Comparison of Traditional, Two-Sided Sediment Passive Sampler Deployment Frame to New, Annular Design for Deployment to Rocky Substrate

A thesis

Presented by:

Alanna Sparagna

To:
The Department of Civil and Environmental Engineering

in partial fulfillment of the requirements for the degree of

Master of Science

In the field of

Environmental Engineering

Northeastern University

Boston, MA

December 2019
Abstract

This work centers around the need for a new sediment passive sampler deployment method for monitoring contaminated sediments across an armored cap or sediments in rocky substrates where traditional sampler frames cannot be used. Armored caps and large cobbles make it difficult for traditional passive samplers to penetrate through to contaminated sediment layers, and therefore a new spike design was made. The new, annular sampler has a solid aluminum core with a pointed end around which the performance reference compound (PRC)-loaded polyethylene (PE) was placed. Perforated tubing was then secured around the PE layer, using stainless steel wire wound in opposing directions. In this study, a side-by-side comparison of the new annular design and a traditional two-sided sampler frame was performed at the Rumney Marsh, Revere, Massachusetts, USA.

In this study we examined the concentrations of polyaromatic hydrocarbons (PAHs) in the water and sediment porewaters of the Rumney Marsh. The two samplers were deployed adjacently (within 0.5 m of each other). After one month, the samplers were retrieved, cleaned, sectioned and extracted. Based on the prototype only being exposed on one side, it was expected that the fractional equilibration ($f_{eq}$) of the PE would be less than that observed in the PE exposed by the traditional sampler frame, and that the concentrations taken up by the sampler would be lower than within the traditional sampler, but that the resulting PRC corrected freely-dissolved concentrations would be similar.

It was found that the $f_{eq}$s were lower in the prototype sampler than in the traditional sampler, however the concentrations did not follow an obvious trend. This could have been due to differences in the sediments, or potential sediment contamination in the extracts. In general,
the prototype functioned as it was expected to and will be further tested in cobbled sediment beds in future studies.
Acknowledgement

I would like to thank my advisor, Doctor Loretta A. Fernandez, who not only made this project possible for me to pursue, but also had the patience of a saint dealing with me through this whole process. I would also like to thank Mike MacNeil and Kurt Braun, without whom we could not have built the prototype this project is based on, as well as Kelsey Walak, the undergraduate Co-Op student that has worked in the lab this past semester for her help in cleaning the samplers once they were retrieved as well as the extraction process, and Dr. Annalisa Onis-Hayden for taking pity on my poor soul.

Additionally, I would like to thank my office mates and friends in the Civil and Environmental Engineering department, especially Cassandra Nickels, who also has the patience of a saint, along with Nicole Catubig, Carolina Venegas-Martinez, Sarah Sanchez, Max Rome and Sadia Khan, for their continued support and encouragement throughout my experiments and writing. I would also like to thank the EnviroChem supergroup for their helpful inputs and suggestions about how to properly handle and process my data.

Finally, I would like to thank my parents for their kind and encouraging words, even when I thought I was at my wit’s end, as well as my siblings, my sisters Kristen and Bridget, and my brother Nick, for actually inquiring about what I was doing despite the fact that ninety-five percent of the time they had no idea what I was talking about when I started throwing acronyms around.
# Table of Contents

Abstract ........................................................................................................................................... 2

Acknowledgement .......................................................................................................................... 3

List of Figures ................................................................................................................................ 6

List of Tables ................................................................................................................................... 7

1. Introduction and Background ........................................................................................................ 8

   1.1 PAHs .......................................................................................................................................... 8

   1.2 Toxicity Risk and Exposure ....................................................................................................... 8

   1.3 Passive Sampling .................................................................................................................... 11

   1.4 Performance Reference Compounds (PRCs) ......................................................................... 12

   1.5 Sampler designs for in situ deployment to engineered sediment cap ..................................... 12

   1.6 Objectives ............................................................................................................................... 13

2. Materials and Methods .................................................................................................................. 15

   2.1 Materials .................................................................................................................................. 15

      2.1.1 Chemicals ......................................................................................................................... 15

      2.1.2 Polyethylene (PE) preparation ......................................................................................... 15

   2.2 Methods ................................................................................................................................... 16

      2.2.1 Prototype .......................................................................................................................... 16

      2.2.2 Traditional PE deployment frame ...................................................................................... 16

      2.2.3 Test Site ........................................................................................................................... 17

      2.2.4 Sampler extraction ............................................................................................................ 17

      2.2.5 GC Analysis ..................................................................................................................... 18

3. Results and Discussion .................................................................................................................... 18

   3.1 Comparison of methods ........................................................................................................... 18
3.1.1 Fractional Equilibration comparison ................................................................. 18
3.1.2 Phenanthrene and Anthracene ........................................................................... 19
3.1.3 Fluoranthene and Pyrene .................................................................................. 20
3.1.4 Benz(a)anthracene and Chrysene ..................................................................... 21
3.1.5 Depth Comparison ............................................................................................. 21
3.2 Sources of Error ..................................................................................................... 22
4. Conclusion ............................................................................................................... 22
  4.1 Conclusions ........................................................................................................... 22
  4.2 Future Work .......................................................................................................... 23
Tables .......................................................................................................................... 24
Figures ......................................................................................................................... 27
Works Cited ............................................................................................................... 33
List of Figures

