Application of Passive Sampling Technology in HOCs Contaminated Sediemnt Management and Remediation

by

Songjing Yan, B.S., M.S.

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Approved

Dr. Danny Reible
Chair of Committee

Dr. Chau-Chyun Chen

Dr. Andrew Jackson

Dr. Jeremy Marston

Mark Sheridan
Dean of the Graduate School

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Abstract

Passive sampling technology is an emerging approach of using sorbents to obtain freely dissolved concentrations of target compounds in air or aquatic environment. This research focuses on using passive sampling technology to determine and monitor hydrophobic organic contaminants (HOCs) in sediment porewater using solid phase micro-extraction (SPME) with polydimethylsiloxane (PDMS) fibers.

The traditional way to obtain porewater concentrations is to convert bulk sediment concentrations. Compared to conventional techniques, passive sampling technology has several advantages. It’s efficient and easy to process. It has less impacts on the surroundings and it can provide lower detection limits. More importantly, passive sampling method can directly obtain sediment porewater concentration which is regarded as a good indicator of bioaccumulation and chemical activity. Therefore, it is essential for risk management. In addition, passive samplers have the capability to capture the concentrations that change over time and don’t need to be corrected for organic carbon or lip species on a temporal or spatial scale. Due to the above advantages, passive sampling approach is a promising method to monitoring pollutants in aquatic environment, especially in contaminated sediment management and remediation.

In this dissertation, three applications of passive sampling technologies in HOCs contaminated sediment management were explored based on *in situ* pilot studies. The SPME PDMS method was employed at two different polychlorinated biphenyl (PCB) contaminated sediment sites, Hunter’s Point Navy Shipyard (San Francisco, CA) and Columbia Slough (Portland, OR). The spatial representativeness of passive sampling method was explored and compared with bulk sediment measurement by developing spatial semivariogram models. The SPME PDMS fibers were used to monitor the concentration change with time after application of activated carbon to the sediment surface as an *in situ* treatment at the Hunter's Point site. The ability of passive sampling to assess site transport conditions was also explored. An analytical model was developed to estimate groundwater upwelling velocities and effective diffusion coefficients using the rate of release of performance reference compounds. The results indicate that passive sampling approach is a viable and promising tool for evaluating exposure and risk of HOC contaminated sediment management, the effectiveness of *in situ* remediation and for characterizing site transport characteristics.

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Chapter 1

Introduction

1.1 BACKGROUND AND PROBLEM STATEMENT

Passive sampling technology is an emerging approach to obtain freely dissolved concentrations of target compounds in air or aquatic environment. The basic approach of passive sampling is to use sorbents to concentrate the contaminants of interest from a target environment, then to process and extract the chemical accumulated sorbents.[1]

The freely dissolved porewater concentration (C_{free}) can be used as a predictor for toxicity, chemical activity, bioaccumulation, flux, and exposure for sediments.[2, 3] However, C_{free} is difficult to measure. By using passive sampling techniques, the freely dissolved porewater concentrations can be obtained through measuring the accumulated compounds concentrations on the sorbent and partition coefficients between the sorbent and porewater. Sorbents like polyethylene (PE), polyoxymethylene (POM), and polydimethysiloxane (PDMS) are commonly used passive sampler materials for hydrophobic organic compounds due to their high sorbent water partition coefficients.

Passive sampling technologies were developed as a reliable and easily implemented approach with minimal disturbance for monitoring of contaminants in sediments. Compared to conventional techniques, passive sampling technologies can obtain sediment porewater concentrations directly from the environment (i.e. *in situ*) and provide low detection limits. Because of the passive sampler sorbent's high absorptivity, only a small amount of sorbent is needed to measure the target compounds to a detectable level. The amount of water required is significantly lower for passive sampling to achieve the same detection limits for traditional methods.[4]

Many studies have shown that with low detection limits, the passive sampling methods perform well for water quality monitoring of HOCs.[5–8] Passive sampling methods can also be used as good surrogates for bioaccumulation measurements and availability to benthic organisms of hydrophobic organic compounds.[9–14]

Evaluating performance of sediment remediation, especially of *in situ* capping management, is an important application for passive sampling techniques. The low detection limit in passive sampling methods indicates theirs availability to obtain low contaminant concentrations after remediation. Moreover, *in situ* sediment risk management strategies are mostly associated with reducing exposure and risk rather than sediment concentration, therefore, the traditional bulk sediment measurements do not work well in evaluating the effectiveness.[15] Different with conventional strategies, passive sampling approach can assess exposure and risk directly by monitoring the sediment porewater concentrations directly. Some studies have shown the effectiveness of employing passive sampling technologies to *in situ* sediment remediation.[15–20]

The limitations of passive sampling technologies includes: (1) slow uptake of contaminants onto the passive sampler sorbent potentially requiring a long time for the passive sampler to achieve equilibrium; (2) uncertainty in achievement of equilibrium and equilibrium material water partition coefficients; (3) concerns about loss of target compounds during processing and analysis; (4) low freely dissolved concentrations of hydrophobic organic compounds; and (5) lack of a long documented history.

The primary focus of this thesis is to use passive sampling methods to determine and monitor hydrophobic organic contaminants (HOCs) in sediment porewater and water column using solid phase micro-extraction (SPME) with polydimethylsiloxane (PDMS) fibers and apply this approach to the evaluation of an *in situ* sediment treatment technology.

1.2 RESEARCH OBJECTIVES

Even though passive sampling techniques have shown advantages for determining and monitoring chemical concentrations and transport in the environment and have a wide range of applications, there is still much work to do for passive sampling to earn regulatory acceptance. Expanding the range of field applications is also of research interest for passive sampling techniques.[2]

This research is dedicated to improve the acceptance and confidence in the use of SPME PDMS passive sampling techniques and expand the applications of passive sampling methods. Several specific objectives were addressed in this dissertation: (1) demonstration of the advantages of *in situ* passive sampling methods over traditional technologies, specifically in terms of spatial resolution; (2) demonstration of the SPME PDMS as a practical tool for accessing the effectiveness of *in situ* sediment remediation; (3) evaluation of geostatistical variations in porewater concentrations using passive sampling approach; (4) use of the equilibration rate of passive sampling to estimate water exchange and/or groundwater mixing rates in surficial sediments.

1.3 DISSERTATION STRUCTURE

The dissertation is divided into the following chapters:

1. this introduction
2. a literature review that will focus on the common types of hydrophobic organic contaminants in sediments, the history and development of passive sampling methods, and current important applications of passive sampling technologies for water quality monitoring, evaluating bioavailability and bioaccumulation and evaluating the performance of sediment remedial strategies
3. a discussion of porewater concentration geostatistics using passive sampling and comparing to representativeness of bulk solid concentration measurement by analyzing the results from field studies conducted at Hunter’s Point Navy Shipyard (San Francisco, CA) and Columbia Slough (Portland, OR)
4. the application of SPME PDMS sampling devices for evaluating performance of *in situ* activated carbon placement on a PCB contaminated sediment at Hunter’s Point Navy Shipyard (San Francisco, CA)

5. the development of a mathematical modeling approach for applying SPME PDMS passive sampling technologies to estimate contaminant flux and ground water upwelling velocity
6. a summary of research conclusions of previous chapters and recommendations for future research work.

1.4 REFERENCES

1. Huckins, J. N., Tubergen, M. W. & Manuweera, G. K. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20,** 533–552 (1990).

2. Greenberg, M. S. *et al.* Passive sampling methods for contaminated sediments: Risk assessment and management. *Integr. Environ. Assess. Manag.* **10,** 224–236 (2014).

3. Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2003. Environmental organic chemistry, 2nd ed. Wiley, Hoboken, N.J.

4. Greenwood, R., Mills, G. A. & Vrana, B. Potential applications of passive sampling for monitoring non-polar industrial pollutants in the aqueous environment in support of REACH. *J. Chromatogr. A* **1216,** 631–639 (2009).

5. Vrana, B. *et al.* Passive sampling techniques for monitoring pollutants in water. *TrAC Trends Anal. Chem.* **24,** 845–868 (2005).

6. Alvarez, D. A. *et al.* Comparison of a novel passive sampler to standard water-column sampling for organic contaminants associated with wastewater effluents entering a New Jersey stream. *Chemosphere* **61,** 610–622 (2005).

7. Adams, R. G., Lohmann, R., Fernandez, L. A. & MacFarlane, J. K. Polyethylene Devices: Passive Samplers for Measuring Dissolved Hydrophobic Organic Compounds in Aquatic Environments. *Environ. Sci. Technol.* **41,** 1317–1323 (2007).

8. Allan, I. J., Harman, C., Ranneklev, S. B., Thomas, K. V. & Grung, M. Passive sampling for target and nontarget analyses of moderately polar and nonpolar substances in water. *Environ. Toxicol. Chem.* **32,** 1718–1726

9. Vinturella, A. E., Burgess, R. M., Coull, B. A., Thompson, K. M. & Shine, J. P. Use of Passive Samplers To Mimic Uptake of Polycyclic Aromatic Hydrocarbons by Benthic Polychaetes. *Environ. Sci. Technol.* **38,** 1154–1160 (2004).

10. Cornelissen, G., Breedveld, G. D., Næs, K., Oen, A. M. P. & Ruus, A. Bioaccumulation of native polycyclic aromatic hydrocarbons from sediment by a polychaete and a gastropod: Freely dissolved concentrations and activated carbon amendment. *Environ. Toxicol. Chem.* **25,** 2349–2355 (2006).

11. Friedman, C. L. *et al.* Comparing Polychaete and Polyethylene Uptake to Assess Sediment Resuspension Effects on PCB Bioavailability. *Environ. Sci. Technol.* **43,** 2865–2870 (2009).

12. Lu, X., Reible, D. D. & Fleeger, J. W. Bioavailability of polycyclic aromatic hydrocarbons in field-contaminated Anacostia River (Washington, DC) sediment. *Environ. Toxicol. Chem.* **25,** 2869–2874 (2006).

13. Lu, X., Skwarski, A., Drake, B. & Reible, D. D. Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environ. Toxicol. Chem.* **30,** 1109–1116 (2011).

14. Rosen, G. *et al.* A sediment ecotoxicity assessment platform for in situ measures of chemistry, bioaccumulation and toxicity. Part 2: Integrated application to a shallow estuary. *Environ. Pollut.* **162,** 457–465 (2012).

15. J. Lampert, D., Lu, X. & D. Reible, D. Long-term PAH monitoring results from the Anacostia River active capping demonstration using polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **15,** 554–562 (2013).

16. Cho, Y.-M. *et al.* Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment. *Environ. Sci. Technol.* **43,** 3815–3823 (2009).

17. Oen, A. M. P. *et al.* In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers. *Environ. Sci. Technol.* **45,** 4053–4059 (2011).

18. Mayer, P. *et al.* Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* **10,** 197–209 (2014).

19. Lampert, D. J., Sarchet, W. V. & Reible, D. D. Assessing the Effectiveness of Thin-Layer Sand Caps for Contaminated Sediment Management through Passive Sampling. *Environ. Sci. Technol.* **45,** 8437–8443 (2011).

20. Thomas, C., Lampert, D. & Reible, D. Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **16,** 445–452 (2014).

Chapter 2

Literature Review

2.1 SEDIMENT CONTAMINATION HYDROPHOBIC ORGANIC CONTAMINANTS (HOCS)

2.1.1 Polychlorinated Biphenyls (PCBs)

Polychlorinated biphenyl, or PCB, are a family of anthropogenic organic compounds which have negative human health and ecological effects. The chemical structure of PCBs is a biphenyl connected with 1 to 10 chlorine atoms. Figure 2-1 shows the chemical structure of PCBs. Due to different numbers and positions of chlorine atoms, there are theoretically 209 PCB congeners listed. PCBs were first used in industry in 1929 and were manufactured till 1977 in the United States. Jensen et al. (1966; 1969), first demonstrated PCBs to be an environmental contaminant and then found that they tended to accumulate in marine organisms.[1, 2] In 1976, all PCB uses in the United States were banned under the Toxic Substances Control Act (TSCA).

Studies have shown that PCBs have negative human health and ecological effects, including an increase in cancer incidence, brain damage, liver damage, skin sores, and immune system problems.[3–7] Similar to PAHs, human beings and wildlife are exposed to PCBs through skin contact with contaminated water or sediment, through breathing contaminated air or indirectly through PCB contaminated food. Of these, the primary sediment concerns are associated with fish exposure, PCB accumulation and the resulting PCB contaminated fish in the human diet.

With low reactivity, high stability and slow biodegradation rate, PCBs tend to be very stable in environment. Elevated levels of PCBs are found in many sediment environments more than forty years after being banned in the United States. In other words, the presence of PCBs in sediments poses potential long-term risks for the environment.

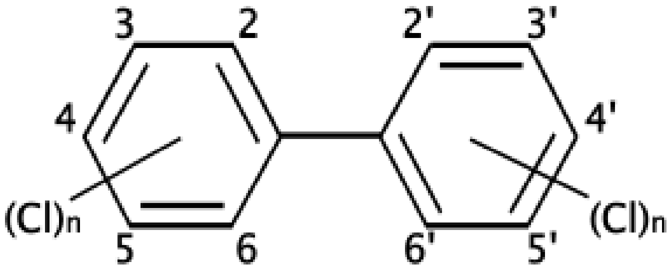


Figure 2-1. Chemical structure of PCBs

2.1.2 Other Organic Compounds

A variety of organic contaminants other than PCBs accumulate in sediment environment. Polycyclic Aromatic Hydrocarbons (PAHs) are one class of organic pollutants that commonly encountered in sediments. The United States Environmental Protection Agency (EPA) has determined some PAHs are probable human carcinogen.[8] People and wildlife are exposed to PAHs through direct contact, indirectly through diet, breathing or skin contacting.

Polychlorinated dibenzodioxins (PCDDs), commonly referred to as dioxins, are significant environmental pollutant as well. Different dioxin compounds exhibit different toxicity levels.[9] Studies have shown that the dioxins can accumulate in humans and cause health problems including blood issues, tumors, and so on.[10]

Dichloro-diphenyl-trichloroethylene (DDT) is another commonly observed contaminant. In 1960s, DDT was noted to be easily accumulated in environment and may cause health problem to human and wildlife.[11] By-products of DDT, for example, dichloro-diphenyl-dichloroethylene (DDE) and dichloro-diphenyl-chloroethane (DDD) are commonly found in DDT-polluted areas and are of environment concern as well.

2.2 FREELY DISSOLVED CONCENTRATIONS

The freely dissolved concentrations in sediment porewater (C_{free}) refers to the concentration of sediment contaminants not bound to particulate matter, colloids, or dissolved organic carbon.[12] They are usually difficult to measure. Some hydrophobic organic contaminants, such as chemicals discussed earlier, PAHs, PCBs, DDT and some other pesticides and insecticides are typically associated with precipitated or suspended particulate matter or colloidal organic carbon. Only a small fraction is freely dissolved in sediment porewater.

The freely dissolved porewater concentrations of these hydrophobic organic contaminants can be used as a predictor for toxicity, bioaccumulation, flux, and exposure for sediment sites risk management.[13] Smedes et al. (2013) discussed using passive sampling methods used for sediment risk assessment by estimating PAHs and PCBs pore water concentrations.[14] Mayer et al. (2014) discussed the application of freely dissolved concentrations for assessing and predicting sediment toxicity to benthic organisms.[15]

The bioaccumulation factor and bioconcentration factor can also be estimated from freely dissolved porewater concentration. Kraaij et al. (2003) and Lu et al. (2003) both described that the bioaccumulations of HOCs can be indicated by porewater concentrations.[16,17] By measuring biota-sediment accumulation factor (BSAF), Cornelissen et al. (2006) reported that the freely dissolved porewater concentrations indicate bioaccumulation better than sediment measurement.[18] Lu et al. (2011) introduced a model to predict bioaccumulation potential and bioavailability of PAHs and PCBs by freely dissolved porewater concentrations:[19]

$$C_{t,predict} = K_{ow} \times C_{free}$$

where $C_{t,predict}$ is the predicted lipid-normalized bioaccumulation and Kow is the octanol–water partition coefficient. This model accurately predicted bioaccumulation in deposit feeding oligochaetes and thus an accurate measure of the freely dissolved concentrations of target compounds is needed to use this model.

2.3 PASSIVE SAMPLING METHODS

2.3.1 Development of Passive Sampling Technologies

Passive sampling is the process of exposing a sorbent passively, i.e. without disturbing the environment, to accumulate a target contaminant. Passive sampling technologies were first used for air quality monitoring of volatile compounds in the early 1970s and have been accepted by regulatory agencies over time.[20] They have primarily been used to define personal exposure, e.g. as a sorbing badge worn on one’s person.

However, the application of passive sampling technologies for sediment and water monitoring were developed later and still need more research for regulatory acceptance.

Hesslein (1976) described a diffusion based dialysis membrane device to obtain *in situ* porewater concentrations.[21] However, this method requires large amount of water to be collected to achieve needed detection limits for hydrophobic compounds. A means of concentrating the target hydrophobic organic is needed to achieved adequate detection limits.

With the development of semi-permeable membrane devices (SPMDs), which concentrated contaminants in an organophyllic gel, researchers sought to apply passive sampling technologies to explore surface water and sediment porewater pollutant bioaccumulation and concentrations in 1990s.[22,23] A SPMD contains a thin film of lipids and is placed into contaminated aquatic environments, then is removed for analysis.[22] The SPMD approaches are more consistent, less costly and more convenient than conventional water extraction methods since they don’t require a pre-filtration step compared to traditional methods.[23] Nevertheless, SPMDs are not widely used in contaminants profile in water and sediments. The drawbacks of SPMD approaches includes: very slow equilibration for highly hydrophobic contaminants, and difficulty in identifying target compounds and toxicity from the extract.[24]

Solid phase micro-extraction (SPME) technologies were developed in 1990s and the first SPME device was fused silica fibers coated with polymers.[25,26] In the following decades, many alternative materials have been explored to be used as polymer extracting phases and solid supports.[27] Polyethylene (PE),[28] polyoxymethylene (POM),[29] and polydimethylsiloxane (PDMS) are the most commonly used passive sampler materials for matrix-SPME.[30] In the study of Mayer et al. (2000), the surrounding sediment matrix was used as a reservoir for an equilibrium extraction and the concentrations of persistent and bioaccumulative pollutants were measured by glass fiber coated with polydimethylsiloxane (PDMS).[30] This approach was termed as matrix solid phase micro-extraction technique and the current thesis is focused on methods that developed from that approach.

2.3.2 Commonly Used Passive Samplers

2.3.2.1 Polyethylene (PE) Sheets

Polyethylene (PE) is a common polymer membrane which has low hardness and rigidity. Figure 2-2 shows the chemical structure formula of the repeating unit for PE. PE has good chemical resistance to strong acid, bases, oxidants and reducing agents. Polyethylene is commonly classified by its density and branching: high-density polyethylene (HDPE) has a density range of 0.93–0.97 g/cm^3 while low-density polyethylene (LDPE) has a density range of 0.91–0.93 g/cm^3. Compared with HDPE, LDPE has lower tensile strength and enhanced ductility. Therefore, LDPE finds applications in both rigid containers and plastic films.

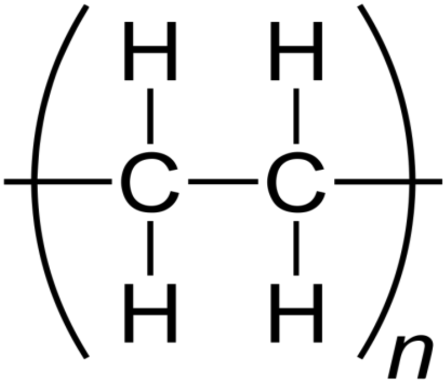


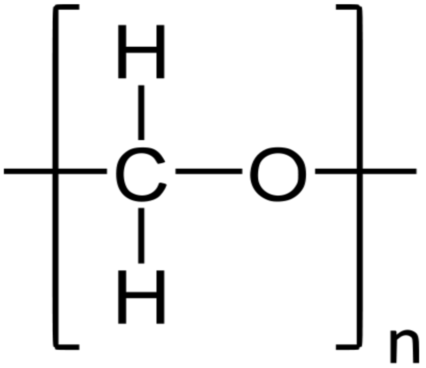
Figure 2-2. Polyethylene Structure Formula of the Repeating Unit

The most commonly used PE devices are LDPE flat sheets, which is produced by free-radical polymerization. Some studies have applied PE as passive samplers for aquatic organic contaminants monitoring.[28, 31, 32] To determine freely dissolved hydrophobic organic contaminant concentrations in surface water and sediment, polyethylene is deployed and passively absorbs target compounds. After allowing time for equilibration, the PE sheets are retrieved and extracted for analyze.

The sizes and thicknesses of PE flat sheets can be easily tuned to meet specific demands. Due to its ubiquity, LDPE has huge advantage of low cost. As a simple and effective method for *in situ* sampling, PE sheets with large volume can collect a large amount of chemicals, which has the potential to lower detection limits.

2.3.2.2 Polyoxymethylene (POM) Sheets

Polyoxymethylene (POM) is a polymer material with high tensile strength, impact strength, and compression strength. It also possesses good abrasion and wear resistance. Due to these advantages, POM has been widely used in many engineering applications since 1960s including in the automobile and electronics industry as an alternative to metals. It is also used as a material for household application, such as door handles and toys.[33–36] POM is produced through the polymerization of formaldehyde and has good chemical stability. Figure 2-3 shows the chemical structure formula of the repeating unit for POM. For water quality monitoring, POM sheets are inserted into aquatic sampling locations, left to equilibrate for some time and then retrieved for chemicals concentration analyze procedure on instruments.[29, 37]



$$\left[-CH_2-O-\right]_n$$

Figure 2-3. Polyoxymethylene structure formula of the repeating unit

The thickness of POM sheets for passive sampling technologies can vary from tens to hundreds micrometers, nevertheless, the POM materials thicker than 100 µm are very slow to achieve equilibrium, which causes problems in practical applications.[38] POM exhibits a high capacity for hydrophobic organics and thus can be used to detect low concentrations in aqueous environment.

2.3.2.3 Polydimethylsiloxane (PDMS) Fibers

Possessing unique rheological properties, polydimethylsiloxane (PDMS) is the most popular silicon-based polymer. It is a widely used surfactant and finds applications in cleaning products, food, lubricants and many other fields. PDMS can be crosslinked and the crosslinked PDMS exhibits a hydrophobic surface, which makes it repel water and alcohols and has the potential of absorbing HOCs. Figure 2-4 shows the chemical structure formula of the repeating unit for PDMS.

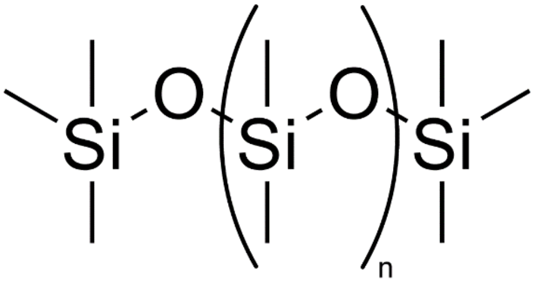


Figure 2-4. Polydimethylsiloxane structure formula of the repeating unit

Polydimethylsiloxane is commonly coated on a cylindrical glass core, for example an optical fiber, and the combination work as passive samplers.[30] The thickness of PDMS fibers can be as small as 10 µm. Similar to other PE and POM, PDMS fibers are deployed in sampling sediment till equilibrium and then processed and extracted for porewater concentration determination. The application and academic research of using PDMS fibers as passive samplers have been reported in many studies.[30, 39–41]

PE and POM are usually used in sheet shape while PDMS is often coated on cylindrical cores. PDMS can also be fabricated as a sheet although the cylindrical fibers have distinct geometrical advantage when inserted into sediments. PE and POM have larger sorptive capacities, which leads to lower detection limits of target compounds. Meanwhile, PDMS fibers have faster kinetics than PE and POM sheets.[37] The SPME PDMS fibers are usually fragile and require protective shielding, particularly in coarse sediments.

2.4 PERFORMANCE REFERENCE COMPOUNDS (PRCS)

The contaminant concentrations absorbed to passive samplers are proportional to freely dissolved porewater concentrations. Therefore, the freely available concentrations of target compounds can be calculated from the passive sampler sorbent concentrations and the compound's sorbent-water partition coefficient by the following equation at equilibrium:

$$C_{free} = \frac{C_{fiber}}{K_{pw}}$$

Different compounds require different exposure time to achieve equilibrium between passive sampler polymer and sediment porewater. Some studies have shown that for many hydrophobic organic compounds to obtain equilibrium, passive sampler sorbents need to be placed in the environment for weeks or months.[29, 31, 32] For samplers where equilibrium is uncertain, some method of evaluation of the extent of equilibration is required.

Performance reference compounds (PRCs) can be used to estimate the non-equilibrium uptake.[42] PRCs are pre-loaded onto a passive sampler and their release indicates the extent to which target compounds of similar characteristics are sorbing to the passive sampler. PRCs are chemicals not present in the sampling sediment or present in substantially different concentrations that typically are analyzed in the same manner and at the same time as the target compounds. Commonly used PRCs are isotopes of the target compounds, such as deuterated or C^{13} labeled PAHs and PCBs.

Huckins et al. first developed a first order release theory of using PRCs to estimate the fraction of equilibrium achieved to obtain accurate porewater concentrations for SPMDs.[42] The depletion of the PRCs is inversely related to the uptake of target compounds with equivalent sorption properties and thus the extent of PRCs' release can be used to correct the non-equilibrium exposure of passive samplers. In the following years, studies applied PRCs approach on SPME passive samplers like PE, POM and PDMS using mass transfer models to describe the exchange between the environment and the passive sampler fiber.[31, 43–46] These models can be used to relate PRC release information on a few compounds to the prediction of the extent of equilibration of other compounds that are homologues but not identical to the PRC compounds.

Fernandez et al. developed a mass transfer model which considered both mass transfer resistances due to retarded diffusion external to the passive sampler sorbent (PE sheet) and the internal mass transfer within the polymer.[44] The thicker the polymer is, the longer the exposure time is required for absorption to reach equilibrium. Therefore, the passive sampler thickness has been reduced for application, which means that for thin passive sampler polymers, the external transport resistances often dominate uptake kinetics over internal transport resistances. Lampert et al. developed a model for thin SPME PDMS fibers neglecting internal transport resistances.[45] Lampert used a practical analytical solution to obtain an effective diffusion coefficient exterior to the PDMS fibers. The analytical solution used Carslaw and Jaeger's analogous heat conduction problem.[47] For PDMS fibers, Shen developed an analytical model for the fate and transport of compounds in a cylindrical system by applying the Laplace transform and asymptotic analysis.[48] Although the external resistance only models are generally valid for thin layers of PDMS, Choi et al. showed that for applications using PE sheets as passive samplers, the internal and external resistance model fits the experimental uptake data better than the external resistances only model.[49] In general, the external resistances model is likely to be valid for thin layers of PDMS while internal resistances may be more important for PE and POM.

In application, since the models are adjusted to the observed behavior of a few PRC compounds, it makes very little difference which model is applied as long as a broad range of hydrophobicites are included as PRCs. The primary difference is that a model that captures the key processes will presumable lead to model parameters that better physically represent the system under study.

2.5 CURRENT USE OF PASSIVE SAMPLING METHODS

Even though passive sampling methods are still an emerging technology, the application of passive sampling devices have been wide. In current research, some key applications of passive sampling technologies includes water quality monitoring of HOCs,[32,50–54] estimating bioavailability and bioaccumulation potential,[19,53,55–59] and evaluating assessment and remediation of contaminated sediment sites.[39,41,60,61]

2.5.1 Passive Sampling Devices Used for Water Quality Monitoring of HOCs

Vrana et al. (2005) reviewed the typical applications of passive sampling methods in accessing the concentration of hydrophobic contaminants in aquatic environment.[50] In this review, fifty-one applications were reviewed. The researchers concluded that passive sampling methods performed as a promising tool for determining HOCs concentrations in water columns. Adams et al., (2007) used polyethylene devices to access the concentrations of eight PAHs and five PCBs in aquatic environments.[32] Ouyang et al. (2007) employed SPME PDMS fibers to determine six PAHs concentrations in water.[51]

Additionally, passive sampling methods show ability to detect, quantify and monitor the HOCs concentrations in sediment porewater as well as water columns. In Allan et al. (2009), seven different passive sampling devices were used for monitoring HOCs in field applications.[52] Mayer et al. (2000) determined sediment porewater concentrations using disposable PDMS fibers.[30] PE stripes were employed for PCBs and PAHs porewater measurement.[43,44] Gschwend et al. (2011) used PE, POM and PDMS fibers to determine PCB concentrations in both tumbled and passive sediment porewater.[53]

In general, the passive sampling technologies can overcome many shortcomings that conventional sediment measurement have in monitoring HOCs concentrations in aquatic environment. For example, the bulk sediment measurement usually require large amount of water to meet detection limits and unable to capture the concentrations that change over time.[50]

Another concern about the bulk sediment measurement is the spatial statistical variability. The sampling procedure for sediment samples are usually not continuous in space, and the bulk sediment concentrations may vary spatially due to the contaminant sources, which indicates the importance of spatial analysis for sediment measurement. Due to the cost and complexity of *in situ* monitoring, the sorbents are often placed at a small number of locations at a given site and generally measure only a small volume of interstitial water. This leads to concerns about the representativeness of passive sampler measurements similar to the concerns about solid measurements. Therefore, the spatial variability and representativeness of porewater concentrations and passive sampling methods needs to be explored and compared with sediment measurements.

2.5.2 Passive Sampling Devices Used as an Indicator for Bioaccumulation Measurements

Since the freely dissolved porewater concentration (C_{pw}) has the ability to estimate the bioaccumulation factor and bioconcentration factor, passive sampling technologies, which can measure C_{pw} directly, can be applied as a surrogate for bioaccumulation measurements of HOCs. Many studies have shown that passive sampling methods can be used as a better prediction to assess the bioavailability and bioaccumulation than traditional measurements.[19,53,56,58] Gomez-Eyles et al., (2012) compared different approaches for PAH bioavailability in earthworms (*Eisenia fetida*) and rye grass (*Lolium multiflorum*) root by: exhaustive acetone/hexane extractions, mild solvent (butanol) extractions, cyclodextrin extractions, and two passive sampling methods—SPME and polyoxymethylene solid phase extraction.[58] The results indicated that passive sampling methods provides better prediction than other approaches used. Lu et al. (2011) evaluated the bioavailability of PAHs and PCBs in the deposit-feeding oligochaete *Ilyodrilus templetoni* by SPME PDMS fibers.[19] In Gschwend et al. (2011), the bioaccumulation of PCBs in marine polychaete, *Neanthes arenaceodentata* was determined by three passive samplers: PE, POM and PDMS.[53] Janssen et al., (2011) showed the POM samplers could evaluate the PCBs bioavailability changes on *Neanthes arenaceodentata*, resulted from activated carbon *in situ* and *ex situ* sediment management.[56] Bioaccumulation in these studies was well predicted by the product of the C_{pw} and the HOCs octanol-water partition coefficient.

Bioaccumulation is proportional to chemical activity rather than concentration in a media. Therefore, a viable and accurate method for determining C_{pw} is important for sediment management.

2.5.3 Passive Sampling Devices Used for Assessing Effectiveness of Sediment Remediation

For in-situ management of sediments by capping or treatment, the traditional approaches to the bulk solid concentrations to evaluate remedy performance are not beneficial. The bulk solid measurements do not indicate reductions in bioavailability (e.g. due to the addition of sorbents to sediments) and are misleading if used to indicate contaminant movement into a non-sorptive material such as sand.[40] Measurements of the most available and mobile fraction, that is, in the porewater, can indicate the effectiveness of in-situ capping or treatment. Porewater measurements by conventional methods, however, usually have high detection limit or it may be difficult to generate representative porewater to measure. Passive sampling is a promising approach because it is conducted in-situ and does not require porewater extraction or sediment disturbance to monitor and evaluate porewater concentrations. Some studies have shown the effectiveness of applying passive sampling methods to sediment management,[15,52] especially in evaluating *in situ* sediment remediation, including SPMDs,[60] PE and POM,[61] and PDMS.[30, 39, 41]

Cho et al. (2009) reported a field application of SPMDs in monitoring the PCBs concentrations in South Basin near San Francisco bay, CA, 18 months after activated carbon treatment.[60] Oen et al., (2011) employed both polyethylene (PE, 51 µm thick) and polyoxymethylene (POM, 17 µm thick) to monitor PCB concentration profiles 30 months after treatment using an activated carbon amendment in an *in situ* study conducted in San Francisco Bay, CA.[61] A study completed by Lampert et al. (2011) used polydimethylsiloxane (PDMS) to assess thin-layer sand capping for polycyclic aromatic hydrocarbons (PAHs) contaminated sediment.[39] In Thomas et al.,(2014), polydimethylsiloxane (PDMS) were used to access three different *in situ* remediation of contaminated sites: Chattanooga Creek (Chattanooga, TN) (PAH contaminated, capped with fresh sand/sediment capped and amendment materials), Eagle Harbor (Bainbridge Island, WA) (PAH contaminated, capped with clean sediments) and Hunter's Point (San Francisco, CA) (PCB contaminated, capped with activated carbon).[41] All these studies show that passive sampling techniques are useful for evaluating the performance of *in*-situ remedial approaches in sediments.

For many *in situ* risk management for HOCs contaminated sediments, the remediation materials, such as activated carbon, are only placed at the surface of sediment sites. Moreover, the activated carbon is designed to reduce the availability and mobility of contaminant and does not change the bulk solid concentration. Therefore, a viable method to monitor the vertical concentration profiles of porewater concentration is necessary for accurate assessment of reductions in availability and mobility, which could be explored as an application of passive sampling methods.

There are limited studies that demonstrate the application of passive sampling in evaluating activated carbon sediment remediation under full scale in congeners and profiles over several years in field conditions. More pilot studies are necessary to work as a bridge to connect the practical application with academic research and fulfill the need for the implementation of passive sampling methods for evaluating *in situ* sediment management.

2.5.4 Passive Sampling Methods for Estimating Contaminant Flux and Groundwater Velocities

The risks that hydrophobic organic compounds in sediments pose to the overlying water column is largely controlled by the contaminant flux from the sediments. For contaminated sediment site management, it is critical to understand contaminant behavior in terms of direction and magnitude of flux.[62] The velocity of groundwater moves upward, is also an important parameter in controlling flux to overlying water.[63] There are several studies explored the ability to estimate effective diffusion coefficients or velocities by passive sampling materials: Schaanning (2006) used SPMDs;[64] Liu et al

(2013) employed LDPE attached to horizontal and vertical plates;[62] Beckinghan and Ghosh (2013) conducted experiments with POM;[65] Thomas (2014) explored diffusive and advective flux models to assess the importance of diffusive-like processes and advection-like processes through PDMS fibers.[41]

The SPME PDMS fibers are commonly used as passive samplers and have faster kinetics than LDPE and POM. Therefore, an exploration of utilizing SPME PDMS fibers to estimate contaminant flux and groundwater upwelling velocity is necessary for expand the passive sampling applications improve the regulatory acceptance.

2.6 SUMMARY

Passive sampling technology is an approach developed to assess freely dissolved concentrations of target compounds in air, sediment porewater or surface water. Since it can obtain freely dissolved porewater concentrations directly, which are related to chemical activity and bioaccumulations, passive sampling method has several advantages over conventional methods for monitoring contaminants fate and transport in environment.

The overall objectives for passive sampling research is to improve the regulatory acceptance and explore more applications. Currently, the key applications of passive sampling techniques includes monitoring HOCs concentrations for water quality monitoring, estimating bioavailability and bioaccumulations potentials, and evaluating the sediment risk management and remediation.

In the following chapters of this dissertation, several applications and problems of passive sampling technologies are addressed expanding on current applications. The spatial representativeness of porewater concentrations will be assessed by passive sampling and compared to that of bulk sediment concentrations by developing spatial semivariogram models. SPME PDMS fibers will also be used to monitor the concentration profiles changes with time caused by placement of an activated carbon amendment at a PCB contaminated sediment site. The ability of passive sampling to obtain vertical concentration profiles of PCBs and estimate groundwater upwelling velocities and effective diffusion coefficients in sediments will also be assessed.

2.7 REFERENCES

1. Jensen, S. Report of a New Chemical Hazard. *New Sci.* **15,** 612 (1966).

2. Jensen, S., Johnels, A. G., Olsson, M. & Otterlind, G. DDT and PCB in Marine Animals from Swedish Waters. *Nature* **224,** 247–250 (1969).

3. Jonsson, H. T. *et al.* Prolonged ingestion of commercial DDT and PCB; effects on progesterone levels and reproduction in the mature female rat. *Arch. Environ. Contam. Toxicol.* **3,** 479–490 (1975).

4. Kimbrough, R. D. Human health effects of polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs). *Annu. Rev. Pharmacol. Toxicol.* **27,** 87–111 (1987).

5. Erickson, M. D. *Analytical Chemistry of PCBs, Second Edition*. (CRC Press, 1997).

6. Jacobson, J. L., Jacobson, S. W. & Humphrey, H. E. B. Effects of exposure to PCBs and related compounds on growth and activity in children. *Neurotoxicol. Teratol.* **12,** 319–326 (1990).

7. Rothman, N. *et al.* A nested case-control study of non-Hodgkin lymphoma and serum organochlorine residues. *The Lancet* **350,** 240–244 (1997).

8. NORRIS, G. EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals & User Guide, US. Environmental Protection Agency. *http://www.epa.gov/heasd/products/pmf/pmf.html* (2008).

9. Haws, L. C. *et al.* Development of a Refined Database of Mammalian Relative Potency Estimates for Dioxin-like Compounds. *Toxicol. Sci.* **89,** 4–30 (2006).

10. Berg, M. V. den, Jongh, J. D., Poiger, H. & Olson, J. R. The Toxicokinetics and Metabolism of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Dibenzofurans (PCDFs) and Their Relevance for Toxicity. *Crit. Rev. Toxicol.* **24,** 1–74 (1994).

11. Carson, N. A. J. & Neill, D. W. Metabolic Abnormalities Detected in a Survey of Mentally Backward Individuals in Northern Ireland. *Arch. Dis. Child.* **37,** 505–513 (1962).

12. Schwarzenbach, R. P. General Introduction and Sorption Processes Involving Organic Matter. *Environ. Org. Chem.* 275–330 (2003).

13. Greenberg, M. S. *et al.* Passive sampling methods for contaminated sediments: Risk assessment and management. *Integr. Environ. Assess. Manag.* **10,** 224–236 (2014).

14. Smedes, F., van Vliet, L. A. & Booij, K. Multi-Ratio Equilibrium Passive Sampling Method to Estimate Accessible and Pore Water Concentrations of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Sediment. *Environ. Sci. Technol.* **47,** 510–517 (2013).

15. Mayer, P. *et al.* Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* **10,** 197–209 (2014).

16. Kraaij, R. *et al.* Measured Pore-Water Concentrations Make Equilibrium Partitioning Work A Data Analysis. *Environ. Sci. Technol.* **37,** 268–274 (2003).

17. Lu, X., Reible, D. D., Fleeger, J. W. & Chai, Y. Bioavailability of desorption-resistant phenanthrene to the oligochaete Ilyodrilus templetoni. *Environ. Toxicol. Chem.* **22,** 153–160 (2003).

18. Cornelissen, G., Breedveld, G. D., Næs, K., Oen, A. M. P. & Ruus, A. Bioaccumulation of native polycyclic aromatic hydrocarbons from sediment by a polychaete and a gastropod: Freely dissolved concentrations and activated carbon amendment. *Environ. Toxicol. Chem.* **25,** 2349–2355 (2006).

19. Lu, X., Skwarski, A., Drake, B. & Reible, D. D. Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environ. Toxicol. Chem.* **30,** 1109–1116 (2011).

