Fall 2012

Depth profiling of PAHs treated with activated carbon using in-situ SPME

Ryan D. Stringer

Department:

DEPTH PROFILING OF PAHS TREATED WITH ACTIVATED CARBON USING IN-SITU SPME

By

RYAN DEAN STRINGER

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

2012

Approved by

Joel G. Burken, Advisor
Andrew C. Elmore
Glenn C Morrison

PUBLICATION THESIS OPTION

Sections 1-5 provide information and data not presented within the journal article which is located on pages 25-50. The article has been formatted as specified by the Journal of Environmental Science and will be submitted in the future.

ABSTRACT

Novel and efficient methods to measure the bioavailability of hydrophobic organic contaminants (HOCs) in contaminated sediments will play an important role in the acceptance of alternative sediment remediation strategies. In this project, solid phase microextraction (SPME) fibers, protected in perforated steel tubes, were used as *in situ* passive samplers to measure the treatment of activated carbon (AC) in polycyclic aromatic hydrocarbon (PAH) contaminated sediment. Contaminated sediment was treated with two modes of AC waterjet amendment. In the first treatment, a single 2-min injection was shot into the center of a test vessel and in the second treatment, multiple 7-sec injections in a grid were placed in sediment. In the single injection no treatment was observed 5 cm away from the injection, while at 2.5 cm greater than 90% removal of PAH pore water concentrations were observed. In the multiple injection experiment greater than 90% PAH pore water reductions were observed throughout the test vessel. Highly contaminated and less contaminated sediments were mixed with 0-5% AC by weight to develop AC treatment curves. Over 99% reduction in PAH bioavailability was observed in the less contaminated sediment at 3% AC while 99% removal was never reached even at 5% AC addition in the highly contaminated sediment. Clear treatment curves were observed for both contaminated sediments, though they were very different. *In situ* equilibration times were 120, 215 and 250 hours for phenanthrene, pyrene and benzo(a)Anthracene respetively. The results show that *in situ* SPME is a viable method to observe AC treatment and evaluate reductions in bioavailability.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Joel Burken, for his advice, patience and assistance throughout the project. Dr. Burken has always had his door open to me to help as problems arose.

Dr. Curt Elmore, I would like to thank for his comments, insight and challenges. His presence has always been a catalyst, helping to move things forward.

I would also like to thank the NIEHS and the Superfund Research Program for their assistance in the funding of the project.

To my fellow students on the project, Aaron Archer, Chris Redell, Gavin Risley and Grace Harper, you have assisted me in many ways both with my work and through the difficulties of graduate studies. Thank you for your assistance and presence.

I would like to thank my lab mates, including Matt Limmer, for their assistance and support. Having a good group of people to discuss and bond with has been a great resource through my studies.

Finally, I would like to thank my family for their support and encouragement throughout. Without the upbringing and guidance my parents given me I would have never been able to succeed.

TABLE OF CONTENTS

LIST OF FIGURES

Page

LIST OF TABLES

Page

NOMENCLATURE

AC	Activated Carbon
ATSDR	Agency for Toxic Substances and Disease Registry
DOC	Dissolved Organic Carbon
EPA	Environmental Protection Agency
GC	Gas Chromatograph
HOC	Hydrophobic Organic Contaminant
HPLC	High Pressure Liquid Chromatograph
ITRC	Interstate Technical and Regulatory Council
Kow	Ocantol-water Partitioning Coefficient
PAH	Polycyclic Aromatic Hydrocarbon
PCB	Polychlorinated Biphenyl
PDMS	Polydimethylsiloxane
POM	Polyoxymethylene
POP	Persistent Organic Pollutant
PRC	Performance Reference Compound
RSD	Relative Standard Deviation
SPME	Solid Phase Microextraction

1. LITERATURE REVIEW

1.1 INTRODUCTION

Contaminated sediment remediation in the United States and around the world is a significant environmental problem. While there are numerous sediment contaminants some of the most difficult and pervasive are HOCs such as PAHs or PCBs (U.S. Environmental Protection Agency, 1998). . HOCs are very hydrophobic, usually with a high K_{ow}Upon entering the water body the majority of HOC contaminants in sediment will concentrate in organic or carbonaceous material (Ghosh et al., 2000). Once HOCs have accumulated in the contaminated sediment they can be very difficult to remediate and can persist in the environment for years (Yongyong et al., 2011).

HOCs in the sediment will equilibrate with the local pore water. Benthic organisms in the sediment will then equilibrate with the HOCs causing toxicity and bioaccumulation (U.S. Environmental Protection Agency, 1998). The contaminants may then bioaccumulate into higher trophic levels causing toxic effects in fish and exposing humans through their consumption as seen in Figure 1.1. HOC contamination in the United States has left millions of river miles and lake acres with major environmental problems; significantly contaminating 10% of U.S. sediments (U.S. Environmental Protection Agency, 2009).

Dredging is the traditional method for remediating contaminated sediments. Physical removal of contaminated sediments ensures contaminants have been removed from the water bodies. Dredging, however, poses challenges such as: requiring disposal or treatment of removed contaminated sediment, the resuspension of contaminated

sediment during dredging transporting contaminants downstream, the natural flora and fauna are excavated, and it can be very difficult to remove all of the contaminated sediment (Francingues et al., 2008).

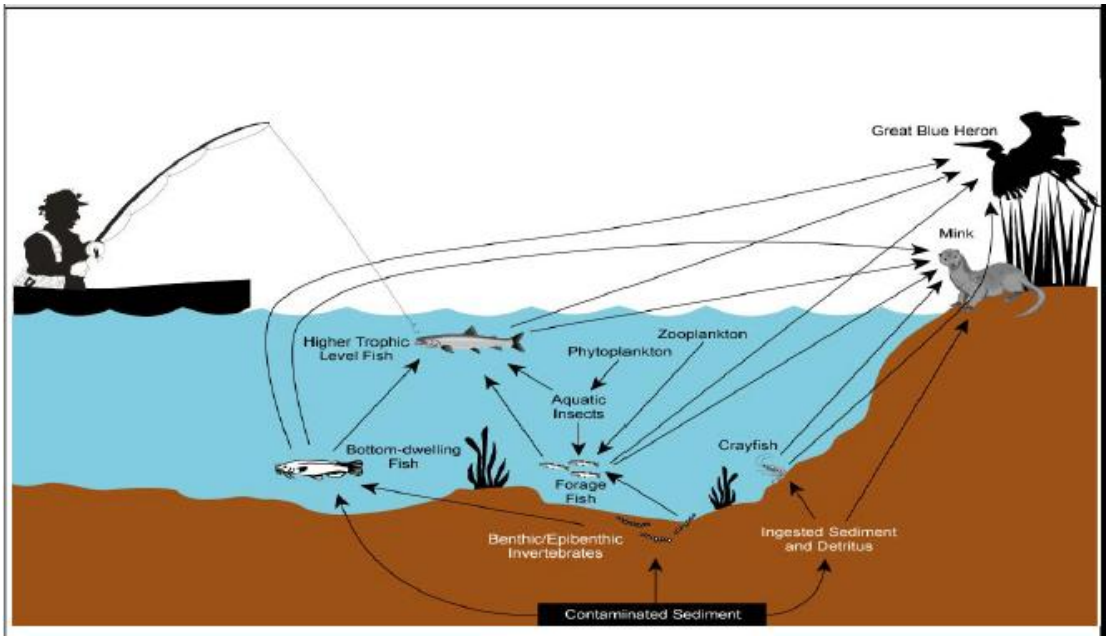


Figure 1.1:Contaminated Sediment Conceptual Site Model of bioaccumulation (U.S. Environmental Protection Agency, 1998)

Alternative treatments to dredging have been introduced to overcome shortfalls of dredging. These include the use of caps to physically separate contaminated sediment with a clean sediment layer and *in sit*u amendments which serve to lower chemical activity or remediate contaminants. Capping requires the placement of layers of material to help isolate contaminants and may eliminate benthic organisms. Cap placement may

also be limited by the water body traffic and river hydraulics (U.S Environmental Protection Agency, 2005).

In situ amendments may be placed into contaminated sediment to lower chemical activity without requiring the placement of a clean sediment layer or removal of sediment (SERDP and ESTCP, 2004). One of the most studied amendments used for HOC remediation is activated carbon (AC) (Ghosh et al., 2011). The AC has very high partitioning coefficients for HOCs and it is able to significantly lower the bioavailability and chemical activity of HOCs in the sediment without destroying the existing benthic organisms.

In situ treatments for sediment contamination require proof to ensure that appropriate treatment has occurred. These treatments do not physically remove contaminated sediment but rather act to impede their migration or lower their bioavailability and require evidence of on-going treatment. Frequent measurement of the contaminant migration of *in situ* treated contaminated sediment may be required as *in situ* sediment treatment becomes more accepted in industry. New methods to measure in situ treatment efficiently with minimal disturbance of the remediation will aid in the advancement of in situ treatment. Developing methods with the ability to perform measurements with depth is also important to show evidence of treatment with depth and to observe if any vertical migration or deposition of contaminated sediment is occurring.

Current in situ chemical sampling techniques use passive sampling to selectively concentrate HOCs into material that can later be extracted. Typical passive sampling materials for HOCs include polyethylene, polyoxymethylene (POM), and

polydimethylsiloxane (PDMS) (Bao and Zeng, 2011; Namieśnik et al., 2005; Oen et al., 2011). These materials may come in sheets or tubes or as the coatings on SPME fibers. When these materials are exposed to sediment they will equilibrate with the sediment pore water. Partitioning coefficients can then be used to determine pore water concentrations, which indicate the contaminant's bioavailability and is the best way to measure the risk to benthic organisms (Hawthorne et al., 2007). There are few methods which use passive sampling to measure contaminant depth profiles in sediment. Methods to measure contaminants with depth may become very important as alternative sediment treatments become more accepted.

1.2 PAH SEDIMENT CONTAMINATION

Contaminated sediments are a major environmental problem in the United States. In the U.S. approximately 18 million lake acres and 1.4 million river miles were under advisory in 2008, representing 43% of the nation's total lake acreage and 39% of the nation's total river miles"(U.S. Environmental Protection Agency, 2009). The EPA estimated that up to 10% of sediments across the United States could be considered contaminated, totaling up to 1.2 billion cubic yards (U.S. Environmental Protection Agency, 1998). Polycyclic aromatic hydrocarbon (PAH) contamination is the largest risk factor at 20% of contaminated sediment sites in the U.S. (U.S. Environmental Protection Agency, 1998). PAH, PCB and other HOC sediment contamination is a major pollution problem in the U.S. and abroad.

PAHs are hydrophobic organic chemicals (HOCs) that can persist in the environment for many years. PAHs are composed of two or more connected benzene rings. PAH contamination sources include petrogenic and pyrogenic sources. Petrogenic

sources include oil and fuel spills that have occurred over the years, especially at manufactured gas plants and natural petroleum seeps (Van Metre et al., 2000). Pyrogenic PAHs are produced through the incomplete combustion of coal or other carbonaceous material and may be produced by natural or anthropogenic sources such as; forest fires , coal combustion, automobiles, cooking and heating fires, and industrial activities such as coal gasification, iron and steel foundries, creosote operations and during coke production (Boffetta et al., 1997; Simonich et al., 2011). While PAHs have been produced throughout history the modern use of fossil fuels has greatly increased their production (Guo et al., 2006) and have led to many of the current environmental contamination concerns related to PAHs. The production from these pyrogenic sources has led to the increasing build up and concentration of PAHs in the environment as POPs, causing problems with contamination effecting natural resources and the health of people consuming fish and other wildlife from these natural resources.

The PAHs produced during pyrogenic processes absorb to the particulate matter produced during combustion and to particulates in the air. Once in the air the contaminated particles will settle in the environment on the ground, buildings and plants in the area as well as directly into water bodies. Research by Simcik et al (1996) revealed the majority of PAH contamination entering Lake Michigan came from atmospheric emissions created during the burning of coal for coke and steel production. The particles are then transported with rain fall or other runoff into storm drains, ditches, streams and rivers. Once PAHs have been transported to bodies of water they partition into the organic matter associated with the sediment or suspended solids in the water column (Ghosh et al., 2000). Modern lake sediment contamination has been shown to be highly

correlated with urban sprawl and the amount of vehicular traffic that occurs in the area, indicating that some modern PAH contamination comes from the operation of vehicles and the use of roads PAH act as POPs in the environment due to their high organic partitioning and low solubility (Ghosh et al., 2000). PAH octanol-water partitioning (K_{ow}) coefficients range from 3.3-6.2 (ter Laak et al., 2006). Large K_{ow} will cause the majority of PAH to be strongly bound to the sediment but, once PAHs have partitioned into carbonaceous material they will release low, but potentially toxic, concentrations into the sediment pore water and water column that should persist over long time periods.

The toxicity of PAHs in contaminated sediment has been shown to affect benthic organisms, fish and other wildlife. In the EPA (1998) Contaminated Sediment Remediation Strategy PAH contaminated sediments and waters were found to cause tumors and fin rot in fish. Many studies have shown the toxic effects of PAHs on benthic organisms and have been documented in many different locations. The Agency for Toxic Substances and Disease Registry PAH toxicology profile reports that many PAHs have been shown to be carcinogenic in animals, benzo(a)pyrene is carcinogenic to humans and others are likely carcinogenic (ATSDR et al., 1995). Other studies attest to PAH contaminated sediments having possible genotoxic effects (White, 2002) and many examples of mortality occurring in PAH contaminated sediments have been documented.

To reduce the impact of these contaminated sediments on the natural resources, many agencies have released sediment quality guidelines to determine what sediments require remediation and which sediments are not significantly impacted by PAHs. Sediment quality guidelines, as seen in Table 1.1, are usually related to sediment concentrations and include several different types of values such as: screening level

concentrations, effects range low, effects range medium, threshold effects level, probable effects level, low apparent effects threshold, high apparent effects threshold, among other specified levels (Fisher et al., 2011; Swartz, 1999; U.S. Environmental Protection Agency, 2003). The guidelines cover a range of metrics from sediment levels that show measurable build up in organisms (screening level concentration (SLC)), to sediment levels which caused toxic effects to organisms in a large data sets of contaminated sediments (effects range low (ERL) and effects range medium (ERM), threshold effects level (TEL), probable effect level (PEL), and high apparent effects threshold (HAET)). These guidelines apply to many individual PAHs as well as mixtures of PAHs.

Table 1.1: PAH Sediment Quality Guidelines (µg/g organic carbon) (adapted from Swartz 1999)

PAH	ERL	ERM	TEL	PEL	SLC	LAET	HAET	EqP	Sim PAH	Sum PAH
Naphthalene	16	210	3	39	41	210	270		13	71
Acenaphthylene	4	64	1	13	5	56	130		3	15
Acenaphthene	2	50	1	9	6	50	200	230	4	23
Fluorene	2	54	2	14	10	54	360		17	90
Phenanthrene	24	150	9	54	37	150	690	240	29	155
Anthracene	9	110	5	24	16	96	1300		21	114
Low Molecular weight PAH	57	368	21	153	115	616	2950		87	468
Fluoranthene	60	510	11	149	64	170	3000	300	69	371
Pyrene	66	260	15	140	66	260	1600		90	481
Benz(a)anthracene	26	160	7	69	26	130	510		21	111
Chrysene	38	280	11	85	38	140	920		31	169
Benzo(b)fluoranthene	32	188	7	71	32	160	445		33	180
Benzo(k)fluoranthene	28	162	6	61	28	160	445		29	155
Benzo(a)pyrene	43	160	9	76	40	160	360		33	179
High Molecular weight PAH	293	1720	66	651	294	1180	7280		306	1646
Total PAH	350	2358	87	804	409	1796	10230	211	393	2114

The variation in guidelines, display the wide variety of standards available for estimating sediment toxicity as well as how difficult it is to describe the toxicity of sediment. Each individual PAH may have a guideline to follow. Also, in most cases, PAHs are present in varying mixtures which lead to more complicated sediment quality guidelines.

Currently, the EPA uses a model to estimate sediment toxicity which assigns toxicity values to PAHs depending on their pore water concentrations (U.S. Environmental Protection Agency, 2003). Pore water concentrations are used because they are closely related to chemical activity, which is a much better indicator of the chemical bioavailability. The more bioavailable a chemical is the more likely it is to accumulate in organisms. If the sum of toxicities contributed by each PAH is greater than one then the sediment is considered toxic. The major problem with this method is that pore water concentrations are usually estimated by assuming certain partitioning behavior based on the PAH's interactions with organic material (Swartz, 1999; U.S. Environmental Protection Agency, 2003). This partitioning behavior, however, is different depending on the characteristics of individual sediments and is not accurately estimated using the recommended method. This results in a gross overestimation of the toxicity of sediments, sometimes up to 3 magnitudes of order above actual toxicity (Hawthorne et al., 2007).

In order to correct the previously mentioned challenge with estimating PAH pore water concentrations, efforts to directly measure pore water concentrations of PAHs have been developed to measure the bioavailable portion of PAHs in sediment (Gschwend et al., 2011; Lu et al., 2011). Results from these measurements show a much better

correlation with actual toxicity in the sediment and highlight the need for innovative contaminated sediment measurement techniques to evaluate PAH concentrations.

1.3 PAH CONTAMINATED SEDIMENT REMEDIATION STRATEGIES

Current methods for the treatment of these contaminated sediments include dredging, capping and in-situ amendment treatments. Each method has advantages and disadvantages. While dredging has been shown to effectively remove volumes of contaminated sediment from a river or lake bottom, several issues make treatment with dredging ineffective in many cases. These issues include: the difficulty of characterizing sites and determining the extent of contamination for removal, predicting possible transport and suspension during and after treatment and determining the effectiveness of treatment (Francingues et al., 2008). Dredging alone has been shown to reduce the abundance and diversity of benthic organisms at sites, damaging fragile ecosystems. These reductions may replenish in months (Van Dolah et al., 1984) or may take years to recover to natural levels (Boyd et al., 2005). Environmental dredging may be an ideal treatment for some contaminated sediment sites. However, in many cases other remediation strategies would be more applicable for the wide range of sites where dredging is not ideal. Along with in-situ remediation alternatives, advances in in-situ assessment approaches are needed to improve all aspects of sediment treatment.

A novel alternative for the treatment of contaminated sediment involves mixing the sediment with amendments in-situ. Amendments may be used to degrade or sequester contaminants to lower bioavailability to benthic organisms and decrease chemical migration into the water column. This method of treatment will reduce the bioavailability of contaminants to benthic organisms in the sediment and act as a barrier

to contaminants migrating up into the water column (Ghosh et al., 2011). The amendments may perform remediation through chemical reaction, sequestration, or enhancing biodegradation (SERDP and ESTCP, 2004). In Fahrenfeld et al (2012) the biodegradation of TNT was enhanced through the mixing of lactate, ethanol or natural organic matter in the sediment to promote reducing conditions. In sediments with metal contamination, amendment with apatite can precipitate metals, eliminating their bioavailability.

Many HOCs can be treated by amending the contaminated sediment with activated carbon or other carbonaceous material. HOCs such as PAHs and PCBs tend to partition into organic and black carbon material such as soot and coal derived particles in sediments(Ghosh et al., 2000). When in the presence of black carbon in sediments the bioavailability of HOCs tend to decrease dramatically compared to the bioavailability of HOCs bound to normal organic material in sediment (Gustafsson et al., 1996; Lohmann et al., 2004). This observation inspired the idea for activated carbon to be used as an in-situ treatment for HOCs. Activated carbon has a large specific surface area and low specific activity coefficient that enhances HOC adsorption, reducing the bioavailability to exposed organisms and decreasing observed bioaccumulation and toxic effects of HOCs (Millward et al., 2005; Paine et al., 1996; Tomaszewski et al., 2007). Activated carbon has been shown to be an effective treatment for PCBs and PAHs in both laboratory and pilot scale tests. PCBs have been significantly reduced in pore water and benthic organisms for several years at Hunters bay in San Francisco where AC was applied in 2006 (Ghosh et al., 2011)

Current amendment placement options for contaminated sediment include the use of a rototiller to mix AC placed on the surface of contaminated sediment during low water periods and through underwater mechanical mixing of AC placed on the surface of sediment using tilling equipment placed on a mechanical arm (Cho et al., 2009,Beckingham & Ghosh, 2011). Current techniques of *in situ* amendment placement may have limited applications due to the difficulty in reaching depths and the high rate of mechanical mixing inciting mortality in benthic organisms. Another technique for administering *in situ* amendments include using natural bioturbation of benthic organisms to mix amendments placed on the sediment surface. This method has a very low impact on the benthic organisms but may take several months for amendments to be well mixed with shallow sediments. Methods to reach greater depths are desirable.

Capping is an *in situ* method for remediating contaminated sediment sites. Capping is a process where contaminated sediment is covered in one or more layers of material that inhibits the transport of pore water and contaminants to the clean overlying sediment, stabilizes contaminated sediment to prevent resuspension, and separates contaminated sediment from benthic organisms (U.S Environmental Protection Agency, 2005). These capping materials can range from a combination of sand and clay to reactive materials or reactive mats that actively retard the transport of contaminants and can improve environmental conditions for benthic organisms (Reible, 2011). The long term integrity of the capping techniques must be considered for each specific site.

Capping contaminated sediments effectively reduces the release of contaminants to the water column, prevents migration to clean overlying sediment and creates a contaminant free environment. Appropriately designed caps may last for years (Murphy

et al., 2006). While capping appears to be an effective technology it is still undergoing pilot scale testing and there are some issues with its implementation in some cases. The river bottom may not allow for placement of a cap due to the following conditions: elevations, river traffic or flow conditions which may erode the cap, upwelling of contaminated water into the river may lower the life of the cap and the deposition of contaminated sediment on top of the cap may negate the benefits provided by the cap in the first place. Quadrini et al (2003) reports using in-situ capping to successfully stop the exposure of contaminated sediments to organisms, even though some cap erosion did occur during unexpected environmental conditions on the Grasse River. Capping requires long term monitoring of sediment contaminant migration to ensure effective continued treatment from the cap. Monitoring treatment with caps requires methods with minimal cap disturbance that can evaluate PAH concentrations over the depth of the cap to observe migration of contaminants through the cap.