Figure 1. The bioavailability process ........................................................................................................28
Figure 2. The traditional PE passive sampler deployed in Rumney Marsh on June 26, 2019 ............ 27
Figure 3. A side by side comparison of the deployed prototype and traditional sampler .................. 28
Figure 4. Comparison of d-chrysene $f_{eq}$ by depth, with the zero centerline being the sediment water interface. Error bars represent the propagation measurement uncertainty through Eqn 1. ...................... 28
Figure 5. Comparison of d-pyrene $f_{eq}$ by depth, with the zero centerline being the sediment water interface. Error bars represent the propagation measurement uncertainty through Eqn 1. ...................... 29
Figure 6. Comparison of d-phenanthrene $f_{eq}$ by depth with the sediment-water interface at y value zero. The error bars represent the propagation of measurement uncertainty through Eqn 1. ...................... 29
Figure 7. Calculated $C_{free}$ for phenanthrene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2. .......................................................... 30
Figure 8. Calculated $C_{free}$ for anthracene for both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2. .......................................................... 30
Figure 9. Calculated $C_{free}$ for fluoranthene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2. .......................................................... 31
Figure 10. Calculated $C_{free}$ for pyrene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2. .......................................................... 31
Figure 11. Calculated $C_{free}$ for benz(a)anthracene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2. .......................................................... 32
Figure 12. Calculated $C_{free}$ for chrysene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2. .......................................................... 32
List of Tables

Table 1. Percent difference analysis according to equivalent depths for phenanthrene (ng/L) and anthracene (ng/L). The shaded portion is the sediment portion .......................................................... 25

Table 2. Percent difference analysis according to equivalent depths for fluoranthene (ng/L) and pyrene (ng/L). The shaded portion is the sediment portion .......................................................... 24

Table 3. Percent difference analysis according to equivalent depths for Benz(a)anthracene (ng/L) and Chrysene (ng/L). The shaded portion is the sediment portion .......................................................... 25

Table 4. The percent recovery of surrogate standards ........................................................................................................ 26
1. Introduction and Background

1.1 PAHs

Hydrophobic organic contaminants (HOCs) are a class of organic pollutants including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) as well as dioxins and some pesticides. HOCs are generally found in topsoil and aquatic systems. Despite increased restrictions, HOCs are still used in industries and are continually added to the environment through new contaminant spills as well as past contaminant spills that were either improperly remediated or not remediated at all (Moyo et al., 2014). Also known as legacy contaminants, HOCs degrade very slowly over time, if at all. Due to their hydrophobicity, they have low solubility in water and thus typically sorb to sediments and soils (Yang et al., 2007).

Polycyclic aromatic hydrocarbons (PAHs) are released into the air and water supply through car exhaust, industrial wastes, and the burning of fossil fuels, as well as chemical and oil spills (Toxicology, 1995).

There are several factors that affect the persistence of PAHs in soil and sediment. Their recalcitrant aromatic structure, low aqueous solubility and high hydrophobicity result in compounds that are resistant to physical and chemical degradation (Couling et al., 2010). These properties raise concerns of bioaccumulation and acute toxicity in living organisms.

1.2 Toxicity Risk and Exposure

The toxicity of the 100+ PAHs in existence varies depending on the molecular formula. Generally speaking, PAHs are known or suspected carcinogens (Lohmann et al., 2004) and have been found to cause tumors in lab animals. As previously stated, PAHs prefer to be sorbed to
sediment rather than free in solution, but this causes an inherent risk of PAHs entering the food chain.

PAHs and HOCs in general may be toxic to benthic organisms that inhabit contaminated sediments, whereas marine and terrestrial biota are indirectly exposed via food web transfer as well as directly through water and air (Maruya et al., 2009). HOCs typically exhibit a narcotic toxicity by sorbing to membrane lipids (which will disrupt membrane function) and travel up the food chain by accumulation in body fat. (Fernandez, 2005; Lohmann et al., 2004) It has been shown that sediment association with PAHs alone is not predictive of consequences at tissue or organism level (Yang et al., 2007). The source of the PAH also matters greatly. PAHs from pyrogenic sources are mainly adsorbed onto charcoal and soot, whereas those from petrogenic sources are less strongly sorbed to natural organic material (Witt et al., 2009). HOCs and by extension PAHs enter aquatic ecosystems via pathways such as dumping, direct discharge into the water, aeolian deposits from the combustion of fossil fuels, and suspended particles entering the waterways through oil or chemical spills (Witt et al., 2013; Witt et al., 2009).

In addition to the toxicity risk associated with PAHs, bioavailability and bioaccessibility must also be considered. Bioavailability is defined as a chemical which is freely available to cross a microorganism’s membrane from the medium in which that organism exists. Bioaccessibility, however, is defined as “that which is available to cross an organism’s cellular membrane freely from the environment, if the organism has access to the chemical”. Accessibility is highly variant and depends on the freely-dissolved concentrations of pollutants, which, due to environmental factors, is not fixed and can vary widely with time (Ehlers et al., 2006). Certain types of PAHs are more readily available to the environment due to their sources. As previously mentioned, PAHs can come from multiple source, including pyrogenic (e.g.,
burning fossil fuels, coal, etc.) versus petrogenic (e.g., oil spills and wastewater). PAHs from pyrogenic sources tend to be less available because they are already strongly bound to carbonaceous matter, whereas petrogenic sources produce PAHs that are sorbed to amorphous organic carbon coatings and are more likely to desorb in the appropriate conditions (Rust et al., 2004).

