

PCBs Time to 95% of Steady State (d)								
Condition	Fiber Type	Temp	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180
Fiber in Sediment	PM 170/110	25°C	20	28			54	93
		12°C		10	16	8	8	
		4°C		16	34	14	13	
	FG 230/210	12°C		2.2	2.4	5.5	3.0	
		4°C		4.3	2.2	8.8	3.2	
Fiber in Rod in Sediment	PM 170/110	25°C	34	65			63	72

Compared to PAH, PCB overall require a significantly longer time to reach steady state in PDMS matrix when exposed to contaminated sediment environments. PCB uptake kinetics were not measured in the water due to problems with sorption losses and volatilization of compounds during the experiment and uncertainty in the time to reach equilibrium. The uncertainty in the time to reach 95% of steady state for PCB is reported in the table below. An uncertainty of 32 days is observed for SPME fiber PM 170/110 within a sampling device in sediment for PCB 180 with a time to steady state estimated as 72 days.

Table 16: Standard Error in Time to 95% of Steady State for PCB.

Standard Error in Time to 95% of Steady State (d)								
Condition	Fiber Type	Temp	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180
Fiber in Sediment	PM 170/110	25°C	4.76	2.26			8.03	32.67
		12°C		4.91	2.13	4.95	4.95	
		4°C		4.49	5.00	8.20	8.14	
	FG 230/210	12°C		0.59	1.00	0.78	0.82	
		4°C		1.05	1.03	2.56	1.15	
Fiber in Rod in Sediment	PM 170/110	25°C	13.38	27.70			27.14	32.10

PCB 52

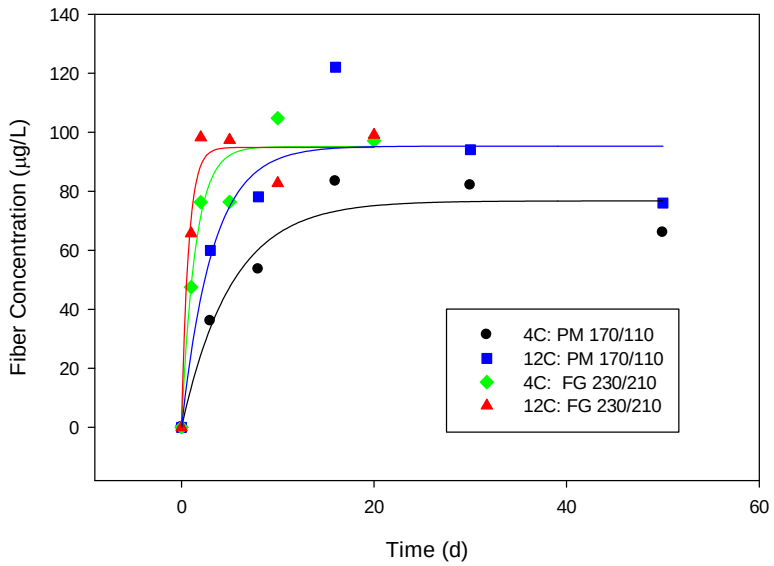

Figure 12: Uptake of PCB 52 in Sediment to SPME Fiber at 4 Different Conditions with 2 Types of SPME Fiber and 2 Constant Temperature (4°C and 12°C)**.**

PCB 138

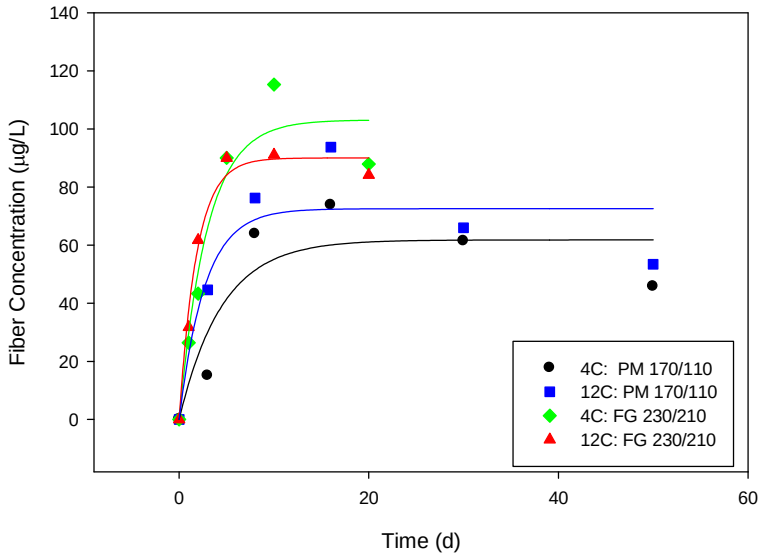

Figure 13: Uptake of PCB 138 in Sediment to SPME Fiber at 4 Different Conditions with 2 Types of SPME Fiber and 2 Constant Temperatures (4°C and 12°C)**.**

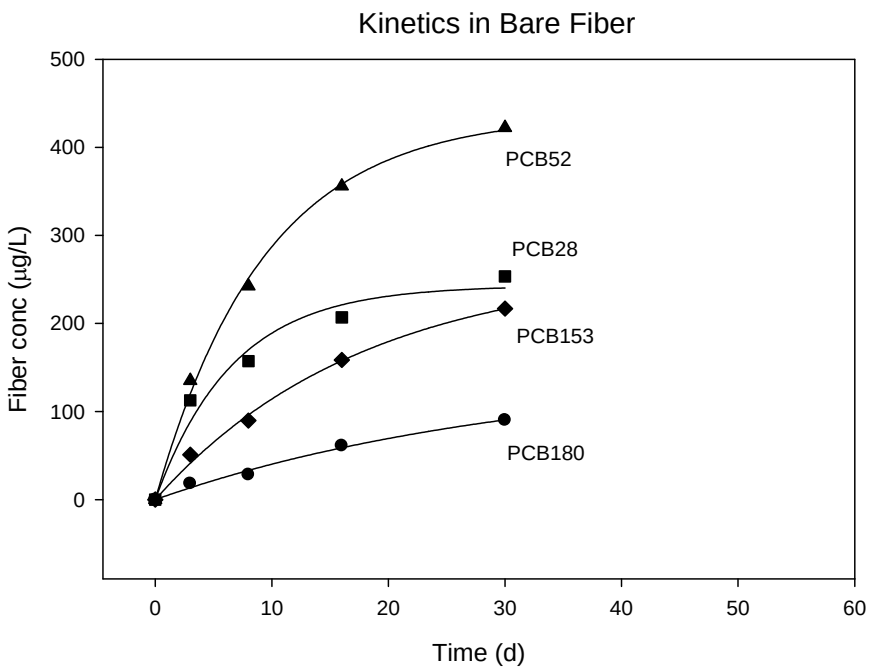

Figure 16: Uptake Kinetics of PCB in Bare Fiber at 25°C with PM 170/110.

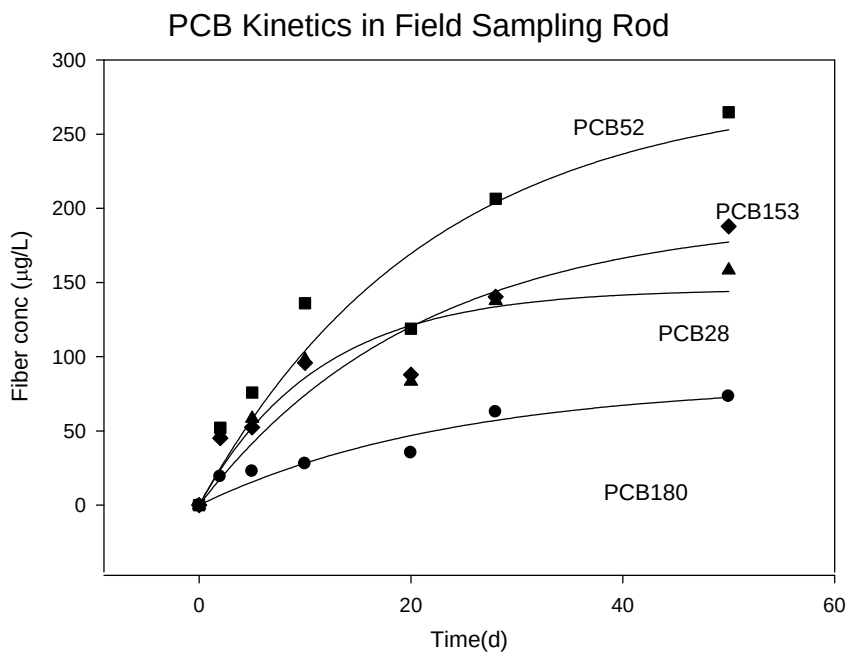

Figure 17: Uptake Kinetics of PCB in Sampling Rod at 25°C with PM 170/110.

The best estimates for the percentage of steady state if a 30-day equilibration time is used for SPME fiber PM 170/110 in the sampling rod is shown below. For the more hydrophobic PCB, only an average 74% of steady state has been reached in a 30 day equilibration period. For field

experiments, either a long equilibration time should be utilized or alternate fiber FG 230/210 should be deployed.

Table 17: Estimate of Steady State Using a 30-day Equilibration Period in SPME Sampling Device with PM 170/110.

Compound	% of Steady State Achieved	Std Error
PCB 28	93%	22%
PCB 52	75%	44%
PCB 153	76%	44%
PCB 180	71%	48%

Research has also been conducted on developing a model of equilibration so that the effect of different geometry, etc; can be evaluated. The model considers mass transfer limited diffusion onto a cylindrical annulus, the geometry of our SPME fibers. The diffusion coefficient for a compound in the SPME fiber can be estimated by transient uptake experiments in a tumbled (well-mixed) system and then the mass transfer coefficient can be estimated for the bare fiber or the sheathed rod experiments by comparison to the tumbled water uptake measurements. The time to achieve a certain fraction of steady state associated with the fraction degree of completion M/M_0 is given by

$$t_1 = \frac{-1}{D\alpha_1^2} \ln \left\{ \frac{\left(M/M_\infty - 1 \right)\left(b^2 - a^2 \right)\alpha_1 \left[\left(1 + \left(D\alpha_1/k \right)^2 \right) J_1^2(a\alpha_1) - \left(D/k\, \alpha_1 J_1(b\alpha_1 - J_0(b\alpha_1) \right) \right]}{2\pi b J_1(a\alpha_1)\left[D/k\, \alpha_1 J_1(b\alpha_1) - J_0(b\alpha_1) \right]\left[Y_1(a\alpha_1) J_1(b\alpha_1) - Y_1(b\alpha_1) J_1(a\alpha_1) \right]} \right\}$$

Where Y and J and Bessel functions. Key parameters in the model include D, diffusivity in the fiber, k, the mass transfer coefficient at the fiber-water interface, and b and a, the outer and inner radius of the fiber, respectively. This also requires solution of the recurrence relationship for the eigenvalues α which are approximately given by (for large values of α) as

$$\alpha_n = \frac{\pi}{b-a}(n - 1/2) .$$

Fitting of the model to observations to determine effective diffusivity and mass transfer coefficient is underway. Existing uptake kinetics in stirred water systems will be used to determine compound diffusivity in the fiber and existing uptake kinetics with the bare fiber and fiber in a sheathed field deployable system will be used to estimate mass transfer resistances external to the fiber. The model will then be used to predict steady state times for different compounds and under different conditions.

The model reduces to a form that is equivalent to Equation 11 when external mass transfer resistances control contaminant uptake into the fiber.

4.3 Limits of Vertical Resolution using a Multiple Layered System

One of the primary advantages of the proposed insertion of a length of vertical fiber into the sediments is the potential to determine profiles in pore water concentration. Vertical resolution is controlled by two factors:

1. Detection limits which define the minimum length of fiber that can be used to measure the pore water concentration
2. Vertical spreading of pore water in the protective sheath of the field deployable rod leading to blurred or smoothed gradients in concentration.

The first factor has been addressed previously. The second factor was addressed by setting up a layered system with a layer of clean sand above a contaminated sediment layer. An SPME fiber with the field deployable sheath was inserted such that 4 cm of the fiber would be exposed to the sand layer and 11 cm would be exposed to the sediments. Anacostia river sediments were again used as the contaminated sediments. A graduated cylinder was partially filled with the sediment and then the rod was placed into cylinder and sand covered the sediment layer. Care was taken to keep the layers from intermixing. The sand was then saturated with distilled water and the top of the cylinder was covered with film and aluminum foil and placed in a 25°C room for 16 days.

After the 16-day period, the rod was removed and fiber cut into varying lengths, 2 cm sections of fiber were cut for the sediment layer and 4-1 cm fiber sections were cut for the overlying sand layer. Fiber samples were inserted into glass insert and 100 µL of acetonitrile was added and then analyzed via HPLC.

Phenanthrene is relatively low sorbing and mobile and thus any intermixing or consolidation within the sediments would give rise to significant phenanthrene migration. This is shown in Figure 14. Although much of the phenanthrene observed in the overlying sand layer was believed due to the intermixing and consolidation, it is not possible to eliminate sampling device associated migration as a cause.

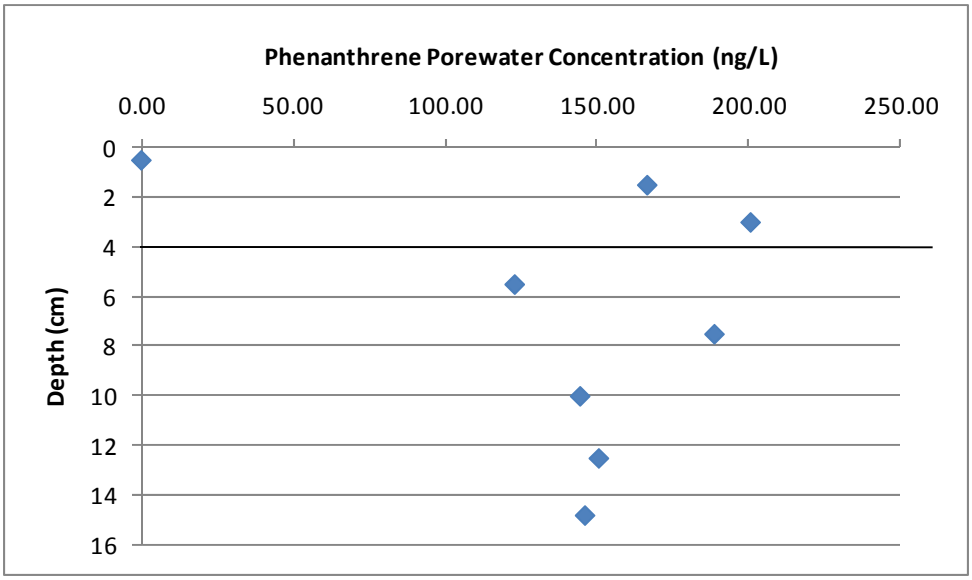

Figure 14: Phenanthrene Concentration Over Depth. The Solid Line Indicates the Location of the Sand Sediment Interface with Sand Above and Sediment Below.

A better indication of the potential for the sampling device to avoid smoothing concentration gradients is from higher molecular weight compounds that would not exhibit significant migration due to the minor intermixing and consolidation processes. A pyrene profile is shown in Figure 19 and illustrates that the device does not itself cause significant intermixing or profile smoothing, at least for compounds more sorbing than phenanthrene. This conclusion was further supported by chrysene profiles, shown in Figure 20. These data suggest that sharp concentration gradients, with a vertical resolution of at least 1 cm, are possible with the sampling device, at least for moderately hydrophobic and hydrophobic compounds that would be minimally disturbed by insertion of the device.

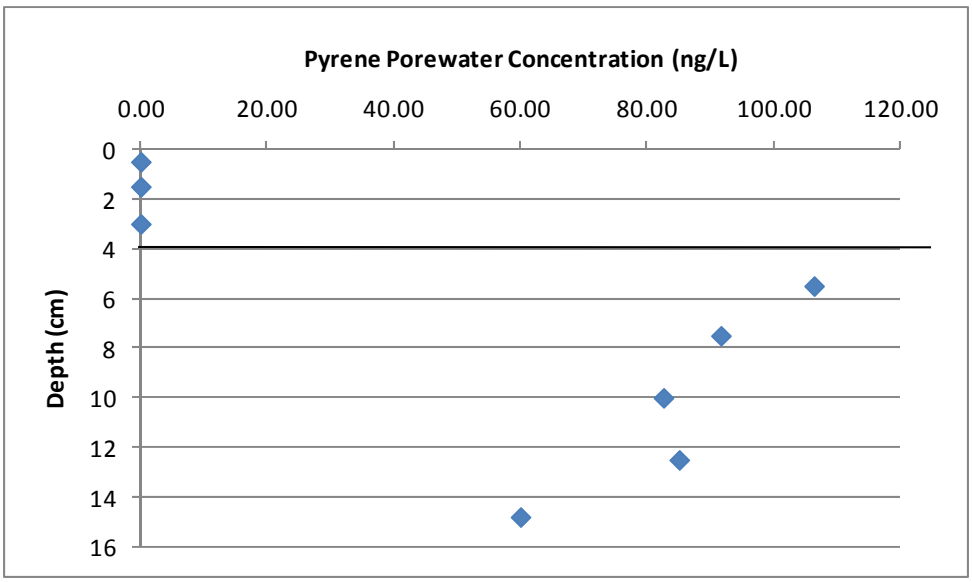

Figure 19: Pyrene Concentration Over Depth. The Solid Line Indicates the Location of the Sand Sediment Interface with Sand Above and Sediment Below.

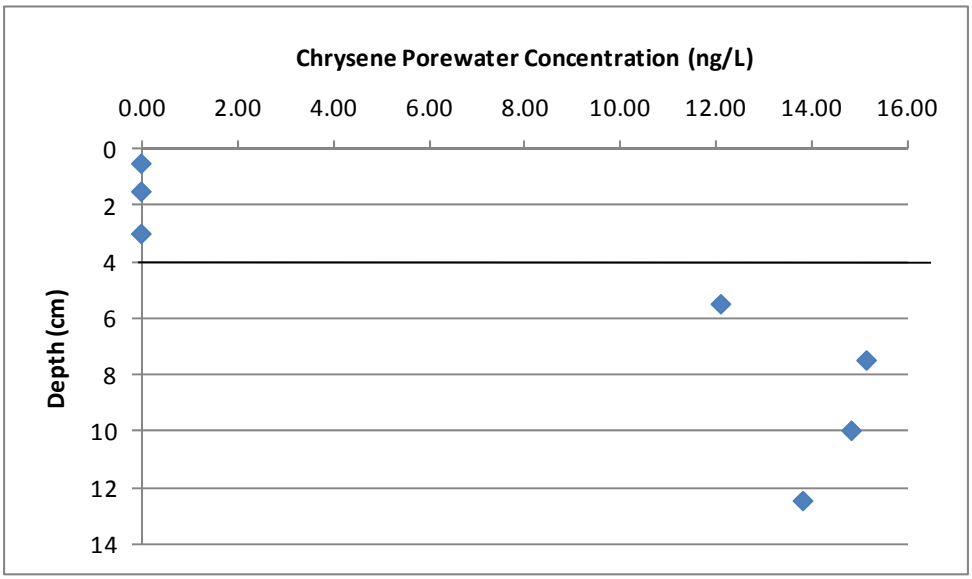

Figure 20: Chrysene Concentration Over Depth. The Solid Line Indicates the Location of the Sand Sediment Interface with Sand Above and Sediment Below.

4.4 Evaluation of Sample Integrity

One concern with the sampling devices is loss of analytes to the air while in transit or while waiting to be analyzed. Experiments were conducted to observe the loss to the air of analytes from the fiber. SPME fiber was exposed to a PAH solution of high concentration (25 µL of 66.82 ppm stock solution) in a 500 mL volume of deionized water. Two fibers (2 replicates) approximately 8 cm were exposed to the solution and allowed to equilibrate for 2 days. The fiber was withdrawn from the water and one sample was analyzed immediately. The remainder of the fiber was exposed to ambient air (22°C, ~50% humidity) for 24 hr, 48 hr, 96 hr, 7 days,

and 14 days. Once each 1 cm of fiber was cut, it was immediately placed into 100 µL of acetonitrile solvent and analyzed using HPLC.

Data for phenanthrene, pyrene, chrysene, and B[a]P are plotted below with the standard error. Significant loss is observed after just 1 day of fiber exposure to the air, especially for more volatile compounds such as phenanthrene (Figure 21). Substantial but manageable losses are also observed with other more sorbing and less volatile compounds such as pyrene, chrysene or benzo[a]pyrene (22, Figure 16, and Figure 17). More volatile species must be analyzed or stabilized by extraction into solvent immediately upon retrieval to avoid this loss. Preliminary data also suggest that shipment cold, wrapped in plastic bags to retain moisture and limit evaporation of water or contaminant would also substantially reduce this lost. Essentially identical concentration profiles were detected in fibers processed on the day of retrieval in the field and upon shipment back to the laboratory prior to processing. These results will be discussed in a field demonstration report. The evaporative losses from room temperature exposure of the fibers to ambient air simply suggests that fibers samples should be handled with a degree of care and control similar to that for conventional liquid samples.