While dredging removes volumes of contaminated sediment from a river or lake bottom there are several issues that may make treatment with dredging ineffective or undesirable. These issues include: the difficulty of characterizing sites and determining the extent of contamination for removal, predicting possible transport and suspension during and after treatment, and determining the effectiveness of treatment (Francingues et al., 2008). Also, dredging alone has been shown to reduce the abundance and diversity of benthic organisms at sites. These reductions may replenish in months (Van Dolah et al., 1984) or may take years to recover to natural levels (Boyd et al., 2005). Dredging essentially removes the existing benthic community, which in many cases is the target for protection.

Dredging can resuspend contaminants in sediments, depending on the type of dredging. Hydraulic dredging methods (sediment pumped from the river bottom in a slurry) usually results in less resuspension than mechanical dredging methods (sediment collected and lifted out of the water body). Hydraulic dredging has been estimated to result in approximately a 0.7% dry weight loss of sediments to resuspension while mechanical dredging results in an average loss of 2.1% (Anchor Environmental CA, 2003). Resuspension can be highly variable and transports contaminants downstream. Resuspension of sediments has been shown to result in increased bioaccumulation in the water column and transport of sediment contaminants during dredging operations (Bocchetti et al., 2008).

Dredging requires the transport and disposal or treatment of the contaminated sediment and any water collected during dredging after it has been removed from the water body. The transport is often over great distances or in off shore disposal impoundments. The types of ex-situ treatment often used for contaminated sediments include bioremediation, chemical treatment, extraction or flushing, stabilization, and thermal oxidation (U.S Environmental Protection Agency, 2005). The additional transport and treatment adds to the cost and difficulty in performing environmental dredging. The drive for cost effective and sustainable treatment has led to the current desire for in-situ treatment options.

1.4 PAH CONTAMINATED SEDIMENT DETECTION METHODS

Detection of PAHs in contaminated sediment traditionally has been performed using whole sediment extraction. These sediment concentrations are then used to estimate sediment toxicity based on inferred pore water concentrations or compared to

previous sediment toxicity data sets (U.S. Environmental Protection Agency, 2003). Research has shown large over estimations of sediment toxicity due to differences between lab derived sediment-organic partitioning coefficient and actual partitioning coefficients (Hawthorne et al., 2007). The difficulty of estimating the actual in-situ sediment-pore water partitioning coefficients and the difficulty and large solvent requirements for sediment PAH extractions has led to the development of new methods aimed at directly measuring pore water concentrations. The direct measurement of pore water concentrations extracted from sediment also has some limitations. Detection limits are high due to the limited solubility of PAHs and due to the small volume of pore water that can be easily extracted from extracted sediment. Also, evaluation of pore water concentrations over a depth can be difficult because it requires separate extractions of smaller volumes of pore water from subsamples of a sediment core. Some extraction techniques, such as liquid-liquid extraction, to concentrate PAHs in the pore water may use significant amounts of solvent.

One of the most promising methods developed, so far, for measuring pore water concentrations uses passive sampling techniques in which pore water is equilibrated with a material into which PAHs will partition. The mass of PAHs concentrated into the passive samplers can then be used along with pre-determined partitioning coefficients or specific activity coefficients to calculate sediment pore water concentrations or chemical activity. Many of these passive sampler detection methods can be used in-situ which can allow for more accurate estimations of in-situ distributions and toxicity of PAHs.

In whole sediment extractions sediment cores are removed from sediment. Subsamples of the sediment are then subjected to extraction methods such as soxhlet

extraction, ultrasonic extraction or other techniques. Also, samples may be cleaned up using solid phase extraction before analysis (Lau et al., 2010). These methods tend to require large volumes of sediments to achieve detection levels along with the consumption of toxic solvents for use in analysis and require complex steps to complete. In the measurement of PAH contaminated sediments it has been observed that toxicity calculations based on total sediment concentrations have displayed a gross overestimation of sediment toxicity, over estimating between 100 and 1000 times the actually sediment toxicity (Hawthorne et al., 2007). This has resulted in a need for the development of pore water measurement techniques.

Pore water concentrations have been shown to be a much better indicator of local chemical activity/bioavailability/toxicity in sediments for HOCs. Methods to measure the pore water concentrations of PAHs and other HOCs include the manual extraction and analysis of pore water from sediment cores, the placement of instruments into the sediments to slowly collect sediment pore water, and the use of passive samplers which are able to selectively accumulate HOCs while being exposed to contaminated pore water and sediment. Manual extraction may be performed *in situ* (Interstate Technology & Regulatory Council, *2005)* or *ex situ* (Hawthorne et al., 2007). After the pore water has been collected the pore water may be analyzed through extraction techniques appropriate for the contaminant being measured.

ITRC defines passive sampling as "any sampler that is able to acquire a sample of a discrete location or interval in a well, without the active transport or purge technique associated with pump or purge technique"(Interstate Technology & Regulatory Council, 2005). These samplers allow for the in-situ measurement of contaminated sediment pore

waters while avoiding complications and small sample sizes associated with manually extracted sediment pore water or poorly calculated estimates based on sediment concentrations.

Passive sampling for PAHs and other HOCs works by exposing a material with a high affinity and selectivity for the contaminant in question to contaminated sediment. The material will then equilibrate with HOCs in the local pore water concentrations. Once the sampler has been exposed it can be removed and the mass of contaminant in the sampler can be extracted for analysis. Based on predetermined partitioning coefficients in-situ pore water concentrations can be calculated. These methods include exposing SPME, polytheylene, POM, and PDMS plastic in a variety of forms to contaminated sediment (Bao and Zeng, 2011; Namieśnik et al., 2005; Oen et al., 2011).

Measuring pore water concentrations with passive sampling requires information about the uptake of the contaminant into the SPME fiber. Each chemical's partitioning coefficient needs to be determined as well as equilibration information. Depending on the tactic for measuring the contaminant, either the equilibration time for the contaminant to completely partition into the passive sampler needs to be known or the kinetics of the contaminants uptake into the sampler must be known. The equilibration time can simply be used to determine the required passive sampler exposure time. An understanding of the kinetic uptake of contaminants into the sampler is required to reduce sampler exposure times (Vrana et al., 2005). Reductions in sampling times are achieved by using passive samplers that have been previously equilibrated with performance reference compounds. Performance reference compounds (PRCs) are similar compounds to the contaminant being measured that, when pre-loaded into passive sampler, will desorb into

the sediment at a similar kinetic rate as the contaminant partitions into the sampler (Booij et al., 2002). With proper modeling of the kinetic uptake, sampling time can be significantly decreased by using the amount of PRC desorption to estimate the uptake of contaminant into the passive sampler.

1.5 SOLID PHASE MICROEXTRACTION

Solid phase microextraction (SPME) is a passive sampling method developed by Arthur and Pawliszyn (1990). The most common application exposes a fused silica core fiber covered with a polymer coating, essentially a fiber optic cable, to a chemical in a solution. The chemical then equilibrates with the fiber coating and the surrounding water. The fiber can then either have the chemical desorbed into a GC for detection or it may be extracted with a solvent for use with an HPLC (Chen and Pawliszyn, 1995). Chemical pore water or vapor concentrations can then be calculated based on the resulting analysis. The GC method of extraction is better suited for volatile compounds as the GC relies on volatility of the compounds, while the HPLC is better suited for semi-volatile and non-volatile chemicals. SPME has been used to measure compounds in various matrices such as: body fluids, food items, and surface and ground water (Prosen and Zupančič-Kralj, 1999). SPME has been shown to be an effective method for extracting organic chemicals from complex matrices while using less solvent than traditional extraction methods. The thin coating and relatively large surface area to mass ratio of the SPME makes the kinetics of equilibration more rapid than other passive sampling devices. SPME requires appropriate time for equilibration to take place to measure contaminants. Equilibration times in SPME fibers will vary based on the

chemical being measured, the matrix the SPME fiber is exposed to, and environmental conditions.

Ex-*situ* SPME measurements may be performed with a variety of techniques. Negligible-depletion SPME measurements are performed when enough freely available contaminant resides in the water or head space volume to replenish without the SPME fiber providing a significant reduction in free concentrations. The sampling volume required is dependent upon the partitioning coefficient between the chemical being measured and the fiber material. Acceptable percent reductions of chemical in the sample range from 1 to 10 percent depending on the source (Heringa and Hermens, 2003).

Another method known as matrix SPME uses the original matrix to replenish chemical concentrations in the sample volume, either aqueous or head space. Matrix SPME allows for pore water or head space concentrations to decrease but must allow time for the chemicals to redistribute from the matrix. Matrix SPME allows for much smaller sample volumes to be used because, usually, the SPME fiber has similar partitioning coefficients to the matrix being sampled which means that instead of a hundred or a thousand times the SPME fiber volume required for the negligible depletion of the matrix SPME method may only require ten or a hundred times the SPME fiber volume. Equilibration times may be extended in matrix SPME because not only must the SPME equilibrate with the water or headspace but the water or head space must equilibrate with the matrix as well (Heringa and Hermens, 2003).

When performing passive sampling in such a complex matrix the effect of DOC is an important consideration. In Haftka et al. (2008) it was determined that DOC enhanced the kinetic uptake of several PAHs in SPME fibers. The DOC was able to reduce equilibration times by increasing diffusion rate of PAH through the unstirred boundary layer, though the overall partitioning coefficients between the PDMS and PAHs appeared to stay constant. In Jahnke & Mayer (2010) measurements of several HOCs were performed under exposure to different DOCs using SPME fibers. It was determined that none of the complex matrices caused large differences in measurements with control fibers with slight elevations being contributed to lipid layers developing on the fiber and binding of proteins on the fiber surface. These studies show that DOC may affect equilibration times but shouldn't interfere with *in situ* or matrix SPME measurements.

In situ SPME techniques main limitation is that the method is dependent on equilibration between the SPME sampler and the soil or sediment. SPME equilibration may require days to months depending on the chemical being sampled and environmental conditions. *In situ* conditions expose the SPME fiber to harsher conditions and may require a protective device to prevent damage to the SPME fiber occurring during placement and extraction. Examples of *in situ* SPME include Maruya et al (2009) where a SPME fiber placed in a perforated copper pipe was covered with glass microfilter was placed into contaminated sediment to measure a variety of HOCs. In Condor et al (2003) SPME fibers were placed into envelopes made with sheets of metal filters to protect the SPME fibers. The envelopes containing SPME fibers were placed into contaminated sediment to measure TNT pore water concentrations and compared well with traditional extractions methods. In Cornelissen et al. (2008) SPME fibers along with other passive

samplers were suspended in water above a contaminated sediment site. Using this process they were able to determine that PAH concentrations above the sediment were greater than pore water concentrations indicating that PAHs were migrating from the sediment into the overlying water.

Several different methods of measuring PAHs using SPME have been developed. These include both *in situ* and *ex situ* methods with different types of SPME fibers being used. *Ex situ* methods developed so far include those used by Hawthorne (2008) which use both traditional SPME fibers placed on a metal rod and fiber optic cable with PDMS coatings. In either method, SPME fibers were exposed to extracted sediment submerged in samples for equilibration, usually assisted with mixing, or sonication to reduce *ex situ* equilibration times. Other studies using SPME fibers have been performed with similar procedures (Doong and Chang, 2000; Lu et al., 2011; Maruya et al., 2009; Mayer et al., 2000; van der Wal et al., 2004).

A method for *in-situ* SPME developed using lengths of SPME fibers placed in contaminated sediment protected inside a perforated metal tube was developed by Reible et al (2008). Using this method PAH concentration profiles with depth in contaminated sediment that had been covered with a cap were measured. Investigators were able to observe differences between the contaminated sediment and the uncontaminated cap indicating that this method is an effective method for *in-situ* measurements of the treatment of contaminated sediments using caps. *In-situ* equilibration at 25˚C took 1.55 days for phenanthrene, 2.83 days for chrysene, 11.39 days for benzo(b)fluorene and 16.07 days for benzo(a)pryene. PDMS-water paritioning coefficients measured for a SPME fiber with a 100 µm diameter glass core with a 30 µm thick coating of PDMS at

25˚C were 3.74 for phenanthrene, 4.27 for pyrene, 4.61 for chrysene, 4.66 for benzo(a)anthracene and 4.64 for benzo(a)pyrene.

SPME fibers, as they are currently used, are mostly limited to studies in the lab. While some *in situ* methods have been developed recently, most do not exploit the ability of disposable SPME fibers to sample contaminants over a depth profile. Currently, the only methods for taking *in situ* HOC pore water concentrations over depth profiles in sediment is through the use of POM passive samplers secured on a metal stand or through the use of a disposable SPME fiber placed into sediment. *In situ* SPME fibers have not been previously used to measure the impact of AC treatment on PAH contaminated sediments.

Alternative treatments to dredging contaminated sediment, such as capping or AC amendment, require monitoring to ensure effective treatment coverage and continued performance. Alternative methods of treatment act to isolate contaminated sediments below treated layers. Monitoring treatment performance requires methods that can measure contaminant profiles with depth with minimal disturbance to the treated sediment or cap. The development of simple methods to measure the impact of AC placement in contaminated sediment will play an important role in making alternative sediment treatments a viable strategy in the remediation of contaminated sediment.

2. GOALS AND OBJECTIVES

The major goal of this project was to develop a method, using *in-situ* SPME samplers, to assess PAH pore water concentration profiles over variable depth in contaminated sediment. Methods developed were assessed in measuring the effectiveness of activated carbon amendment in contaminated sediments treated with novel water jet technologies. To accomplish this goal, specific objectives were established as follows:

2.1 OBJECTIVE ONE: MEASUREMENT ERROR QUANTIFICATION

Determine a variability of PAH depth profile measurements with long fiber SPME methods.

Hypothesis

Less than a 10% relative standard deviation will be observed with depth when depth profiles are measured on well mixed aqueous solutions of PAHs.

Experimental approach

SPME fibers were placed into aqueous solutions of PAHs which were kept at constant concentrations by dosed silicone o-rings which were suspended in the water. Equilibration curves were developed from multiple measurements with SPME fibers exposed for different time periods. This allowed for the error associated with this measurement to be determined as well as kinetic equilibration curves to be developed. SPME fibers were also placed in aqueous solutions while in SPME samplers to test how the SPME sampler may affect measurements in an aqueous environment.

2.2 OBJECTIVE TWO: ERROR SOURCES AND QUANTIFICATION

Evaluate sampling and analysis methods to quantify possible sources of error and variability in measurements.

Hypothesis

Minimal error is introduced during HPLC analysis, solvent extraction steps , and during the SPME sampling process.

Experiment 1

Data from repeated measurements was used to evaluate the error introduced during HPLC analysis.

Experiment 2

Spiked aqueous concentrations of PAHs were measured with SPME fibers to calculate the error induced by the use of SPME samplers.

Experiment 3

SPME samplers were placed into well-mixed contaminated sediment to determine error introduced over depth in uniform PAH concentrations.

2.3 OBJECTIVE THREE: MEASURING ACTIVATED CARBON PLACEMENT

Evaluate the impact of the placement of powdered activated carbon into contaminated sediments by observing changes in PAH pore water concentrations before and after amendment of activated carbon.

Hypothesis

The approximate distribution of activated carbon can be found by measuring the decrease in pore water concentrations before and after activated carbon amendment and then comparing those decreases with pore water concentrations of contaminated sediment mixed with different portions of activated carbon.

Experiment

Different amounts of activated carbon were mixed with contaminated sediment. Each of these treated contaminated sediments was then measured with in-situ SPME sampling. Based on the treatment provided by each amount of activated carbon an estimate of the amount of activated carbon placed into the contaminated sediment was determined.

PAPER

I. *IN SITU* SPME FOR DEPTH PROFILING OF PAHS IN SEDIMENTS TREATED WITH ACTIVATED CARBON

Ryan D. Stringer, Joel G. Burken, Andrew C. Elmore, Danny D. Reible

R.D. Stringer, J.G. Burken, C. Elmore,

Missouri University of Science and Technology, 309 Butler Carlton Hall 1401 N. Pine Street Rolla, MO 65409

D.D. Reible

University of Texas at Austin, 301 E. Dean Keeton St. Stop C1786 Austin, TX 78712-1173

Corresponding Author

Ryan D. Stringer

Tel: (573) 341-6670

e-mail: rdsqkc@mst.edu

Abstract

Novel and efficient methods to measure the bioavailability of hydrophobic organic contaminants (HOCs) in contaminated sediments will play an important role in the acceptance of alternative sediment remediation strategies. In this project, solid phase microextraction (SPME) fibers, protected in perforated steel tubes, were used as *in situ* passive samplers to measure the treatment of activated carbon (AC) in polycyclic aromatic hydrocarbon (PAH) contaminated sediment. Contaminated sediment was treated with two modes of AC waterjet amendment. In the first treatment, a single 2-min injection was shot into the center of a test vessel and in the second treatment, multiple 7-sec injections in a grid were placed in sediment. In the single injection no treatment was observed 5 cm away from the injection, while at 2.5 cm greater than 90% removal of PAH pore water concentrations were observed. In the multiple injection experiment greater than 90% PAH pore water reductions were observed throughout the test vessel. Highly contaminated and less contaminated sediments were mixed with 0-5% AC by weight to develop AC treatment curves. Over 99% reduction in PAH bioavailability was observed in the less contaminated sediment at 3% AC while 99% removal was never reached even at 5% AC addition in the highly contaminated sediment. Clear treatment curves were observed for both contaminated sediments, though they were very different. *In situ* equilibration times were 120, 215 and 250 hours for phenanthrene, pyrene and benzo(a)Anthracene respectively. The results show that *in situ* SPME is a viable method to observe AC treatment and evaluate reductions in bioavailability.

Introduction

Contaminated sediment is a major problem in the United States and globally. The U.S. has an estimated 1.2 billion cubic yards of significantly contaminated sediment (U.S. Environmental Protection Agency, 1998) resulting in fishing advisories for more than 18 million lake acres and 1.4 million river miles (U.S. Environmental Protection Agency, 2009). The US Navy estimates that remediation of contaminated sediment under their control alone will cost more than a billion dollars (SERDP and ESTCP, 2004). Traditionally contaminated sediments have been remediated through environmental dredging, removing contaminated sediments from the area and treating them or disposing them elsewhere. Dredging, however, has some significant drawbacks such as: the resuspension of contaminated sediments resulting in increased bioaccumulation and potential exposure downstream (Anchor Environmental CA, 2003; Boyd et al., 2005), the extraction of benthic communities (Boyd et al., 2005; Van Dolah et al., 1984), and the large cost of removing contaminated sediment from a site (Bridges et al., 2008). These limitations encourage the use of alternative remediation methods to replace or supplement dredging.

Alternatives to dredging include the placement of *in situ* caps and *in situ* amendments. While these methods may not destroy or remove the contaminants they can act to limit bioavailability vectors of ecological exposure. Capping of contaminated sediment may involve several different techniques, but generally a cap is made up of a confining layer, usually a low darcy velocity clay possibly mixed with a reactive amendment, a layer of sand for further separation and the placement of clean sediment (U.S Environmental Protection Agency, 2005). The cap physically separates

contaminated sediment from the water column, provides clean sediment for benthic organisms to repopulate, prevents the resuspension of contaminated sediment and provides a buffer layer slowing the migration of contaminants. Capping may not work effectively in areas where flow patterns or ship traffic may erode the cap or where the upwelling of groundwater can compromise the cap.

The *in situ* amendment of contaminated sediment is a novel technique for treating contaminated sediment. Amendments can reduce the chemical activity and bioavailability by sorption or degrade the contaminant or enhance biodegradation (SERDP and ESTCP, 2004). Adsorbent amendments result in reduced risk to benthic organisms and act as a barrier to retard the migration of contaminants into the water column (Ghosh et al., 2011). *In situ* amendments provide a cost effective alternative to both dredging and capping while providing *in situ* treatment options where capping is not possible.

Activated carbon (AC) is the most studied amendment for hydrophobic organic contaminants (HOCs) such as PCBs or PAHs. Laboratory and field tests show effective treatment of HOCs with reductions in pore water concentrations usually greater than 90% (Hale et al., 2010) and significant reductions in the bioaccumulation to various benthic organisms (Ghosh et al., 2011; Millward et al., 2005). The effective dose of activated carbon to contaminated sediment occurs at around a 3% by weight addition and the addition of activated carbon has very few detrimental effects to benthic organisms and generally improves the health of organisms in contaminated sediment (Kupryianchyk et al., 2011). Current methods for placing activated carbon into contaminated sediment include using mechanical incorporation either in shallow tidal flats or suspended on track

hoes placed on barges to mix in activated carbon slurries pumped into the mixing units, or through liquid injections of slurries directly into sediment (Beckingham and Ghosh, 2011; Redell et al., 2011).

Assessing sediment contamination poses unique challenges, as distribution can be highly heterogeneous in three dimensions in a media that is difficult to access. *In situ* treatment options offer new challenges as these dredging alternatives do not physically remove the contaminants, placing a higher burden of proof on monitoring *in situ* to ensure proper treatment. Traditional sampling methods to measure bioavailaibility utilize sediment cores or *in situ* biological exposure which require extensive labor, extraction and cleanup and may not provide appropriate resolution with depth. New methods to measure remediation are required which may reduce the sampling work load and the disturbance of treated areas while allowing for more samples to be obtained. Analysis techniques that can provide noninvasive, high resolution measurements of sediment contaminant profiles are required (SERDP and ESTCP, 2004).

Bioavailability assessment in the environment is often performed either through direct exposure of the organisms to contaminated sediment or through the use of models to predict risk based on the extraction of sediment contaminants . The use of live organisms for testing the effects of contaminated sediments can directly measure bioavailability, though measurements do vary between different organisms. The tests are, however, difficult to perform considering that organisms must be kept alive during their exposure, exposure must be representative and uptake analysis must be measured by extracting contaminants from the organism's remains (Muijs and Jonker, 2011). These tests require equilibration between the sediment and the organisms and are difficult to

perform, especially in-situ. Such methods with live organisms also do not allow for contaminant bioavailability assessment with depth.