The bioavailability process (Figure 1) is difficult to model due to the complex set of factors that vary from organism to organism. Originally, harsh, exhaustive extraction procedures were used to try and predict the bioavailability of the contaminant and each time it resulted in overestimations of the bioavailability due to the process extracting non-bioaccessible HOCs from their sorbed surfaces (Ehlers et al., 2006). The most accurate way of predicting bioavailability is testing the tissues of organisms. However, this is both costly and time consuming. According to Tuikka et. al, in their study of a two-carbon model versus dissolved porewater concentration, the concentration of freely-dissolved PAHs and PCBs in porewater was the most predictive of bioaccumulation seen in tissue samples (Tuikka et al., 2016).

Biota to sediment accumulation factors (BSAFs), which relate lipid normalized organism tissues to organic carbon normalized bulk sediment HOC concentrations of hydrophobic organic compounds are highly variable for deposit feeders. As a result, one can conclude that equilibrium partitioning (EqP) models that depend on a compound sorption to a single organic carbon pool are not accurate when trying to derive bioavailability. Variability in BSAFs can be attributed to differences in sequestration or the presence of slowly desorbing fractions of contaminants in sediment (Kraaij et al., 2002).
1.3 Passive Sampling

Passive sampling is a relatively new method for measuring organic contaminants in water and air that is more efficient than traditional sampling. It involves exposing some form of polymer sheets such as low density polyethylene (PE) or polyoxymethylene (POM), or glass fibers coated with a polymer such as polydimethylsiloxane (PDMS) (also known as solid phase microextraction (SPME)) (Zhou et al., 2007) to the media to be sampled and using laboratory determined partition coefficients to find the equivalent water concentration. Passive sampling is advantageous over traditional sampling because it allows for the detection of dissolved HOCs at very low levels, as well as negates the need to collect or filter large volumes of water. Furthermore, passive sampling avoids many of the estimations and models associated with traditional methods that result in over- and under-estimating dissolved concentrations (Fernandez et al., 2012). Passive sampling functions by creating a gradient across which organic materials will sorb to the polymer due to lower concentrations outside the samplers or higher concentration.

As previously stated, passive sampling is a much more consistent and precise method of determining dissolved concentrations of HOCs than using EqP models considering a single organic carbon pool (Fernandez et al., 2015; Lohmann et al., 2004). In addition to implications when predicting bioavailability, accurately determining sediment porewater concentrations is important when calculating contaminant flux across the sediment-water interface. According to Fernandez et al. (2014), the flux of PCBs between sediment and water at sites on the Palos Verdes Shelf differed by more than an order of magnitude when using passive sampler determined porewater concentrations and EqP determined concentrations (Fernandez et al., 2014).
1.4 Performance Reference Compounds (PRCs)

It may take anywhere from weeks to years for polymer type passive samplers to reach equilibrium with sediment beds depending on the sampler type and target compounds. Performance reference compounds are used to correct sampler concentrations for non-equilibrium conditions in laboratory and field deployments (Adams et al., 2007; Huckins et al., 2002). The desorption of the PRCs from polymer samplers is used as an indicator of approach to equilibrium between sampler and sampled media (Joyce et al., 2018). To analyze air and water samples, PRCs are loaded into smaller PE coupons and deployed with clean samplers. When sampling sediment, however, the PRCs are loaded into the sampler itself prior to deployment.

1.5 Sampler designs for in situ deployment to engineered sediment cap

Sediment passive samplers are traditionally PRC loaded strips of polyethylene that are placed between two metal frames. Wire mesh over the polyethylene is occasionally used with large samplers (Figure 2). Using this geometry, the PE is exposed to the sediment on two sides, making the diffusion thickness of the PE one half of the full thickness. Unlike surface water samplers, the diffusion distance within the sediment layer increases with time, a phenomenon referred to as the “depletion zone” (Apell et al., 2015). Across multiple studies, passive samplers have been found to be a very effective way of analyzing porewater concentration as well as monitoring contaminated sediment remediation. Oen et. al (2011) made the point that contaminated sediment that has been remediated by dredging, capping or other amendment techniques will require longer deployment times due to the potential decrease in free contaminant concentration, extending the deployment time to 4-8 weeks (Oen et al., 2011).

Capping, or the process of covering up contaminated sediment with sand or clean sediment, sometimes both, is as previously stated a common remediation technique. It can be
used for organic contamination as well as nutrient or even metal contamination. The cap material varies depending on the contaminant but can range from fine sand to sandy sediment with armored stone to plastic liners and sandy sediment (Palermo, 1998). Sediment caps are often several feet thick to provide confidence of complete isolation of the underlying contaminants. (Lampert et al., 2011). To deploy a sediment sampler through the sediment cap, armored or not, beyond several inches is difficult due to their relatively flimsy construction. When it was attempted at the Grasse River field site, traditional metal frames could not be hammered into cobble filled sediments more than ~10 cm despite the use of a 16 lb. sledge hammer by divers. Therefore, to sample through an armored sediment cap, a new sampler apparatus was required.

The prototype that was built is different than the traditional passive sampling method in two ways. The first way is in the general shape of the apparatus. It is a cylindrical aluminum rod that has an end tapered into a cone, around which the passive sampler and perforated tubing is attached by winding wires in opposing directions (Figure 3). This structure lends itself to the second difference, which is that the passive sampler is only exposed on one side, as compared to both sides of the traditional sampler.

