ACTIVE AND PASSIVE SAMPLING OF TACONY-FRANKFORD CREEK IN

PHILADELPHIA, PA

By

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ABSTRACT OF THE DISSERTATION

ACTIVE AND PASSIVE SAMPLING OF TACONY-FRANKFORD CREEK IN PHILADELPHIA, PA

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Water, sediment and fish were sampled at various times and locations between 2008 and 2011 on the Tacony-Frankford Creek, a tributary to the Delaware River in Philadelphia, PA. The study sought to identify spatial and temporal trends, identify the sources and fate of polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) compounds, and explore an alternative sampling method for PAH and PCB compounds in the stream. Grab samples of sediments and whole water were collected between November 2008 and April 2010, and fish samples were collected in June 2010 and analyzed for 28 PAH compounds. Total sediment concentrations of Σ PAH ranged from 3,200 ng/g to 72,000 ng/g at various locations in the tidal and non-tidal regions of the tributary and 25,000 ng/L in the Delaware River. The Σ PAH concentration in water ranged between 170 ng/L and 580 ng/L in the tributary and between 130 ng/L and 150 ng/L in the Delaware River. The concentration of Σ PAH varied greatly depending on the type of fish and tissue, and ranged from 43 ng/g in catfish livers to 1,300 ng/g in white

perch organs (minus livers). The PAH concentration in water and sediment samples exhibited spatial trends but no identifiable temporal trend. The primary source of PAHs to the stream for the time period was motor vehicle emissions.

In June 2011, grab samples of whole water were collected at different times in the tidal cycle at a single location and filtered to separate suspended particles from the aqueous samples. Both fractions were analyzed for PAH and PCB concentrations to determine whether sampling depth and time impact the concentrations in a tidal stream. The sum of 16 PAH compounds ranged from 74 to 160 ng/L and the sum of 41 PCB compounds ranged from 2.7 to 7.9 ng/L in the whole water samples. The results showed that sampling depth impacts both classes of compounds, with concentrations higher near the sediment bed than near the surface and affected mostly by the portion that was associated with particles. Timing of sampling during the tide had a much larger impact on the concentration of PAHs than PCBs. Passive sampling was explored as a technique to mitigate the temporal variability that was evident in the study stream. Polyoxymethylene (POM) was investigated as a material to collect passive samples in small aquatic systems. In the laboratory, 76 µm thick POM sheets exhibited fast sorption, coming to equilibrium with aqueous-phase phenanthrene within 2 weeks at 23°C and 5 weeks at 4°C. Partitioning coefficients $log(K_{POM})$ were calculated for 16 PAH and 41 PCB compounds and ranged from 3.1 to 6.4, and 4.1 to 6.1, respectively. The $log(K_{POM})$ values were used with collected POM concentrations to predict PAH and PCB concentrations in the aqueous phase and were found to underpredict the aqueous phase for most compounds. Correlations between POM films and sediments or biota were not very strong, except for samples of white sucker fish and catfish livers.

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DEDICATION

This dissertation is dedicated to the memory of my father

Rowland Francisco

I know that he would have been proud.

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"All we have to decide is what to do with the time that is given us." -Gandalf

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LIST OF ABBREVIATIONS

А	Anthracene
ACE	Acenaphthene
ACY	Acenaphthylene
BAA	Benz[a]anthracene
BAF	Benzo[a]fluorene
BAP	Benzo[a]pyrene
BBF	Benzo[b]fluorene
BBFL	Benzo[b]fluoranthene
BEP	Benzo[e]pyrene
BKFL	Benzo[k]fluoranthene
BNT	Benzo[b]naptho[2,1-d]thiophene
BPE	Benzo[g,h,i]perylene
С	Chrysene
COR	Coronene
СР	Cyclopenta[cd]pyrene
DBA	Dibenzo[a,h]anthracene
DBT	Dibenzothiophene
DMP	3,6-Dimethylphenanthrene
F	Fluorene
FL	Fluoranthene
IP	Indeno[1,2,3-cd]pyrene
MEP	4,5Methylenephenanthrene
MFL	1Methylfluorene
NA	Naphthacene
Р	Phenanthrene
PE	Perylene
PY	Pyrene
RET	Retene
Т	Triphenylene
	1
PCB 17	2,2',4-Trichlorobiphenyl
PCB 18	2,2',5-Trichlorobiphenyl
PCB 28	2,4,4'-Trichlorobiphenyl
PCB 31	2,4',5-Trichlorobiphenyl
PCB 33	2',3,4-Trichlorobiphenyl
PCB 44	2,2',3,5'-Tetrachlorobiphenyl