20. Palmes, E. D. & Gunnison, A. F. Personal Monitoring Device for Gaseous Contaminants. *Am. Ind. Hyg. Assoc. J.* **34,** 78–81 (1973).

21. Hesslein, R. H. An in situ sampler for close interval pore water studies1. *Limnol. Oceanogr.* **21,** 912–914 (1976).

22. Huckins, J. N., Tubergen, M. W. & Manuweera, G. K. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20,** 533–552 (1990).

23. Huckins, J. N., Booij, K. & Petty, J. D. Introduction to Passive Sampling. in *Monitors of Organic Chemicals in the Environment* 1–28 (Springer, Boston, MA, 2006).

24. Namieśnik, J., Zabiegała, B., Kot-Wasik, A., Partyka, M. & Wasik, A. Passive sampling and/or extraction techniques in environmental analysis: a review. *Anal. Bioanal. Chem.* **381,** 279–301 (2005).

25. Belardi, R. P. & Pawliszyn, J. B. The Application of Chemically Modified Fused Silica Fibers in the Extraction of Organics from Water Matrix Samples and their Rapid Transfer to Capillary Columns. *Water Qual. Res. J.* **24,** 179–191 (1989).

26. Arthur, C. L. & Pawliszyn, J. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem.* **62,** 2145–2148 (1990).

27. Lord, H. & Pawliszyn, J. Evolution of solid-phase microextraction technology. *J. Chromatogr. A* **885,** 153–193 (2000).

28. Allan, I. J., Ruus, A., Schaanning, M. T., Macrae, K. J. & Næs, K. Measuring nonpolar organic contaminant partitioning in three Norwegian sediments using polyethylene passive samplers. *Sci. Total Environ.* **423,** 125–131 (2012).

29. Cornelissen, G., Pettersen, A., Broman, D., Mayer, P. & Breedveld, G. D. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environ. Toxicol. Chem.* **27,** 499–508 (2008).

30. Mayer, P. *et al.* Sensing Dissolved Sediment Porewater Concentrations of Persistent and Bioaccumulative Pollutants Using Disposable Solid-Phase Microextraction Fibers. *Environ. Sci. Technol.* **34,** 5177–5183 (2000).

31. Booij, K., Smedes, F. & van Weerlee, E. M. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **46,** 1157–1161 (2002).

32. Adams, R. G., Lohmann, R., Fernandez, L. A. & MacFarlane, J. K. Polyethylene Devices: Passive Samplers for Measuring Dissolved Hydrophobic Organic Compounds in Aquatic Environments. *Environ. Sci. Technol.* **41,** 1317–1323 (2007).

33. Schweitzer, C. E., Macdonald, R. N. & Punderson, J. O. Thermally stable high molecular weight polyoxymethylenes. *J. Appl. Polym. Sci.* **1,** 158–163 (1959).

34. Koch, T. A. & Lindvig, P. E. Molecular structure of high molecular weight acetal resins. *J. Appl. Polym. Sci.* **1,** 164–168 (1959).

35. Linton, W. H. & Goodman, H. H. Physical properties of high molecular weight acetal resins. *J. Appl. Polym. Sci.* **1,** 179–184 (1959).

36. Lorthioir, C. *et al.* Solid-State Organization and Morphological Partitioning in Polyoxymethylene-Based Copolymers: A Solid-State NMR and WAXS Study. *Macromolecules* **40,** 5001–5013 (2007).

37. Jonker, M. T. O. & Koelmans, A. A. Polyoxymethylene Solid Phase Extraction as a Partitioning Method for Hydrophobic Organic Chemicals in Sediment and Soot. *Environ. Sci. Technol.* **35,** 3742–3748 (2001).

38. Arp, H. P. H. *et al.* Review of polyoxymethylene passive sampling methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants. *Environ. Toxicol. Chem.* **34,** 710–720 (2015).

39. Lampert, D. J., Sarchet, W. V. & Reible, D. D. Assessing the Effectiveness of Thin-Layer Sand Caps for Contaminated Sediment Management through Passive Sampling. *Environ. Sci. Technol.* **45,** 8437–8443 (2011).

40. J. Lampert, D., Lu, X. & D. Reible, D. Long-term PAH monitoring results from the Anacostia River active capping demonstration using polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **15,** 554–562 (2013).

41. Thomas, C. L. Passive sampling to evaluate performance of in situ sediment remediation. (2014).

42. Huckins, J. N., Manuweera, G. K., Petty, J. D., Mackay, D. & Lebo, J. A. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27,** 2489–2496 (1993).

43. Tomaszewski, J. E. & Luthy, R. G. Field Deployment of Polyethylene Devices to Measure PCB Concentrations in Pore Water of Contaminated Sediment. *Environ. Sci. Technol.* **42,** 6086–6091 (2008).

44. Fernandez, L. A., MacFarlane, J. K., Tcaciuc, A. P. & Gschwend, P. M. Measurement of Freely Dissolved PAH Concentrations in Sediment Beds Using Passive Sampling with Low-Density Polyethylene Strips. *Environ. Sci. Technol.* **43,** 1430–1436 (2009).

45. Lampert, D. J., Thomas, C. & Reible, D. D. Internal and external transport significance for predicting contaminant uptake rates in passive samplers. *Chemosphere* **119,** 910–916 (2015).

46. Schmidt, S. N. *et al.* Cross Validation of Two Partitioning-Based Sampling Approaches in Mesocosms Containing PCB Contaminated Field Sediment, Biota, and Activated Carbon Amendment. *Environ. Sci. Technol.* **51,** 9996–10004 (2017).

47. Carslaw, H. S. & Jaeger, J. C. *Conduction of heat in solids*. (Oxford University Press, 1986).

48. Shen, X. Developing models for the assessment and the design of the in situ remediation of contaminated sediments. (2017).

49. Choi, Y., Wu, Y., Luthy, R. G. & Kang, S. Non-equilibrium passive sampling of hydrophobic organic contaminants in sediment pore-water: PCB exchange kinetics. *J. Hazard. Mater.* **318,** 579–586 (2016).

50. Vrana, B. *et al.* Passive sampling techniques for monitoring pollutants in water. *TrAC Trends Anal. Chem.* **24,** 845–868 (2005).

51. Ouyang, G. & Pawliszyn, J. Configurations and calibration methods for passive sampling techniques. *J. Chromatogr. A* **1168,** 226–235 (2007).

52. Allan, I. J. *et al.* Field Performance of Seven Passive Sampling Devices for Monitoring of Hydrophobic Substances. *Environ. Sci. Technol.* **43,** 5383–5390 (2009).

53. Gschwend, P. M. *et al.* Comparison of polymeric samplers for accurately assessing PCBs in pore waters. *Environ. Toxicol. Chem.* **30,** 1288–1296 (2011).

54. Schintu, M., Marrucci, A. & Marras, B. Passive Sampling Technologies for the Monitoring of Organic and Inorganic Contaminants in Seawater. in *Current Environmental Issues and Challenges* 217–237 (Springer, Dordrecht, 2014).

55. Lu, X., Reible, D. D. & Fleeger, J. W. Bioavailability of polycyclic aromatic hydrocarbons in field-contaminated Anacostia River (Washington, DC) sediment. *Environ. Toxicol. Chem.* **25,** 2869–2874 (2006).

56. Janssen, E. M.-L., Oen, A. M. P., Luoma, S. N. & Luthy, R. G. Assessment of field-related influences on polychlorinated biphenyl exposures and sorbent amendment using polychaete bioassays and passive sampler measurements. *Environ. Toxicol. Chem.* **30,** 173–180 (2011).

57. Rosen, G. *et al.* A sediment ecotoxicity assessment platform for in situ measures of chemistry, bioaccumulation and toxicity. Part 2: Integrated application to a shallow estuary. *Environ. Pollut.* **162,** 457–465 (2012).

58. Gomez-Eyles, J. L., Jonker, M. T. O., Hodson, M. E. & Collins, C. D. Passive Samplers Provide a Better Prediction of PAH Bioaccumulation in Earthworms and Plant Roots than Exhaustive, Mild Solvent, and Cyclodextrin Extractions. *Environ. Sci. Technol.* **46,** 962–969 (2012).

59. Wang, J., Taylor, A., Xu, C., Schlenk, D. & Gan, J. Evaluation of different methods for assessing bioavailability of DDT residues during soil remediation. *Environ. Pollut.* **238,** 462–470 (2018).

60. Cho, Y.-M. *et al.* Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment. *Environ. Sci. Technol.* **43,** 3815–3823 (2009).

61. Oen, A. M. P. *et al.* In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers. *Environ. Sci. Technol.* **45,** 4053–4059 (2011).

62. Liu, H.-H. *et al.* Novel Passive Sampling Device for Measuring Sediment–Water Diffusion Fluxes of Hydrophobic Organic Chemicals. *Environ. Sci. Technol.* **47,** 9866–9873 (2013).

63. Murphy Paul, Marquette Andre, Reible Danny & Lowry Gregory V. Predicting the Performance of Activated Carbon-, Coke-, and Soil-Amended Thin Layer Sediment Caps. *J. Environ. Eng.* **132,** 787–794 (2006).

64. Schaanning, M., Breyholtz, B. & Skei, J. Experimental results on effects of capping on fluxes of persistent organic pollutants (POPs) from historically contaminated sediments. *Mar. Chem.* **102,** 46–59 (2006).

65. Beckingham, B. & Ghosh, U. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* **91,** 1401–1407 (2013).

Chapter 3

Spatial Variations of Bulk Sediment and Porewater Concentration Determined by Passive Sampling in Complex Sediment Matrices

3.1 ABSTRACT

Sediment porewater concentrations of hydrophobic organic contaminants (HOCs) measured by passive sampling methods are often used to indicate bioavailability and potential risks to aquatic organisms over more traditional bulk solid concentration measurements. Due to the cost and complexity of *in situ* monitoring, the sorbents are often placed at a small number of locations at a given site and generally measure only a small volume of interstitial water. This leads to concerns that the individual measurements of passive samplers are less representative than bulk solids.

The aim of this study was to evaluate and compare the spatial correlations of *in situ* hydrophobic organic compounds' porewater concentrations determined by passive sampling approaches and bulk sediment concentrations to evaluate representativeness using geostatistical analysis.

In this chapter a discussion of passive sampling methods' advantages over bulk solid concentration measurement in spatial resolution by analyzing the results from field studies conducted at Hunter's Point Navy Shipyard (San Francisco, CA) and Columbia Slough (Portland, OR), and a potential application of employing passive sampling to determine contaminated sediment hot-spots.

3.2 INTRODUCTION

Sediment porewater concentrations of hydrophobic organic contaminants (HOCs) measured by passive sampling are often used to indicate bioavailability and potential risks to aquatic organisms over more traditional bulk solid concentration measurements.

Passive sampling is the process of exposing a sorbent passively, i.e. without disturbing the environment, to accumulate a target contaminant. Passive sampling technologies were first developed in the 1990s and have been used for detecting, quantifying and monitoring contaminant concentrations in sediment porewater and surface water.[1, 2] Initial efforts employed an oily substance in polyethylene bags to simulate lipids in biological organisms. More recently, polymer sorbents have been used as passive samplers, which act via achieving chemical equilibrium with freely dissolved concentrations of contaminants through matrix solid phase microextraction (SPME).[3] Commonly used polymer samplers are polyethylene (PE),[4] polyoxymethylene (POM),[5] and polydimethylsiloxane (PDMS).[3, 6–8] PDMS is usually coated as a thin layer on a glass fiber while PE and POM are used in flat sheet form. PE and POM have larger sorptive capacities, which leads to lower detection limits of target compounds. Meanwhile, PDMS fibers have faster kinetics than PE and POM sheets of the same thickness.[9]

In general, passive sampling has several advantages over conventional bulk sediment measurement: it’s efficient, it’s easy to process and it has less impacts on the surroundings. Passive sampling has much lower detection limits than traditional sediment measurements.[2,4] In addition, the freely dissolved porewater concentration obtained by passive sampling methods can be regarded as a better indicator of bioaccumulation and chemical activity than traditional bulk solid concentration measurements.[6,10,11] Another major advantage of passive samplers over conventional sediment sampling is that passive samplers are able to capture the concentrations that change over time.[12] And passive sampling approaches can better control the statistical variance on a temporal or spatial scale.[13] Based on the above advantages, passive sampling approach are a promising method for determining and monitoring pollutants in aquatic environment.

Several researches have applied passive sampling methods to characterize the spatial and temporal variability of HOCs, pesticides, and metals in field study.[14, 15] Due to the cost and complexity of in-situ monitoring, the sorbents are often placed at a small number of locations at a given site and generally measure only a small volume of interstitial water. This leads to concerns that the individual measurements of passive samplers are less representative than bulk solids.

In this work, solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers were used to determine the freely dissolved porewater of polychlorinated biphenyls (PCBs). The representativeness and spatial variability of dissolved PCB porewater concentrations in open water near Hunters Point Navy Shipyard (San Francisco, CA) and Columbia Slough (Portland, OR) were characterized and compared with bulk sediment concentration measurements. These two sites were contaminated with PCBs as a result of historical activities. Twenty sampling locations were sampled at each sampling site by both passive sampling method and bulk sediment measurement. Semivariogram models were developed for each sited to analyze the spatial variability of porewater concentrations as well as bulk solid concentrations to provide an estimate of spatial variability of the two measurements.

3.3 MATERIALS AND METHODS

3.3.1 Sediment Site—Hunter's Point Navy Shipyard

Hunter's Point Navy Shipyard (HPNS) is located southeast of San Francisco, California. (Figure 3-1 and Figure 3-2). The shipyard has been occupied by the United States Department of the Navy (Navy) since 1939. It was predominantly used as a repair facility and was closed in 1991. It is currently divided into eleven parcels, among which, Parcel F is offshore and is the focus of this study (Figure 3-3). Parcel F includes approximately 457 acres of offshore sediment impacted by the release of PCBs from site historical activities.

Twenty locations within two half-acre plots of Parcel F sediments in South Basin were identified for multiple end-point monitoring, including porewater concentrations, bulk sediment concentrations, and total organic carbon analysis.

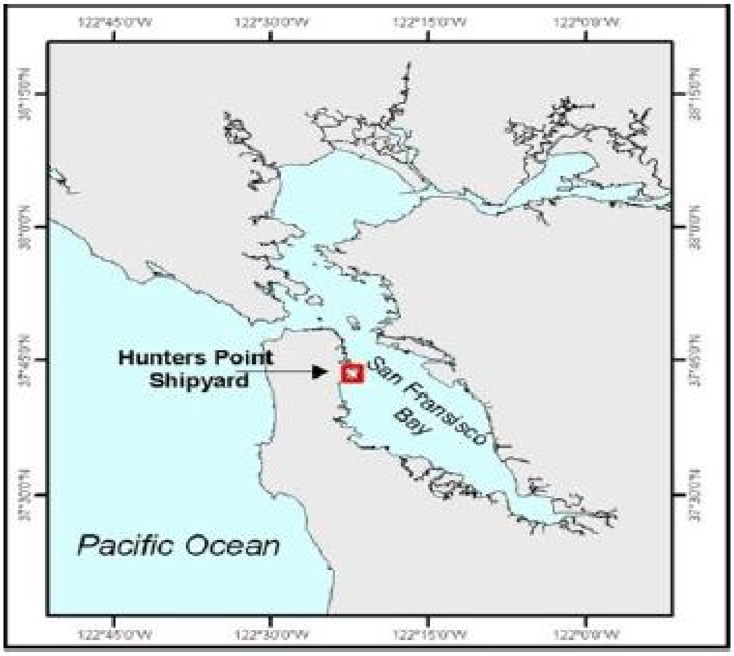
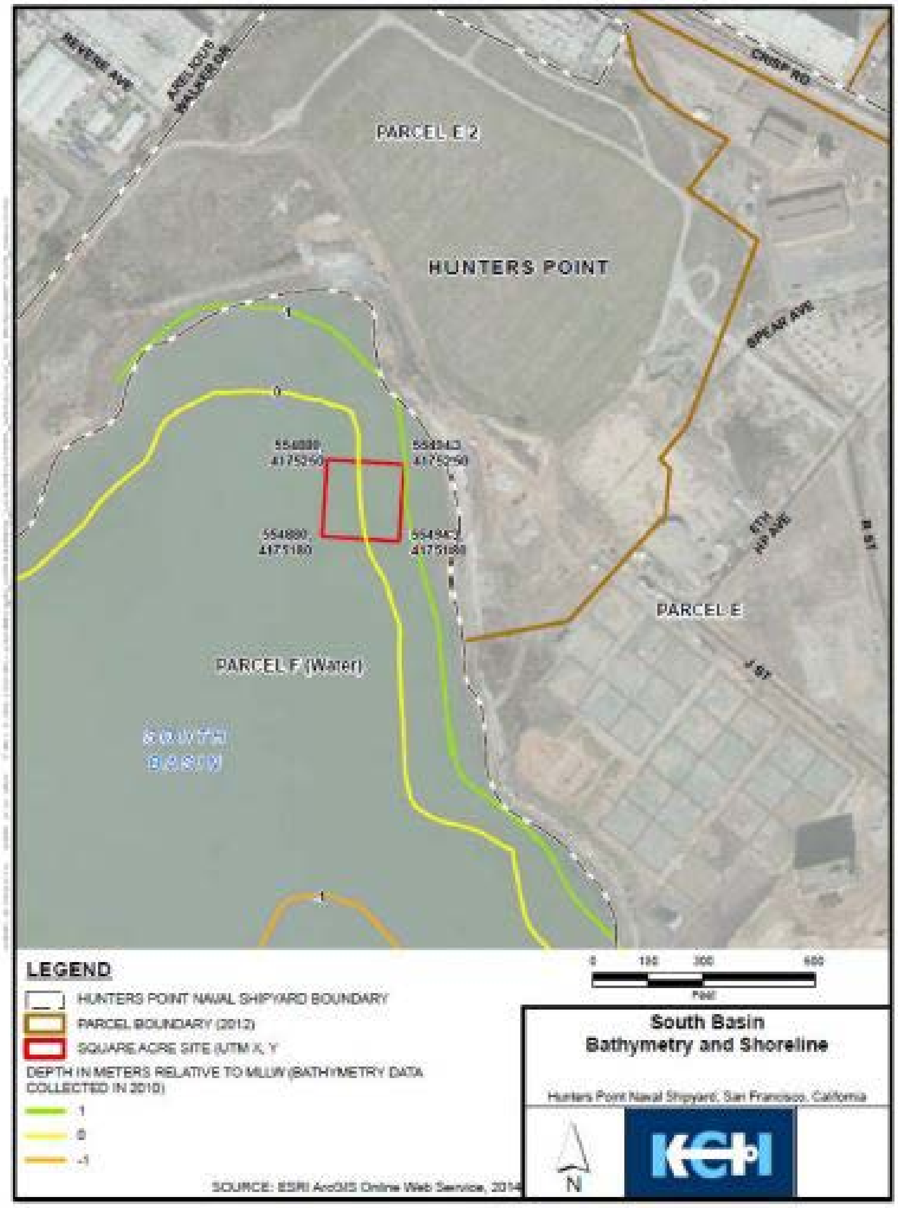


Figure 3-1. Facility location, Hunter's Point Navy Shipyard



SOURCE: ESRI ArcGIS Online Web Service, 2014

Figure 3-2. PDMS passive sampling plot at Hunter’s Point Navy Shipyard

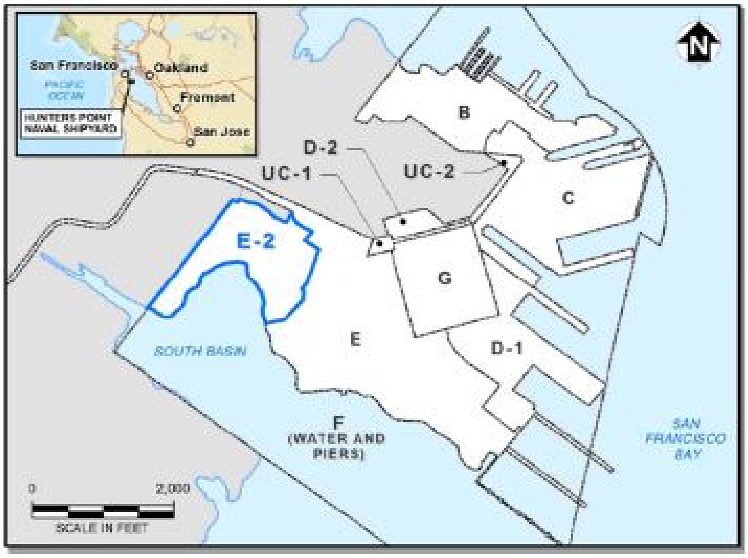
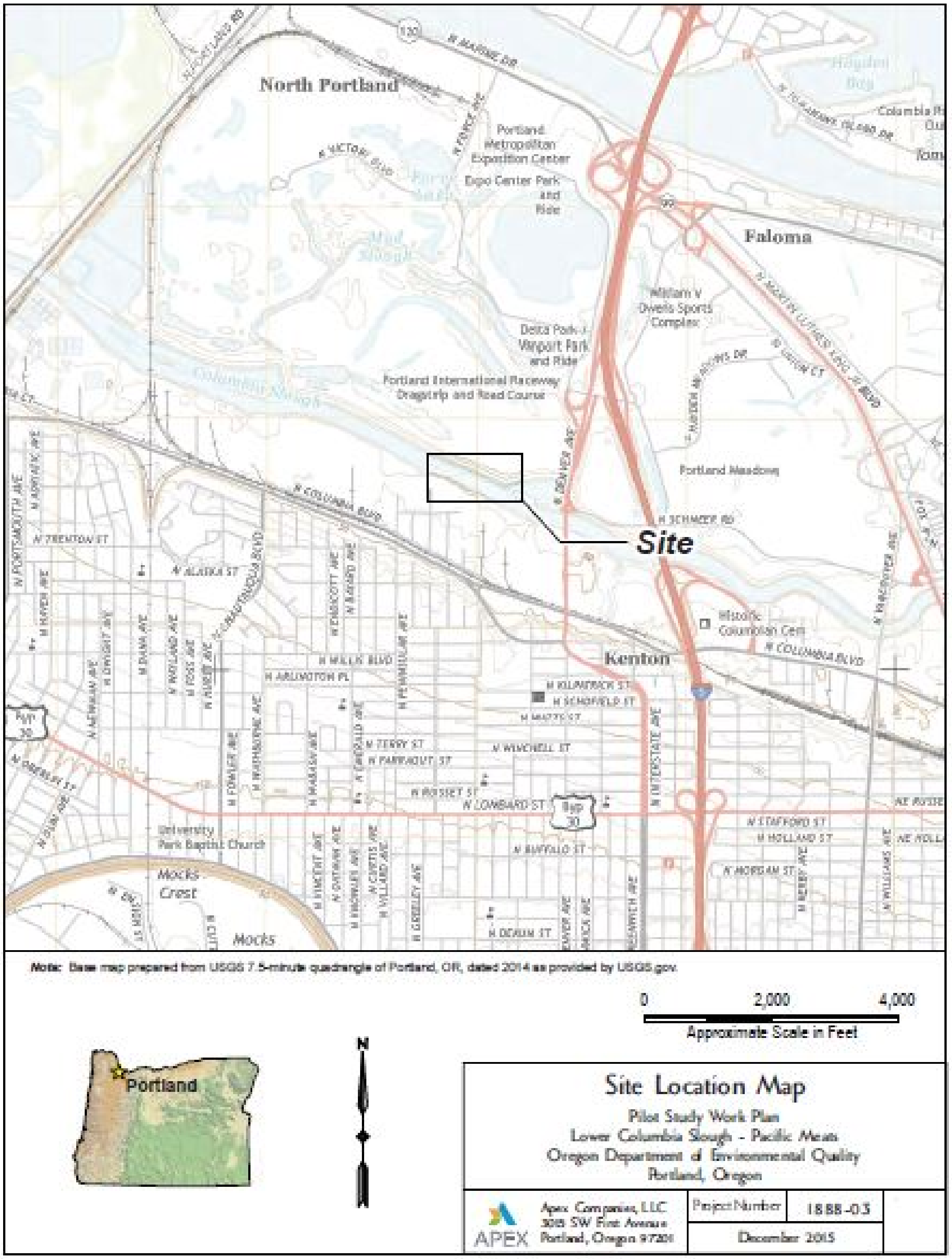


Figure 3-3. Site location, Parcel F, Hunter’s Point Navy Shipyard

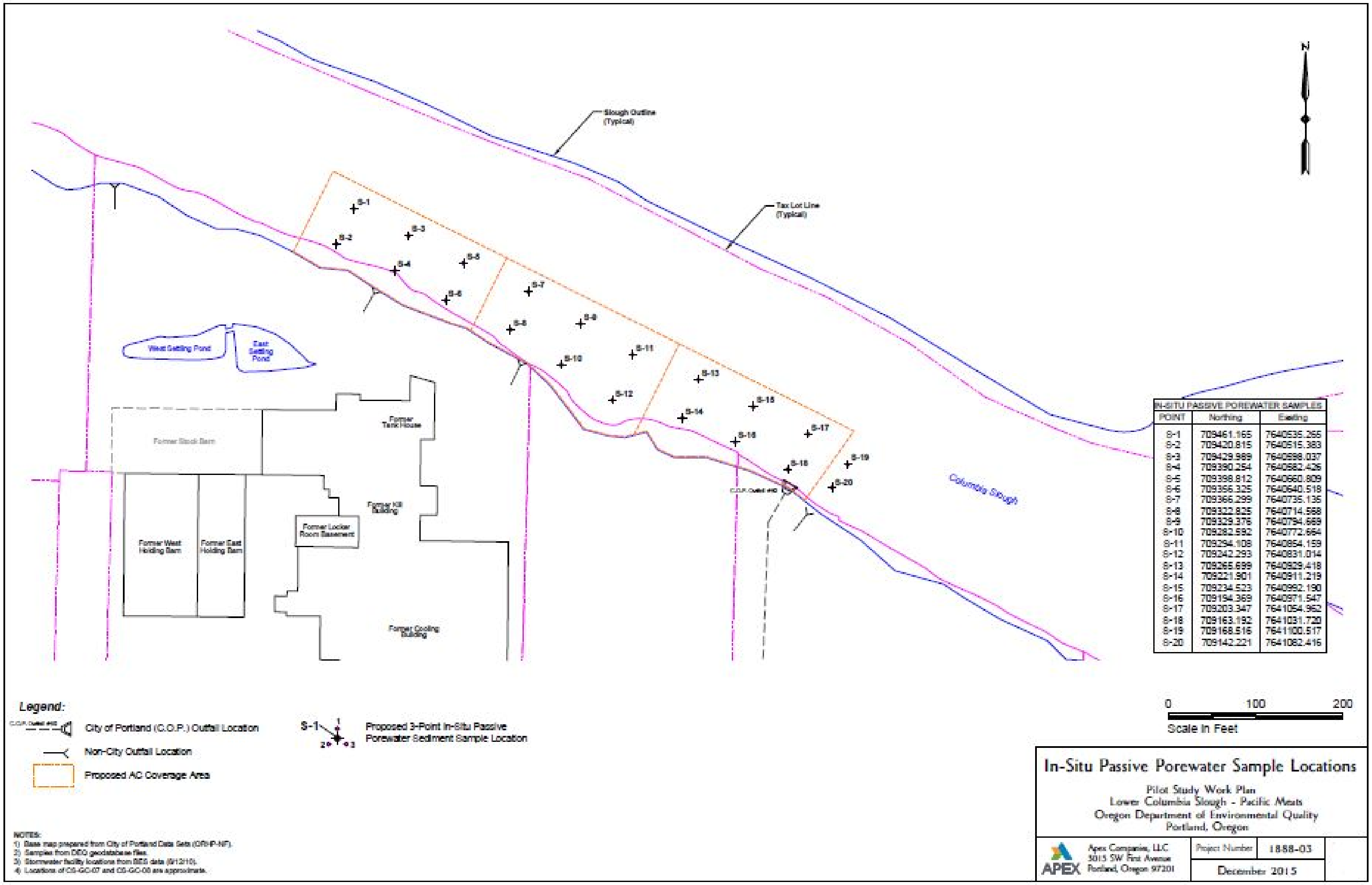
3.3.2 Sediment Site—Columbia Slough

The pilot study area of Columbia Slough (CS) is a waterway located northwest of the City of Portland, Oregon (Figure 3-4). The sediment is affected by PCB contaminants. The study area extends approximately 600 feet along the shoreline and approximately 100 feet wide. Within this pilot study area, twenty locations were identified for sampling. Twenty locations were arranged in two rows along the shoreline and each row has ten sampling locations (Figure 3-5). Among these twenty sites, site S8, S10 and S20 were close to the historical contaminants outfalls.



Note: Base map prepared from USGS 7.5-minute quadrangle of Portland, OR, dated 2014 as provided by USGS.gov.

Figure 3-4. Facility location, Columbia Slough



IN-SITU PASSIVE POREWATER SAMPLES

POINT	Northing	Easting
S-1	709461.165	7640535.265
S-2	709420.815	7640515.383
S-3	709429.989	7640598.037
S-4	709390.254	7640582.426
S-5	709398.812	7640660.909
S-6	709356.325	7640640.518
S-7	709366.299	7640735.135
S-8	709322.825	7640714.568
S-9	709329.376	7640794.669
S-10	709282.592	7640772.664
S-11	709294.108	7640854.159
S-12	709242.293	7640831.014
S-13	709265.699	7640929.418
S-14	709221.901	7640911.219
S-15	709234.523	7640992.190
S-16	709194.369	7640971.547
S-17	709203.347	7641054.962
S-18	709163.192	7641031.720
S-19	709168.516	7641100.517
S-20	709142.221	7641082.416

Figure 3-5. PDMS passive sampling plot at Columbia Slough

3.3.3 Chemicals

Pure grade hexane and acetonitrile purchased from Fisher (Hampton, NH) were used to clean PDMS fibers and sampling devices before deployment. A methanol (Fisher, ultra-pure grade): water solution (20:80) was used to help obtain better loading of performance reference compounds (PRCs).[16, 17] The PCB extract solvent was hexane (Fisher, ultra-pure grade). In the preparation and spiking step, all water used was Milli-Q water (Millipore Corporation).

Analytical standards were made from stock solution of PCB Mix from AccuStandard (detailed list of studied congeners can be found in Supporting Information). C^{13} labeled mix containing PCBs: 28/52/101/153/138/180/209 were used as performance reference compounds and C^{13} labeled PCB 9, 118 and 188 were used as internal standards (Cambridge Isotope Laboratories).

3.3.4 Polydimethylsiloxane (PDMS) Fibers

Solid phase micro-extraction (SPME) polydimethylsiloxane (PDMS) fibers with PDMS coating of different thickness were purchased from Polymicro Technologies, (Phoenix, AZ). For Hunter's Point study, the glass core was coated with a 36 µm PDMS layer on a 486 µm glass core, while for Columbia Slough study, a 30.5 um PDMS layer on a 497 µm glass core was used.

The PDMS fibers were cleaned with hexane and acetonitrile, then rinsed with MiliQ water several times and then dried. The solvent washed fibers were submerged in 80:20 (v:v) water: methanol solution in a 4L amber bottle. Following this procedure

PDMS fibers were preloaded with performance reference compounds (PRCs) to assess the fraction of steady-state achieved during the sampler deployment. The C^{13} labeled mix containing PCBs: 28/52/101/153/138/180/209 was used as the PRCs. The 4L bottle was placed on a shaking Table for 4 weeks.

3.3.5 Sampling Approach

The PDMS fibers were placed in sample holders fabricated from ¼” stainless steel rods that formed the legs of a tripod approximately 30 cm on a side (Figure 3-6). The cleaned and PRC-loaded fibers were placed in a 30 cm long groove cut into the stainless steel rods and attached with approximately 1 cm of waterproof silicone caulk (hydrocarbon-free silicon) at both ends.

Figure 3-6. Passive sampling tripod employed at each field location

As shown in Figure 3-5 and Figure 3-7, there were 20 sampling locations designed for passive sampling approach in both HPNS and CS pilot study. At each sampling location, a tripod was embedded vertically into the sediment by using a long sleeved pipe. A buoy marked with sampling the site number was attached to each tripod via cords and used for identification for retrieval. After 28 days exposure, the samplers were retrieved from the sampling plot, disassembled and the fibers sectioned and placed in solvent for analysis. Initial efforts involved field processing of samples but testing showed that sectioning and extraction in solvent could be conducted after shipment to the laboratory.

Bulk sediment samples were collected from the surficial sediments, about 4 inches, at each porewater sample sampling location using an Ekman dredge immediately after passive sampler retrieval. The samples were homogenized and shipped overnight at 4˚C for laboratory analysis. For HPNS, sediment samples from 11 locations (Site 17, 19, 22, 24, 28, 30, 33, 36, 38, 40, and 42) were taken, while for CS, samples from all 20 locations where PDMS samplers were located were taken.

The Hunter's Point Navy Shipyard pilot study deployed in May 2015 and retrieved in June 2015, while the Columbia Slough study deployed in September 2015 and retrieved in October 2015.

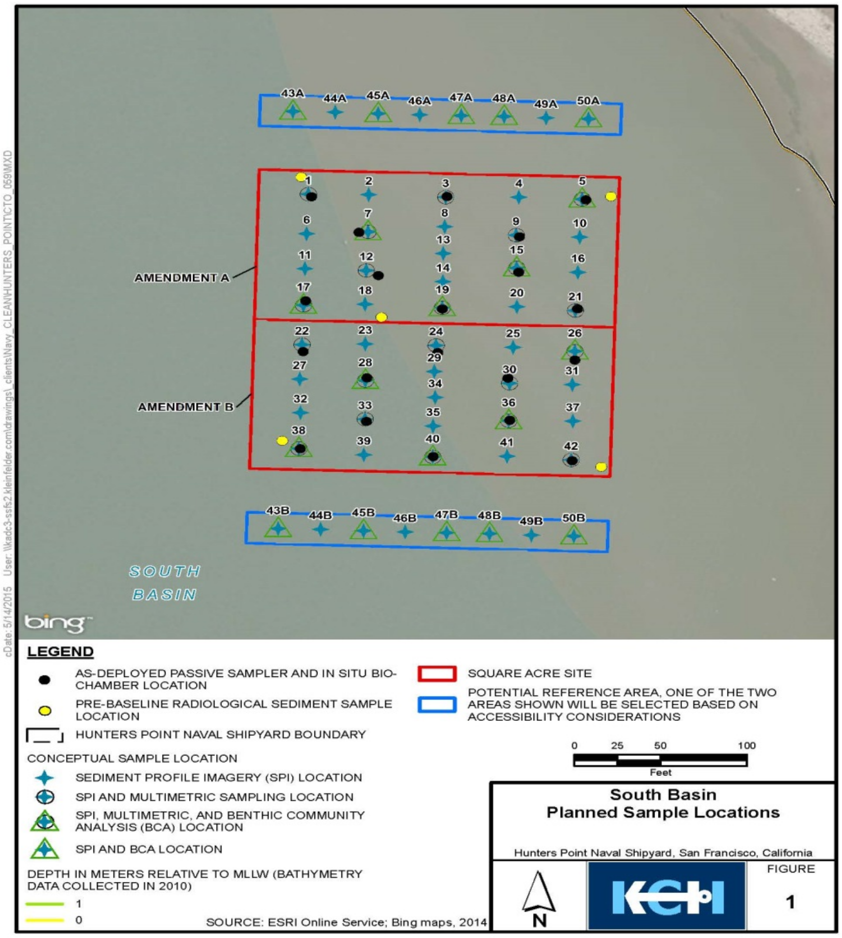


Figure 3-7. Detailed PDMS passive sampling locations at Hunter’s Point Navy Shipyard

3.3.6 Analytical Procedures

For Hunter’s Point Navy Shipyard samples, the 30 cm PDMS fibers were segmented and measured at different depth layers: bioactive top layer (1-6cm), middle layer (11-16cm), and deeper layer (21-26cm) to evaluate deeper contamination or potential for migration into the biologically active zone.

For Columbia Slough samples, the retrieved PDMS fibers were sectioned into two different depth: the top layer (1-13.5cm) and a deeper layer (13.5-27cm).

The passive sampling fibers were sectioned into short segments, about 1 cm, and placed into a 2 mL auto sampling vial with insert containing 150 μL of hexane to extract target compounds and PRCs. PDMS fibers were soaked in hexane overnight and every sample was vortexed for at least 2 minutes to ensure full extraction. The volume of extract was reduced to 50 μL. Internal standards (C^{13} labeled PCB 9, PCB 118 and PCB 188) were added to a target concentration of 50 μg/L.

Samples were analyzed for PRCs and 111 PCB congeners using gas chromatography with a triple quadrupole mass selective detector (GCTQMS, Agilent 7890B) using a modified EPA method 1668c. The calibration range used for analysis in GCTQMS was 0.08 to 5 µg/L.

3.3.7 Solid Sample Analysis

The homogenized sediment samples were dried and spiked with 7 C^{13} labeled PCBs: 28/52/101/153/138/180/209 (Cambridge Isotope Laboratories). Samples were extracted with Accelerated Solvent Extraction (ASE 350, Dionex) for 8 hours with a mixture of hexane/acetone (3:1, v/v) at 100˚C. Each extract was concentrated from volume of 60mL to 1.5 – 2 mL using a Rocket evaporator (Genevac) and cleaned up over sodium sulphate and florisil columns with 30 mL of hexane. Afterwards, the obtained extracts were condensed to 1mL by Rocket evaporator and desulphurised using copper powder in an ultrasonic bath (Branson 8800). The extracted samples in hexane were analyzed for PCB congeners as noted above.

3.3.8 Modeling Tool for Spatial Analysis—Semivariogram

The separation of the samples varied from approximately 1 foot (the separation of the tripod legs) to several hundred feet. The variations over these distances in solid and porewater samples were analyzed by constructing a semivariogram which describes the spatial autocorrelation of the measured data points. The following equation describes the definition of semivariogram value:

$$\gamma(\mathrm{h}) = \frac{1}{2N(h)}\sum_{i=1}^{N(h)}(Z(x_i) - Z(x_i + h))^2$$

where ϒ(h) is the semivariance value; N is the number of data points; Z is the target value, which is C_{pw} or C_{sed} in this work; $Z(x_i)$ and $Z(x_i+h)$ are the target value at location x_i and at location with a distance h to location x_i.

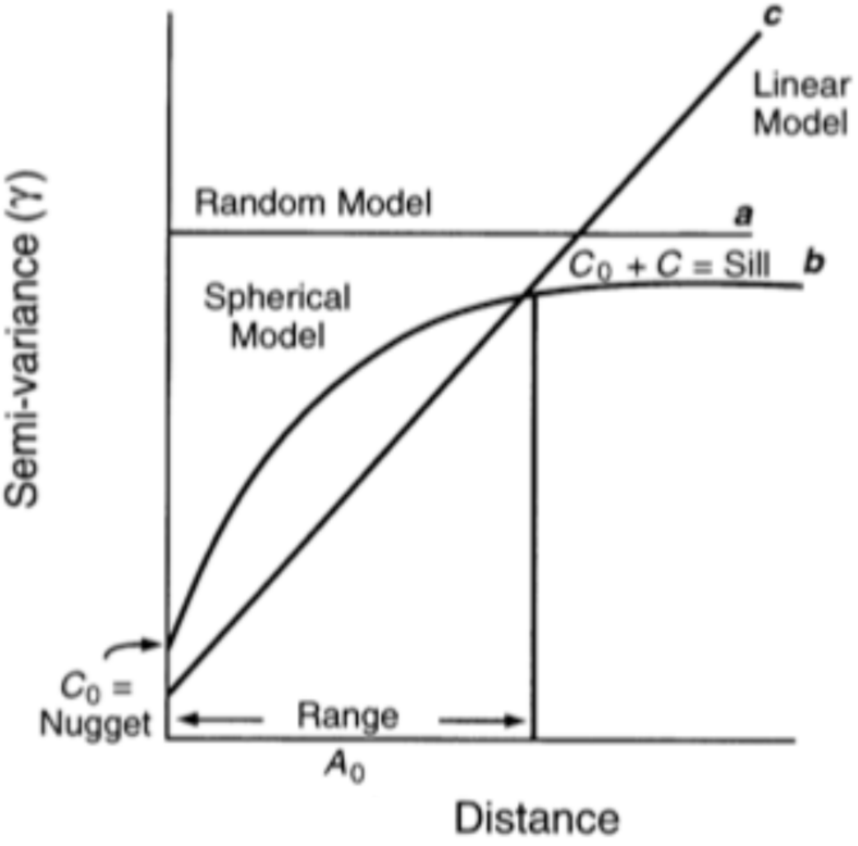


Figure 3-8. Anatomy of a typical semivariogram

Figure 3-8 shows the anatomy of a typical semivariogram. The x-axis shows the distance (h) between different sampling locations while the y axis is the semi-variance value (ϒ). The most commonly used parameters to describe the model includes nugget C_0, range A_0, and still/constant value:

- Nugget C_0: spatial discontinuity or observation error;
- Range A_0: the distance within which positive spatial autocorrelation exists;
- Still/Constant value: maximum semivariance.