1.6 Objectives

Conventionally, passive samplers of PE strips are placed into aluminum frames and deployed to the environment with both sides of the PE exposed. Samplers that are pre-loaded with PRCs are exposed to sediment beds and the mass transfer of PRCs to sediment beds are used to determine the fractional equilibration of samplers and sediments.

\[ F_{eq} = \left( C_{PRC0} - C_{PRC,t} \right) / C_{PRC0} \]

where \( C_{PRC0} \) is the concentration of PRCs in the PE before deployment, and \( C_{PRC,t} \) is the concentration of PRC in the PE after deployment. The mass of target chemical taken up by the
samplers, $C_{PE,t}$, are then corrected for disequilibrium by dividing by the fraction of equilibrium reached during deployment (Gschwend et al., 2014) and the concentration of freely-dissolved HOC in water of porewater, $C_{free}$, can be calculated by dividing the equilibrium concentration in the PE by the compound specific PE-water partition coefficient, $K_{PEW}$ (Lohmann, 2012).

$$C_{free} = \frac{C_{PE,t}}{F_{eq}K_{PEW}} \quad (2)$$

This traditional sampler design was tested for use across an engineered remedial cap at the Grasse River Superfund site that included two layers of armoring with cobbles and gravel. Although the goal was to sample PCBs in porewater within the cap and bed sediment to a depth of 1 m, the samplers were too wide and bulky to pass by the surface armoring material. The prototype sampler design was able to be inserted past the armoring material, but it has not been tested for how the cylindrical design will affect rate of mass exchange between sampler material and sediments.

The objective of this work is to compare the two sampler designs in terms of necessary deployment times and to validate the use of the cylindrical design against previously validated two-sided, flat deployment. It is expected that the cylindrical design will reach approximately half the fraction of equilibration as the two-sided design during the same deployment period but will still provide equivalent dissolved porewater concentrations for a suite of PAHs.

2. Materials and Methods

2.1 Materials

2.1.1 Chemicals

Laboratory filtered water (Milli-Q water) with > 18MOhm/cm resistance (Milli-Q Reference, Millipore, Darmstadt, Germany) was used for all rinsing and loading of preparation
of PRC spiking solution. Organic solvents, methanol (Fisher Chemical, Pittsburg, Pennsylvania, USA) and dichloromethane (Honeywell, Morris Plains, New Jersey, USA) were both HPLC grade. Deuterated PAH standards used as PRCs (Phenanthrene-d10, Pyrene-d10, and Chrysene-d12) were purchased from Agilent Technologies (Kingston, RI, USA). The injection (p-terphenyl) and surrogate standards (d10-anthracene, 10-fluoranthene, and 12-benz(a)anthracene) were purchased from AccuStandard (New Haven, CT, USA). All glassware used was pre-combusted at 450 °C for 24 hours, rinsed with DCM and all caps were lined with DCM-rinsed foil.

2.1.2 Polyethylene (PE) preparation

Samplers were prepared from low density polyethylene (LDPE) sheeting (25 µm thickness, Ace Hardware, Boston, MA, USA). PE strips were cut to size (10 cm by 100 cm) before being cleaned by rinsing twice for 24 hours each with DCM, Methanol and finally Milli-Q water. Strips were then stored in Milli-Q water at room temperature until use.

Two samplers were loaded with PRCs together in a 1 L mixture of 80:20 methanol/water solution containing 7 mg of d10-phenanthrene, 4 mg of d10-pyrene, and 1.5 mg of d12-chrysene, with the aim of having a nominal concentration of 10 µg/g PE after equilibration. The jar was set on an orbital shaker set to 45 rpm (Apell et al., 2018). After six weeks, the PE strips were moved to a 1L jar containing Milli-Q water to remove any residual methanol.

2.2 Methods

2.2.1 Prototype

For this experiment, two prototype samplers were constructed using aluminum cylinders machined to have a 60° cone on the end forming a spike. The cylinders were further machined to have an outside diameter matching the inside diameter of a perforated stainless-steel pipe which
had been sawed in half to form two sides of a tight-fitting shell around the metal cylinder. Two additional holes were drilled through the cylinder at the bottom and near the top of the perforated tubing to allow for wire wrapping. It is noted that this sampler deployment device was designed for deployment in a fresh water system where corrosion due to contacting unlike metals was not expected. The sampler was designed so that when the PE strip was wrapped around the cylinder and covered with the perforated pipe, diffusion of chemicals from the PE would only occur in one radial direction, away from the center core (Figure 1). Furthermore, the snug fit between perforated pipe, PE, and metal core would not allow for water to move vertically along the sampler housing. To prepare the sampler for deployment, the PE strip was laid flat in one half of the perforated pipe, the remaining PE was then wrapped around the aluminum spike and covered with the other half of the perforated pipe. Aircraft grade stainless steel wire (20 gauge) was inserted through a hole in the bottom of the cylinder and the two ends were twisted in opposite directions along the length of the sampler. After tightening the wire at the top of the cylinder the ends were passed through another hole at the top and secured by twisting.