PCB 49	2,2',4,5'-Tetrachlorobiphenyl
PCB 52	2,2',5,5'-Tetrachlorobiphenyl
PCB 70	2,3',4',5-Tetrachlorobiphenyl
PCB 74	2,4,4',5-Tetrachlorobiphenyl
PCB 82	2,2',3,3',4-Pentachlorobiphenyl
PCB 87	2,2',3,4,5'-Pentachlorobiphenyl
PCB 95	2,2',3,5',6-Pentachlorobiphenyl
PCB 99	2,2',4,4',5-Pentachlorobiphenyl
PCB 101	2,2',4,5,5'-Pentachlorobiphenyl
PCB 105	2,3,3',4,4'-Pentachlorobiphenyl
PCB 110	2,3,3',4',6-Pentachlorobiphenyl
PCB 118	2,3',4,4',5-Pentachlorobiphenyl
PCB 132	2,2',3,3',4,6'-Hexachlorobiphenyl
PCB 149	2,2',3,4',5',6-Hexachlorobiphenyl
PCB 151	2,2',3,5,5',6-Hexachlorobiphenyl
PCB 153	2,2',4,4',5,5'-Hexachlorobiphenyl
PCB 128	2,2',3,3',4,4'-Hexachlorobiphenyl
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PCB 171	2,2',3,3',4,4',6-Heptachlorobiphenyl
PCB 177	2,2',3,3',4',5,6-Heptachlorobiphenyl
PCB 180	2,2',3,4,4',5,5'-Heptachlorobiphenyl
PCB 183	2,2',3,4,4',5',6-Heptachlorobiphenyl
PCB 187	2,2',3,4',5,5',6-Heptachlorobiphenyl
PCB 191	2,3,3',4,4',5',6-Heptachlorobiphenyl
PCB 194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl
PCB 195	2,2',3,3',4,4',5,6-Octachlorobiphenyl
PCB 199	2,2',3,3',4,5,5',6'-Octachlorobiphenyl
PCB 205	2,3,3',4,4',5,5',6-Octachlorobiphenyl
PCB 206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl
PCB 208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl
PCB 209	2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl

Chapter 1: Introduction

1.1 Importance

Water is a vital resource for humans and as such, many urban centers have been located near rivers and coastlines. Unfortunately, this is often to the detriment of the body of water. In order to maintain water that is safe to use, scientists must study the water, sediment and biota. Most of these studies focus on larger rivers, as they can have several inputs that might affect the health of the river, but fewer studies have looked at the tributaries that feed into the larger rivers. These small tributaries can be a source or sink of pollutants for the larger river. In addition, it is important to assess the health of these smaller tributaries, as they are often the streams that the general public lives near and is interacting with.

This dissertation investigated an urban tributary to the Delaware River and attempt to address a lack of knowledge pertaining to the extent of influence that small streams can have on the waterways that they feed into. This work specifically looked at two classes of organic pollutants. Organic compounds were chosen over another type of pollutant because of their tendency to partition to sediments and biota in the aqueous environment. In urban settings, sediments are an important reservoir for pollution due to frequent dredging of sediments to ensure transportation routes and fish may be caught and consumed by portions of the general public that are not knowledgeable about the prevalence of organic pollution in small streams. Therefore, the benefit of this work was not only in gaining a broader insight into sources of pollution to larger rivers, but also in having a deeper knowledge about the challenges facing the smaller ecosystems and the communities surrounding it.

1.2 Objectives

The purposes of this work were to describe the variability of an urban tidal stream by looking at how spatial and temporal difference in sampling can affect the results, and to examine a different method of sampling that can resolve some of the issues surrounding grab sampling in a dynamic system. To that end, the individual questions that we sought to answer were:

- 1. What is the extent of variability of hydrophobic organic compounds (HOCs) measured during different seasons?
- 2. What is the extent of variability of HOCs measured at different locations between the non-tidal portion and the Delaware?
- 3. What are the relative concentrations of HOCs in the water column, sediments and biota?
- 4. What is the extent of variability of HOCs measured at different depths in the same location?
- 5. What is the extent of variability of HOCs measured at different times during a tidal cycle?
- 6. Can another method to measure HOCs in water be used that reduces the uncertainty created by temporal variability in small streams?
- 7. Can the new method be used to predict HOC concentrations or patterns in water, sediments or biota?

1.3 Overview

This dissertation contains 6 chapters. The objectives of this work were addressed in the following chapters:

- Chapter 2 describes the background information on the compounds studied and their prevalence in the environment. This chapter also delineates the selected methods of active and passive sampling of water from the field.
- Chapter 3 defines the urban system included in the studies by examining differences in the water column concentrations of hydrophobic organic compounds at different locations on the stream and during different seasons of the year.
- Chapter 4 further addresses the variability of the water column by looking at two separate classes of HOC over the course of a single tidal cycle.
- Chapter 5 presents the study of a passive sampling method in an effort to reduce the effects of variability in dynamic tidal systems and to predict concentrations in various phases.
- Chapter 6 summarizes the research, its implications and points out the areas in which further study can emerge.

Chapter 2: Background and Previous Studies

2.1 Urban Streams and Tidal Range

Due to the importance of marine transport throughout history, many urban environments occur in coastal areas and have streams that are influenced by tidal flow due to an adjacent estuary or ocean. Examples include the Anacostia River (Hwang and Foster 2006), Caloosahatchee River (Fernandez, Marot, and Holmes 1999), Elbe River (Götz et al. 1998), Hudson River (Butcher and Garvey 2004; Farley, Wands, and Cooney III 2014), Hugli River (Guzzella et al. 2005), and Pearl River (Chen et al. 2013). Each of these river systems is unique from upland systems in that tidal forces impact the fate and transport of contaminants in the stream. In addition, their location within the urban environment means that the surrounding population uses these waterways in diverse ways. The general public uses streams in urban areas for swimming, fishing, recreation, and sustenance and as a water supply for industrial and municipal purposes. In addition, many of these streams serve as transportation corridors as well as receiving water for excess precipitation and treated or untreated wastewater, any of which can introduce pollutants to the system.