Pore water concentrations are the best indicator of HOC contaminant bioavailability (Hawthorne et al., 2007). For PAHs, the EPA uses ratios of these inferred pore water concentrations to convert individual PAH concentrations into toxicity units to estimate possible harm to organisms (U.S. Environmental Protection Agency, 2003). Using sediment concentrations, the sediment organic content, and contaminant organic partitioning constants, pore water concentrations can be estimated (U.S. Environmental Protection Agency, 2003). Unfortunately, this method for determining sediment toxicity has been shown to be inaccurate causing overestimation of contaminant bioavailability by up to three orders of magnitude (Paine et al., 1996). The overestimation is due to the difference between partitioning between normal organics in the sediment and black carbon materials in the sediment (Koelmans et al., 2006; Paine et al., 1996). Black carbon material partitioning coefficients for HOCs are much greater than other organics, decreasing bioavailable concentrations of HOCs (Brändli et al., 2008). The shortfalls of inferring sediment pore water concentrations from sediment extractions have encouraged the development of new techniques to directly measure HOC pore water concentrations.

Methods to directly measure pore water concentrations have been developed to better estimate PAH bioavailability and to measure the effectiveness of sediment remediation. Pore water measurements include the use of passive samplers such as SPME fibers, POM strips and polyethylene strips. In Heidjen et al. (2009), several different methods for determining PAH bioavailability in sediments were tested. The different methods tested include: the exposure of sediment to organisms, SPME, POM

passive samplers and traditional extraction and through the *in situ* sampling of benthic organisms, and *in situ* SPME. *In situ* tests using organisms correlated best with *in situ* SPME samples and laboratory POM samples. Cornelissen (2008) also found that SPME fibers and POM were able to effectively measure PAH pore water concentrations in situ and were able to reach equilibration within 23 to 63 days for 2-6-ring PAHs. Other methods of directly measuring sediment pore water concentrations include: *ex situ* SPME (Hawthorne et al. 2008), the use of *in situ* SPME fibers to measure TNT contaminated sediments (Conder et al 2003), and the use of peepers to measure less hydrophobic contaminants (Teasdale et al., 1995).

Measuring contaminated sediments that have been treated *in situ* with amendments or capping has been accompanied with the development of innovative sampling techniques. A field site treated with AC in Oen et al (2011) was assessed using POM passive samplers that were placed on metal rods that could be inserted in the sediment to provide a profile of PCB pore water concentrations with depth. Beckingham and Ghosh (2011) present data on controlled *in situ* exposures of oligochaete worms used to observe reductions in PCB bioavailability between 69 and 99% in AC amended sediments. In Cho et al (2009) SPMDs were used to observe a 46-66% decrease in the bioavailability of PCBs in AC treated sediment. Cho also found that after 18 months decreases in *in situ* bioaccumulation of *M. nasuta* were not observed due to the deposition of contaminated sediment due to shallow burrowing. Passive sampling with the capability of profiling contaminant concentrations with depth may have been helpful in confirming these results.

In this paper, a method developed to measure the bioavailability of PCB depth profiles in capped sediments (Lu et al., 2011; Reible et al., 2008) was used to measure the amendment of sediments with waterjet injected AC (Redell et al., 2011). The objective of the research was to develop a method to quickly and easily measure the treatment of activated carbon with depth into contaminated sediment. Accurate measurement of treatment efficiency of *in situ* amendments over depth and area is a necessary assessment tool that could save money, increase the efficiency of treatment, and prevent the need for more expensive solvent intensive sampling and analysis techniques.

Methods and Materials

SPME Sampling

Disposable PDMS SPME fibers used in these experiments were obtained from Polymicro Technologies. Fibers were composed of a 1 mm diameter glass rod core with a 33µm PDMS coating. Samplers to contain the fibers, as seen in Figure 1, were constructed of 1.6 mm thick, 6.35 mm diameter stainless steel tubing. 1-mm diameter holes were placed 1 cm apart on four sides of each SPME sampler using a water-jet. A steel tip was placed into the bottom of each sampler to allow the sample to be easily inserted into sediment and a Teflon cover was placed over each sampler to prevent sediment from falling into the sampler.

SPME samplers were inserted into contaminated sediment and allowed to equilibrate for 7 days. After 7 days the SPME fibers were removed from the sampler, any visible soil residue was rinsed off of the fibers with deionized water and any visible water drops were removed by lightly padding the SPME fiber with a Kimwipe. The SPME fiber was then placed on a glass and scored at 1 cm intervals. Each piece of

SPME fiber was extracted in a 1-ml shell vial with 0.5 ml of acetonitrile (ACN) for a minimum of 200 minutes and analysis was performed using high-performance liquid chromatography (HPLC) coupled with fluorescence detection. PAH concentrations in the ACN were then determined with pre-made external calibration curves.

Fiber concentrations were calculated from the PAH concentrations in the ACN with the sample concentration (C_{sample}), the ACN volume (V_{ACN}) and the volume of PDMS (V_{PDMS}) in each SPME sample (Equation 1).

$$C_{fiber} = \frac{C_{sample} \cdot V_{ACN}}{V_{PDMS}} \qquad \text{Equation 1}$$

Once the fiber concentration is known the pore water concentration can be estimated using fiber-water partition coefficients (K_f) for each PAH, Equation 2.

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

Contaminated Sediment

Contaminated sediment was obtained from a former manufactured gas plant in Centralia, Illinois. A soil analysis showed that the sediment has an organic content of 0.6%, a pH of 7.6 and a water content of 19%. Sediment was collected in 20-L buckets during excavation and held for experiments. Prior to experiments, sediment was mixed in 75 to 80-liter batches for >30 minutes with water added to help homogenize the sediment. The contaminated sediment was then stored in buckets until it was used in various experiments.

HPLC Analysis

The samples taken from the SPME fibers were analyzed on a Waters 600 HPLC system equipped with a fluorescence detector and an auto sampler. Analysis was adapted from EPA method 8310 and was performed under gradient conditions with ACN and milli-q water. Gradient conditions began with 60:40 ratio of water to ACN and switched to 100% ACN over 15 minutes with the total analysis taking 50 minutes. Fluorescence excitation and emission wavelengths were 280 and 389 nm respectively. PAH concentrations in samples were quantified with external standard calibration curves.

Matrix Free Testing

Matrix free testing was performed to observe kinetic uptake and variability in SPME measurements in an environment free of matrix interferences. The experiment was performed in a 2-liter glass reactor filled with deionized water. The water was continuously dosed with PAHs from food grade silicone o-rings that were dosed with Naphthalene, Phenanthrene, and Pyrene as described previously (Smith et al., 2009). The dosed O-rings were suspended in the water on a wire which was looped through the O-rings. SPME fibers were placed into solution through sealable chambers that were placed into the reactor lid. This allowed SPME fibers to be suspended in the solution and removed easily without removing the O-rings and with negligible disturbance. SPME fibers, 8-cm long, were suspended in the solution in pairs and exposed for varying amounts of time to develop equilibration curves and confidence intervals for the SPME measurements.

The RSD was measured by comparing differences in measurements in either well mixed aqueous conditions or homogenized contaminated sediment along the length of SPME fibers. Under well mixed conditions, any error between measurements can be attributed to the method. This allowed the error associated with PAH measurements to be evaluated with and without matrix effects.

AC Treatment Testing

Measuring the effects of AC treatment on contaminated sediment using *in situ* SPME was performed to evaluate impacts of AC treatment levels via *in situ* SPME measurements. Contaminated sediment noted above was mixed with 0.1%, 0.5%, 1.0%, 3.0% and 5.0% by wet weight AC and placed in duplicate 150-mL amber glass jars. DI water was added to fill the jar. SPME samplers 6 cm long were placed into the contaminated sediment with SPME fibers. After exposure for 7 days the SPME fibers were removed and analyzed as noted above to determine porewater concentrations and assess AC reduction of PAH bioavailability.

Contaminated Sediment Column Testing

For several tests, columns of well mixed contaminated sediment were placed into 60 cm tall, 29.5 cm diameter PVC pipes in which the bottom was sealed with the corresponding PVC cap and a standing water layer at least 4 inches deep was placed over the sediment. In each test a batch of well-mixed contaminated sediment was used to fill two or three test columns and each column was covered with aluminum foil maintained at room temperature. SPME samplers were added to each column after treatment was performed.

The first column test was a single injection test comprised of two columns of contaminated sediment. In one of the columns a waterjet was used to inject a single stream of 20% by weight AC and water mixture for two minutes into the center of a column of contaminated sediment. The other column was kept as a control without any treatment. SPME samplers were placed 3.8 and 7.6 cm from the center of each column so comparisons between the treated and control column could be made (Reible et al., 2008).

A second test was performed in which multiple, short-duration injections were performed in contaminated sediment (Redell et al., 2011). Multiple shorter duration injections were hypothesized to result in better AC mixing into the sediment. 54 injections were performed at 2.5 cm intervals in a 15.2 cm by 22.9 cm rectangle within the contaminated sediment column. Following injections, SPME samplers were placed in the center of the injection area, 5 cm from the injection area and 10 cm from the center of injections. The sampler placed 10 cm from the center of injection was placed outside of the injection area. Another column was also kept as an untreated control.

Results and Discussion

Error Measurement

Error measurement results for *in situ* SPME PAH assessment in aqueous and *in situ* scenarios are shown in Table 1. Relative standard deviations were found to be greatest using the *in situ* measurements as expected. Error measured in the aqueous solutions was much lower than those measured *in situ*. The error due to these measurements may be attributed to variation in the length of SPME fiber cut (1.03 cm –

1.1 cm) resulting in 6.5% variation of pore water measurements, variation in the amount of ACN in each vial (pipette error range +/-0.6%) resulting in 1% variation in pore water measurements and variation in the PDMS coating covering the SPME fiber over the length. Increases in *in situ* standard deviation in the data were much larger than in the aqueous measurements. Errors were expected to be due to variable contact with the SPME fibers, however increases in SPME PAH concentrations with depth were observed. Some of the variability in the *in situ* samples may be due to the deposition of sediment inside sampler or from the transport of PAHs inside the sampler. Improved SPME sampler/holders may be needed to improve the precision and decrease variability of *in situ* measurements.

In-situ and Aqueous Equilibration

Measurement of true pore water concentrations with passive samplers can only be determined once the SPME fiber has reached equilibrium with the surrounding pore water and sediment. The equilibration time in passive samplers can range from days to months, depending on the chemical being studied and the passive sampler being used (Bao and Zeng, 2011; Zabiegała et al., 2010) . Equilibration curves for the 1000 µm core-33µm coating SPME fibers developed in this sediment are shown in figure 2 , the single compartment model (equation 3) as seen in Reible et al (2008) was used to model the equilibration using PROC NLIN regression function in SAS (SAS Institute, Cary NC).

$$C_f = C_{f\infty}(1 - e^{-k_e t}) \qquad \text{Equation 3}$$

Equilibration of each PAH was established as the time in which the model concentration reached 99% of $C_{f\infty}$. Results are shown in Table 2, where equilibration was reached 120 – 240 hours in sediment and between 10.2 and 25.6 hours in aqueous solution. Reible et al (2008) found equilibration time for SPME fibers sediment with phenanthrene and chrysene to be 1.55 days and 2.83 days respectively. Equilibration times were longer in this study. The increased equilibration time may be due to differences in sediment, and the SPME sampler arrangement. The equilibration period in the aqueous solution was around 10% of the sediment equilibration time indicating that water-SPME transfer is not a rate limitation for the *in situ* equilibration process and that the contaminant mass transfer rate from the sediment to water is clearly the limiting process and should be further studied. Overall, desorption kinetics are likely sediment specific and should be evaluated in different *in situ* testing as sediment-contaminant interactions are highly variable.

AC Treatment Curve

The results of the variable AC treatment tests (Figure 3) show that sediments with different levels of contamination may behave very differently. In the less contaminated sediment the addition of AC at 0.1% and 0.5% resulted in a slight average decrease though they are not very different from the untreated sediment. Average bioavailability reductions with 0.1% and 0.5% AC addition were 0.04 and 0.13 log reduction respectively. AC additions of 1.0% by weight resulted in a log reduction of 0.88 with Pyrene pore water concentrations dropping to 5.6 µg/L from the initial concentration of 43 µg/L. Treatment at 3% and 5% resulted in greater than 2.3 log reductions in bioavailability. Both reduced bioavailability from the 1% sample, though were not very

different from each other. The measurements show that variable AC treatments could be distinguished for this contaminated sediment using in-situ SPME fibers. Recommended treatment levels of 3-5% by weight of AC noted in literature were adequate to reach 0.88, 1.3 and 1.22 log reductions in sediment pore water concentrations (Beckingham et al., Hale et al., Tomaszewski et al., 2007; Zimmerman et al., 2004). In the highly contaminated sediment no reduction in PAH pore water concentrations at 69 µg/L were observed until the 2% addition of AC in which Pyrene pore water concentrations were 50.9 µg/L. Distinct reductions were also observed at 3, 4 and 5% AC with Pyrene concentrations of 23.2, 3.6 and 0.8 µg/L respectively. The highly contaminated sediment never reached a 2-log removal of PAH and showed higher bioavailabilities than in the less contaminated sediment. Based on these results, SPME measurements of PAH bioavailabilities were able to indicate appropriate AC treatment levels and if target levels in concentration and bioavailability were reached.

Lab-scale Demonstrations

Measurement of contaminated sediments treated with waterjet injected AC was performed in two bench-scale tests. In the single injection test, results show that the pore water reduction of PAHs in the sediment in the 3.8 cm sample are between 2 and 3.5 log reduction. In the sample 7.8 cm from the injection center the log reduction of PAHs in the pore water was negligible indicating that there was little to no removal 7.8 cm from the injection area. This indicates that the single injection was able to treat the sediment with-in 3.8 cm area but somewhere between the 3.8 cm sampler and the 7.8 cm sampler the AC mixing with sediment was not sufficient to reduce bioavailability.

In this scenario the samplers were able to identify both treated and untreated sediments rapidly using *in situ* SPME sampling to determine treatment efficacy.

In another bench scale experiment in Redell et al (2011) contaminated sediment placed in columns as highlighted above was instead treated with multiple short-duration injections of AC. Experimental results showed that more than a 1-log removal of PAHs was observed throughout the treatment, Figure 3. In this instance, the *in situ* SPME fibers were able to measure treatment efficacy outside of the actual area of injection. Considering the equilibration periods noted above, the fibers that were exposed for 7 days were not expected to be at equilibrium for all the PAHs measured Phenanthrene would be at equilibrium while Pyrene and Benzo(a)Anthracene would be at 71% and 60% of equilibrium respectively but they were still able to observe decreases in PAH bioavailability just like the AC treatment tests. They indicated that mixing of the contaminated sediment occurred outside of the injection area unlike the previously mentioned test where an area of untreated sediment was observed outside of the injection area. The use of the *in situ* SPME fibers allowed the reduction of PAH porewater concentrations outside of the actual zone of treatment to be quantified which was not observed in the previous treatment experiment.

Conclusions

In situ SPME sampling was able to measure the efficacy of waterjet AC placement into contaminated sediments at concentrations significant to results given in the literature. The method is able to perform measurements in the same or less time than other passive samplers such as POM at 10 days (Cornelissen et al 2008) or PE at 21 days (Hale et al 2010). In *situ* SPME sampling was able to indicate possible treatment

impacts outside of a zone of treatment in the multiple injection experiment and was able to observe a zone where treatment did not occur in the single injection experiment. This highlights the ability for the method to determine where treatment does and does not occur with spatial resolution.

SPME enables a convenient approach to perform measurements with depth, with samplers that are small and unobtrusive, reducing sediment disturbance and cost. The simplicity of the method should also allow testing at greater spatial density with less time and expense compared to sediment coring throughout a site. Some shortfalls, however, for *in situ* SPME sampling include the requirement to both place and remove SPME samplers for analysis and the required time to wait for equilibration with the sediment. Sediment and contaminant-specific mass transfer limitations cause variability in sampling precision and equilibration periods and such variability should be assessed at individual sites where SPME are deployed. Some changes in PAH concentrations were observed with depth and indicate that further studies on PAH and sediment transport in the samplers may be required to ensure accurate depth profiling.

Acknowledgements

This project could not have been completed without the help of many individuals. Some of the most influential include Honglan Shi, Gregorz Galecki, D. Scott Parker, Aaron Archer, Chris Redell, Grace Harper, and Matt Limmer. Funding for the project was provided by NIEHS and the Superfund Research Program through grants 3R01ES016158 and 5R01ES016158.

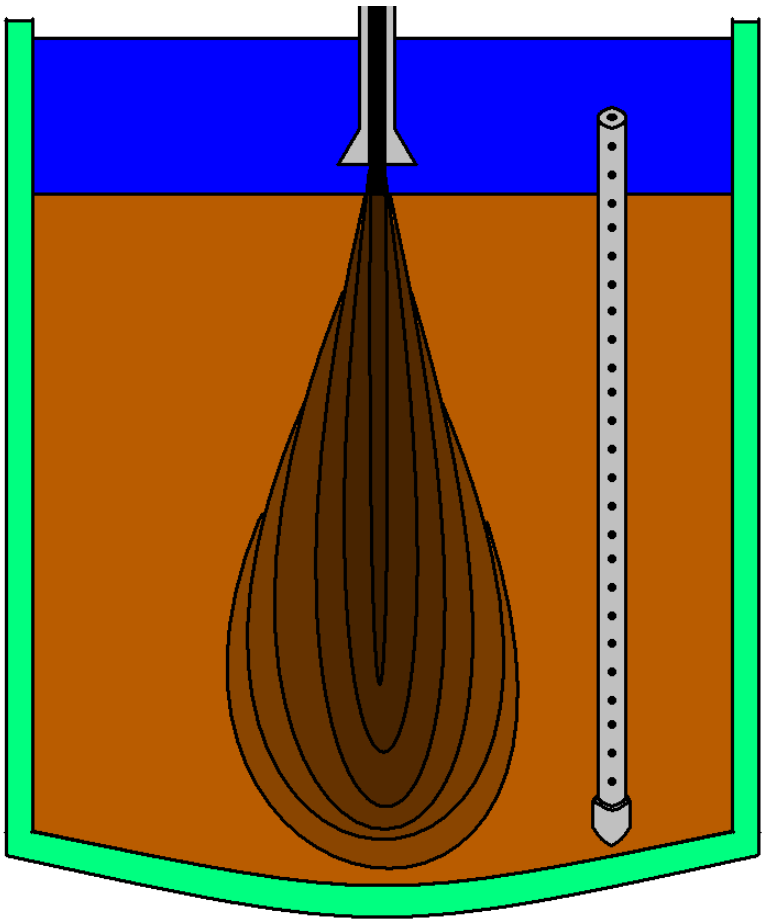


Fig 1: SPME sampler in *situ*. This is a diagram of the SPME sampler placed into contaminated sediment next to an injection of AC into sediment using a waterjet.

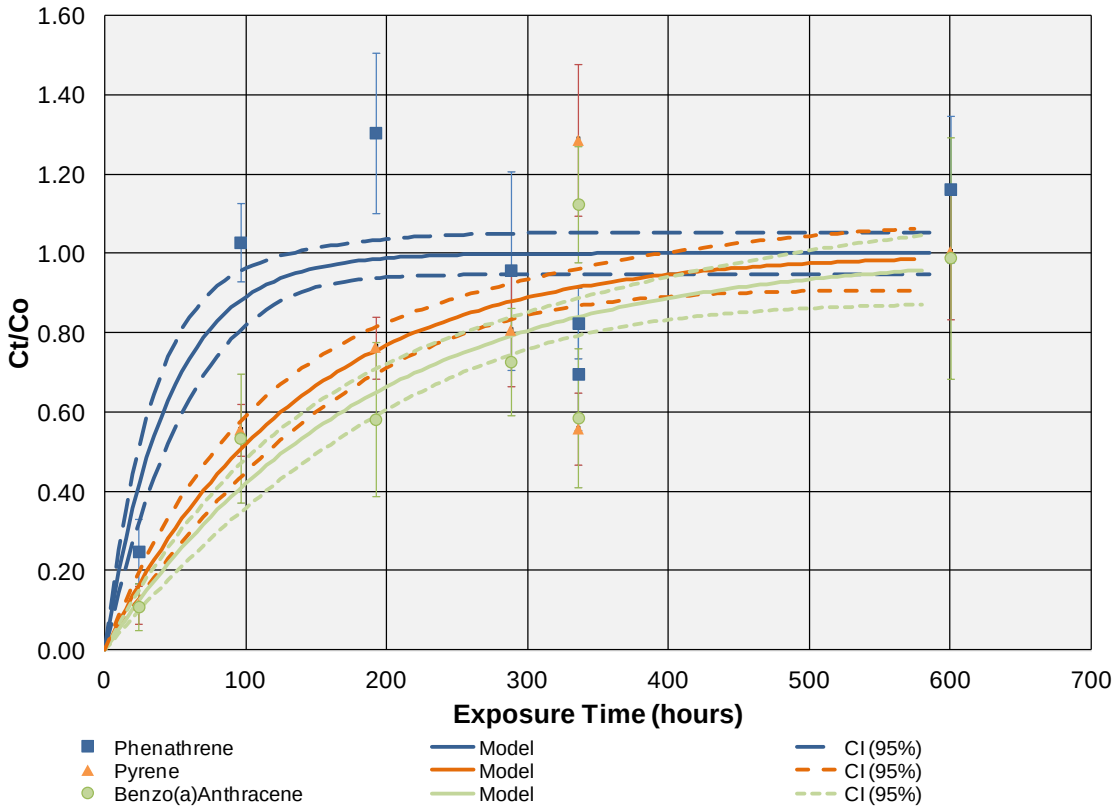


Fig 2: PAH In-situ Equilibration: 30 cm long SPME fibers were placed into a column of PAH contaminated sediment and exposed for up to 600 hours. Values are displayed as the final concentration divided by the concentration at each time period. Equilibration data was modeled with a single compartment model (equation 1) with a nonlinear regression, equation 3, using SAS.