2.2.2 Traditional PE deployment frame

A metal frame and wire mesh were prepared to hold the PE at the two ends and allow the PE to be pushed into the sediment in the field. The frame, mesh, and fasteners were washed using Extran 300 Detergent (Millipore EMD, Darmstadt, Germany) then rinsed in DCM. The PE strip was then attached between the two layers of mesh and the two sides of the frame and wrapped in DCM rinsed aluminum foil before being deployed in the field. The metal of the prototype was washed in a similar manner and was wrapped in aluminum foil before being brought out to the field to equilibrate.
2.2.3 Test Site

While the Superfund site where sediment samplers will eventually be used is a freshwater site with polychlorinated biphenyl (PCB) contamination, the prototype will be tested in a brackish marsh environment where PAHs are expected to be the primary contaminants. The conventional passive sampler and the new prototype were co-deployed in the Rumney Marsh in Revere, MA, USA. Both samplers were pushed into the sediment up to approximately 80 cm. Although we would not expect PCB contamination at the marsh, we would expect to see both PCBs and PAHs in the contaminated Grasse River sediment.

Rumney Marsh is a site where PAHs would be expected to be present due to several factors. The waterways have been exposed to tannery operation and other heavy industries as well as waste incineration ((MAPC), 2010-2017). It is also bisected by a railroad and is near urban areas of industry including Revere and Boston, Massachusetts.

2.2.4 Sampler extraction

Samplers were retrieved from the field after 30 days, rinsed with Milli-Q water to remove adhering sediment in the field, wrapped in solvent rinsed aluminum foil, and returned to the laboratory on ice. PE strips were immediately cut into 4 cm sections, rinsed with Milli-Q water, wiped with a laboratory tissue and placed in 40 mL amber glass vials. Recovery compounds (100 µg of d10-anthracene, 10-fluoranthene, and 12-benz(a)anthracene in 100 µL DCM), included to assess extraction efficiency, were added to each vial prior to the first extraction. The PE strips were then extracted three times in 15 mL of dichloromethane. Combined extracts were blown down to approximately 1 mL under a gentle stream of nitrogen and transferred to autosampler vials. Injection standard (100 µL of 1 µg/mL p-terphenyl in dichloromethane) was added to each extract just prior to instrumental analysis.
2.2.5 GC Analysis

All extracts were analyzed using gas chromatography-mass spectrometry (GCMS, TRACE 1310, TSQ Quantum XLS Ultra, Thermo Scientific, Waltham, MA, USA). Splitless 1 µL injections were made onto a 30 m Agilent HP-5MSI capillary column (0.25 mm internal diameter with a 0.25 µm film thickness). The injection port temperature was 300°C. The initial column temperature was set to 60°C and was increased at a rate of 12 °C/minute until the oven temperature reached 210 °C. Following this, the temperature was raised at a slower rate of 8 °C per minute until it achieved a final temperature of 320 °C, at which time the temperature was held for four minutes. The MS was operated in selection reaction monitoring (SRM) and EI+ modes. A calibration standard containing 23 PAHs, including the PRCs, surrogate standards and injection standard was run after every four samples to monitor the stability of the instrument and help detect any drift.

3. Results and Discussion

3.1 Comparison of methods

3.1.1 Fractional Equilibration comparison

Based on the design for the prototype, we would expect the fractional equilibrations of the PE deployed using the prototype to be less than those for the PE deployed using the traditional sampler, because the PRCs within the prototype have twice the distance to diffuse. This is exactly what was found. The water layers were generally disregarded except for the layer just above the sediment-water interface due to their potential exposure to air during extreme low tides.

The $f_{eq}$s for the performance reference compounds (PRCs) in each 4 cm section of the samplers were calculated using Eqn. 1 and compared (Figure 4, Figure 5 and Figure 6).
Uncertainty in $f_{eq}$ were calculated by propagating measurement uncertainty (one standard deviation of calibration standard run throughout the sample analysis (n=8)) through Eqn 1. In all cases, the $f_{eq}$ observed in PE of the new annular deployment design were lower than those observed using the traditional two-sided deployment. The observed differences were largest for d10-phenanthrene, where the calculated $f_{eq}$ for the prototype were often below 50% and lower than the $f_{eq}$ for larger PRCs, d10-pyrene and d12-chrysene. This is very unexpected and explanations for why d10-phenanthrene would appear to be more retained are still being sought.

3.1.2 Phenanthrene and Anthracene

The first direct comparison between each layer corresponding to the same depth is within the concentrations of phenanthrene and anthracene. $C_{free}$ in the porewater of each sediment section were calculated using Eqn 2. Fractional equilibration for d10-phenanthrene was used to calculate the equilibrium concentration of both phenanthrene and anthracene in PE sections. These two PAHs have the same molecular weight and are expected to behave similarly in the samplers and the environment, although they are not expected to necessarily have the same concentrations in the environment. The percent difference of the two sampler-determined $C_{free}$ was calculated with regards to the concentrations of the traditional sampler. The percent difference for the concentrations of phenanthrene between the prototype and the traditional sampler range from 20% to -553% (Table 1). The percent difference for anthracene ranges from 28.8% to 1106% (Table 1). The large differences in calculated $C_{free}$ are likely due to the unexpectedly low calculated $f_{eq}$ for d10-phenanthrene in the prototype sampler.

The concentration profiles down to 28 cm of depth into sediments can be seen in the tables and figures section. However, when including propagation of error into the concentration by depth profile of anthracene and phenanthrene (Figures 7-8) it was discovered that we could
only statistically determine a difference between these numbers at deeper layers, which may indicate a change in concentration within the sediment system itself.