Transportation and recreation activities in urban waterways add motor fluids directly to the water. During a precipitation event, runoff from surrounding streets and land makes its way to local streams either through overland flow or through storm drains. This runoff carries with it many types of pollution including organic and inorganic chemicals, metals, road salts, automotive fluids, litter and excess sediments and nutrients. Additionally, in urban areas with combined sanitary sewers and storm drain systems, high amounts of precipitation can mean that some of the municipal wastewater containing untreated sewage, high levels of nutrients and bacteria or viruses will be released directly to the stream. These forms of pollution are detrimental to the biota and result in impaired aquatic ecosystems near urban areas. Many of these streams are used for navigation and even once the pollution sources have ceased, dredging to maintain deep channels can cause contaminated sediments to come back onto contact with the water column. These sediments can act as a sink or a source for HOCs in streams. Since the compounds are so hydrophobic, they are associated strongly with the sediment, which in turn acts as a sink for the water column. However, hydrodynamic forces and bioturbation from stream biota can act to resuspend the sediment particles and the HOCs can desorb, with sediment acting as a source to the overlying water (Schaffner et al, 1997).

Much of the research on HOCs has been conducted in freshwater, non-tidal systems. These systems are relatively straightforward in terms of fate and transport of HOCs when compared to tidal streams in urban areas. Salinity and ionic strength have an impact on the movement of a compound through the system by affecting the sorption and partitioning behavior. Differences in ionic strength and salinity change the chemical activity of the compound. Salinity is regarded as a factor in urban environments that are located in coastal regions, but ionic strength can be a factor even in non-coastal regions due to the various dissolved chemicals in the runoff from roadways. These dissolved chemicals are present year-round, but can have a disproportionate effect in winter months, when northern locations use salt compounds to prevent icy conditions on roadways. Another difference between streams in coastal areas and inland streams is the

bidirectional flow. Combined with salinity changes, the movement of water with higher ionic strength upstream will impact the chemical distribution between sediments and the water column. When the tide changes, fresher water will wash back out over the sediments, creating a highly dynamic system with partitioning behavior varying throughout each tidal cycle. In addition, the fish community is different near a coast than inland. Some species might be year-round residents, but there is also a community of fish that frequently migrate from the fresh water streams to the ocean and back.

2.2 Hydrophobic Organic Compounds

One purpose of this research is to determine how hydrophobic organic compound (HOC) concentrations vary in tidal streams. While HOC partitioning behavior in large freshwater systems and under laboratory conditions is well documented (McGroddy, Farrington, and Gschwend 1996; Gschwend and Wu 1985; Qiao, Huang, and Wang 2007; Farrington 1991), this research is important to add to that knowledge by including field studies in small tidal streams that can be important reservoirs and sources of HOCs. There are two classes of HOCs that are included in these studies: polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). These two compound classes were chosen to represent both compounds that are continuously added to the environment (PAHs) and historic pollutants that are no longer generated in large quantities but persist in the environment (PCBs). PAHs are of interest because of their pervasive, continuous and unintentional release by numerous activities in modern life. Urban areas are especially susceptible to this type of pollution due to the high concentration of industry and transportation. PCBs were manufactured and intentionally

used in the environment until the late 1970s. They have been banned for decades but are still found in the environment, especially near industry. The Delaware River is an example of a system with measureable concentrations of PCBs, even though these compounds are not currently in use. They are quantified in this work to show the relative concentrations of compounds from historic sources to ongoing sources.

2.2.1 PAHs

2.2.1.1 Structure and Sources

Polycyclic aromatic hydrocarbons are a class of organic compounds that are comprised of fused benzene rings. Each benzene ring is connected to at least one other benzene ring through a shared carbon-carbon double bond, and due to this bond they are planar compounds. There are over one hundred individual PAHs, ranging from two to six complete benzene rings. PAHs are most often found in the environment as mixtures, rather than single compounds due to their formation as a result of combustion of organic materials.

Some ways that PAHs are released to the environment are the burning of wood or coal for heating and energy production, gasoline and diesel engine exhaust and residential or wild fires. Other sources include the manufacture and production of coal tar, dyes and commercial chemicals. PAHs may also be released into the environment through accidental spills of crude oil, grease and gasoline, especially near land and marine transportation routes (Li et al. 2015; Yanik et al. 2003; Aislabie et al. 2004). While these compounds are also formed through natural processes, the anthropogenic generation of PAHs tends to be the largest source in the post-industrial world. For this reason, urban

areas with high population numbers, extensive transportation routes and numerous industrial areas have high levels of PAHs.