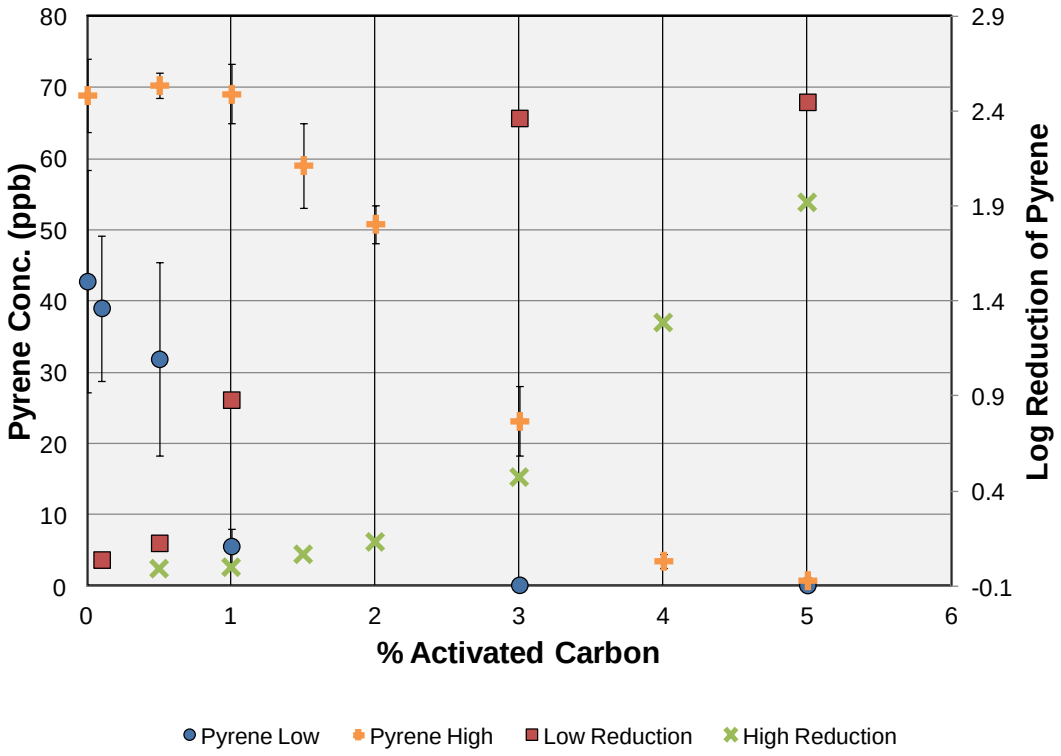


Fig 3: Pyrene pore water concentrations (left) and bioavailability reduction (right) with variable AC additions for two types of contaminated sediment. The highly contaminated sediment is represented with the (X)'s and the plus signs while the less contaminated sediment is represented with the circles and sqares. SPME samplers were equilibrated for 7 days. Two sediments were tested; one sediment having higher PAH levels than another. Similar reductions were observed in Phenanthrene and Benzo(a)Anthracene. (error bars are 95% CI)

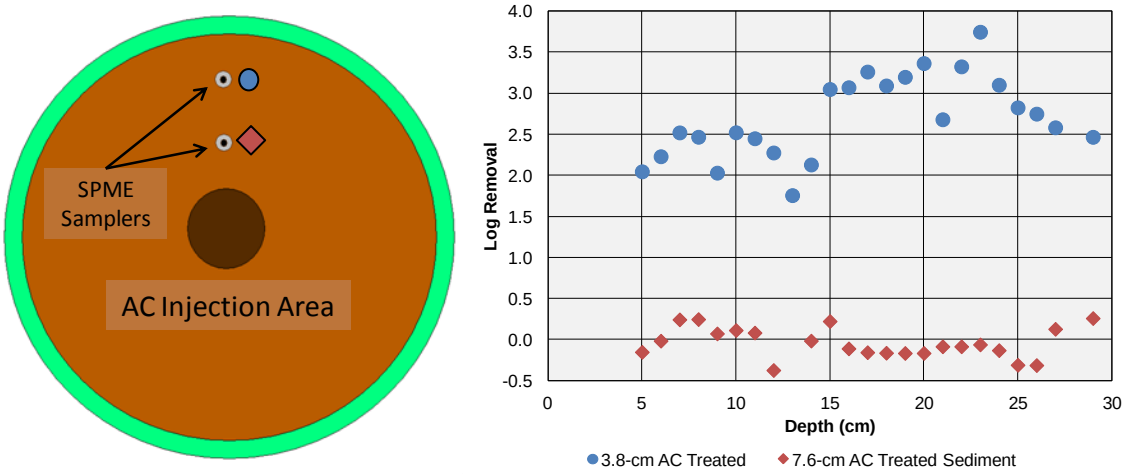


Fig 4: AC efficacy measured with *in situ* SPME in a single injection experiment. The diagram (left) shows the layout of the experiment. 30-cm SPME samplers placed 3.8 and 7.6 cm from the center to equilibrate for 7 days. The graph (right) shows the log reduction in pyrene pore water concentrations for both samplers placed in the column. Log reductions were calculated by comparing measurements with those in a control column that was not treated with AC.

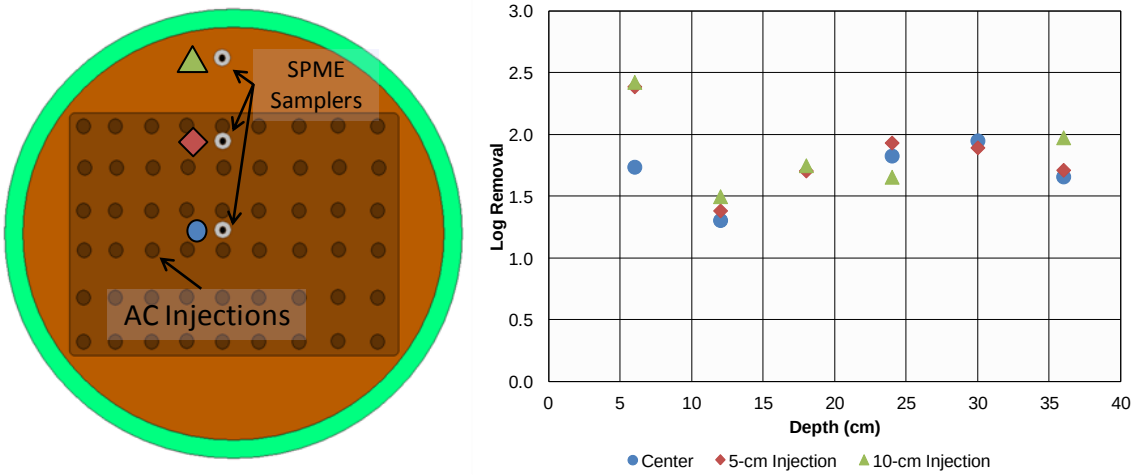


Fig 5: Pyrene pore water reduction in multiple AC injection treated contaminated sediment: The diagram (left) shows the layout of the experiment. 30-cm SPME samplers were placed in the zero, 3.8 and 7.6 cm from the center of the injection area and 30 cm SPME fibers were placed into the samplers to equilibrate for 7 days. The graph (right) shows the log reduction in Pyrene pore water concentrations for each sampler placed in the column. Log reductions were calculated by comparing measurements with those in a control column that was not treated with AC.

Table 1: Relative Standard Deviation (RSD) of select PAHs measured with *in situ* SPME fibers: The HPLC RSD was determined from multiple standard analysis. Aqueous RSDs were determined by performing multiple SPME measurements in a 1-liter aqueous chamber kept under constant PAH concentrations by being dosed with PAHs from preloaded silicon o-rings. In-situ RSD was measured by looking at deviation with depth in 30 cm long samplers placed in well mixed contaminated sediment.

PAH	**In-Situ (RSD)**	**Aqueous (RSD)**	**HPLC (RSD)**
Phenanthrene	35%	11%	4%
Pyrene	20%	11%	5%
Benzo(a)Pyrene	77%	17%	5%

Table 2: Equilibration times of PAHs in quiescent *in situ* and well mixed aqueous conditions: Once concentrations changed by less than one percent in the model equilibrium was assumed to have been reached, modeled in SAS.

PAH	In-Situ		Aqueous	
	Equil. Time	Ke	Equil. Time	ke
Phenanthrene	120 hours	0.0221/hour	10.3 hours	0.4681
Pyrene	215 hours	0.00732/hour	25.6 hours	0.1803/hour
Benzo(a)Anthracene	250 hours	0.0054/hour	Not Available	

References

Anchor Environmental CA L.P. (2003) Literature review of effects of resuspended sediments due to dredging operations., Prepared for Los Angeles Contaminated Sediments Task Force, Los Angeles, CA.

Bao L.-J., Zeng E.Y. (2011) Passive sampling techniques for sensing freely dissolved hydrophobic organic chemicals in sediment porewater. Trends in Analytical Chemistry 30:1422-1428.

Beckingham B., Ghosh U. (2011) Field-Scale Reduction of PCB Bioavailability with Activated Carbon Amendment to River Sediments. Environmental Science & Technology 45:10567-10574. DOI: 10.1021/es202218p.

Boyd S.E., Limpenny D.S., Rees H.L., Cooper K.M. (2005) The effects of marine sand and gravel extraction on the macrobenthos at a commercial dredging site (results 6 years post-dredging). ICES Journal of Marine Science 62:145-162.

Brändli R.C., Hartnik T., Henriksen T., Cornelissen G. (2008) Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. Chemosphere 73:1805-1810.

Bridges T.S., Ells S., Hayes D., Mount D., Nadeau S.C., Palermo M.R., Patmont C., Schroeder P. (2008) The four Rs of Environmental Dredging: Resuspension, Release, Residual and Risk, in: Dredging Operations and Environmental Research Program (Ed.), US Army Crops of Engineers Engineer Research and Development Center, Washington, DC.

Cho Y.-M., Ghosh U., Kennedy A.J., Grossman A., Ray G., Tomaszewski J.E., Smithenry D.W., Bridges T.S., Luthy R.G. (2009) Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment. Environmental Science & Technology 43:3815-3823. DOI: 10.1021/es802931c.

Conder, J.M., La Point, T.W., Lotufo, G.R., Steevens, J.A. (2003) Nondestructive Minimal-Disturbance, Direct-Burial Solid-Phase Microextraction Fiber Technique for Measuring TNT in Sediment. Environmental Science & Technology 37:1625-1632

Cornelissen G., Pettersen A., Broman D., Mayer P., BreedVeld G.D. (2008) Field Testing of Equilibrium Passive Samplers to Determine Freely Dissolved Native Polycyclic Aromatic Hydrocarbon Concentrations. Environmental Toxicology & Chemistry 27:499-508. DOI: 0730-7268/08.

Ghosh U., Luthy R.G., Cornelissen G., Werner D., Menzie C.A. (2011) In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. Environmental Science & Technology 45:1163-1168. DOI: 10.1021/es102694h.

Hale S.E., Meynet P., Davenport R.J., Martin Jones D., Werner D. (2010) Changes in polycyclic aromatic hydrocarbon availability in River Tyne sediment following bioremediation treatments or activated carbon amendment. Water Research 44:4529-4536.

Hawthorne S.B., St. Germain R.W., Azzolina N.A. (2008) Laser-Induced Fluorescence Coupled with Solid-Phase Microextraction for In Situ Determination of PAHs in Sediment Pore Water. Environmental Science & Technology 42:8021-8026. DOI: 10.1021/es8011673.

Hawthorne S.B., Azzolina N.A., Neuhauser E.F., Kreitinger J.P. (2007) Predicting Bioavailability of Sediment Polycyclic Aromatic Hydrocarbons to Hyalella azteca using Equilibrium Partitioning, Supercritical Fluid Extraction, and Pore Water Concentrations. Environmental Science & Technology 41:6297-6304. DOI: 10.1021/es0702162.

Heijden S.A.v.d., Jonker M.T.O. (2009) PAH Bioavailability in Field Sediments: Comparing Different Methods for Predicting in Situ Bioaccumulation. Environmental Science & Technology 43:3757-3763. DOI: 10.1021/es803329p.

Koelmans A.A., Jonker M.T.O., Cornelissen G., Bucheli T.D., Van Noort P.C.M., Gustafsson Ö. (2006) Black carbon: The reverse of its dark side. Chemosphere 63:365-377.

Kupryianchyk D., Reichman E.P., Rakowska M.I., Peeters E.T.H.M., Grotenhuis J.T.C., Koelmans A.A. (2011) Ecotoxicological Effects of Activated Carbon Amendments on Macroinvertebrates in Nonpolluted and Polluted Sediments. Environmental Science & Technology 45:8567-8574. DOI: 10.1021/es2014538.

Lu X., Skwarski A., Drake B., Reible D.D. (2011) Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. Enivornmental Toxicology and Chemistry 30:1109-1116. DOI: 10.1002/etc.495.

Millward R.N., Bridges T.S., Ghosh U., Zimmerman J.R., Luthy R.G. (2005) Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulosus). Environmental Science & Technology 39:2880-2887. DOI: 10.1021/es048768x.

Muijs B., Jonker M.T.O. (2011) Does Equilibrium Passive Sampling Reflect Actual in Situ Bioaccumulation of PAHs and Petroleum Hydrocarbon Mixtures in Aquatic Worms? Environmental Science & Technology 46:937-944. DOI: 10.1021/es202951w.

Oen A.M.P., Janssen E.M.L., Cornelissen G., Breedveld G.D., Eek E., Luthy R.G. (2011) In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers. Environmental Science & Technology 45:4053-4059. DOI: 10.1021/es200174v.

Paine M.D., Chapman P.M., Allard P.J., Murdoch M.H., Minifie D. (1996) Limited bioavailability of sediment pah near an aluminum smelter: Contamination does not equal effects. Environmental Toxicology and Chemistry 15:2003-2018. DOI: 10.1002/etc.5620151119.

Redell C., Elmore A., Burken J., Stringer R. (2011) Waterjet injection of powdered activated carbon for sediment remediation. Journal of Soils and Sediments 11:1115-1124. DOI: 10.1007/s11368-011-0392-x.

Reible D.D., Lotufo G., Skwarski A., Lampert D., Lu X. (2008) Demonstration and evaluation of solid phase microextraction for the assessment of bioavailability and contaminant mobility, in: Environmental Security Technology Certification Program (Ed.), Laboroatory Study Report.

SERDP, ESTCP. (2004) SERDP and ESTCP Expert Panel Workshop on Research and Development Needs for the In Situ Management of Contaminated Sediments, Strategic Environmental Research and Development Program, Arlington, VA.

Smith K.E.C., Oostingh G.J., Mayer P. (2009) Passive Dosing for Producing Defined and Constant Exposure of Hydrophobic Organic Compounds during in Vitro Toxicity Tests. Chemical Research in Toxicology 23:55-65. DOI: 10.1021/tx900274j.

Teasdale P.R., Batley G.E., Apte S.C., Webster I.T. (1995) Pore water sampling with sediment peepers. TrAC Trends in Analytical Chemistry 14:250-256.

Tomaszewski J.E., Werner D., Luthy R.G. (2007) Activated carbon amendment as a treatment for residual ddt in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. Environmental Toxicology and Chemistry 26:2143-2150. DOI: 10.1897/07-179r.1.

U.S Environmental Protection Agency. (2005) Contaminated Sediment Remediation Guidance, in: U. EPA (Ed.), Office of Solid waste and Emergency Response, Washington DC.

U.S. Environmental Protection Agency. (1998) Field Applications of In Situ Remediation Technologies., U.S. Environmental Protection Agency, Washington, DC.

U.S. Environmental Protection Agency. (2003) Procedures for the Derivation of Equilibrium Partition Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures, in: Office of Research and Development (Ed.), Washington, DC.

U.S. Environmental Protection Agency. (2009) 2008 Biennial National Listing of Fish Advisories, in: Office of Science and Technology (Ed.), U.S. EPA,, Washington, DC.

Van Dolah R.F., Calder D.R., Knott D.M. (1984) Effects of dredging and open-water disposal on benthic macroinvertebrates in a South Carolina estuary. Estuaries 7:28-37.

Zabiegała B., Kot-Wasik A., Urbanowicz M., Namieśnik J. (2010) Passive sampling as a tool for obtaining reliable analytical information in environmental quality monitoring. Analytical and Bioanalytical Chemistry 396:273-296. DOI: 10.1007/s00216-009-3244-4.

Zimmerman J.R., Ghosh U., Millward R.N., Bridges T.S., Luthy R.G. (2004) Addition of Carbon Sorbents to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests. Environmental Science & Technology 38:5458-5464. DOI: 10.1021/es034992v.

SECTION

3. RECOMMENDATIONS FOR FUTURE WORK

The results of this work have shown that impacts of AC placement were observed through the application of in-*situ* SPME fibers in lab-scale tests. The SPME fibers were able to measure varying degrees of treatment observed from different additions of AC in different sediments. Some unexpected results were observed in well mixed contaminated sediment tests which, put into question the methods ability to provide accurate depth profiles. Increases in PAH concentrations were observed with depth in the samplers despite the samplers being placed in well mixed contaminated sediment. Changes to the sampler design may be necessary to address these issues.

Long fiber SPME has potential to rapidly access contaminants profiles with depth, but steps in the scale-up require further refinement and development. Contaminant transport appears to occur in the samplers as used in this study and redesign of the SPME holder/sampler is a target for future research. To prepare this method for use in field sites a sturdier sampler is necessary which should be able to be easily place and removed in sediment. A device with a screw on lid may be the best alternative for convenient addition and removal of the SPME fibers. Also, developing a deployment and capture system to pick up and place samplers without requiring a diver would add additional utility to the method.

APPENDIX A

IN SITU EQUILIBRATION CURVE

PHENANTHRENE	1 DAY EXPOSURE		4 DAY EXPOSURE		8 DAY EXPOSURE		12 DAY EXPOSURE	
DEPTH	PEAK AREA	CONC. (PPM)	PEAK AREA)	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)
1	4.865E+07	0.432	2.069E+08	1.976	2.081E+08	2.125	2.056E+08	2.099
2	4.352E+07	0.385	1.962E+08	1.869	2.280E+08	2.330	N/M	N/M
3	5.668E+07	0.507	1.759E+08	1.666	2.339E+08	2.390	1.898E+08	1.936
4	3.910E+07	0.344	1.858E+08	1.765	1.820E+08	1.856	1.257E+08	1.278
5	5.078E+07	0.452	2.332E+08	2.241	2.108E+08	2.152	1.454E+08	1.479
6	5.008E+07	0.446	1.967E+08	1.874	2.290E+08	2.340	1.281E+08	1.302
7	4.313E+07	0.381	2.295E+08	2.203	2.177E+08	2.223	1.302E+08	1.324
8	4.463E+07	0.395	2.327E+08	2.235	2.296E+08	2.346	1.214E+08	1.234
9	4.403E+07	0.389	2.051E+08	1.957	2.454E+08	2.509	1.561E+08	1.589
10	4.320E+07	0.382	2.404E+08	2.313	2.346E+08	2.398	1.716E+08	1.749
11	4.603E+07	0.408	2.232E+08	2.140	2.515E+08	2.572	1.764E+08	1.798
12	6.322E+07	0.569	2.176E+08	2.083	2.767E+08	2.832	1.876E+08	1.913
13	4.423E+07	0.391	N/M	N/M	2.542E+08	2.600	1.864E+08	1.901
14	4.480E+07	0.396	1.925E+08	1.832	2.656E+08	2.718	1.756E+08	1.790
15	5.422E+07	0.484	N/M	N/M	2.773E+08	2.838	1.789E+08	1.823
16	3.974E+07	0.350	2.048E+08	1.955	3.352E+08	3.437	2.197E+08	2.244
17	5.985E+07	0.537	2.207E+08	2.114	2.374E+08	2.426	2.611E+08	2.672
18	1.041E+08	0.961	1.907E+08	1.813	3.114E+08	3.191	2.588E+08	2.647
19	8.692E+07	0.795	2.072E+08	1.979	2.979E+08	3.051	2.532E+08	2.590
20	6.756E+07	0.610	1.872E+08	1.779	2.090E+08	2.134	2.442E+08	2.497

PHENANTHRENE	14 DAY EXPOSURE 1		14 DAY EXPOSURE 2		14 DAY EXPOSURE 3		25 DAY EXPOSURE	
DEPTH	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)
1	1.575E+08	1.484	1.951E+08	1.917	9.404E+07	1.072	2.238E+08	2.286
2	1.442E+08	1.353	1.752E+08	1.731	9.258E+07	1.056	2.226E+08	2.274
3	1.281E+08	1.194	1.671E+08	1.655	9.764E+07	1.114	2.059E+08	2.102
4	9.830E+07	0.905	1.626E+08	1.612	1.118E+08	1.274	N/M	N/M
5	1.376E+08	1.287	1.670E+08	1.654	1.101E+08	1.255	2.171E+08	2.217
6	1.167E+08	1.084	1.498E+08	1.491	1.010E+08	1.151	2.326E+08	2.377
7	1.424E+08	1.335	1.424E+08	1.421	8.152E+07	0.930	2.306E+08	2.356
8	1.501E+08	1.411	1.368E+08	1.368	9.614E+07	1.096	2.751E+08	2.816
9	1.344E+08	1.256	1.323E+08	1.325	8.737E+07	0.996	2.638E+08	2.699
10	1.757E+08	1.664	1.291E+08	1.294	8.829E+07	1.007	2.679E+08	2.741
11	2.100E+08	2.007	1.462E+08	1.457	8.050E+07	0.918	2.155E+08	2.201
12	1.960E+08	1.867	1.468E+08	1.462	8.882E+07	1.013	2.253E+08	2.302
13	1.718E+08	1.625	1.582E+08	1.570	7.897E+07	0.901	1.809E+08	1.845
14	1.287E+08	1.201	1.597E+08	1.585	7.963E+07	0.908	1.739E+08	1.773
15	1.316E+08	1.229	1.771E+08	1.749	8.417E+07	0.960	1.772E+08	1.807
16	1.178E+08	1.094	1.864E+08	1.836	8.320E+07	0.949	1.604E+08	1.633
17	1.215E+08	1.130	1.850E+08	1.823	8.284E+07	0.945	1.790E+08	1.825
18	1.180E+08	1.096	1.721E+08	1.702	8.685E+07	0.991	2.345E+08	2.396
19	1.515E+08	1.424	1.619E+08	1.606	1.333E+08	1.520	2.226E+08	2.274
20	1.376E+08	1.288	1.641E+08	1.627	1.307E+08	1.490	2.731E+08	2.795