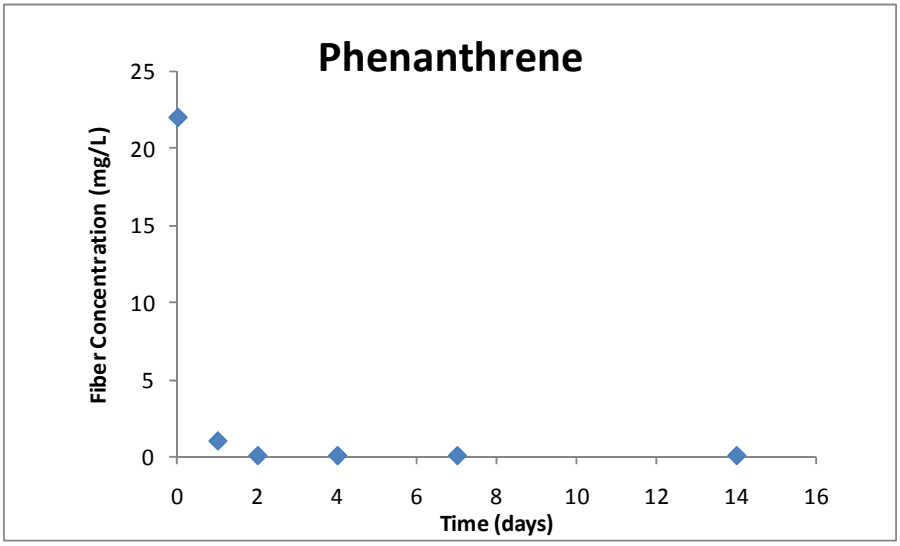

Figure 21: Phenanthrene Loss from Fiber Over Time After Exposure to Ambient Air.

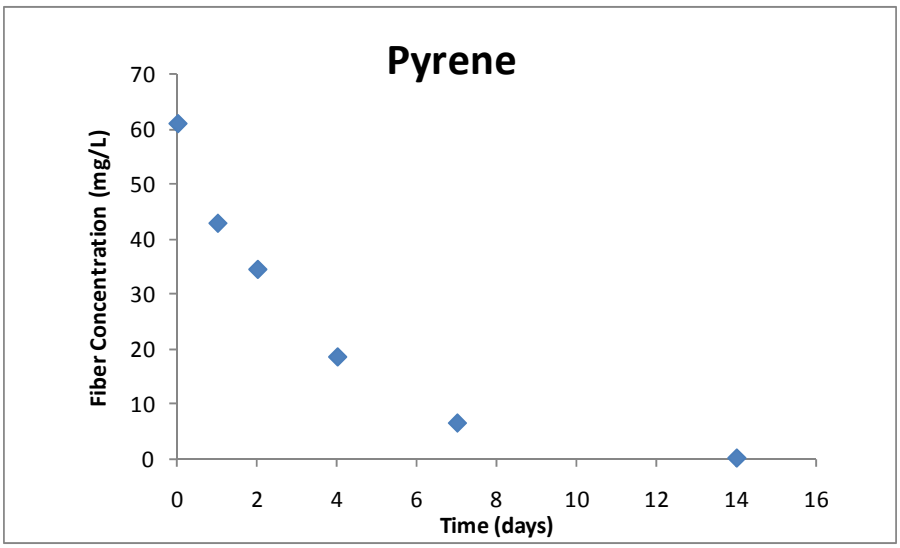

Figure 15: Pyrene Loss from Fiber Over Time After Exposure to Ambient Air.

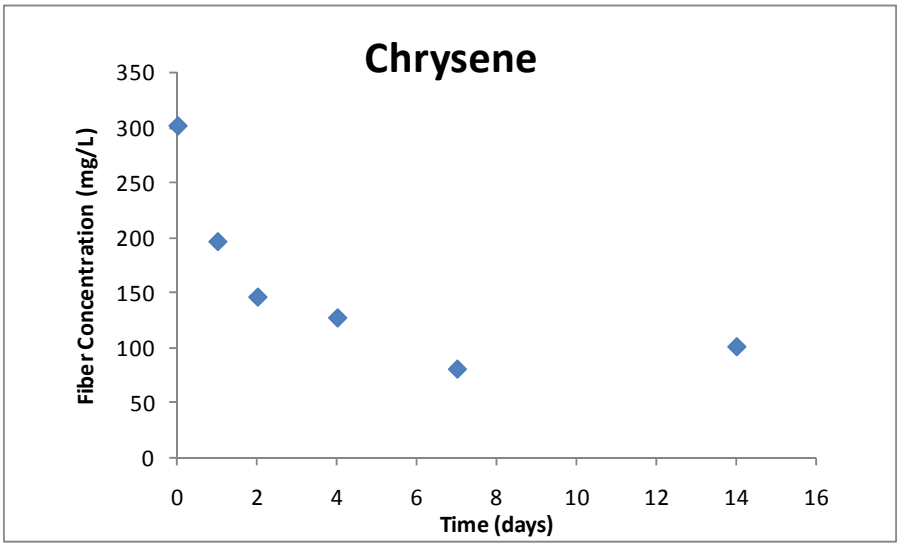

Figure 16: Chrysene Loss from Fiber Over Time After Exposure to Ambient Air.

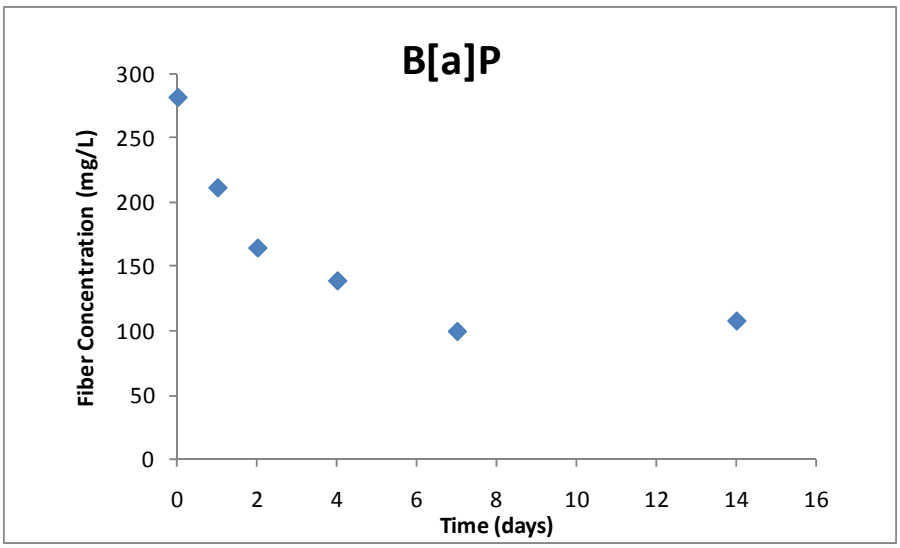

Figure 17: Benzo[a]pyrene Loss from Fiber Over Time After Exposure to Ambient Air.

5. SPME USED TO PREDICT BIOAVAILABILITY

5.1 Bioaccumulation of PAH and PCB by *Ilyodrilus templetoni* in Anacostia River Sediment

The primary purpose of the field deployable or laboratory measurement of pore water by SPME is to use pore water concentrations as an indicator of bioavailability. The focus of our efforts in this regard is on a dose proportional response in benthic organisms, i.e. bioaccumulation, rather than on a threshold dose response such as toxicity. The benthic organisms of primary interest are deposit feeding organisms oligochaetes and polychaetes that are responsible for the most intense sediment reworking and are typically present in high densities in contaminated sediments (e.g. Reible et al. 1996). Due to their ability to tolerate significant environmental stresses, they are often the only organisms found in heavily contaminated environments or are found in the highest densities. Lu et al. (2003), Lu et al. (2004) and Lu et al. (2006) in our group had previously shown that pore water concentration measurements by conventional means correlate well with uptake in freshwater tubificids. Other groups had shown similar data (e.g. Kraiij et al. 2003).

An experiment was designed to assess the bioavailability and bioaccumulation of PAH and PCB from Anacostia River, Washington D.C. sediments, to a deposit-feeding freshwater oligochaete, *Ilyodrilus templetoni*. This is effectively an extension of the work of Lu et al. (2006) using more compounds and SPME to evaluate pore water concentrations. Sediment from the Anacostia River, Washington D.C. was collected as part of a continuing evaluation of active sediment capping. Surficial sediments were collected from a control area at a water depth between 10 and 15 ft. Total PAH concentration is approximately 20 mg/kg with phenanthrene 1.67 mg/kg, pyrene 4.64 mg/kg, chrysene 1.54 mg/kg, benzo(k)fluoranthene 0.74 mg/kg, and benzo (a) pyrene 1.57 mg/kg. Total organic carbon (TOC) is 5.4-5.8%.

This initial test was a randomized design of 3 replicates per sample interval. Although prior work within the Reible group showed that *I. templetoni* reached apparent steady state within 7 days (Lu 2003), more hydrophobic PCB were likely to take longer to equilibrate in tissue, so experiments were conducted for up to 50 days to ensure steady-state tissue concentrations had been reached. Accumulation experiments were conducted in 50 mL polypropylene centrifuge tubes (Lotufo and Fleeger 1996). At the beginning of the experiment, approximately 50 g wet sediment (~50% water content) was added to each tube and allowed to settle, then 20 sexually mature *I. templetoni* worms of similar size were added to each tube. After all worms burrowed into the sediment, a thin layer of cheesecloth was placed on the sediment surface and secured with a polyvinyl chloride split ring. Roughly 2 cm overlying tap water was placed in each tube. Tubes were held in a rack and water was replaced every other day. Tissue samples were analyzed for PAH and PCB concentration on days 0, 7, 14, 28, and 50 of the experiment to determine when steady state accumulation was approached.

Steady state was achieved within 28 days for all compounds as illustrated by PCB 180, the most hydrophobic constituent monitored, in Figure 25.

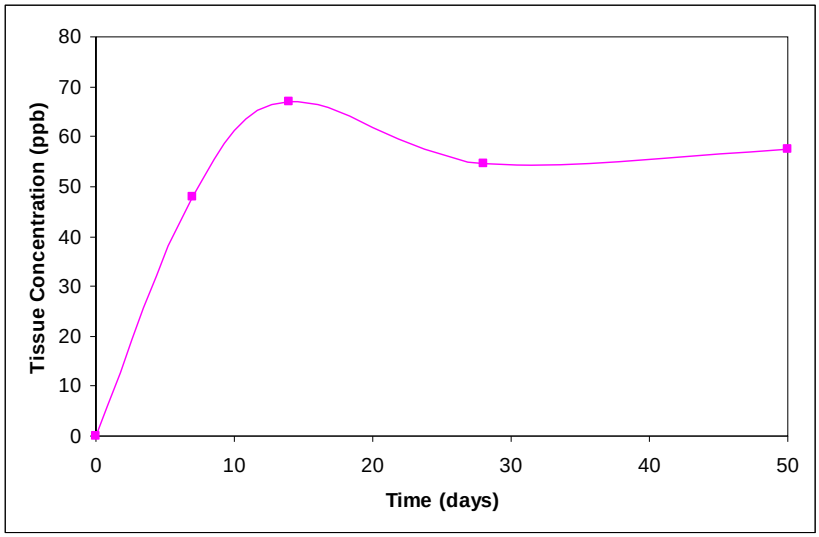

Figure 18: Tissue Concentration Versus Time for Highly Hydrophobic PCB 180.

Steady state accumulation of contaminants in the organisms was compared to bulk sediment concentrations and pore water concentrations measured in this study. Two sets of experiments were conducted and sediment and pore water concentrations of 5 PAH and 5 PCB were measured in both as shown in Table 18.

Table 18: Phase Concentrations (Ilyodrilus Templetoni in Anacostia River Sediment)**.**

Compound	Batch 1 (f_{oc}=0.0585)					Batch 2 (f_{oc}=0.0535)				
	C_{sed} ng/g	C_f ng/mL	C_{pw} ng/L	C_t/f_{lipid} ng/g	BSAF	C_{sed} ng/g	C_f ng/mL	C_{pw} ng/L	C_t/f_{lipid} ng/g	BSAF
Phenanthrene	2420	1082	213	8025	0.19	2160	1160	228	11052	0.27
Pyrene	5400	10911	1124	14519	0.16	5612	17832	999	30108	0.29
Chrysene	2170	325	5.6	3740	0.10	1522	335	5.8	3472	0.12
Benzo[b]fluoranthene	2510	205	2.1	2622	0.06	2020	144	1.5	2545	0.07
Benzo[k]fluoranthene	1970	88	0.8	1342	0.04	1130	87	0.8	1251	0.06
Benzo[a]pyrene	2670	142	1.0	3552	0.08	2580	159	1.1	3195	0.07
PCB#28	23.9	241	2.1	743	1.81	56.3	312	2.7	1454	1.38
PCB #52	33.6	432	1.8	2034	3.53	34.7	680	2.8	3635	5.60
PCB #153	177	438	0.31	1604	0.53	91.3	515	0.37	2593	1.52
PCB#138	155	428	0.27	1928	0.72	89.8	399	0.25	2795	1.67
PCB#180	124	251	0.10	969	0.46	63.9	212	0.0085	1407	1.18

C_{sed} –Sediment concentration, C_f – Fiber Concentration, C_{pw}- pore water concentration, C_t-organism tissue concentration, f_{lipid}- fraction lipid, f_{oc}- fraction organic carbon in sediments

Measured tissue concentrations are also shown in Table 18 as biota-sediment accumulation factors (BSAF). The BSAF is the ratio of the tissue concentration normalized by lipid fraction to the sediment concentration normalized by organic carbon fraction.

$$BSAF = \frac{C_t / f_{lipid}}{C_{sed} / f_{oc}}$$ **Equation 18**

Where C_t /f_{lipid} is the lipid normalized tissue concentration of a contaminant and C_{sed}/f_{oc} is the organic carbon normalized sediment concentration. Bulk sediment concentration does not describe the observed tissue accumulation as illustrated in Figure 19 for PCB. From the definition of the BSAF, the data plotted as in Figure 19 should describe a constant, i.e. a constant BSAF.

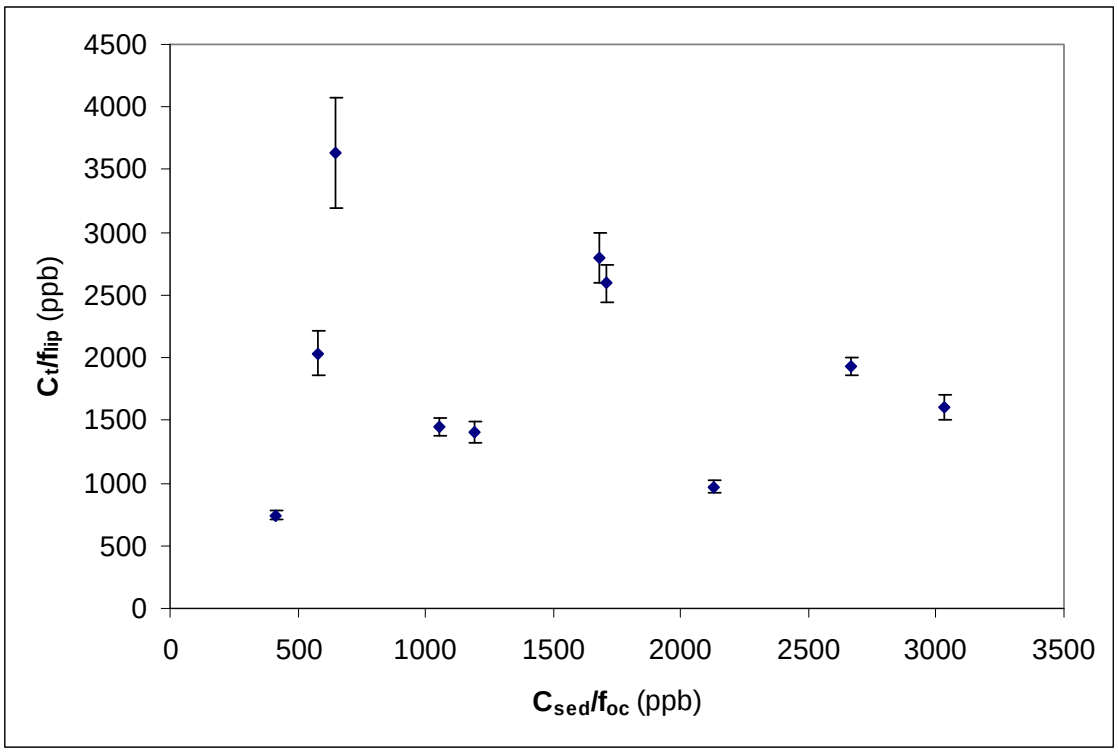

Figure 19: PCB Mean Lipid-normalized tissue (+/- Std Error) **Versus Bulk Sediment Concentration** (*Ilyodrilus* in Anacostia River Sediments)**.**

The presumption in the current work is that the pore water concentration or the surrogate of SPME fiber concentration would better indicate availability for uptake and accumulation in the benthic organism. The results of experiments completed in this research are compared to these earlier studies. Results from experiments completed with Anacostia River sediment are shown below specifically displaying the relationship between measured fiber concentration and lipid normalized tissue, pore water concentration and lipid normalized tissue, and K_{ow} and BCF.

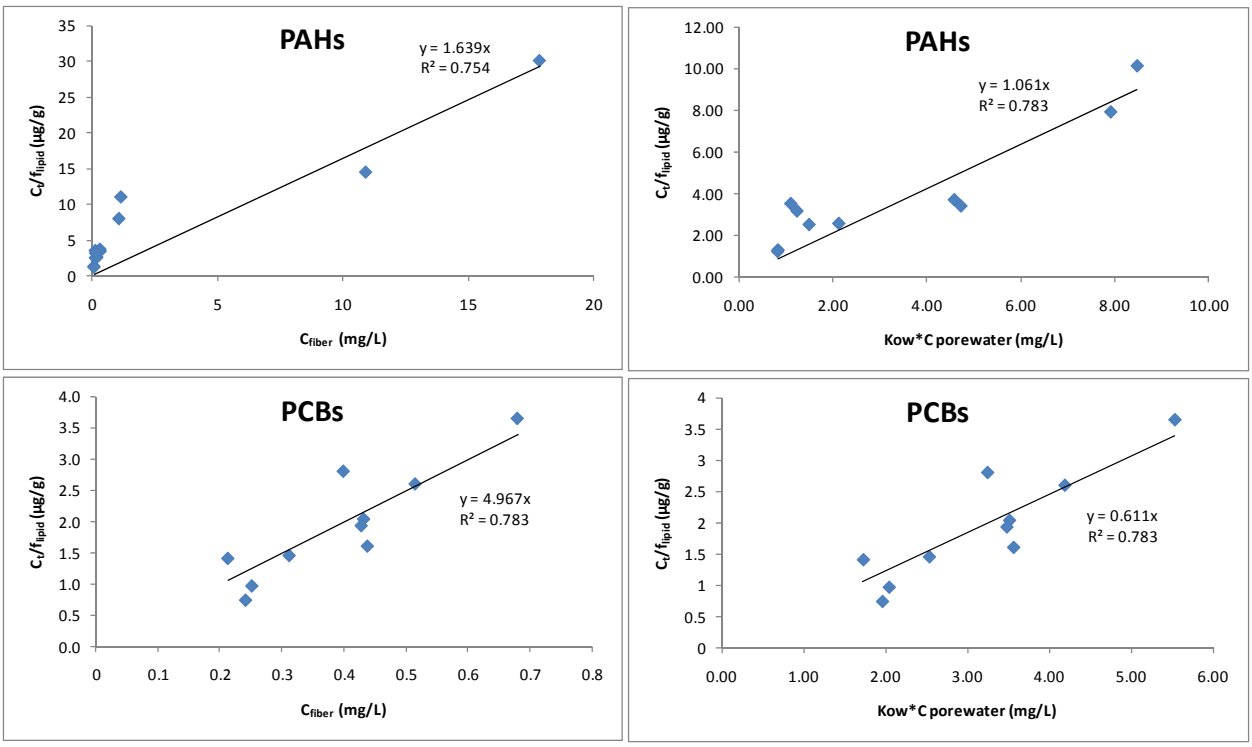

Figure 20: Correlation of PAH and PCB SPME Fiber (left) **and Pore Water Concentration** (right) **to Organism Lipid Normalized Body Burden** (*Ilyodrilus* in Anacostia River Sediments) (Drake 2007)**.**

Comparing tissue concentrations to SPME fiber measurements displays the effectiveness of using SPME to determine and predict bioavailability. The correlation between tissue and pore water multiplied by the K_{ow} illustrates the relationship of organism body burden to abundance of contaminants in pore water and hydrophobicity. Bioconcentration factors (BCF) were used to assess accumulation as a direct function of the measured pore water concentrations for water-borne routes of exposure. The BCF is described as the ratio of chemical concentration in an organism to that of the surrounding water and therefore characterizes the accumulation of pollutants through chemical partitioning from the aqueous phase into an organic phase. High correlation between the measured and predicted BCF defines a good relationship between the tissue and pore water concentrations.