When they are released into the environment as a spill, PAHs have a moderate to very low solubility in water and will partition to non-polar surfaces such as soils and sediments (Kayal and Connell 1990; Z. Guo et al. 2007; Hyötyläinen and Olkari 1999). The solubility decreases with increasing number of aromatic rings, but is also lower for a compound that has the same number of rings arranged linearly. The range of values for aqueous solubility varies from 0.001 mg/L for benzo[g,h,i]perylene to 32 mg/L for naphthalene (May, Wasik, and Freeman 1978; Pearlman, Yalkowsky, and Banerjee 1984). In air, the low molecular weight PAHs (2- and 3-ring) have higher vapor pressures (10 – 10⁻³ Pa) and can remain in the gaseous phase, but high molecular weight PAHs tend to be associated with aerosol or dust particles due to their very low vapor pressures (10⁻⁵ – 10⁻¹⁰ Pa) (Dachs and Eisenreich 2000).

In general, the higher the number of aromatic rings, the more stable that the PAH is in the environment. Prior studies showed that PAHs are subject to microbial degradation but this process can take from several days to several months depending on the compound and the overall pollution of the surrounding stream ecosystem (Delaune, Patrick, and Casselman 1981; Heitkamp and Cerniglia 1987; Bauer and Capone 1985). PAH compounds can also be removed from the environment through photooxidation. Low molecular weight PAHs attached to dust particles or soils can be photooxidized readily, while photooxidation of PAHs dissolved or attached to suspended particles in water has been shown to be inhibited (Zafiriou 1977). Overall, medium to high molecular weight PAHs are considered persistent in the environment once released (Wild, Berrow,

and Jones 1991; Wilcock et al. 1996). This, coupled with the toxicity of PAHs is the reason why many of the compounds have been listed as the priority pollutants by the USEPA (*40 CFR Part 423* 2015).

2.2.1.2 *Toxicity*

The 17 PAHs discussed in detail in the ATSDR (1995) are acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, benzo[a]pyrene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*g,h,i*]perylene, benzo[*k*]fluoranthene, chrysene, dibenz[*a,h*]anthracene, fluoranthene, fluorene, indeno[1,2,3-*c,d*]pyrene, phenanthrene and pyrene. These compounds are considered a priority due to their prevalence at sites where PAH pollution is found, as well as their known or suspected toxicity. The typical routes of exposure to PAHs are inhalation, ingestion and dermal contact (Menzie, Potocki, and Santodonato 1992). In studies, PAH exposure has been shown to produce mutagenic and carcinogenic effects (Hermann 1981; Luch 2005).

2.2.2 PCBs

2.2.2.1 Structure and Sources

Polychlorinated biphenyls are similar to PAHs in that they are hydrophobic, stable and persistent in the environment, but their formation and history may be different. During the twentieth century, PCB mixtures were used as dielectric insulators. Due to their persistence in the environment and toxicity, the manufacture of PCBs in the US ceased in the 1970s (*40 CFR Part 761* 1976). However, some PCBs are still generated as a by-product of other manufacturing processes (J. Guo et al. 2014). The backbone structure of all PCBs is two benzene rings connected by a single carbon-carbon bond. The other ten carbon molecules in the rings can either be bonded to hydrogen or chlorine. There are 209 possible congeners, each with a common name (PCB-1 through PCB-209). The congeners are often grouped by into homolog groups by the number of chlorine they contain. Since there is only a single carbon-carbon bond, chlorine substitution at the ortho positions results in non-planarity of the congener.

All PCBs have low aqueous solubility that decreases as the number of chlorine atoms increases. Individual congeners vary in solubility from 5.5×10^{-3} g/L for PCB-1 to 1.2×10^{-9} g/L for PCB-209 (Abramowitz and Yalkowsky 1990; Dunnivant and Elzerman 1988). Therefore, they are typically found associated with air particles, soils and sediments in the environment. The vapor pressures of PCB congeners varies from 2.5 Pa to 3.5×10^{-6} Pa for PCB-1 and PCB-209, respectively (Site 1997) so that lower chlorinated homologs can also be found in the gaseous phase. The fact that they are chemically inert is why they were so widely produced, but also contributes to their extreme persistence in the environment. Microbial degradation happens to some extent, but dechlorinating bacteria usually require anaerobic conditions that are generally not met in much of the natural environment (Unterman 1996).

2.2.2.2 *Toxicity*

Ingestion and inhalation are the two major pathways of exposure to PCBs for the public (Freels et al. 2007; Currado and Harrad 1998). PCBs accumulate in fatty tissue both in fish (Stow, Jackson, and Amrhein 1997) and humans (Biros, Walker, and Medbery 2013; Aronson et al. 2000) and can be passed from mother to child through breast milk (Kuwabara et al. 1978). The individual congeners vary in toxicity, but the effects include skin rashes, endocrine issues, neurologic problems, immune system impacts and liver damage (ATSDR 2000). Many of the more chlorinated congeners are

considered probable human carcinogens, with recent studies showing links to non-Hodgkin's lymphoma and prostate cancer (Cogliano 1998).