PYRENE	1 DAY EXPOSURE		4 DAY EXPOSURE		8 DAY EXPOSURE		12 DAY EXPOSURE	
DEPTH	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)
1	3.564E+07	0.138	1.029E+08	0.398	1.23E+08	0.477	1.257E+08	0.610
2	3.905E+07	0.151	1.136E+08	0.440	1.66E+08	0.642	1.438E+08	0.696
3	4.403E+07	0.170	1.055E+08	0.409	1.64E+08	0.636	1.425E+08	0.690
4	2.721E+07	0.105	1.197E+08	0.463	1.62E+08	0.627	1.291E+08	0.626
5	1.665E+07	0.064	1.112E+08	0.430	1.73E+08	0.670	1.623E+08	0.785
6	4.499E+06	0.017	N/M	N/M	1.58E+08	0.613	1.508E+08	0.730
7	2.420E+07	0.094	1.161E+08	0.449	1.52E+08	0.587	1.295E+08	0.628
8	2.379E+07	0.092	1.164E+08	0.451	1.44E+08	0.556	1.311E+08	0.636
9	3.230E+07	0.125	1.135E+08	0.439	1.56E+08	0.603	1.357E+08	0.658
10	2.013E+07	0.078	1.197E+08	0.464	1.59E+08	0.617	1.252E+08	0.607
11	1.865E+07	0.072	1.244E+08	0.482	1.52E+08	0.587	1.266E+08	0.614
12	1.832E+07	0.071	9.924E+07	0.384	1.60E+08	0.618	1.231E+08	0.597
13	1.825E+07	0.071	1.132E+08	0.438	1.46E+08	0.564	1.247E+08	0.605
14	1.631E+07	0.063	1.245E+08	0.482	1.41E+08	0.545	9.236E+07	0.450
15	2.044E+07	0.079	9.031E+07	0.350	1.52E+08	0.589	9.108E+07	0.444
16	2.044E+07	0.079	1.064E+08	0.412	1.36E+08	0.526	9.696E+07	0.472
17	1.410E+07	0.055	N/M	N/M	1.18E+08	0.457	9.211E+07	0.449
18	1.953E+07	0.076	8.414E+07	0.326	1.40E+08	0.544	1.011E+08	0.492
19	1.482E+07	0.057	9.191E+07	0.356	1.40E+08	0.541	1.401E+08	0.679
20	1.520E+07	0.0588	8.689E+07	0.336	1.22E+08	0.474	1.600E+08	0.774

PYRENE	14 DAY EXPOSURE 1		14 DAY EXPOSURE 2		14 DAY EXPOSURE 3		25 DAY EXPOSURE	
DEPTH	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)
1	9.827E+07	0.380	1.819E+08	1.005	1.120E+08	0.579	1.153E+08	0.560
2	9.979E+07	0.386	1.778E+08	0.982	1.076E+08	0.557	1.218E+08	0.591
3	9.252E+07	0.358	1.777E+08	0.982	1.129E+08	0.584	1.148E+08	0.558
4	7.556E+07	0.292	1.894E+08	1.045	1.323E+08	0.683	1.470E+08	0.712
5	1.120E+08	0.434	1.976E+08	1.089	1.253E+08	0.647	1.560E+08	0.755
6	9.702E+07	0.376	1.987E+08	1.096	1.058E+08	0.548	1.599E+08	0.773
7	1.189E+08	0.460	1.712E+08	0.947	8.296E+07	0.431	2.001E+08	0.965
8	1.114E+08	0.431	1.759E+08	0.972	9.807E+07	0.508	1.808E+08	0.873
9	9.626E+07	0.373	1.675E+08	0.926	8.718E+07	0.453	2.006E+08	0.967
10	1.260E+08	0.488	1.542E+08	0.854	9.325E+07	0.484	1.494E+08	0.723
11	1.432E+08	0.554	1.303E+08	0.724	8.961E+07	0.465	1.647E+08	0.797
12	1.329E+08	0.514	1.320E+08	0.733	9.361E+07	0.485	1.518E+08	0.735
13	1.187E+08	0.459	1.402E+08	0.777	8.454E+07	0.439	1.350E+08	0.654
14	9.569E+07	0.370	1.452E+08	0.805	8.760E+07	0.455	1.450E+08	0.702
15	9.568E+07	0.370	1.544E+08	0.855	8.825E+07	0.458	1.346E+08	0.652
16	9.067E+07	0.351	1.751E+08	0.968	8.737E+07	0.454	N/M	N/M
17	1.008E+08	0.390	1.743E+08	0.963	8.879E+07	0.461	1.401E+08	0.679
18	1.002E+08	0.388	1.851E+08	1.022	9.514E+07	0.493	1.834E+08	0.885
19	1.349E+08	0.522	1.956E+08	1.079	1.464E+08	0.754	1.711E+08	0.827
20	1.240E+08	0.480	2.086E+08	1.149	1.388E+08	0.715	1.928E+08	0.930

BENZO(A)ANTHRACENE	1 DAY EXPOSURE		4 DAY EXPOSURE		8 DAY EXPOSURE		12 DAY EXPOSURE	
DEPTH	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)
1	5.285E+07	0.025	1.291E+08	0.061	5.804E+07	0.027	1.893E+08	0.115
2	4.428E+07	0.021	1.402E+08	0.066	7.218E+07	0.034	1.558E+08	0.095
3	4.400E+07	0.021	1.298E+08	0.061	7.883E+07	0.037	1.179E+08	0.072
4	2.894E+07	0.014	1.361E+08	0.064	7.363E+07	0.035	1.074E+08	0.066
5	1.611E+07	0.008	1.240E+08	0.058	8.554E+07	0.040	1.038E+08	0.063
6	3.027E+07	0.014	N/M	N/M	9.693E+07	0.045	1.010E+08	0.062
7	2.896E+07	0.014	1.533E+08	0.072	9.195E+07	0.043	1.051E+08	0.064
8	2.674E+07	0.013	1.546E+08	0.072	1.017E+08	0.048	1.053E+08	0.064
9	3.539E+07	0.017	1.336E+08	0.063	1.268E+08	0.059	1.259E+08	0.077
10	1.998E+07	0.009	1.333E+08	0.062	1.284E+08	0.060	1.248E+08	0.076
11	1.523E+07	0.007	1.393E+08	0.065	1.322E+08	0.062	1.291E+08	0.079
12	1.753E+07	0.008	1.160E+08	0.054	1.395E+08	0.065	1.281E+08	0.078
13	1.821E+07	0.009	1.336E+08	0.063	1.400E+08	0.066	1.319E+08	0.080
14	1.380E+07	0.007	1.322E+08	0.062	1.529E+08	0.072	1.300E+08	0.079
15	1.741E+07	0.008	9.496E+07	0.045	1.699E+08	0.080	1.265E+08	0.077
16	1.647E+07	0.008	8.024E+07	0.038	1.898E+08	0.089	1.348E+08	0.082
17	9.723E+06	0.005	N/M	N/M	1.906E+08	0.089	1.323E+08	0.081
18	1.348E+07	0.006	4.901E+07	0.023	1.874E+08	0.088	1.062E+08	0.065
19	1.085E+07	0.005	5.353E+07	0.025	1.703E+08	0.080	1.006E+08	0.061
20	1.059E+07	0.005	4.766E+07	0.022	1.311E+08	0.061	8.246E+07	0.050

BENZO(A)ANTHRACENE	14 DAY EXPOSURE 1		14 DAY EXPOSURE 2		14 DAY EXPOSURE 3		25 DAY EXPOSURE	
DEPTH	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)	PEAK AREA	CONC. (PPM)
1	9.775E+07	0.046	1.819E+08	0.121	7.186E+07	0.046	1.074E+08	0.066
2	9.537E+07	0.045	1.778E+08	0.118	6.641E+07	0.043	1.147E+08	0.070
3	7.488E+07	0.035	1.777E+08	0.118	7.172E+07	0.046	1.252E+08	0.076
4	1.198E+08	0.056	1.894E+08	0.126	9.720E+07	0.063	1.510E+08	0.092
5	2.191E+07	0.010	1.976E+08	0.131	9.093E+07	0.059	1.747E+08	0.106
6	1.077E+08	0.051	1.987E+08	0.132	8.683E+07	0.056	1.907E+08	0.116
7	1.380E+08	0.065	1.712E+08	0.114	7.382E+07	0.048	2.027E+08	0.123
8	1.367E+08	0.064	1.759E+08	0.117	8.571E+07	0.055	2.098E+08	0.127
9	1.173E+08	0.055	1.675E+08	0.111	7.449E+07	0.048	2.028E+08	0.123
10	1.533E+08	0.072	1.542E+08	0.102	8.000E+07	0.052	1.668E+08	0.101
11	1.705E+08	0.080	1.303E+08	0.087	7.902E+07	0.051	1.841E+08	0.112
12	1.497E+08	0.070	1.320E+08	0.088	8.385E+07	0.054	1.549E+08	0.094
13	1.360E+08	0.064	1.402E+08	0.093	8.125E+07	0.052	1.569E+08	0.095
14	1.200E+08	0.056	1.452E+08	0.096	8.727E+07	0.056	1.737E+08	0.106
15	1.258E+08	0.059	1.544E+08	0.103	8.480E+07	0.055	1.540E+08	0.094
16	1.181E+08	0.055	1.751E+08	0.116	8.171E+07	0.053	1.603E+08	0.098
17	1.336E+08	0.063	1.743E+08	0.116	8.381E+07	0.054		
18	1.458E+08	0.068	1.851E+08	0.123	9.106E+07	0.059	2.311E+08	0.140
19	1.912E+08	0.089	1.956E+08	0.130	1.393E+08	0.089	2.083E+07	0.013
20	1.814E+08	0.085	2.086E+08	0.138	1.318E+08	0.084	2.530E+08	0.153

SAS MODELLING

PHENANTHRENE					
Source	Degrees of Freedom	Sum of Squares	Mean Squares	Approx F Value	Pr>P
Model	2	432.7	216.3	834.90	<0.0001
Error	135	34.9826	0.2591		
Uncorrected Total	137	467.7			

Parameter	Estimate	Std Error	95% Confidence Limits		Skewness
PA	1.9344	0.0523	1.8309	2.0379	0.0446
k1	0.0221	0.0036	0.015	0.0292	0.5534

PYRENE					
Source	Degrees of Freedom	Sum of Squares	Mean Squares	Approx F Value	Pr>P
Model	2	48.3144	24.1572	763.68	<0.0001
Error	137	4.3337	0.0316		
Uncorrected Total	139	52.6481			

Parameter	Estimate	Std Error	95% Confidence Limits		Skewness
PA	0.7517	0.0361	0.6802	0.8231	0.4072
k1	0.00732	0.00113	0.00508	0.00956	0.4714

BENZO(A)ANTHRACENE					
Source	Degrees of Freedom	Sum of Squares	Mean Squares	Approx F Value	Pr>P
Model	2	48.3144	24.1572	763.68	<0.0001
Error	137	4.3337	0.0316		
Uncorrected Total	139	52.6481			

Parameter	Estimate	Std Error	95% Confidence Limits		Skewness
PA	0.7517	0.0361	0.6802	0.8231	0.4072
k1	0.00732	0.00113	0.00508	0.00956	0.4714

APPENDIX B
MATRIX FREE EQUILIBRATION

PHENANTHRENE									
Time	Sample ID	Order	Depth	Conc		Time	Sample ID	Order	Depth	Conc
25	25 min a	1	1	0.953		480	480 min A	7	1	2.668
25	25 min a	1	2	0.820		480	480 min A	7	2	2.968
25	25 min a	1	3	0.644		480	480 min A	7	3	3.589
25	25 min a	1	4	0.711		480	480 min A	7	4	3.824
25	25 min a	1	5	0.722		480	480 min A	7	5	4.180
25	25 min b	1	1	0.975		480	480 min B	7	1	2.758
25	25 min b	1	2	0.962		480	480 min B	7	2	2.695
25	25 min b	1	3	0.868		480	480 min B	7	3	2.829
25	25 min b	1	4	0.792		480	480 min B	7	4	2.691
25	25 min b	1	5	0.785		480	480 min B	7	5	2.800
120	120 min a	2	1	2.535		720	720 min A	8	1	4.391
120	120 min a	2	2	2.409		720	720 min A	8	2	3.206
120	120 min a	2	3	2.358		720	720 min A	8	3	3.269
120	120 min a	2	4	2.313		720	720 min A	8	4	3.646
120	120 min a	2	5	2.047		720	720 min A	8	5	3.057
120	120 min b	2	1	2.144		720	720 min B	8	1	3.049
120	120 min b	2	2	1.844		720	720 min B	8	2	4.763
120	120 min b	2	3	2.221		720	720 min B	8	3	4.384
120	120 min b	2	4	2.084		720	720 min B	8	4	3.641
120	120 min b	2	5	2.390		720	720 min B	8	5	4.276
240	240 min A	3	1	2.377		1020	1020 min A	5	1	0.000

240	240 min A	3	2	2.718	1020	1020 min A	5	2	4.092
240	240 min A	3	3	2.276	1020	1020 min A	5	3	2.947
240	240 min A	3	4	2.200	1020	1020 min A	5	4	3.232
240	240 min A	3	5	2.478	1020	1020 min A	5	5	3.424
240	240 min b	3	1	2.979	1020	1020 min B	5	5	N/M
240	240 min b	3	2	2.716	1020	1020 min B	5	4	3.424
240	240 min b	3	3	3.118	1020	1020 min B	5	3	0.487
240	240 min b	3	4	3.263	1020	1020 min B	5	2	0.142
240	240 min b	3	5	3.583	1020	1020 min B	5	1	2.776

PHENANTHRENE									
Time	Sample ID	Order	Depth	Conc		Time	Sample ID	Order	Depth	Conc
1290	1020 min A	4	4	2.797		1620	1620 min A	6	5	3.560
1290	1020 min A	4	3	2.792		1620	1620 min A	6	4	3.520
1290	1020 min A	4	2	3.070		1620	1620 min A	6	3	3.125
1290	1020 min A	4	1	3.903		1620	1620 min A	6	2	3.362
1290	1290 min A	4	5	3.12		1620	1620 min A	6	1	3.391
1290	1290 min A	4	4	2.80		1620	1620 min B	6	5	3.745
1290	1290 min A	4	3	2.79		1620	1620 min B	6	4	3.507
1290	1290 min A	4	2	3.07		1620	1620 min B	6	3	3.529
1290	1290 min A	4	1	3.90		1620	1620 min B	6	2	3.637
1290	1290 min B	4	5	2.86		1620	1620 min B	6	1	3.572

PYRENE									
Time	Sample ID	Order	Depth	Conc		Time	Sample ID	Order	Depth	Conc
25	25 min a	1	5	2.070		120	120 min b	2	5	9.343
25	25 min a	1	4	1.991		120	120 min b	2	4	8.006
25	25 min a	1	3	1.787		120	120 min b	2	3	8.133
25	25 min a	1	2	2.328		120	120 min b	2	2	6.401
25	25 min a	1	1	2.742		120	120 min b	2	1	7.688
25	25 min b	1	5	2.324		240	240 min a	3	5	10.083
25	25 min b	1	4	2.343		240	240 min a	3	4	9.311
25	25 min b	1	3	2.577		240	240 min a	3	3	10.964
25	25 min b	1	2	2.869		240	240 min a	3	2	14.567
25	25 min b	1	1	2.899		240	240 min a	3	1	12.902
120	120 min a	2	5	6.875		240	240 min b	3	5	14.718
120	120 min a	2	4	8.452		240	240 min b	3	4	13.215
120	120 min a	2	3	9.102		240	240 min b	3	3	13.507

120	120 min a	2	2	9.465		240	240 min b	3	2	12.488
120	120 min a	2	1	10.115		240	240 min b	3	1	14.857

PYRENE										
Time	Sample ID	Order	Depth	Conc		Time	Sample ID	Order	Depth	Conc
480	480 min A	7	5	20.074		1020	1020 min B	5	5	22.827
480	480 min A	7	4	16.212		1020	1020 min B	5	4	26.232
480	480 min A	7	3	17.161		1020	1020 min B	5	3	21.206
480	480 min A	7	2	16.005		1020	1020 min B	5	2	25.017
480	480 min A	7	1	15.104		1020	1020 min B	5	1	23.255
480	480 min B	7	5	16.245		1290	1290 min A	6	5	28.285
480	480 min B	7	4	15.569		1290	1290 min A	6	4	22.196
480	480 min B	7	3	15.214		1290	1290 min A	6	3	19.605
480	480 min B	7	2	14.175		1290	1290 min A	6	2	19.480
480	480 min B	7	1	14.225		1290	1290 min A	6	1	21.057
720	720 min A	8	5	19.886		1290	1290 min B	6	5	25.439
720	720 min A	8	4	21.013		1290	1290 min B	6	4	22.972
720	720 min A	8	3	18.780		1290	1290 min B	6	3	22.192
720	720 min A	8	2	19.399		1290	1290 min B	6	2	19.471
720	720 min A	8	1	24.099		1290	1290 min B	6	1	20.407
720	720 min b	8	5	26.164		1620	1620 min a	4	5	24.575
720	720 min b	8	4	21.437		1620	1620 min a	4	4	24.144
720	720 min b	8	3	24.400		1620	1620 min a	4	3	21.838
720	720 min b	8	2	26.797		1620	1620 min a	4	2	23.740
720	720 min b	8	1	17.813		1620	1620 min a	4	1	24.027
1020	1020 min a	5	5	22.575		1620	1620 min b	4	5	26.580
1020	1020 min	5	4	22.022		162	1620 min b	4	4	24.858

	a					0				
1020	1020 min a	5	3	19.976		1620	1620 min b	4	3	24.556
1020	1020 min a	5	2	24.808		1620	1620 min b	4	2	25.539
1020	1020 min a	5	1	N/M		1620	1620 min b	4	1	25.186

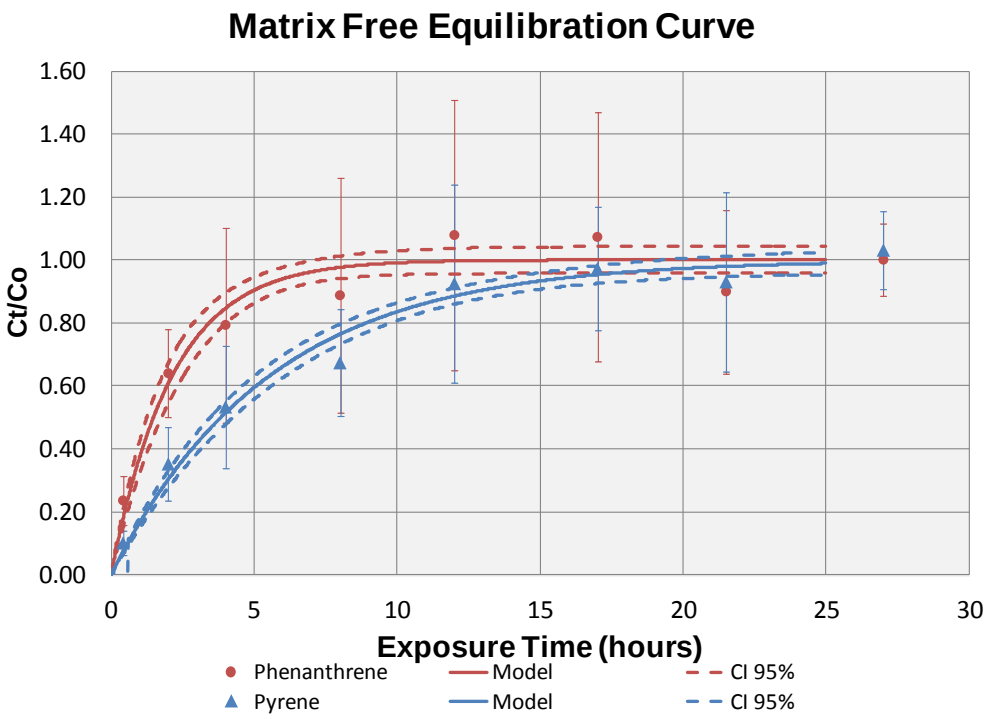
SAS MODELLING

PHENANTHRENE					
Source	Degrees of Freedom	Sum of Squares	Mean Squares	Approx F Value	Pr>P
Model	2	666.1	333.0	1492.63	<0.0001
Error	72	16.0642	0.2231		
Uncorrected Total	74	682.1			

Parameter	**Estimate**	**Std Error**	**95% Confidence Limits**		**Skewness**
PA	3.4919	0.0746	3.3432	3.6406	0.0339
k1	0.4681	0.0466	0.3752	0.5610	0.3779

PYRENE					
Source	Degrees of Freedom	Sum of Squares	Mean Squares	Approx F Value	Pr>P
Model	2	25346.6	12673.3	2542.12	<0.0001
Error	72	389.9	4.9853		
Uncorrected Total	74	25730.4			

Parameter	**Estimate**	**Std Error**	**95% Confidence Limits**		**Skewness**
PA	23.761	0.492	22.781	24.741	0.1165
k1	0.1803	0.0126	0.1553	0.2054	0.1987


Matrix Free Equilibration Curve
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
Ct/Co
0
5
10
15
20
25
30
Exposure Time (hours)
Phenanthrene
Model
CI 95%
Pyrene
Model
CI 95%