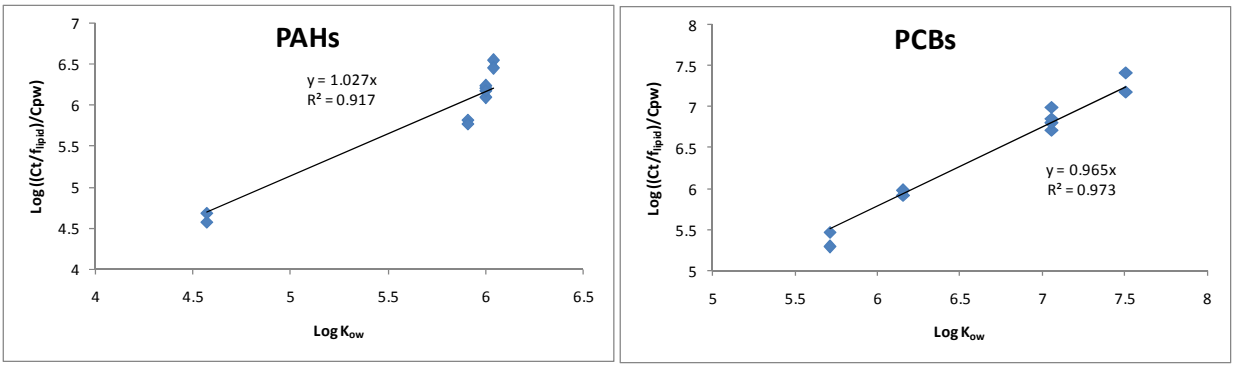

Figure 21: Measured and Predicted BCF Values for PAH and PCB (*Ilydorilus* in Anacostia River Sediment) (Drake 2007)**.**

The concept of a BSAF is that the partitioning of the pore water to sediment organic carbon and pore water to organism lipids is analogous and differing by at most a constant, the ratio of the partition coefficient to lipids versus that to sediment organic carbon, K_{lipid} / K_{oc}. The difficulty is that the relationship of the sediment concentration to pore water concentration is distorted by desorption resistant phenomena. That is, the desorption from the sediments, which is the source of the contamination, does not describe the sorption to the organism lipids. This suggests that the ratio of the actual pore water concentration to that predicted by reversible desorption from the sediments (that is, in the absence of desorption resistance) would be a better indication of the BSAF.

$$BSAF_{predicted} = \frac{K_{lipid}}{K_{oc}} \times \left(\frac{C_{porewater,observed}}{C_{porewater,theoretical}} \right) \qquad \textbf{Equation 19}$$

This relationship is supported by the measured pore water data using SPME as shown in Figure 29 and Figure 30. In these figures, the ratio of K_{lipid}/K_{oc} is assumed approximately 1.8.

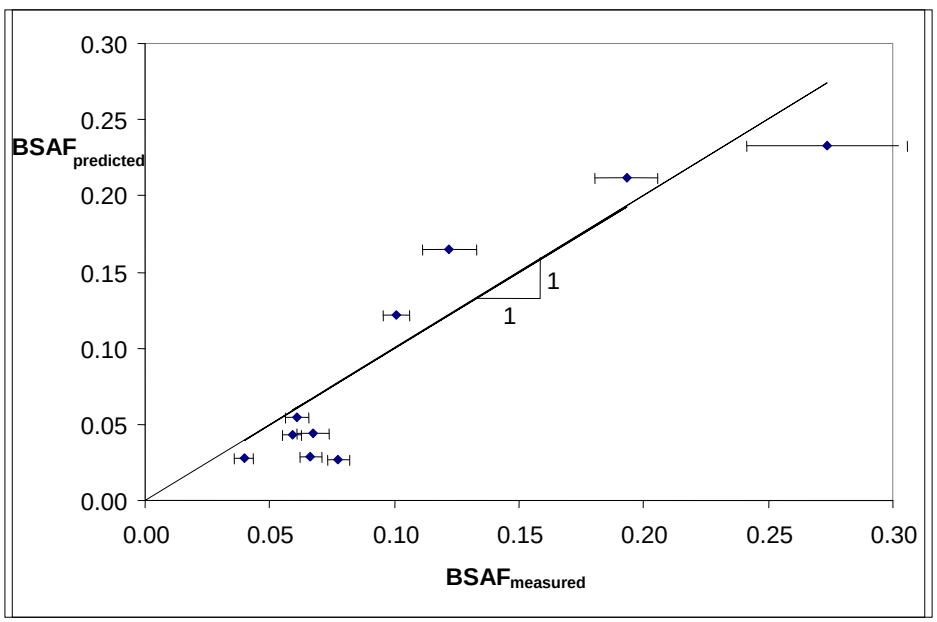

Figure 29: BSAF Predictions for PAH Assuming K_{lipid}/K_{oc}=1.8.

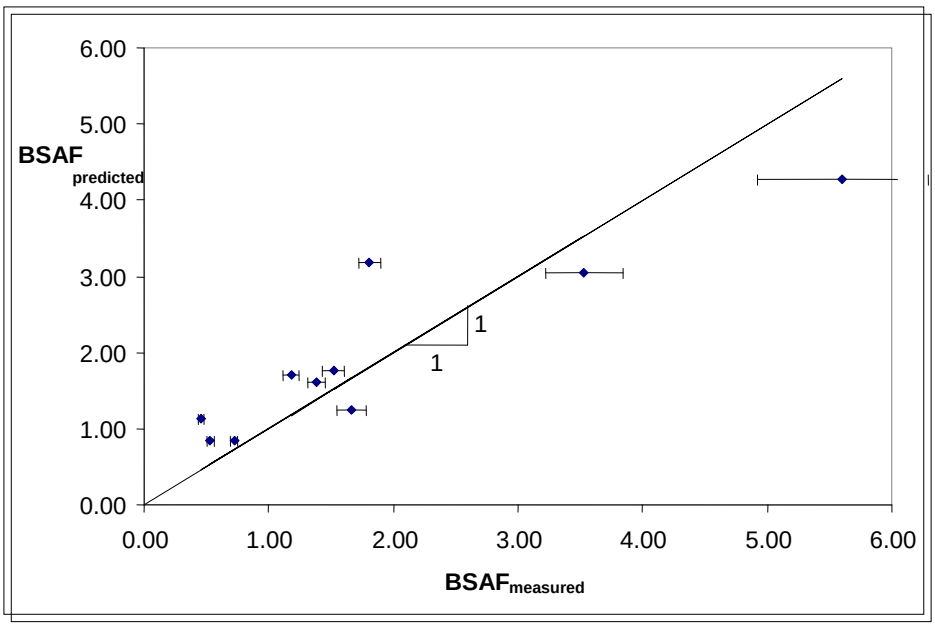

Figure 30: BSAF Predictions for PCB Assuming K_{lipid}/K_{oc}=1.8.

These data are strong support for the use of pore water concentrations to predict accumulation in organisms although not all organisms and sediment combinations would be expected to have this specific correlation. In addition, the use of BSAFs implies that we know the organic carbon based partition coefficient that for many compounds is subject to significant uncertainty. It does appear, however, that SPME fiber concentration or pore water concentration can be a good indicator of potential for accumulation for both PAH and PCB.

5.2 Bioaccumulation of PAH and PCB by *Ilyodrilus templetoni* in Sequential Dilution Experiment

A second set of experiments were conducted using sediment more highly contaminated with PCB. New Bedford Harbor sediment was diluted with freshwater sediment from Brown Lake, in Vicksburg, Mississippi. The dilution with freshwater sediment allowed the use of the *Ilyodrilus templetoni,* a freshwater deposit feeding oligochaete that was used in the preceding study. Sediment from the subtidal zone of New Bedford Harbor, New Bedford, Massachusetts, was collected in the Spring of 2001. Measured concentrations in the collected sediment were 124 mg/kg total PCB and 27 mg/kg of 16 Environmental Protection Agency (EPA) priority pollutant PAH. The organic carbon content of the sediment is approximately 4 %. Sediment from Browns Lake (Vicksburg., Mississippi) was collected in the fall of 2006 from a deep portion of the lake. The total PCB and 16 EPA priority pollutant PAH concentration was below the laboratory reporting limit. The organic carbon content was 0.7 %. This sediment was used to prepare sequential dilutions of New Bedford Harbor sediment. Four dilution treatments were employed (25%, 12%, 6%, and 3% New Bedford Harbor sediment by dry weight with the remainder Brown Lake sediment). Prior to the experiments, the sediment was homogenized.

Eighteen glass jars were utilized for the bioaccumulation experiment. Four replicates for each of the four sequential dilutions and two control jars were filled with 200 mL of sediment. The

volume of sediment added was based on a dry to weight ratio of approximately 50% for each of the samples. Figure 31 indicates the bulk sediment concentration of PAH was proportional to the dilution with clean sediment. The linear relationship shown below in Figure 31 displays how accurate the dilutions percentages are with regard to the measured concentrations. The organic carbon fractions of the 3, 6, 12 and 25% dilutions were 0.94, 0.83, 1.11, and 1.49% , respectively, approximately consistent with the desired dilutions although the 3 and 6% dilutions were significantly different in organic carbon content from each other or from pure Brown's Lake sediment. Additional analytical results for Figure 31 can be found in Appendix C (Table C3 and C4).

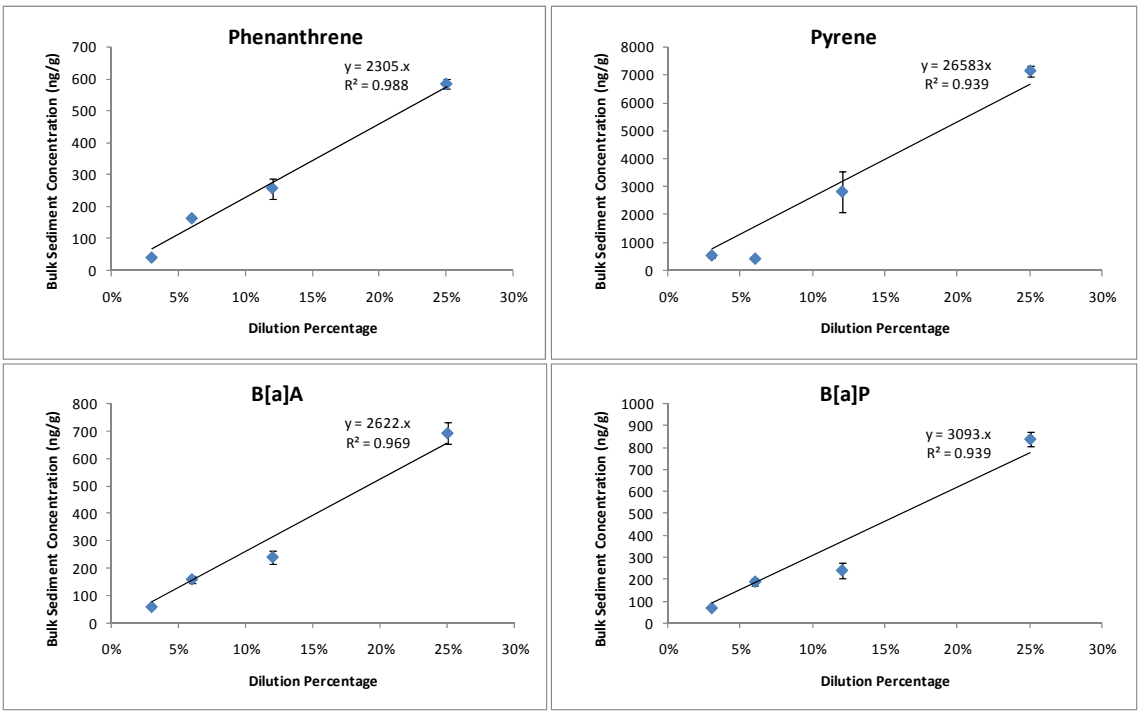

Figure 31: Comparing Bulk Sediment Concentration (ng/g) **to the Dilution of New Bedford Harbor Sediment with Brown's Lake Sediment.**

150 mL of artificial pond water (APW) was created (0.5 mM NaCl, 0.2mM $NaHCO_3$, 0.05 mM KCl, 0.4 mM $CaCl_3$) and added for each jar. After overnight consolidation, SPME fibers were introduced to the sediment. Both PAH and PCB concentrations were measured using the SPME fibers. Four fibers of 2.5 cm were cut and injected through a septa of a 2 mL autosampler cap and then placed into the bottom of the sediment and its location was marked for retrieval. These fibers were retrieved at the termination of the experiment before the organisms were removed. *Ilyodrilus templetoni maintained* in cultures at University of Texas were introduced to the sediment in groups of sixty worms per jar. Two groups of twenty were used for PAH and PCB tissue analysis and the other group were used for lipid analysis. The worms were allowed to burrow into the sediment before the overlying 150 mL of APW was added slowly so as not to disturb the sediment or the organisms. Aluminum foil was placed over the jars with holes for aeration and the jars were stored in a controlled temperature (25°C) room for 28 days. The overlying water was changed three times a week by siphoning off without disturbing the sediment layer.

Figure 32 depicts one of the worm environments from the side indicating the intensity of the burrowing activity by the organisms.

Figure 32: Side View of Microcosm with Evidence of Burrowing into the New Bedford Harbor Marine Sediment Diluted with Brown's Lake freshwater Sediment.

The artificial pond water alone contained 6.88 mg/L dissolved oxygen while the experiment jars ranged from roughly 3-5 mg/L. The organisms are tolerant of low oxygen levels and these oxygen levels are sufficient to maintain good organism activity.

After a 28-day period, the organisms were removed by sieving the sediment through a 0.5 mm sieve and then placed in clean artificial pond water to depurate their gut contents. A sediment-purging period of 6 hour was employed for all experimental organisms to minimize excessive depuration of chemicals from tissue. After depuration, worms were weighed in groups of twenty and transferred to either glass scintillation vials for PAH and PCB analysis or 15 mL centrifuge tubes for lipid analysis. From each jar with 60 worms, one of each analysis using 20 worms was performed. Samples were then placed in the freezer until analysis. Twenty worms were extracted from each jar and the individual worm weights from the dilution replicates can be found in Appendix C (Tables C7 and C8).

SPME analysis was conducted for both PAH and PCB. The SPME within the Teflon cap was extracted from the sediment with tweezers before the organisms were extracted by sieving. The fiber was rinsed with distilled water to remove any sediment debris. Five cm of fiber was used for PAH analysis and 5 cm of fiber was used for PCB analysis. The fiber was transferred to the bottom of a glass vial insert and 100 µL of either acetonitrile (PAH) or hexane (PCB) was added to the insert in a 2 mL glass sample vial with cap. SPME fiber concentrations were converted to pore water concentrations by using a fiber-water partition coefficient. For PAH compounds, the

K_f values used were determined experimentally, as described in earlier sections. For PCB compounds, K_f values were estimated using Mayer's correlation Log K_f = Log K_{ow} – 0.9 and K_{ow} values were estimated using a correlation based on the chlorine number of the specific PCB, Log K_{ow}=0.45N_{Cl}+4.36 (deBruijn, 1989).

Tissue analysis was completed by first grinding tissue with sodium sulfate followed by addition of solvent, dichloromethane (20 mL) and then sonicating for 25 minutes. This solvent was then analyzed the following day by first extracting 2 mL of the 20 mL, concentrating, and exchanging DCM for acetonitrile (PAH) or hexane (PCB). PAH samples were further concentrated and analyzed by HPLC while PCB samples were cleaned using a silica gel column based on EPA method 3630C. The cleaned PCB sample was then concentrated and analyzed using gas chromatography.

Table 19 summarizes the accumulated tissue concentrations of PAH and PCB, respectively. Further information regarding data analysis and statistics can be found in Appendix C (Tables C7 and C8).

Table 19: Average PAH and PCB Tissue Concentrations.

	Tissue Concentration (ng/g)			
	3%	6%	12%	25%
PAHS				
Phenanthrene	272	413	433	300
Pyrene	554	699	694	1682
Chrysene	156	131	230	207
B[a]A	199	298	434	398
B[b]F	176	210	349	335
B[k]F	82	88	164	151
B[a]P	134	187	318	329
PCBs				
PCB 10	584	902	1070	1147
PCB 28	19059	29815	35789	30038
PCB 52	20158	31479	35293	32609
PCB 153	5904	8697	10903	9770
PCB 139	3478	5250	6986	6374
PCB 180	695	936	1150	1027

For lipid analysis, a 5 mL aliquot of methanol and chloroform was added to the centrifuge tube containing worm tissue. The sample was then sonicated for 30 seconds and allowed to equilibrate at room temperature for four hours. After centrifuging, the liquid phase of each tube was transferred. This was repeated a second time. To remove proteins, 2 mL of distilled water was added to each liquid phase and shaken until the two phases separated. After centrifuging, the overlying phase was decanted into a waste bottle and the bottom phase with lipids was transferred to aluminum planchets and then put on a heated surface to dry overnight. The difference between the two weights (the planchet and the lipid+planchet) is the total weight of lipid and solvent residues. Method blanks and standards were utilized for all of the analysis to check efficiency and potential error. Table 20 displays the lipid analysis results.

Table 20: Average Lipid Percentages.

Dilution	Average % Lipid
3	7.71
6	6.03
12	5.80
25	7.91

The magnitude of the pore water concentrations inferred from the fiber concentrations in this experiment is shown in Table 21. PAH concentrations for each of the analytes increase with increasing dilution schemes. However, the concentrations are not in direct proportion to the dilution. Similar behavior was noted with PCB

Table 21: Measured Pore Water Concentrations for PAH and PCB.

	Porewater Concentrations (ng/L)			
	3%	6%	12%	25%
PAHs				
Phenanthrene	21	32	38	45
Pyrene	52	54	85	133
B[a]A	1.13	2.56	2.63	5.33
B[b]F	0.83	1.02	1.52	2.49
B[k]F	0.26	0.44	0.55	0.83
B[a]P	0.32	0.55	0.70	1.34
PCBs				
PCB10	49	73	95	167
PCB28	144	198	208	404
PCB52	71	97	105	191
PCB153	0.64	0.90	0.98	1.90
PCB138	0.35	0.49	0.56	1.03
PCB180	0.01	0.02	0.03	0.05

The following figures display the relationships between measured fiber concentration and pore water concentration with lipid normalized tissue concentration for both PAH and PCB in the sequential dilution experiment. For both PAH and PCB, the data display a linear trend while regression for PAH not passing through the origin. The slopes of these plots represent the degree to which the organism body burden can be predicted from both the measured SPME fiber concentration and the calculated pore water concentration. For example, if the data displayed a linear slope of unity the relationship between the measured fiber or pore water concentration (ng/L) and the measured organism tissue concentration would be one to one, the SPME fiber could predict the organism contamination.

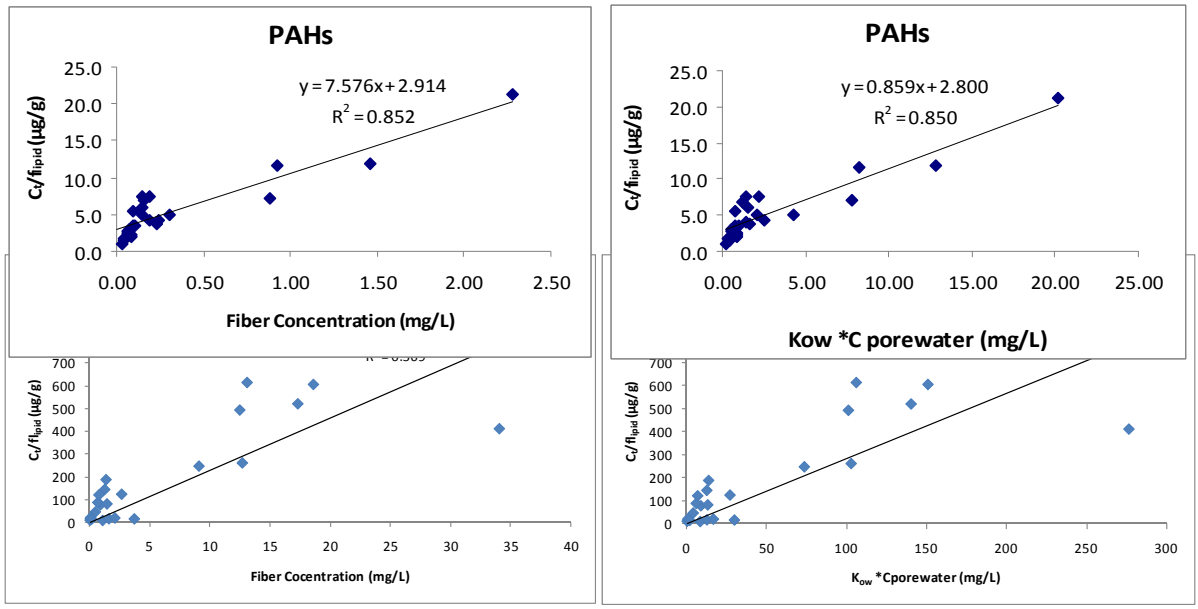

Figure 22: Correlation of PAH and PCB SPME Fiber (left) **and Pore Water Concentration** (right) **to Organism Lipid Normalized Body Burden** (*Ilyodrilus* in Sequential Dilution Experiment)**.**

For measured PCB pore water concentrations, PCB 153, 138, and 180 had not reached equilibrium in the 28-day duration of the experiment. For these congeners, the pore water concentrations were corrected for this non-steady state factor using data analysis from studies concerning kinetics and equilibrium found in Table 15. Corrected values for the select PCB congeners are shown in the table below.