2.3 Passive Sampling

Sampling for and measurement of HOCs can be performed via many different methods. Due to their ubiquitous nature, passive sampling approaches can be helpful in measuring environmental concentrations of HOCs because such approaches do not require a power source, and therefore can be deployed almost anywhere. Passive sampling was used in this study due to the lack of available power supply as well as the need to collect samples that were integrated across the tidal cycle. Passive sampling methods can be useful for environmental analysis due to their ability to collect a composite of conditions over a longer exposure period, rather than the snapshot of conditions that a grab sample represents. They are also unobtrusive since they do not require mechanical sampling or removal of any components of the ecosystem other than the compound of interest.

2.3.1 Theory

Passive sampling refers to methods that install a material into the environment that will sample chemical compounds through diffusion and partitioning onto the material. Sampling passively is dependent upon the mass transfer of each compound from the freely dissolved phase across the boundary layer to the sampler material. The driving force is the concentration gradient between the dissolved aqueous phase concentration and the aqueous phase concentration corresponding to the adsorbed concentrations before attainment of equilibrium. When choosing a passive sampling material, it is important to use a material that has a relatively high sorption capacity for the compound(s) of interest (Ghosh et al. 2014).

2.3.2 Materials

There are several different materials that are used for passive sampling. The choice of material depends on the compound of interest and the environmental medium. The most common materials used for passive sampling in aquatic systems are polyoxymethylene (POM), polyethylene (PE) and polydimethylsiloxane (PDMS) (Ghosh et al. 2014). POM and PE are usually sold as a solid pliable material or film that can be directly deposited into an aquatic system for sampling, while PDMS is usually deployed as a coating on glass fibers (Maruya et al. 2009). Due to the thinner film thickness of PDMS in most applications, it is quicker to come to equilibrium in the environment but also does not have detection limits as low as POM or PE (Perron et al. 2013).

2.3.3 Methods

All three materials can be used for collection of both PAHs and PCBs, but for longer deployment times and systems in which there may be a high concentration of nonaqueous phase liquids or black carbon, POM and PDMS have been shown to be superior to PE, which may be subject to fouling (van der Heijden and Jonker 2009). The advantage of PDMS is that it can be coated onto a stiff surface that can be deposited directly into sediments to measure pore water HOC concentration (Cam et al. 2000). POM and PE can also be obtained in thicknesses that would allow direct insertion into sediments, but equilibrium times are inhibitive at such thickness (Belles, Alary, and Mamindy-Pajany 2016; X. Guo et al. 2012). More commonly, POM and PE is used as a film with a thickness of less than 100 μ m, and therefore require a sampling structure to be placed in the environment with the films secured to it (Oen et al. 2011; Ghosh et al. 2014). The pre-cleaning and extraction procedures typically involve either Soxhlet extraction or sonication with various solvents including hexane, acetone, methanol and dichloromethane, depending on the analytes of interest. For PAH and PCB analysis, either dichloromethane or a hexane/methanol mixture yield acceptable recoveries (Arp et al. 2015; Rusina et al. 2007).

Laboratory studies have been performed to determine the partitioning behavior of PAHs (Josefsson et al. 2015; Cornelissen, Pettersen, et al. 2008; Hawthorne et al. 2011) and PCBs (Hawthorne, Miller, and Grabanski 2009) to POM. These studies have primarily focused on partitioning of select compounds in freshwater at standard laboratory conditions, but a couple have also looked at temperature (Booij et al. 2003) and salinity (Arp et al. 2015) effects on the POM/water partitioning coefficient K_{POM} values. Partitioning equilibrium between the aqueous phase and POM can be achieved for both classes of compounds in 4 weeks (Jonker and Koelmans 2001). POM films have also been used in the field to determine the PAH and PCB concentrations in sediments (Smedes, van Vliet, and Booij 2013; Beckingham and Ghosh 2013), landfill leachate (Cornelissen et al. 2009) soil samples impacted by oil (Hong and Luthy 2008) and harbor water affected by contaminated sediments (Cornelissen, Arp, et al. 2008). This study adds to the knowledge base by further investigating combined temperature and salinity effects on partitioning constants and by deploying POM into a tidal stream system to determine the efficacy of using passive sampling in small streams.

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Chapter 3: PAH Concentration in Water, Sediments and Fish of the Tacony-Frankford Creek, Philadelphia, PA

Abstract

Water, sediment and fish were sampled at various times and locations in a tributary to the Delaware River in Philadelphia, PA and analyzed for polycyclic aromatic hydrocarbon (PAH) concentrations. This study sought to identify spatial and temporal trends and to identify the sources and fate of 28 PAH compounds in the stream. Grab samples of sediments and whole water were collected between November 2008 and April 2010. In addition, fish samples were collected in June 2010 and consisted of five species commonly found in the stream. Total sediment concentrations of Σ PAH ranged from 3,200 ng/g to 72,000 ng/g at various locations in tidal and non-tidal region of the tributary and 25,000 ng/L in the Delaware River. The Σ PAH concentration in water ranged between 170 ng/L and 580 ng/L in the tributary and between 130 ng/L and 150 ng/L in the Delaware River. The concentration of Σ PAH varied greatly depending on the type of fish and tissue, and ranged from 43 ng/g in catfish livers to 1,300 ng/g in white perch organs (minus livers). The PAH concentration in water and sediment samples exhibited spatial trends but no identifiable temporal trend, the primary source of PAHs to the stream is motor vehicle emissions, and the fish organs and sediments were the primary reservoirs of PAH concentration in the stream.
3.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of compounds that are ubiquitous pollutants that can be found in water, air, soils and sediments around the globe. They are comprised of carbon and hydrogen atoms forming two or more fused aromatic rings. While there are more than 100 compounds in this group, the US EPA has designated 17 PAH compounds as priority pollutants due to higher potential for adverse effects in humans and aquatic species than the rest of the group. These 17 compounds are: acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz[*a*,*h*]anthracene, fluoranthene, benzo[*g*,*h*,*i*]perylene and indeno[*1*,*2*,*3*-*c*,*d*]pyrene. The main anthropogenic sources of PAHs are incomplete combustion of organic matter, releases of petroleumbased products and waste, and urban runoff (Cavalcante et al. 2012; Z. Wang, Liu, and Yang 2014; Yunker et al. 2002; Chen, Teng, and Wang 2012).