3.1.3 Fluoranthene and Pyrene

The $f_{eq}$ for d10-pyrene was used with equations 1 and 2 to calculate $C_{free}$ for pyrene and fluoranthene within each sampler section. Again, the same PRC could be used for both compounds because they have the same molecular weight. Percent differences were calculated in the same fashion as phenanthrene and anthracene and produced a percent difference ranging from -32 to 69.7% (Table 2). The smaller range of difference is likely due to smaller uncertainties and the more predictable behavior of PRCs in the systems. $C_{free}$ of these larger PAHs in the sediment are generally higher than for the other PAHs as has been previously observed for sediments near urban areas (Fernandez et al., 2015; Lohmann et al., 2005), but the trend of the prototype having slightly higher concentrations in the sediment layers might be because of sediment contamination within the extracts. It was observed that not all the sediment had been wiped from the prototype-deployed PE sampler before extraction.

When conducting propagation error analysis on the concentrations of fluoranthene and pyrene (Figures 9-10) they were found to be statistically similar enough that except for one layer in pyrene (12 cm below the surface), it cannot be reported that these concentrations are different enough to be confident in their difference. This reflects favorably upon the possibility of this prototype functioning similarly to the traditional sampler when deployed for organic contaminant monitoring purposes.

3.1.4 Benz(a)anthracene and Chrysene

Finally, calculated $C_{free}$ of benz(a)anthracene and chrysene were calculated using equations 1 and 2. Benz(a)anthracene concentrations determined using the PE from the prototype
sampler are overall higher than those determined using the traditional sampler within the sediment layers. Again, this may be due to the possibility of having extracted sediment adhering to the PE deployed using the prototype along with the PE. Although the percent differences were high (ranging from -1 to -185%) the concentrations matched within uncertainty for chrysene and were within a factor of 3 for benz(a)anthracene (Table 3).

When accounting for error propagation, at no point are we able to determine any concentration within chrysene (Figure 12) to be statistically different in either sampler. The benz(a)anthracene concentrations (Figure 11) were found to be statistically different at 12 cm depth and below. This could either be due to heterogeneity in the sediment bed or to sample processing errors described above.

3.1.5 Depth Comparison

The concentration profiles for PAHs in the Rumney Marsh observed in this study indicate higher PAH porewater concentrations with depth. This might be an indication of PAHs being flushed from sediments at shallower sediment depths or might indicate that PAH contamination rates have been reduced over time, leading to high contaminant loads in older, deeper sediments. Additional measurements including the collection of sediment cores and sediment dating would be necessary to determine what might have led to the contaminant profile observed in this study.

3.2 Sources of Error

As previously stated, concentration comparisons are not the best method for comparing similarities because there are too many sources of error. In addition to human error, there was clearly some form of error within the PRC loading in terms of the phenanthrene concentrations, and as can be seen by the percent recovery of surrogate standards which can be found in the tables and figures section (Table 4). Within d-10 anthracene the recovery ranges from as low as
62.1% to as high as 79.21%, while d-10 fluoranthene reports ranges from 60.2% to 78.5%, and from 60.5% to 79.5% for d12-benz(a)anthracene. While these recoveries are within acceptable ranges, the pattern of recoveries are unexpected. More frequently, recoveries are higher for larger compounds than their smaller counterparts due to the volatility of small compounds. Other sources of error include chromatography errors as well as peak integration errors. There was an issue with the GC-MS when the samples were first run where it had to be rebooted, therefore whatever potentially caused that could also have produced some residual errors.

Another possible source of error would be that there was only one sampler of each deployed at the time. This does not allow for complete statistical analysis of the test area of Rumney Marsh. There are differences within the sediment that could have accounted for the difference in concentration, and this would have been more thoroughly analyzed if there had been time to repeat the experiment with multiple samplers of each type.

4. Conclusion

4.1 Conclusions

The results of this work indicate that the prototype passive sampler did function as it was expected to. The narrower design makes it capable of penetrating the armored cap (as observed during preliminary testing by divers at the Grasse River Superfund site in Masena, NY) and the perforated tubing around the spike protects the polyethylene from tearing as it is hammered into the sediment. The propagation of error also allows us to see that this would be an excellent substitute for the traditional passive sampler in that it yields similar results within the certainty of propagated error.
4.2 Future Work

Future work involves repeating the experiment in duplicate or triplicate to acquire significant statistical analysis and trends. Additionally, deploying the samplers to the superfund site and analyzing the results of that deployment would be an important next step.
Tables

Table 1. Percent difference analysis according to equivalent depths for phenanthrene (ng/L) and anthracene (ng/L). The shaded portion is the sediment portion.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Phenanthrene (ng/L)</th>
<th>Anthracene (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Traditional</td>
<td>Prototype</td>
</tr>
<tr>
<td>28</td>
<td>31.079</td>
<td>24.645</td>
</tr>
<tr>
<td>24</td>
<td>33.964</td>
<td>25.543</td>
</tr>
<tr>
<td>20</td>
<td>57.304</td>
<td>26.596</td>
</tr>
<tr>
<td>16</td>
<td>167.747</td>
<td>27.418</td>
</tr>
<tr>
<td>12</td>
<td>126.931</td>
<td>17.152</td>
</tr>
<tr>
<td>8</td>
<td>84.186</td>
<td>23.920</td>
</tr>
<tr>
<td>4</td>
<td>52.510</td>
<td>18.025</td>
</tr>
<tr>
<td>-4</td>
<td>31.481</td>
<td>68.937</td>
</tr>
<tr>
<td>-8</td>
<td>28.796</td>
<td>80.605</td>
</tr>
<tr>
<td>-12</td>
<td>35.742</td>
<td>151.278</td>
</tr>
<tr>
<td>-16</td>
<td>47.200</td>
<td>133.926</td>
</tr>
<tr>
<td>-20</td>
<td>52.654</td>
<td>138.383</td>
</tr>
<tr>
<td>-24</td>
<td>30.194</td>
<td>197.408</td>
</tr>
<tr>
<td>-28</td>
<td>54.547</td>
<td>231.011</td>
</tr>
</tbody>
</table>