Table 22: Corrected Pore Water Concentrations for More Hydrophobic PCB.

		PCB Compound		
		#153	#138	#180
Fraction to steady state		0.79	0.87	0.59
Measured Pore water (ng/L)	3%	0.644	0.350	0.015
Corrected Pore water (ng/L)		0.815	0.402	0.025
Measured Pore water (ng/L)	6%	0.901	0.492	0.023
Corrected Pore water (ng/L)		1.141	0.565	0.039
Measured Pore water (ng/L)	12%	0.979	0.560	0.025
Corrected Pore water (ng/L)		1.239	0.644	0.043
Measured Pore water (ng/L)	25%	1.896	1.035	0.046
Corrected Pore water (ng/L)		2.400	1.189	0.078

Although the degree of fit of the correlation is similar between the sequential dilution experiment results (Figure 22) and those from studies completed previously with sediment from the Anacostia River (Figure 20), the tissue concentrations measured in the sequential dilution experiment for PCB are approximately 5 times larger than those observed in the Anacostia River for a given pore water. For PAH, the tissue concentrations measured for a given pore water in

the sequential dilution experiment are shown similar to those observed in experiments completed using Anacostia sediment.

An alternative way to look at accumulation in lipids is through a bioconcentration factor that relates water concentration, in this case, pore water, to organism body burdens. A bioconcentration factor can be predicted from the contaminant octanol-water partition coefficient (Mackay, 1982) and then related to measured BCF conducted in laboratory investigations. Literature correlations of BCF provide the following estimates:

$$\text{For PCBs}: BCF_{predicted} = K_{ow} \qquad \text{For PAHs}: BCF_{predicted} = K_{ow}$$ **Equation 20** **Equation 21**

$$BCF_{measured} = \frac{\text{lipid normalized tissue concentration}}{\text{SPME measured porewater concentration}}$$ **Equation 22**

Figure 23 shows the correlation between the measured and predicted PAH and PCB bioconcentration factors explained in the above equations.

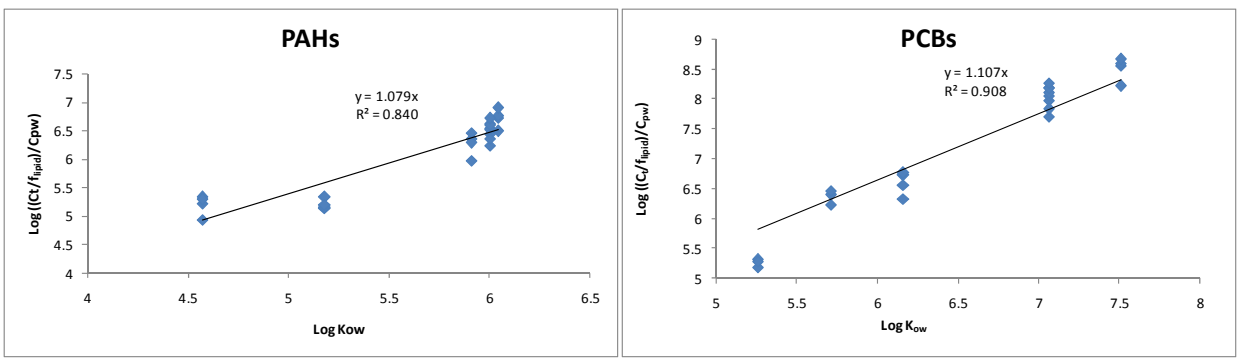

Figure 23: Measured and Predicted BCF Values for PAH and PCB (*Ilydorilus* in New Bedford Harbor Sediment Diluted with Brown's Lake Sediment)**.**

Measured and predicted BCF correlations for both PAH and PCB show a slope of approximately unity (y=1.079x for PAH and y=1.107x for PCB) implying a one to one correlation between the organism tissue concentration and the level of contamination found in the surrounding pore water. For PAH and PCB, the measured bioconcentration factor from both lipid normalized tissue and measured pore water is correlated closely with the reported octanol-water partition coefficient. Predictions of organism body burden can be determined if pore water concentration and contaminant properties are known.

5.3 Bioaccumulation of PCB from Hunter's Point Sediment

A third sediment was included in the laboratory evaluation as part of a collaborative effort with other Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) projects. Surficial sediment was collected from Hunter's Point Naval Shipyard and distributed to the collaborating groups after homogenization and sieving through a #5 (4 mm) sieve. Bioaccumulation experiments similar to those described above were conducted with a marine organism, the polychaete *Neanthes arenaceodentata*.

For this experiment five replicates were used for both tissue and lipid analysis. A total of 10 1-L beakers were filled with 200 mL of sediment (wet weight). This sediment was allowed to consolidate overnight. Organisms were added to the 1 L beakers containing 200 mL of sediment and 600 mL of artificial seawater (30 ppt Instant Ocean, 30 g per L) was slowly added using a syringe to avoid disturbance of sediment layer. Beakers were kept at 25°C and the overlying water was exchanged once a week. After a 3-week period, the experiment was terminated and the organisms were recovered using a 1 mm sieve. After depuration in water to clear the organisms of any sediment, the organisms were extracted as described previously and analyzed for PCB body burden. For complete survival/mortality and extracted worm weights, see Appendix C (Table C12).

Figure 24: Hunter's Point Sediment Microcosm – Side View with Evidence of *Neanthes* Burrowing.

The contaminants of concern in the Hunter's Point Sediments are PCB and bioaccumulation of only these constituents were evaluated in the exposed N*eanthes.*

Similar bioaccumulation studies were completed with the marine organism *Neanthes arenaceodentata* exposed to surficial sediments collected from PCB contaminated Hunter's Point Naval Academy. Nineteen PCB congeners were analyzed in this study with the same data analysis as presented in the previous section, correlating lipid normalized tissue concentration with SPME fiber concentration and pore water concentration. Analytical data pertaining to this experiment can be found in Appendix C.3 (Tables C14-C18). The quality of the correlation is similar to that observed in the previous experiments but the lipid normalized tissue concentrations for a given SPME fiber concentration are approximately 2-3 times greater than was observed in the diluted New Bedford Harbor sediment and approximately 10 times greater than was observed in the freshwater Anacostia River sediment. This may be a reflection of the marine sediments in the latter experiments.

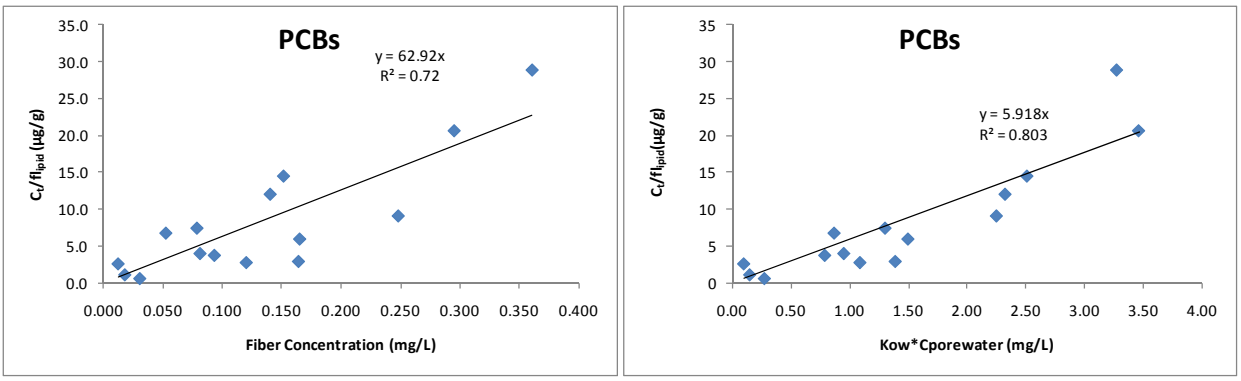

Figure 25: Correlation of PAH and PCB SPME Fiber (left) **and Pore Water Concentration** (right) **to Organism Lipid Normalized Body Burden** (*Neanthes* in Hunter's Point Sediments)**.**

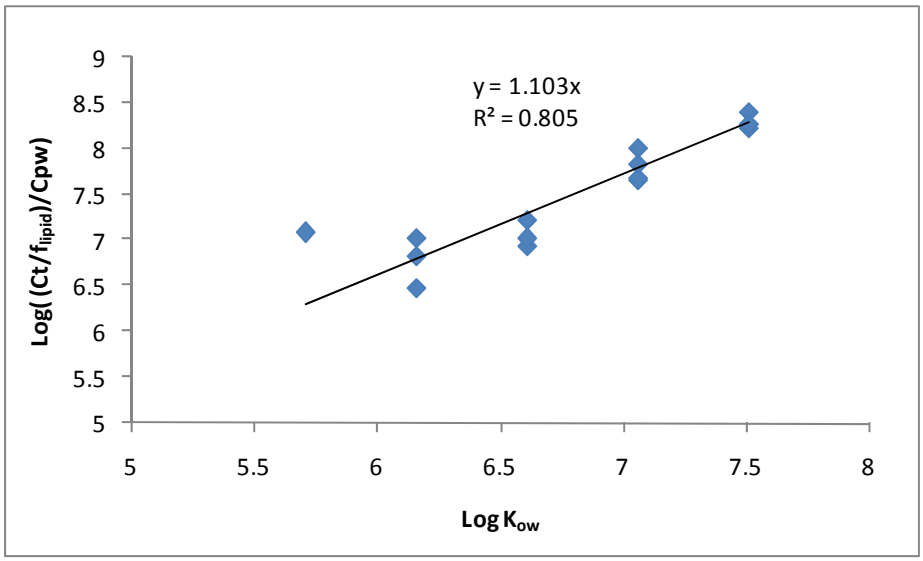

Figure 26: Measured and Predicted BCF Values for PAH and PCB (*Neanthes* in Hunter's Point sediment)**.**

The relationship observed between bioconcentration factors predicted by the octanol-water partition coefficient and those measured during experiments completed with Hunter's Point sediment displays similarities to previous experiments (y=1.127x). The table below summarizes the results from all bioaccumulation experiments showing the best-fit slope values for each of the three relationships. For the correlation between predicted and measured BCF values, a standard error of the regression has been included. The slope increases as the ionic strength (as indicated by salinity of source sediments) increases. Anacostia River sediment is fresh water, the sequential dilution experiment was a mixture of both marine and fresh water, and Hunter's Point was marine sediment. Such inconsistencies in the type of sediment used for the experiment may account for the discrepancies in the measured slopes. With regard to measured and predicted bioconcentration factors, all experiments display a similar slope of approximately unity. The reported standard error is logarithmic with the average for all experiments roughly 0.255 log units or a factor of 1.8.

Table 23: Bioaccumulation Summary.

PAHs							
	Normalized Tissue and SPME fiber		Normalized Tissue and Porewater		Measured and Predicted Log BCF		
Experiment	Slope	r^2	Slope	r^2	Slope	r^2	Std Error
Anacostia River (Drake 2007)	1.639	0.754	1.061	0.783	1.027	0.917	0.198
Sequential Dilution, New Bedford Harbor + Brown Lake	10.08	0.53	1.137	0.561	1.079	0.84	0.262
PCBs							
	Normalized Tissue and SPME fiber		Normalized Tissue and Porewater		Measured and Predicted Log BCF		
Experiment	Slope	r^2	Slope	r^2	Slope	r^2	Std Error
Anacostia River (Drake 2007)	4.967	0.783	0.611	0.783	0.965	0.973	0.121
Sequential Dilution, New Bedford Harbor + Brown Lake	22.98	0.569	2.831	0.578	1.107	0.908	0.369
Hunter's Point	62.92	0.72	5.918	0.803	1.103	0.805	0.275

Due to the substantial similarities in BCF correlations between the bioaccumulation experiments, an overall governing equation can relate pore water and hydrophobicity with organism tissue concentrations. Data from all experiments was combined and graphed below in Figure 27. The standard error in regression for the figure below was reported as 0.414 log units or a factor of 2.6.

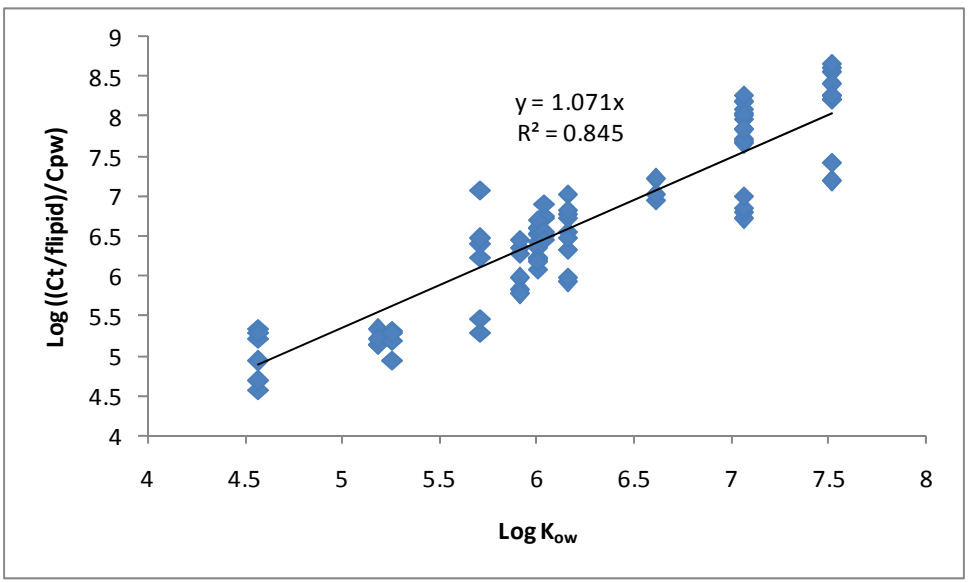

Figure 27: Summary BCF Correlation for all Bioaccumulation Experiments Including Freshwater and Marine Sediment and Organisms.

The overall governing equation:

$$Log\left(\frac{C_t / f_{lipid}}{C_{porewater}}\right) = 1.071 Log K_{ow}$$

Using this equation and pore water concentrations measured using SPME, organism body burden for specific contaminants can be estimated. Greater accuracy can be obtained through use of the site and sediment specific correlations.

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Appendix A: Laboratory SPME Studies

Analytical results for SPME fiber extraction efficiency

Three extractions were utilized, direct injection, heating and shaking samples before analyzing. Direct extraction samples were taken initially and then at a time three hours later. Samples that were heated were analyzed at 1 hr and 3 hr time intervals and samples on the shaker table were analyzed at 1 hr and 20 hr.

Table A.1: Fiber Concentration for PAHs (mg/L)

	Direct extraction				Heating		Shaking	
Compound	0hr-d	3hr-d	0hr-d	3hr-d	1hr-h	3hr-h	1hr-s	20hr-s
Phenanthrene	11	9	9	10	7	10	8	10
Pyrene	24	24	24	24	19	25	36	24
B[a]A	162	169	169	164	128	167	148	166
BbF	65	67	67	68	51	69	59	68
BkF	225	229	229	231	175	234	201	234
BaP	35	37	37	37	28	37	32	38

Similar experiments were completed with PCB compounds.

Table A.2: Fiber Concentrations for PCBs (mg/L)

	Direct injection			Heating at 50C		Shaking	
Compounds	0hr-d	0hr-d	2hr-d	1hr-h	3hr-h	1hr-s	20hr-s
PCB28	11.4	10.7	10.6	11.4	11.6	11.3	13.1
PCB52	22.6	20.5	19.6	21.1	21.5	20.6	25.2
PCB153	22.3	12.2	11.6	10.8	10.9	10.6	19.6
PCB138	22.0	11.9	11.3	10.6	14.2	10.3	19.4
PCB180	21.3	8.5	7.5	7.2	7.3	7.2	17.1

Samples were injected a second time to determine if the entire analyte had completely desorbed from the fiber coating. The following table displays the GC response and fraction of the original response for two of the samples – 0 hr direct injection and 3 hr heating. The fraction of the second injection is simply the ratio of the machine response for the second injection to the first injection. Each sample was injected twice during GC analysis and the fractions were averaged for the two results. Results can be found in Section 1.2 of the report.

Fiber-water partition coefficients

Table A.3: Static measurements – single concentration

Compounds	$C_{w,initial}$, µg/L		$C_{w,final}$, µg/L		C_{fiber}, µg/L		Log K_f (C_{fiber}/ $C_{w,final}$)		Mass balance,%
Phenanthrene	Replicate	3.64	Replicate	2.84	Replicate	14965	Replicate	3.72	81
		3.43		3		15659		3.72	86
				3.32		16051		3.68	95
				3.22		17454		3.73	92
	Average	3.53	Average	3.1	Average	16032	Average	3.71	88
	Std Dev		Std Dev	0.22	Std Dev	1049	Std Dev	0.02	6.2
Pyrene	Replicate	3.74	Replicate	2.28	Replicate	46353	Replicate	4.31	52
		5.18		2.41		50360		4.32	55
				3.47		54712		4.2	79
				3.31		54874		4.22	76
	Average	4.46	Average	2.87	Average	51575	Average	4.26	66
	Std Dev		Std Dev	0.61	Std Dev	4061	Std Dev	0.06	14
Chrysene	Replicate	1.27	Replicate	1.17	Replicate	83608	Replicate	4.86	105
		1.13		1.27		93602		4.87	114
				0.97		57082		4.77	86
				1.56		56025		4.55	135
	Average	1.2	Average	1.24	Average	72579	Average	4.76	110
	Std Dev		Std Dev	0.25	Std Dev	18954	Std Dev	0.15	20
B[a]A	Replicate	1.77	Replicate	1.73	Replicate	111402	Replicate	4.81	103
		1.93		1.83		122862		4.83	109
				1.76		78532		4.65	102
				1.67		85785		4.71	98
	Average	1.8	Average	1.75	Average	99645	Average	4.75	103
	Std Dev		Std Dev	0.07	Std Dev	20937	Std Dev	0.08	4.6
B[b]F	Replicate	1.4	Replicate	1.76	Replicate	146596	Replicate	4.92	162
		0.95		1.72		188036		5.04	163
				1.63		116916		4.85	149
				1.58		117416		4.87	145
	Average	1.18	Average	1.67	Average	142241	Average	4.92	155
	Std Dev		Std Dev	0.08	Std Dev	33535	Std Dev	0.08	9
B[k]F	Replicate	1.03	Replicate	0.88	Replicate	91475	Replicate	5.02	121
		0.59		0.99		104971		5.02	136
				0.65		55332		4.93	87
				0.6		45070		4.87	81
	Average	0.81	Average	0.78	Average	74212	Average	4.96	106
	Std Dev		Std Dev	0.19	Std Dev	28576	Std Dev	0.07	27
B[a]P	Replicate	0.98	Replicate	0.72	Replicate	99628	Replicate	5.14	94
		0.73		0.8		113645		5.15	105
				0.51		71539		5.15	66
				0.44		57839		5.12	58
	Average	0.88	Average	0.62	Average	85663	Average	5.14	81
	Std Dev		Std Dev	0.17	Std Dev	25506	Std Dev	0.02	22

Isotherm – multiple concentration measurements

Table A.4: Isotherm Measurements – 5 times diluted

Water Sample 2 - Diluted 5 times							
Compound		$C_{w,\ initial}$ (µg/L)	$C_{w,\ final}$ (µg/L)	C_{fiber} (µg/L)	% Mass	% Loss	Log Kf
Phenanthrene	Replicate	1.09	1.05	6983	97	3.09	3.82
			1.34	9160	123		3.84
			1.01	6707	93	7.0	3.82
	Average		1.13	7617	104	5.06	3.83
	Std Dev		0.18	1344	17		0.01
Pyrene	Replicate	1.23	0.84	20312	69	31	4.39
			1.32	19857	109		4.18
			0.95	20599	78	22	4.34
	Average		1.03	20256	85	26	4.30
	Std Dev		0.25	374	21		0.11
Chrysene	Replicate	0.47	0.48	28978	107		4.78
			0.57	48022	129		4.92
			0.47	27870	104		4.77
	Average		0.51	34957	113		4.82
	Std Dev		0.06	11329	13		0.09
B[a]A	Replicate	0.52	0.63	31004	125		4.69
			0.67	48100	134		4.86
			0.65	32428	128		4.70
	Average		0.65	37177	129		4.75
	Std Dev		0.02	9486	5		0.09
B[b]F	Replicate	0.42	0.47	37300	116		4.90
			0.48	68473	123		5.16
			0.56	38193	138		4.84
	Average		0.50	47989	126		4.96
	Std Dev		0.05	17746	11		0.17
B[k]F	Replicate	0.31	0.25	25077	84	16	5.01
			0.25	58894	92	8.3	5.37
			0.26	29408	88	12	5.06
	Average		0.25	37793	88	12	5.15
	Std Dev		0.01	18402	4	4	0.20
B[a]P	Replicate	0.31	0.27	25209	92	8.3	4.97
			0.27	54531	97	2.9	5.31
			0.34	28743	115		4.93
	Average		0.29	36161	101	5.6	5.07
	Std Dev		0.04	16007	12		0.21