Figure 3-9 shows several commoly used semivariogram model types: spherical, linear, exponential, gaussian and stable. These models are designed to best fit different types of data. Once the variance data of each pair of locations is plotted, a fitted model can be used to predict data values at unsampled locations.

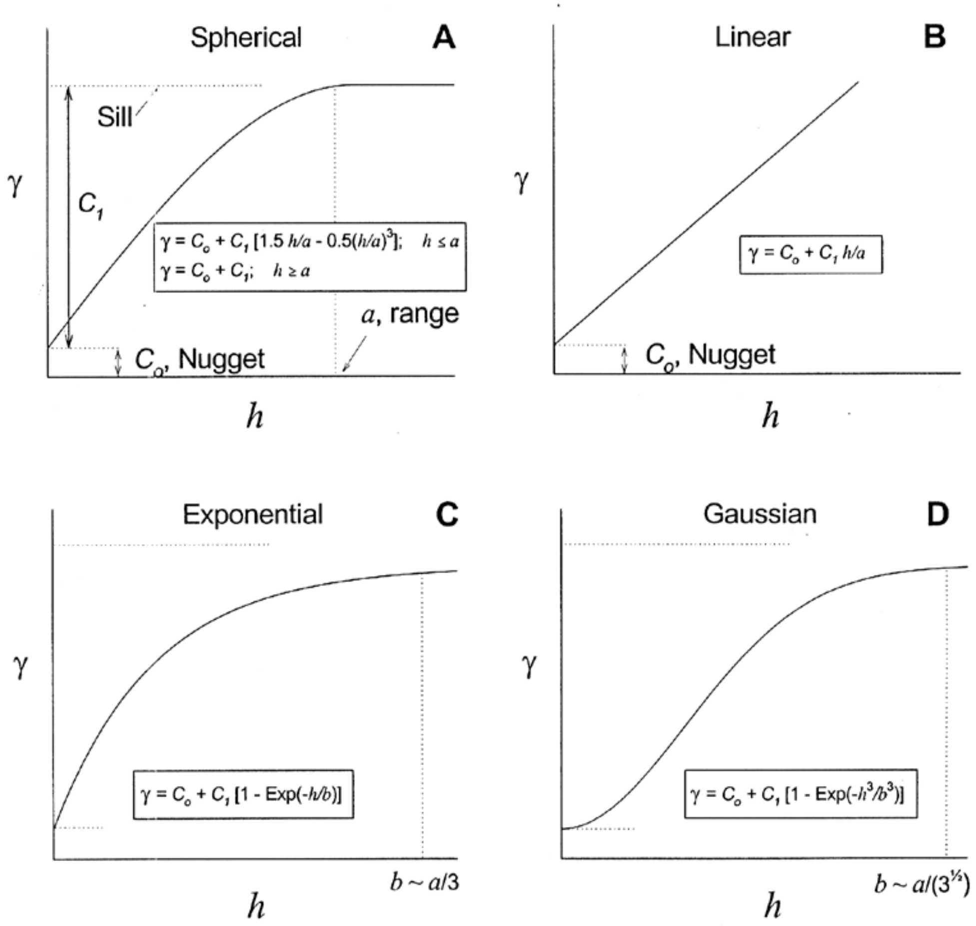


Figure 3-9. Most commonly used semivariogram models

3.4 RESULTS AND DISCUSSIONS

3.4.1 Performance Reference Compounds (PRCs) Results

The degree of non-equilibrium kinetics for PRCs, that is, the fractional approach to steady state can be estimated by the following equation:

$$f_{ss} = \frac{M_t}{M_0}$$

Where M_t and M_0 are the absorbed mass of PRCs on PDMS fibers at deployment time t and time 0 (before deployment). Twelve 5 cm PDMS fiber replicates taken prior to sediment deployments were used as PRC C_0s, which shows the initial PRCs impregnated into the fibers. The model of Lampert et al. (2015) was applied here for the PDMS uptake.[8]

$$M(t) = K_f C_0 L_f v_f \left[1 - \exp\left(\frac{RDt}{l^2 K_f^2}\right) erfc\left(\frac{\sqrt{RDt}}{lK_f}\right)\right] = K_f C_0 L_f v_f f_{ss}$$

M (t) –contaminant mass absorbed on the fiber at time t;

K_f –fiber–water partition coefficient; C_0 is the pore water concentration;

L_f –fiber length;

v_f –fiber volume per unit length;

l –volume to area ratio of the fiber coating;

RD –product of R and D, a parameter expected to increase linearly with K_{ow}

R –retardation factor;

D –effective diffusivity;

fss –fraction of equilibrium achieved.

K_f values are unique to each compound and are correlated with the hydrophobicity of the compounds and the octanol-water partition coefficient (K_{ow}). The K_{ow} values for target PCB congeners were taken from Hawker and Connell (1988).[18] For PCB compounds on PDMS fibers, Ghosh et al. (2014) estimate K_f from K_{ow} for PCBs by the following equation[17]:

$$logK_f = 0.947logK_{ow} - 0.017$$

Table 3-1 list the estimated K_f for PRCs by the model.

Table 3-1. Octanol-water partition coefficient (K_{ow}) and fiber–water partition coefficient (K_f) values for 7 PCB compounds

	(Hawker and Connell)	(Ghosh et al, 2014)
Compound	log K_{ow}	log K_f
PCB-28	5.67	5.35
PCB-52	5.84	5.51
PCB-101	6.38	6.02
PCB-153	6.92	6.54
PCB-138	6.83	6.45
PCB-180	7.36	6.95
PCB-209	8.18	7.73

The media retardation factor (R) is typically a linear function of compound hydrophobicity while D is approximately constant within a homologous series of compounds of similar molecular weight. Figure 3-10 and Figure 3-12 show a linear relationships between the logarithm of the product RD and logK_{ow} for PRC compounds at the two locations. Based on the linear relationship, the RD values for individual PCB congeners can be calculated by their K_{ow} and therefore, the fraction to steady state can be estimated. The corresponding estimated relationship of *fss* for target PCB compounds with K_{ow} for these two sites are showed in Figure 3-11 and Figure 3-13. In general, low molecular weight PCBs reached approximately 70-80% of steady state, whereas, high chlorinated PCBs the fraction obtained was estimated to be 10% (PCB 209) for HPNS and 30% (PCB 209) for CS.

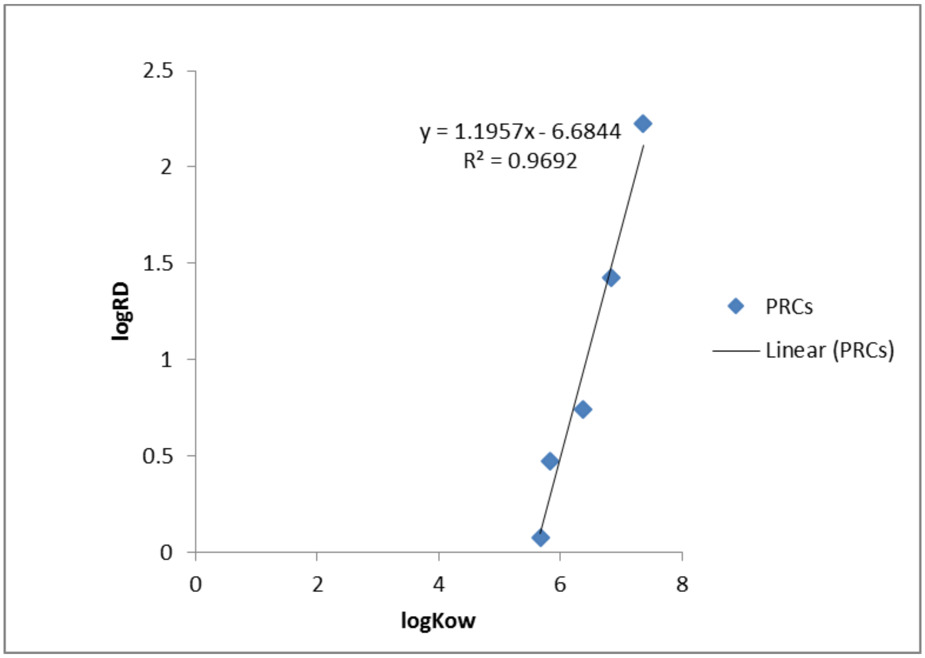


Figure 3-10. logRD values found for PRCs and the line of best linear fit for Hunter’s Point Navy Shipyard

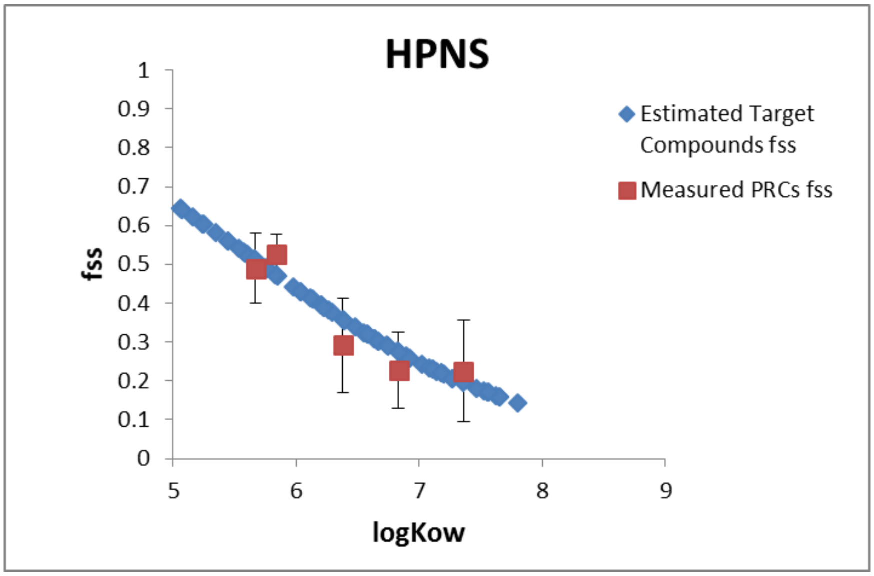


Figure 3-11. Fractional approach to steady state (fss) of PCBs estimated for Hunter's Point Navy Shipyard

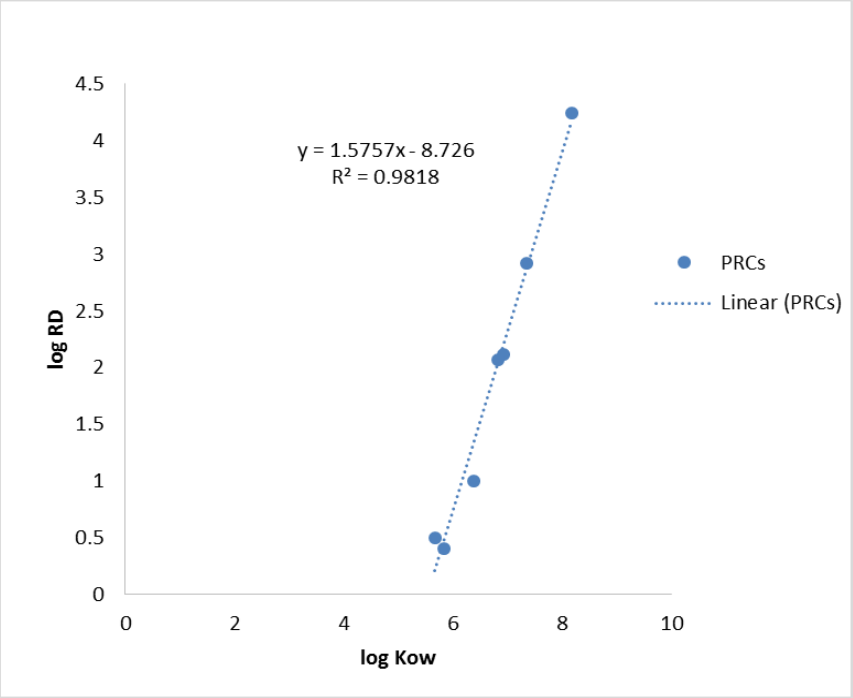


Figure 3-12. logRD values found for PRCs and the line of best linear fit for Columbia Slough

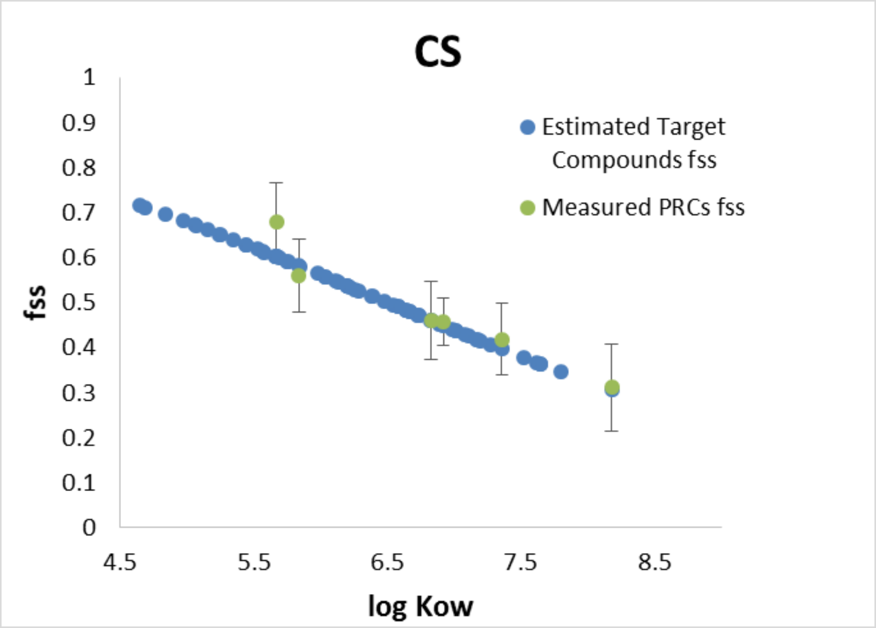


Figure 3-13. Fractional approach to steady state (fss) of PCBs estimated for Columbia Slough

3.4.2 Measured pore water concentrations by SPME PDMS

The freely dissolved porewater concentrations (C_{pw}) were converted by the measured PDMS fibers concentrations (C_{fiber}) by the following equation:

$$C_{pw} = \frac{C_{fiber}}{\mathrm{K}_f \times f_{ss}}$$

The fiber concentrations were estimated by extracted concentration ($C_{extract}$) and volume ratio:

$$C_{fiber} = \frac{C_{extract} \times V_{extract}}{V_{fiber}}$$

3.4.2.1 Hunter's Point Navy Shipyard Cpw Results

The lowest detected calibration point for the extract concentration was 0.2 µg/L and 74 PCB congeners were detected in the HPNS project in total. The average total PCB porewater concentration (sum of 74 congeners) was 2.4 ng/L with a standard deviation of 0.2 ng/L. The sum *in situ* C_{pw} of 74 PCB congeners across the 20 sampling sites at the upper sediment layer (1-6 cm), middle layer (11-16cm) and at depth layer (21-26 cm) are shown in Figure 3-14.

The porewater concentration at surficial layer and middle layer tends to show laterally even distribution and only small variations were observed. At depth, the maximum PCB concentration was found at site 1 and site 3, while were close to shore and the source of the contamination.

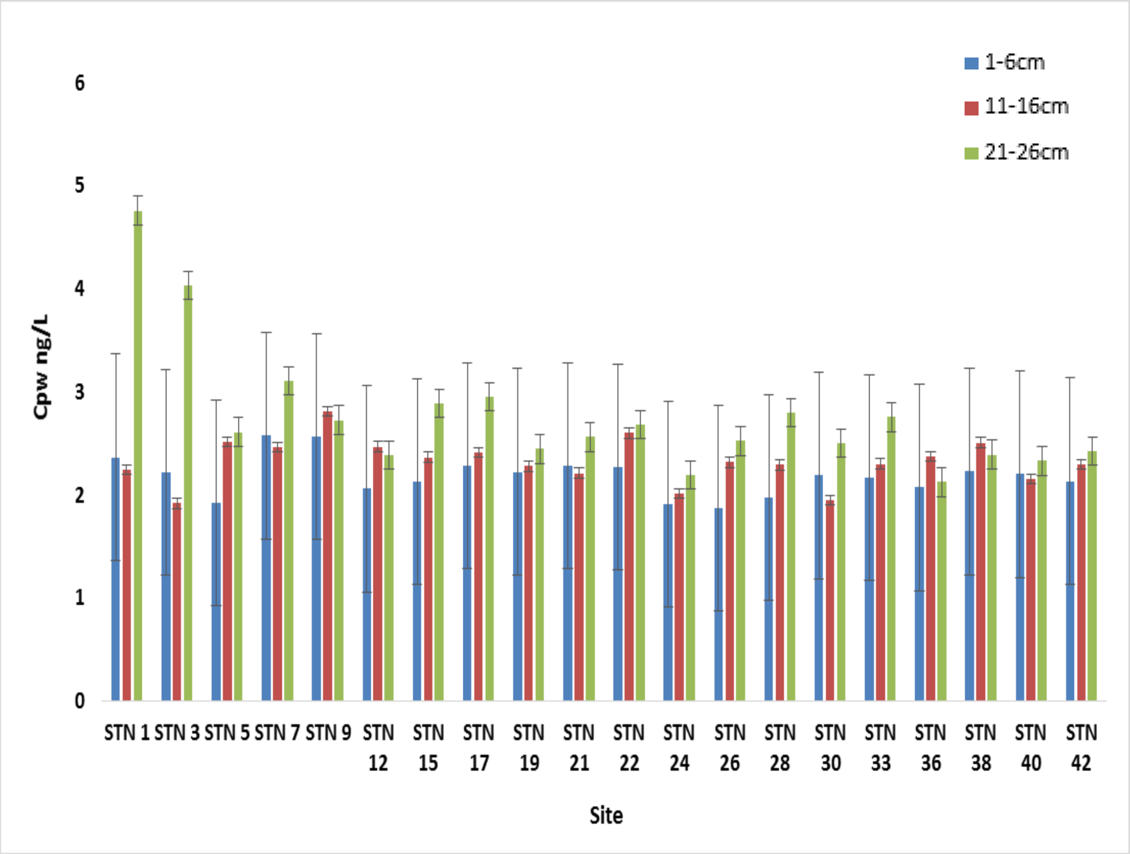


Figure 3-14. Average PCB porewater concentrations at each sampling location– Hunter's Point Navy Shipyard results

3.4.2.2 Columbia Slough Cpw Results

111 PCB congeners were analyzed for Columbia Slough study and 94 PCB were above the detection limit (0.2 µg/L). Figure 3-12 shows the sum PCB Cpw obtained by SPME PDMS fibers at each sampling location at the surficial sediment layer (1-13.5 cm) and at lower layer (13.5-29 cm) are plotted in Figure 3-15.

In general, the sampling locations closer to the shore (with even site numbers) show higher PCB concentrations than the further locations (with odd site numbers) by a factor of approximately 2 to 10. At deeper layer (13.5-29cm), the highest PCB porewater concentrations was detected in sampling site 20, and site 8 and site 10 showed higher concentration than other sampling locations as well. All these three locations are adjacent to effluent outfalls.

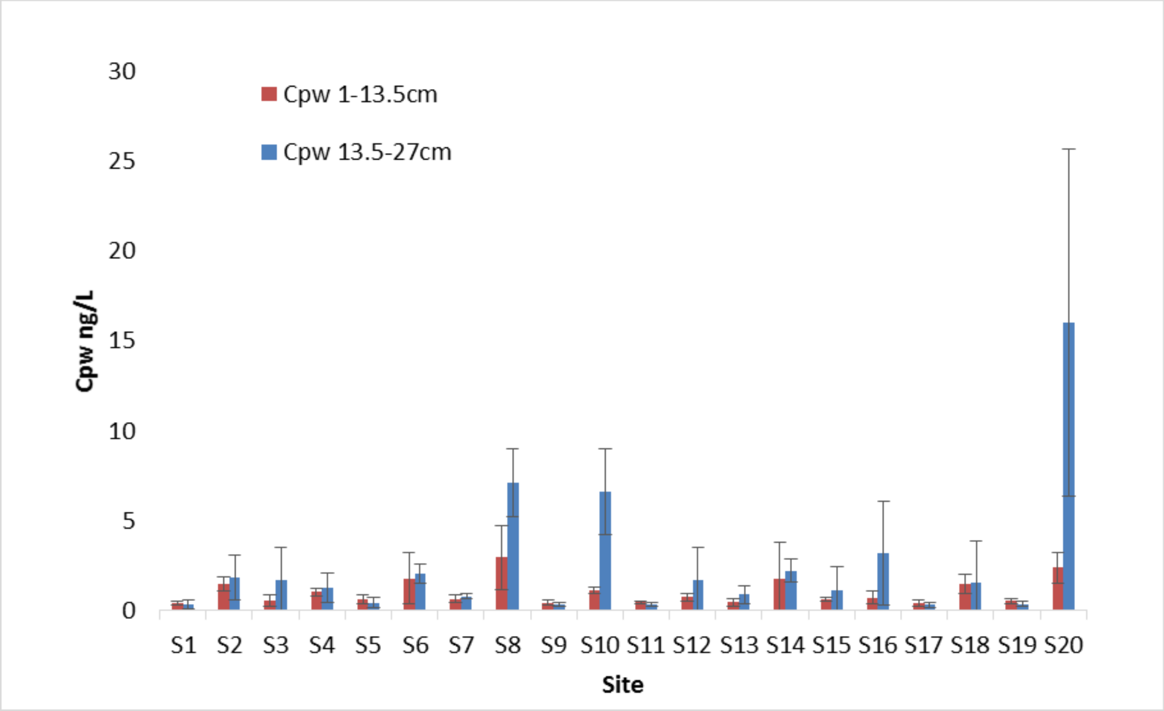


Figure 3-15. Average PCB porewater concentrations at each sampling location–Columbia Slough results

3.4.3 Measured bulk solid concentrations

3.4.3.1 Hunter's Point Navy Shipyard Csed Results

Surficial sediment samples from 11 sampling locations (Site 17, 19, 22, 24, 28, 30, 33, 36, 38, 40, and 42) were taken to measure bulk sediment concentrations (C_{sed}) in Hunter's Point Navy Shipyard. Sum of the bulk sediment concentrations of PCBs are shown in Figure 3-16. The bulk sediment concentrations showed more variability than the porewater results. Site 38, 40 and 42 are approximately a factor of 2 higher in concentration than the locations further from the shore.

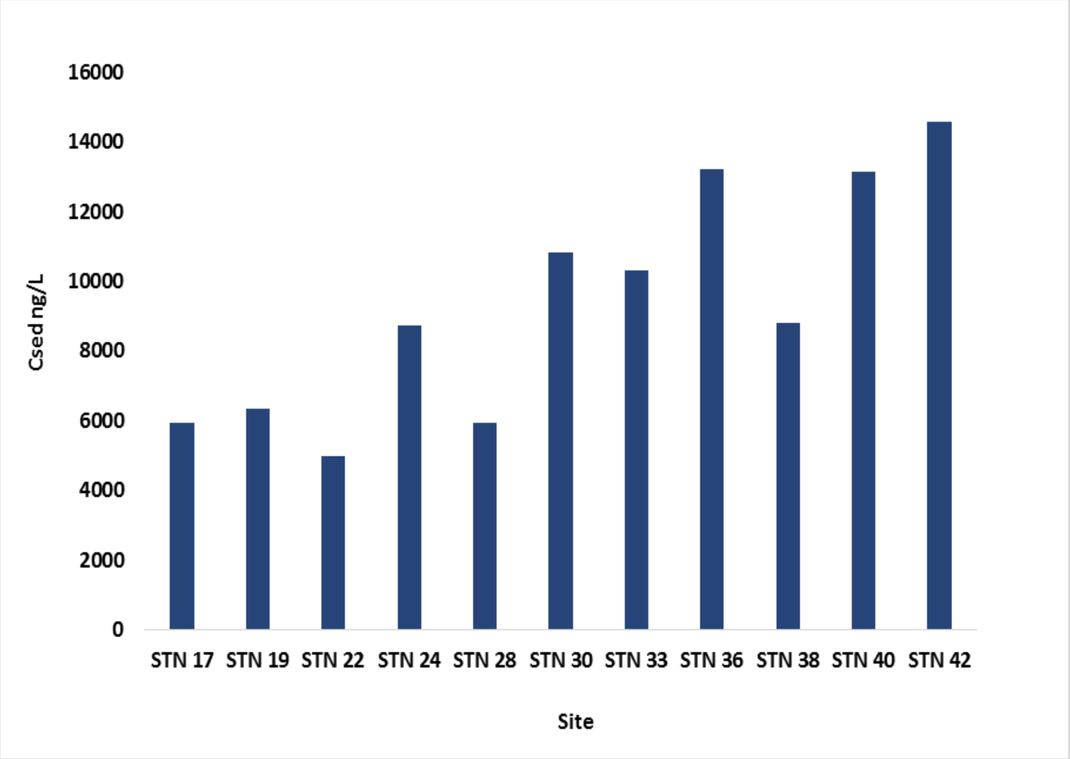


Figure 3-16. Measured PCB bulk sediment concentrations at each sampling location–Hunter's Point Navy Shipyard results

3.4.3.2 Columbia Slough Csed Results

Among the 20 sampling locations, site 8, 10 and 20 are identified to be near the historical contaminants outfalls. Figure 3-17 shows the measured PCB bulk sediment concentrations in Columbia Slough. Sampling site 10 was much higher than other sampling locations, which likely reflects a historical outfall. However, the surficial sediment in site 8 and 20 didn't show elevations, likely as are result of deposition of cleaner sediment at the surface.

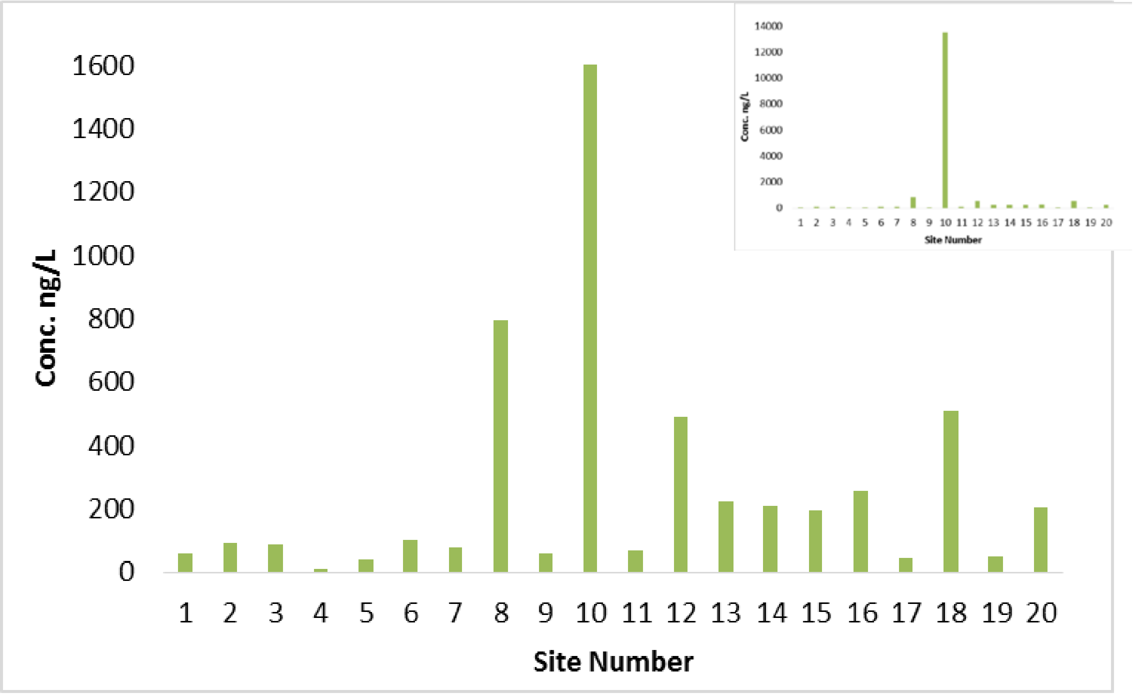


Figure 3-17. Measured PCB bulk sediment concentrations at each sampling location – Columbia Slough results

The solid-water partition coefficients are defined by porewater concentrations and sediment concentrations. Figure 3-18 and 3-19 show the comparison for both Hunter's Point Navy Shipyard and Columbia Slough. The porewater concentrations vary little compared to the variations in sediment concentration. The sediment concentrations likely reflect local variations in sediment composition and organic carbon content while the porewater concentrations appear to be more integrative of conditions across the site.

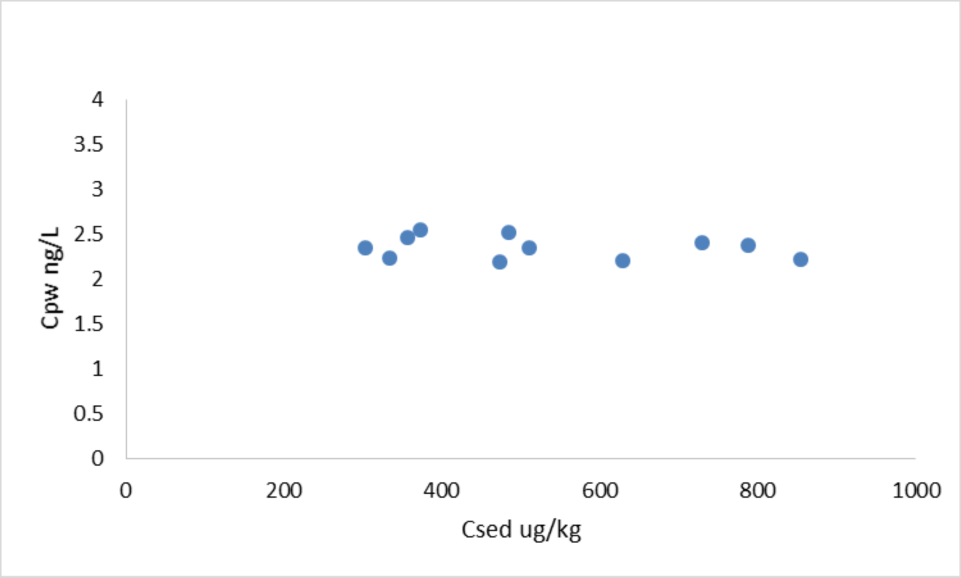


Figure 3-18. Measured PCB porewater concentrations compared to sediment concentrations at Hunter’s Point Navy Shipyard

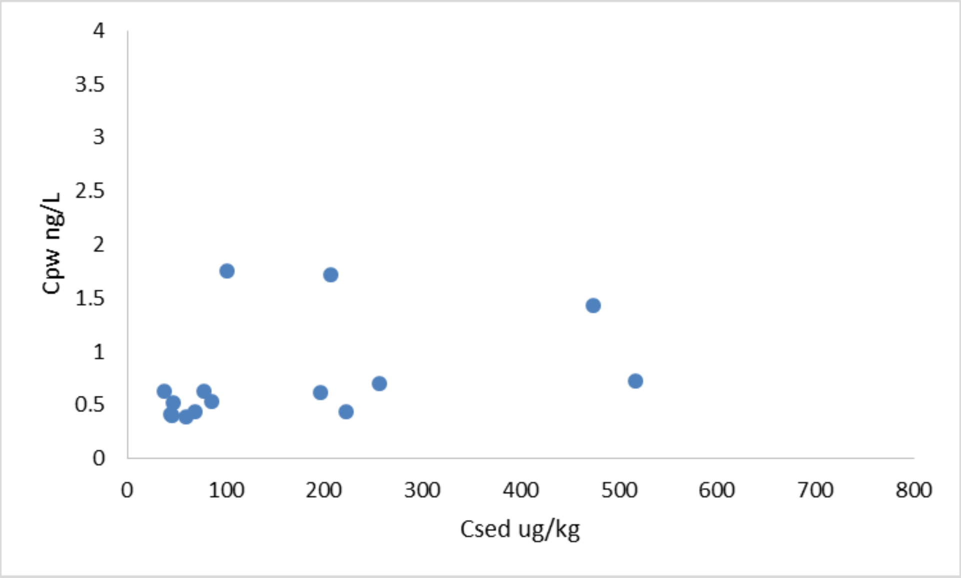


Figure 3-19. Measured PCB porewater concentrations compared to sediment concentrations at Columbia Slough

3.4.4 Spatial Analysis Results

3.4.4.1 Cpw Variance in the Horizontal Direction

The smallest distance interval employed was the separation of the replicates within each sampling site, which is 1 foot. To enable the detection of low concentrations, however, these samples were often combined into a single sample. Thus the sample horizontal separation range is from 9 m (sampling location 15 to 17, and 14 to 16) to 56 m (sampling site 8 to site 20) in HPNS. For Columbia Slough study, the sample horizontal separation ranges from 6.7m (sampling locations 3 to 4, and 15 to 16) to 97 m (sampling site 1 to site 19). Table 3-3 and Table 3-4 shows the Geo information of the sampling locations (latitude and longitude). The data are grouped and averaged over 8 m, approximately the minimum sample location separation.

Table 3-2. Geology information for Hunter’s Point Navy Shipyard pilot study area

object_ID	latitude	longitude
STN1	37.722787 °	-122.377152°
STN3	37.722789°	-122.376888°
STN5	37.722802°	-122.376595°
STN7	37.722719°	-122.377049°
STN9	37.72273°	-122.376737°
STN12	37.722635°	-122.377014°
STN15	37.722654°	-122.376738°
STN17	37.72259°	-122.377171°
STN19	37.722574°	-122.376883°
STN21	37.72258°	-122.376622°
STN22	37.722494°	-122.377167°
STN24	37.722497°	-122.376912°
STN26	37.722486°	-122.376614°
STN28	37.722444°	-122.377029°
STN30	37.722453°	-122.376762°
STN33	37.722354°	-122.377037°
STN36	37.722365°	-122.376755°
STN38	37.722307°	-122.377169°
STN40	37.722294°	-122.376902°
STN42	37.722298°	-122.376621°

Table 3-3. Geology information for Columbia Slough pilot study area

object_ID	latitude	longitude
1	45.5917384°	-122.6939895°
2	45.5916263°	-122.6940628°
3	45.5916577°	-122.6937411°
4	45.5915476°	-122.6937978°
5	45.5915768°	-122.6934926°
6	45.5914589°	-122.6935674°
7	45.5914932°	-122.6931989°
8	45.5913725°	-122.6932746°
9	45.5913964°	-122.6929625°
10	45.5912665°	-122.6930435°
11	45.5913042°	-122.6927265°
12	45.5911604°	-122.6928114°
13	45.5912319°	-122.6924296°
14	45.5911105°	-122.6924960°
15	45.5911511°	-122.6921812°
16	45.5910395°	-122.6922575°
17	45.5910703°	-122.6919327°
18	45.5909585°	-122.6920193°
19	45.5909782°	-122.6917512°
20	45.5909048°	-122.6918191°

To make the freely dissolved porewater concentration and bulk sediment concentrations comparable with each other, the measured concentration data are normalized by their respective averages:

$$\mathrm{C} = \frac{C(x_i)}{\mu}$$

where μ is the average data for Cpw or Csed.

At Hunter’s Point Navy Shipyard the concentrations show little variance, especially for porewater in the upper layer. For C_{pw} in the surface layer there is a stable variance while at depth the best fit semivariogram is the exponential model. For surficial sediment, the best fit semivariogram is also the exponential model indicating that there is a spatial variation in solid concentration that is not indicated by the porewater concentration. This may be due to the importance of surface water-sediment exchange on the surficial porewater concentrations. Because flux and risk may be better related to porewater concentration, however, the porewater may better indicate risk than the more variable bulk solids.

The best fit models for HPNS study are:

$$\Upsilon_{Cpw,top\ layer} = 0.0078$$

$$\Upsilon_{Cpw,depth\ layer} = 0.014e^{0.038h}, R^2 = 0.95$$

$$\Upsilon_{Csed} = 0.015e^{0.068h}, R^2 = 0.95$$

Figure 3-19 shows the measured variance and the fitted models for C_{pw} and C_{sed}. The exponential models should increasing variance with distance simply indicating that the total sampling distance was insufficient to achieve a stable variance value.

For Columbia Slough, the best fit models are the exponential models as well. The best semivariogram models and the measured data for Columbia Slough are plotted in Figure 3-21. The expression for fitted exponential models are：

$$\Upsilon_{Cpw,top\ layer} = -0.05 + 0.42(1 - e^{-\frac{h}{1.65}}), R^2 = 0.65$$

$$\Upsilon_{Cpw,depth\ layer} = -0.04 + 0.56(1 - e^{-\frac{h}{2.94}}), R^2 = 0.76$$

$$\Upsilon_{Csed} = -0.01 + 1.81(1 - e^{-\frac{h}{10.4}}), R^2 = 0.66$$

The C_{pw} has much smaller parameters for the model. Figure 3-21 shows that porewater concentration variance reaches a constant value (0.4 for surface layer and 0.5 for depth layer) at a distance less than 10 m, while for bulk sediment, the distance range is more than 30 m with a constant value of 1.2.

When two sampling locations are separated by the same distance, the variance in C_{pw} is much lower than for the C_{sed}. This suggests that porewater concentrations at both locations show less variability than bulk solid concentration and suggest that surficial sampling for site characterization of porewater could be conducted with a coarser sampling grid than for bulk solids. For example, the relevant variance in bulk sediment concentration at locations separated by 20 m at Columbia Slough are approximately double the normalized variance in porewater concentration.