Owing to both population density and proximity of industry, many urban areas have elevated levels of PAHs in their air, water and soil (Crunkilton and DeVita 1997; X.-T. Wang et al. 2013; Cavalcante et al. 2012; Foster et al. 2000). Philadelphia, PA is one such urban area in which there is a heightened potential for PAH pollution. The streams and watersheds of Philadelphia are mostly buried (Levine 2014) and those that remain uncovered receive effluent from industrial sites and sewage treatment facilities, as well as runoff from numerous roadways. The stream selected for this research is the Tacony-Frankford Creek in Philadelphia, PA, which has a drainage area of 75 square km (Figure 3.1). The Tookany/Tacony Creek originates in Montgomery County northwest of Philadelphia and then travels through suburban and urban residential areas as well as industrial and recreational areas before emptying into the Delaware River. The portion of the stream between Castor Avenue and Torresdale Avenue is channelized. In the 1950s, the lower portion of the creek, below Interstate 95, was diverted from its original sinuous path through Bridesburg to a straight path that directly connects to the Delaware River. The Tacony-Frankford Creek is tidally influenced by the Delaware River below the dam at Frankford Avenue.

The primary objectives of this study are to determine the PAH concentrations in the Tacony-Frankford Creek and to examine possible spatial and temporal variability of PAHs in the stream. Previous studies have measured the concentrations of PCBs in the sediments (Praipipat, Rodenburg, and Cavallo 2013), water (Du, Belton, and Rodenburg 2008; Guo 2013), air (Du et al. 2009; Totten et al. 2006) and biota (Romanok et al. 2006) of the Delaware River and surrounding areas. PAHs have been also measured in the air (Du 2011) and sediments (Fischer and (U.S.) 2004) in the Delaware River, but the contribution of smaller tributaries to the Delaware River has not been examined. A secondary objective of the study is to use the measured PAH concentrations in the sediments, water, suspended sediments and fish to better understand the sources and fate of PAHs in the stream. To that end, source apportionment and partitioning coefficients will be derived for the compounds of interest.

3.2 Method and Materials

3.2 1 Sample Collection

3.2.1.1 Water/TSS

Whole water samples were collected as grab samples near the water surface at Sites 1-4 shown in Figure 3.1 on November 19, 2008 and May 6, 2009. Additional whole water samples were taken only at Site 2 on a weekly basis from October 29, 2009 through November 19, 2009. Finally, whole water samples were collected from Site 2 at four times during the course of a full tide on April 19, 2010.

The November 19, 2008 sampling occurred during average to wet conditions, with 5.4 cm of precipitation occurring in the week prior to sampling (Weather Underground 2015). For the week previous to sampling, USGS streamflow data indicates that the stream had a median flow that was comparable to the statistical mean daily discharge with two elevated flow events on November 13, 2008 and November 15-16, 2008 where the flow peaked at 10 times the baseline flow (USGS 2015). The May 9, 2009 sampling occurred during average to wet conditions, with 7.1 cm of precipitation occurring in the week prior to sampling (Weather Underground 2015). For the week previous to sampling, the stream had a median flow comparable to the statistical mean daily discharge with a high flow event occurring on May 6, 2009 that peaked at 20 times the baseline and had the potential to scour sediment (USGS 2015).

The October 29 through November 19, 2009 samplings occurred during dry conditions, with 0.5 cm to 0.9 cm of precipitation occurring each week prior to sampling,

except for the week of October 22-29, 2009, which had 8.6 cm of precipitation (Weather Underground 2015). For the week previous to each sampling, the stream had a median flow slightly above the statistical mean daily discharge with a high flow event on October 24, 2009 and a moderately elevated flow event on October 28, 2009 (USGS 2015).



Figure 3.1 Map of Tacony-Frankford watershed boundaries with June 2007 aerial photograph showing the sampling locations for studies in the Tacony-Frankford Creek, Philadelphia, PA.

The April 19, 2010 sampling occurred during average to dry conditions, with 0.6 cm of precipitation occurring in the week prior to sampling (Weather Underground 2015). For the week previous to sampling, the stream had a median flow comparable to the

statistical mean daily discharge and no anomalous flow events (USGS 2015). All discharge statistics and data for the Tacony-Frankford Creek were collected by the USGS at Station 01467087.