APPENDIX C
AC TREATMENT CURVES

BENZO(A)ANTHRACENE HIGHLY CONTAMINATED AC TREATMENT CURVE						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
0% A1	29.092	0.0	6.40E+08	2.61	1331.24	7.3157
0% A2	29.040	0.0	6.03E+08	2.46	1255.53	6.8997
0% A3	N/M	0.0	N/M	N/M	N/M	N/M
0% B1	29.022	0.0	4.45E+08	1.83	931.68	5.1200
0% B2	29.188	0.0	3.83E+08	1.57	802.49	4.4100
0% B3	29.118	0.0	3.89E+08	1.60	815.15	4.4796
0.5% A1	29.237	0.5	5.04E+08	2.06	1051.89	5.7806
0.5% A2	29.169	0.5	4.21E+08	1.73	882.75	4.8511
0.5% A3	29.254	0.5	4.00E+08	1.64	838.35	4.6071
0.5% B1	29.189	0.5	4.63E+08	1.90	968.65	5.3231
0.5% B2	29.465	0.5	4.82E+08	1.98	1008.28	5.5409
0.5% B3	29.179	0.5	4.86E+08	1.99	1015.24	5.5792
1% A1	29.565	1.0	4.43E+08	1.82	927.54	5.0972
1% A3	30.051	1.0	4.26E+08	1.75	891.06	4.8967
1% A2	N/M	1.0	N/M	N/M	N/M	N/M
1% B1	29.239	1.0	5.04E+08	2.06	1051.89	5.7806
1% B2	29.239	1.0	4.96E+08	2.03	1036.01	5.6933
1% B3	29.163	1.0	4.39E+08	1.80	919.77	5.0545
1.5% A1	29.553	1.5	5.87E+08	2.40	1223.45	6.7234
1.5% A2	29.160	1.5	4.27E+08	1.75	893.87	4.9122
1.5% A3	29.165	1.5	2.99E+08	1.23	629.33	3.4584
1.5% B1	29.195	1.5	3.78E+08	1.55	792.41	4.3546
1.5% B2	29.152	1.5	3.14E+08	1.30	660.96	3.6322
1.5% B3	29.984	1.5	2.63E+08	1.09	555.27	3.0514
2% A1	29.277	2.0	3.51E+08	1.44	736.38	4.0467
2% A2	29.204	2.0	3.27E+08	1.35	688.55	3.7839
2% A3	29.182	2.0	3.31E+08	1.36	695.21	3.8205
2% B1	29.194	2.0	3.09E+08	1.28	650.94	3.5772
2% B2	28.983	2.0	3.13E+08	1.29	658.80	3.6204
2% B3	29.297	2.0	2.38E+08	0.99	502.39	2.7608
3% A1	30.194	3.0	1.10E+08	0.46	235.85	1.2961
3% A2	30.440	3.0	1.09E+08	0.46	233.41	1.2827
3% A3	29.031	3.0	1.20E+08	0.50	255.73	1.4054
3% B1	29.232	3.0	2.80E+08	1.16	590.97	3.2476
3% B2	29.591	3.0	1.64E+08	0.69	349.78	1.9222
3% B3	29.054	3.0	6.10E+07	0.26	131.79	0.7242
4% A1	29.501	4.0	4.18E+07	0.18	90.78	0.4989
4% A2	29.935	4.0	1.10E+07	0.05	24.38	0.1340
4% A3	29.188	4.0	1.15E+07	0.05	25.47	0.1400

4% B1	29.317	4.0	4.26E+07	0.18	92.49	0.5083
4% B2	29.042	4.0	1.86E+07	0.08	41.02	0.2254
4% B3	29.158	4.0	1.50E+07	0.07	33.17	0.1823
5% A1	27.980	5.0	1.45E+07	0.06	31.98	0.1757
BENZO(A)ANTHRACENE HIGHLY CONTAMINATED AC TREATMENT CURVE (CONT.)						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
5% A2	29.246	5.0	7.29E+06	0.03	16.29	0.0895
5% A3	28.866	5.0	6.65E+06	0.03	14.90	0.0819
5% A3	29.235	5.0	7.48E+06	0.03	16.72	0.0919
5% B1	29.598	5.0	8.21E+06	0.04	18.33	0.1007
5% B2	29.235	5.0	3.60E+06	0.02	8.15	0.0448
5% B3	29.228	5.0	6.29E+06	0.03	14.09	0.0774

PYRENE HIGHLY CONTAMINATED AC TREATMENT CURVE						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
0% A1	26.534	0.0	6.13E+08	3.09	1.57E+03	88.531
0% A2	26.483	0.0	5.31E+08	2.68	1.37E+03	76.938
0% A3	N/M	0.0	N/M	N/M	N/M	N/M
0% B1	26.459	0.0	4.25E+08	2.16	1.10E+03	61.803
0% B2	26.634	0.0	4.11E+08	2.08	1.06E+03	59.734
0% B3	26.560	0.0	3.96E+08	2.01	1.02E+03	57.600
0.5% A1	26.706	0.5	5.45E+08	2.75	1.40E+03	78.845
0.5% A2	26.615	0.5	4.77E+08	2.41	1.23E+03	69.186
0.5% A3	26.697	0.5	4.77E+08	2.41	1.23E+03	69.104
0.5% B1	26.644	0.5	4.80E+08	2.43	1.24E+03	69.571
0.5% B2	26.869	0.5	4.84E+08	2.45	1.25E+03	70.163
0.5% B3	26.631	0.5	4.48E+08	2.27	1.16E+03	65.062
1% A1	26.952	1.0	4.57E+08	2.31	1.18E+03	66.290
1% A3	27.368	1.0	3.66E+08	1.86	9.48E+02	53.324
1% A2	N/M	1.0	N/M	N/M	N/M	N/M
1% B1	26.683	1.0	5.31E+08	2.68	1.37E+03	76.920
1% B2	26.684	1.0	5.61E+08	2.83	1.44E+03	81.151
1% B3	26.600	1.0	4.67E+08	2.36	1.20E+03	67.744
1.5% A1	26.942	1.5	6.03E+08	3.04	1.55E+03	87.093
1.5% A2	26.555	1.5	4.63E+08	2.34	1.19E+03	67.166
1.5% A3	26.556	1.5	3.69E+08	1.87	9.54E+02	53.654
1.5% B1	26.654	1.5	3.58E+08	1.82	9.26E+02	52.076

1.5% B2	26.601	1.5	3.51E+08	1.78	9.09E+02	51.120
1.5% B3	27.318	1.5	2.97E+08	1.51	7.72E+02	43.423
2% A1	26.728	2.0	4.14E+08	2.10	1.07E+03	60.186
2% A2	26.636	2.0	3.92E+08	1.99	1.01E+03	56.948
2% A3	26.627	2.0	2.97E+08	1.52	7.73E+02	43.453
2% B1	26.633	2.0	3.65E+08	1.86	9.46E+02	53.219
2% B2	26.414	2.0	3.28E+08	1.67	8.52E+02	47.898
2% B3	26.765	2.0	2.97E+08	1.52	7.73E+02	43.455
PYRENE HIGHLY CONTAMINATED AC TREATMENT CURVE (CONT.)						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
3% A1	27.493	3.0	1.20E+08	0.62	3.17E+02	17.809
3% A2	27.711	3.0	1.19E+08	0.61	3.13E+02	17.585
3% A3	26.459	3.0	1.22E+08	0.63	3.21E+02	18.070
3% B1	26.685	3.0	3.18E+08	1.62	8.26E+02	46.435
3% B2	26.954	3.0	2.01E+08	1.03	5.25E+02	29.521
3% B3	26.482	3.0	6.52E+07	0.34	1.73E+02	9.750
4% A1	26.892	4.0	5.06E+07	0.26	1.35E+02	7.597
4% A2	27.274	4.0	8.61E+06	0.05	2.36E+01	1.328
4% A3	26.644	4.0	9.60E+06	0.05	2.63E+01	1.478
4% B1	26.758	4.0	3.70E+07	0.19	9.93E+01	5.584
4% B2	26.467	4.0	1.93E+07	0.10	5.22E+01	2.938
4% B3	26.611	4.0	1.60E+07	0.09	4.34E+01	2.442
5% A1	25.181	5.0	7.81E+06	0.04	2.15E+01	1.207
5% A2	26.698	5.0	4.59E+06	0.02	1.27E+01	0.715
5% A3	26.377	5.0	4.05E+06	0.02	1.12E+01	0.632
5% A3	26.685	5.0	5.93E+06	0.03	1.64E+01	0.921
5% B1	26.962	5.0	7.54E+06	0.04	2.07E+01	1.166
5% B2	26.689	5.0	2.76E+06	0.02	7.72E+00	0.434
5% B3	26.677	5.0	4.72E+06	0.03	1.31E+01	0.736

PHENANTHRENE HIGHLY CONTAMINATED AC TREATMENT CURVE						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
0% A1	23.417	0.000	4.38E+08	4.99	2542.90	495.8259
0% A2	23.371	0.000	3.88E+08	4.42	2256.17	439.9175
0% A3	N/M	0.000	N/M	N/M	N/M	
0% B1	23.354	0.000	3.10E+08	3.53	1802.28	351.4170

0% B2	23.537	0.000	3.03E+08	3.46	1763.14	343.7850
0% B3	23.443	0.000	2.82E+08	3.22	1640.62	319.8948
0.5% A1	23.622	0.500	3.79E+08	4.32	2201.85	429.3263
0.5% A2	23.515	0.500	3.28E+08	3.74	1907.54	371.9405
0.5% A3	23.599	0.500	3.45E+08	3.93	2003.89	390.7273
0.5% B1	23.538	0.500	3.21E+08	3.66	1868.13	364.2567
0.5% B2	23.742	0.500	3.32E+08	3.79	1932.43	376.7946
0.5% B3	23.529	0.500	3.05E+08	3.47	1772.03	345.5183
1% A1	23.803	1.000	3.19E+08	3.64	1856.82	362.0510
1% A3	24.136	1.000	2.52E+08	2.87	1464.36	285.5271
1% A2	N/M	1.000	N/M	N/M	N/M	N/M
1% B1	23.564	1.000	3.77E+08	4.29	2188.30	426.6836

PHENANTHRENE HIGHLY CONTAMINATED AC TREATMENT CURVE (CONT.)

Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
1% B2	23.562	1.000	3.99E+08	4.55	2319.46	452.2582
1% B3	23.504	1.000	3.34E+08	3.81	1942.81	378.8177
1.5% A1	23.796	1.500	4.19E+08	4.77	2433.49	474.4932
1.5% A2	23.409	1.500	3.02E+08	3.44	1754.08	342.0184
1.5% A3	23.406	1.500	2.52E+08	2.87	1464.15	285.4863
1.5% B1	23.564	1.500	2.57E+08	2.93	1492.11	290.9374
1.5% B2	23.496	1.500	2.36E+08	2.69	1374.20	267.9472
1.5% B3	24.097	1.500	2.11E+08	2.41	1229.34	239.7017
2% A1	23.626	2.000	3.12E+08	3.55	1811.42	353.1985
2% A2	23.531	2.000	2.89E+08	3.30	1682.04	327.9718
2% A3	23.539	2.000	2.26E+08	2.58	1315.99	256.5985
2% B1	23.545	2.000	2.82E+08	3.22	1641.08	319.9859
2% B2	23.323	2.000	2.57E+08	2.93	1494.61	291.4255
2% B3	23.665	2.000	2.37E+08	2.70	1374.83	268.0707
3% A1	24.235	3.000	1.09E+08	1.25	635.29	123.8726
3% A2	24.446	3.000	1.07E+08	1.22	622.20	121.3188
3% A3	23.351	3.000	1.15E+08	1.31	668.64	130.3735
3% B1	23.585	3.000	2.60E+08	2.96	1508.89	294.2106
3% B2	23.789	3.000	1.69E+08	1.93	982.11	191.4957
3% B3	23.384	3.000	6.10E+07	0.70	354.78	69.1767
4% A1	23.756	4.000	4.62E+07	0.53	268.77	52.4054
4% A2	24.075	4.000	6.82E+06	0.08	39.71	7.7419
4% A3	23.543	4.000	7.93E+06	0.09	46.17	9.0025
4% B1	23.643	4.000	2.76E+07	0.31	160.47	31.2890
4% B2	23.369	4.000	1.74E+07	0.20	101.56	19.8020
4% B3	23.517	4.000	1.47E+07	0.17	85.72	16.7144

5% A1	21.730	5.000	5.70E+06	0.07	33.17	6.4683
5% A2	23.598	5.000	3.44E+06	0.04	20.06	3.9115
5% A3	23.276	5.000	3.66E+06	0.04	21.30	4.1522
5% A3	23.597	5.000	4.54E+06	0.05	26.45	5.1570
5% B1	23.805	5.000	7.32E+06	0.08	42.60	8.3071
5% B2	23.586	5.000	2.32E+06	0.03	13.50	2.6330
5% B3	23.569	5.000	3.80E+06	0.04	22.16	4.3207

BENZO(A)ANTHRACENE LESS CONTAMINATED AC TREATMENT CURVE						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
0% AC PAH A1 11/3	18.978	0	2.42E+08	0.114	118.907	0.653
0% AC PAH A2 11/3	19.008	0	1.55E+08	0.073	76.301	0.419
0% AC PAH A3 11/3	19.000	0	1.08E+08	0.051	52.954	0.291
0% AC PAH B1 11/3	19.012	0	2.00E+08	0.094	98.416	0.541
0% AC PAH B2 11/3	19.036	0	9.97E+07	0.047	49.010	0.269
0% AC PAH B3 11/3	19.027	0	7.03E+07	0.033	34.539	0.190
0.1% AC PAH A1 11/3	19.034	0.1	1.94E+08	0.091	95.471	0.525
0.1% AC PAH A2 11/3	19.039	0.1	1.66E+08	0.078	81.596	0.448
0.1% AC PAH A3 11/3	19.047	0.1	1.30E+08	0.061	64.026	0.352
0.1% AC PAH B1 11/3	19.050	0.1	1.38E+08	0.065	67.965	0.373
0.1% AC PAH B2 11/3	19.007	0.1	7.86E+07	0.037	38.657	0.212
0.1% AC PAH B3 11/3	18.973	0.1	4.86E+07	0.023	23.902	0.131
0.5% AC PAH A1 11/3	18.841	0.5	1.07E+08	0.051	52.834	0.290
0.5% AC PAH A2 11/3	18.867	0.5	1.26E+08	0.059	62.072	0.341
0.5% AC PAH A3 11/3	18.867	0.5	1.39E+08	0.066	68.540	0.377
0.5% AC PAH B1 11/3	18.852	0.5	5.61E+07	0.026	27.555	0.151
0.5% AC PAH B2 11/3	18.860	0.5	3.16E+07	0.015	15.553	0.085
0.5% AC PAH B3 11/3	18.833	0.5	3.54E+07	0.017	17.428	0.096
1.0 AC PAH B3 11/3	18.650	1	1.65E+07	0.008	8.123	0.045
1.0% AC PAH A1 11/3	18.825	1	1.47E+07	0.007	7.229	0.040
1.0% AC PAH A2 11/3	18.816	1	1.20E+07	0.006	5.922	0.033
1.0% AC PAH A3 11/3	18.828	1	5.26E+06	0.002	2.592	0.014
1.0% AC PAH B1 11/3	18.706	1	2.30E+07	0.011	11.299	0.062
1.0% AC PAH B2	18.657	1	1.85E+07	0.009	9.089	0.050

11/3						
3.0% AC PAH A1 11/3	18.639	3	3.44E+06	0.002	1.698	0.009
3.0% AC PAH A2 11/3	18.601	3	2.30E+06	0.001	1.138	0.006
3.0% AC PAH A3 11/3	18.679	3	1.58E+06	0.001	0.784	0.004
3.0% AC PAH B1 11/3	18.590	3	3.31E+06	0.002	1.632	0.009
3.0% AC PAH B2 11/3	18.636	3	1.71E+06	0.001	0.846	0.005
3.0% AC PAH B3 11/3	18.667	3	1.47E+06	0.001	0.728	0.004
5.0% AC PAH A1 11/3	18.662	5	4.31E+06	0.002	2.126	0.012
5.0% AC PAH A2 11/3	18.685	5	4.31E+05	0.000	0.217	0.001
5.0% AC PAH A3 11/3	18.699	5	7.45E+05	0.000	0.372	0.002
5.0% AC PAH B1 11/3	18.709	5	1.40E+06	0.001	0.693	0.004
5.0% AC PAH B2 11/3	18.731	5	7.90E+05	0.000	0.394	0.002

PYRENE LESS CONTAMINATED AC TREATMENT CURVE						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
0% AC PAH A1 11/3	16.378	0.0	2.34E+08	1.082	1131.006	63.601
0% AC PAH A2 11/3	16.398	0.0	1.44E+08	0.664	694.4746	39.053
0% AC PAH A3 11/3	16.393	0.0	9.61E+07	0.444	464.1674	26.102
0% AC PAH B1 11/3	16.398	0.0	2.18E+08	1.007	1052.501	59.186
0% AC PAH B2 11/3	16.419	0.0	9.60E+07	0.443	463.5673	26.068
0% AC PAH B3 11/3	16.414	0.0	5.10E+07	0.235	246.1581	13.842
0.1% AC PAH A1 11/3	16.416	0.1	1.93E+08	0.890	930.8956	52.348
0.1% AC PAH A2 11/3	16.421	0.1	1.67E+08	0.769	804.3004	45.229
0.1% AC PAH A3 11/3	16.428	0.1	1.23E+08	0.569	594.3325	33.422
0.1% AC PAH B1 11/3	16.428	0.1	1.55E+08	0.717	749.8262	42.166
0.1% AC PAH B2 11/3	16.402	0.1	8.13E+07	0.376	392.8371	22.091
0.1% AC PAH B3 11/3	16.380	0.1	4.65E+07	0.215	224.5416	12.627
0.5% AC PAH A1 11/3	16.294	0.5	1.32E+08	0.609	636.725	35.806
0.5% AC PAH A2 11/3	16.312	0.5	1.64E+08	0.756	790.3064	44.442
0.5% AC PAH A3 11/3	16.312	0.5	1.72E+08	0.796	832.3706	46.808
0.5% AC PAH B1 11/3	16.298	0.5	8.24E+07	0.381	398.1067	22.387
0.5% AC PAH B2 11/3	16.306	0.5	3.70E+07	0.171	178.7363	10.051
0.5% AC PAH B3 11/3	16.289	0.5	2.85E+07	0.131	137.3689	7.725
1.0 AC PAH B3 11/3	16.171	1.0	1.91E+07	0.088	92.22782	5.186
1.0% AC PAH A1 11/3	16.279	1.0	2.50E+07	0.116	120.901	6.799
1.0% AC PAH A2 11/3	16.272	1.0	1.75E+07	0.081	84.29789	4.740
1.0% AC PAH A3 11/3	16.284	1.0	7.47E+06	0.034	36.02915	2.026
1.0% AC PAH B1 11/3	16.201	1.0	3.45E+07	0.159	166.4918	9.363
1.0% AC PAH B2	16.171	1.0	2.46E+07	0.114	118.9049	6.687

11/3						
3.0% AC PAH A1 11/3	16.168	3.0	7.62E+05	0.003	3.648159	0.205
3.0% AC PAH A2 11/3	16.098	3.0	8.05E+05	0.004	3.857819	0.217
3.0% AC PAH A3 11/3	16.183	3.0	5.36E+05	0.002	2.55918	0.144
3.0% AC PAH B1 11/3	16.130	3.0	9.03E+05	0.004	4.33061	0.244
3.0% AC PAH B2 11/3	16.156	3.0	4.34E+05	0.002	2.064908	0.116
3.0% AC PAH B3 11/3	16.177	3.0	4.52E+05	0.002	2.153543	0.121
5.0% AC PAH A1 11/3	16.179	5.0	1.43E+06	0.007	6.853381	0.385
5.0% AC PAH A2 11/3	16.195	5.0	2.61E+05	0.001	1.227734	0.069
5.0% AC PAH A3 11/3	16.191	5.0	4.58E+05	0.002	2.182191	0.123
5.0% AC PAH B1 11/3	16.218	5.0	4.32E+05	0.002	2.057053	0.116
5.0% AC PAH B2 11/3	16.231	5.0	2.59E+05	0.001	1.2189	0.069

PHENANTHRENE LESS CONTAMINATED AC TREATMENT CURVE						
Sample ID	Ret Time	% AC	Peak Area	ACN Conc	PDMS Conc. (ppm)	Pore Water Conc (ppb)
0% AC PAH A1 11/3	13.727	0	3.18E+08	2.869	2999.531	0.5849
0% AC PAH A2 11/3	13.738	0	1.97E+08	1.775	1855.514	0.3618
0% AC PAH A3 11/3	13.736	0	1.31E+08	1.184	1237.916	0.2414
0% AC PAH B1 11/3	13.742	0	3.18E+08	2.868	2997.882	0.5845
0% AC PAH B2 11/3	13.756	0	1.50E+08	1.349	1410.488	0.2750
0% AC PAH B3 11/3	13.749	0	6.46E+07	0.583	609.118	0.1188
0.1% AC PAH A1 11/3	13.748	0.1	2.84E+08	2.561	2677.508	0.5221
0.1% AC PAH A2 11/3	13.754	0.1	2.32E+08	2.091	2186.306	0.4263
0.1% AC PAH A3 11/3	13.766	0.1	1.69E+08	1.523	1592.310	0.3105
0.1% AC PAH B1 11/3	13.764	0.1	2.34E+08	2.115	2210.714	0.4311
0.1% AC PAH B2 11/3	13.748	0.1	1.34E+08	1.207	1261.697	0.2460
0.1% AC PAH B3 11/3	13.725	0.1	8.32E+07	0.751	784.603	0.1530
0.5% AC PAH A1 11/3	13.684	0.5	2.49E+08	2.249	2351.353	0.4585
0.5% AC PAH A2 11/3	13.692	0.5	3.14E+08	2.834	2962.743	0.5777
0.5% AC PAH A3 11/3	13.692	0.5	3.20E+08	2.889	3019.657	0.5888
0.5% AC PAH B1 11/3	13.683	0.5	1.73E+08	1.560	1631.133	0.3180
0.5% AC PAH B2 11/3	13.690	0.5	8.06E+07	0.727	759.822	0.1482
0.5% AC PAH B3 11/3	13.671	0.5	5.57E+07	0.503	525.338	0.1024
1.0 AC PAH B3 11/3	13.590	1	3.43E+07	0.309	323.443	0.0631
1.0% AC PAH A1 11/3	13.669	1	6.15E+07	0.555	579.916	0.1131
1.0% AC PAH A2 11/3	13.663	1	4.17E+07	0.376	393.365	0.0767
1.0% AC PAH A3 11/3	13.671	1	1.81E+07	0.164	171.309	0.0334
1.0% AC PAH B1 11/3	13.615	1	8.63E+07	0.779	814.229	0.1588
1.0% AC PAH B2	13.590	1	5.20E+07	0.469	490.522	0.0956