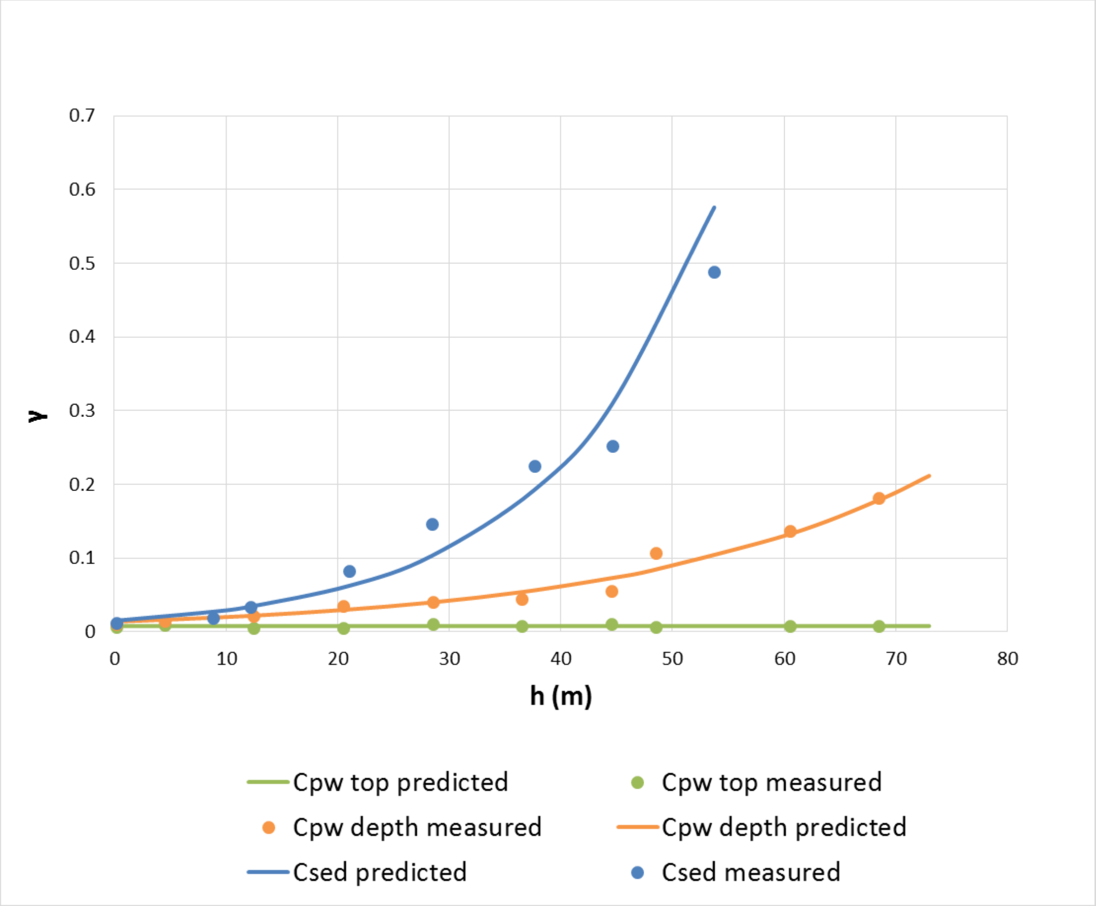


Figure 3-20. Fitted semivariogram models for measured concentrations of detected PCB at Hunter's Point Navy Shipyard (HPNS)

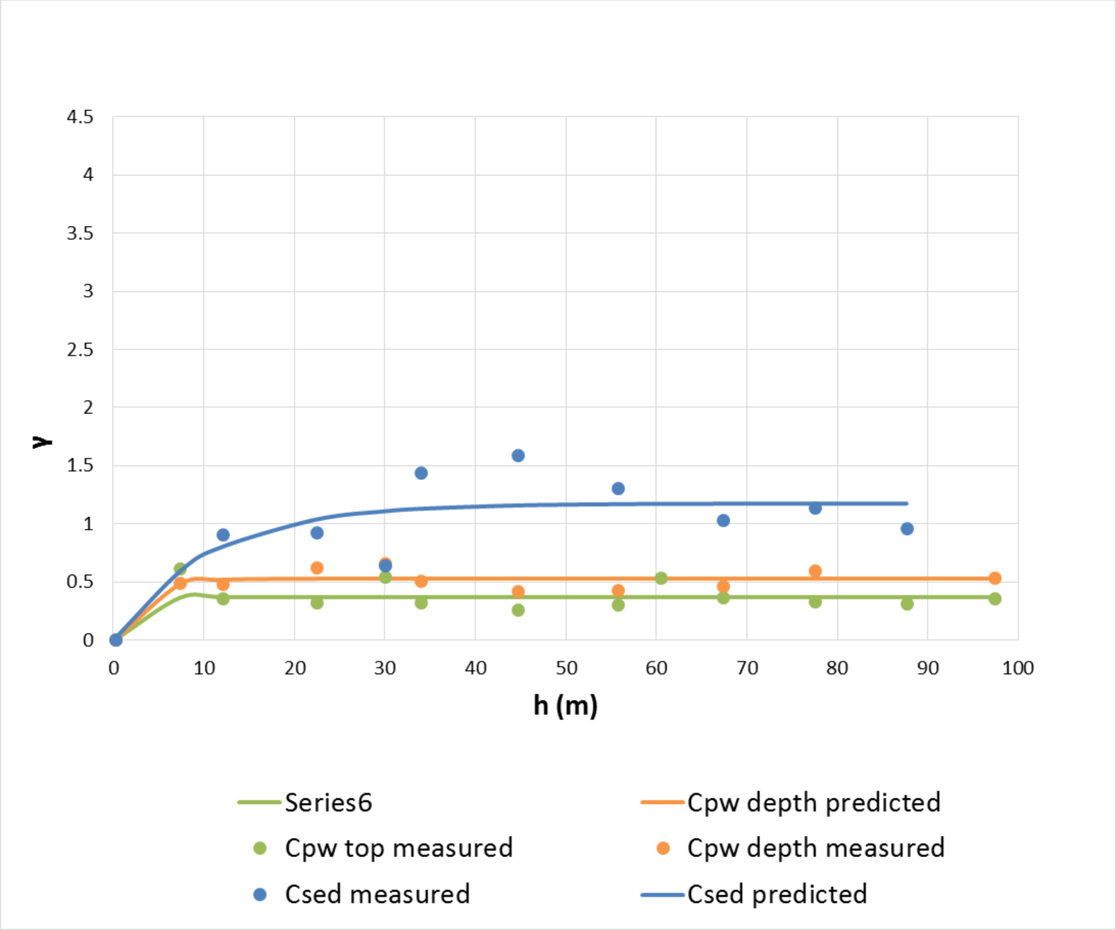


Figure 3-21. Fitted semivariogram models for measured concentrations of detected PCB at Columbia Slough (CS)

In addition, the fitted model can be used to estimate the concentrations at unsampled location based on the spatial distance and the average measured data. Another potential application of these spatial models is to determine uncorrelated “hot-spots”.

In Columbia Study, for example, the porewater and bulk sediment concentrations at all twenty sampling locations were used initially. However, the measured concentrations in Figure 3-15 and Figure 3-17 show that sampling site S8, S10, and S20 have an abnormally high concentration compared to other locations. These selected sites were removed from the analysis and the remainder fit to a variance model. The variance among these three areas in Columbia Slough were compared to the stable variance of the remainder of the site as listed in Table 3-4 and Table 3-5. The normalized variance between these sites and the adjacent sites are all much larger than the stable normalized variance across the site of 0.4 for surficial layer concentrations and 0.5 for depth layer concentrations. These results indicate S8, S10 and S20 represent hot spots with substantially greater concentrations and site to site variances that are much greater than the remainder of the sites.

Table 3-4. Normalized semi-variance of surficial layer (1-13.5cm) porewater concentrations at three sampling sites with adjacent locations at Columbia Slough

Normalized ϒ	S7	S9	S11	S19
S8	1.2	1.4		
S10		0.7	0.7	
S20				0.8

Table 3-5. Normalized semi-variance of depth layer (13.5-27cm) porewater concentrations at three sampling sites with adjacent locations at Columbia Slough

Normalized ϒ	S7	S9	S11	S19
S8	2.7	3.1		
S10		2.7	1.35	
S20				8.35

3.4.4.2 Statistical Approach

Statistics were used to evaluate the significance of the differences in the spatial variance of the surficial porewater data, the deeper porewater data and surficial sediment data. In this dissertation, the statistical analysis was processed by IBM SPSS software. The input variance is the normalized semi-variance value within locations. Three groups of semi-variance data: top layer porewater concentration variance, depth layer porewater concentration variance, and sediment concentration variance, are compared with each other for both Hunter's Point Navy Shipyard study and Columbia Slough study. The variance data was tested for normality and the normally distributed datasets were evaluated for homogeneity.

Columbia Slough was not significantly inhomogeneous ($p>0.05$) which suggested that ANOVA can be employed to determine the differences in variance between the paired datasets. The ANOVA suggested that there were significant differences in the variances of the three datasets ($p<<<0.01$). Multiple pairwise comparisons by the Game-Howell model are presented in Table 3-6. The difference between the top and bottom layer C_{pw} were not significant but there were significant differences between either of them and the sediment concentrations.

Table 3-6. Significance of Pairwise Differences in Variances between the concentration datasets- Columbia Slough (p values shown)

P value	$C_{pw, depth}$	$C_{pw, depth}$	C_{sed}
$C_{pw, top}$		0.21	0.00
$C_{pw, depth}$	0.21		0.00
C_{sed}	0.00	0.00	

For Hunter's Point, the variances were significantly inhomogeneous ($p<0.05$), so the Welch model and Brown-Forsythe model was used instead of ANOVA. Table 3-7 shows the p-value results for these two approaches and indicates that a significant difference exists between the porewater concentration and bulk sediment concentration spatial variances. Multiple pairwise comparisons were evaluated by the Game-Howell model. There were significant differences between the porewater concentration variances in the surface layer, the deeper layer and the sediment concentration variances.

Table 3-7. Significance of Differences in Variances among the three concentration datasets- Hunter's Point Navy Shipyard (p values shown)

Model	Welch	Brown-Forsythe
p value	0.005	0.036

3.5 CONCLUSIONS

The results from the field deployment in this chapter indicate that the SPME PDMS passive sampling can be used to characterize porewater concentrations across a site and with depth at specific locations as well as to identify and locate hot spots or source locations.

Surficial porewater concentrations are closely correlated across each site, probably due to dominant influence of sediment-surface water exchange. The variability in measured porewater concentrations are typically smaller than that in bulk sediment concentrations, which indicate that porewater is an integrative medium. This suggests that the sampling resolution to measure surficial porewater concentrations can be more coarse than might be used to measure bulk solid concentration. Moreover, surficial porewater concentration better represents flux to the overlying water and potentially risk to benthic organisms. The variability in surficial porewater concentrations is smaller than the variability at depth. The interlocation variances can also be used to identify hot spots as was demonstrated for three specific locations at Columbia Slough.

3.6 REFERENCES

1. Huckins, J. N., Tubergen, M. W. & Manuweera, G. K. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20,** 533–552 (1990).

2. Huckins, J. N., Booij, K. & Petty, J. D. Introduction to Passive Sampling. in *Monitors of Organic Chemicals in the Environment* 1–28 (Springer, Boston, MA, 2006).

3. Mayer, P. *et al.* Sensing Dissolved Sediment Porewater Concentrations of Persistent and Bioaccumulative Pollutants Using Disposable Solid-Phase Microextraction Fibers. *Environ. Sci. Technol.* **34,** 5177–5183 (2000).

4. Allan, I. J., Ruus, A., Schaanning, M. T., Macrae, K. J. & Næs, K. Measuring nonpolar organic contaminant partitioning in three Norwegian sediments using polyethylene passive samplers. *Sci. Total Environ.* **423,** 125–131 (2012).

5. Cornelissen, G., Pettersen, A., Broman, D., Mayer, P. & Breedveld, G. D. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environ. Toxicol. Chem.* **27,** 499–508 (2008).

6. Lu, X., Skwarski, A., Drake, B. & Reible, D. D. Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environ. Toxicol. Chem.* **30,** 1109–1116 (2011).

7. Thomas, C., Lampert, D. & Reible, D. Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **16,** 445–452 (2014).

8. Lampert, D. J., Thomas, C. & Reible, D. D. Internal and external transport significance for predicting contaminant uptake rates in passive samplers. *Chemosphere* **119,** 910–916 (2015).

9. Jonker, M. T. O. & Koelmans, A. A. Polyoxymethylene Solid Phase Extraction as a Partitioning Method for Hydrophobic Organic Chemicals in Sediment and Soot. *Environ. Sci. Technol.* **35,** 3742–3748 (2001).

10. Kraaij, R. *et al.* Measured Pore-Water Concentrations Make Equilibrium Partitioning Work A Data Analysis. *Environ. Sci. Technol.* **37,** 268–274 (2003).

11. Lu, X., Reible, D. D. & Fleeger, J. W. Bioavailability of polycyclic aromatic hydrocarbons in field-contaminated Anacostia River (Washington, DC) sediment. *Environ. Toxicol. Chem.* **25,** 2869–2874 (2006).

12. Vrana, B. *et al.* Passive sampling techniques for monitoring pollutants in water. *TrAC Trends Anal. Chem.* **24,** 845–868 (2005).

13. Lohmann, R., Booij, K., Smedes, F. & Vrana, B. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environ. Sci. Pollut. Res.* **19,** 1885–1895 (2012).

14. Vrana, B. *et al.* Passive sampling: An effective method for monitoring seasonal and spatial variability of dissolved hydrophobic organic contaminants and metals in the Danube river. *Environ. Pollut.* **184,** 101–112 (2014).

15. Chepchirchir, B. S., Paschke, A. & Schüürmann, G. Passive sampling for spatial and temporal monitoring of organic pollutants in surface water of a rural-urban river in Kenya. *Sci. Total Environ.* **601–602,** 453–460 (2017).

16. Booij, K., Smedes, F. & van Weerlee, E. M. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **46,** 1157–1161 (2002).

17. Ghosh, U. *et al.* Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integr. Environ. Assess. Manag.* **10,** 210–223 (2014).

18. Hawker, D. W. & Connell, D. W. Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* **22,** 382–387 (1988).

Chapter 4

Solid Phase Microextraction (SPME) Polydimethylsiloxane (PDMS) Passive sampling for Evaluation of Carbon Amendment Performance

4.1 ABSTRACT

In this chapter, passive sampling approaches were evaluated to assess the performance of activated carbon remediation of polychlorinated biphenyl (PCB) contaminated sediment offshore of Hunter's Point Navy Shipyard (HPNS) (San Francisco, California). Two different activated carbon materials, AquaGate+PAC and Sedimite^{TM}, were placed on the sediment surface and their performance evaluated. Polydimethylsiloxane (PDMS) fibers were applied to evaluate and monitor PCB porewater concentrations before placement of the activated carbon and at 8 months, 14 months and 26 months after the activated carbon capping layer placed. The concentration at 4 different depths into the sediment were analyzed. The results show that AquaGate+PAC reduced PCB concentrations by 83.7% after 8 months and 85.6% at 14 and 26 months, while Sedimite resulted a reduction by 72.5% after 8 month and 87.6 after 26 months. Although carbon was placed only at the surface, 80% reductions were observed to a depth of 16 cm after 8 months and 26 cm after 26 months in AquaGate+PAC treatment plot. Low molecular weight PCBs showed more rapid uptake on the carbon than high molecular weight PCBs. Hexachlorobiphenyls showed only 70% reduction after 26 months.

4.2 INTRODUCTION

Approaches to manage risks of contaminated sediments includes: source control, natural attenuation and recovery, *in situ* treatment or capping and removal and *ex situ* treatment or disposal.[1] Capping and *in situ* treatment of contaminated sediment are effective approaches for remediation. A capping layer or sorbent material can isolate chemical contaminants from the overlying water and reduce the flux and transport to the water column.[2–4] Capping materials are often sand, gravel or other coarse media and sorbents such as activated carbon can be used as a cap component or an in-situ treatment.[5]

Activated carbon (AC) has been proposed for contaminated sediment management and remediation has increased interest in recent years due to its high sorpobility.[6,7] Activated carbon has been used as composite material for sediment management with contaminants of PAHs,[4] PCBs,[8–11] mercury and methylmercury,[12] and organochlorine pesticide.[13] Activated carbon has been applied in a variety of ways including working into the sediment and placement onto the surface of the sediment to allow natural processes such as bioturbation to work the carbon into the sediment.[7] The latter approach is relatively simple but there are concerns that it may lead to a loss of the carbon sorbent prior to being effectively mixed within the sediment by bioturbation or other sediment mixing processes.

For *in situ* sediment management, traditional monitoring approaches focused on bulk solid concentrations to monitor remedy performance are not helpful. *In situ* management of refractory contaminants is a containment approach and does not generally degrade or reduce contaminants. Instead, measures that focus on contaminant availability and mobility are required. Contaminants present in porewater are mobile and generally more available than contaminants on solids. Passive sampling is a means of measuring the porewater concentration in-place without removing the sediment or treatment materials. In this study, solid phase microextaction (SPME) is used to measure freely dissolved porewater concentrations in as an indicator of bioaccumulation and chemical activity.[14–19] Polyethylene (PE), polyoxymethylene (POM), and polydimethylsiloxane (PDMS) are commonly used sorbents for passive samplers. Several studies have shown the effectiveness of applying passive sampling to sediment assessment,[20–23] and for evaluating the effectiveness of *in situ* sediment remediation.[4, 8, 9, 24–26]

In this work, SPME polydimethylsiloxane (PDMS) fibers were used to assess the effectiveness of activated carbon materials capping at contaminated sediment sites in open water near Hunters Point Navy Shipyard, San Francisco, California. The site was contaminated with PCBs as a result of historical activities. Two types of composite materials, AquaGate+PAC and Sedimite were used as *in situ* capping remedies. The activated carbon was placed directly on the sediment surface, and *in situ* passive sampling samplers were deployed 8 months, 14 months and 26 months after AC placement. The changes in porewater concentration of target compounds were determined to monitor the performance and persistence of the remediation of the contaminated site.

The objectives of this work were to:

1) evaluate the effectiveness of the two activated carbon *in situ* treatment remedies by employing SPME PDMS passive sampling methods to determine porewater concentration over time

2) evaluate changes in the congener distribution of PCB porewater concentration by time and depth

3) evaluate the vertical mixing of AC over time after surface placement and the resulting vertical profiles in freely dissolved PCB porewater concentration.

4.3 MATERIALS AND METHODS

4.3.1 Site Description

Hunter's Point Navy Shipyard (HPNS) is located southeast of the City and County of San Francisco, California on a promontory extending eastward into San Francisco Bay (Figure 4-1 and Figure 4-2). The site was first used as a commercial dry dock facility, and then occupied by the United States Department of the Navy before it turned into a commercial ship repair facility. The shipyard was closed in 1991. Offshore sediments are affected by the release of PCBs from historical activities.

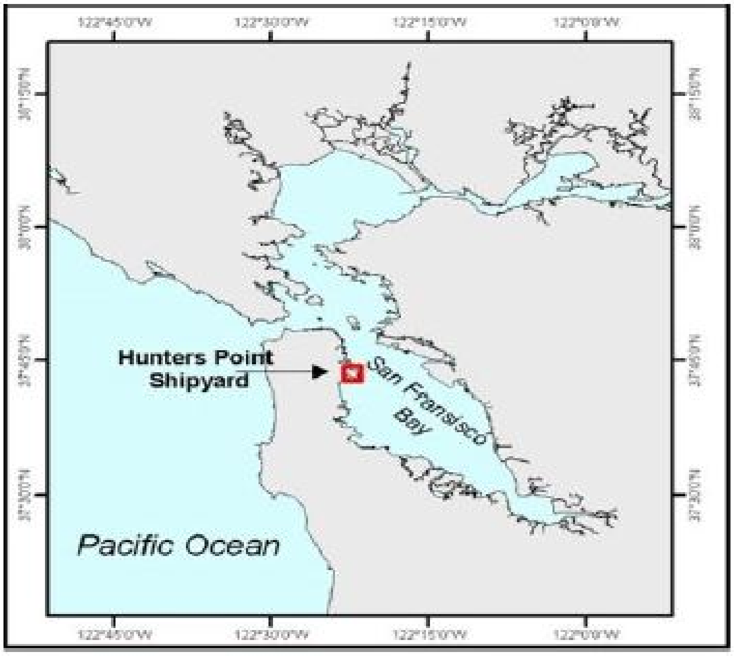
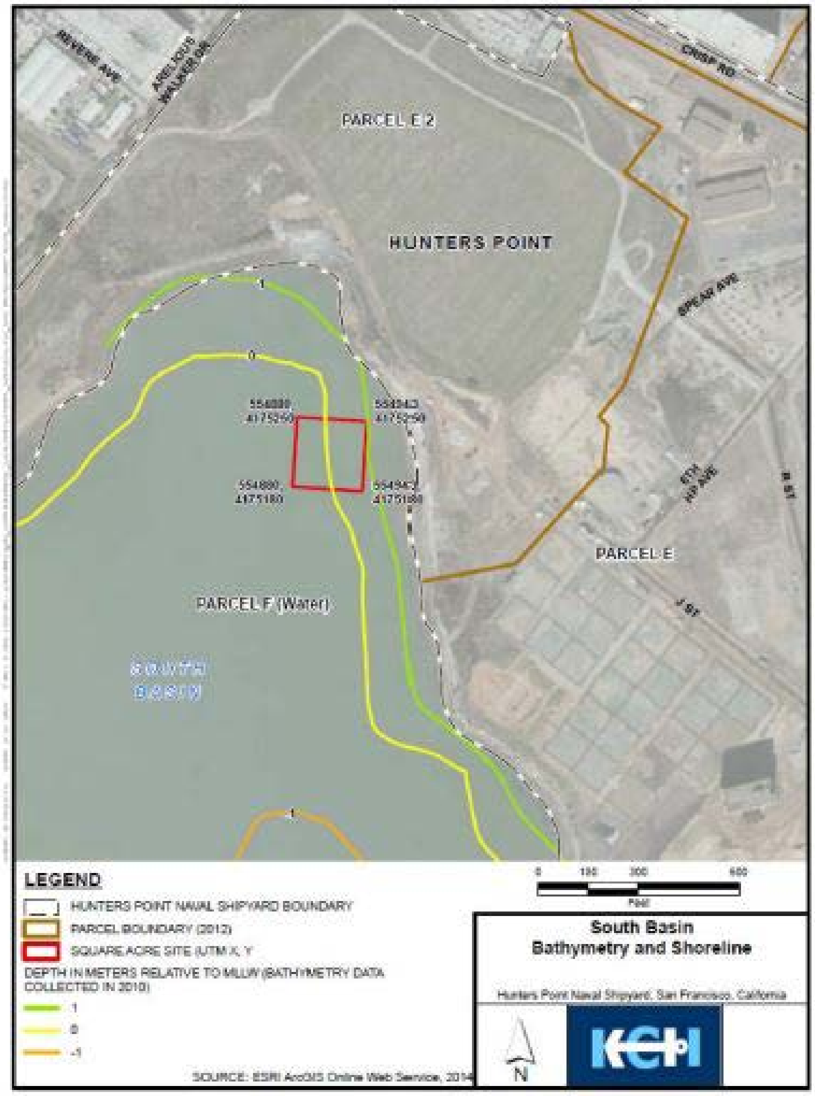


Figure 4-1. Site location, Hunter’s Point Navy Shipyard



SOURCE: ESRI ArcGIS Online Web Service, 2014

Figure 4-2. Location of activated carbon amendment study site at Hunter’s Point Navy Shipyard

4.3.2 Activated Carbon Materials and Placement

Twenty locations within two half-acre plots of the study are (Figure 4-3) were identified for baseline monitoring and for monitoring post AC placement. Two different types of commercial activated carbon materials were placed at two different plots as shown in Figure 4-3: AquaGate+PAC (Powdered Activated Carbon) for plot 1 (site 1, 3, 5, 7, 9, 12, and 15) and Sedimite for plot 2 (site 28, 30, 33, 36, 38, 40, and 42) in June 2015. Both formulations were designed to aid in delivery of activated carbon to the surface of the sediment. The two distinct AC amendment plots were separated by a buffer zone approximately 45 feet wide, which included six sampling locations (site 17, 19, 21, 22, 24, and 26). With no activated carbon placed, three locations (site 43A, 45A, and 48A) about 10 meters north of the AC amendment area were used as reference sites in the post-treatment studies.

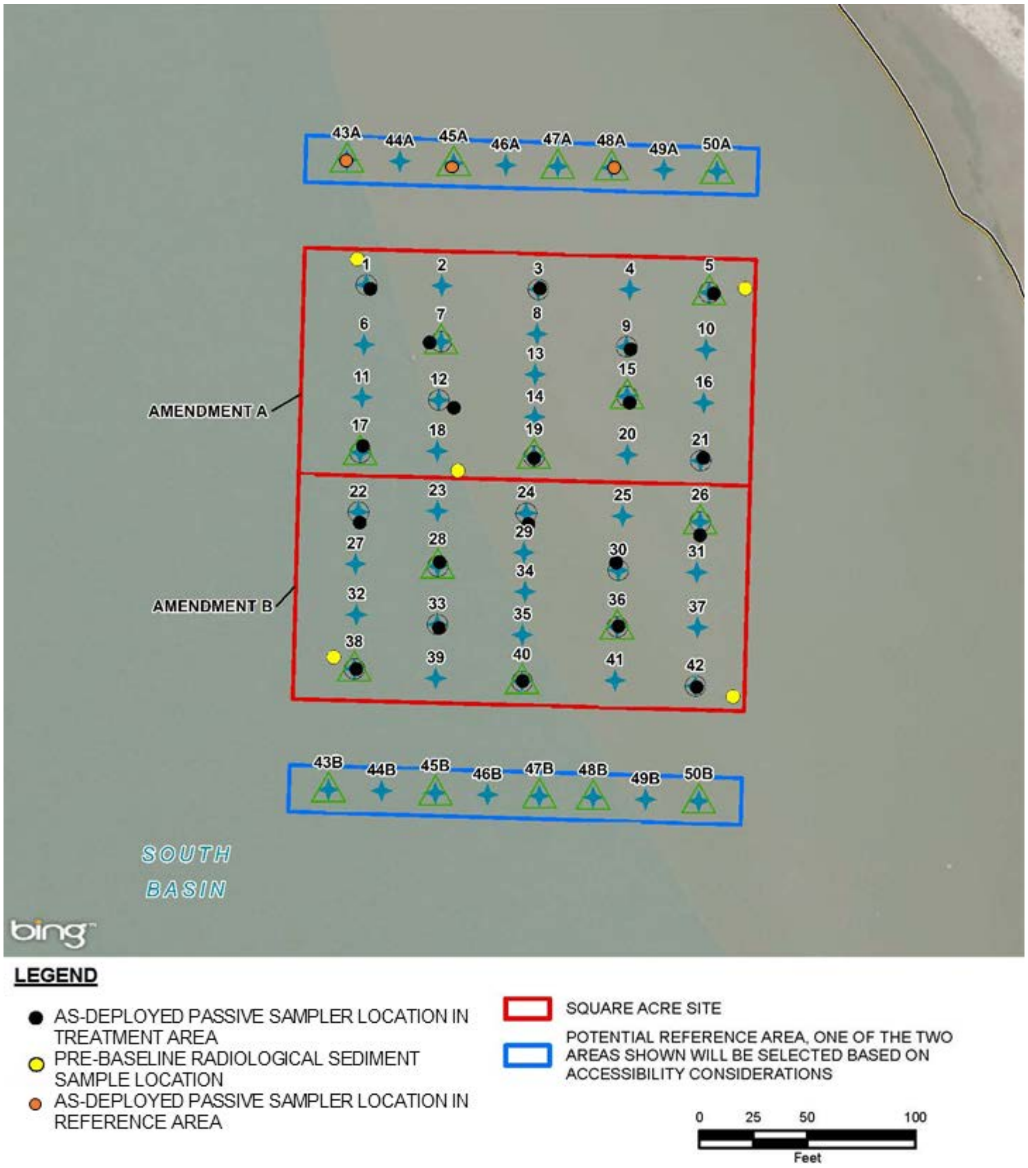


Figure 4-3. PDMS Passive sampling locations at Hunter’s Point Navy Shipyard

AquaGate +PAC (AquaBlok, Ltd, Toledo, Ohio) and Sedimite (Sediment Solutions, Ellicott City, MD) both are patented technologies which can serve as capping materials and deliver activated carbon to sediment for in-situ remediation, especially in aquatic environments (Figure 4-4). They have been proposed for a wide range of contaminants, including HOCs (PAHs, PCBs, dioxins, TBT) and metals (mercury).[27, 28] By combining AC within a more dense aggregate material, the activated carbon can settle onto the sediment surface and be less subject to erosive forces and slowly be integrated into the sediments through bioturbation or settling. The target carbon dose was determined to be 4 to 6 percent (mass carbon /mass dry sediment). Target total amendment mass was calculated based on a sediment thickness of 6 inches and a dry sediment bulk density of 600 kilograms per cubic meter. Activated carbon placement parameters are summarized in Table 4-1.

Figure 4-4. Two type of amendment materials used at Hunter’s Point Navy Shipyard: AquaGate+PAC (left) and sedimite (right)

Table 4-1. Summary of determined AC dose

Summary of Determined AC Doses			
Amendment Type:		AquaGate	SediMite
Activated carbon by weight	% by weight	10%	40%
Applied values			
Area treated	Acres	0.41	0.39
	Square feet	17,860	16,800
Total mass amendment applied	Pounds	190,000	53,200
Effective placement thickness	Inches	1.7	0.8
Calculated applied carbon dose	% by weight	5.7%	6.6%

4.3.3 Sampling Approach

The baseline study was conducted in May 2015. The passive sampling devices were placed at 20 sampling locations and retrieved in June 2015. At each location, three PDMS samplers were attached to a weighted tripod at each end and used as triplicates. The post-treatment sampling were conducted in January 2016, July 2016 and July 2017, which were as 8 months, 14 months and 26 months post amendment. In each study, the passive sampling devices were placed in the sediment and retrieved 28 days later. In addition to the 20 sampling locations, several sites north of the AC treatment area were served as reference sites in 8 months (site 45a), 14 months (site 45a and 48a) and 26 months (site 43a, 45a and 48a).

4.3.4 Bulk Sediment Sampling

Bulk sediment samples were collected at each porewater sampling location using an Ekman dredge immediately after passive sampler retrieval. The sediement samples were collected from the surficial sediments, about 4 inches, and homogenized. The sediment samples were then shipped overnight at 4˚C to complete laboratory analysis, including *ex situ* PCB porewater concentrations, bulk sediment concentrations, and TOC analysis.

4.3.5 Chemicals, Fibers and Samplers

The following solvents were used in the experimental and field procedures: Hexane and acetone (Fisher, ultra-pure grade), methanol (Fisher, ultra-pure grade), acetonitrile (Fisher, ultra-pure grade), and Nano-pure water (Barnstead). Other water preparations used Milli-Q water (Millipore Corporation).

The PDMS fibers used for porewater concentration determination were manufactured by Polymicro Technologies (Phoenix, AZ). For baseline study and at 8 months post-placement, the coated layer of PDMS was 36 µm with fibers diameter of 558 µm outside diameter and 486 µm diameter of the glass core. At 14 and 26 months, a slightly thinner PDMS layer was employed of 34.5 µm. The PDMS fibers were cleaned with hexane and acetonitrile, then rinsed with MiliQ water several times and then dried. The solvent washed fibers were submerged by 80:20(v:v) water: methanol solution in a 4L amber bottle and spiked with 7 performance reference compounds (PRCs) to provide an indication of the extent of equilibration of the fibers during deployment. The 4L bottle was placed on a shaking table for 4 weeks. Seven C^{13} labeled PCBs were used as performance reference compounds (PRCs): PCB 28/52/101/153/138/180/209.

The PDMS fibers were placed in sample holders fabricated from ¼” stainless steel rods that formed the legs of a tripod approximately 30 cm on a side. The fiber was placed in a 30 cm long groove cut into the stainless steel rods. The samplers were deployed in the field for approximately 30 days and then retrieved for analysis. The PDMS fiber was segmented into a surface layer (1-6cm), middle layer (6-11cm and 11-16cm) and depth layer (21-26cm). Due to the low concentrations after AC placement, a second 30 cm long groove was cut into the opposite side of each stainless steel rod and equal depth segments from all three tripod legs and both grooves on each leg were combined to ensure the achievement of sufficient detection limits.

The passive sampling fibers were sectioned into short segments, about 1 cm, and placed into a 2 mL auto sampling vial with insert. 150 µL of hexane was added to extract target compounds and PRCs. PDMS fibers were soaked in hexane overnight and every sample was vortexed for at least 2 minutes to ensure full extraction. The volume of extract was reduced to 50 µL. Internal standards (C^{13} labeled PCB9, PCB118 and PCB188) were added to a target concentration of 50 µg/L.

Samples were analyzed for PRCs and 111 PCB congeners using gas chromatography with a triple quadrupole mass selective detector (GCTQMS, Agilent 7890B) using a modified EPA method 1668c. The calibration range used for analysis in GCTQMS was 0.08 to 5 µg/L.

Bulk sediment samples were extracted by Accelerated Solvent Extraction (ASE 350, Dionex) and the extract were analyzed as noted above. Solid TOC samples were analyzed on an Elementar Vario EL instrument (Mt. Laurel, NJ). For BC determination, samples were heated to 375 ºC in muffle furnace for 24 hours before acidification and analysis on the TOC.[29] The instrument TOC measurement is of volatile carbon only, therefore the percentage TOC will only measure the non-ash component of the Activated Carbon. Standard Reference Material (SRM) 1941b were used as quality assurance and quality check (QAQC). The reference TOC value for SRM is 3.10% and reference BC percentage is 0.58%. The low TOC standard samples, which has theoretical TC% of 1.55, and Na_2CO_3, with theoretical a TC% of 11.3, were used for calibration standards and QAQC.

4.4 RESULTS AND DISCUSSIONS

4.4.1 TOC Analysis and Correlation with AC Dosage

The TOC in the sediments compared to the TOC during baseline measurements was used to indicate the amount of activated carbon in the sediment samples. A summary of total organic carbon results is provided in Figure 4-5 and Table 4-2. The difference between the post amendment TOC value (TOC%p) and the TOC percentage at baseline (TOC%b) were used to estimate the AC amount in this study, which were also shown in Figure 4-5 and Table 4-2. In the baseline study, the sediment samples had an average TOC of 1.4 wt. % and an average BC of 0.14 wt. %. The averaged TOC content measured at 8 months after placement of the activated carbon materials increased significantly to 11.7% in plot 1 (AquaGate+PAC) and 13.8% in plot 2 (Sedimite). The measured AC percentage in the surficial (4 inches) sediment samples are higher than targeted values, which may reflect the lack of complete intermixing over a 6-inch layer and the greater collection of the placed materials in the surficial solids collection. In later sampling events, the TOC% was reduced as a result of both intermixing into the sediments and potentially some loss of the activated carbon.

Black carbon measurements were also conducted on collected solid samples. The black carbon was not a useful indicator of AC since some loss of AC would occur at temperatures below that used to define black carbon. At 26 months after the activated carbon placed, the Aquagate+PAC plot and Sedimite area showed an average black carbon of 0.24 wt. % and 0.22 wt. %, respectively, while the baseline value was 0.14 wt. %.

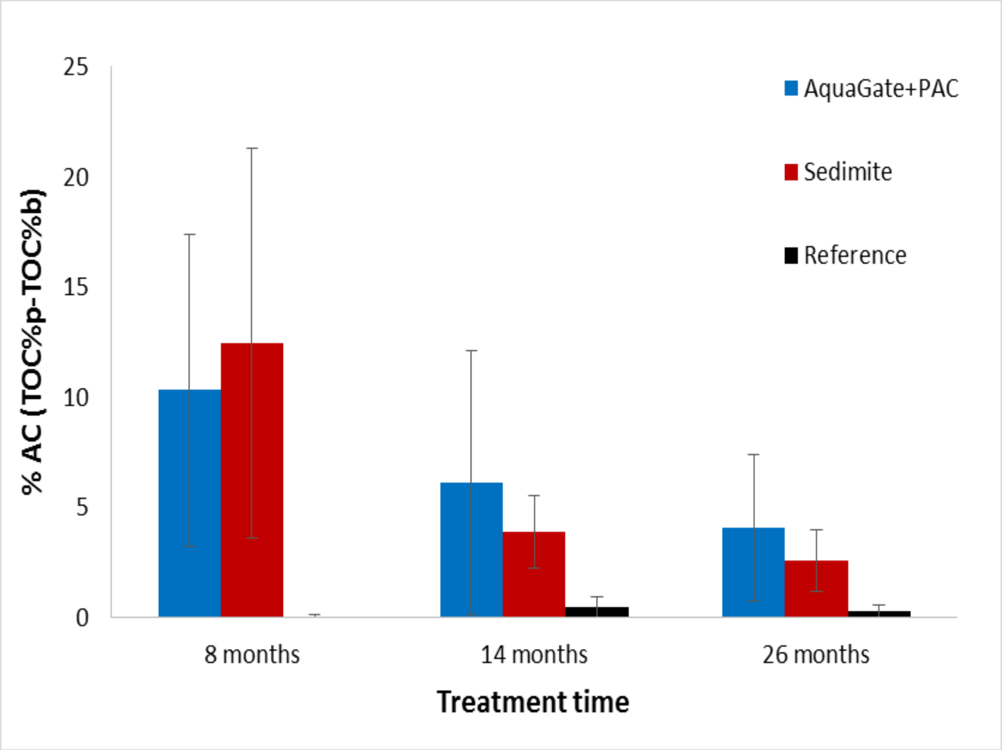


Figure 4-5. Estimate AC% (post amendment TOC %- baseline TOC %) in sediment with comparison to different treatment time

Table 4-2. Summary of measured TOC (%) in different AC treated plots

	Baseline	Postamendment TOC%			% AC (TOC%p-TOC%b)		
	TOC%	8 months	14 months	26 months	8 months	14 months	26 months
AquaGate+PAC	1.4±0.08	11.7±7.1	7.6±6.0	5.5±3.3	10.3	6.1	4.1
Sedimite		13.8±8.8	5.3±1.7	4.0±1.4	12.4	3.9	2.6
Reference Sites		1.5±0.1	1.9±0.5	1.7±0.1	0.1	0.5	0.3

4.4.2 Performance Reference Compound (PRC) Results

Performance Reference Compound (PRC) data were used to extent of equilibration of the passive samplers as indicated by the fraction of steady state (*fss*). In short, the fractional approach to steady state of a PRC desorbing from the passive sampler is given by

$$f_{ss} = 1 - \frac{C}{C_0}$$

Where C_0 is the initial concentration of the PRC at time 0, and C is its concentration at time of retrieval. This should also represent the fractional approach to steady state of an equivalent adsorbing compound. The PRCs used for HPNS studies were C^{13} labeled PCB 28, 52, 101, 138, 153, 180 and 209. For target congeners the data from the PRCs was fit to the model of Lampert et al. (2011) in which the fractional approach to steady state was a function of the product of a media sorption-related retardation factor and effective diffusivity for each compound (RD).[24]

The calculated logRD (m^2/d) values were fit to a linear relationship with $\log K_{ow}$ ($\log RD = \alpha \log K_{ow} + \log\beta$) recognizing that R should be approximately linear with the hydrophobicity of a target compound and D is approximately constant for a homologous series of similar molecular weight. The relationship between estimated *fss* for target PCB congeners with K_{ow} based upon PRC release and the measured PRC *fss* at baseline study is shown in Figure 4-6. The estimated fractional approach to steady state in deeper layers post amendment (i.e. below the activated carbon) was essentially identical to the fractional approach to steady state estimated at all depths during the baseline studies. In the surficial layer, however, activated carbon enhanced release of PRCs. This suggests a more rapid approach to steady state than actually occurs associated with strongly nonlinear sorption of the AC and is the subject of ongoing research (Shen, personal communication, 2018). Numerical simulations conducted by Shen suggest that the AC provides a more rapid approach to steady state of the desorbing PRC compounds relative to the uptake of the target compounds from water and thus use of the PRC information from the post-AC sampling periods may be misleading. Because the mixing processes at the site are likely to be unchanged and in order to provide a conservative estimate of the performance of the AC, the same relative approach to steady state was assumed post AC placement as was observed prior to AC placement.

The fractions of steady state for both baseline and post-treatment study at Hunter's Point ranged from 0.1 to 0.75. Overall, PCBs with low molecular weight reached higher fraction of steady state than the heavy PCB compounds.