Whole water samples were collected in 20 liter acetone and hexane rinsed stainless steel cans following the techniques described in Rowe et al. (2007). The samples were taken by submerging the can completely in the stream water and capping underwater with a watertight seal to ensure no headspace. Samples were then transported to the laboratory for immediate filtering.

3.2.1.2 Sediments

Sediment samples were collected on November 19, 2008 at the five sites on the Tacony-Frankford Creek shown in Figure 3.1. Site 1 is located on the Delaware River at the mouth of the Tacony-Frankford Creek. Site 2 is located in a newer section of the stream that was dug in the 1950s to remove meandering and prevent flooding in the neighborhood surrounding the original stream path. Site 3 is approximately halfway up the tidal portion of the stream, located near the Interstate 95 overpass and on the edge of the newer and older portion of the stream. Site 4 is located downstream of the channelized portion and just below the dam that is considered the breakpoint between the tidal and non-tidal portion. It should be noted that at high tide during wet periods, water has been observed flowing upstream over this dam. Upstream of the channelized portion are Site 5, which is adjacent to the USGS gauge (Station 01467087) and Site 6, which is below the silt dam within Juniata Golf Course.

All sediment samples were collected using a Ponar dredge to collect the top 5 cm of sediment, and stored in clean 1-liter glass jars on ice for transport to the laboratory. The samples were freeze-dried at -59°C and 0.133 mbar to remove moisture and stored at 0°C until they were processed. Prior to extraction or carbon analysis, a homogenized subsample was ground using a mortar and pestle to a uniform particle size.

3.2.1.3 Fish

Fish samples were collected by electrofishing in the lower reaches of the stream (between Site 1 and Site 3) on June 6, 2010 by Philadelphia Water Department personnel. The whole fish were placed on ice immediately upon collection and brought back to the laboratory to be divided into three fractions: fillet, liver and other organs, which were freeze-dried at -59°C and 0.133 mbar to remove moisture and stored in borosilicate glass jars at 0°C until extraction.

3.2.2 Chemicals and Materials

All solvents and Whatman GF/F glass microfiber filters (142 mm) were purchased from VWR International (Radnor, PA). The solvents were EMD OmniSolv High Purity high-resolution GC grade hexane, Burdick & Jackson ACS/HPLC grade methanol, JT Baker HPLC grade acetone and JT Baker HPLC grade methylene chloride. Ultra high-purity nitrogen gas was purchased from Airgas (Malvern, PA). Deuteriumlabeled D_{10} -anthracene, D_{10} -fluoranthene and D_{12} -benzo[*e*]pyrene were purchased as surrogate standards and deuterium-labeled D_{10} -phenanthrene, D_{10} -pyrene and D_{12} benzo[*a*]pyrene were purchased as internal standards from Cambridge Isotope (Andover, MA). The twenty-eight PAH compounds for the calibration standard were purchased from Sigma Aldrich (St. Louis, MO) and included fluorene, phenanthrene, anthracene, 1methylfluorene, dibenzothiophene, 4,5-methylphenanthrene, fluoranthene, pyrene, 3,6dimethylphenanthrene, benzo[*a*]fluorene, benzo[*b*]fluorene, retene, benzo[*b*]naphtha[2,1*d*]thiophene, cyclopenta[*cd*]pyrene, benz[*a*]anthracene, chrysene/triphenylene (co-elute), naphthacene, benzo[*b*+*k*]fluoranthene (co-elute), benzo[*a*]pyrene, benzo[*e*]pyrene, perylene, indeno[1,2,3-*cd*]pyrene, benzo[*g*,*h*,*i*]perylene and dibenz[*a*,*h*+*a*,*c*]anthracene (co-elute), and coronene.

Prior to sampling, Amberlite XAD-2 resin was purchased from Sigma-Aldrich (St. Louis, MO) and cleaned by extracting in a soxhlet for 24 hours each in methanol, acetone, hexane, acetone and methanol and then rinsing completely and storing in high purity Milli-Q water. Sodium sulfate was purchased from VWR International (Radnor, PA) and dehydrated at 450°C for 24 hours, then stored at 100°C prior to use. Neutral alumina (60-325 mesh) was purchased from Fisher Scientific (Pittsburgh, PA) and was activated for 24 hours at 550°C and deactivated with 3% high purity Milli-Q water 12 hours prior to use and stored in an airtight desiccator. The SX-3 Bio-Beads used for lipid cleanup were purchased from Bio-Rad Laboratories (Hercules, CA, USA). Florisil (60-100 mesh) was purchased from Fisher Scientific (Pittsburgh, PA) and was cleaned and activated for 24 hours at 550°C, then deactivated with 2.5% high purity Milli-Q water immediately prior to use. The Whatman glass fiber filters were combusted at 450°C for 4 hours to remove trace volatile compounds. The stainless steel sample containers were rinsed three times with acetone and hexane, and air-dried prior to sampling. All

glassware was washed using Alconox, rinsed with Milli-Q water and dried for 5 hours at 450°C. Additionally, each piece of glassware was rinsed two times each with hexane and acetone just prior to use.