11/3						
3.0% AC PAH A1 11/3	13.577	3	4.88E+05	0.005	4.754	0.0009
3.0% AC PAH A2 11/3	13.497	3	4.10E+05	0.004	4.023	0.0008
3.0% AC PAH A3 11/3	13.589	3	5.30E+05	0.005	5.154	0.0010
3.0% AC PAH B1 11/3	13.554	3	6.41E+05	0.006	6.199	0.0012
3.0% AC PAH B2 11/3	13.576	3	6.50E+05	0.006	6.288	0.0012
3.0% AC PAH B3 11/3	13.598	3	6.25E+05	0.006	6.047	0.0012
5.0% AC PAH A1 11/3	13.590	5	7.91E+05	0.007	7.610	0.0015
5.0% AC PAH A2 11/3	13.602	5	2.72E+05	0.003	2.720	0.0005
5.0% AC PAH A3 11/3	13.618	5	3.92E+05	0.004	3.852	0.0008
5.0% AC PAH B1 11/3	13.623	5	3.61E+05	0.003	3.557	0.0007
5.0% AC PAH B2 11/3	13.636	5	1.38E+05	0.001	1.457	0.0003

APPENDIX D
SINGLE AC INJECTION

PHENANTHRENE 3.8 CM SPME CARBON INJECTED TUBE				
Depth	Peak Area	Conc. (µg/ml)	C (pdms) (ppm)	C(H2O) (ppm)
1	5.02E+06	0.0454	47.488	9.259
2	1.34E+06	0.0122	12.795	2.495
3	1.42E+06	0.0129	13.532	2.639
4	4.37E+05	0.0041	4.275	0.833
5	3.27E+05	0.0031	3.238	0.631
6	2.36E+05	0.0023	2.377	0.463
7	2.28E+05	0.0022	2.308	0.450
8	3.03E+05	0.0029	3.015	0.588
9	4.79E+05	0.0045	4.672	0.911
10	2.46E+05	0.0024	2.470	0.482
11	3.32E+05	0.0031	3.283	0.640
12	3.10E+05	0.0029	3.077	0.600
13	7.31E+05	0.0067	7.051	1.375
14	5.99E+05	0.0055	5.799	1.131
15	2.06E+05	0.0020	2.092	0.408
16	1.78E+05	0.0018	1.833	0.357
17	1.22E+05	0.0013	1.307	0.255
18	1.32E+05	0.0013	1.399	0.273
19	1.04E+05	0.0011	1.139	0.222
20	1.19E+05	0.0012	1.275	0.249
21	9.49E+04	0.0010	1.049	0.204
22	9.32E+04	0.0010	1.033	0.201
23	1.02E+05	0.0011	1.120	0.218
24	1.49E+05	0.0015	1.562	0.305
25	1.22E+05	0.0013	1.308	0.255
26	1.67E+05	0.0017	1.727	0.337
27	3.10E+05	0.0029	3.075	0.600
28	6.10E+05	0.0056	5.905	1.151
29	2.94E+05	0.0028	2.926	0.571

PHENANTHRENE 7.2 CM SPME CARBON INJECTED TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (pdms) (ppm)	C(H2O) (ppb)
1	7.19E+05	0.007	6.935	1.352
2	3.09E+06	0.028	29.291	5.711
3	2.37E+07	0.214	223.370	43.554
4	7.79E+07	0.703	734.704	143.256
5	1.00E+08	0.906	947.214	184.692
6	8.79E+07	0.793	829.048	161.652
7	7.86E+07	0.709	741.561	144.593
8	8.60E+07	0.776	811.162	158.164
9	8.87E+07	0.801	837.017	163.205
10	1.02E+08	0.924	965.715	188.299
11	1.11E+08	0.997	1042.665	203.303
12	1.11E+08	1.000	1045.301	203.817
13	1.10E+08	0.994	1038.918	202.573
14	1.02E+08	0.924	966.337	188.421
15	1.07E+08	0.967	1011.035	197.136
16	2.65E+08	2.395	2503.603	488.164
17	2.79E+08	2.520	2634.026	513.594
18	2.78E+08	2.508	2622.303	511.308
19	2.89E+08	2.605	2722.791	530.902
20	2.87E+08	2.587	2703.979	527.234
21	2.15E+08	1.939	2027.146	395.262
22	2.25E+08	2.034	2126.588	414.652
23	2.08E+08	1.873	1958.187	381.816
24	1.86E+08	1.682	1758.616	342.903
25	3.11E+08	2.810	2937.690	572.804
26	3.12E+08	2.814	2941.732	573.592
27	1.24E+08	1.119	1169.326	228.000
28	7.73E+07	0.698	729.156	142.174
29	6.91E+07	0.624	651.961	127.122

PHENANTHRENE 7.2 CM SPME CONTROL TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (pdms) (ppm)	C(H2O) (ppb)
1	5.26E+06	0.04763	49.79546	9.709
2	1.09E+07	0.09879	103.27232	20.136
3	3.33E+07	0.30079	314.43246	61.309
4	5.95E+07	0.53661	560.95855	109.378
5	7.63E+07	0.68883	720.08633	140.406
6	6.95E+07	0.62699	655.43206	127.799
7	1.02E+08	0.91680	958.39625	186.872
8	1.13E+08	1.01952	1065.77007	207.809
9	1.04E+08	0.94164	984.35901	191.935
10	1.20E+08	1.07938	1128.34822	220.010
11	1.15E+08	1.03956	1086.72336	211.894
12	6.61E+07	0.59681	623.88978	121.649
13	7.19E+07	0.64836	677.77847	132.156
14	1.21E+08	1.08839	1137.77070	221.848
15	1.74E+08	1.56925	1640.44690	319.862
16	1.49E+08	1.34301	1403.93908	273.746
17	1.40E+08	1.26149	1318.72119	257.130
18	1.50E+08	1.35018	1411.44028	275.209
19	1.56E+08	1.40499	1468.72979	286.379
20	1.61E+08	1.45631	1522.37810	296.840
21	1.56E+08	1.40355	1467.22945	286.087
22	1.56E+08	1.40634	1470.14027	286.655
23	1.48E+08	1.33973	1400.51603	273.079
24	1.37E+08	1.23753	1293.67727	252.247
25	1.38E+08	1.24678	1303.34861	254.133
26	1.25E+08	1.13159	1182.92734	230.652
27	1.47E+08	1.32947	1389.78386	270.986
28	N/M	N/M	N/M	N/M
29	1.14E+08	1.02468	1071.16994	208.861

PYRENE 3.8 CM SPME CARBON INJECTED TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (pdms) (ppm)	C(H2O) (ppb)
1	1.16E+07	0.05371	56.150	3.1575
2	1.73E+06	0.00798	8.345	0.4693
3	2.14E+06	0.00987	10.313	0.5799
4	3.86E+05	0.00175	1.833	0.1031
5	4.34E+05	0.00197	2.064	0.1161
6	3.66E+05	0.00166	1.738	0.0977
7	3.14E+05	0.00142	1.486	0.0835
8	4.48E+05	0.00204	2.133	0.1200
9	8.46E+05	0.00388	4.054	0.2280
10	3.60E+05	0.00163	1.707	0.0960
11	4.45E+05	0.00203	2.117	0.1191
12	2.50E+05	0.00113	1.179	0.0663
13	7.22E+05	0.00331	3.455	0.1943
14	6.40E+05	0.00293	3.060	0.1720
15	1.62E+05	0.00072	0.752	0.0423
16	1.42E+05	0.00063	0.655	0.0368
17	9.23E+04	0.00040	0.415	0.0234
18	1.29E+05	0.00057	0.593	0.0334
19	1.08E+05	0.00047	0.493	0.0277
20	7.75E+04	0.00033	0.344	0.0193
21	3.30E+05	0.00150	1.563	0.0879
22	8.22E+04	0.00035	0.366	0.0206
23	3.52E+04	0.00013	0.139	0.0078
24	1.34E+05	0.00059	0.618	0.0348
25	2.43E+05	0.00109	1.142	0.0642
26	2.84E+05	0.00128	1.343	0.0755
27	4.51E+05	0.00205	2.148	0.1208
28	1.28E+06	0.00587	6.133	0.3449
29	4.89E+05	0.00223	2.329	0.1309

PYRENE 7.2 CM SPME CARBON INJECTED TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (PDMS) (ppm)	C(H2O) (ppb)
1	6.70E+05	0.001	1.309	0.074
2	1.05E+06	0.003	3.211	0.181
3	1.47E+07	0.068	71.118	3.999
4	5.90E+07	0.278	291.394	16.386
5	6.58E+07	0.311	325.524	18.306
6	6.19E+07	0.292	305.763	17.194
7	5.68E+07	0.268	280.630	15.781
8	7.15E+07	0.338	353.878	19.900
9	7.43E+07	0.351	367.407	20.661
10	8.81E+07	0.417	436.502	24.546
11	9.92E+07	0.470	491.356	27.631
12	1.06E+08	0.501	524.439	29.491
13	N/M	N/M	N/M	N/M
14	8.61E+07	0.407	426.268	23.971
15	1.01E+08	0.480	502.694	28.269
16	1.99E+08	0.945	989.332	55.634
17	2.18E+08	1.035	1083.033	60.903
18	2.14E+08	1.017	1064.515	59.862
19	2.28E+08	1.084	1134.513	63.798
20	2.34E+08	1.110	1161.793	65.332
21	1.83E+08	0.868	907.875	51.054
22	1.89E+08	0.897	938.155	52.756
23	1.79E+08	0.851	890.469	50.075
24	2.12E+08	1.005	1051.652	59.139
25	3.13E+08	1.486	1554.488	87.415
26	3.11E+08	1.477	1545.032	86.884
27	1.23E+08	0.583	609.783	34.291
28	8.96E+07	0.424	443.968	24.966
29	7.57E+07	0.358	374.616	21.066

PYRENE 3.8 CM SPME CONTROL TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (PDMS) (ppm)	C(H2O) (ppb)
1	1.55E+07	0.00730	7.635	0.04196
2	1.33E+06	0.00063	0.660	0.00363
3	7.44E+05	0.00036	0.371	0.00204
4	1.75E+05	0.00009	0.091	0.00050
5	1.39E+05	0.00007	0.073	0.00040
6	2.27E+05	0.00011	0.117	0.00064
7	1.78E+05	0.00009	0.093	0.00051
8	3.16E+05	0.00015	0.161	0.00088
9	3.84E+05	0.00019	0.194	0.00106
10	2.19E+05	0.00011	0.113	0.00062
11	2.01E+05	0.00010	0.104	0.00057
12	1.46E+05	0.00007	0.077	0.00042
13	2.03E+05	0.00010	0.105	0.00058
14	2.41E+05	0.00012	0.124	0.00068
15	7.20E+04	0.00004	0.041	0.00022
16	3.47E+04	0.00002	0.022	0.00012
17	2.12E+04	0.00002	0.016	0.00009
18	3.01E+04	0.00002	0.020	0.00011
19	1.33E+05	0.00007	0.070	0.00039
20	1.04E+05	0.00005	0.056	0.00031
21	N/M	N/M	N/M	N/M
22	1.74E+05	0.00009	0.091	0.00050
23	1.80E+05	0.00009	0.094	0.00052
24	3.77E+04	0.00002	0.024	0.00013
25	2.12E+05	0.00010	0.109	0.00060
26	2.04E+05	0.00010	0.106	0.00058
27	4.74E+05	0.00023	0.238	0.00131
28	2.79E+06	0.00132	1.375	0.00756
29	7.73E+05	0.00037	0.385	0.00212

BENZO(A)ANTHRACENE 3.8 CM SPME AC INJECTION TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (PDMS) (ppm)	C(H2O) (ppb)
1	1.50E+07	0.069	72.551	4.080
2	9.29E+06	0.042	44.174	2.484
3	2.08E+07	0.097	101.619	5.714
4	2.84E+07	0.133	139.144	7.825
5	4.65E+07	0.219	229.189	12.888
6	5.96E+07	0.281	294.471	16.559
7	9.91E+07	0.469	491.110	27.617
8	1.26E+08	0.597	624.442	35.115
9	8.76E+07	0.415	433.740	24.391
10	1.14E+08	0.541	566.125	31.836
11	1.20E+08	0.568	593.934	33.399
12	4.50E+07	0.212	221.930	12.480
13	4.00E+07	0.188	196.810	11.067
14	8.31E+07	0.393	411.409	23.135
15	1.69E+08	0.802	839.294	47.197
16	1.55E+08	0.734	767.911	43.183
17	1.52E+08	0.722	755.498	42.485
18	1.47E+08	0.699	731.278	41.123
19	1.56E+08	0.740	774.177	43.535
20	1.60E+08	0.758	792.905	44.588
21	1.51E+08	0.714	746.822	41.997
22	1.55E+08	0.737	771.446	43.382
23	1.56E+08	0.738	772.435	43.437
24	1.57E+08	0.743	777.141	43.702
25	1.53E+08	0.728	761.268	42.809
26	1.51E+08	0.718	751.130	42.239
27	1.65E+08	0.783	818.933	46.052
28	N/M	N/M	N/M	N/M
29	1.37E+08	0.650	680.324	38.257

BENZO(A)ANTHRACENE 7.2 CM SPME AC INJECTION TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (PDMS) (ppm)	C(H2O) (ppb)
1	1.21E+06	0.00045	0.469	0.003
2	7.54E+05	0.00021	0.215	0.001
3	4.93E+06	0.00244	2.554	0.014
4	2.19E+07	0.01152	12.043	0.066
5	2.11E+07	0.01110	11.600	0.064
6	2.88E+07	0.01520	15.893	0.087
7	3.80E+07	0.02018	21.095	0.116
8	5.72E+07	0.03041	31.792	0.175
9	6.52E+07	0.03474	36.317	0.200
10	8.05E+07	0.04291	44.861	0.247
11	9.72E+07	0.05188	54.238	0.298
12	1.09E+08	0.05815	60.786	0.334
13	9.82E+07	0.05241	54.792	0.301
14	8.17E+07	0.04355	45.531	0.250
15	1.02E+08	0.05438	56.848	0.312
16	2.06E+08	0.10993	114.919	0.632
17	2.25E+08	0.12011	125.561	0.690
18	2.18E+08	0.11649	121.777	0.669
19	2.37E+08	0.12691	132.664	0.729
20	2.65E+08	0.14151	147.931	0.813
21	2.24E+08	0.11982	125.251	0.688
22	2.59E+08	0.13835	144.626	0.795
23	2.63E+08	0.14067	147.052	0.808
24	2.68E+08	0.14326	149.757	0.823
25	3.72E+08	0.19881	207.831	1.142
26	3.85E+08	0.20610	215.452	1.184
27	1.60E+08	0.08525	89.118	0.490
28	1.30E+08	0.06955	72.701	0.400
29	9.68E+07	0.05167	54.013	0.297

BENZO(A)ANTHRACENE 3.8 CM SPME CONTROL TUBE				
Depth (cm)	Peak Area	Conc. (µg/ml)	C (PDMS) (ppm)	C(H2O) (ppb)
1	1.51E+07	0.00791	8.268	0.0454
2	1.06E+07	0.00549	5.740	0.0315
3	1.62E+07	0.00846	8.845	0.0486
4	2.04E+07	0.01071	11.198	0.0615
5	4.35E+07	0.02311	24.157	0.1328
6	7.59E+07	0.04045	42.285	0.2324
7	1.02E+08	0.05439	56.859	0.3125
8	1.21E+08	0.06454	67.472	0.3708
9	7.62E+07	0.04063	42.474	0.2334
10	1.04E+08	0.05549	58.009	0.3188
11	2.06E+07	0.01086	11.350	0.0624
12	3.82E+07	0.02026	21.183	0.1164
13	3.03E+07	0.01604	16.773	0.0922
14	7.16E+07	0.03818	39.908	0.2193
15	1.70E+08	0.09065	94.766	0.5208
16	1.63E+08	0.08696	90.907	0.4996
17	1.56E+08	0.08350	87.289	0.4797
18	1.39E+08	0.07421	77.582	0.4263
19	1.49E+08	0.07977	83.385	0.4582
20	1.56E+08	0.08347	87.262	0.4795
21	1.50E+08	0.08035	83.991	0.4616
22	1.62E+08	0.08666	90.589	0.4978
23	1.67E+08	0.08935	93.405	0.5133
24	1.77E+08	0.09472	99.015	0.5441
25	1.71E+08	0.09130	95.446	0.5245
26	1.75E+08	0.09342	97.654	0.5366
27	1.88E+08	0.10075	105.324	0.5788
28	N/M	N/M	N/M	N/M
29	1.46E+08	0.07779	81.318	0.4469

APPENDIX E
MULTIPLE AC INJECTION DATA

BENZO(A)ANTHRACENE 7-SECOND BURST SHOT INJECTION TUBE								
Sample ID	Ret Time	Depth (cm)	Area per 2 cm	Conc. in ACN	Mass in PDMS (µg)	Conc. In PDMS (µg/mL)	Conc. In Pore Water (ppm)	Conc. In Pore Water (ppb)
7-0-1 11/3 11/5	18.678	30	4.66E+06	0.0023	0.0011	1.072	0.00021	0.2091
7-0-4 11/3 11/5	18.678	24	4.66E+06	0.0023	0.0011	1.072	0.00021	0.2091
7-0-7 11/3 11/5	18.706	18	5.49E+06	0.0027	0.0014	1.280	0.00025	0.2496
7-0-10 11/3 11/5	18.713	12	4.29E+06	0.0021	0.0010	0.979	0.00019	0.1909
7-0-13 11/3 11/5	18.691	6	2.60E+06	0.0012	0.0006	0.558	0.00011	0.1089
7-0-16 11/3 11/5	18.693	0	4.44E+06	0.0022	0.0011	1.018	0.00020	0.1986
7-2.5-1 11/5 11/3	18.709	30	1.13E+07	0.0059	0.0029	2.743	0.00053	0.5348
7-2.5-4 11/3 11/5	18.715	24	7.35E+06	0.0037	0.0019	1.746	0.00034	0.3404
7-2.5-7 11/3 11/5	18.703	18	6.60E+06	0.0033	0.0017	1.558	0.00030	0.3038
7-2.5-10 11/3 11/5	18.695	12	6.43E+06	0.0032	0.0016	1.515	0.00030	0.2953
7-2.5-13 11/3 11/5/10	18.713	6	4.44E+06	0.0022	0.0011	1.017	0.00020	0.1982
7-2.5-16 11/3 11/5/10	18.730	0	4.09E+06	0.0020	0.0010	0.929	0.00018	0.1811
7-4-1 11/3 11/5	18.714	30	2.23E+07	0.0117	0.0059	5.473	0.00107	1.0671
7-4-4 11/3 11/5	18.706	24	4.36E+07	0.0231	0.0116	10.802	0.00211	2.1062
7-4-7 11/3 11/5	18.689	18	1.50E+07	0.0078	0.0039	3.661	0.00071	0.7138
7-4-10 11/3 11/5	18.697	12	5.35E+06	0.0027	0.0013	1.245	0.00024	0.2428
7-4-13 11/3 11/5	18.715	6	7.18E+06	0.0036	0.0018	1.703	0.00033	0.3320
7-4-16 11/3 11/5/10	18.698	0	6.89E+06	0.0035	0.0017	1.631	0.00032	0.3180

BENZO(A)ANTHRACENE 7-SECOND BURST SHOT INJECTION CONTROL TUBE								
Sample ID	Ret Time	Depth (cm)	Area per 2 cm	Conc. in ACN	Mass in PDMS (µg)	Conc. In PDMS (µg/mL)	Conc. In Pore Water (ppm)	Conc. In Pore Water (ppb)
C-0-1 11/3 11/6	18.578	30	5.15E+08	0.276	0.138	128.724	0.0251	25.099
C-0-4 11/3 11/6	18.589	24	5.84E+08	0.312	0.156	145.862	0.0284	28.441
C-0-7 11/3 11/6	18.599	18	5.62E+08	0.301	0.150	140.529	0.0274	27.401
C-0-10 11/3 11/6	18.594	12	4.92E+08	0.263	0.132	122.881	0.0240	23.960
C-0-13 11/3 11/6	18.610	6	3.57E+08	0.191	0.096	89.179	0.0174	17.389
C-0-16 11/3 11/6	18.612	0	2.42E+08	0.129	0.065	60.364	0.0118	11.770
C-4-1 11/3 11/6	18.612	30	6.16E+08	0.330	0.165	154.060	0.0300	30.039
C-4-4 11/3 11/6	18.601	24	6.71E+08	0.359	0.180	167.635	0.0327	32.686
C-4-7 11/3 11/6	18.608	18	5.05E+08	0.270	0.135	126.234	0.0246	24.614
C-4-10 11/3 11/6	18.623	12	4.39E+08	0.235	0.117	109.677	0.0214	21.385
C-4-13 11/3 11/6	18.620	6	3.93E+08	0.210	0.105	98.094	0.0191	19.127
C-4-16 11/3 11/6	18.618	0	1.72E+08	0.092	0.046	43.013	0.0084	8.387

PYRENE 7-SECOND BURST SHOT INJECTION TUBE								
Sample ID	Ret Time	Depth (cm)	Area per 2 cm	Conc. in ACN	Mass in PDMS (µg)	Conc. In PDMS (µg/mL)	Conc. In Pore Water (ppm)	Conc. In Pore Water (ppb)
7-0-1 11/3 11/5	16.16203	1	8183744.056	0.0378	0.019	17.638	0.0010	0.992
7-01-4 11/3 11/5	16.16203	4	8183744.056	0.0378	0.019	17.638	0.0010	0.992
7-0-7 11/3 11/5	16.18057	7	7896914.08	0.0365	0.018	17.019	0.0010	0.957
7-0-10 11/3 11/5	16.1945	10	6449882.849	0.0298	0.015	13.898	0.0008	0.782
7-0-13 11/3 11/5	16.17188	13	7419761.716	0.0342	0.017	15.990	0.0009	0.899
7-0-16 11/3 11/5	16.17747	16	5444168.375	0.0251	0.013	11.729	0.0007	0.660
7-2.5-1 11/5 11/3	16.19111	1	10406850.39	0.0480	0.024	22.433	0.0013	1.262
7-2.5-4 11/3 11/5	16.19701	4	6207101.103	0.0286	0.014	13.375	0.0008	0.752
7-2.5-7 11/3 11/5	16.18861	7	8441081.659	0.0390	0.019	18.193	0.0010	1.023
7-2.5-10 11/3 11/5	16.17439	10	11777758.04	0.0544	0.027	25.390	0.0014	1.428
7-2.5-13 11/3 11/5/10	16.18607	13	6823047.672	0.0315	0.016	14.703	0.0008	0.827
7-2.5-16 11/3 11/5/10	16.20232	16	4298215.165	0.0198	0.010	9.257	0.0005	0.521
7-4-1 11/3 11/5	16.19623	1	17109646.37	0.0790	0.040	36.891	0.0021	2.075
7-4-4 11/3 11/5	16.18698	4	55242095.85	0.2552	0.128	119.140	0.0067	6.700
7-4-7 11/3 11/5	16.16625	7	29627102.33	0.1368	0.068	63.890	0.0036	3.593
7-4-10 11/3 11/5	16.1735	10	11444623.98	0.0528	0.026	24.672	0.0014	1.387
7-4-13 11/3 11/5	16.19154	13	5970644.735	0.0276	0.014	12.865	0.0007	0.723
7-4-16 11/3 11/5/10	16.17972	16	6566417.333	0.0303	0.015	14.150	0.0008	0.796