Table A.5: Isotherm Measurements – 4 times diluted

Water Sample 3 - Diluted 4 times							
Compound		$C_{w,\ initial}$ (µg/L)	$C_{w,\ final}$ (µg/L)	C_{fiber} (µg/L)	% Mass	% Loss	Log Kf
Phenanthrene	Replicate	1.21	1.158	6868	96	3.7	3.77
			1.194	7536	99	0.64	3.80
			1.259	7016	105		3.75
	Average		1.20	7140	100	2.2	3.77
	Std Dev		0.05	351	4.2		0.03
Pyrene	Replicate	1.36	1.978	17190	147		3.94
			1.366	25291	102		4.27
			1.525	18645	113		4.09
	Average		1.62	20375	121		4.10
	Std Dev		0.32	4319	23		0.16
Chrysene	Replicate	0.77	0.654	17855	86	14	4.44
			0.570	20791	75	25	4.56
			0.552	25534	73	27	4.67
	Average		0.59	21394	78	22	4.55
	Std Dev		0.05	3875	6.8	6.8	0.11
B[a]A	Replicate	0.70	0.683	20574	99	0.67	4.48
			0.655	25305	96	4.3	4.59
			0.693	29915	101		4.64
	Average		0.68	25264	99	2.5	4.57
	Std Dev		0.02	4670	2.9		0.08
B[b]F	Replicate	0.61	0.523	19010	88	11.9	4.56
			0.557	26029	94	5.7	4.67
			0.574	31139	97	2.5	4.73
	Average		0.55	25393	93	6.7	4.65
	Std Dev		0.03	6090	4.8	4.8	0.09
B[k]F	Replicate	0.72	0.275	12152	39	61	4.64
			0.288	15919	41	59	4.74
			0.279	20604	40	60	4.87
	Average		0.28	16225	40	60	4.75
	Std Dev		0.01	4234	1.0	1.0	0.11
B[a]P	Replicate	0.65	0.322	12993	51	49	4.61
			0.320	17136	51	49	4.73
			0.284	21648	46	54	4.88
	Average		0.31	17259	49	51	4.74
	Std Dev		0.02	4329	3.0	3.0	0.14

Table A.6: Isotherm Measurements – 3 times diluted

Water Sample 4 - Diluted 3 times							
Compound		$C_{w,\ initial}$ (µg/L)	$C_{w,\ final}$ (µg/L)	C_{fiber} (µg/L)	% Mass	% Loss	Log Kf
Phenanthrene	Replicate	1.57	1.57	9449	100		3.78
			1.59	8845	102		3.74
			1.57	9100	100		3.76
	Average		1.58	9131	101		3.76
	Std Dev		0.01	303	0.80		0.02
Pyrene	Replicate	1.89	2.25	23501	120		4.02
			2.20	26188	117		4.08
			1.68	27051	90		4.21
	Average		2.04	25580	109		4.10
	Std Dev		0.31	1851	17		0.10
Chrysene	Replicate	0.59	0.72	32716	125		4.66
			0.70	28833	121		4.62
			0.59	25869	103		4.64
	Average		0.67	29139	116		4.64
	Std Dev		0.07	3434	12		0.02
B[a]A	Replicate	0.74	0.83	38017	115		4.66
			0.88	33892	121		4.59
			0.79	30749	109		4.59
	Average		0.83	34219	115		4.61
	Std Dev		0.04	3645	5.7		0.04
B[b]F	Replicate	0.58	0.81	42812	144		4.72
			0.78	35163	138		4.66
			0.49	29488	87	13	4.78
	Average		0.69	35821	123		4.72
	Std Dev		0.18	6686	31		0.06
B[k]F	Replicate	0.39	0.43	26291	114		4.79
			0.36	20236	95	5.1	4.76
			0.26	19760	71	29	4.88
	Average		0.35	22096	93	17.2	4.81
	Std Dev		0.08	3641	21.6		0.06
B[a]P	Replicate	0.36	0.46	29027	132		4.80
			0.40	23412	114		4.77
			0.26	20528	75	25	4.91
	Average		0.37	24322	107		4.83
	Std Dev		0.10	4322	30		0.07

Table A.7: Isotherm Measurements – 2 times diluted

Water Sample 5 - Diluted 2 times							
Compound		$C_{w,\ initial}$ (µg/L)	$C_{w,\ final}$ (µg/L)	C_{fiber} (µg/L)	% Mass	% Loss	Log Kf
Phenanthrene	Replicate	2.24	2.34	13966	105		3.78
			2.45	13619	110		3.74
			2.28	13934	102		3.79
	Average		2.36	13840	106		3.77
	Std Dev		0.09	192	4.1		0.02
Pyrene	Replicate	2.12	2.05	41395	98	2.4	4.31
			3.05	33033	145		4.03
			2.75	35701	131		4.11
	Average		2.62	36710	124		4.15
	Std Dev		0.52	4271	24		0.14
Chrysene	Replicate	0.95	1.02	53975	110		4.72
			0.81	30946	86	14	4.58
			0.84	37591	91	9.4	4.65
	Average		0.89	40837	96	12	4.65
	Std Dev		0.12	11853	13		0.07
B[a]A	Replicate	1.03	1.22	63985	122		4.72
			1.11	40329	110		4.56
			1.15	45432	114		4.60
	Average		1.16	49915	116		4.62
	Std Dev		0.06	12449	6.1		0.08
B[b]F	Replicate	0.74	1.10	72374	154		4.82
			0.83	39301	114		4.68
			0.97	48346	134		4.70
	Average		0.97	53340	134		4.73
	Std Dev		0.14	17093	20		0.08
B[k]F	Replicate	0.71	0.47	46550	71	29	4.99
			0.35	20042	51	49	4.76
			0.41	27078	60	40	4.82
	Average		0.41	31223	61	39	4.86
	Std Dev		0.06	13732	10	10	0.12
B[a]P	Replicate	0.56	0.55	50730	104		4.96
			0.38	23982	71	29	4.80
			0.46	31298	85	15	4.84
	Average		0.46	35337	86	22	4.87
	Std Dev		0.09	13824	17		0.09

Table A.8: Isotherm Measurements – Original Solution

Water Sample 1 - Original Solution							
Compound		$C_{w,\ initial}$ (µg/L)	$C_{w,\ final}$ (µg/L)	C_{fiber} (µg/L)	% Mass	% Loss	Log Kf
Phenanthrene	Replicate	4.14	4.43	26737	107		3.78
			4.27	25310	103		3.77
			4.56	24792	110		3.74
	Average		4.42	25613	107		3.76
	Std Dev		0.15	1007	3.5		0.02
Pyrene	Replicate	3.77	3.91	77662	105		4.30
			5.14	74890	137		4.16
			5.08	70695	136		4.14
	Average		4.71	74416	126		4.20
	Std Dev		0.69	3508	18		0.08
Chrysene	Replicate	1.17	1.37	59666	121		4.64
			1.24	50148	109		4.61
			1.10	45939	97	3.2	4.62
	Average		1.24	51918	109		4.62
	Std Dev		0.13	7032	12		0.02
B[a]A	Replicate	1.63	2.16	92353	135		4.63
			1.97	77140	123		4.59
			1.87	71906	117		4.58
	Average		2.00	80466	125		4.60
	Std Dev		0.15	10621	9.2		0.03
B[b]F	Replicate	1.24	1.64	95909	137		4.77
			1.36	76877	113		4.75
			1.13	70280	94	6.1	4.80
	Average		1.37	81022	114		4.77
	Std Dev		0.26	13307	21		0.02
B[k]F	Replicate	0.65	0.66	41806	105		4.80
			0.57	30837	90	10	4.73
			0.52	28563	83	17	4.74
	Average		0.58	33735	92	14	4.76
	Std Dev		0.07	7081	11		0.04
B[a]P	Replicate	0.60	0.66	54331	115		4.92
			0.58	42247	100		4.86
			0.50	37815	87	13	4.88
	Average		0.58	44798	101		4.89
	Std Dev		0.08	8549	14		0.03

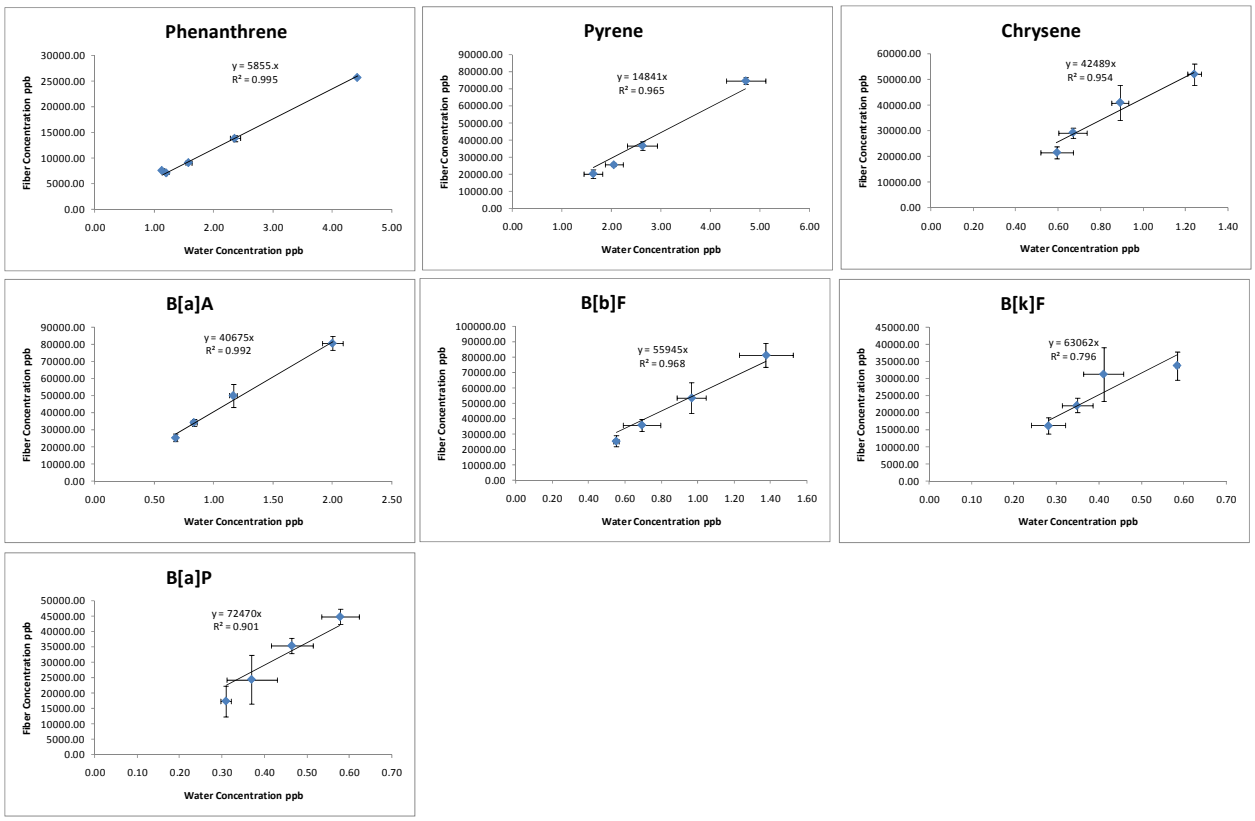


Figure A.1: Partition Coefficients determined from slopes of averaged fiber and water concentrations for four dilutions (#2 concentration level was removed because of its deviation from the other four treatments. Fiber to water ratio for #2 is 1 cm fiber to 125 ml water, while fiber to water ratio of the other four concentrations is 1 cm fiber to 250 ml water)

Partition coefficients from the multi-concentration experiment are compared below to those measured from the single concentration (1 point calibration) experiment and also to literature values from Ter Laak (Environ Sci Technol. 2006, 40, 2184-2190).

Kinetic measurements – SPME fiber in water

Table A.9: Fiber Kinetics PM 170/110 at 25C

	Phenanthrene					
Time (hrs)	5	10	24	48	76	168
C_{water} (μg/L)	5.51	5.51	5.51	5.51	5.51	5.51
C_{fiber} (μg/L)	28054	29320	30716	28732	30930	29892
	39755	30105	31158	30481	31135	29802
C_f/C_w	5092	5321	5575	5214	5613	5425
	7215	5464	5655	5532	5651	5409
	Pyrene					
Time (hrs)	5	10	24	48	76	168
C_{water} (μg/L)	5.12	5.12	5.12	5.12	5.12	5.12
C_{fiber} (μg/L)	50354	60950	79139	90473	95784	96312
	90125	59952	99385	97505	92779	94241
C_f/C_w	9835	11904	15457	17671	18708	18811
	17603	11709	19411	19044	18121	18406
	Chrysene					
Time (hrs)	5	10	24	48	76	168
C_{water} (μg/L)	1.81	1.81	1.81	1.81	1.81	1.81
C_{fiber} (μg/L)	31503	39104	30393	71493	75243	73962
	243490	37170	81598	136736	49174	77809
C_f/C_w	17405	21604	16792	39499	41571	40863
	134525	20536	45082	75545	27168	42988
	B[a]A					
Time (hrs)	5	10	24	48	76	168
C_{water} (μg/L)	2.50	2.50	2.50	2.50	2.50	2.50
C_{fiber} (μg/L)	36931	48194	50687	102155	113725	111994
	133645	46805	107294	120900	87225	111151
C_f/C_w	14772	19278	20275	40862	45490	44798
	53458	18722	42918	48360	34890	44461
	B[b]F					
Time (hrs)	5	10	24	48	76	168
C_{water} (μg/L)	1.54	1.54	1.54	1.54	1.54	1.54
C_{fiber} (μg/L)	30792	40851	33043	115214	148957	146773
	157645	39868	122032	141072	81126	155546
C_f/C_w	19995	26527	21456	74814	96725	95307
	102367	25888	79242	91605	52679	101004
	B[k]F					
Time (hrs)	5	10	24	48	76	168
C_{water} (μg/L)	1.11	1.11	1.11	1.11	1.11	1.11
C_{fiber} (μg/L)	25201	31331	12039	43267	47238	45417
	66196	29164	46075	57904	21995	47248
C_f/C_w	22704	28226	10846	38980	42557	40916
	59636	26274	41509	52166	19815	42566

	B[a]P					
Time (hrs)	5	10	24	48	76	168
C_{water} (μg/L)	1.65	1.65	1.65	1.65	1.65	1.65
C_{fiber} (μg/L)	27958	38589	20350	64115	75807	70068
	90973	36168	67567	80107	45500	72304
C_f/C_w	16944	23387	12334	38858	45944	42466
	55135	21920	40950	48550	27576	43820

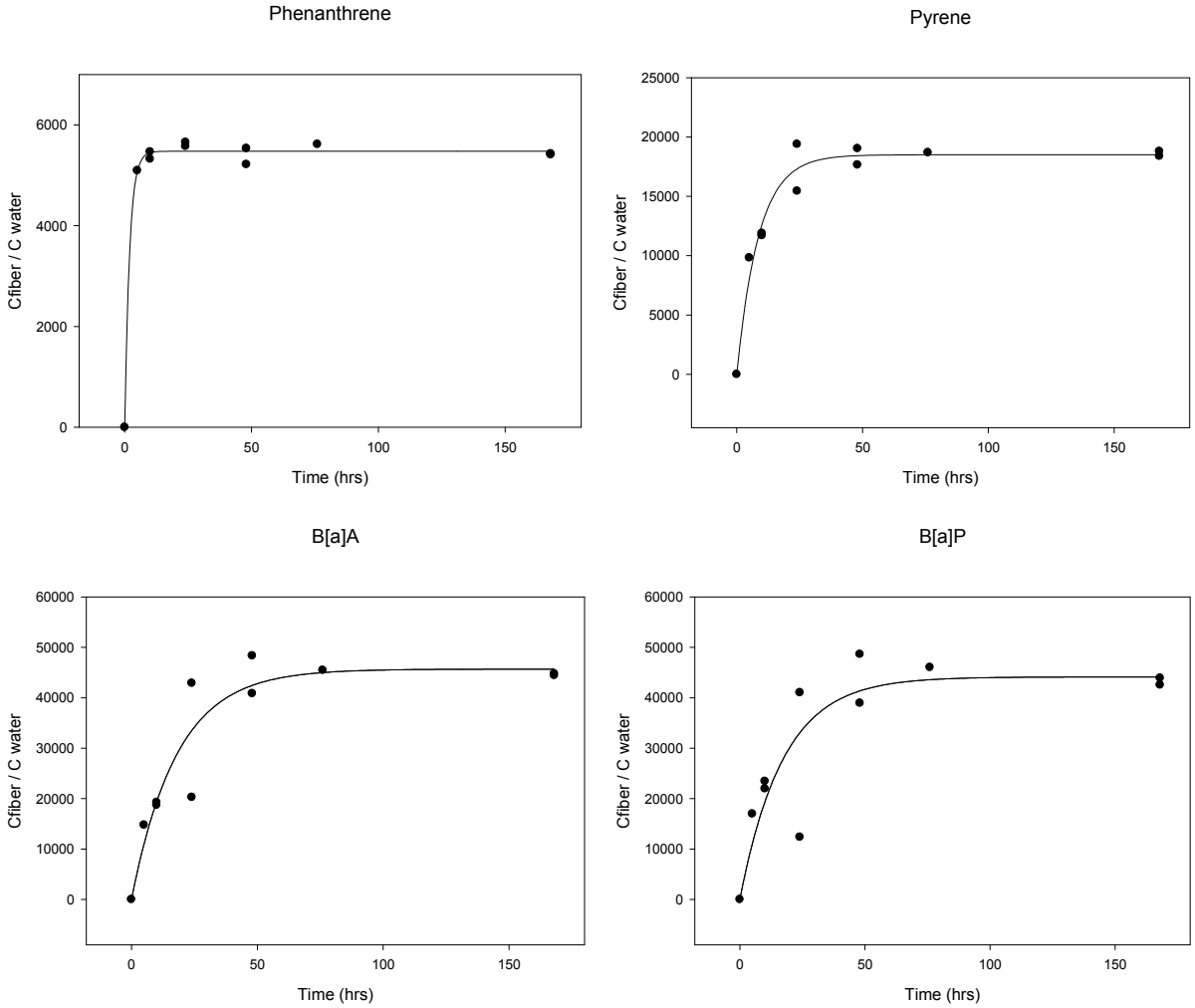


Figure A.2: Select PAHs for kinetics of PM 170/110 at 25C

Table A.10: Fiber Kinetics FG 230/210 at 25C

	Phenanthrene					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	3.27	3.31	3.25	3.35	3.26	3.27
	3.22	3.29	3.28	3.48	3.25	3.29
C_{fiber} (μg/L)	12205	20564	17481	19470	19887	20455
	19200	28577	22804	22684	21962	18647
C_f/C_w	3727	6205	5382	5807	6109	6251
	5958	8699	6952	6517	6767	5673
	Pyrene					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	3.72	4.03	1.91	3.36	3.54	3.22
	2.30	4.38	3.94	3.84	3.54	3.65
C_{fiber} (μg/L)	19441	53790	44518	60368	49864	64956
	51899	78910	71498	70041	66459	62128
C_f/C_w	5221	13341	23297	17989	14083	20158
	22589	18000	18144	18246	18772	17009
	Chrysene					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	1.38	1.64	0.87	0.94	0.73	1.51
	1.71	1.75	2.07	1.68	1.18	1.49
C_{fiber} (μg/L)	6290	42260	23009	39705	19175	70739
	34506	161073	67360	106222	90832	58512
C_f/C_w	4572	25822	26475	42055	26272	46969
	20131	92140	32518	63376	76973	39364
	B[a]A					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	1.48	1.81	0.91	1.06	0.84	1.70
	1.80	1.96	2.07	1.93	1.59	1.76
C_{fiber} (μg/L)	9257	54770	33581	58681	36536	99676
	44481	169156	96549	134151	120023	92902
C_f/C_w	6272	30278	36727	55535	43490	58801
	24733	86112	46739	69666	75686	52841
	B[b]F					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	1.06	1.46	0.70	0.44	0.52	0.97
	1.42	1.87	1.58	1.71	0.72	1.25
C_{fiber} (μg/L)	6189	48293	30437	63628	33881	123280
	39251	230380	116120	211659	143241	159040
C_f/C_w	5818	33181	43387	145223	65761	127357
	27707	123399	73475	124031	197672	127183
	B[k]F					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	0.84	1.22	0.64	0.57	0.70	1.07
	1.23	1.60	1.64	1.34	0.91	1.35
C_{fiber} (μg/L)	2087	31417	17240	37060	21442	68236
	23905	96197	61161	84060	82322	64794
C_f/C_w	2471	25681	26755	65104	30652	63823
	19357	60012	37321	62732	90941	47859

	B[a]P					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	0.98	1.34	0.70	0.53	0.73	1.02
	1.29	1.84	1.79	1.52	0.91	1.31
C_{fiber} (μg/L)	2987	34865	24045	35273	27747	77793
	28235	130835	81316	117989	108812	89531
C_f/C_w	3047	26063	34536	66546	37912	75959
	21935	71207	45328	77509	119769	68354