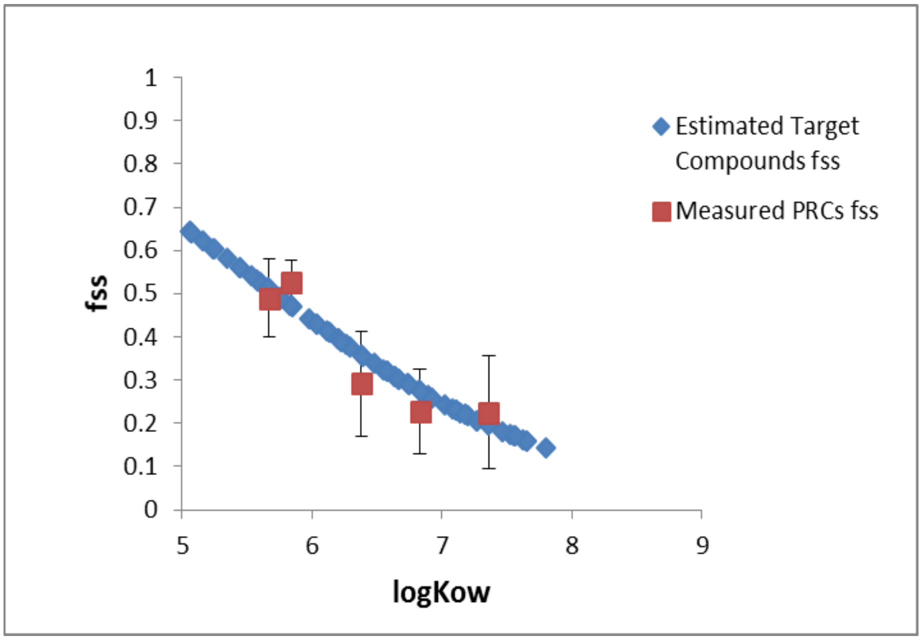


Figure 4-6. Fractional approach to steady state (fss) of PCBs based upon PRC release compared to the PRC fss estimated during baseline study

The error in measured PRCs may lead to uncertainty to the estimated porewater concentration of the target PCB congeners. Table 4-3 shows the measured $\frac{C_{PRC,t}}{C_{PRC,0}}$ of different PRCs at Hunter’s Point Navy Shipyard. The uncertainty in PRC concentration results represents the variability by sampling locations, which leads to uncertainty of 10%-20% in estimated concentration results.

Table 4-3. SPME PDMS measured ratio of remained PRC concentrations to original preloaded PRC concentrations (with standard deviation among locations) in Hunter's Point Navy Shipyard (HPNS)

$\frac{C_{PRC,t}}{C_{PRC,0}}$ (or 1-fss)	101	153	138	180
1-6cm	0.61±0.11	0.70±0.16	0.68±0.11	0.66±0.14
21-26cm	0.71±0.13	0.76±0.20	0.83±0.12	0.77±0.17

4.4.3 *In situ* PCB Porewater Concentrations

The *in situ* porewater concentrations of target PCBs at baseline study were measured in June 2015 and summarized in Chapter 3. The porewater concentrations were relatively uniform in distribution in baseline study. In total, 78 PCB congeners were detected and the determined PCB porewater concentration at baseline study across site averaged 2.4 ng/L. The primary focus of the post-treatment studies is to profile and monitor the changes of PCB porewater concentrations over treatment time.

By adding an additional 30 cm PDMS fiber to each sample holder and combing 3 replicates together, we could obtain lower porewater concentration detection limit in post-treatment studies and only 74 PCB congeners were still detected in total in each sampling event.

The sum concentration (ng/L) of all detected PCB congeners at baseline and three different treatment time periods and percent reductions are shown in Table 4-4.

Table 4-4. Summary of measured porewater concentrations (sum of identified congeners in ng/L) and concentration reductions (%)

		Baseline	8 months	14 months	26 months
AquaGate+ PAC	C_{pw} (ng/L)	2.63±0.28	0.46±0.25	0.44±0.12	0.37±0.11
	Reductions (%)		83.7±8.7	83.8±6.2	85.6±2.6
Sedimite	C_{pw} (ng/L)	2.29±0.09	0.66±0.25	0.49±0.16	0.28±0.11
	Reductions (%)		72.5±12.0	78.9±7.9	87.6±4.9

Samples collected at 14 months and 26 months generally showed similar concentrations with 8 months measurement, especially for samples from sediment surface (Figure 4-7). This indicates that activated carbon resulted in a relatively rapid C_{pw} reduction in the first 8 month and that reduction was maintained throughout the remainder of the study period. Note that this occurred despite reduction in the average amount of AC in the surficial sediments due to intermixing with depth and any potential loss of AC. In addition, there were porewater reductions that were deeper than vertical extent of AC missing across the amendment sites, particularly at the initial post-treatment sampling period when essentially all of the AC could be accounted for in the surficial sample.

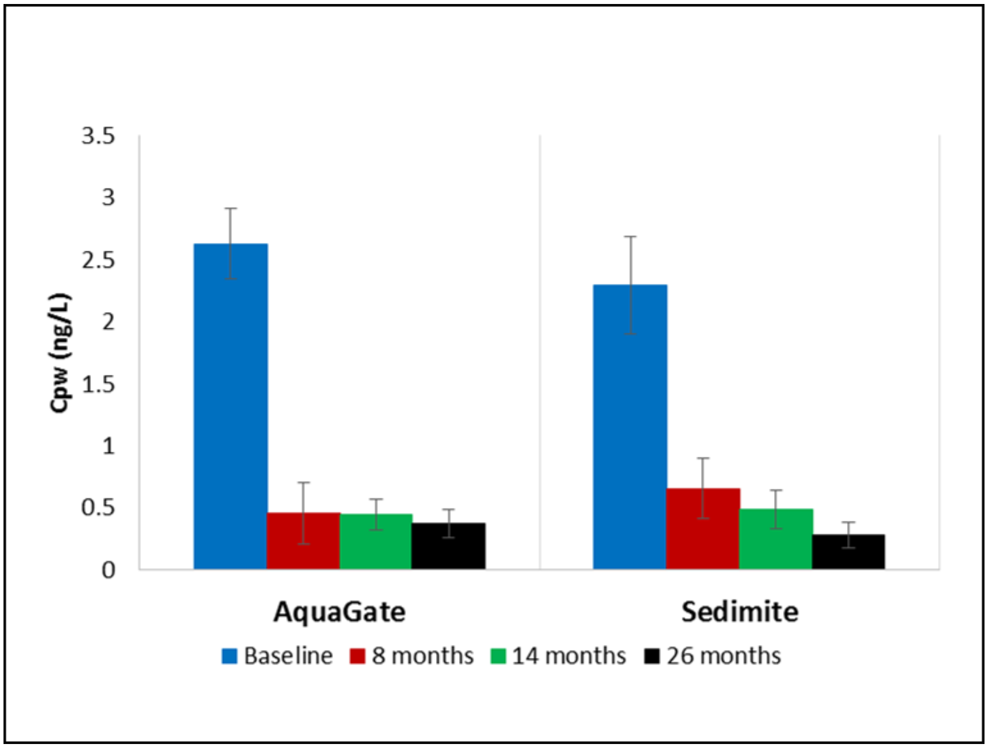


Figure 4-7. Measured PCBs porewater concentrations change with time across the AC treatment plots

26 months after AC placement, the measured average total PCB porewater concentrations at surface layer (1-6cm) was 0.24±0.08 ng/L in the Aquagate+PAC treatment plot and 0.19±0.09 ng/L in the Sedimite plot. This means that the Aquagate+PAC treatment resulted in an 89% decrease and Sedimite plot shows a reduction of 91% of surficial porewater concentrations.

In the baseline study, the concentration weighted average congener was found to be PCB 37 ($\log K_{ow} = 5.83$). That is, this is the congener whereby half of the PCB concentration was associated with lower molecular weight congeners and half with higher molecular weight congeners. The median congener turned to be PCB 66 ($\log K_{ow} =$

6.2) at 8 months sampling event and PCB 146 ($\log K_{ow}$ = 6.89) and PCB 183 ($\log K_{ow}$ = 7.2) at 14 and 26 months sampling events. The median congener increased in the post treatment sampling events due to the more rapid sorption of the low molecular weight congeners and the relatively slow sorption of higher molecular weight congeners.

The PCB congeners were grouped and analyzed by homologs as well as individual compounds. Table 4-5 lists the porewater concentration reductions by PCB homologs and treatment time. Monochloro PCBs were almost completely absorbed by the AC at the 8 months sampling event while the heptachloro PCBs still showed less than 70% sorption after 26 months. Figure 4-8 shows the PCB homologs at both top (1-6cm) and depth (21-26cm) layer at AquaGate+PAC and Sedimite plots. At both AC amendment plots, the largest concentration reductions were observed in the low molecular weight PCB homologs (mono-, di-, tri-), which were consistent with HOCs sorption to activated carbon kinetic studies[31-33]. The slow sorption of high molecular weight PCBs is likely due to high sorption capacity (high retardation) as well as size and steric effects in the AC

Table 4-5. Porewater concentration reduction (%) by PCB homologs and treatment time

Reduction (%)		Mono chloro	Di chloro	Tri chloro	Tetra chloro	Penta chloro	Hexa chloro	Hepta chloro	Octa chloro
AquaGate +PAC	8 months	0.99	0.88	0.91	0.87	0.73	0.64	0.63	0.88
	14 months	1	0.90	0.95	0.84	0.75	0.54	0.68	0.83
	26 months	1	0.95	0.94	0.92	0.77	0.69	0.59	0.81
Sedimite	8 months	0.68	0.81	0.87	0.78	0.57	0.54	0.51	0.81
	14 months	1	0.86	0.93	0.81	0.71	0.49	0.58	0.74
	26 months	1	0.94	0.94	0.93	0.81	0.77	0.67	0.79

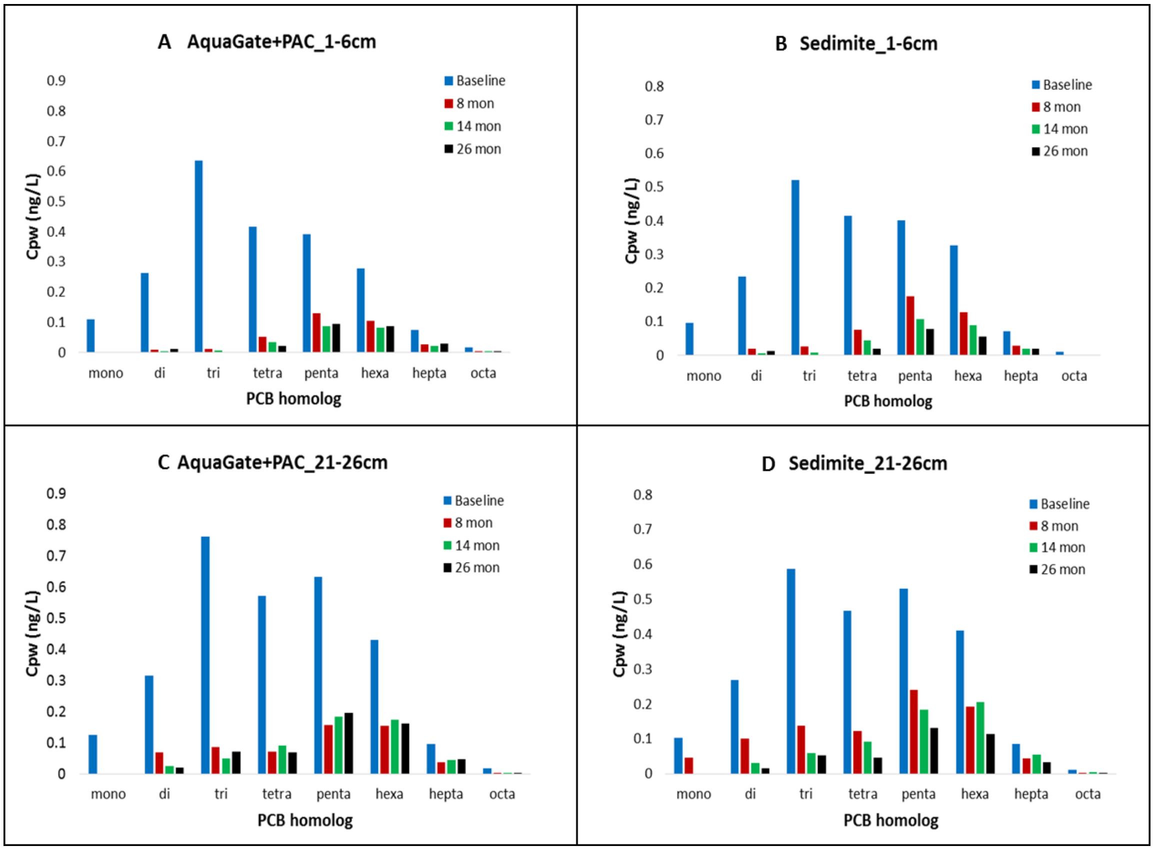


Figure 4-8. PCB homologs concentrations comparison in sediment porewater in (A) AquaGate+PAC plot at upper layer (1-6cm); (B) Sedimite plot at upper layer; (C) AquaGate+PAC plot at depth layer (21-26cm); and (D) Sedimite plot at depth layer (21-26cm)

4.4.4 AC Treatment Effect of C_{pw} at Different Depth

Since the remediation materials were placed at the surface of the sediment, the rate and effects of movement deeper into the sediment is of interest.

The measured total porewater concentration of all detected PCB compounds at four sampling horizons (1-6 cm depth, 6-11 cm depth, 11-16 cm depth and 21-26 cm depth) were analyzed and compared. The average C_{pw} results of AquaGate+PAC amendment plot and Sedimite amendment plot are shown in Table 4-6, Figure 4-19 and Figure 4-10.

For both amendments, the surficial layer showed the greatest reduction of PCB porewater concentrations. The C_{pw} decreased dramatically within 8 months after activated carbon materials placed by approximately a magnitude, and then maintained a relatively stable level in the following sampling events. Smaller but significant reductions in porewater concentrations were also noted at the deeper intervals. An 83% reduction of PCB porewater concentration was ultimately observed at 26 months between 21 cm to 26 cm below sediment surface in the Aquagate+PAC plot while Sedimite treatment led to approximately 85% decrease of PCB C_{pw} at the same horizion. This indicate that activated carbon effects not only at surface layer, but also at depth. This may correlate to the TOC and AC redistribution. As AC materials move down deeper, the porewater concentrations at depth could reduce than the early stage of capping.

Table 4-6. Summary of measured porewater concentrations in AquaGate+PAC plot and Sedimite plot

Cpw (ng/L)		Baseline	8 months	14 months	26 months
AquaGate+PAC	1-6cm	2.26±0.25	0.30±0.23	0.23±0.12	0.23±0.08
	6-11cm	NA	0.40±0.33	0.53±0.25	0.28±0.11
	11-16cm	2.40±0.27	0.46±0.31	0.52±0.13	0.36±0.11
	21-26cm	3.22±0.86	0.51±0.23	0.49±0.40	0.56±0.26
Sedimite	1-6cm	2.14±0.09	0.42±0.20	0.28±0.20	0.33±0.13
	6-11cm	NA	0.51±0.24	0.49±0.23	0.32±0.14
	11-16cm	2.47±0.18	0.68±0.30	0.70±0.33	0.28±0.15
	21-26cm	2.47±0.24	0.80±0.45	0.63±0.49	0.40±0.28

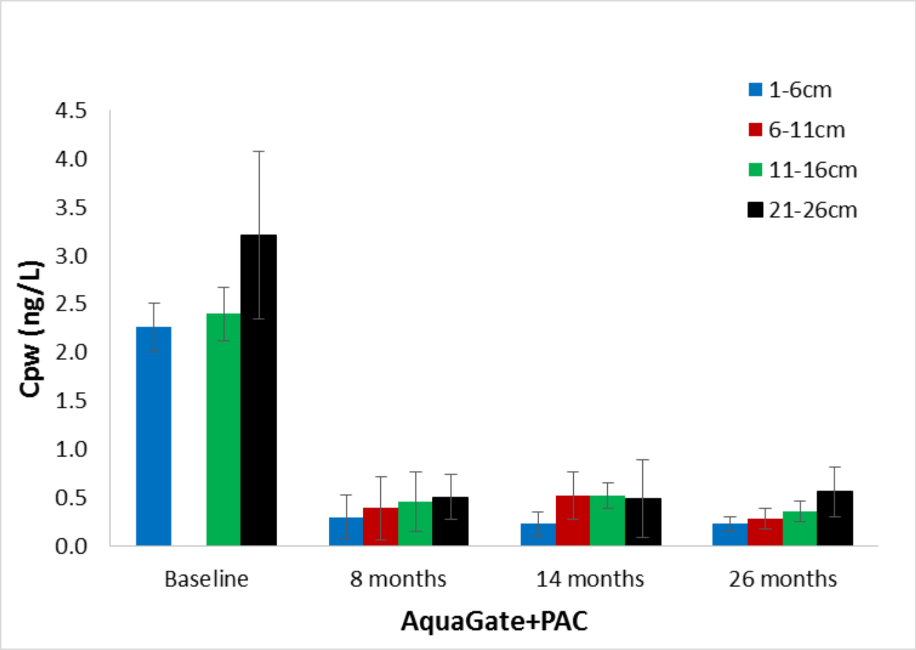


Figure 4-9. Mesured PCB concentrations in porewater across the Aquagate+PAC sites at four layer depth

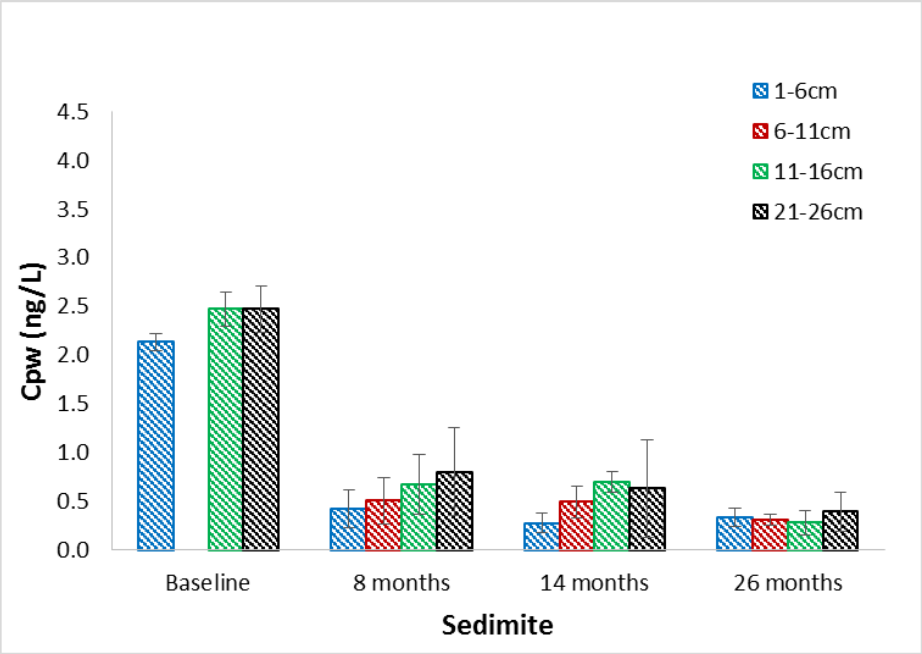


Figure 4-10. Measured PCB concentrations in porewater across the sedimite sites at four layer depth

4.4.5 Statistical Approach

Statistics were used to determine if the activated carbon amendment led to significant changes in concentration in each of the sampling time periods. The concentration datasets were first tested for normality and normality was satisfied for all data. The test for homogeneity showed that the datasets had variances that were significantly different ($p<0.05$).

The Welch model and Brown-Forsythe model were used to determine whether significant differences within the datasets (Table 4-7) were. The pairwise comparisons by the Game-Howell model are presented in Table 4-8 showing that porewater concentration data for all time periods are significantly different except for the 8 and 14 month data.

Table 4-7. Test of significance of differences within the porewater concentration datasets Hunter’s Point Navy Shipyard

Model	Welch	Brown-Forsythe
p value	0.00	0.00

Table 4-8. Pairwise comparison of porewater concentrations at different times for Hunter’s Point Navy Shipyard

p value	Baseline	8 months	14 months	26 months
Baseline		0.00	0.00	0.00
8 months	0.00		0.66	0.00
14 months	0.00	0.66		0.00
26 months	0.00	0.00	0.00	

4.5 CONCLUSIONS AND IMPLICATIONS

This chapter discussed the application of SPME PDMS fibers for evaluating PCB contaminated sediment remediation of activated carbon materials capping. The results from the activated carbon post-treatment analysis at Hunter’s Point Navy Shipyard demonstrated:

1. Both activated carbon materials, AquaGate+PAC and Sedimite performed well in PCB contaminated sediment management. Significant reductions were observed in the first 8 months amendment and that reduction was maintained throughout the remainder of the study period. AquaGate+PAC reduced total PCB concentrations by 83.7% after 8 months and 85.6% at 14 and 26 months, while Sedimite resulted a reduction by 72.5% after 8 month and 87.6 after 26 months.

2. Low molecular weight PCBs (mono-, di-, and tri-) show the largest concentration reductions in both activated carbon remediation. This may be related to the structure properties of PCB congeners and uptake kinetics to AC.

3. The surficial layer (1-6 cm depth) showed the greatest reduction of PCB porewater concentrations. Smaller but significant reductions in porewater concentrations were also noted at the deeper intervals (up to 26 cm). This is probably due to activated carbon intermixing and migrating happened during the treatment time.

This pilot study can be used as an example to prove that passive sampling can be used to illustrate the utility of the passive sampling approach and work as a bridge between academic research and practical application of passive sampling.

4.6 REFERENCES

1. *Processes, Assessment and Remediation of Contaminated Sediments*. (Springer-Verlag, 2014).

2. Wang, X. Q., Thibodeaux, L. J., Valsaraj, K. T. & Reible, D. D. Efficiency of capping contaminated bed sediments in situ. 1. Laboratory-scale experiments on diffusion-adsorption in the capping layer. *Environ. Sci. Technol.* **25,** 1578–1584 (1991).

3. Lampert, D. J. & Reible, D. An Analytical Modeling Approach for Evaluation of Capping of Contaminated Sediments. *Soil Sediment Contam. Int. J.* **18,** 470–488 (2009).

4. Thomas, C., Lampert, D. & Reible, D. Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **16,** 445–452 (2014).

5. Palermo, M.; Maynord, S.; Miller, J.; Reible, D., Assessment and remediation of contaminated sediments (ARCS) program: Guidance for in situ subaqueous capping of contaminated sediments. EPA 905-B96-004 1998.

6. Reible, D., Lampert, D., Constant, D., Jr, R. D. M. & Zhu, Y. Active capping demonstration in the Anacostia river, Washington, D.C. *Remediat. J.* **17,** 39–53 (2006).

7. Ghosh, U., Luthy, R. G., Cornelissen, G., Werner, D. & Menzie, C. A. In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. *Environ. Sci. Technol.* **45,** 1163–1168 (2011).

8. Cho, Y.-M. *et al.* Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment. *Environ. Sci. Technol.* **43,** 3815–3823 (2009).

9. Oen, A. M. P. *et al.* In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers. *Environ. Sci. Technol.* **45,** 4053–4059 (2011).

10. Nybom, I. *et al.* Effects of Activated Carbon on PCB Bioaccumulation and Biological Responses of Chironomus riparius in Full Life Cycle Test. *Environ. Sci. Technol.* **50,** 5252–5260 (2016).

11. Abel, S. & Akkanen, J. A Combined Field and Laboratory Study on Activated Carbon-Based Thin Layer Capping in a PCB-Contaminated Boreal Lake. *Environ. Sci. Technol.* **52,** 4702–4710 (2018).

12. Gilmour, C. C. *et al.* Activated Carbon Mitigates Mercury and Methylmercury Bioavailability in Contaminated Sediments. *Environ. Sci. Technol.* **47,** 13001–13010 (2013).

13. Thompson, J. M., Hsieh, C.-H., Hoelen, T. P., Weston, D. P. & Luthy, R. G. Measuring and Modeling Organochlorine Pesticide Response to Activated Carbon Amendment in Tidal Sediment Mesocosms. *Environ. Sci. Technol.* **50,** 4769–4777 (2016).

14. Booij, K., Smedes, F. & van Weerlee, E. M. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **46,** 1157–1161 (2002).

15. Kraaij, R. *et al.* Measured Pore-Water Concentrations Make Equilibrium Partitioning Work A Data Analysis. *Environ. Sci. Technol.* **37,** 268–274 (2003).

16. Lu, X., Reible, D. D., Fleeger, J. W. & Chai, Y. Bioavailability of desorption-resistant phenanthrene to the oligochaete Ilyodrilus templetoni. *Environ. Toxicol. Chem.* **22,** 153–160 (2003).

17. Schäfer, R. B., Hearn, L., Kefford, B. J., Mueller, J. F. & Nugegoda, D. Using silicone passive samplers to detect polycyclic aromatic hydrocarbons from wildfires in streams and potential acute effects for invertebrate communities. *Water Res.* **44,** 4590–4600 (2010).

18. Lu, X., Skwarski, A., Drake, B. & Reible, D. D. Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environ. Toxicol. Chem.* **30,** 1109–1116 (2011).

19. Gomez-Eyles, J. L., Jonker, M. T. O., Hodson, M. E. & Collins, C. D. Passive Samplers Provide a Better Prediction of PAH Bioaccumulation in Earthworms and Plant Roots than Exhaustive, Mild Solvent, and Cyclodextrin Extractions. *Environ. Sci. Technol.* **46,** 962–969 (2012).

20. Allan, I. J. *et al.* Field Performance of Seven Passive Sampling Devices for Monitoring of Hydrophobic Substances. *Environ. Sci. Technol.* **43,** 5383–5390 (2009).

21. Mayer, P. *et al.* Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* **10,** 197–209 (2014).

22. Ghosh, U. *et al.* Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integr. Environ. Assess. Manag.* **10,** 210–223 (2014).

23. Greenberg, M. S. *et al.* Passive sampling methods for contaminated sediments: Risk assessment and management. *Integr. Environ. Assess. Manag.* **10,** 224–236 (2014).

24. Lampert, D. J., Sarchet, W. V. & Reible, D. D. Assessing the Effectiveness of Thin-Layer Sand Caps for Contaminated Sediment Management through Passive Sampling. *Environ. Sci. Technol.* **45,** 8437–8443 (2011).

25. J. Lampert, D., Lu, X. & D. Reible, D. Long-term PAH monitoring results from the Anacostia River active capping demonstration using polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **15,** 554–562 (2013).

26. Beckingham, B. & Ghosh, U. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* **91,** 1401–1407 (2013).

27. Johnston, R. *et al.* Monitoring to assess the effectiveness of an activated carbon sediment amendment to remediate contamination at a site located at the Puget Sound Naval Shipyard & Intermediate Maintenance Facility, Bremerton, WA. in *Salish Sea Ecosystem Conference* (2014).

28. Patmont, C. R. *et al.* In situ sediment treatment using activated carbon: A demonstrated sediment cleanup technology. *Integr. Environ. Assess. Manag.* **11,** 195–207 (2015).

29. Gustafsson, Ö. *et al.* Evaluation of a protocol for the quantification of black carbon in sediments. *Glob. Biogeochem. Cycles* **15,** 881–890 (2001).

30. Hale, S. E., Kwon, S., Ghosh, U., & Werner, D. Polychlorinated biphenyl sorption to activated carbon and the attenuation caused by sediment. *Global NEST Journal* **12**, 318-326 (2010).

31. Kupryianchyk, D., *et al.* In situ sorption of hydrophobic organic compounds to sediment amended with activated carbon. *Environmental pollution* **161**, 23-29 (2012).

32. Rakowska, M., *et al.* Equilibrium and kinetic modeling of contaminant immobilization by activated carbon amended to sediments in the field. *Water research* **67**, 96-104 (2014).

Chapter 5

Employing Passive Sampling to Estimate Contaminant Flux and Ground Water Upwelling Velocity

5.1 ABSTRACT

Passive sampling technologies employ solid phase microextraction (SPME) using polymers such as polydimethylsiloxane (PDMS), polyethylene (PE), and polyoxymethylene (POM) to directly access the freely dissolved concentration in sediment porewater or overlying water columns. They have been used as emerging methods to detect, determine, and monitor the concentrations of hydrophobic organic contaminants (HOCs) like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediment pore waters. The risks to overlying water, however, is not just associated with concentration but flux, a quantity typically controlled by the rate of groundwater upwelling.

In this work, a model of mass transfer is used to predict groundwater upwelling velocity and contaminant flux using the rate of equilibration of passive samplers. The mass transfer coefficient is estimated by the rate of release of performance reference compound (PRCs) that can be used to assess the deviation from equilibrium in the passive sampler. The results are applied to two sediment sites, Hunter's Point Naval Shipyard, San Francisco, California and Columbia Slough, Portland, Oregon to illustrate the utility and usefulness of the SPME PDMS approach at evaluating contaminant flux.

5.2 INTRODUCTION

Hydrophobic organic compounds such as PAHs, PCBs, dioxins and some pesticides have accumulated in sediments as a result of poor management of industrial and municipal effluents. The risks that these compounds pose the overlying water is controlled by the contaminant flux from the sediments. This is true for undisturbed sediments as well as sediments managed by in-situ treatment or capping with a clean substrate. For both long-term and short-term monitoring goals, it is critical to understand contaminant behavior in terms of direction and magnitude of flux.[1] Therefore, the velocity of groundwater moves upward, also known as Darcy velocity, is an important parameter in controlling flux to overlying water.[2]

Passive sampling technologies were first developed in the 1990s and have been used for detecting, quantifying and monitoring contaminant concentrations in sediment porewater and surface water.[3, 4] Initial efforts employed an oily substance in polyethylene bags to simulate lipids in biological organisms. More recently, polymer sorbents have been used as passive samplers, which act via achieving chemical equilibrium with freely dissolved concentrations of contaminants through matrix solid phase microextraction (SPME).[5] Commonly used polymer samplers are polyethylene (PE),[6] polyoxymethylene (POM),[7] and polydimethylsiloxane (PDMS).[5, 8, 9] PDMS is usually coated to a cylinder while PE and POM are used in flat sheet form.

SPME passive sampling has many advantages: it’s efficient, it’s easy to process and it has less impacts on the surroundings. Passive sampling has much lower detection limits than traditional bulk sediment measurements.[4,6] Moreover, it can directly access the freely-dissolve porewater concentrations (C_{free}), which are the aqueous concentrations not bound to particulate matter or dissolved organic carbon.[10] The determination of C_{free}

is important for the management of contaminated sites due to its relationship to chemical activity, bioavailability and bioaccumulation potential.[8, 10, 11]

Performance reference compounds (PRCs) are used in passive sampling methods to indicate the rate of release of specific compounds and to estimate the expected rate of uptake of equivalent compounds, i.e. to estimate the extent of equilibrium of target compounds.[12, 13] The PRCs are not found in the surroundings (e.g. deuterated or C^{13} labeled homologs) and spiked to the sampler before use.

In this study, we attempt to employ *in situ* SPME passive sampling methods to estimate contaminant flux at the sediment-water interface. The method is based upon analytical solution to the PRC transport equations. In particular, we can obtain an expression to estimate the groundwater velocity and contaminant flux PRCs kinetics on polymer samplers.

The method is applied to two polychlorinated biphenyls (PCBs) contaminated sediments site, Hunter’s Point Naval Shipyard (San Francisco, California) and Columbia Slough (Portland, Oregon) to show the ability of the SPME PDMS passive sampling technique to measure flux from sediment to water column.

5.3 THEORETICAL CONSIDERATIONS

5.3.1 2-D Advective-diffusive System

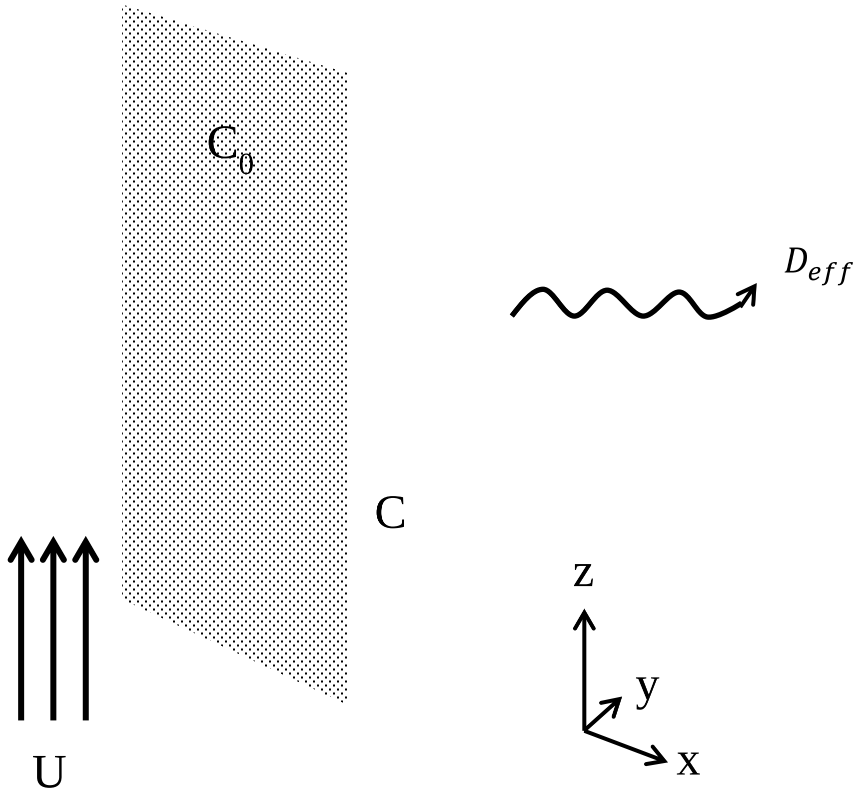


Figure 5-1. Passive sampling fiber placed in porous sediment bed subject to advective and diffusive fluxes

Figure 5-1 shows a planar or nearly flat passive sampling fiber placed in a saturated sediment bed. It is subject to diffusive and advective mass transport processes external to the sorbent layer. For cylindrical PDMS fibers with thin coat, when the characteristic length of distance, or the concentration gradient is small compared to the fiber diameter, the flat model can be used as a close approximation. Shen (2017) calculated that in non advective case, during 30 days sampling time, a typical hydrophobic contaminant with sorption coefficient $K_d=10^6$ L/kg and molecular diffusivity D=5×10^{-6} cm^2/s will diffuse approximate 0.5 mm in the sediment, which is roughly the same scale as the fiber outer radius. With higher velocity, the boundary layer on fibers decrease and lead to smaller characteristic diffusion distance.[14]

The general transport equation for a non-reactive contaminant subject to diffusive and advective transport in a porous media at quasi steady state is given by the equation:[15]

$$U\nabla C = D_Z\nabla^2 C \qquad \text{Eq. 5-1}$$

In a 2-D rectangular system at a quasi-steady state, Eq. 1 can be expressed by assuming the concentration and the upwelling groundwater flow rate are uniform on the y-axis:

$$\mathrm{U}\frac{dC}{dz} = D_{eff}(\frac{d^2C}{d^2x} + \frac{d^2C}{d^2y} + \frac{d^2C}{d^2z}) \qquad \text{Eq. 5-2}$$

where C is the freely dissolved target compounds' porewater concentration, D_{eff} is the effective diffusivity of the contaminant at z direction, x is the lateral coordinate, z is longitudinal axis parallel to the sampler sheet, and U is the fluid's upwelling velocity. In porous media, the velocity can be taken as a constant.

Transport in the direction perpendicular to the fiber was assumed to occur only via diffusion and advection could be assumed to dominate on z-axis. Then the Eq. 5-2 can be written as:

$$\mathrm{U}_z\frac{dC}{dz} = D_{eff}\frac{d^2C}{d^2x} \qquad \text{Eq. 5-3}$$

The approximation at the sampler-sediment interface requires a slender transport region, so the thickness of the layer **δ**, must be much smaller than the length z: $\delta \ll z$.

Define dimensionless variables,

$\theta = \frac{C_* - C_0}{C_\infty - C_0}$, where Define dimensionless variables, Then Eq.5-3 turns into

$$\mathrm{U}_z \frac{d\theta}{dz} = D_{eff} \frac{d^2\theta}{d^2x} \qquad \text{Eq. 5-4}$$

The relative magnitude of advective to diffusive mass transfer processes is expressed as the Peclet number (Pe):

$$Pe_z = \frac{U_z z}{D_{eff}} \qquad \text{Eq. 5-5}$$

Introducing a similarity variable suggested by the scaling law:

$$\eta = \frac{x}{z} Pe_z^{1/2} \qquad \text{Eq. 5-6}$$

Then the equation becomes

$$\theta'' + \frac{1}{2}\eta\theta' = 0 \qquad \text{Eq. 5-7}$$

With boundary conditions

$$\theta(0) = 0,\ \theta(\infty) = 1$$

Using separation of variable methods to solve the equation with these boundary conditions, the solution can be expressed as:

$$\theta = \mathrm{erf}(\frac{\eta}{2}) \qquad \text{Eq. 5-8}$$

The derivative of the error function follows from its definition and leads to a following expression:

$$\left(\frac{d\theta}{d\eta}\right)_{\eta=0} = \pi^{-\frac{1}{2}} = 0.564 \qquad \text{Eq. 5-9}$$

According to this similarity solution, the local Sherwood number, which represents the ratio of the convective mass transfer to the rate of diffusive mass transport can be estimated by Pe number:

$$Sh = \frac{kz_*}{D_{eff}} = \frac{flux}{C_0 - C_\infty}\frac{z}{D_{eff}} = \left(\frac{d\theta}{d\eta}\right)_{\eta=0} Pe_z^{1/2} = 0.564 Pe_z^{1/2} \qquad \text{Eq. 5-10}$$

The analytical relationship between Sh number and Pe number was developed by Bejan (1984), and Cheng (1977) found the same result by numerical methods.[16, 17]

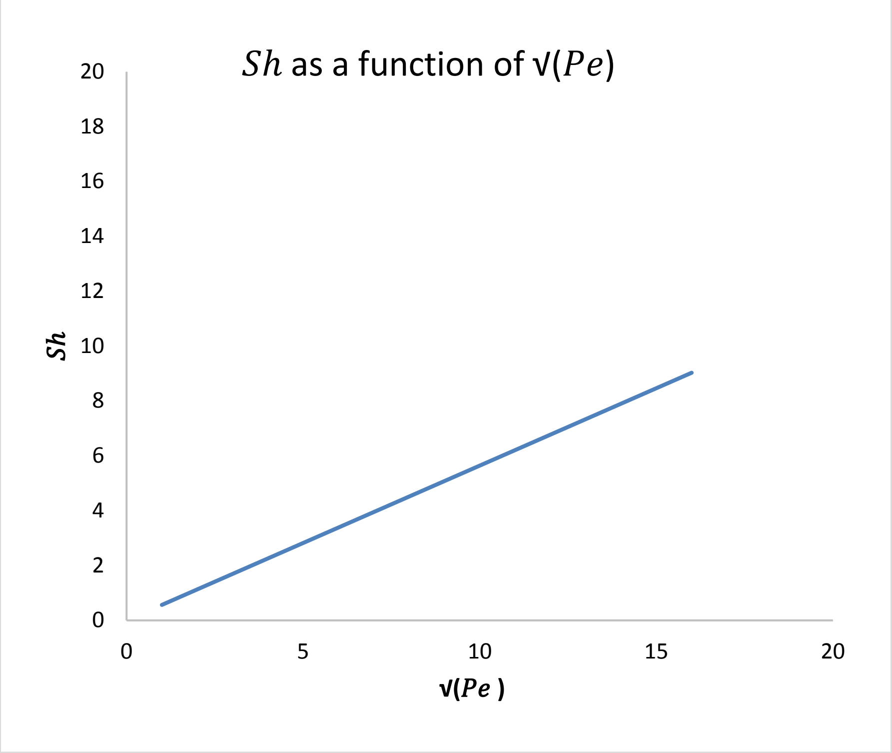


Figure 5-2. Sh as a function of $\sqrt{Pe_z}$ in rectangular system

5.3.2 Local Sherwood Number

The local Sherwood number can be determined by k, z and D_{eff}. The mass transfer coefficient k can be obtained from the loss of PRCs from the passive sampling fiber layer:

$$F_{PRC} = V\frac{dC_{PRC,fiber}}{dt} = kA(C_{PRC}|_{z\to\infty} - C_{PRC}|_{z=0}) \quad \text{Eq. 5-11}$$

where V is volume of the SPME fiber layer and A is the surface area of the SPME sorbent. The difference of PRC concentration at distance (z→∞) and at the fiber-water interface is the driving force of the PRC mass transfer. C_{PRC} at (z→∞) is zero since the PRC is not present naturally.