PYRENE 7-SECOND CONTROL TUBE								
Sample ID	Ret Time	Depth (cm)	Area per 2 cm	Conc. in ACN	Mass in PDMS (µg)	Conc. In PDMS (µg/mL)	Conc. In Pore Water (ppm)	Conc. In Pore Water (ppb)
C-0-1 11/3 11/6	15.43587	1	296427335.7	1.4074	0.704	657.065	0.0369	36.949
C-0-4 11/3 11/6	15.44519	4	328245004.6	1.5586	0.779	727.690	0.0409	40.921
C-0-7 11/3 11/6	15.45435	7	329509351	1.5646	0.782	730.496	0.0411	41.079
C-0-10 11/3 11/6	15.44986	10	266562691.5	1.2654	0.633	590.776	0.0332	33.222
C-0-13 11/3 11/6	15.46087	13	206591864.5	0.9803	0.490	457.661	0.0257	25.736
C-0-16 11/3 11/6	15.46512	16	175452452.4	0.8322	0.416	388.542	0.0218	21.849
C-4-1 11/3 11/6	15.45586	1	317365618.3	1.5069	0.753	703.541	0.0396	39.563
C-4-4 11/3 11/6	15.4515	4	382042543.5	1.8144	0.907	847.102	0.0476	47.636
C-4-7 11/3 11/6	15.45626	7	273491922.1	1.2983	0.649	606.156	0.0341	34.087
C-4-10 11/3 11/6	15.46435	10	241536136.3	1.1464	0.573	535.225	0.0301	30.098
C-4-13 11/3 11/6	15.46441	13	253048565.9	1.2011	0.601	560.779	0.0315	31.535
C-4-16 11/3 11/6	15.46677	16	111674467.5	0.5290	0.264	246.976	0.0139	13.888
C-0-1 11/3 11/6	15.43587	1	296427335.7	1.4074	0.704	657.065	0.0369	36.949

PHENANTHRENE 7-SECOND BURST SHOT INJECTION TUBE								
Sample ID	Ret Time	Depth (cm)	Area per 2 cm	Conc. in ACN	Mass in PDMS (µg)	Conc. In PDMS (µg/mL)	Conc. In Pore Water (ppm)	Conc. In Pore Water (ppb)
7-0-1 11/3 11/5	13.576	30	8916712.233	0.0806	0.040	37.626	0.0073	7.337
7-01-4 11/3 11/5	13.576	24	8916712.233	0.0806	0.040	37.626	0.0073	7.337
7-0-7 11/3 11/5	13.586	18	7456162.995	0.0674	0.034	31.474	0.0061	6.137
7-0-10 11/3 11/5	13.595	12	6180493.672	0.0559	0.028	26.101	0.0051	5.089
7-0-13 11/3 11/5	13.585	6	11268813.36	0.1018	0.051	47.533	0.0093	9.268
7-0-16 11/3 11/5	13.585	0	5870926.059	0.0531	0.027	24.797	0.0048	4.835
7-2.5-1 11/5 11/3	13.592	30	5980233.158	0.0541	0.027	25.258	0.0049	4.925
7-2.5-4 11/3 11/5	13.599	24	4075507.211	0.0369	0.018	17.235	0.0034	3.361
7-2.5-7 11/3 11/5	13.595	18	7431740.139	0.0672	0.034	31.371	0.0061	6.117
7-2.5-10 11/3 11/5	13.585	12	12265608.06	0.1108	0.055	51.732	0.0101	10.087
7-2.5-13 11/3 11/5/10	13.596	6	7216284.984	0.0653	0.033	30.464	0.0059	5.940
7-2.5-16 11/3 11/5/10	13.602	0	3983839.974	0.0361	0.018	16.849	0.0033	3.285
							0.0000	
7-4-1 11/3 11/5	13.598	30	9901281.793	0.0895	0.045	41.773	0.0081	8.145
7-4-4 11/3 11/5	13.594	24	81939736.71	0.7394	0.370	345.201	0.0673	67.309
7-4-7 11/3 11/5	13.579	18	61240442.03	0.5526	0.276	258.015	0.0503	50.309
7-4-10 11/3 11/5	13.585	12	12922074.08	0.1167	0.058	54.497	0.0106	10.626
7-4-13 11/3 11/5	13.596	6	4762498.162	0.0431	0.022	20.129	0.0039	3.925
7-4-16 11/3 11/5/10	13.591	0	5628543.233	0.0509	0.025	23.776	0.0046	4.636

PHENANTHRENE 7-SECOND CONTROL TUBE								
Sample ID	Ret Time	Depth (cm)	Area per 2 cm	Conc. in ACN	Mass in PDMS (µg)	Conc. In PDMS (µg/mL)	Conc. In Pore Water (ppm)	Conc. In Pore Water (ppb)
C-0-1 11/3 11/6	13.520	30	795860290	7.180	3.590	3352.26	0.654	653.638
C-0-4 11/3 11/6	13.525	24	867026364.2	7.822	3.911	3652.01	0.712	712.085
C-0-7 11/3 11/6	13.529	18	921985353.6	8.318	4.159	3883.50	0.757	757.222
C-0-10 11/3 11/6	13.528	12	745545886.5	6.726	3.363	3140.33	0.612	612.316
C-0-13 11/3 11/6	13.537	6	590951009.2	5.331	2.666	2489.17	0.485	485.350
C-0-16 11/3 11/6	13.540	0	131998661.3	1.191	0.595	556.05	0.108	108.421
C-4-1 11/3 11/6	13.536	30	907744674.4	8.189	4.095	3823.52	0.746	745.526
C-4-4 11/3 11/6	13.531	24	1137147108	10.259	5.130	4789.77	0.934	933.930
C-4-7 11/3 11/6	13.535	18	771892476.1	6.964	3.482	3251.30	0.634	633.953
C-4-10 11/3 11/6	13.541	12	708826915	6.395	3.197	2985.67	0.582	582.159
C-4-13 11/3 11/6	13.541	6	592129806.9	5.342	2.671	2494.14	0.486	486.318
C-4-16 11/3 11/6	13.541	0	92412147.65	0.834	0.417	389.31	0.076	75.910
C-0-1 11/3 11/6	13.520	30	795860290	7.180	3.590	3352.26	0.654	653.638

REFERENCES

Anchor Environmental CA L.P. (2003) Literature review of effects of resuspended sediments due to dredging operations., Prepared for Los Angeles Contaminated Sediments Task Force, Los Angeles, CA.

Arthur C.L., Pawliszyn J. (1990) Solid phase microextraction with thermal desorption using fused silica optical fibers. Analytical Chemistry 62:2145-2148. DOI: 10.1021/ac00218a019.

ATSDR, Mumatz M., George J. (1995) Toxicological Profile for Polycyclic Aromatic Hydrocarbons, in: Agency for Toxic Substances and Disease Registry (Ed.), U.S. Government Printing Office,, Atlanta, GA.

Bao L.-J., Zeng E.Y. (2011) Passive sampling techniques for sensing freely dissolved hydrophobic organic chemicals in sediment porewater. Trends in Analytical Chemistry 30:1422-1428.

Bocchetti R., Fattorini D., Pisanelli B., Macchia S., Oliviero L., Pilato F., Pellegrini D., Regoli F. (2008) Contaminant accumulation and biomarker responses in caged mussels, Mytilus galloprovincialis, to evaluate bioavailability and toxicological effects of remobilized chemicals during dredging and disposal operations in harbour areas. Aquatic Toxicology 89:257-266.

Boffetta P., Jourenkova N., Gustavsson P. (1997) Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons. Cancer Causes and Control 8:444-472. DOI: 10.1023/a:1018465507029.

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

Boyd S.E., Limpenny D.S., Rees H.L., Cooper K.M. (2005) The effects of marine sand and gravel extraction on the macrobenthos at a commercial dredging site (results 6 years post-dredging). ICES Journal of Marine Science 62:145-162.

Chen J., Pawliszyn J.B. (1995) Solid Phase Microextraction Coupled to High-Performance Liquid Chromatography. Analytical Chemistry 67:2530-2533. DOI: 10.1021/ac00111a006.

Cho Y.-M., Ghosh U., Kennedy A.J., Grossman A., Ray G., Tomaszewski J.E., Smithenry D.W., Bridges T.S., Luthy R.G. (2009) Field Application of Activated Carbon Amendment for In-Situ Stabilization of Polychlorinated Biphenyls in Marine Sediment. Environmental Science & Technology 43:3815-3823. DOI: 10.1021/es802931c.

Conder J.M., La Point T.W., Lotufo G.R., Steevens J.A. (2003) Nondestructive, Minimal-Disturbance, Direct-Burial Solid-Phase Microextraction Fiber Technique for Measuring TNT in Sediment. Environmental Science & Technology 37:1625-1632. DOI: 10.1021/es0260770.

Cornelissen G., Pettersen A., Broman D., Mayer P., BreedVeld G.D. (2008) Field Testing of Equilibrium Passive Samplers to Determine Freely Dissolved Native Polycyclic Aromatic Hydrocarbon Concentrations. Environmental Toxicology & Chemistry 27:499-508. DOI: 0730-7268/08.

Doong R.-a., Chang S.-m. (2000) Determination of Distribution Coefficients of Priority Polycyclic Aromatic Hydrocarbons Using Solid-Phase Microextraction. Analytical Chemistry 72:3647-3652. DOI: 10.1021/ac000040l.

Fahrenfeld, N., Zoeckler, J., Widdowson, M.A., Pruden, A. (2012) Effect of biostimulants on 2,4,6-trinitrotoluene and bacterial community composition in contaminated aquifer sediment enrichments. Biodegradation, DOI 10.1007/s10532-012-9569-2

Fisher T.T., Law R.J., Rumney H.S., Kirby M.F., Kelly C. (2011) Towards a scheme of toxic equivalency factors (TEFs) for the acute toxicity of PAHs in sediment. Ecotoxicology and Environmental Safety 74:2245-2251.

Francingues K.E.G., Burton G.A., Norman R., Wolfe, Jr., Danny D.R., Donna J.V., John R. (2008) Evaluating the Effectiveness of Contaminated-Sediment Dredging. Environmental Science & Technology 42:5042-5047. DOI: 10.1021/es087185a.

Ghosh U., Gillette J.S., Luthy R.G., Zare R.N. (2000) Microscale Location, Characterization, and Association of Polycyclic Aromatic Hydrocarbons on Harbor Sediment Particles. Environmental Science & Technology 34:1729-1736. DOI: 10.1021/es991032t.

Ghosh U., Luthy R.G., Cornelissen G., Werner D., Menzie C.A. (2011) In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. Environmental Science & Technology 45:1163-1168. DOI: 10.1021/es102694h.

Gschwend P.M., MacFarlane J.K., Reible D.D., Lu X., Hawthorne S.B., Nakles D.V., Thompson T. (2011) Comparison of polymeric samplers for accurately assessing PCBs in pore waters. Environmental Toxicology and Chemistry 30:1288-1296. DOI: 10.1002/etc.510.

Guo Z., Lin T., Zhang G., Yang Z., Fang M. (2006) High-Resolution Depositional Records of Polycyclic Aromatic Hydrocarbons in the Central Continental Shelf Mud of the East China Sea. Environmental Science & Technology 40:5304-5311. DOI: 10.1021/es060878b.

Gustafsson Ö., Haghseta F., Chan C., MacFarlane J., Gschwend P.M. (1996) Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability. Environmental Science & Technology 31:203-209. DOI: 10.1021/es960317s.

Haftka J.J.H., Parsons J.R., Govers H.A.J., Ortega-Calvo J.-J. (2008) Enhanced kinetics of solid-phase microextraction and biodegradation of polycyclic aromatic hydrocarbons in the presence of dissolved organic matter. Environmental Toxicology and Chemistry 27:1526-1532. DOI: 10.1897/07-544.1.

Hale, S.E., Meynet, P., Davenport, R.J., Jones, D.M., Werner, D. (2012) Changes in polycyclic aromatic hydrocarbon availability in River Tyne sediment following bioremediation treatments or activated carbon amendment. Water Research 44:4529-4536. DOI: 10.1016/j.watres.2010.06.027

Hawthorne S.B., St. Germain R.W., Azzolina N.A. (2008) Laser-Induced Fluorescence Coupled with Solid-Phase Microextraction for In Situ Determination of PAHs in Sediment Pore Water. Environmental Science & Technology 42:8021-8026. DOI: 10.1021/es8011673.

Hawthorne S.B., Azzolina N.A., Neuhauser E.F., Kreitinger J.P. (2007) Predicting Bioavailability of Sediment Polycyclic Aromatic Hydrocarbons to Hyalella azteca using Equilibrium Partitioning, Supercritical Fluid Extraction, and Pore Water Concentrations. Environmental Science & Technology 41:6297-6304. DOI: 10.1021/es0702162.

Heringa M.B., Hermens J.L.M. (2003) Measurement of free concentrations using negligible depletion-solid phase microextraction (nd-SPME). TrAC Trends in Analytical Chemistry 22:575-587.

Interstate Technology & Regulatory Council. (2005) Technology overview of passive sampler technologies, in: Diffusion Sampler Team (Ed.), Technology Overview, Washington, D.C.

Jahnke A., Mayer P. (2010) Do complex matrices modify the sorptive properties of polydimethylsiloxane (PDMS) for non-polar organic chemicals? Journal of Chromatography A 1217:4765-4770.

Lau E.V., Gan S., Ng H.K. (2010) Extraction Techniques for Polycyclic Aromatic Hydrocarbons in Soils. International Journal of Analytical Chemistry 2010. DOI: 10.1155/2010/398381.

Lohmann R., MacFarlane J.K., Gschwend P.M. (2004) Importance of Black Carbon to Sorption of Native PAHs, PCBs, and PCDDs in Boston and New York Harbor Sediments. Environmental Science & Technology 39:141-148. DOI: 10.1021/es049424+.

Lu X., Skwarski A., Drake B., Reible D.D. (2011) Predicting bioavailability of PAHs and PCBs with porewater concentrations measured by solid-phase microextraction fibers. Enivornmental Toxicology and Chemistry 30:1109-1116. DOI: 10.1002/etc.495.

Maruya K.A., Zeng E.Y., Tsukada D., Bay S.M. (2009) A passive sampler based on solid-phase microextraction for quantifying hydrophobic organic contaminants in sediment pore water. Environmental Toxicology and Chemistry 28:733-740. DOI: 10.1897/08-322r.1.

Mayer P., Vaes W.H.J., Wijnker F., Legierse K.C.H.M., Kraaij R., Tolls J., Hermens J.L.M. (2000) Sensing Dissolved Sediment Porewater Concentrations of Persistent and Bioaccumulative Pollutants Using Disposable Solid-Phase Microextraction Fibers. Environmental Science & Technology 34:5177-5183. DOI: 10.1021/es001179g.

Millward R.N., Bridges T.S., Ghosh U., Zimmerman J.R., Luthy R.G. (2005) Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulosus). Environmental Science & Technology 39:2880-2887. DOI: 10.1021/es048768x.

Murphy P., Marquette A., Reible D., Lowry G. (2006) Predicting the Performance of Activated Carbon-, Coke-, and Soil-Amended Thin Layer Sediment Caps. Journal of Environmental Engineering 132:787-794. DOI: doi:10.1061/(ASCE)0733-9372(2006)132:7(787).

Namieśnik J., Zabiegała B., Kot-Wasik A., Partyka M., Wasik A. (2005) Passive sampling and/or extraction techniques in environmental analysis: a review. Analytical and Bioanalytical Chemistry 381:279-301. DOI: 10.1007/s00216-004-2830-8.

Oen A.M.P., Janssen E.M.L., Cornelissen G., Breedveld G.D., Eek E., Luthy R.G. (2011) In Situ Measurement of PCB Pore Water Concentration Profiles in Activated Carbon-Amended Sediment Using Passive Samplers. Environmental Science & Technology 45:4053-4059. DOI: 10.1021/es200174v.

Paine M.D., Chapman P.M., Allard P.J., Murdoch M.H., Minifie D. (1996) Limited bioavailability of sediment pah near an aluminum smelter: Contamination does not equal effects. Environmental Toxicology and Chemistry 15:2003-2018. DOI: 10.1002/etc.5620151119.

Prosen H., Zupančič-Kralj L. (1999) Solid-phase microextraction. Trends in Analytical Chemistry 18:272-282.

Quadrini J.D., VanDewalker H.M., Mihm J.E., McShea L.J. (2003) Pilot-scale demonstration of in situ capping of PCB-containing sediments in the lower Grasse River. Remediation Journal 14:33-53. DOI: 10.1002/rem.10093.

Reible D.D., Lotufo G., Skwarski A., Lampert D., Lu X. (2008) Demonstration and evaluation of solid phase microextraction for the assessment of bioavailability and contaminant mobility, in: Environmental Security Technology Certification Program (Ed.), Laboroatory Study Report.

SERDP, ESTCP. (2004) SERDP and ESTCP Expert Panel Workshop on Research and Development Needs for the In Situ Management of Contaminated Sediments, Strategic Environmental Research and Development Program, Arlington, VA.

Simcik M.F., Eisenreich S.J., Golden K.A., Liu S.-P., Lipiatou E., Swackhamer D.L., Long D.T. (1996) Atmospheric Loading of Polycyclic Aromatic Hydrocarbons to Lake Michigan as Recorded in the Sediments. Environmental Science & Technology 30:3039-3046. DOI: 10.1021/es960102i.

Simonich S.L.M., Motorykin O., Jariyasopit N. (2011) PAH intermediates: Links between the atmosphere and biological systems. Chemico-Biological Interactions 192:26-29.

Swartz R.C. (1999) Consensus sediment quality guidelines for polycyclic aromatic hydrocarbon mixtures. Environmental Toxicology and Chemistry 18:780-787. DOI: 10.1002/etc.5620180426.

Ter Laak T.L., Barendregt A., Hermens J.L.M. (2006) Freely Dissolved Pore Water Concentrations and Sorption Coefficients of PAHs in Spiked, Aged, and Field-Contaminated Soils. Environmental Science & Technology 40:2184-2190. DOI: 10.1021/es0524548.

Tomaszewski J.E., Werner D., Luthy R.G. (2007) Activated carbon amendment as a treatment for residual ddt in sediment from a superfund site in San Francisco Bay, Richmond, California, USA. Environmental Toxicology and Chemistry 26:2143-2150. DOI: 10.1897/07-179r.1.

U.S Environmental Protection Agency. (2005) Contaminated Sediment Remediation Guidance, in: U. EPA, Office of Solid waste and Emergency Response, Washington DC.

U.S. Environmental Protection Agency. (1998) Field Applications of In Situ Remediation Technologies., U.S. Environmental Protection Agency, Washington, DC.

U.S. Environmental Protection Agency. (2003) Procedures for the Derivation of Equilibrium Partition Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures, in: Office of Research and Development, Washington, DC.

U.S. Environmental Protection Agency. (2009) 2008 Biennial National Listing of Fish Advisories, in: Office of Science and Technology, U.S. EPA,, Washington, DC.

Van der Wal L., Jager T., Fleuren R.H.L.J., Barendregt A., Sinnige T.L., van Gestel C.A.M., Hermens J.L.M. (2004) Solid-Phase Microextraction To Predict Bioavailability and Accumulation of Organic Micropollutants in Terrestrial Organisms after Exposure to a Field-Contaminated Soil. Environmental Science & Technology 38:4842-4848. DOI: 10.1021/es035318g.

Van Dolah R.F., Calder D.R., Knott D.M. (1984) Effects of dredging and open-water disposal on benthic macroinvertebrates in a South Carolina estuary. Estuaries 7:28-37.

Van Metre P.C., Mahler B.J., Furlong E.T. (2000) Urban Sprawl Leaves Its PAH Signature. Environmental Science & Technology 34:4064-4070. DOI: 10.1021/es991007n.

Vrana B., Allan I.J., Greenwood R., Mills G.A., Dominiak E., Svensson K., Knutsson J., Morrison G. (2005) Passive sampling techniques for monitoring pollutants in water. TrAC Trends in Analytical Chemistry 24:845-868.

White P.A. (2002) The genotoxicity of priority polycyclic aromatic hydrocarbons in complex mixtures. Mutation Research/Genetic Toxicology and Environmental Mutagenesis 515:85-98.

Yongyong G., Kusheng W., Xia H., Xijin X. (2011) Sources, Distribution, and Toxicity of Polycyclic Aromatic Hydrocarbons. Journal of Environmental Health 73:22-25.

VITA

Ryan Stringer was born to Kenny and Gina Stringer in Exeter, Missouri. Growing up, he participated in baseball and basketball and loved the challenge of a competition. He attended Exeter high school where he graduated valedictorian of his class and, due to his interest in science and mathematics, decided to attend the University of Missouri Rolla to pursue a degree in engineering in the fall of 2005. During his undergraduate career Ryan participated in student government as a resident hall treasurer and a Vice President of Business and Operations for the Student Union Board. He was also an RA, performed undergraduate research and was a member of the engineering honors society Chi Epsilon. In 2010, Ryan graduated Magna Cum Laude with a B.S. in Environmental Engineering and immediately began working on a Master's Degree in Environmental Engineering. Ryan graduated summa cum laude with his Master's Degree in Environmental Engineering in December of 2012.