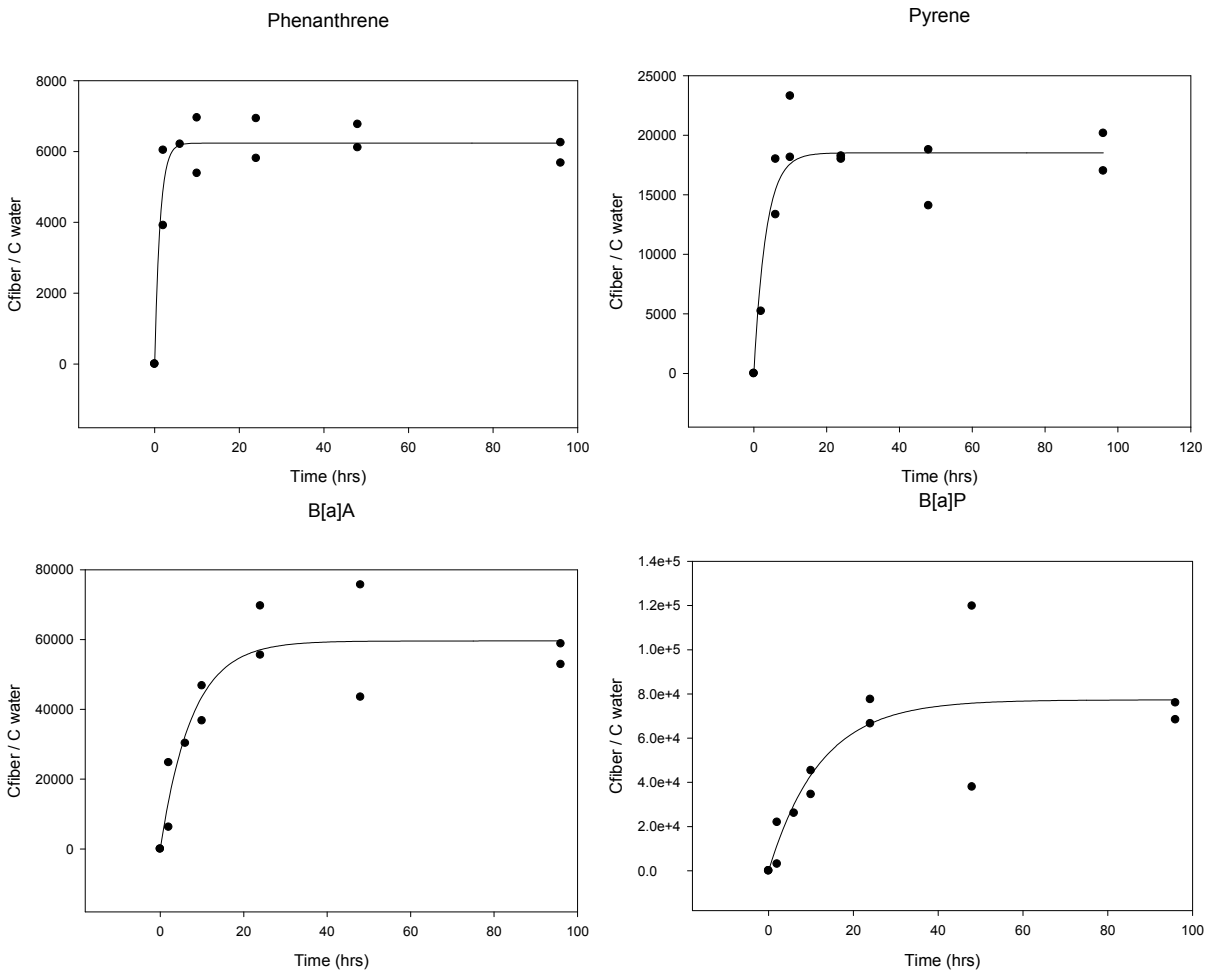


Figure A.3: Select PAHs for kinetics of FG 230/210 at 25C

Table A.11: Fiber Kinetics PM 170/110 at 12C

	Phenanthrene					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	3.35	3.11	3.09	3.26	3.54	3.71
	3.34	3.38	3.25	3.13	3.27	3.71
C_{fiber} (μg/L)	20297	22417	21032	23817	22478	35809
	20297	26232	23034	20919	20687	43219
C_f/C_w	6065	7209	6803	7306	6358	9659
	6068	7751	7092	6685	6325	11657
	Pyrene					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	3.51	3.33	3.32	3.63	3.12	2.97
	3.96	3.29	3.40	3.24	3.11	2.97
C_{fiber} (μg/L)	34782	73688	63735	82960	61692	67266
	17153	78357	76702	73097	59887	86543
C_f/C_w	9919	22122	19217	22827	19804	22678
	4330	23834	22578	22579	19267	29177
	Chrysene					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	0.92	1.08	1.08	0.78	0.73	0.71
	0.89	1.01	1.02	0.81	0.59	0.71
C_{fiber} (μg/L)	16538	50431	45557	62446	26553	37498
	13326	70597	57767	40175	18506	71337
C_f/C_w	17879	46902	42033	79721	36478	53024
	14898	69566	56520	49906	31416	100873
	B[a]A					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	1.15	1.07	1.09	1.26	0.93	1.21
	1.20	1.28	1.36	1.64	0.89	1.21
C_{fiber} (μg/L)	20389	77620	64636	110461	65291	87589
	14824	87439	92714	70292	49255	135117
C_f/C_w	17704	72223	59489	87427	70449	72444
	12384	68221	68029	42881	55424	111754
	B[b]F					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	0.84	0.55	0.59	0.65	0.52	0.96
	0.74	0.79	1.00	0.69	0.53	0.96
C_{fiber} (μg/L)	16646	88335	63005	133085	78820	113186
	14146	83912	114429	64398	49051	164969
C_f/C_w	19773	159649	106626	203761	152386	117940
	19040	106801	114173	93307	91707	171897
	B[k]F					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	0.84	0.74	0.77	0.51	0.42	0.91
	0.72	0.76	0.78	0.44	0.42	0.91
C_{fiber} (μg/L)	12465	46028	42890	59849	39736	54109
	13395	64957	62830	30767	24644	107106
C_f/C_w	14873	61921	55572	116912	95665	59585
	18560	85591	80966	69660	59063	117946

	B[a]P					
Time	10	24	48	96	168	240
C_{water} (μg/L)	0.81	0.66	0.73	0.54	0.42	0.93
	0.70	0.80	0.84	0.48	0.45	0.93
C_{fiber} (μg/L)	11595	52282	41733	68436	54878	81555
	12274	65684	77485	33387	36038	148888
C_f/C_w	14385	78832	57383	126768	131022	87670
	17641	82313	92248	69522	80037	160051

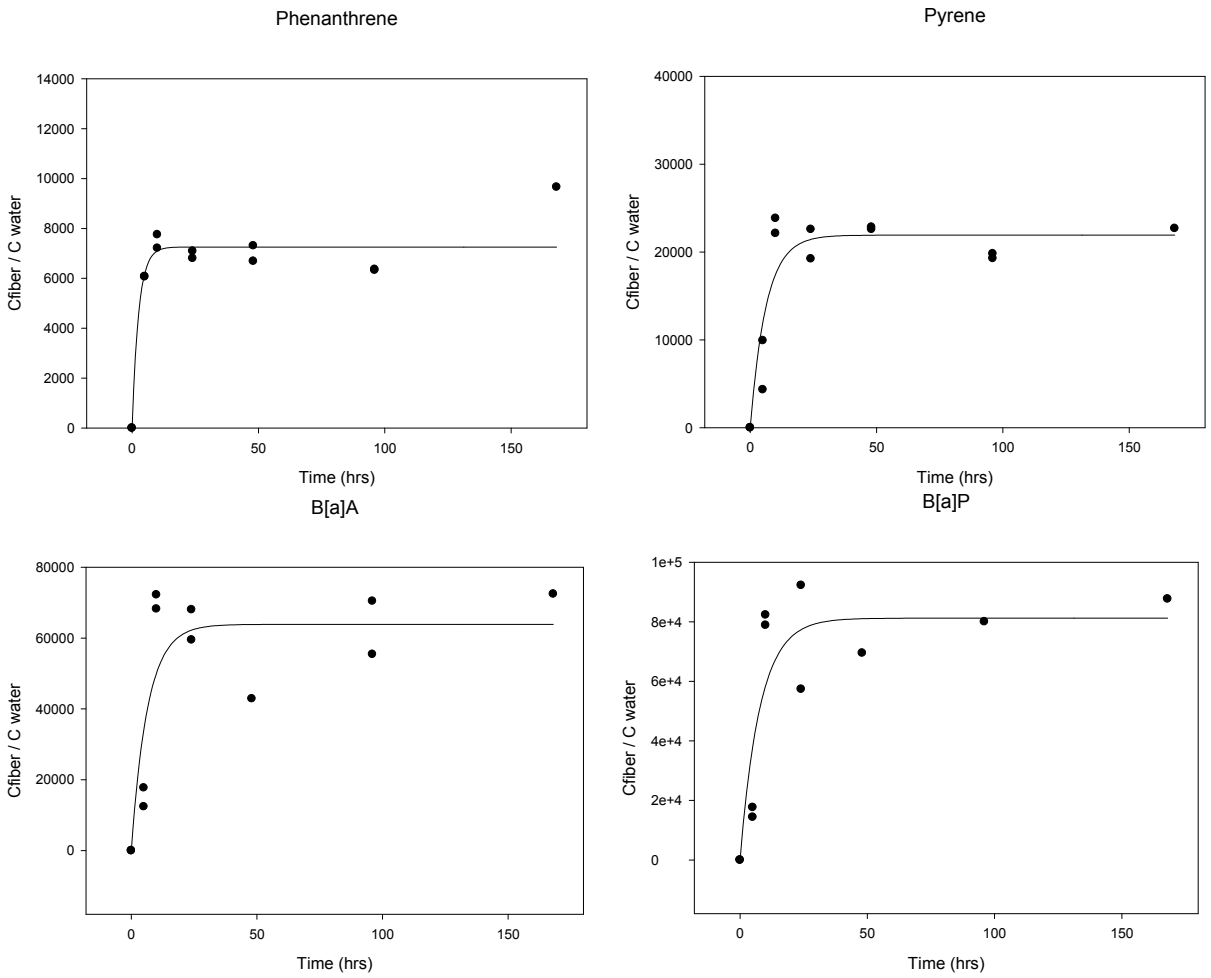


Figure A.4: Select PAHs for kinetics of PM 170/110 at 12C

Table A.12: Fiber Kinetics FG 230/210 at 12C

	Phenanthrene					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	3.17	3.02	3.17	3.06	3.33	3.21
	3.19	3.02	3.34	3.29	3.34	3.01
C_{fiber} (μg/L)	22496	16001	20236	20116	25961	19713
	23149	25476	39524	26171	25935	20208
C_f/C_w	7103	5305	6377	6573	7786	6149
	7256	8449	11829	7947	7770	6724
	Pyrene					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	3.57	2.97	3.17	2.79	3.60	3.18
	3.31	3.39	3.12	3.45	3.55	2.98
C_{fiber} (μg/L)	44568	25088	61222	54185	83262	63442
	45901	71549	104776	81530	80270	51817
C_f/C_w	12500	8445	19337	19407	23128	19963
	13886	21087	33613	23657	22625	17365
	Chrysene					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	1.23	1.08	0.73	0.74	1.23	1.09
	0.85	1.08	0.98	0.70	1.43	0.47
C_{fiber} (μg/L)	41535	14181	40951	24526	64336	27796
	54841	88188	174559	87532	88578	21834
C_f/C_w	33740	13161	56297	33010	52158	25531
	64867	81403	177895	124356	62035	46127
	B[a]A					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	1.30	1.15	0.91	0.82	1.38	0.97
	1.03	1.13	1.21	1.02	1.44	0.55
C_{fiber} (μg/L)	46649	17136	57494	38340	95012	57329
	59906	109421	176919	118402	114779	35112
C_f/C_w	35956	14890	63363	46963	69051	59060
	58011	96941	145969	116191	79957	63741
	B[b]F					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	0.96	0.94	0.60	0.48	0.97	0.70
	0.84	0.90	0.92	0.46	1.15	0.24
C_{fiber} (μg/L)	48592	15620	60026	41740	95440	58315
	64321	145180	204567	164179	157380	29643
C_f/C_w	50688	16583	100797	87170	98363	83166
	76965	161677	221401	356712	136392	125125
	B[k]F					
Time (hrs)	2	6	10	24	48	96
C_{water} (μg/L)	1.06	0.83	0.65	0.61	1.06	1.02
	0.89	1.01	0.86	0.54	1.28	0.23
C_{fiber} (μg/L)	42898	12789	41276	27455	62717	31550
	58732	79763	96222	81555	80514	18141
C_f/C_w	40638	15370	63121	44654	58898	30930
	66103	78763	112301	151595	63137	79577

	B[a]P					
Time	2	6	10	24	48	96
C_{water} (μg/L)	1.05	0.90	0.68	0.59	1.05	0.98
	0.85	0.95	0.89	0.56	1.25	0.21
C_{fiber} (μg/L)	38502	12487	46680	27351	73478	40425
	54539	100564	127149	106223	99412	19862
C_f/C_w	36709	13915	69076	46452	69720	41159
	64350	105783	142415	189767	79781	95645

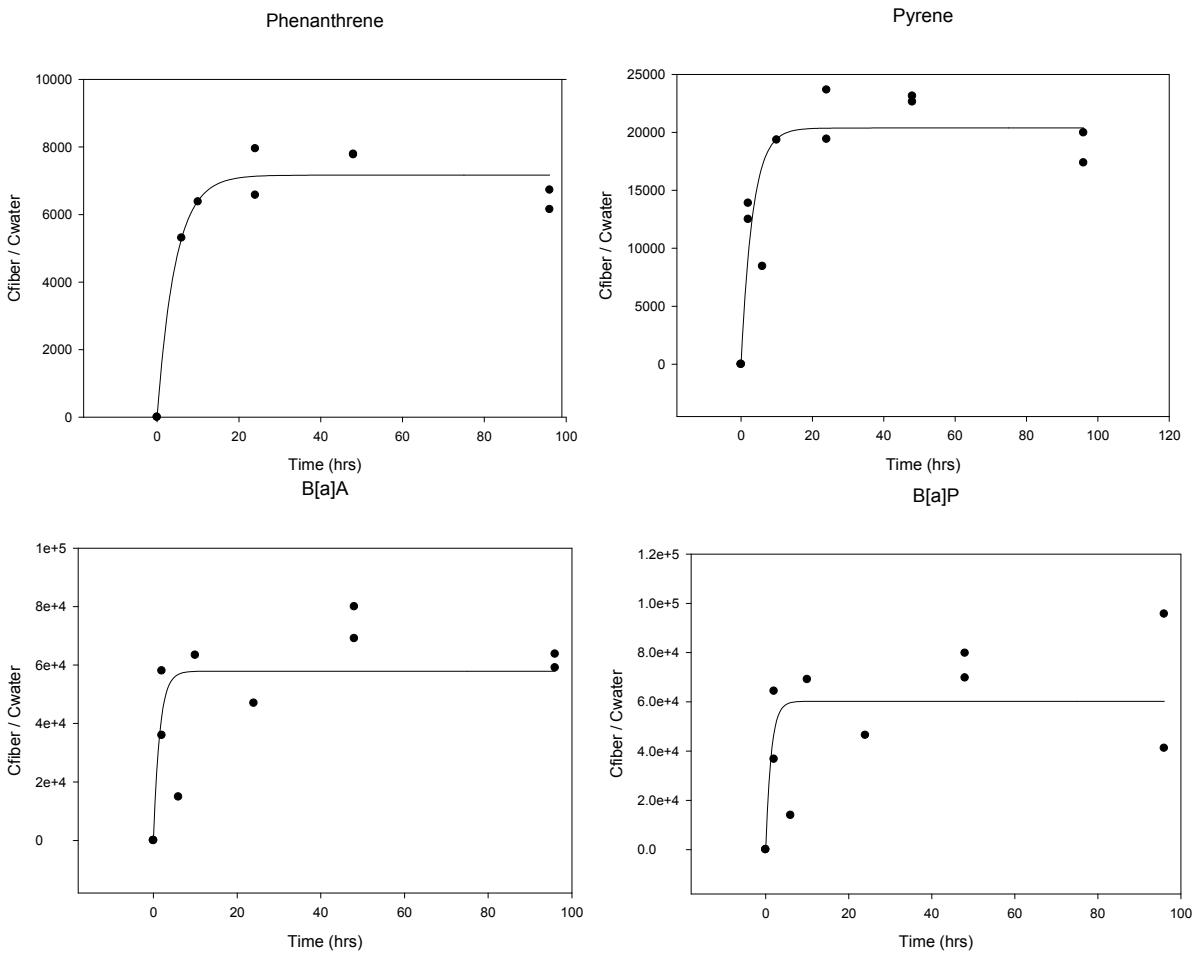


Figure A.5: Select PAHs for kinetics of FG 230/210 at 12C

Table A.13: Fiber Kinetics PM 170/110 at 4C

	Phenanthrene					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	3.43	3.18	3.38	3.21	3.50	3.34
	3.15	3.12	3.26	3.15	3.47	3.33
C_{fiber} (μg/L)	9620	23568	27071	26629	31824	28643
	24840	24316	27861	26866	45772	26819
C_f/C_w	2802	7418	8000	8302	9100	8567
	7885	7804	8549	8529	13197	8046
	Pyrene					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	3.47	2.92	2.86	2.86	4.13	3.43
	2.95	2.89	2.80	2.81	3.36	3.67
C_{fiber} (μg/L)	10800	59297	89484	79465	118474	97099
	46721	48177	97417	94624	147117	93785
C_f/C_w	3113	20321	31289	27759	28652	28286
	15844	16698	34840	33730	43754	25521
	Chrysene					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	1.61	1.31	1.26	0.81	0.59	1.10
	1.13	0.66	2.11	0.58	0.49	0.87
C_{fiber} (μg/L)	5294	46066	38389	26342	58706	44001
	19402	12370	49608	28442	138575	32801
C_f/C_w	3278	35298	30516	32698	99997	40000
	17229	18759	23515	49185	284938	37656
	B[a]A					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	1.70	1.38	1.46	1.08	1.00	1.29
	1.29	0.96	2.12	0.89	0.86	1.10
C_{fiber} (μg/L)	5621	57504	61630	43683	105752	76636
	24591	18832	80679	67991	170225	73390
C_f/C_w	3304	41599	42346	40409	105774	59520
	19123	19542	38142	76021	197860	66495
	B[b]F					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	1.43	1.03	1.12	0.79	0.67	1.02
	0.96	0.68	1.93	0.62	0.46	0.80
C_{fiber} (μg/L)	4652	72700	43676	34907	114466	70679
	19601	13036	70536	56947	214835	63479
C_f/C_w	3264	70283	38958	44265	170385	69018
	20500	19311	36561	92506	467476	79163
	B[k]F					
Time (hrs)	10	24	48	96	168	240
C_{water} (μg/L)	1.43	1.06	1.15	0.61	0.35	0.91
	0.90	0.54	2.02	0.45	0.31	0.69
C_{fiber} (μg/L)	4205	46570	29420	17892	52109	36958
	15263	6760	43262	14862	88301	19684
C_f/C_w	2946	43795	25556	29161	147524	40773
	16910	12482	21470	32786	285458	28391

	B[a]P					
Time	10	24	48	96	168	240
C_{water} (μg/L)	1.55	1.14	1.22	0.72	0.47	1.03
	0.96	0.60	2.08	0.52	0.41	0.81
C_{fiber} (μg/L)	4309	51943	30507	25982	68394	53553
	16207	8457	51525	31740	122070	37214
C_f/C_w	2780	45539	24972	36307	145048	52107
	16880	14067	24764	61568	294152	45680

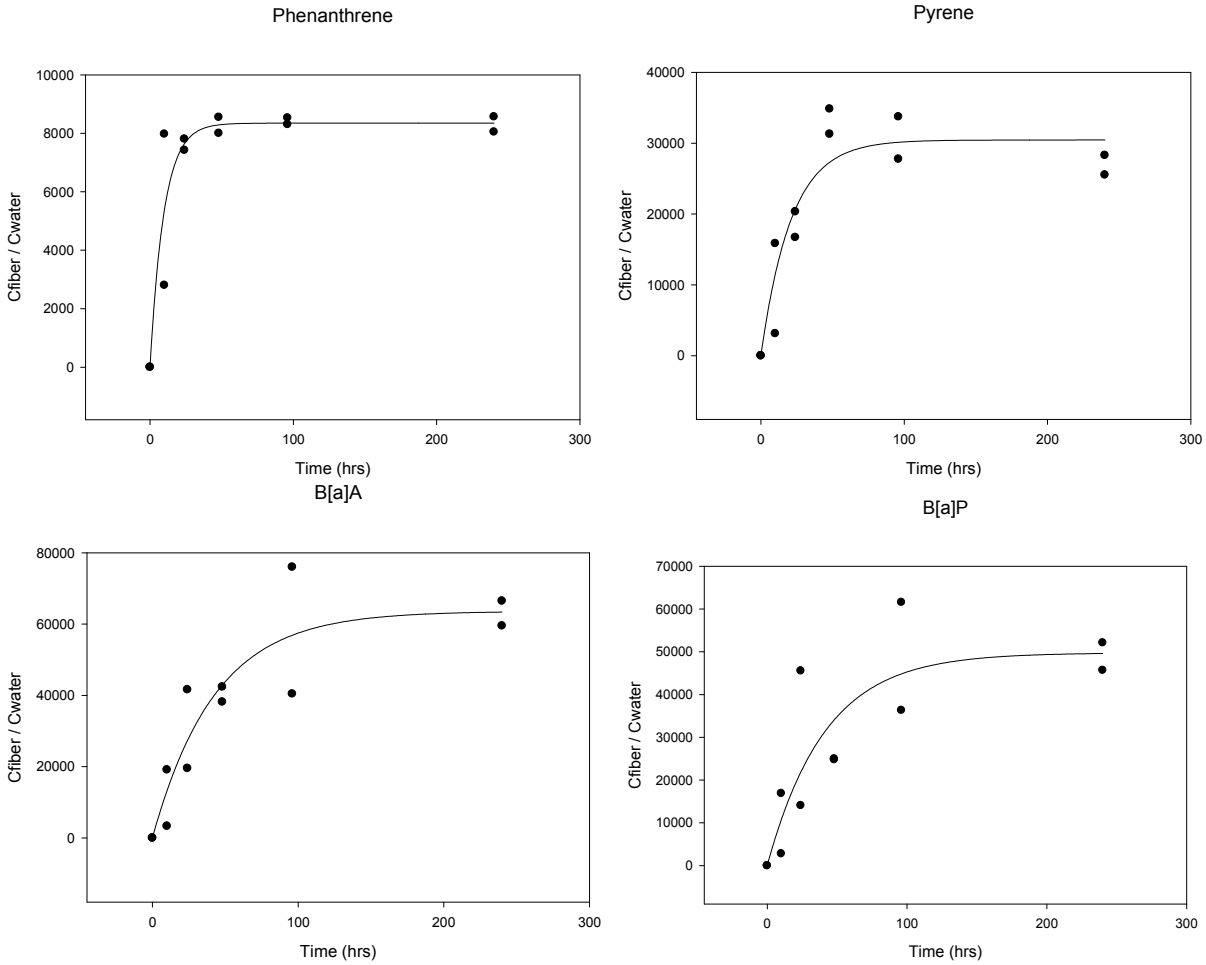


Figure A.6: Select PAHs for kinetics of PM 170/110 at 4C

Uniformity of PDMS coating on fiber is very important as it determines reproducibility of fiber. The table below shows fiber mass at different lengths. The average and standard deviation is shown in the table.