At z=0 the PRC release from the polymer equilibrates with the adjacent sediment where the total concentration includes both a dissolved and sorbed component.

$$C_{PRC} = \varepsilon\frac{C_{PRC,fiber}}{K_{fiber}} + \rho_b(1-\varepsilon)K_d\frac{C_{PRC,fiber}}{K_{fiber}} \qquad \text{Eq. 5-12}$$

where **ε** is the sediment bed's porosity, ρ is the density of sediment or other capping material, K_{fiber} is the passive sampling fiber-water partition coefficient, which in this case, is the PDMS-water partition coefficient, K_{PDMS}. K_d is the sediment-water partition coefficient, which in the case of diffusion only in sediment media, can be estimated by the following equation:

$$K_d = K_{oc} \times f_{oc} \qquad \text{Eq. 5-13}$$

where f_{oc} is the fraction organic carbon (assumed 1%) and K_{oc} is the organic carbon partition coefficient. The K_{oc} values for PCB congeners have be reported by Hansen et at. (1999).[18] Note that a measured sediment-water partition coefficient in contaminated sediments is often more reflective of the long-term desorption and is heavily influenced by slowly desorbing phases such as so-called "black" carbon. Here we assume that the short term PRC partitioning to the sediment is largely driven by sorption to the labile organic matter.

For some common hydrophobic organic chemicals like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), the K_{PDMS} can be predicted by octanol-water partition coefficient (K_{ow}) by the model presented by Ghosh et al., (2014).[19] For example, the correlations for PDMS are:

$$\log K_{PDMS} = 0.725 logK_{ow} + 0.479 \text{ for PAH} \qquad \text{Eq. 5-14}$$

$$\log K_{PDMS} = 0.725 log K_{ow} + 0.479 \text{ for PCB} \qquad \text{Eq. 5-15}$$

Solving for k from Equation 5-11 yields:

$$k = -\ln(\frac{C_{PRC,t}}{C_{PRC,0}}) \frac{V}{At} \frac{K_{PDMS}}{\varepsilon + \rho(1-\varepsilon)K_d} \qquad \text{Eq. 5-16}$$

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

For a fully saturated porous media composed of granular solids, the effective diffusivity of the contaminant D_{eff} can be estimated using the relationship developed by Millington and Quirk (1961):[20]

$$D_{eff} = D_w \frac{\boldsymbol{\varepsilon}}{\boldsymbol{\tau}} \qquad \text{Eq. 5-17}$$

$$D_{eff} = D_w \varepsilon^{4/3} \qquad \text{Eq. 5-18}$$

where $\boldsymbol{\varepsilon}$ is the porosity of the medium, τ is the factor representing the tortuosity of the flow path, and D_w is the diffusion coefficient value in water phase. The D_w values for a large number of chemical species in air and water have been reported in many papers. Corrections for different temperatures and pressures are discussed by Bird, et al. (1960).[21]

In summary, this equation provides an approach estimating advective velocity, U, by measuring the Sherwood number (Sh) from PRC release information and soil and PRC properties.

5.3.3 Freely-dissolved Porewater Concentrations

The freely-dissolved pore water concentrations were calculated from the accumulated concentrations in the fiber and the fiber-water partition coefficients as shown in the following equation:

$$C_{pw} = \frac{C_{fiber}}{K_{fiber} f_{ss}} \qquad \text{Eq. 5-19}$$

where fss is the fraction steady-state achieved from PRC data.[9]

5.4 FIELD TESTING METHODS

The method is applied to two polychlorinated biphenyls (PCBs) contaminated sites, Hunters Point Naval Shipyard (HPNS), San Francisco, California and Columbia Slough (CS), Portland, Oregon. SPME PDMS fibers are used in HPNS to determine porewater concentrations of PCBs for both sites.

5.4.1 Sediment Sampling Sites

5.4.1.1 Hunter's Point Naval Shipyard (San Francisco, California)

Hunters Point Naval Shipyard (HPNS) is located in southeast San Francisco on a peninsula that extends east into the San Francisco Bay. The shipyard is currently divided into eleven Parcels. Parcel F is the offshore parcel and the focus of this study. Due to historical site activities, sediments on and surrounding this site have been affected by the release of polychlorinated biphenyls (PCBs) mainly during 1960s. The vertical process of water at Hunter's Point Navy Shipyard sampling site is regarded to be purely tidal.

In May 2015, passive sampling was used to measure porewater concentrations in this area to define a baseline for a study of activated carbon in situ treatment. At each location, three samplers with PDMS were attached at each corner of a weighted tripod. The passive sampling devices were placed in the sediment and retrieved 28 days later. The rate of equilibration as measured by PRCs was used to estimate net equivalent upwelling velocity.

5.4.1.2 Columbia Slough-Pacific Meats (Portland, Oregon)

This area for the pilot study is located within the upper portion of the Columbia Slough, west of the City of Portland, Oregon. Oregon Department of Environmental Quality seeks to evaluate freely dissolved concentrations of PCBs in support of a pilot study evaluating activated carbon as a remedial option in this pilot. An in-situ baseline passive sampling study was conducted in July 2015. The same sampling devices used at Hunter's Point were also used at Columbia Slough. Thirty centimeter of the PDMS fibers were used in 20 different locations, which were arranged in two rows along the shoreline and each row has ten sampling locations. For sampling locations at channel, the vertical movement is probably just tidal, while for bank locations, it may be tidal with some groundwater flow.

5.4.2 PDMS Fibers

Solid phase micro-extraction (SPME) polydimethylsiloxane (PDMS) fibers (558 outside diameter/486um inner diameter) with PDMS coating thickness of 36 µm were purchased from Polymicro Technologies, (Phoenix, AZ).

Prior to use, the fibers had been cut into 30 and 5 cm length pieces and washed twice with hexane and acetonitrile sequentially for at least 30 minutes each. After the solvent wash, the fibers were rinsed with MiliQ water at least three times and then dried with Kimwipes™. Following this procedure, PDMS fibers were preloaded with performance reference compounds (PRCs) to assess the fraction of steady-state achieved during the sampler deployment and estimate the D_{eff} values. In this study, the C^{13} labeled mix containing PCBs was used as the PRCs. C^{13} labeled PCBs were selected as PRCs based on similarity to the target compounds, ease of detection, and coverage of a wide range of partition coefficients. Fibers were exposed for 30 days on a shaking table to an 80:20 (v/v) methanol: water solution spiked with PRCs to achieve 50 μg/L in final extract.

5.4.3 *In situ* Sampling Process

5.4.3.1 Preparation

Before loading the SPME fibers, the sampling devices were disassembled and washed with detergent and hot water, and then rinsed sequentially by rinsing with hexane, acetonitrile and distilled water, and then dried overnight.

The cleaned PRC C^{13} loaded fibers were assembled into grooves of each sampler and affixed with approximately 1 cm of waterproof caulk (hydrocarbon-free silicon) at both ends. After the silicon caulk dried, samplers were wrapped with clean aluminum foil individually and shipped overnight to field sites with ice bags to reduce evaporation loss.

5.4.3.2 Deployment

The assembled SPME insertion devices were placed within a tripod and then were driven perpendicular to the sediment interface from the water surface. For both Hunter's Point pilot and Columbia Slough pilot, twenty tripods were deployed at each target site which were recorded within the accuracy of differential GPS. All tripods were connected via nylon cords to surface-deployed buoys marked with site numbers.

5.4.3.3 Retrieval

Passive samplers were allowed to partially equilibrate for 28 days (the actual extent of equilibration measured with performance reference compounds) before they were withdrawn from the sediment by retrieval of the locating line. During processing, the insertion tools were dismantled, and both fibers were removed from the inner rod and wiped with damp tissue to remove sediment particles and sampled from top to bottom simultaneously.

5.5 ANALYTICAL METHODS

The 30 cm PDMS fibers were segmented into shorter parts (e.g. 5cm) to evaluate contaminant concentration at different depths with a ceramic column cutter. The first cm was discarded due to the silicon caulk. Two different depths (1-6cm and 21-26cm) were measured based upon the objectives of the Hunter's Point project. For Columbia Slough, the two target depths were 1-12.5cm and 12.5-27cm. The 5 cm segments of each sample were further cut into 1 cm lengths and pooled together in 2 mL labeled auto-sampling vials prefilled with 150 µL of hexane. The concentrations of PRCs impregnated into the fibers prior to insertion in the sediments were obtained by analysis a batch of 5 cm original fiber segments.

After removing the fibers, SPME extracts in hexane were analyzed for 111 target PCB congeners and remained spiked PCB C^{13} congeners by Gas Chromatography with a triple quadrupole mass selective detector (Agilent 7890B) using a SIM/SIM mode (modified Method 1668). 50ppb internal standard containing C^{13} labeled PCBs (9/118/188) were added to the SPME extracts prior to analysis. A modified EPA method 1668c was employed for the chemical analysis.

Calibration standards ranging from 0.2 to 5 µg/L in hexane were prepared from a 10000 µg/L PCB stock solution (Accustandards). A six point calibration led to a linear calibration with R^2>0.997 for all compounds. 5 µg/L PCB mix standard was added every 15 samples for quality assurance and quality control (QAQC).

5.6 RESULTS

5.6.1 Estimation of the Site Specific Effective Diffusivities

The mass transfer parameters of the pure compounds needed for the model can be found in Mackay (2006), Ghosh (2014), and an online website tool, LookChem.[19, 22] The effective diffusivity of contaminant D_{eff} were determined by the diffusion coefficient in water phase, D_w, and the sediment bed's porosity, $\boldsymbol{\varepsilon}$. The sediment bed's porosity, $\boldsymbol{\varepsilon}$ can be obtained by measured moisture content.

$$moisture\ content = \frac{\varepsilon \times \rho_{water}}{\varepsilon \times \rho_{water} + (1-\varepsilon) \times \rho_{sed}} \qquad \text{Eq. 5-20}$$

The sediment grain density ρ_{sed} is estimated to be 2.6g/cm^3, and water density ρ_{water} is 1g/cm^3. Moisture content is calculated by the measured bulk mass and dry mass. The porosity results for two sites are shown in Table 5-1.

Table 5-1. Moisture content and porosity for Hunter's Point Navy Shipyard (HPNS) and Columbia Slough (CS)

	Moisture Content	Sediment Bed's Porosity
Hunter's Point	51.95%	0.738
Columbia Slough	51.38%	0.733

Therefore, the D_{eff} can be determined by Eq. 5-18:

$$D_{eff} = D_w \varepsilon^{4/3} \qquad \text{Eq. 5-18}$$

The calculated D_{eff} for PCB 101, 153, 138 and 180 are listed in Table 2. C^{13} labeled homologue of these congeners were used as PRCs for Hunter's Point while Columbia Slough used PCB C^{13} 52, 101, 153 and 180.

Table 5-2. Pure Compound mass transport parameters for Hunter's Point Navy Shipyard (HPNS) and Columbia Slough (CS)

PCB Congener	52	101	153	138	180
Structure	2,2',5,5'-	2,2',4,5,5'-	2,2',4,4',5,5'-	2,2',3,4,4',5'-	2,2',3,4,4',5,5'-
M_w (g/mole)	291.99	326.43	360.88	360.88	395.32
Density (g/mL) @ 20˚C	1.2024	1.2803	1.3482	1.3482	1.3702
logK_{ow}	5.84	6.38	6.92	6.83	7.36
logK_{PDMS} (Ghosh 2014)	5.51	6.02	6.54	6.45	6.95
logK_{oc} (Hansen 1999)	5.20±0.07	5.64±0.20	6.06±0.24	6.19±0.21	6.53±0.36
D_w (cm^2/s) @ 20˚C	5.37E-06	5.19E-06	5.03E-06	5.03E-06	4.88E-06
D_{eff} (cm^2/s) @ HP	3.58E-06	3.46E-06	3.35E-06	3.35E-06	3.25E-06
D_{eff} (cm^2/s) @ CS	3.55E-06	3.43E-06	3.32E-06	3.32E-06	3.26E-06

5.6.2 Preferred Reference Compounds (PRCs) Fractional to Steady State (fss) Results

The corrections for non-equilibrium kinetics, that is, the fractional of equilibrium achieved (*fss*) can be expressed as Equation 5-21:

$$f_{ss} = \frac{M_t}{M_0} \qquad \text{Eq. 5-21}$$

Where M_t and M_0 are the absorbed mass on PDMS fibers at deployment time t and time 0 (before deployment). For preloaded PRCs, Eq. 5-21 can also be expressed in terms of concentrations:

$$f_{ss} = 1 - \frac{C_{PRC,t}}{C_{PRC,0}} \qquad \text{Eq. 5-22}$$

Twelve 5 cm PDMS fiber replicates taken prior to sediment deployments were used as PRC $C_{PRC,\,0}$, which shows the initial PRCs impregnated into the fibers. $C_{PRC,t}$ is the PRC remaining sorbed to the polymer layer after an exposure time t. Figure 5-3 and Figure 5-4 show relationships between the calculated *fss* and logKow for PRC compounds at different sampling locations at Hunter’s Point Navy Shipyard and Columbia Slough, respectively. The error bar in each figure represents for the standard deviation of different sampling location results.

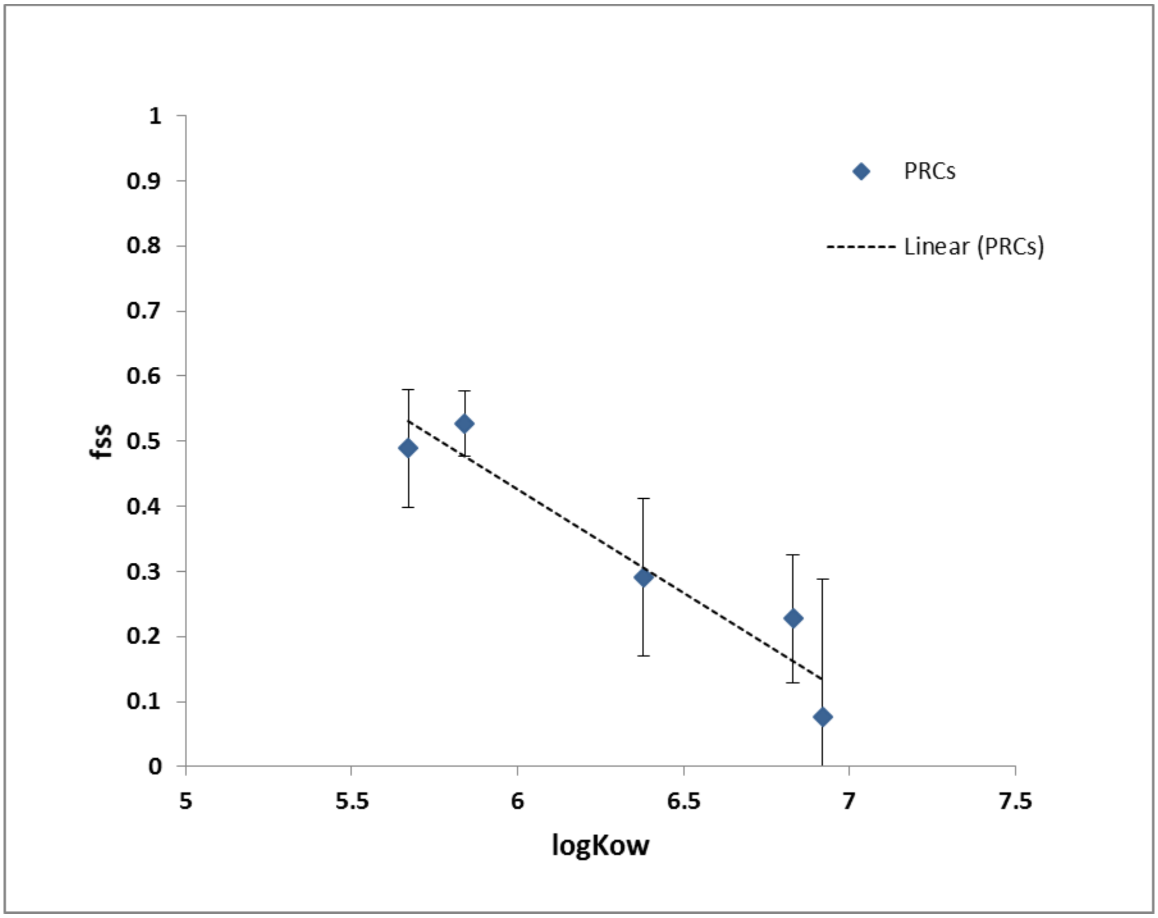


Figure 5-3. Relationship between fractions to steady state (*fss*) with logKow at Hunter's Point Navy Shipyard

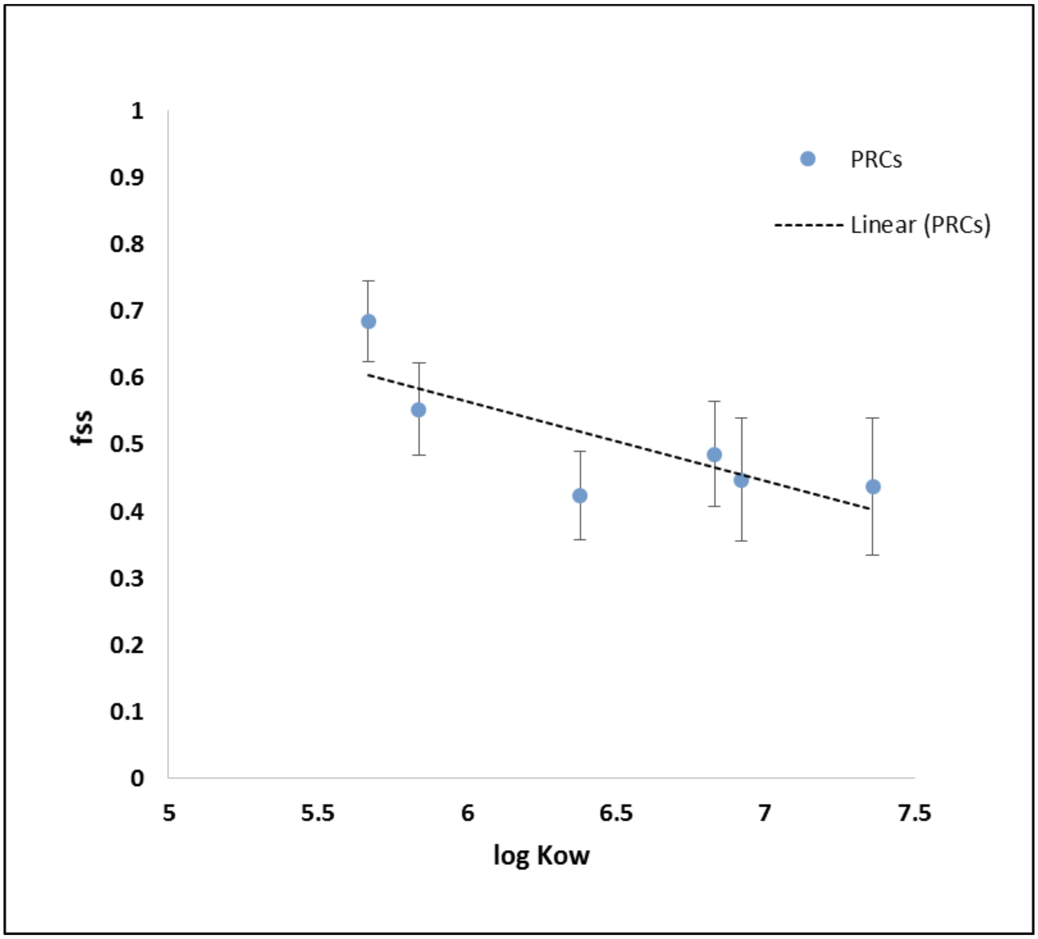


Figure 5-4. Relationship between fractions to steady state (*fss*) with logKow at Columbia Slough

Table 5-3 and Table 5-4 show the measured $\frac{C_{PRC,t}}{C_{PRC,0}}$ of different PRCs at Hunter's Point Navy Shipyard and Columbia Slough. The uncertainty in PRC concentration results represents the variability by sampling locations, which may lead to uncertainty in model estimations. In general, the uncertainty caused by location variations is in the range of 10% to 20% for both sampling sites.

Table 5-3. SPME PDMS measured ratio of remained PRC concentrations to original preloaded PRC concentrations (with standard deviation among locations) in Hunter's Point Navy Shipyard (HPNS)

$\frac{C_{PRC,t}}{C_{PRC,0}}$ (or 1-fss)	101	153	138	180
1-6cm	0.61±0.11	0.70±0.16	0.68±0.11	0.66±0.14
21-26cm	0.71±0.13	0.76±0.20	0.83±0.12	0.77±0.17

Table 5-4. SPME PDMS measured ratio of remained PRC concentrations to original preloaded PRC concentrations (with standard deviation among locations) in Columbia Slough (CS)

$\frac{C_{PRC,t}}{C_{PRC,0}}$ (or 1-fss)	101	153	138	180
1-13.5cm	0.66±0.08	0.61±0.10	0.63±0.10	0.68±0.10
13.5-27cm	0.64±0.07	0.58±0.09	0.59±0.09	0.65±0.12

5.6.3 Mass Transfer Coefficient k Determined by SPME PDMS

As discussed earlier, the mass transfer coefficients can be determined by Eq. 5-16:

$$k = -\ln\left(\frac{C_{PRC,t}}{C_{PRC,0}}\right)\frac{V}{At}\frac{K_{fiber}}{\varepsilon+\rho(1-\varepsilon)K_d} = -\ln(1-fss)\frac{V}{At}\frac{K_{fiber}}{\varepsilon+\rho(1-\varepsilon)K_{oc}f_{oc}} \qquad \text{Eq. 5-16}$$

In this equation, the fraction to steady state (*fss*) and sediment porewater partition coefficient (K_d) values are measured by passive sampling method while the fiber volume (V), area (A), deployment time (t) and fiber water partitioning coefficient (K_{fiber}) are parameters used in passive sampling approach. The sediment grain density ρ is estimated to be 2.6g/cm^3.

The uncertainty in this calculations may be caused by both the experimental measurement, for example the $C_{PRC,t}$ and $C_{PRC,0}$ measured in different sampling locations and among replicates, and the theoretical estimations in partitioning coefficient K_{oc} and K_{fiber}.

The calculated mass transfer coefficient k values for Hunter's Point and Columbia Slough study at different depths are listed in Table 5-5 and Table 5-6, and plotted in Figure 5-5 and Figure 5-6, in which the listed uncertainty in mass transfer coefficient reflects the uncertainty in PRC result. Mass transfer coefficients estimated by different PRCs show consistent results for both field sites.

Table 5-5. Calculated mass transport parameters for Hunter's Point (HP)

PCB Congener		101	153	138	180
1-6cm	k (cm/d)	0.029	0.025	0.024	0.025
	Uncertainty (%)	16.3	19.8	14.7	18.2
21-26cm	k (cm/d)	0.019	0.010	0.015	0.014
	Uncertainty (%)	16.6	22.5	13.3	15.7

Table 5-6. Calculated mass transport parameters for Columbia Slough (CS)

PCB Congener		101	153	138	180
1-13.5cm	k (cm/d)	0.018	0.018	0.021	0.018
	Uncertainty (%)	11.2	14.6	14.4	13.0
13.5-27cm	k (cm/d)	0.019	0.017	0.023	0.019
	Uncertainty (%)	10.2	13.9	13.9	16.1

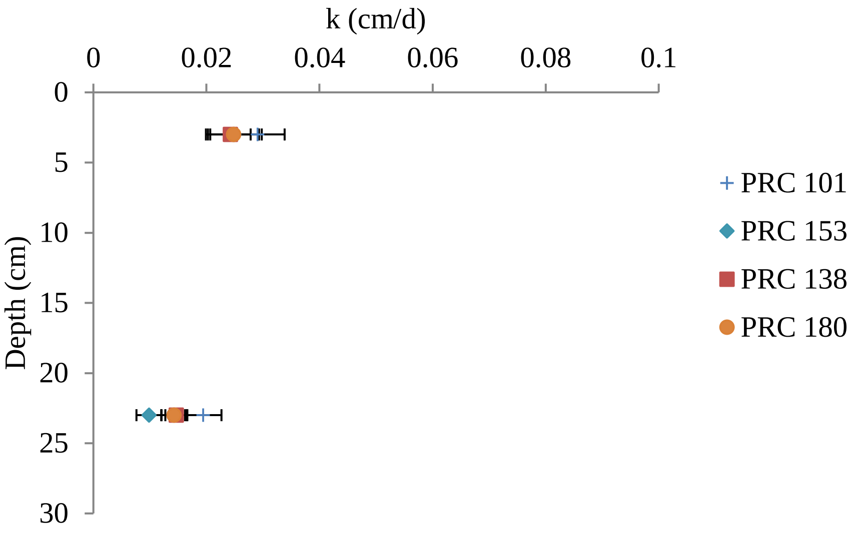


Figure 5-5. Mass transfer coefficient estimates for Hunter's Point Navy Shipyard (HPNS)

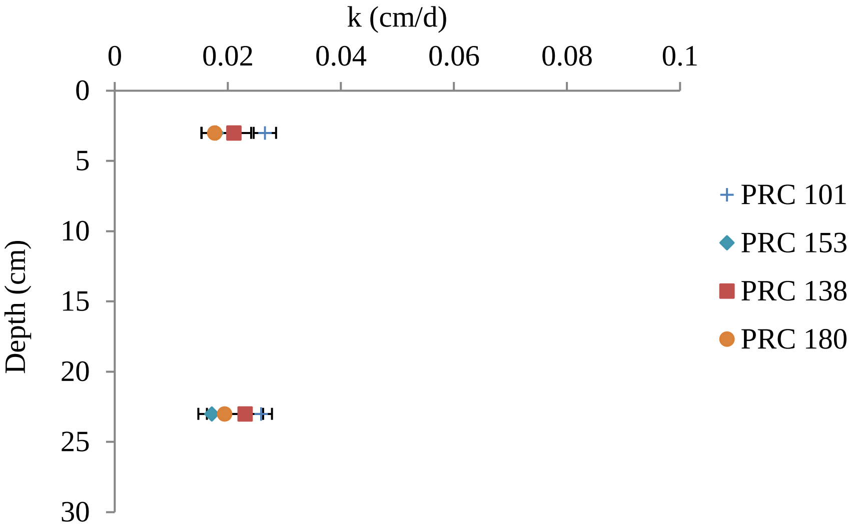


Figure 5-6. Mass transfer coefficient estimates for Columbia Slough (CS)

In Hunter's Point study, two sampling locations, STN 05 and STN 26 are analyzed for variations in locations. The estimated mass transfer coefficients are shown in Figure 5-7, which show that the results at different locations are consistent with each other and the variance may due to the PRC measurement uncertainty.

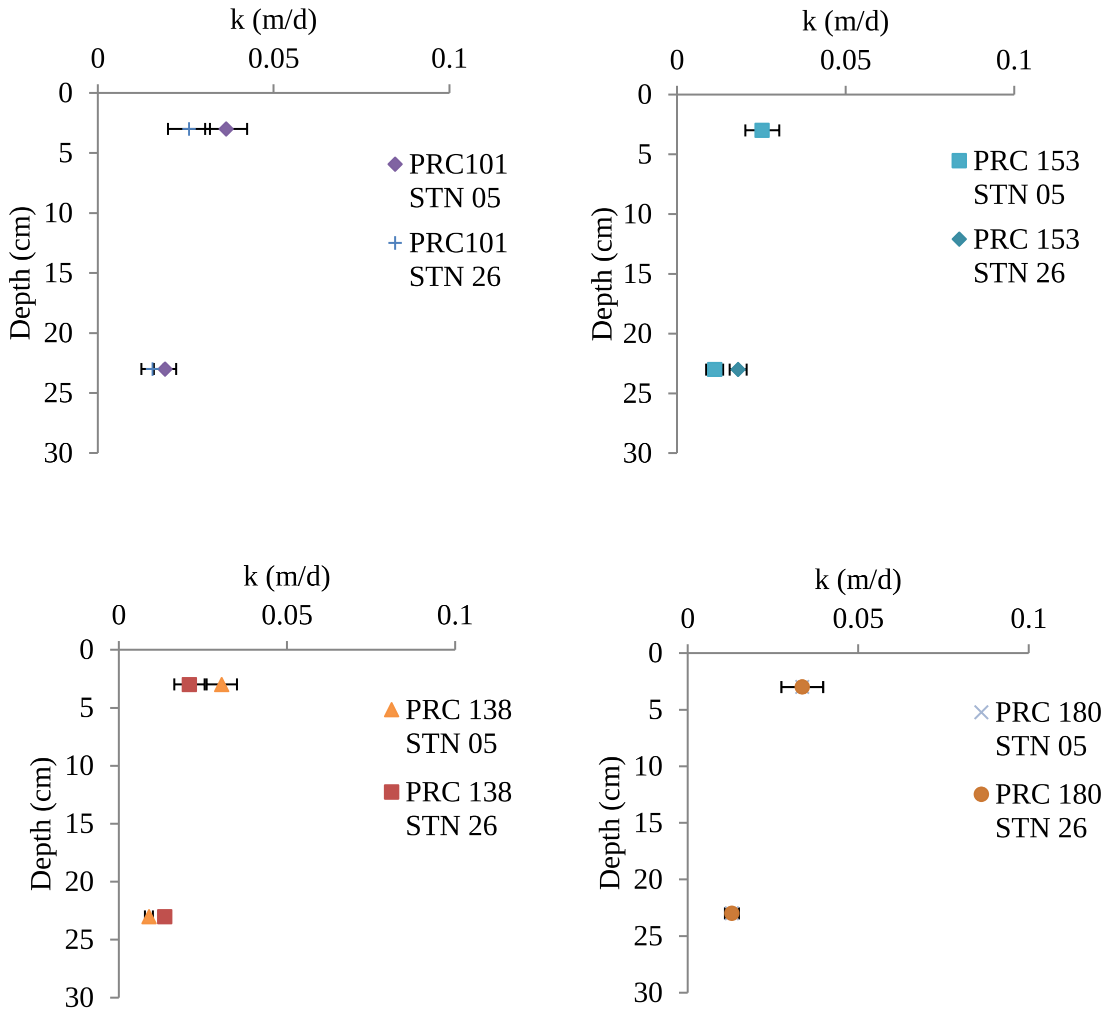


Figure 5-7. Mass transfer coefficient estimates for Hunter's Point (HP) at two different sampling locations

5.6.4 Sherwood Number and Water Velocities Determined by SPME PDMS

The value of Sh numbers could be calculated based upon the measured PRC release rate over the period of deployment by Eq. 5-10:

$$Sh = \frac{kz_*}{D_{eff}} \qquad \text{Eq. 5-10}$$

The Peclet number can be estimated by the Sh- Pe correlations (Eq.5-10) accordingly. Figure 5-8 shows the estimated groundwater upwelling velocity at Hunter's Point Navy Shipyard. The velocity should be same but appears lower at depth. This might be due to the tidal affect, which leads to decreasing velocity with depth. The groundwater upwelling velocity results at Columbia Slough were shown in Figure 5-9. Figure 5-10 shows the groundwater velocity estimated by different PRCs at two sampling sites at both HP. There are some differences among these sites, but not significantly. The differences may be caused by the geometric characteristics, differences, complex fluid transfer and measure errors.

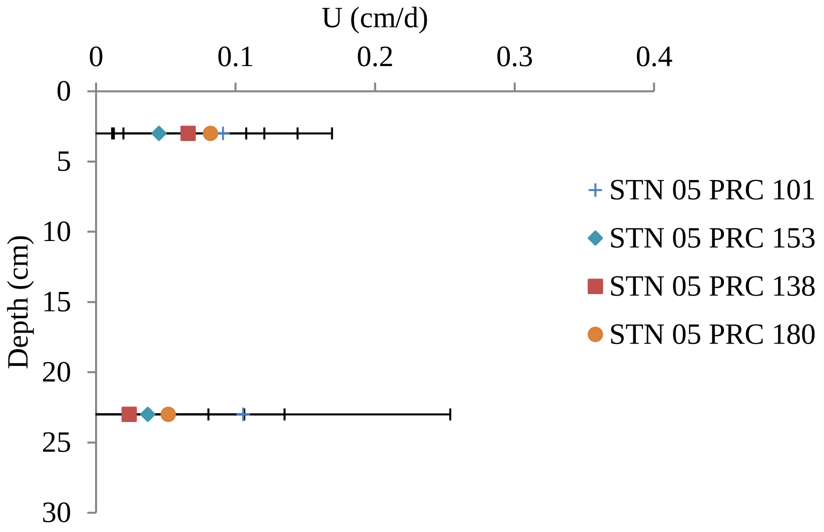


Figure 5-8. Groundwater velocity estimates for Hunter's Point Navy Shipyard (HPNS)

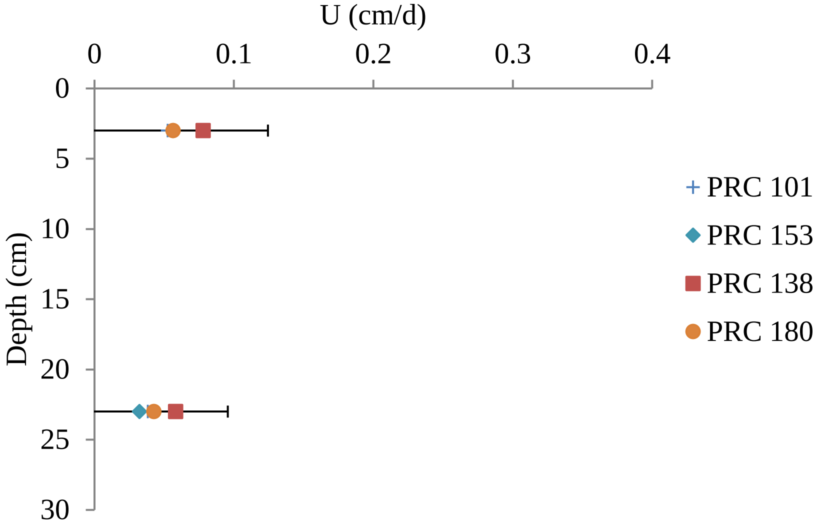


Figure 5-9. Groundwater velocity estimates for Columbia Slough (CS)

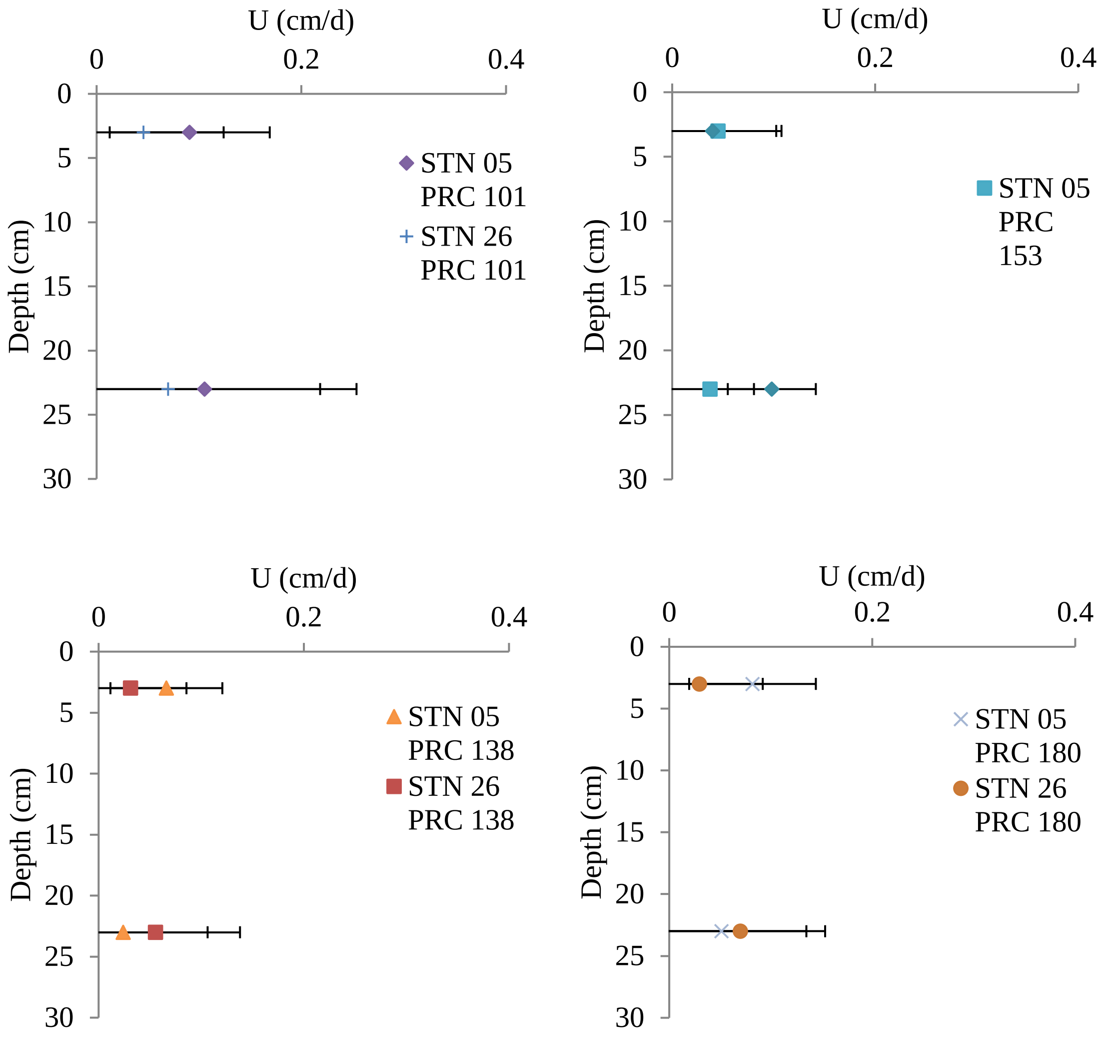


Figure 5-10. Groundwater velocity estimates by PRCs at different sites at Hunter’s Point (HP)

5.6.4 Porewater Concentrations Determined by SPME PDMS

The porewater concentrations for PCB congeners determined by SPME PDMS sorbent concentrations and the fraction steady state. In total, 111 PCB congeners were detected by instrument and the total PCB concentrations at Hunter’s Point and 70 PCB congeners were detected at Columbia Slough.

For Hunter’s Point, the average concentrations in lower layer (21-26cm) was 2.76 ng/L, higher than upper layer (1-6cm) concentration of 2.18 ng/L. In general, the concentrations measured at Hunter's Point sites did not present significant trend except site 1 and site 3. Therefore, the following analysis were use the average data among these sites. The relative high concentrations at site 1 and site 3 might be that they are close to the shore and were affected more by the contamination.

For Columbia Slough, the average concentrations in lower layer (12.5-27cm) was 5.06 ng/L, higher than upper layer (1-12.5cm) concentration of 6.03 ng/L. The concentration differences among sites at Columbia Slough are higher than at Hunter's Point. The relative high concentrations at site 18 to 20 might be that they are close to the contaminants source.