Table 2. Percent difference analysis according to equivalent depths for fluoranthene (ng/L) and pyrene (ng/L). The shaded portion is the sediment portion.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Fluoranthene (ng/L)</th>
<th>Pyrene (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Traditional</td>
<td>Prototype</td>
</tr>
<tr>
<td>28</td>
<td>57.043</td>
<td>17.303</td>
</tr>
<tr>
<td>24</td>
<td>41.151</td>
<td>16.187</td>
</tr>
<tr>
<td>20</td>
<td>29.681</td>
<td>9.515</td>
</tr>
<tr>
<td>16</td>
<td>34.488</td>
<td>10.381</td>
</tr>
<tr>
<td>12</td>
<td>10.496</td>
<td>15.027</td>
</tr>
<tr>
<td>8</td>
<td>16.851</td>
<td>14.576</td>
</tr>
<tr>
<td>4</td>
<td>11.617</td>
<td>14.741</td>
</tr>
<tr>
<td>-4</td>
<td>23.929</td>
<td>19.230</td>
</tr>
<tr>
<td>-8</td>
<td>24.453</td>
<td>22.307</td>
</tr>
<tr>
<td>-12</td>
<td>28.736</td>
<td>38.597</td>
</tr>
<tr>
<td>-16</td>
<td>37.784</td>
<td>47.811</td>
</tr>
<tr>
<td>-20</td>
<td>38.664</td>
<td>51.166</td>
</tr>
<tr>
<td>-24</td>
<td>42.225</td>
<td>55.276</td>
</tr>
<tr>
<td>-28</td>
<td>65.229</td>
<td>56.558</td>
</tr>
</tbody>
</table>
Table 3. Percent difference analysis according to equivalent depths for Benz(a)anthracene (ng/L) and Chrysene (ng/L). The shaded portion is the sediment portion.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Benz(a)anthracene (ng/L)</th>
<th>Chrysene (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Traditional</td>
<td>Prototype</td>
</tr>
<tr>
<td>28</td>
<td>3.229099198</td>
<td>1.45157</td>
</tr>
<tr>
<td>24</td>
<td>0.197046847</td>
<td>1.648624</td>
</tr>
<tr>
<td>20</td>
<td>0.180815495</td>
<td>1.785564</td>
</tr>
<tr>
<td>16</td>
<td>0.365473062</td>
<td>1.426866</td>
</tr>
<tr>
<td>12</td>
<td>1.945422933</td>
<td>1.272738</td>
</tr>
<tr>
<td>8</td>
<td>1.373875275</td>
<td>1.028853</td>
</tr>
<tr>
<td>-4</td>
<td>0.382576398</td>
<td>0.975065</td>
</tr>
<tr>
<td>-8</td>
<td>1.51522124</td>
<td>1.473185</td>
</tr>
<tr>
<td>-12</td>
<td>1.419677586</td>
<td>2.053315</td>
</tr>
<tr>
<td>-16</td>
<td>1.558637562</td>
<td>3.732425</td>
</tr>
<tr>
<td>-20</td>
<td>1.73813513</td>
<td>4.420637</td>
</tr>
<tr>
<td>-24</td>
<td>2.145708578</td>
<td>4.916223</td>
</tr>
<tr>
<td>-28</td>
<td>2.780848438</td>
<td>7.702008</td>
</tr>
</tbody>
</table>

-4, -8, -12, -16, -20, -24, and -28 cm readings are shaded to indicate the sediment portion.
Table 4. The percent recovery of surrogate standards