Table A.14: Weight/unit length ratios of SPME fiber

Length (cm)	Mass (g)	Mass (mg)	Weight / Unit Length (mg/cm)
8	0.0024	2.4	0.3000
10	0.0037	3.7	0.3700
8	0.0026	2.6	0.3250
7	0.0022	2.2	0.3143
7	0.0021	2.1	0.3000
6.5	0.0022	2.2	0.3385
8	0.0032	3.2	0.4000
8	0.0025	2.5	0.3125
8	0.0027	2.7	0.3375
8	0.0031	3.1	0.3875
8	0.0026	2.6	0.3250
		Average	**0.3373**
		STD	**0.0343**

Table A.15: PAH Fiber-sediment kinetics PM 170/110 4°C

	Fiber Concentration (μg/L)						
Time (d)	Phen	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
1	376	2358	56	63	54	46	56
1	227	3526	70	60	53	20	20
2	241	4273	75	90	71	46	57
2	338	4169	132	167	156	129	165
5	318	4586	68	97	108	60	96
5	319	5178	88	89	87	37	58
10							
10	443	4636	142	226	231	177	210
20	1284	5265	152	196	230	137	218
20	1198	5781		147	178	127	153

Table A.16: PAH Fiber-sediment kinetics FG 170/110 4°C

	Fiber Concentration (μg/L)						
Time (d)	Phen	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
0.33	435	3314	46	71	76	30	34
0.33	521	4465	61	79	68	29	51
1	393	4631	95	92	99	48	70
1	414	4514	55	84	87	36	47
2	552	5935	145	193	172	152	192
2	522	5242	144	159	133	120	160
4	605	5659					
4	551	4850	192	219	239	191	235
8	1057	6191	117	167	186	95	120
8	1355	7943	96	196	241	106	140

Table A.17: PAH Fiber-sediment kinetics PM 170/110 12°C

	Fiber Concentration (μg/L)						
Time (d)	Phen	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
1	315	4658	65	96	53	20	37
1	388	4735	78	71	40	15	25
2	398	5373	77	101	97	38	63
2	375	5313	95	114	77	36	61
5	381	6843	129	177	178	71	128
5	351	6005	141	153	156	101	142
10	370	4245	91	176	158	78	115
10	386	6942	192	302	352	187	242
20		6819	164	223	234	113	186
20		6796	147	172	202	101	169

Table A.18: PAH Fiber-sediment kinetics FG 230/210 12°C

	Fiber Concentration (µg/L)						
Time (d)	Phen	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
0.33	508	4173	68	65	76	25	49
0.33	612	5678	101	125	92	36	69
1	386	5460	81	122	94	40	77
1	457	4809	112	104	106	45	74
2	514	7920	200	240	189	146	209
2	627		229	307	335	212	
4	729		294	367	351	190	272
4	746		291	264	346	186	317
8	680	7436	182	281	293	165	236
8		6510	140	239	248	134	
10	398	4476	175	291	384	231	282

Table A.19: PCB Fiber-sediment kinetics PM 170/110 4°C

	Fiber Concentration (µg/L)									
	Time (d)									
PCB	3	3	8	8	16	16	30	30	50	50
5		98	165	219	228	267	361	292	267	258
18	37	46	127	100			237	279	145	187
31	39	32	103	98	208	130	321	283	251	260
44	125	101	179	129	182	175	226	210	167	147
52	41	31	60	47	85	82	89	75	65	67
66	43	39	86	69	90	98	102	87	101	107
87	45	38	50	42	115	126	165	110	164	151
101	104	93	158	129	218	233	334	266	249	349
110	47	43	78	72	87	95	144	109	97	116
138	15	15	90	37	62	86	63	60	46	45
141	51	44	92	71	87	121	81	69	63	66
151	15	13	52	33	40	66	25	20	16	15
153	42	22	96	81	113	136	92	73	72	69
170	29	30	106	82	91	89	53	40	29	27
180	0	0	29	26	46	52			5	7
183	14	11	19	16	26	21	31	29	25	
187	11	10	20	19			18	15	15	5

Table A.20: PCB Fiber-sediment kinetics FG 230/210 4°C

	Fiber Concentration (µg/L)				
	Time (d)				
PCB	1	3	5	10	20
5	149	261	224	283	312
18	57	131	147	0	121
31	81	103	100	117	140
44	152	241	203	273	181
52	48	76	76	105	97
66	52	115	92	108	107
87	80	151	80	121	144
101	193	335	229	261	288
110	70	134	91	119	106
138	26	43	90	115	88
141	84	128	98	125	118
151	20	30	32	57	58
153	77	110	97	148	127
170	51	69	75	117	92
180	10	23		27	26
183	34	42	36	38	61
187	18	24	29	18	

Table A.21: PCB Fiber-sediment kinetics PM 170/110 12°C

	Fiber Concentration (µg/L)									
	Time (d)									
PCB	3	3	8	8	16	16	30	30	50	50
5	177	130	230	216	217	308	339	243	283	289
18	45	46	188	168	146	254	314	207	203	200
31	58	55	139	133	181	278	167	112	86	93
44	107	101	177	190	190	278	224	178	172	103
52	76	44	74	83	97	147	106	82	72	80
66	73	56	105	105	106	142	152	112	122	129
87	97	91	96	89	86	124	148	96	171	141
101	171	144	243	235	257	408	372	307	298	332
110	83	74	106	103	106	145	131	112	109	124
138	45	44	82	71	66	122	69	63	51	56
141	82	92	94	105	139	142	95	85	68	77
151	16	15	46	38	46	86	24	20	21	18
153	78	70	88	86	131	147	91	65	80	85
170	99	113	85	91	131	153	48	43	31	54
180	18	16	31	25	49	56	0	0	6	4
183	31	34	29	28	35	48	32	25	26	33
187	19	19	18	25	33		19	18	19	19

Table A.22: PCB Fiber-sediment kinetics FG 230/210 12°C

	Fiber Concentration (µg/L)				
	Time (d)				
PCB	1	3	5	10	20
5	153	285	346	248	319
18	102	101	213	128	168
31	114	93	119	104	177
44	121	211	214	196	148
52	66	98	97	83	99
66	79	174	123	97	138
87	107	249	176	196	136
101	230	404	368	326	287
110	94	170	138	104	122
138	32	62	90	91	84
141	86	115	119	121	108
151	19	27	39	45	43
153	79	99	123	102	136
170	48	55	103	92	98
180	17	20	40	45	0
183	39	42	42	35	65
187	18	21	23	24	32

Appendix B: Optimization of Field Sampling

Table B.1: PAH Kinetics in bare fiber

	Fiber Conc (μg/L) Bare Fiber			
Time (d)	Phen	Chrysene	B[b]F	B[a]P
0	0	0	0	0
1	521.87	183.13	67.85	43.62
2	529.16	201.62	93.23	58.58
4	530.26	218.67	168.28	109.00
8	547.61	278.85	141.98	146.44
19	570.58	304.04	172.80	175.80

Table B.2: PAH Kinetics in sampling rod

	Phen	Chrysene	B[b]F	B[a]P
Time(d)	Fiber concentration (μg/L)			
1	379.21	92.02	61.16	44.77
2	381.03	127.89	114.18	66.53
5	346.41	80.69	79.22	44.58
10	433.11	139.23	162.54	118.03
20	440.37	141.35	139.68	120.78
28	466.36	147.64	209.54	134.22
50	490.19	183.59	183.78	130.29

Table B.3: PCB Kinetics in bare fiber

	PCB28	PCB52	PCB153	PCB180
Time(d)	Fiber concentration (μg/L)			
3	112.71	135.20	51.07	18.20
8	157.23	242.52	89.83	28.32
16	206.97	355.90	158.52	61.09
30	253.43	422.32	216.94	90.15

Table B.4: PCB Kinetics in sampling rod

	PCB28	PCB52	PCB153	PCB180
Time(d)	Fiber concentration (μg/L)			
2	47.79	52.18	45.10	19.17
5	58.38	75.79	52.32	22.66
10	98.04	136.03	95.87	27.84
20	83.41	118.89	87.85	35.12
28	137.76	206.49	140.37	62.72
50	158.35	264.77	187.82	73.25

Table B.5: Time to 95% steady state and standard error of coefficients for PAHs

PAHs Time to 95% of Steady State (d)									
Condition	Fiber Type	Temp	Phen	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
Fiber in Water	PM 170/110	25°C	0.24	1.09	1.79	2.27	3.86	1.44	2.17
		12°C	0.33	0.79	0.63	0.82	0.87	0.81	0.98
		4°C	1.21	2.64	3.56	5.34	5.41	2.28	5.19
	FG 230/210	20°C	0.16	0.42	1.06	0.95	1.71	1.31	1.52
		12°C	0.56	0.41	0.61	0.19	0.71	0.57	0.16
Fiber in Sediment	PM 170/110	25°C	0.97		3.63		5.74		13.15
		12°C	1.09	2.34	5.81	8.02	11.93	12.65	12.84
		4°C	1.58	3.53	3.84	20.17	12.72	13.04	19.19
	FG 230/210	12°C	0.55	0.92	2.60	3.59	4.80	4.21	5.63
		4°C	0.35	1.10	2.55	3.31	4.57	3.66	2.07
Fiber in Rod in Sediment	PM 170/110	25°C	1.55		2.83		11.39		16.07
Standard Error in Time to 95% Steady State									
Condition	Fiber Type	Temp	Phen	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
Fiber in Water	PM 170/110	25°C	0.0064	0.0015	0.0026	0.0015	0.0011	0.0042	0.0022
		12°C	0.0158	0.0056	0.0124	0.0075	0.0084	0.0077	0.0057
		4°C	0.0034	0.0015	0.0013	0.0008	0.0012	0.0035	0.0011
	FG 230/210	20°C	0.0249	0.0097	0.0062	0.0041	0.0036	0.0047	0.0041
		12°C	0.0040	0.0127	0.0119	0.0555	0.0095	0.0147	0.0871
Fiber in Sediment	PM 170/110	25°C	0.0955		0.0310		0.0167		0.0023
		12°C	0.1034	0.0430	0.0206	0.0147	0.0125	0.0139	0.0094
		4°C	0.1464	0.0163	0.0497	0.0092	0.0114	0.0167	0.0114
	FG 230/210	12°C	0.4796	0.1088	0.0601	0.0297	0.0239	0.0361	0.0165
		4°C	0.7755	0.1133	0.0600	0.0270	0.0184	0.0499	0.1035
Fiber in Rod in Sediment	PM 170/110	25°C	0.1026		0.0709		0.0142		0.0082

Table B.6: Time to 95% steady state and standard error of coefficients for PCBs

PCBs Time to 95% of Steady State (d)								
Condition	Fiber Type	Temp	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180
Fiber in Sediment	PM 170/110	25°C	20	28			54	93
		12°C		10	16	8	8	
		4°C		16	34	14	13	
	FG 230/210	12°C		2.2	2.4	5.5	3.0	
		4°C		4.3	2.2	8.8	3.2	
Fiber in Rod in Sediment	PM 170/110	25°C	34	65			63	72
Standard Error in Time to 95% of Steady State (d)								
Condition	Fiber Type	Temp	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180
Fiber in Sediment	PM 170/110	25°C	0.11	0.03			0.03	0.03
		12°C		0.42	0.14	0.62	0.62	
		4°C		0.13	0.06	0.38	0.34	
	FG 230/210	12°C		1.10	1.59	0.23	0.82	
		4°C		0.51	1.87	0.30	1.01	
Fiber in Rod in Sediment	PM 170/110	25°C	0.11	0.06			0.06	0.06

Table B.7: Concentration profile over depth – Two layer sediment and sand cap

Depth	Mid-Depth	Phen	Pyr	Chrys	B[a]A	B[b]F	B[k]F	B[a]P
1	0.5	0	0	0	0	0	0	0
2	1.5	166.76	0	0	0	0	0	0
4	3	200.85	0	0	0	0	0	0
7	5.5	123.08	106.40	12.10	4.46	0	0	0
9	7.5	188.94	91.67	15.14	6.43	1.56	0	0
11	10	144.66	82.60	14.82	5.78	3.81	1.79	1.25
14	12.5	150.82	85.08	13.81	4.42	2.37	1.14	2.09
15	14.8	146.27	60.00	0	4.57	0	0	0

Analyte loss to the air

Two 8cm fibers (2 replicates) were exposed to 500 ml spiked water solution and allowed to equilibrate for 2 days. The fiber was withdrawn from the water and one sample was analyzed immediately. The remainder of the fiber was placed in aluminum foil and exposed to room temperature conditions for 24 hr, 48 hr, 96 hr, 7 days, and 14 days. At each exposure period, 1 cm of fiber was cut, it was immediately placed into 100 µL of acetonitrile solvent and analyzed by HPLC. The concentration at each exposure was the average of the two replicates. The following table displays the changes in average concentration over 14 days.

Table B.8: Fiber concentration loss while exposed to room temperature conditions

	Average Fiber Concentration ppb						
Days	Phen	Pyr	Chrys	B[a]A	B[b]F	B[k]F	B[a]P
0	21983	60693	301227	216203	186290	279234	281495
1	953	42608	195857	180220	211684	222426	210865
2	0	34231	145381	150175	184711	183670	163738
4	0	18353	126508	128698	169875	160843	138073
7	0	6349	79834	96554	165731	108491	98468
14	0	0	100236	94580	165171	138210	106671

Appendix C: SPME to predict bioavailability

C.1: New Bedford/Brown Lake sediment – Sequential Dilution

Table C.1: Soil Properties

Sample %	Trial 1		Trial 2		Average ratio
	Moisture Content %	Dry/Wet	Moisture Content %	Dry/Wet	
Control	47.11	0.53	47.46	0.53	0.53
3	48.97	0.51	48.22	0.52	0.51
6	50.45	0.50	49.34	0.51	0.50
12	51.38	0.49	51.70	0.48	0.48
25	52.72	0.47	52.27	0.48	0.48

Table C.2: Sediment mass added to jars

25 A	Mass (g)
Empty jar	213.57
Full (200 mL)	475
Wet sediment	261.43
3 B	Mass (g)
Empty jar	213.96
Full (200 mL)	490
Wet sediment	276.04

Table C.3: PAH Sediment Concentrations

PAH Sediment Concentrations ng/g						
		TOC	0.848	1.074	1.461	2.493
	Log K_{ow}	Log K_{oc}	3%	6%	12%	25%
Phen	4.57	4.36	40	163	257	583
Pyrene	5.18	4.97	549	430	2824	7131
Chrysene	5.86	5.65	31	113	160	387
B[a]A	5.91	5.7	59	160	241	693
B[b]F	6.00	5.79	84	152	270	804
B[k]F	6.00	5.79	33	88	128	379
B[a]P	6.04	5.83	71	190	242	837

Table C.4: PCB Sediment Concentrations

PCB Sediment Concentrations ng/g						
		TOC	0.848	1.074	1.461	2.493
PCB	Log K_{ow}	Log K_{oc}	3%	6%	12%	25%
PCB10	5.26	4.81	22	46	49	241
PCB28	5.71	5.27	753	1468	1816	7052
PCB52	6.16	5.73	952	1762	2254	8210
PCB153	7.06	6.66	337	585	828	2776
PCB138	7.06	6.66	187	358	579	1516
PCB180	7.51	7.13	53	74	94	354

Table C.5: PAH porewater concentration measured with SPME Fiber, New Bedford/Brown Lake sediment

Pore Water Concentration (ng/L)

	3A	3B	3C	3D	Average	STD
Phenanthrene	27.51			14.81	21.16	8.98
Pyrene	50.36			53.11	51.74	1.94
B[a]A	1.093			1.166	1.13	0.05
B[b]F	0.730			0.929	0.83	0.14
B[k]F	0.302			0.213	0.26	0.06
B[a]P	0.403			0.244	0.32	0.11

Pore Water Concentration (ng/L)

	6A	6B	6C	6D	Average	STD
Phenanthrene	38.24	30.32	20.88	37.56	31.75	8.08
Pyrene	45.70	63.46	48.52	59.40	54.27	8.51
B[a]A	2.508	2.870	2.042	2.802	2.56	0.38
B[b]F	0.681	1.412	1.367	0.631	1.02	0.42
B[k]F	0.467	0.377	0.299	0.618	0.44	0.14
B[a]P	0.510	0.427	0.458	0.785	0.55	0.16

Pore Water Concentration (ng/L)

	12A	12B	12C	12D	Average	STD
Phenanthrene	26.40	44.17	37.56	44.78	38.23	8.54
Pyrene	98.58	84.55	82.00	75.19	85.08	9.83
B[a]A	2.580	2.659	2.680	2.609	2.63	0.05
B[b]F	1.377	1.713	1.096	1.904	1.52	0.36
B[k]F	0.629	0.660	0.447	0.467	0.55	0.11
B[a]P	0.590	0.857	0.583	0.753	0.70	0.13

Pore Water Concentration (ng/L)

	25A	25B	25C	25D	Average	STD
Phenanthrene	44.02	45.11	42.19	47.85	44.79	2.37
Pyrene	148.19	167.37	121.61	95.86	133.26	31.20
B[a]A	4.932	5.045	4.925	6.404	5.33	0.72
B[b]F	3.018	3.602	1.285	2.056	2.49	1.03
B[k]F	0.972	0.669	0.802	0.872	0.83	0.13
B[a]P	1.457	1.427	1.260	1.209	1.34	0.12

Table C.6: PCB porewater concentration measured with SPME Fiber, New Bedford/Brown Lake sediment

Pore Water Concentration (ng/L)

	3A	3B	3C	3D	Average	STD
PCB10	53.42	50.27	39.72	53.46	49.22	6.51
PCB28	145.39	135.31	134.33	161.97	144.25	12.83
PCB52	53.56	49.92	50.34	57.91	52.93	3.693
PCB153	0.640	0.603	0.657	0.677	0.64	0.032
PCB138	0.308	0.287	0.322	0.328	0.31	0.018
PCB180	0.022	0.020	0.026	0.026	0.02	0.003

Pore Water Concentration (ng/L)

	6A	6B	6C	6D	Average	STD
PCB10	85.43	54.58	85.91	64.09	72.50	15.69
PCB28	217.10	162.25	201.36	210.99	197.92	24.65
PCB52	80.95	60.79	72.66	74.15	72.14	8.384
PCB153	1.030	0.770	0.918	0.887	0.90	0.107
PCB138	0.498	0.377	0.442	0.436	0.44	0.050
PCB180	0.038	0.033	0.037	0.037	0.04	0.002

Pore Water Concentration (ng/L)

	12A	12B	12C	12D	Average	STD
PCB10	103.95	93.83	91.51	88.74	94.51	6.63
PCB28	220.90	192.65	201.20	215.33	207.52	12.92
PCB52	82.95	75.21	73.23	78.75	77.53	4.27
PCB153	1.006	0.964	0.908	1.037	0.98	0.056
PCB138	0.496	0.470	0.542	0.489	0.50	0.031
PCB180	0.041	0.038	0.039	0.041	0.04	0.002

Pore Water Concentration (ng/L)

	25A	25B	25C	25D	Average	STD
PCB10	158.23	184.28	169.36	154.59	166.61	13.35
PCB28	387.96	445.91	367.54	415.89	404.33	34.08
PCB52	142.03	151.42	129.95	144.15	141.89	8.91
PCB153	1.954	2.065	1.626	1.939	1.90	0.189
PCB138	0.971	1.005	0.770	0.943	0.92	0.104
PCB180	0.078	0.076	0.060	0.077	0.07	0.009

Table C.7: PAH tissue concentrations (µg/g) ppm, New Bedford/Brown Lake sediment

	Phenanthrene	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
3A	1.053	0.242	0.259	0.199	0.255	0.093	0.162
3B	0.203	0.880	0.180	0.153	0.164	0.057	0.098
3C	0.223	0.717	0.084	0.193	0.112	0.091	0.112
3D	0.391	0.376	0.100	0.251	0.171	0.084	0.162
Average	0.272	0.554	0.156	0.199	0.176	0.082	0.134
STD	0.399	0.295	0.081	0.040	0.059	0.016	0.033
CV	1.467	0.533	0.517	0.203	0.338	0.202	0.250

	Phenanthrene	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
6A	0.179	1.087	0.146	0.333	0.157	0.067	0.247
6B	0.692	1.029	0.165	0.305	0.183	0.090	0.168
6C	0.483	0.405	0.121	0.328	0.322	0.124	0.228
6D	0.297	0.273	0.090	0.225	0.178	0.073	0.104
Average	0.413	0.699	0.131	0.298	0.210	0.088	0.187
STD	0.224	0.419	0.033	0.050	0.076	0.026	0.064
CV	0.543	0.600	0.251	0.169	0.360	0.291	0.346

	Phenanthrene	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
12A	0.348	0.880	0.180	0.266	0.230	0.106	0.269
12B	4.215	6.963	1.663	19.244	0.964	0.674	1.928
12C	0.512	0.654	0.314	0.598	0.419	0.212	0.424
12D	0.438	0.549	0.196	0.437	0.398	0.173	0.260
Average	0.43	0.69	0.23	0.43	0.35	0.16	0.32
STD	0.08	0.17	0.07	0.17	0.10	0.05	0.09
CV	0.19	0.24	0.32	0.38	0.296	0.326	0.29

	Phenanthrene	Pyrene	Chrysene	B[a]A	B[b]F	B[k]F	B[a]P
25A	0.918	6.881	0.698	1.171	0.963	0.474	1.016
25B	0.293	2.947	0.242	0.420	0.347	0.159	0.400
25C	4.549	7.668	1.700	2.012	1.173	0.732	2.115
25D	0.308	0.416	0.172	0.376	0.322	0.144	0.257
Average	0.30	1.68	0.21	0.40	0.33	0.15	0.33
STD	0.36	3.26	0.29	0.45	0.36	0.19	0.40
CV	1.19	1.937	1.38	1.123	1.086	1.236	1.226

Highlighted values were removed from the average and standard deviation due to its bias valus.