5.6.5 Estimating Contaminant Upwelling Flux

The vertical contaminant flux ($F_{a/d}$) includes both advective and diffusive ones and can be estimated by Eq. 5-24:

$$F = -(D_{eff}\nabla c + \boldsymbol{CU}) \qquad \text{Eq. 5-24}$$

where the first term represents for the diffusive flux (F_d) and the second term represents for advective flux (F_a).

The parameters needed in Eq. 5-24 has been determined by PDMS passive samplers and the estimated fluxes at z-direction for both Hunter's Point Navy Shipyard and Columbia Slough are shown in Table 5-8. The results show that the advective flux is dominant.

Table 5-8. Estimated Flux at z-direction for Hunter's Point Navy Shipyard (HPNS) and Columbia Slough (CS)

F (ng/cm^2/yr)	F_a	F_d	$F_a/F_{a/d}$
HPNS top layer	0.034	0.003	92%
HPNS depth layer	0.064	0.003	95%
CS top layer	0.10	0.017	85%
CS depth layer	0.071	0.017	81%

5.7 DISCUSSION

The method developed provides an estimate of groundwater upwelling velocity but we have no independent estimates to evaluate the validity of the results. At the very least, however, the method allows the relative transport or mixing rates to be compared at different locations. The method also cannot indicate flow direction, that is it does not differentiate between upwelling or downwelling. Tidal velocities are presumably represented by the average magnitude of flow.

Based on the definition of Pe number (Eq. 5-5), Sh number and their relationship (Eq. 5-10), the groundwater velocity can be expressed as a function of effective diffusivity:

$$U_Z = \frac{z}{D_{eff}}\left(\frac{k}{0.564}\right)^2 \qquad \text{Eq. 5-26}$$

When the dispersion model is considered, the estimated velocity would decrease with increase diffusivities.

One important assumption of this method is the boundary layer approximation. The concentration boundary layer region should be slender and the thickness of the layer **δ**, must be much smaller than the length z: $\delta \ll z$. Another critical assumption is that on the z direction, advection is the dominant fluid transport, which indicate that when the groundwater upwelling velocity is very low, say tend to be zero velocity, this method may be not applicable.

The uncertainty of this approach contains two parts: errors in experimental measurement and theoretical estimation of parameters like the partitioning coefficients K_{oc} and K_{fiber}. The uncertainty in estimated mass transfer coefficient was estimated to be 10% to 20% for specific sites based upon variability between sites. The uncertainty in partitioning coefficients, however, might be as much as factor of 2-3 dwarfing this estimated uncertainty, At this point, the estimated velocity should be considered an order of magnitude estimate.

5.8 CONCLUSIONS& IMPLICATIONS

The contaminant flux is an important endpoint to estimate the contaminant fate and transport, and is of great research valued in the design and assessment of contaminated sediment sites remediation.

This work shows the ability, in principle, to determine the ground water upwelling velocity and contaminant flux through the use of the rate of equilibration of performance reference compounds. Sherwood number can be estimated via passive sampling and used to estimate effective Peclet number or velocity. The model is developed for planar passive samplers like POM and PE sheets, but for PDMS samplers with a thin coat, when a compound has character diffusion length smaller or the scale as the fiber outer radius, the model can also be used as a close approximation. This method has advantages includes effective, convenient, and can obtain low groundwater rates. Future works should be to apply the method to other field work systems with higher velocity to verify the ability and accuracy of the method. An *Ex situ* experiment with several set porewater velocities could also be conducted to verify the methods accuracy.

5.8 REFERENCES

1. Liu, H.-H. *et al.* Novel Passive Sampling Device for Measuring Sediment–Water Diffusion Fluxes of Hydrophobic Organic Chemicals. *Environ. Sci. Technol.* **47,** 9866–9873 (2013).

2. Murphy Paul, Marquette Andre, Reible Danny & Lowry Gregory V. Predicting the Performance of Activated Carbon-, Coke-, and Soil-Amended Thin Layer Sediment Caps. *J. Environ. Eng.* **132,** 787–794 (2006).

3. Huckins, J. N., Tubergen, M. W. & Manuweera, G. K. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20,** 533–552 (1990).

4. Huckins, J. N., Booij, K. & Petty, J. D. Introduction to Passive Sampling. in *Monitors of Organic Chemicals in the Environment* 1–28 (Springer, Boston, MA, 2006).

5. Mayer, P. *et al.* Sensing Dissolved Sediment Porewater Concentrations of Persistent and Bioaccumulative Pollutants Using Disposable Solid-Phase Microextraction Fibers. *Environ. Sci. Technol.* **34,** 5177–5183 (2000).

6. Allan, I. J., Harman, C., Ranneklev, S. B., Thomas, K. V. & Grung, M. Passive sampling for target and nontarget analyses of moderately polar and nonpolar substances in water. *Environ. Toxicol. Chem.* **32,** 1718–1726

7. Cornelissen, G., Pettersen, A., Broman, D., Mayer, P. & Breedveld, G. D. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environ. Toxicol. Chem.* **27,** 499–508 (2008).

8. Lu, X., Reible, D. D., Fleeger, J. W. & Chai, Y. Bioavailability of desorption-resistant phenanthrene to the oligochaete Ilyodrilus templetoni. *Environ. Toxicol. Chem.* **22,** 153–160 (2003).

9. Lampert, D. J., Thomas, C. & Reible, D. D. Internal and external transport significance for predicting contaminant uptake rates in passive samplers. *Chemosphere* **119,** 910–916 (2015).

10. Schwarzenbach R P, Gschwend P M, Imboden D M. Organic liquid–water partitioning. Environmental Organic Chemistry. Wiley, Hoboken, New Jersey, 2003: 213-244.

11. Schwarzenbach, R. P. General Introduction and Sorption Processes Involving Organic Matter. *Environ. Org. Chem.* 275–330 (2003).

12. Huckins, J. N., Manuweera, G. K., Petty, J. D., Mackay, D. & Lebo, J. A. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27,** 2489–2496 (1993).

13. Huckins, J. N. *et al.* Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. *Environ. Sci. Technol.* **36,** 85–91 (2002).

14. Shen, X. Developing models for the assessment and the design of the in situ remediation of contaminated sediments. (2017).

15. Choy, B. & Reible, D. D. *Diffusion Models of Environmental Transport*. (CRC Press, 2000).

16. Bejan, A. & Poulikakos, D. The nondarcy regime for vertical boundary layer natural convection in a porous medium. *Int. J. Heat Mass Transf.* **27,** 717–722 (1984).

17. Ping, C. Combined free and forced convection flow about inclined surfaces in porous media. *Int. J. Heat Mass Transf.* **20,** 807–814 (1977).

18. Hansen, B. G., Paya-Perez, A. B., Rahman, M., & Larsen, B. R. QSARs for Kow and Koc of PCB congeners: a critical examination of data, assumptions and statistical approaches. *Chemosphere*, **39**(13), 2209-2228 (1999).

19. Ghosh, U. *et al.* Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integr. Environ. Assess. Manag.* **10,** 210–223 (2014).

20. Millington, R. J. & Quirk, J. P. Permeability of porous solids. *Trans. Faraday Soc.* **57,** 1200–1207 (1961).

21. Transport phenomena, R. B. Bird, W. E. Stewart, and E. N. Lightfoot, John Wiley and Sons, Inc., New York (1960). 780 pages. $11.50. *AIChE J.* **7,** 5J–6J (1961).

22. Wakao, N. & Funazkri, T. Effect of fluid dispersion coefficients on particle-to-fluid mass transfer coefficients in packed beds: Correlation of sherwood numbers. *Chem. Eng. Sci.* **33,** 1375–1384 (1978).

23. Mackay, D., Shiu, W.-Y., Ma, K.-C. & Lee, S. C. *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Second Edition*. (CRC Press, 2006).

Chapter 6

Summary and Conclusions

6.1 RESEARCH OBJECTIVES

The research presented in this dissertation demonstrated the ability of passive sampling techniques to obtain freely dissolved hydrophobic organic compounds (HOCs) in aquatic environment and expanded the applications of passive sampling methods.

This dissertation had the following:

1. To demonstrate the ability of *in situ* passive sampling method to monitor HOCs contaminants fate and transport and its advantages over conventional technologies, specifically in terms of spatial resolutions;
2. To demonstrate the SPME PDMS practical application in evaluating the effectiveness of sediment remediation using sorbent addition by monitoring the freely dissolved sediment porewater concentrations;
3. To demonstrate the potential of passive sampler for site characterization by identifying hot spots based upon a geospatial analysis and to estimate transport rates including groundwater upwelling rates using performance reference compounds.

The objectives were through laboratory work and modeling and with field demonstrations at HOCs contaminated sediment sites Hunter’s Point (San Francisco, CA) and Columbia Slough (Portland, OR).

6.2 RESEARCH CONCLUSIONS

The results from the field deployment at Hunter’s Point Navy Shipyard (San Francisco, CA) and Columbia Slough (Portland, OR) show that the passive sampling method can be a viable technology to show the vertical profile changes of porewater concentrations of HOCs like PCBs and illustrate that the porewater may be less variable than corresponding solid concentrations. The spatial autocorrelations show that the variability in measured porewater concentrations are typically smaller than that in bulk sediment concentrations. Porewater can be regarded as an integrative medium and the sample grid resolution required to characterize porewater concentrations at a site may be coarser than that required for bulk solids. The variability in surficial porewater concentrations at the sites studied was relatively small due to dominant influence of sediment-surface water exchange. Evaluation of spatial variability in porewater concentrations also allowed the identification of hot-spots with uncharacteristic variability compared to the remainder of the site.

The pilot study at Hunter’s Point Navy Shipyard (San Francisco, CA) showed that the passive sampling methods can be a viable technology to monitor the performance of activated carbon placed for *in situ* sediment remediation. The freely dissolved porewater concentration profiles indicate that both activated carbon materials employed at the site, AquaGate+PAC and Sedimite, significantly reduced PCB porewater concentrations. Significant reductions were observed in the first 8 months amendment and were maintained throughout 26 months after AC materials placement. In addition, the low molecular weight PCB homologs obtained larger concentration reductions than the higher molecular weight homologs due to the more rapid uptake of these congeners on the AC. This work also demonstrates that passive sampling has the ability to measure vertical profile changes in porewater concentrations. Even though the AC materials were placed at the sediment surface, smaller but significant concentration reduction were also noted at deeper intervals up to 26cm.

The contaminant flux is an important indicator of contaminant fate and transport and the potential effects of contaminated sediment on the overlying water. This work showed the ability to determine the ground water upwelling velocity and contaminant flux by passive sampling approaches. The site-specific parameters like Sh and Pe numbers can also be estimated by passive sampling using performance reference compounds (PRCs) as an indicator of the rate of transport in the sediments. An analytical model is used to predict interstitial mixing and transport parameters by analyzing the PRCs release. The method is applied to two polychlorinated biphenyls (PCBs) contaminated sediments site, Hunter's Point Naval Shipyard (San Francisco, California) and Columbia Slough (Portland, Oregon) to show the ability of the SPME PDMS passive sampling technique to measure flux from sediment to water column. This method has advantages includes effective, convenient, and can obtain low groundwater rates.

6.3 RECOMMENDATIONS FOR FUTURE WORK

With lack of a long documented history, passive sampling technologies remains a relatively new technology. Therefore, there are still many outstanding issues to address to achieve better regulatory acceptance. Some potential future topics for this research could include:

- *Exploring certainty in achievement of equilibrium and passive sampler uptake kinetics*—the achievement of equilibrium is one of the basis of passive sampling technologies and the uncertainty is a major challenge for passive sampling. More comprehensive research on mass transfer model and uptake kinetics on passive samplers are necessary for regulatory acceptance of passive sampling. For example, the mass transfer process is assumed to have linear sorption on passive sampler. But with activated carbon placement, the PRC releases may be nonlinear for amended systems.

- *Expanding list of target compounds*—Passive sampling methods are most commonly used for hydrophobic organic compounds, especially polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The application on some emerging pollutant, like polybrominated diphenyl ethers and perfluorinated compounds could be explored.
- *Demonstrate the representativeness of porewater concentrations*— The results herein have shown that porewater is an integrative media that shows less variability than bulk solids concentrations. This result needs to be tested at other sites and the implications understood.
- *Evaluation of the transport characteristics model under experimental or field applications*—The groundwater upwelling model developed in this dissertation needs to be verified by experimental results either in the laboratory in the field. At this time, the approach can best be described as a relative indicator of transport and mixing with uncertain quantitative accuracy. And the spatial semivariogram model needs to be supported by additional field deployments with large spatial scale and more sampling points over a range of distances.

Appendices

APPENDIX A: POLYCHLORINATED BIPHENYLS (PCBS) UPTAKE KINETIC STUDY ON POLYDIMETHYLSILOXANE (PDMS)

To determine the loading time needed for the PRCs to be absorbed on the polydimethylsiloxane (PDMS) fibers, a laboratory experimental was conducted by using 7 C^{13} labeled PCB congeners (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180 and PCB 209). The PDMS fibers with a diameter of 558/486 µm. Figure A-1 shows the changes of PDMS fiber concentrations in 6 weeks. The results show that 4 weeks is a proper loading time for PRCs compounds absorb to PDMS fibers before field deployment.

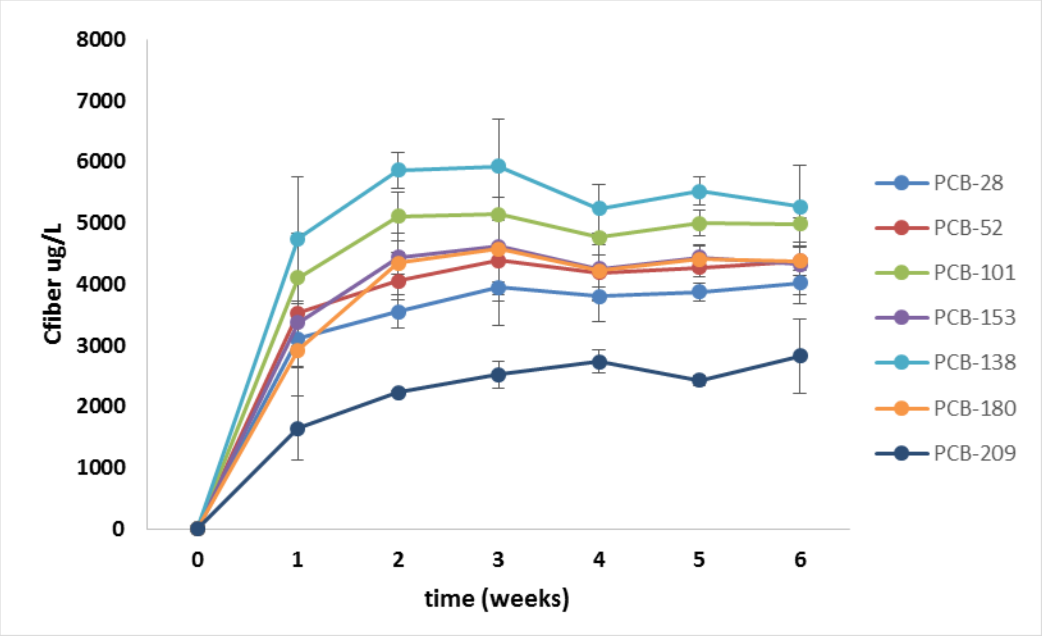


Figure A-1. Polychlorinated biphenyls (PCBs) uptake kinetic study on polydimethylsiloxane (PDMS)

APPENDIX B: POLYCHLORINATED BIPHENYLS (PCBS) CALIBRATION STANDARD LIST

Table B-1. Polychlorinated Biphenyls (PCBs) calibration standard—PCB MIX 1

Analyte	CAS-Number	Analyte	CAS-Number
2-Chlorobiphenyl	2051-60-7	2,2',3,3',4-Pentachlorobiphenyl	52663-62-4
3-Chlorobiphenyl	2051-61-8	2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8
4-Chlorobiphenyl	2051-62-9	2,2',4,4',5-Pentachlorobiphenyl	38380-01-7
2,2'-Dichlorobiphenyl	13029-08-8	2,3,3',4',6-Pentachlorobiphenyl	38380-03-9
2,3'-Dichlorobiphenyl	25569-80-6	2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2
2,4'-Dichlorobiphenyl	34883-43-7	2,2',3,4',5,5'-Hexachlorobiphenyl	51908-16-8
2,5-Dichlorobiphenyl	34883-39-1	2,2',3,4',5,6-Hexachlorobiphenyl	68194-13-8
2,2',3-Trichlorobiphenyl	38444-78-9	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1
2,2',5-Trichlorobiphenyl	37680-65-2	2,2',3,3',4,5,6-Heptachlorobiphenyl	68194-16-1
2,2',6-Trichlorobiphenyl	38444-73-4	2,2',3,3',4,5,6'-Heptachlorobiphenyl	38411-25-5
2,3,4'-Trichlorobiphenyl	38444-85-8	2,2',3,3',4',5,6-Heptachlorobiphenyl	52663-70-4
2,3',4-Trichlorobiphenyl	55712-37-3	2,2',3,3',5,6,6'-Heptachlorobiphenyl	52663-64-6
2,4,4'-Trichlorobiphenyl	7012-37-5	2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	35694-08-7
2,3,3',4'-Tetrachlorobiphenyl	41464-43-1	2,2',3,3',4,4',5,6-Octachlorobiphenyl	52663-78-2
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	52663-75-9
2,3',4,5-Tetrachlorobiphenyl	73575-53-8	2,2',3,4,4',5,5',6-Octachlorobiphenyl	52663-76-0
2,3',4',6-Tetrachlorobiphenyl	41464-46-4	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9
2,4,4',5-Tetrachlorobiphenyl	32690-93-0		

Table B-2. Polychlorinated Biphenyls (PCBs) calibration standard—PCB MIX 2

Analyte	CAS-Number	Analyte	CAS-Number
2,3-Dichlorobiphenyl	16605-91-7	2,2',4,5',6-Pentachlorobiphenyl	60145-21-3
2,4-Dichlorobiphenyl	33284-50-3	2,3,3',4',5-Pentachlorobiphenyl	70424-68-9
2,6-Dichlorobiphenyl	33146-45-1	2,3,4,4',6-Pentachlorobiphenyl	74472-38-1
2,2',4-Trichlorobiphenyl	37680-66-3	2,2',3,3',4,6-Hexachlorobiphenyl	61798-70-7
2,3,6-Trichlorobiphenyl	55702-45-9	2,2',3,3',4,6'-Hexachlorobiphenyl	38380-05-1
2,3',5-Trichlorobiphenyl	38444-81-4	2,2',3,3',5,6'-Hexachlorobiphenyl	52744-13-5
2,4',5-Trichlorobiphenyl	16606-02-3	2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6
2,4',6-Trichlorobiphenyl	38444-77-8	2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0
3,4,4'-Trichlorobiphenyl	38444-90-5	2,3,3',4',5',6-Hexachlorobiphenyl	74472-45-0
2,2',3,4-Tetrachlorobiphenyl	52663-59-9	2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6
2,2',3,6-Tetrachlorobiphenyl	70362-45-7	2,2',3,3',4,4',6-Heptachlorobiphenyl	52663-71-5
2,2',3,6'-Tetrachlorobiphenyl	41464-47-5	2,2',3,3',4,5,5'-Heptachlorobiphenyl	52663-74-8
2,2',4,5-Tetrachlorobiphenyl	70362-47-9	2,2',3,3',5,5',6-Heptachlorobiphenyl	52663-67-9
2,3,4,4'-Tetrachlorobiphenyl	33025-41-1	2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1
2,3',4',5-Tetrachlorobiphenyl	32598-11-1	2,3,3',4',5,5',6-Heptachlorobiphenyl	69782-91-8
2,2',3,3',5-Pentachlorobiphenyl	60145-20-2	2,2',3,3',4,4',5,6'-Octachlorobiphenyl	42740-50-1
2,2',3,3',6-Pentachlorobiphenyl	52663-60-2	2,2',3,3',4,4',6,6'-Octachlorobiphenyl	33091-17-7
2,2',3,5',6-Pentachlorobiphenyl	38379-99-6	2,3,3',4,4',5,5',6-Octachlorobiphenyl	74472-53-0

Table B-3. Polychlorinated Biphenyls (PCBs) calibration standard—PCB MIX 3

Analyte	CAS-Number
2,2',5-Trichlorobiphenyl	37680-65-2
2,4,4'-Trichlorobiphenyl	7012-37-5
2,4',5-Trichlorobiphenyl	16606-02-3
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2
2,3',4,4',5-Pentachlorobiphenyl	31508-00-6
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2
2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6
2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	35694-08-7
Decachlorobiphenyl	2051-24-3

APPENDIX C: INDIVIDUAL IDENTIFIED CONGENERS AT PQL OF 0.2 μG/L - METHOD 1668C (GC-HRMS)

	PCB congener no	Retention time [min]		PCB congener no	Retention time [min]		
chloro	1	14.757	hexachloro	151	30.213		Mode:splitless
chloro	2	16.108	hexachloro	135	30.389		inlet temp=280 C
chloro	3	16.262	hexachloro	144	30.433		injection vol= 1 uL
dichloro	10	17.096	pentachloro	107	30.574		flow=1.2 ml/min
dichloro	4	17.098	hexachloro	147	30.58		oven temp=80 C
dichloro	9	18.059	hexachloro	149	30.73		column length = 60 m
dichloro	7	18.076	pentachloro	118	30.814		run time = 56.5 min
dichloro	6	18.515	hexachloro	134	31.25		
dichloro	8	18.765	hexachloro	131	31.43		
dichloro	5	18.808	hexachloro	146	31.531		
trichloro	19	19.648	hexachloro	153	31.795		
trichloro	18	20.561	hexachloro	132	31.969		
trichloro	17	20.653	pentachloro	105	32.034		
dichloro	15	20.68	hexachloro	141	32.369		
trichloro	27	21.025	heptachloro	179	32.503		
trichloro	24	21.042	hexachloro	164	33.003		
trichloro	32	21.38	hexachloro	138	33.059		
trichloro	16	21.413	hexachloro	158	33.181		
trichloro	23	21.756	heptachloro	178	33.41		
trichloro	29	21.966	heptachloro	175	33.785		
trichloro	26	22.129	heptachloro	183	34.003		
trichloro	25	22.274	hexachloro	128	34.302		
trichloro	31	22.504	heptachloro	185	34.834		
trichloro	28	22.593	heptachloro	174	35.084		
trichloro	20	23.037	heptachloro	171	35.273		
trichloro	22	23.372	hexachloro	157	35.566		
tetrachloro	45	23.602	heptachloro	173	35.573		
tetrachloro	46	23.957	heptachloro	172	35.722		
tetrachloro	69	24.033	octachloro	197	35.883		
tetrachloro	52	24.092	heptachloro	180	36.014		
tetrachloro	47	24.436	heptachloro	193	36.124		
tetrachloro	48	24.482	heptachloro	191	36.328		
tetrachloro	44	25.048	heptachloro	170	37.312		
trichloro	37	25.203	heptachloro	190	37.386		
tetrachloro	42	25.218	octachloro	201	37.683		
tetrachloro	71	25.541	octachloro	203	37.905		
tetrachloro	41	25.616	octachloro	196	37.924		
pentachloro	105	25.93	nonachloro	208	39.163		
tetrachloro	40	25.997	octachloro	195	39.23		
tetrachloro	67	26.197	nonachloro	207	39.504		
tetrachloro	74	26.627	octachloro	194	40.041		
tetrachloro	70	26.768	octachloro	205	40.283		
tetrachloro	66	26.963	nonachloro	206	41.792		
pentachloro	95	26.985	decachloro	209	43.385		
pentachloro	93	27.021					
tetrachloro	56	27.732		Additional Congeners			
pentachloro	92	27.741		77	TBD		
tetrachloro	60	27.749		81	TBD		
pentachloro	84	27.97		105	TBD		
pentachloro	101	27.997		114	TBD		
pentachloro	99	28.245		118	TBD		
pentachloro	119	28.544		123	TBD		
pentachloro	83	28.746		126	TBD		
pentachloro	115	29.221		156	TBD		
pentachloro	87	29.264		157	TBD		
hexachloro	136	29.577		167	TBD		
pentachloro	110	29.666		169	TBD		
pentachloro	82	30.209		189	TBD		

APPENDIX D: TOTAL ORGANIC CARBON (TOC) PROFILES IN HUNTER'S POINT NAVY SHIPYARD AFTER ACTIVATED CARBON (AC) TREATMENT

Table D-1. Summary of measured TOC (%) in AC treated plots in Hunter's Point Navy Shipyard

baseline TOC=1.4%, p=postamendment, b=baseline

	Site Number	**Baseline**	**Postamendment**			**% AC (TOC%p-TOC%b)**		
			8months	**14months**	**26months**	**8 months**	**14 months**	**26months**
AquaGate+PAC	**#1**	NA	10.89	3.82	2.43	9.47	2.40	1.01
	#3	NA	5.84	4.42	2.79	4.42	3.01	1.37
	#5	NA	16.18	8.08	8.78	14.76	6.67	7.36
	#7	NA	4.57	4.71	5.51	3.15	3.30	4.09
	#9	NA	18.96	3.47	7.51	17.54	2.05	6.10
	#12	NA	21.17	20.47	9.79	19.75	19.05	8.37
	#15	NA	4.55	7.93	1.54	3.13	6.52	0.13
	average	NA	**11.74**	**7.56**	**5.48**	**10.32**	**6.14**	**4.06**
	stdev	NA	**7.06**	**6.00**	**3.31**	**7.06**	**6.00**	**3.31**
Buffer Zone	**#17**	1.45	17.80	7.98	1.33	16.38	6.57	-0.09
	#19	1.51	2.59	1.60	1.58	1.17	0.18	0.17
	#21		1.88	2.41	1.39	0.46	1.00	-0.02
	#22	1.58	2.36	2.03	1.96	0.95	0.61	0.54
	#24	1.35	3.00	1.69	1.51	1.58	0.27	0.09
	#26		2.63	5.90	1.34	1.22	4.48	-0.08
	average	**1.47**	**5.04**	**3.60**	**1.52**	**3.63**	**2.18**	**0.10**
	stdev	**0.10**	**6.26**	**2.68**	**0.24**	**6.26**	**2.68**	**0.24**
Sedimite	**#28**	1.43	7.27	6.09	3.54	5.86	4.68	2.12
	#30	1.37	10.15	3.16	2.51	8.74	1.74	1.10
	#33	1.45	18.09	5.50	5.28	16.67	4.08	3.87
	#36	1.44	7.83	5.52	3.31	6.41	4.10	1.89
	#38	1.40	30.64	3.24	3.80	29.22	1.82	2.39
	#40	1.32	5.91	7.95	3.02	4.49	6.53	1.61
	#42	1.29	17.18	5.65	6.45	15.77	4.24	5.03
	average	**1.39**	**13.87**	**5.30**	**3.99**	**12.45**	**3.88**	**2.57**
	stdev	**0.06**	**8.82**	**1.67**	**1.39**	**8.82**	**1.67**	**1.39**
	overall average	**1.42**	**12.80**	**6.43**	**4.73**	**9.06**	**4.16**	**2.35**
Reference site	**#43**	NA	NA	NA	1.65	NA	NA	NA
	#45	NA	1.56	2.26	1.79	0.14	0.84	0.37
	#48	NA	1.41	1.53	1.69	-0.01	0.11	0.28
	average	NA	**1.49**	**1.89**	**1.71**	**0.07**	**0.48**	**0.32**
	stdev	NA	**0.11**	**0.52**	**0.07**	**0.11**	**0.52**	**0.07**

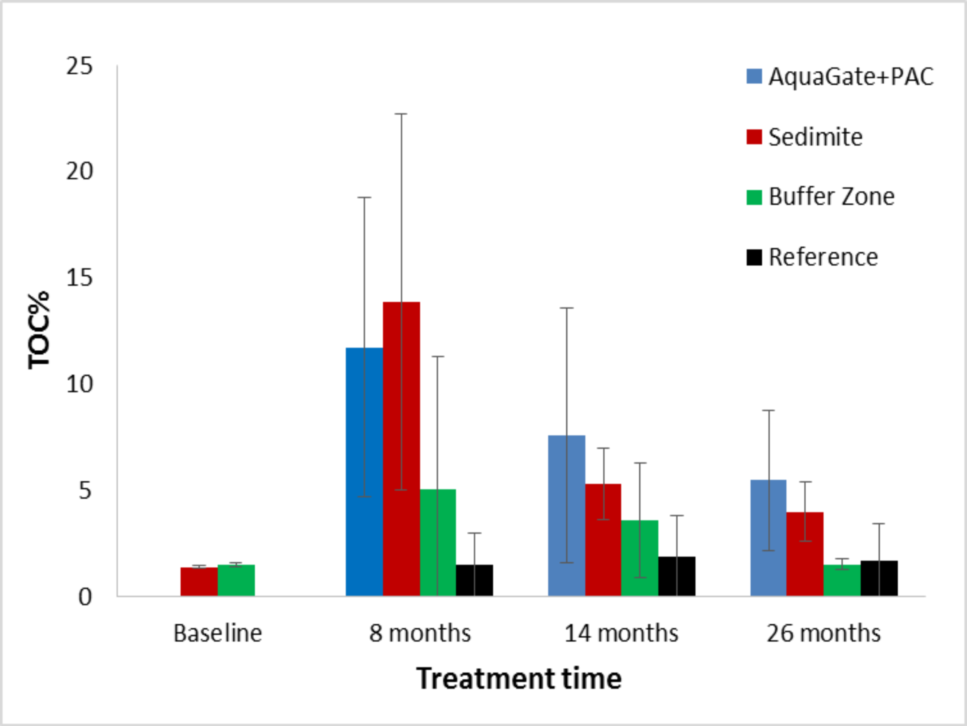


Figure D-1. Detected TOC% in Hunter's Point Navy Shipyard sediment with comparison to different treatment time and the baseline results

APPENDIX E: POREWATER CONCENTRATION PROFILES IN HUNTER'S POINT NAVY SHIPYARD AFTER ACTIVATED CARBON (AC) TREATMENT

Some supporting information about the porewater concentration changes with Activated Carbon placement at Hunter's Point Navy Shipyard are summarized. The sum concentration (ng/L) of all detected PCB congeners at four different depth (1-6 cm, 6-11 cm, 11-16 cm and 21-16 cm) at each sampling location are shown in Table E-1. The measured percent reductions in the 26 months, 14 months and 8 months post-placement sampling event are summarized in Table G-2.

Figure E-1 shows the measured porewater concentrations of individual PCB congeners at three different depth in baseline study. A comparison of each PCB congener porewater concentration determined at different activated carbon treatment time and baseline study at Aquagate+PAC plot and Sedimite plot is shown in Figure E-2 and Figure E-3, respectively. Figure G-4 shows the averaged 26 months post amendment PCB porewater concentration at AquaGate+PAC Plot and Sedimite plot, and their comparison with baseline results.

Table E-1. Summary of measured porewater concentrations (sum of identified congeners in ng/L) in Hunter's Point Navy Shipyard

		Baseline				**Post amendment 8 months**					**Post amendment 14 months**					**Post amendment 26 months**				
						depth	depth	depth	depth		depth	depth	depth	depth		depth	depth	depth	depth	
		1-6cm	**11-16cm**	**21-26cm**	**average**	**1-6cm**	**6-11cm**	**11-16cm**	**21-26 cm**	**average**	**1-6cm**	**6-11cm**	**11-16cm**	**21-26 cm**	**average**	**1-6cm**	**6-11cm**	**11-16cm**	**21-26 cm**	**average**
	SUM PCB	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
AquaGate+PAC	STN 1	2.36	2.25	4.76	3.12	0.73	1.03	1.08	0.61	0.89	0.06	0.24	0.40	0.54	0.31	0.16	0.41	0.56	1.07	0.57
	STN 3	2.22	1.92	4.04	2.72	0.25	0.33	0.45	0.78	0.51	0.41	0.68	0.76	0.53	0.60	0.36	0.36	0.31	0.62	0.43
	STN 5	1.92	2.52	2.61	2.35	0.45	0.59	0.52	0.65	0.59	0.28	0.98	0.56	0.00	0.45	0.34	0.24	0.30	0.37	0.32
	STN 7	2.57	2.46	3.11	2.71	0.33	0.38	0.49	0.47	0.45	0.12	0.37	0.41	1.20	0.52	0.26	0.14	0.35	0.47	0.31
	STN 9	2.57	2.81	2.73	2.70	0.11	0.16	0.36	0.63	0.38	0.22	0.44	0.43	0.21	0.32	0.22	0.40	0.46	0.70	0.45
	STN 12	2.06	2.47	2.39	2.30	0.10	0.10	0.13	0.09	0.12	0.34	0.57	0.61	0.74	0.57	0.18	0.22	0.26	0.36	0.26
	STN 15	2.13	2.37	2.89	2.46	0.14	0.18	0.20	0.32	0.25	0.20	0.39	0.48	0.20	0.32	0.19	0.21	0.28	0.37	0.27
	Average	**2.26**	**2.40**	**3.22**	**2.63**	**0.30**	**0.40**	**0.46**	**0.51**	**0.46**	**0.23**	**0.53**	**0.52**	**0.49**	**0.44**	**0.24**	**0.28**	**0.36**	**0.56**	**0.37**
	Stdev	**0.25**	**0.27**	**0.86**	**0.28**	**0.23**	**0.33**	**0.31**	**0.23**	**0.25**	**0.12**	**0.25**	**0.13**	**0.40**	**0.12**	**0.08**	**0.11**	**0.11**	**0.26**	**0.11**
Buffer zone	STN 17	2.28	2.41	2.95	2.55	0.31	0.38	0.57	0.77	0.59	0.84	1.14	1.09	0.76	0.96	0.47	0.51	0.56	0.91	0.61
	STN 19	2.22	2.28	2.44	2.32	0.91	0.96	1.16	0.67	0.96	0.50	0.48	0.88	0.94	0.70	0.31	0.30	0.43	0.56	0.40
	STN 21	2.28	2.21	2.56	2.35	0.67	0.94	1.46	2.67	1.48	ND	ND	1.61	1.62	0.84	0.35	0.33	0.45	0.62	0.44
	STN 22	2.27	2.60	2.68	2.52	0.54	0.91	1.11	1.18	0.98	0.32	0.52	0.52	1.48	0.71	0.56	0.69	0.75	1.05	0.76
	STN 24	1.91	2.01	2.19	2.04	0.94	0.94	1.13	1.53	1.17	0.36	0.44	1.26	1.08	0.79	0.43	0.45	0.42	0.57	0.47
	STN 26	1.87	2.32	2.52	2.24	0.60	0.89	0.97	2.36	1.29	0.76	0.61	1.08	1.04	0.87	0.32	0.42	0.48	1.05	0.57
	Average	**2.14**	**2.31**	**2.56**	**2.33**	**0.66**	**0.83**	**1.07**	**1.53**	**1.08**	**0.56**	**0.64**	**1.08**	**1.15**	**0.81**	**0.41**	**0.45**	**0.51**	**0.79**	**0.54**
	Stdev	**0.20**	**0.20**	**0.25**	**0.19**	**0.24**	**0.22**	**0.29**	**0.83**	**0.31**	**0.23**	**0.29**	**0.36**	**0.33**	**0.10**	**0.10**	**0.14**	**0.13**	**0.24**	**0.13**
Sedimite	STN 28	2.18	1.94	2.50	2.21	0.50	0.76	1.16	1.60	1.07	0.32	0.67	0.54	0.65	0.55	0.37	0.32	0.32	0.34	0.34
	STN 30	1.98	2.29	2.80	2.36	0.73	0.47	0.66	1.05	0.79	0.45	0.60	0.65	0.24	0.48	0.24	0.30	0.55	0.84	0.50
	STN 33	2.17	2.30	2.75	2.41	0.24	0.19	0.32	0.71	0.48	0.15	0.38	0.46	0.52	0.38	0.14	0.20	0.29	0.30	0.24
	STN 36	2.07	2.37	2.12	2.19	0.31	0.51	0.67	0.49	0.53	0.24	0.46	0.47	0.43	0.40	0.20	0.23	0.22	0.29	0.24
	STN 38	2.23	2.51	2.39	2.37	0.29	0.49	0.72	0.99	0.69	0.35	0.64	0.60	0.35	0.49	0.10	0.17	0.15	0.28	0.18
	STN 40	2.20	2.15	2.33	2.23	0.26	0.27	0.31	0.28	0.31	0.17	0.20	0.43	0.49	0.32	0.14	0.21	0.23	0.35	0.24
	STN 42	2.13	2.30	2.42	2.29	0.64	0.84	0.90	0.47	0.73	0.27	0.50	0.70	1.73	0.80	0.13	0.19	0.21	0.37	0.23
	Average	**2.14**	**2.27**	**2.47**	**2.29**	**0.42**	**0.51**	**0.68**	**0.80**	**0.66**	**0.28**	**0.49**	**0.55**	**0.63**	**0.49**	**0.19**	**0.23**	**0.28**	**0.40**	**0.28**
	Stdev	**0.09**	**0.18**	**0.24**	**0.09**	**0.20**	**0.24**	**0.30**	**0.45**	**0.25**	**0.10**	**0.17**	**0.10**	**0.50**	**0.16**	**0.09**	**0.06**	**0.13**	**0.20**	**0.11**
Overall sites	**Average**	**2.18**	**2.32**	**2.76**	**2.42**	**0.45**	**0.57**	**0.72**	**0.92**	**0.71**	**0.33**	**0.54**	**0.70**	**0.74**	**0.57**	**0.27**	**0.32**	**0.38**	**0.57**	**0.39**
	Stdev	**0.19**	**0.22**	**0.62**	**0.25**	**0.26**	**0.31**	**0.38**	**0.67**	**0.36**	**0.20**	**0.23**	**0.33**	**0.49**	**0.21**	**0.13**	**0.14**	**0.15**	**0.28**	**0.15**
Reference site	**Ref Sites**					**1.67**	**1.23**	**1.52**	**1.49**	**1.44**	**1.26**	**1.27**	**1.33**	**1.63**	**1.38**	**1.10**	**1.39**	**1.36**	**1.84**	**1.42**

Table E-2. Summary of measured porewater concentration reductions (%) in Hunter's Point Navy Shipyard