<table>
<thead>
<tr>
<th></th>
<th>Percent Recovery Surrogate Standards</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>d10 anthracene</td>
<td>d10 fluoranthene</td>
<td>d12 benz(a)anthracene</td>
<td></td>
</tr>
<tr>
<td>W1</td>
<td>79.2196577</td>
<td>72.53085855</td>
<td>77.11510103</td>
<td></td>
</tr>
<tr>
<td>W2</td>
<td>75.68136096</td>
<td>69.73189432</td>
<td>70.37942649</td>
<td></td>
</tr>
<tr>
<td>W3</td>
<td>74.82804866</td>
<td>76.66689405</td>
<td>64.9058805</td>
<td></td>
</tr>
<tr>
<td>W4</td>
<td>65.73894086</td>
<td>78.22310697</td>
<td>79.52085051</td>
<td></td>
</tr>
<tr>
<td>W5</td>
<td>70.79525331</td>
<td>76.6813947</td>
<td>69.2798364</td>
<td></td>
</tr>
<tr>
<td>W6</td>
<td>72.72141064</td>
<td>76.78665505</td>
<td>78.53715911</td>
<td></td>
</tr>
<tr>
<td>W7</td>
<td>76.84790907</td>
<td>78.52359029</td>
<td>77.11770539</td>
<td></td>
</tr>
<tr>
<td>W8</td>
<td>69.80656978</td>
<td>77.22080672</td>
<td>75.60780637</td>
<td></td>
</tr>
<tr>
<td>W9</td>
<td>76.54834099</td>
<td>61.36458574</td>
<td>74.85506526</td>
<td></td>
</tr>
<tr>
<td>W10</td>
<td>75.42341996</td>
<td>60.22302527</td>
<td>65.83343249</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>62.13535094</td>
<td>67.15566241</td>
<td>63.12848482</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>64.50016844</td>
<td>74.50867067</td>
<td>67.91680036</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>66.14774596</td>
<td>73.25858036</td>
<td>67.86063401</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>67.37811196</td>
<td>73.16023098</td>
<td>67.85114052</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>65.03202451</td>
<td>73.94172914</td>
<td>60.60134088</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>69.25848032</td>
<td>71.68804833</td>
<td>63.18283281</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>62.66966291</td>
<td>70.63216894</td>
<td>68.61551254</td>
<td></td>
</tr>
<tr>
<td>W1pro</td>
<td>66.68575008</td>
<td>61.75754559</td>
<td>65.35708191</td>
<td></td>
</tr>
<tr>
<td>W2pro</td>
<td>66.99487379</td>
<td>69.54356394</td>
<td>60.51833592</td>
<td></td>
</tr>
<tr>
<td>W3pro</td>
<td>78.49809907</td>
<td>65.64033129</td>
<td>60.48577127</td>
<td></td>
</tr>
<tr>
<td>W4pro</td>
<td>64.63711204</td>
<td>70.94629972</td>
<td>79.45064575</td>
<td></td>
</tr>
<tr>
<td>W5pro</td>
<td>72.09190745</td>
<td>69.78828716</td>
<td>64.96915584</td>
<td></td>
</tr>
<tr>
<td>W6pro</td>
<td>66.11859112</td>
<td>77.83818677</td>
<td>61.09302646</td>
<td></td>
</tr>
<tr>
<td>W7pro</td>
<td>71.49579045</td>
<td>72.94272267</td>
<td>67.31898538</td>
<td></td>
</tr>
<tr>
<td>S1pro</td>
<td>73.5102379</td>
<td>63.88512773</td>
<td>76.61151377</td>
<td></td>
</tr>
<tr>
<td>S2pro</td>
<td>67.81248688</td>
<td>71.93969757</td>
<td>79.21876917</td>
<td></td>
</tr>
<tr>
<td>S3pro</td>
<td>71.04043379</td>
<td>67.68326503</td>
<td>74.96451889</td>
<td></td>
</tr>
<tr>
<td>S4pro</td>
<td>68.49131763</td>
<td>62.40547731</td>
<td>62.78267823</td>
<td></td>
</tr>
<tr>
<td>S5pro</td>
<td>70.51743977</td>
<td>66.19843658</td>
<td>64.5445578</td>
<td></td>
</tr>
<tr>
<td>S6pro</td>
<td>63.31186338</td>
<td>71.05906063</td>
<td>73.91531418</td>
<td></td>
</tr>
<tr>
<td>S7pro</td>
<td>63.94489832</td>
<td>75.5204747</td>
<td>70.54873613</td>
<td></td>
</tr>
<tr>
<td>S8pro</td>
<td>61.78820183</td>
<td>75.81391751</td>
<td>66.508155</td>
<td></td>
</tr>
<tr>
<td>S9pro</td>
<td>62.41833713</td>
<td>67.2988793</td>
<td>69.49108413</td>
<td></td>
</tr>
<tr>
<td>S10pro</td>
<td>65.94000401</td>
<td>61.82918076</td>
<td>78.21879337</td>
<td></td>
</tr>
<tr>
<td>S11pro</td>
<td>64.65315579</td>
<td>65.12569907</td>
<td>68.21880739</td>
<td></td>
</tr>
</tbody>
</table>
Figures

Figure 1. The bioavailability process

Figure 2. The traditional PE passive sampler deployed in Rumney Marsh on June 26, 2019
Figure 3. A side by side comparison of the deployed prototype and traditional sampler.

Figure 4. Comparison of d-chrysene $f_{eq}$ by depth, with the zero centerline being the sediment water interface. Error bars represent the propagation measurement uncertainty through Eqn 1.
Figure 5. Comparison of d-pyrene $f_{eq}$ by depth, with the zero centerline being the sediment water interface. Error bars represent the propagation measurement uncertainty through Eqn 1.

Figure 6. Comparison of d-phenanthrene $f_{eq}$ by depth with the sediment-water interface at y value zero. The error bars represent the propagation of measurement uncertainty through Eqn 1.
Figure 7. Calculated $C_{\text{free}}$ for phenanthrene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2.

Figure 8. Calculated $C_{\text{free}}$ for anthracene for both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2.
Figure 9. Calculated $C_{\text{free}}$ for fluoranthene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2.

Figure 10. Calculated $C_{\text{free}}$ for pyrene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2.
Figure 11. Calculated $C_{\text{free}}$ for benz(a)anthracene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2.

Figure 12. Calculated $C_{\text{free}}$ for chrysene using both sampler types. The error bars are based on the propagation of measurement uncertainty through Eqns 1 and 2.
Works Cited