Table C.8: PCB tissue concentrations (µg/g) ppm, New Bedford/Brown Lake sediment

	PCB10	PCB28	PCB52	PCB153	PCB138	PCB180
3A	0.609	20.085	16.034	5.745	3.783	0.879
3B	0.484	15.830	16.121	4.372	2.475	0.474
3C	0.453	15.238	18.795	5.649	3.160	0.580
3D	0.789	25.084	29.684	7.850	4.492	0.847
Average	0.584	19.059	20.158	5.904	3.478	0.695
STD	0.153	4.560	6.478	1.440	0.862	0.199
CV	0.262	0.239	0.321	0.244	0.248	0.287

	PCB10	PCB28	PCB52	PCB153	PCB138	PCB180
6A	0.653	23.583	22.458	7.052	4.280	0.801
6B	1.029	31.610	35.555	8.483	4.828	0.778
6C	0.806	27.348	30.012	8.323	5.278	0.934
6D	1.120	36.718	37.891	10.932	6.613	1.231
Average	0.902	29.815	31.479	8.697	5.250	0.936
STD	0.212	5.651	6.862	1.621	0.996	0.208
CV	0.235	0.190	0.218	0.186	0.190	0.223

	PCB10	PCB28	PCB52	PCB153	PCB138	PCB180
12A	0.833	26.804	22.745	7.172	4.748	0.790
12B	1.088	38.922	39.518	12.616	7.541	1.191
12C	1.102	36.131	36.452	10.139	6.755	1.126
12D	1.258	41.299	42.457	13.686	8.900	1.494
Average	1.070	35.789	35.293	10.903	6.986	1.150
STD	0.176	6.351	8.717	2.897	1.736	0.289
CV	0.164	0.177	0.247	0.266	0.248	0.251

	PCB10	PCB28	PCB52	PCB153	PCB138	PCB180
25A	1.691	23.938	35.490	10.800	7.111	1.224
25B	0.600	24.027	22.477	7.338	4.736	0.811
25C	0.931	33.679	33.908	10.703	6.858	1.001
25D	1.364	38.509	38.561	10.242	6.792	1.073
Average	1.147	30.038	32.609	9.770	6.374	1.027
STD	0.479	7.265	7.025	1.640	1.101	0.171
CV	0.418	0.242	0.215	0.168	0.173	0.167

Table C.9: Worm Weights Extracted

Replicate	Worm Weights Extracted (mg)
3A	43.1
3B	58.4
3C	44.8
3D	80.9
6A	56.1
6B	52.4
6C	56.3
6D	67.6
12A	72.9
12B	39.7
12C	59.7
12D	62.8
25A	55.2
25B	60.6
25C	50.6
25D	68.9

Table C.10: Time line of all the laboratory work completed

Date	Task Completed
3/2/2007	Moisture contents
3/5/2007	Moisture contents
3/6/2007	Worm dry/wet weights
3/7/2007	Worms into sediment
3/19/2007	Dissolved oxygen measured
	Artificial Pond Water changed 3 times a week
3/28/2007	Worms extracted from sediment
3/28/2007	Fiber extracted from sediment
4/3 - 6/5	Tissue analysis
4/30/2007	Sediment concentration 6, 12% + mositure content
6/4/2007	Sediment concentration 3, 25% + moisture content
6/7/2007	Lipid analysis
6/19/2007	Sediment concentration all dilutions + moisture content

C.3: Hunter's Point Bioaccumulation

Table C.11: Worms Survival

Jar	Worms released	Worms retrieved	Recovery %
1	10	8	80
2	10	7	70
3	10	9	90
4	10	10	100
5	10	9	90
6	10	10	100
7	10	6	60
8	10	9	90
9	10	8	80
10	10	8	80
		Average	**84**

Table C.12: Worm Weight Extracted

Replicate	Worm Weights (mg)
1	102.4
2	101.4
3	121.0
4	116.6
5	118.4
6	118.6
7	54.8
8	101.6
9	109.8
10	121.0

Table C.13: Wet/Dry Ratio

	Dry/Wet
	0.21
	0.16
	0.26
	0.20
	0.18
	0.29
	0.18
	0.07
	0.16
	0.15
Mean	0.18
STD	0.06

Table C.14: Lipid Content

	% Lipid
	9.99
	11.49
	8.38
	7.76
	15.30
Average	10.59

Table C.15: Tissue Concentration

Tissue Concentration Summary ppb								
PCB	Jar 1	Jar 2	Jar 3	Jar 4	Jar 5		Average	STD
#31			309	289	229		276	42
#52	465	453	340	405	324		397	64
#44	112	116	157	76	129		118	29
#66	349	621	143	283	154		310	195
#101	1225	1411	456	1115	612		964	410
#87	75	82	32	76	54		64	21
#110	359	445	117	380	168		294	143
#151	768	1012	314	803	264		632	328
#153	3681	4676	1418	3727	1798		3060	1390
#141	476	652	154	491	348		424	185
#138	2692	3317	977	2669	1281		2187	1006
#187	1385	1797	401	1373	1420		1275	519
#183	807	1022	251	807	699		717	286
#180	1906	2579	578	2042	574		1536	911
#170	834	1184	262	905	755		788	336
#206	67	104	72	104			87	20

Table C.16: Porewater Concentrations

Porewater Concentration ppt		
PCB	Average	Std Dev
#31	0.22	0.08
#28	0.28	0.14
#52	1.10	0.14
#44	0.26	0.09
#66	0.84	0.13
#101	0.84	0.11
#87	0.13	0.03
#110	0.32	0.04
#151	0.31	0.04
#153	0.35	0.04
#141	0.10	0.01
#138	0.35	0.04
#187	0.08	0.01
#183	0.03	0.00
#180	0.05	0.01
#170	0.03	0.00
Total PCB	5.29	

Table C.17: Moisture content and dry/wet ratios

Moisture Content	54.67%
Dry/Wet Ratio	0.453

Table C.18: Sediment Concentrations

Sediment Concentration ng/g		
PCB	Average	Std Dev
#5	11	0.7
#18	15	5.3
#31	64	21.8
#28	55	10.5
#52	5	1.2
#44	53	13.0
#66	113	29.8
#101	16	3.9
#87	59	13.0
#110	107	32.3
#151	348	97.6
#153	88	27.6
#141	313	91.9
#138	211	72.3
#187	101	32.9
#183	372	122.1
#180	192	59.0
#170	27	12.3

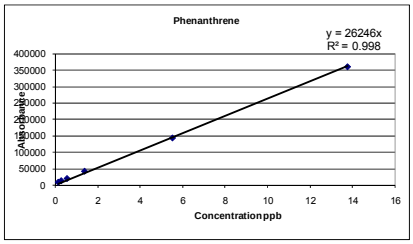
Table C.11: Timeline of completed tasks

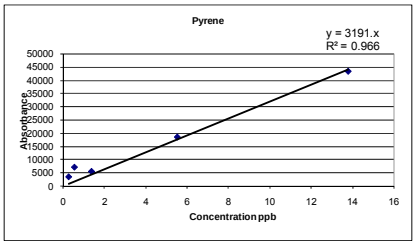
Date	Task Completed
8/20/2007	Hunter's Point sediment received
8/22/2007	Moisture content
8/30/2007	Worms received
8/30/2007	Worm dry/wet ratio - 10 replicates
8/30/2007	Clean worms for analysis
8/30/2007	200 mL sediment poured into beakers
8/31/2007	Worms introduced to sediment environment
9/7/2007	Dissolved oxygen measured
9/7/2007	Water changed
9/14/2007	Dissolved oxygen measured
9/14/2007	Water changed
9/21/2007	Worms removed from sediment

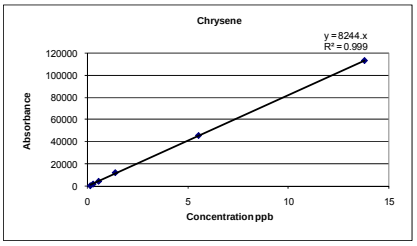
Appendix D: Calibration curves and QA/QC

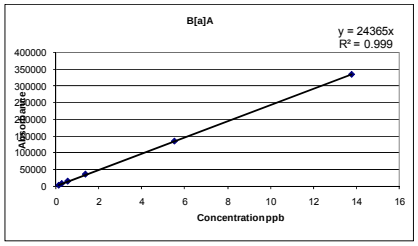
Table D.1: HPLC Fluresecence Detector Method #6 – low concentrations (fiber concentrations, worm concentrations)

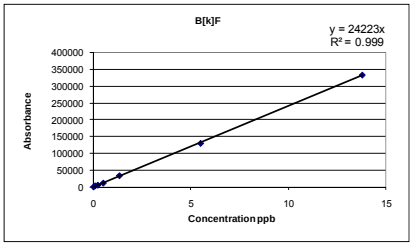
Retention Time	7.56	11.412	15.347	18.822	19.47	25.114	26.047	27.264
Standard	Naphthalene	Phen	Pyr	Chrys	B[a]A	B[b]F	B[k]F	B[a]P
0.0552		8093	3040			1379	5168	5174
0.1377		9808		413	1846	4464	15047	10706
0.276		14257	3437	1922	7106	6609	23525	20654
0.552		20916	7079	4402	14103	12856	46297	35026
1.377		43053	5469	12222	35239	34665	124164	95867
5.52	3051	144170	18439	45767	134517	131076	477879	368123
13.77	7122	360546	43246	113358	335309	334489	1184523	907604
RSF(Area/ppb)		26246	3191.50	8244.6	24365	24223	86132	66051
RSF(ppb/area)		3.81E-05	3.13E-04	1.21E-04	4.10E-05	4.13E-05	1.16E-05	1.51E-05
r2		0.9981	0.9661	0.9998	0.9999	0.9999	1	1

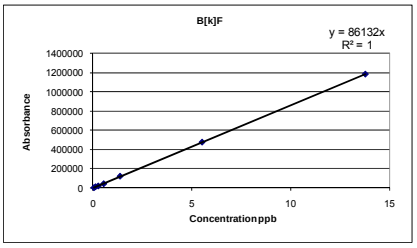












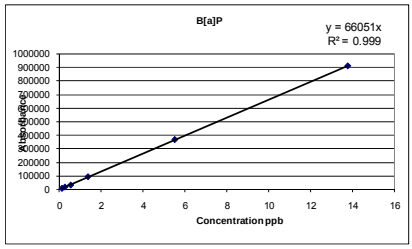


Table D.2: HPLC Fluorescence Detector Method #1 – high concentrations (spiked samples, soil concentrations)

Retention Time	7.994	12.182	16.504	20.464	21.208	27.552	28.593	29.846
Standard	Naphthalene	Phen	Pyr	Chrys	B[a]A	B[b]F	B[k]F	B[a]P
1.377		2330		949	1540	1689	8422	6372
5.52		8064	1349	3360	7178	6868	23711	19555
13.77	394	17851	3025	6715	18210	17470	58852	45851
55.22	1863	72941	10385	25372	70318	65625	232892	187474
137.77	5367	178958	30271	59630	170720	166041	583287	464014
	38.15	1302	560.30	437.2	1244	1203	4232	3371
RSF(ppb/area)	0.02621232	0.00077	0.00178	0.00229	0.0008	0.00083	0.00024	0.0003
r2	0.993	0.999	0.985	0.998	0.999	0.999	1	1

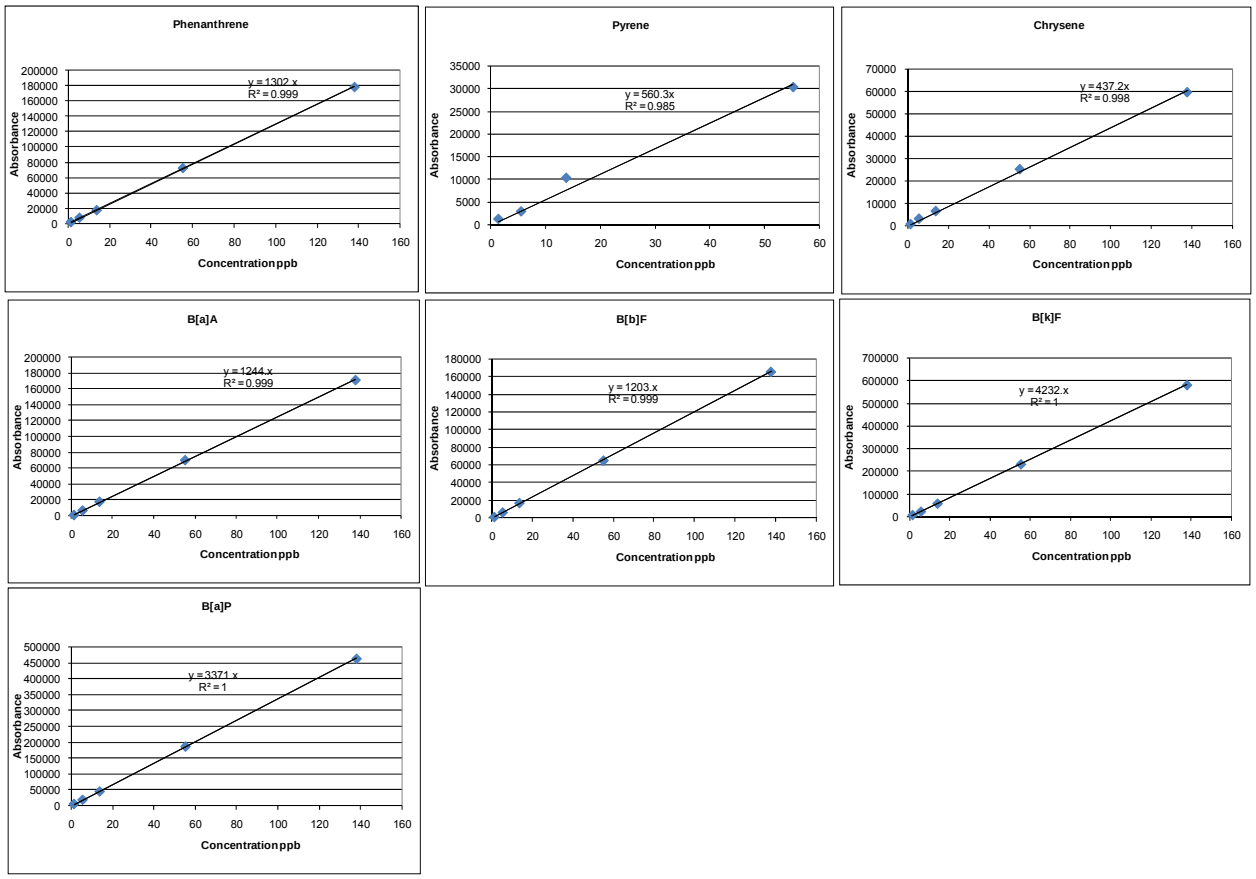
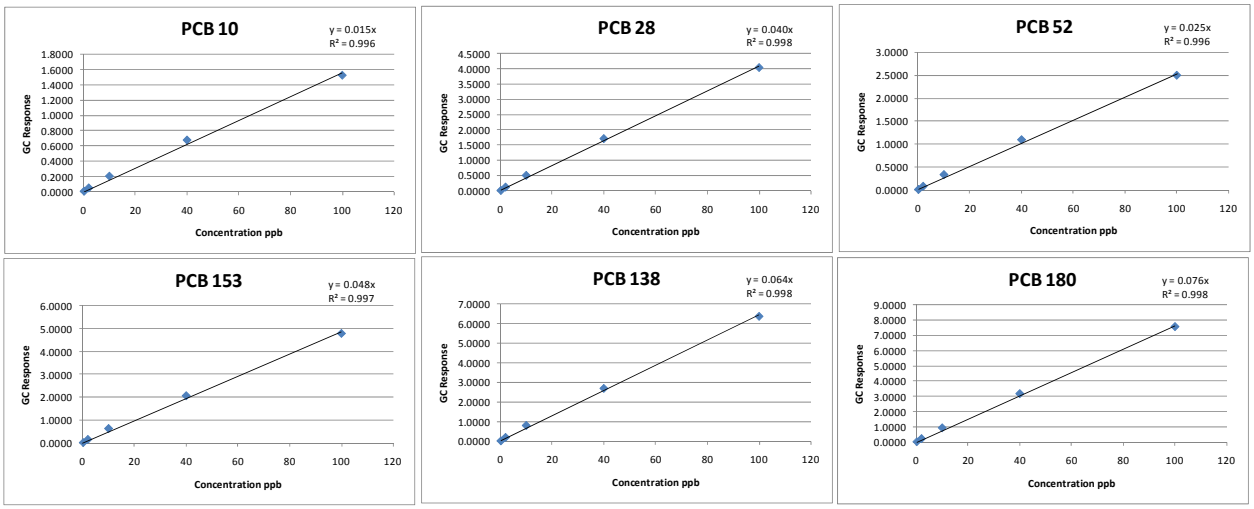


Table D.3 GC Calibration for PCBs in SPME fiber using diluted internal standard

Retention Time	11.523	15.958	17.2	23.629	24.677	27.183
Standard	PCB 10	PCB 28	PCB 52	PCB 153	PCB 138	PCB 180
0.2	0.0048	0.0121	0.0094	0.0169	0.0216	0.0257
2	0.0492	0.1215	0.0809	0.1571	0.2014	0.2315
10	0.2041	0.5036	0.3347	0.6355	0.8101	0.9389
40	0.6791	1.7086	1.0956	2.0761	2.7036	3.1764
100	1.5319	4.0359	2.4993	4.8095	6.3868	7.5649
RSF (area/ppb)	0.0150	0.0400	0.0250	0.0480	0.0640	0.0760
RSF(ppb/area)	66.67	25.00	40.00	20.83	15.63	13.16
r2	0.996	0.998	0.996	0.997	0.998	0.998



Laboratory Control Samples

Efficiency of extraction method and concentration of the sample

Table D.4: PAHs Percentage of measured value to expected value

Sample Set	Phen	Pyr	Chrys	B[a]A	B[b]F	B[k]F	B[a]P
New Bedford/Brown Lake worms	98.33	128.19	103.38	102.85	106.19	99.79	110.42
New Bedford/Brown Lake worms	66.11	11.49	56.37	57.02	61.29	59.85	53.15
Anacostia worm cages	87.71	13.27	112.66	111.58	111.18	110.32	110.83

Table D.5 PCBs Percentage of measured value to expected value

	PCB 10	PCB 28	PCB 52	PCB 153	PCB 138	PCB 180
Average	85.74	95.61	96.73	96.67	96.14	96.23
STD	0.095	0.058	0.045	0.062	0.061	0.068