	Reduction%	**Post amendment 8 months**				**Post amendment 14 months**				**Post amendment 26 months**			
		depth	depth	depth	depth	depth	depth	depth	depth	depth	depth	depth	depth
		1-6cm	**11-16cm**	**21-26 cm**	**average**	**1-6cm**	**11-16cm**	**21-26 cm**	**average**	**1-6cm**	**11-16cm**	**21-26 cm**	**average**
	SUM PCB				ng/L				ng/L				ng/L
AquaGate+PAC	STN 1	69.3	51.7	87.1	69.4	97.4	82.3	88.7	89.5	93.2	75.0	77.5	81.9
	STN 3	88.7	76.6	80.7	82.0	81.5	60.2	86.9	76.2	83.8	83.7	84.6	84.0
	STN 5	76.7	79.2	75.1	77.0	85.4	77.8	100.0	87.7	82.5	88.1	85.9	85.5
	STN 7	87.0	80.3	84.8	84.1	95.4	83.4	61.2	80.0	90.0	85.6	84.8	86.8
	STN 9	95.5	87.4	77.0	86.6	91.5	84.8	92.2	89.5	91.6	83.7	74.5	83.3
	STN 12	95.1	94.8	96.0	95.3	83.3	75.2	69.1	75.9	91.3	89.5	85.0	88.6
	STN 15	93.2	91.5	88.9	91.2	90.4	79.8	92.9	87.7	91.0	88.0	87.1	88.7
	Average	**86.5**	**80.2**	**84.2**	**83.7**	**89.3**	**77.7**	**84.4**	**83.8**	**89.1**	**84.8**	**82.8**	**85.6**
	Stdev	**10.0**	**14.2**	**7.3**	**8.7**	**6.1**	**8.4**	**14.0**	**6.2**	**4.1**	**4.9**	**4.8**	**2.6**
Buffer zone	STN 17	86.6	76.2	74.1	78.9	63.0	54.6	74.2	64.0	79.5	76.9	69.2	75.2
	STN 19	59.0	48.9	72.5	60.1	77.5	61.2	61.6	66.7	86.1	81.1	77.1	81.5
	STN 21	70.4	34.2	-4.1	33.5	ND	27.2	36.6	31.9	84.5	79.9	75.7	80.0
	STN 22	76.3	57.2	56.0	63.2	85.7	80.0	44.7	70.1	75.4	71.1	60.7	69.1
	STN 24	50.4	43.7	30.2	41.4	81.3	37.2	50.7	56.4	77.3	79.3	74.2	76.9
	STN 26	67.9	58.0	6.5	44.1	59.3	53.3	58.9	57.2	83.0	79.5	58.4	73.6
	Average	**68.4**	**53.0**	**39.2**	**53.6**	**73.4**	**52.3**	**54.4**	**57.7**	**70.0**	**67.5**	**69.2**	**65.6**
	Stdev	**12.7**	**14.4**	**33.6**	**16.8**	**11.6**	**18.5**	**13.4**	**13.7**	**29.3**	**27.8**	**8.0**	**28.0**
Sedimite	STN 28	77.2	40.4	35.8	51.1	85.5	72.0	73.8	77.1	83.1	83.7	86.5	84.5
	STN 30	63.1	71.3	62.5	65.7	77.4	71.9	91.3	80.2	87.8	76.1	69.8	77.9
	STN 33	88.8	86.3	74.2	83.1	93.1	80.1	81.2	84.8	93.6	87.4	89.0	90.0
	STN 36	85.2	71.8	76.7	77.9	88.6	80.4	79.8	82.9	90.4	90.7	86.5	89.2
	STN 38	86.8	71.2	58.6	72.2	84.1	75.9	85.4	81.8	95.5	93.9	88.3	92.6
	STN 40	88.3	85.6	87.9	87.3	92.1	80.0	79.0	83.7	93.6	89.5	85.1	89.4
	STN 42	70.2	60.6	80.5	70.5	87.6	69.7	28.6	61.9	94.1	90.7	84.9	89.9
	Average	**79.9**	**69.6**	**68.0**	**72.5**	**86.9**	**75.7**	**74.2**	**78.9**	**91.2**	**87.4**	**84.3**	**87.6**
	Stdev	**10.1**	**15.7**	**17.4**	**12.0**	**5.3**	**4.6**	**20.8**	**7.9**	**4.4**	**5.9**	**6.5**	**4.9**
Overall sites	**Average**	**78.8**	**68.4**	**65.1**	**70.7**	**84.2**	**69.3**	**71.8**	**74.3**	**87.4**	**83.7**	**79.2**	**83.4**
	Stdev	**12.7**	**18.0**	**27.6**	**17.3**	**9.8**	**15.8**	**20.0**	**14.5**	**6.0**	**6.2**	**9.1**	**6.4**

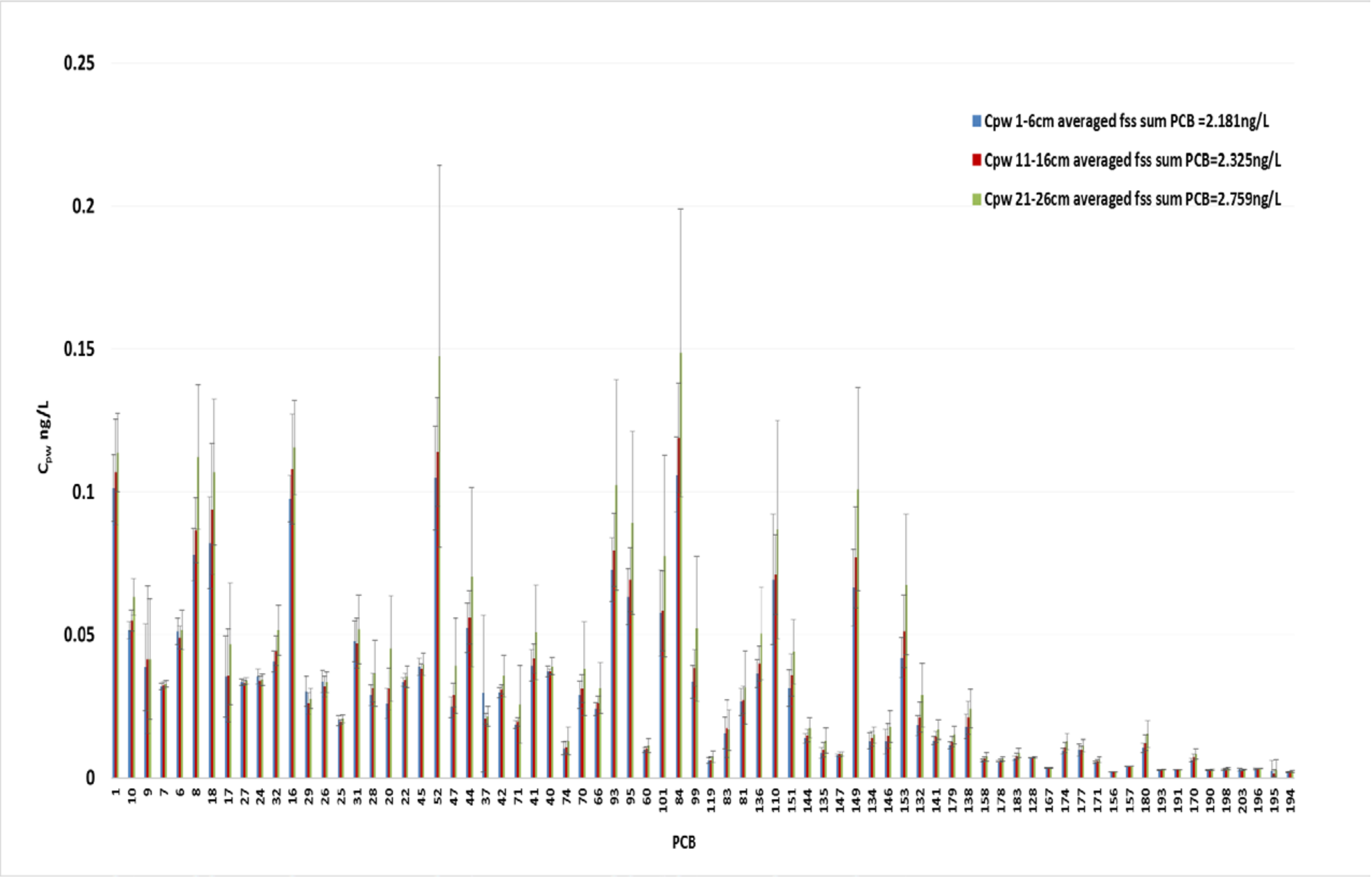


Figure E-1. Average concentration of detected PCB concentrations in Hunter’s Point Navy Shipyard sediment porewater – baseline results

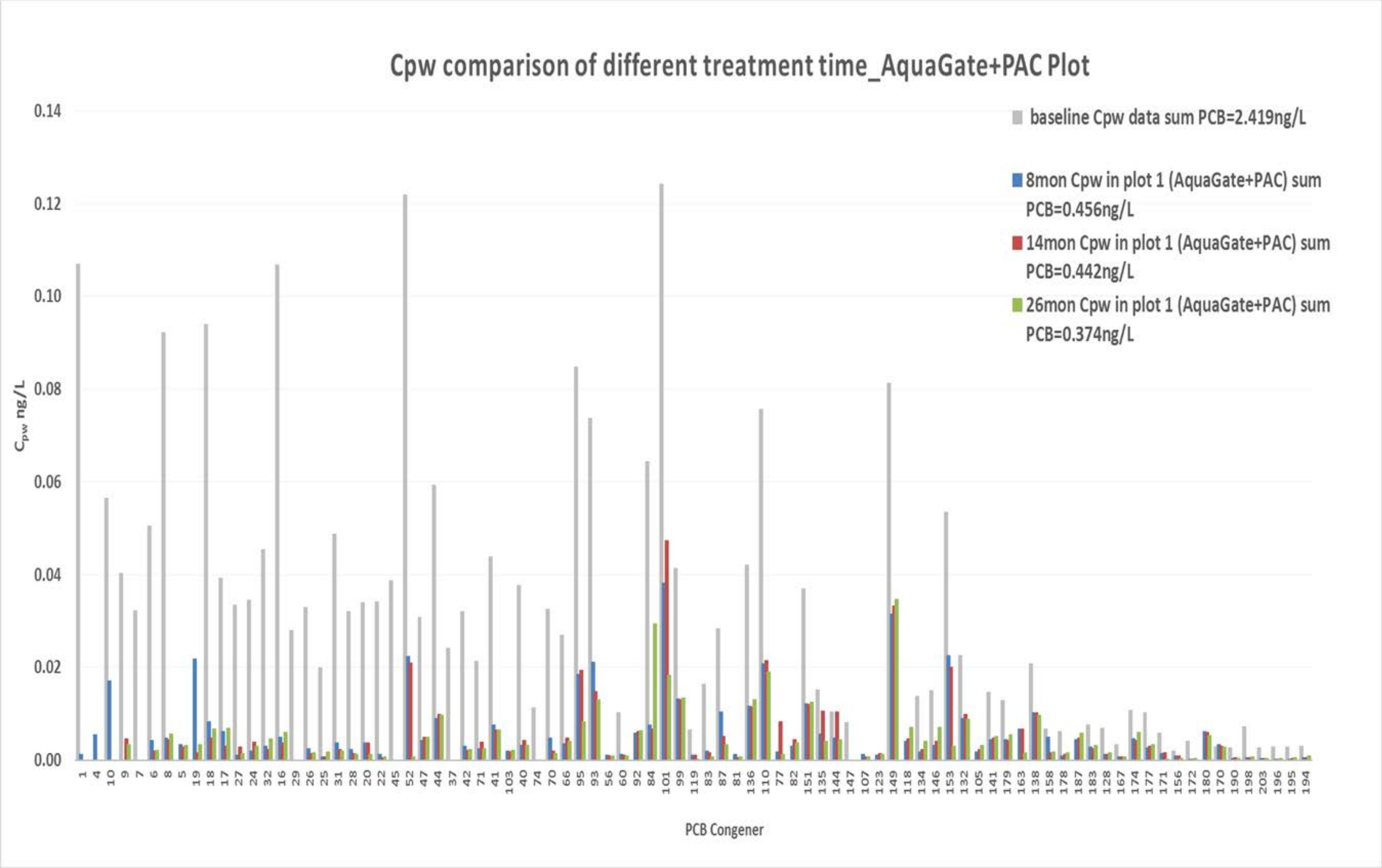


Figure E-2. Average concentration of detected PCB concentrations in sediment porewater in Hunter’s Point Navy Shipyard AquaGate+PAC Plot after 26 months treatment with comparison to 14 months, 8 months treatment and baseline results

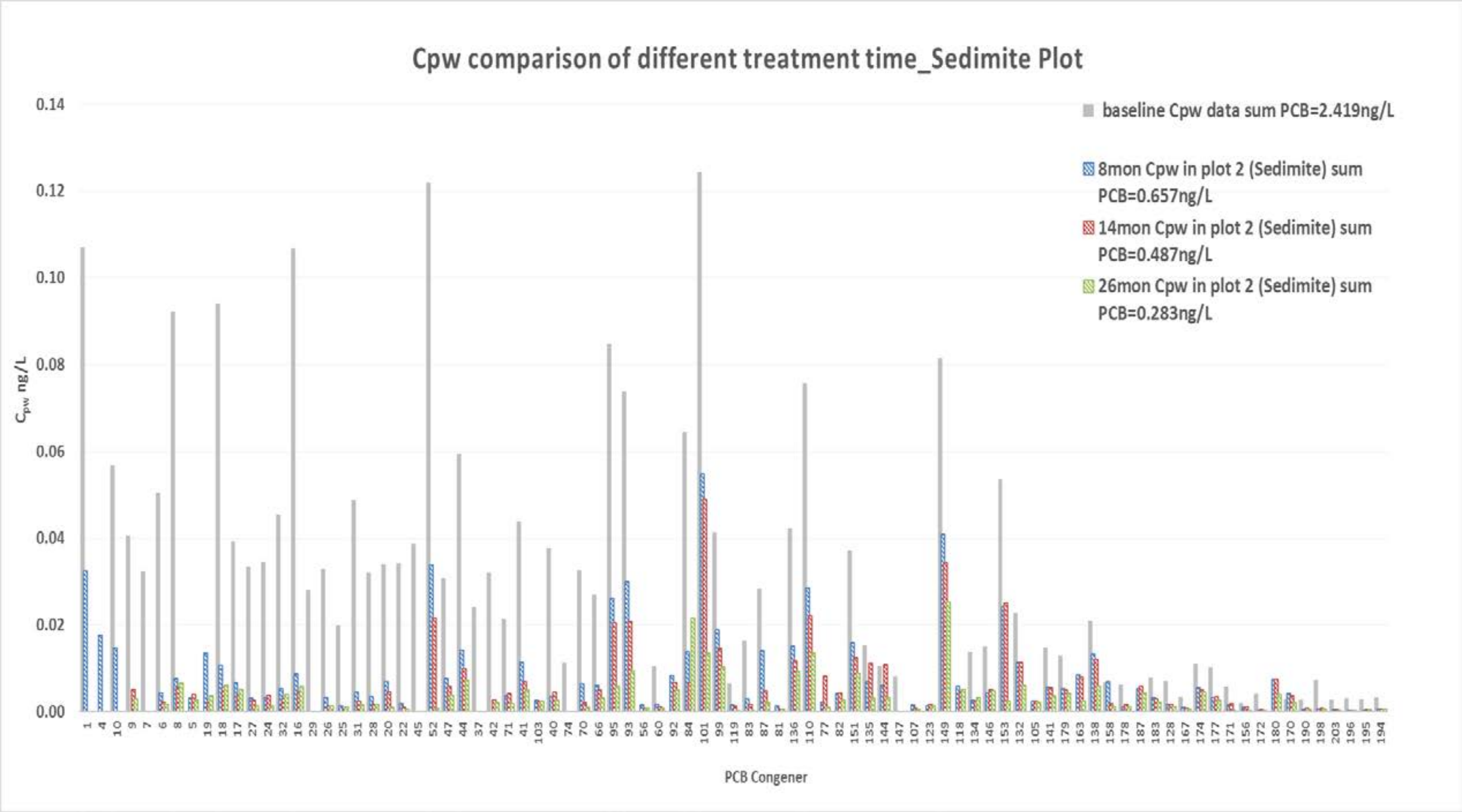


Figure E-3. Average concentration of detected PCB concentrations in sediment porewater in Hunter’s Point Navy Shipyard Sedimite Plot after 26 months treatment with comparison to 14month, 8 months treatment and baseline results

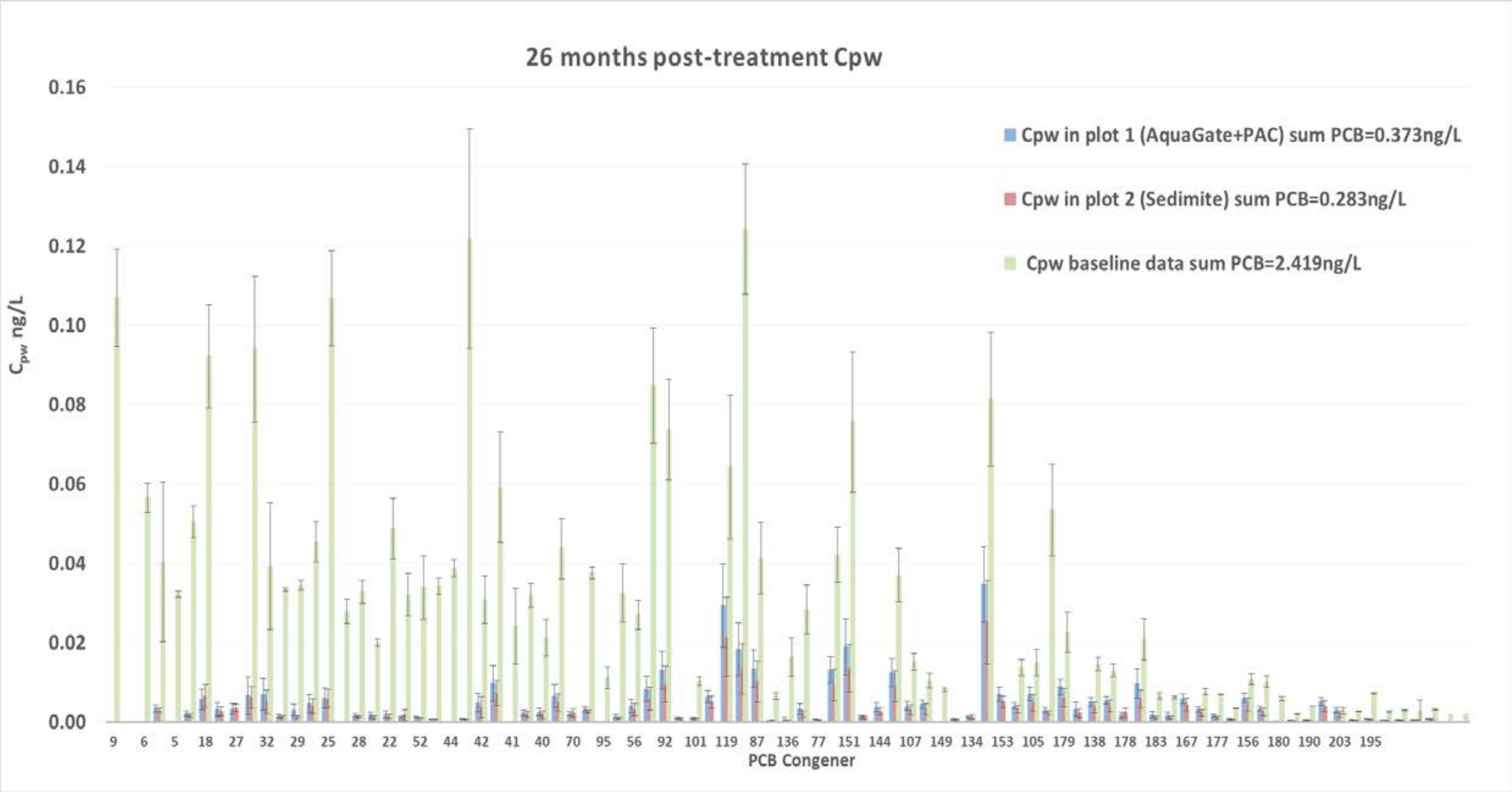


Figure E-4. Average concentration of detected PCB concentrations in sediment porewater in AquaGate+PAC Plot and Sedimite Plot in Hunter’s Point Navy Shipyard after 26 months treatment with comparison to baseline results

Bibliography

1. Huckins, J. N., Tubergen, M. W. & Manuweera, G. K. Semipermeable membrane devices containing model lipid: A new approach to monitoring the bioavaiiability of lipophilic contaminants and estimating their bioconcentration potential. *Chemosphere* **20,** 533–552 (1990).

2. Greenberg, M. S. *et al.* Passive sampling methods for contaminated sediments: Risk assessment and management. *Integr. Environ. Assess. Manag.* **10,** 224–236 (2014).

3. Schwarzenbach, R. P. General Introduction and Sorption Processes Involving Organic Matter. *Environ. Org. Chem.* 275–330 (2003).

4. Greenwood, R., Mills, G. A. & Vrana, B. Potential applications of passive sampling for monitoring non-polar industrial pollutants in the aqueous environment in support of REACH. *J. Chromatogr. A* **1216,** 631–639 (2009).

5. Vrana, B. *et al.* Passive sampling techniques for monitoring pollutants in water. *TrAC Trends Anal. Chem.* **24,** 845–868 (2005).

6. Alvarez, D. A. *et al.* Comparison of a novel passive sampler to standard water-column sampling for organic contaminants associated with wastewater effluents entering a New Jersey stream. *Chemosphere* **61,** 610–622 (2005).

7. Adams, R. G., Lohmann, R., Fernandez, L. A. & MacFarlane, J. K. Polyethylene Devices: Passive Samplers for Measuring Dissolved Hydrophobic Organic Compounds in Aquatic Environments. *Environ. Sci. Technol.* **41,** 1317–1323 (2007).

8. Allan, I. J., Harman, C., Ranneklev, S. B., Thomas, K. V. & Grung, M. Passive sampling for target and nontarget analyses of moderately polar and nonpolar substances in water. *Environ. Toxicol. Chem.* **32,** 1718–1726

9. Vinturella, A. E., Burgess, R. M., Coull, B. A., Thompson, K. M. & Shine, J. P. Use of Passive Samplers To Mimic Uptake of Polycyclic Aromatic Hydrocarbons by Benthic Polychaetes. *Environ. Sci. Technol.* **38,** 1154–1160 (2004).

10. Cornelissen, G., Breedveld, G. D., Næs, K., Oen, A. M. P. & Ruus, A. Bioaccumulation of native polycyclic aromatic hydrocarbons from sediment by a polychaete and a gastropod: Freely dissolved concentrations and activated carbon amendment. *Environ. Toxicol. Chem.* **25,** 2349–2355 (2006).

11. Friedman, C. L. *et al.* Comparing Polychaete and Polyethylene Uptake to Assess Sediment Resuspension Effects on PCB Bioavailability. *Environ. Sci. Technol.* **43,** 2865–2870 (2009).

12. Lu, X., Reible, D. D. & Fleeger, J. W. Bioavailability of polycyclic aromatic hydrocarbons in field-contaminated Anacostia River (Washington, DC) sediment. *Environ. Toxicol. Chem.* **25,** 2869–2874 (2006).

13. Lu, X., Skwarski, A., Drake, B. & Reible, D. D. Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. *Environ. Toxicol. Chem.* **30,** 1109–1116 (2011).

14. Rosen, G. *et al.* A sediment ecotoxicity assessment platform for in situ measures of chemistry, bioaccumulation and toxicity. Part 2: Integrated application to a shallow estuary. *Environ. Pollut.* **162,** 457–465 (2012).

15. J. Lampert, D., Lu, X. & D. Reible, D. Long-term PAH monitoring results from the Anacostia River active capping demonstration using polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **15,** 554–562 (2013).

16. Cho, Y.-M. *et al.* Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment. *Environ. Sci. Technol.* **43,** 3815–3823 (2009).

17. Oen, A. M. P. *et al.* In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers. *Environ. Sci. Technol.* **45,** 4053–4059 (2011).

18. Mayer, P. *et al.* Passive sampling methods for contaminated sediments: Scientific rationale supporting use of freely dissolved concentrations. *Integr. Environ. Assess. Manag.* **10,** 197–209 (2014).

19. Lampert, D. J., Sarchet, W. V. & Reible, D. D. Assessing the Effectiveness of Thin-Layer Sand Caps for Contaminated Sediment Management through Passive Sampling. *Environ. Sci. Technol.* **45,** 8437–8443 (2011).

20. Thomas, C., Lampert, D. & Reible, D. Remedy performance monitoring at contaminated sediment sites using profiling solid phase microextraction (SPME) polydimethylsiloxane (PDMS) fibers. *Environ. Sci. Process. Impacts* **16,** 445–452 (2014).

21. JENSEN, S. Report of a New Chemical Hazard. *New Sci.* **15,** 612 (1966).

22. Jensen, S., Johnels, A. G., Olsson, M. & Otterlind, G. DDT and PCB in Marine Animals from Swedish Waters. *Nature* **224,** 247–250 (1969).

23. Jonsson, H. T. *et al.* Prolonged ingestion of commercial DDT and PCB; effects on progesterone levels and reproduction in the mature female rat. *Arch. Environ. Contam. Toxicol.* **3,** 479–490 (1975).

24. Kimbrough, R. D. Human health effects of polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs). *Annu. Rev. Pharmacol. Toxicol.* **27,** 87–111 (1987).

25. Erickson, M. D. *Analytical Chemistry of PCBs, Second Edition*. (CRC Press, 1997).

26. Jacobson, J. L., Jacobson, S. W. & Humphrey, H. E. B. Effects of exposure to PCBs and related compounds on growth and activity in children. *Neurotoxicol. Teratol.* **12,** 319–326 (1990).

27. Rothman, N. *et al.* A nested case-control study of non-Hodgkin lymphoma and serum organochlorine residues. *The Lancet* **350,** 240–244 (1997).

28. NORRIS, G. EPA Positive Matrix Factorization (PMF) 3.0 Fundamentals & User Guide, US. Environmental Protection Agency. *http://www.epa.gov/heasd/products/pmf/pmf.html* (2008).

29. Haws, L. C. *et al.* Development of a Refined Database of Mammalian Relative Potency Estimates for Dioxin-like Compounds. *Toxicol. Sci.* **89,** 4–30 (2006).

30. Berg, M. V. den, Jongh, J. D., Poiger, H. & Olson, J. R. The Toxicokinetics and Metabolism of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Dibenzofurans (PCDFs) and Their Relevance for Toxicity. *Crit. Rev. Toxicol.* **24,** 1–74 (1994).

31. Carson, N. A. J. & Neill, D. W. Metabolic Abnormalities Detected in a Survey of Mentally Backward Individuals in Northern Ireland. *Arch. Dis. Child.* **37,** 505–513 (1962).

32. Smedes, F., van Vliet, L. A. & Booij, K. Multi-Ratio Equilibrium Passive Sampling Method to Estimate Accessible and Pore Water Concentrations of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls in Sediment. *Environ. Sci. Technol.* **47,** 510–517 (2013).

33. Kraaij, R. *et al.* Measured Pore-Water Concentrations Make Equilibrium Partitioning Work A Data Analysis. *Environ. Sci. Technol.* **37,** 268–274 (2003).

34. Lu, X., Reible, D. D., Fleeger, J. W. & Chai, Y. Bioavailability of desorption-resistant phenanthrene to the oligochaete Ilyodrilus templetoni. *Environ. Toxicol. Chem.* **22,** 153–160 (2003).

35. Palmes, E. D. & Gunnison, A. F. Personal Monitoring Device for Gaseous Contaminants. *Am. Ind. Hyg. Assoc. J.* **34,** 78–81 (1973).

36. Hesslein, R. H. An in situ sampler for close interval pore water studies1. *Limnol. Oceanogr.* **21,** 912–914 (1976).

37. Huckins, J. N., Booij, K. & Petty, J. D. Introduction to Passive Sampling. in *Monitors of Organic Chemicals in the Environment* 1–28 (Springer, Boston, MA, 2006).

38. Namieśnik, J., Zabiegała, B., Kot-Wasik, A., Partyka, M. & Wasik, A. Passive sampling and/or extraction techniques in environmental analysis: a review. *Anal. Bioanal. Chem.* **381,** 279–301 (2005).

39. Belardi, R. P. & Pawliszyn, J. B. The Application of Chemically Modified Fused Silica Fibers in the Extraction of Organics from Water Matrix Samples and their Rapid Transfer to Capillary Columns. *Water Qual. Res. J.* **24,** 179–191 (1989).

40. Arthur, C. L. & Pawliszyn, J. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem.* **62,** 2145–2148 (1990).

41. Lord, H. & Pawliszyn, J. Evolution of solid-phase microextraction technology. *J. Chromatogr. A* **885,** 153–193 (2000).

42. Allan, I. J., Ruus, A., Schaanning, M. T., Macrae, K. J. & Næs, K. Measuring nonpolar organic contaminant partitioning in three Norwegian sediments using polyethylene passive samplers. *Sci. Total Environ.* **423,** 125–131 (2012).

43. Cornelissen, G., Pettersen, A., Broman, D., Mayer, P. & Breedveld, G. D. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environ. Toxicol. Chem.* **27,** 499–508 (2008).

44. Mayer, P. *et al.* Sensing Dissolved Sediment Porewater Concentrations of Persistent and Bioaccumulative Pollutants Using Disposable Solid-Phase Microextraction Fibers. *Environ. Sci. Technol.* **34,** 5177–5183 (2000).

45. Booij, K., Smedes, F. & van Weerlee, E. M. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **46,** 1157–1161 (2002).

46. Schweitzer, C. E., Macdonald, R. N. & Punderson, J. O. Thermally stable high molecular weight polyoxymethylenes. *J. Appl. Polym. Sci.* **1,** 158–163 (1959).

47. Koch, T. A. & Lindvig, P. E. Molecular structure of high molecular weight acetal resins. *J. Appl. Polym. Sci.* **1,** 164–168 (1959).

48. Linton, W. H. & Goodman, H. H. Physical properties of high molecular weight acetal resins. *J. Appl. Polym. Sci.* **1,** 179–184 (1959).

49. Lorthioir, C. *et al.* Solid-State Organization and Morphological Partitioning in Polyoxymethylene-Based Copolymers: A Solid-State NMR and WAXS Study. *Macromolecules* **40,** 5001–5013 (2007).

50. Jonker, M. T. O. & Koelmans, A. A. Polyoxymethylene Solid Phase Extraction as a Partitioning Method for Hydrophobic Organic Chemicals in Sediment and Soot. *Environ. Sci. Technol.* **35,** 3742–3748 (2001).

51. Arp, H. P. H. *et al.* Review of polyoxymethylene passive sampling methods for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants. *Environ. Toxicol. Chem.* **34,** 710–720 (2015).

52. Thomas, C. L. Passive sampling to evaluate performance of in situ sediment remediation. (2014).

53. Huckins, J. N., Manuweera, G. K., Petty, J. D., Mackay, D. & Lebo, J. A. Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water. *Environ. Sci. Technol.* **27,** 2489–2496 (1993).

54. Tomaszewski, J. E. & Luthy, R. G. Field Deployment of Polyethylene Devices to Measure PCB Concentrations in Pore Water of Contaminated Sediment. *Environ. Sci. Technol.* **42,** 6086–6091 (2008).

55. Fernandez, L. A., MacFarlane, J. K., Tcaciuc, A. P. & Gschwend, P. M. Measurement of Freely Dissolved PAH Concentrations in Sediment Beds Using Passive Sampling with Low-Density Polyethylene Strips. *Environ. Sci. Technol.* **43,** 1430–1436 (2009).

56. Lampert, D. J., Thomas, C. & Reible, D. D. Internal and external transport significance for predicting contaminant uptake rates in passive samplers. *Chemosphere* **119,** 910–916 (2015).

57. Schmidt, S. N. *et al.* Cross Validation of Two Partitioning-Based Sampling Approaches in Mesocosms Containing PCB Contaminated Field Sediment, Biota, and Activated Carbon Amendment. *Environ. Sci. Technol.* **51,** 9996–10004 (2017).

58. Carslaw, H. S. & Jaeger, J. C. *Conduction of heat in solids*. (Oxford University Press, 1986).

59. Shen, X. Developing models for the assessment and the design of the in situ remediation of contaminated sediments. (2017).

60. Choi, Y., Wu, Y., Luthy, R. G. & Kang, S. Non-equilibrium passive sampling of hydrophobic organic contaminants in sediment pore-water: PCB exchange kinetics. *J. Hazard. Mater.* **318,** 579–586 (2016).

61. Ouyang, G. & Pawliszyn, J. Configurations and calibration methods for passive sampling techniques. *J. Chromatogr. A* **1168,** 226–235 (2007).

62. Allan, I. J. *et al.* Field Performance of Seven Passive Sampling Devices for Monitoring of Hydrophobic Substances. *Environ. Sci. Technol.* **43,** 5383–5390 (2009).

63. Gschwend, P. M. *et al.* Comparison of polymeric samplers for accurately assessing PCBs in pore waters. *Environ. Toxicol. Chem.* **30,** 1288–1296 (2011).

64. Schintu, M., Marrucci, A. & Marras, B. Passive Sampling Technologies for the Monitoring of Organic and Inorganic Contaminants in Seawater. in *Current Environmental Issues and Challenges* 217–237 (Springer, Dordrecht, 2014).

65. Lu, X., Reible, D. D. & Fleeger, J. W. Bioavailability of polycyclic aromatic hydrocarbons in field-contaminated Anacostia River (Washington, DC) sediment. *Environ. Toxicol. Chem.* **25,** 2869–2874 (2006).

66. Janssen, E. M.-L., Oen, A. M. P., Luoma, S. N. & Luthy, R. G. Assessment of field-related influences on polychlorinated biphenyl exposures and sorbent amendment using polychaete bioassays and passive sampler measurements. *Environ. Toxicol. Chem.* **30,** 173–180 (2011).

67. Gomez-Eyles, J. L., Jonker, M. T. O., Hodson, M. E. & Collins, C. D. Passive Samplers Provide a Better Prediction of PAH Bioaccumulation in Earthworms and Plant

Roots than Exhaustive, Mild Solvent, and Cyclodextrin Extractions. *Environ. Sci. Technol.* **46,** 962–969 (2012).

68. Wang, J., Taylor, A., Xu, C., Schlenk, D. & Gan, J. Evaluation of different methods for assessing bioavailability of DDT residues during soil remediation. *Environ. Pollut.* **238,** 462–470 (2018).

69. Liu, H.-H. *et al.* Novel Passive Sampling Device for Measuring Sediment–Water Diffusion Fluxes of Hydrophobic Organic Chemicals. *Environ. Sci. Technol.* **47,** 9866–9873 (2013).

70. Murphy Paul, Marquette Andre, Reible Danny & Lowry Gregory V. Predicting the Performance of Activated Carbon-, Coke-, and Soil-Amended Thin Layer Sediment Caps. *J. Environ. Eng.* **132,** 787–794 (2006).

71. Schaanning, M., Breyholtz, B. & Skei, J. Experimental results on effects of capping on fluxes of persistent organic pollutants (POPs) from historically contaminated sediments. *Mar. Chem.* **102,** 46–59 (2006).

72. Beckingham, B. & Ghosh, U. Polyoxymethylene passive samplers to monitor changes in bioavailability and flux of PCBs after activated carbon amendment to sediment in the field. *Chemosphere* **91,** 1401–1407 (2013).

73. Lohmann, R., Booij, K., Smedes, F. & Vrana, B. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environ. Sci. Pollut. Res.* **19,** 1885–1895 (2012).

74. Vrana, B. *et al.* Passive sampling: An effective method for monitoring seasonal and spatial variability of dissolved hydrophobic organic contaminants and metals in the Danube river. *Environ. Pollut.* **184,** 101–112 (2014).

75. Chepchirchir, B. S., Paschke, A. & Schüürmann, G. Passive sampling for spatial and temporal monitoring of organic pollutants in surface water of a rural-urban river in Kenya. *Sci. Total Environ.* **601–602,** 453–460 (2017).

76. Ghosh, U. *et al.* Passive sampling methods for contaminated sediments: Practical guidance for selection, calibration, and implementation. *Integr. Environ. Assess. Manag.* **10,** 210–223 (2014).

77. Hawker, D. W. & Connell, D. W. Octanol-water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* **22,** 382–387 (1988).

78. *Processes, Assessment and Remediation of Contaminated Sediments*. (Springer-Verlag, 2014).

79. Wang, X. Q., Thibodeaux, L. J., Valsaraj, K. T. & Reible, D. D. Efficiency of capping contaminated bed sediments in situ. 1. Laboratory-scale experiments on diffusion-adsorption in the capping layer. *Environ. Sci. Technol.* **25,** 1578–1584 (1991).

80. Lampert, D. J. & Reible, D. An Analytical Modeling Approach for Evaluation of Capping of Contaminated Sediments. *Soil Sediment Contam. Int. J.* **18,** 470–488 (2009).

81. Aissou, K. *et al.* Sub-10 nm Features Obtained from Directed Self-Assembly of Semicrystalline Polycarbosilane-Based Block Copolymer Thin Films. *Adv. Mater.* **27,** 261–265 (2015).

82. Reible, D., Lampert, D., Constant, D., Jr, R. D. M. & Zhu, Y. Active capping demonstration in the Anacostia river, Washington, D.C. *Remediat. J.* **17,** 39–53 (2006).

83. Ghosh, U., Luthy, R. G., Cornelissen, G., Werner, D. & Menzie, C. A. In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. *Environ. Sci. Technol.* **45,** 1163–1168 (2011).

84. Nybom, I. *et al.* Effects of Activated Carbon on PCB Bioaccumulation and Biological Responses of Chironomus riparius in Full Life Cycle Test. *Environ. Sci. Technol.* **50,** 5252–5260 (2016).

85. Abel, S. & Akkanen, J. A Combined Field and Laboratory Study on Activated Carbon-Based Thin Layer Capping in a PCB-Contaminated Boreal Lake. *Environ. Sci. Technol.* **52,** 4702–4710 (2018).

86. Gilmour, C. C. *et al.* Activated Carbon Mitigates Mercury and Methylmercury Bioavailability in Contaminated Sediments. *Environ. Sci. Technol.* **47,** 13001–13010 (2013).

87. Thompson, J. M., Hsieh, C.-H., Hoelen, T. P., Weston, D. P. & Luthy, R. G. Measuring and Modeling Organochlorine Pesticide Response to Activated Carbon Amendment in Tidal Sediment Mesocosms. *Environ. Sci. Technol.* **50,** 4769–4777 (2016).

88. Schäfer, R. B., Hearn, L., Kefford, B. J., Mueller, J. F. & Nugegoda, D. Using silicone passive samplers to detect polycyclic aromatic hydrocarbons from wildfires in

streams and potential acute effects for invertebrate communities. *Water Res.* **44,** 4590–4600 (2010).

89. Johnston, R. *et al.* Monitoring to assess the effectiveness of an activated carbon sediment amendment to remediate contamination at a site located at the Puget Sound Naval Shipyard & Intermediate Maintenance Facility, Bremerton, WA. in *Salish Sea Ecosystem Conference* (2014).

90. Patmont, C. R. *et al.* In situ sediment treatment using activated carbon: A demonstrated sediment cleanup technology. *Integr. Environ. Assess. Manag.* **11,** 195–207 (2015).

91. Gustafsson, Ö. *et al.* Evaluation of a protocol for the quantification of black carbon in sediments. *Glob. Biogeochem. Cycles* **15,** 881–890 (2001).

92. Cornelissen, G., Pettersen, A., Broman, D., Mayer, P. & Breedveld, G. D. Field testing of equilibrium passive samplers to determine freely dissolved native polycyclic aromatic hydrocarbon concentrations. *Environ. Toxicol. Chem.* **27,** 499–508 (2008).

93. Huckins, J. N. *et al.* Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. *Environ. Sci. Technol.* **36,** 85–91 (2002).

94. Choy, B. & Reible, D. D. *Diffusion Models of Environmental Transport*. (CRC Press, 2000).

95. Bejan, A. & Poulikakos, D. The nondarcy regime for vertical boundary layer natural convection in a porous medium. *Int. J. Heat Mass Transf.* **27,** 717–722 (1984).

96. Ping, C. Combined free and forced convection flow about inclined surfaces in porous media. *Int. J. Heat Mass Transf.* **20,** 807–814 (1977).

97. Millington, R. J. & Quirk, J. P. Permeability of porous solids. *Trans. Faraday Soc.* **57,** 1200–1207 (1961).

98. Transport phenomena, R. B. Bird, W. E. Stewart, and E. N. Lightfoot, John Wiley and Sons, Inc., New York (1960). 780 pages. $11.50. *AIChE J.* **7,** 5J–6J (1961).

99. Wakao, N. & Funazkri, T. Effect of fluid dispersion coefficients on particle-to-fluid mass transfer coefficients in packed beds: Correlation of sherwood numbers. *Chem. Eng. Sci.* **33,** 1375–1384 (1978).

100. Mackay, D., Shiu, W.-Y., Ma, K.-C. & Lee, S. C. *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Second Edition*. (CRC Press, 2006).