3.2.3 Analysis

3.2.3.1 Water/TSS

The procedures for analyzing the water samples are described in Rowe et al. (2007) and are summarized here. After collection, the whole water samples were immediately transported to the laboratory and a peristaltic pump was used with Nalgene tubing to filter the each sample into dissolved and particulate fractions. The samples were first pumped through PTFE supports containing glass fiber filters (0.7 μ m) to collect the total suspended sediments (TSS) portion and then passed through a PTFE column packed with XAD-2 resin to sorb the dissolved organic components. There was a small amount of breakthrough of solids to the XAD column visible on most samples, determined by the slight discoloration of the glass wool packed around the XAD-2 resin. This breakthrough was far smaller than the total amount of suspended sediment captured on the filters. The filter samples and XAD-2 resin samples were Soxhlet extracted separately in a 1:1 hexane:acetone mixture for 24 hrs. Three deuterated PAH compounds (D₁₀-anthracene, D₁₀-fluoranthene and D₁₂-benzo[*e*]pyrene) were added as surrogate standards to all samples at the beginning of Soxhlet extraction.

A liquid/liquid extraction was performed with 60 ml of Milli-Q water containing 1g NaCl to separate the organic fraction from the aqueous–dissolved fraction. The aqueous fraction was then extracted three times with 50 ml of fresh hexane to partition the analytes from the aqueous phase to the organic phase. The volume was reduced to ~1ml using rotary evaporation and ultra-high purity N₂ gas to evaporate the sample. The samples were purified and fractionated using a glass column packed with 4 g of prepared alumina (3% deactivated) and 1 g of sodium sulfate and the PAH analytes were eluted with 15 mL of a 2:1 (v:v) dichloromethane:hexane mixture. Samples were concentrated to 0.5 mL using rotary evaporation and ultra high purity N₂ gas, and internal standards (D₁₀-phenanthrene, D₁₀-pyrene and D₁₂-benzo[*a*]pyrene) were added before instrumental analysis.

3.2.3.2 Sediments

The organic carbon content in the sediments was determined using obtained by differential subtraction (TC minus IC) using a Shimatzu TOC analyzer with a Solid Sample Combustion Unit (SSM-5000A). The total carbon in each sample was determined using a maximum temperature of 900°C and inorganic carbon was determined using a maximum combustion temperature of 200°C.

Sediment samples were prepared for PAH analysis by Soxhlet extraction for 24 hours in 1:1 (v:v) acetone:methylene chloride. Three deuterated PAH compounds (D_{10} anthracene, D_{10} -fluoranthene and D_{12} -benzo[*e*]pyrene) were added as surrogate standards to all samples at the beginning of Soxhlet extraction. Excess sulfur was removed from the extract using acid-washed copper. The volume was reduced to ~1ml using rotary evaporation and ultra high purity N_2 to evaporate the sample. The samples were purified and fractionated using a glass column packed with 8 g of prepared florisil (2.5% deactivated) and 1 g of sodium sulfate and the PAH analytes were eluted with 35 mL of a 2:1 (v:v) dichloromethane:petroleum ether mixture. Samples were concentrated to 0.5 mL using rotary evaporation and ultra high purity N₂ gas, and internal standards (D₁₀-phenanthrene, D₁₀-pyrene and D₁₂-benzo[*a*]pyrene) were added before instrumental analysis.

3.2.3.3 Fish

Fish samples were Soxhlet extracted with 250 ml of 1:1 (v:v) hexane:acetone mixture for 72 h. The lipid content was determined by gravimetric measurement from an aliquot of the extract. The remainder of each sample was subjected to gel permeation chromatography, using a 50 cm glass column with a 2.5 cm inner diameter packed with 40 g of SX-3 Bio-Beads, and eluted with 1:1 (v:v) dichloromethane:hexane to remove lipids. The eluate containing the target compounds was collected and concentrated to 1 ml by rotary evaporation. The concentrated extract was further cleaned and fractionated on a 30 cm glass column with a 10 mm inner diameter packed with 6 cm deactivated neutral alumina and 12 cm of deactivated neutral silica gel topped with sodium sulfate. The PAH analytes were eluted with 70 ml of 1:1 (v:v) dichloromethane: hexane and concentrated to 1 ml and internal standards (D₁₀-phenanthrene, D₁₀-pyrene and D₁₂benzo[*a*]pyrene) were added prior to instrumental analysis.

3.2.4 Quantification

All samples were analyzed on a Hewlett-Packard 6890N gas chromatograph with a Hewlett-Packard 5973 mass spectrometer detector with a 30 m x 0.25 mm internal diameter HP-5ms capillary column and a 0.25 µm film thickness. The GC-MS method for PAH analysis was as follows: 1 µL pulsed splitless injection at 310°C and 67.2psi, oven temperature held at 50 °C for 1.1 min, then increased by 25°C/min to 125°C, then increased by 8°C/min to 260°C, and finally increased by 3.5°C/min to 310°C and held for 10 min. Chromatograms were integrated using Agilent MSD Chemstation software. Due to the linearity of the calibration curve over the range of sample concentrations, it was determined that a single point curve could be used for quantification ("Method 8000D Determinative Chromatographic Separations" 2015).

Relative response factors (RRFs) were calculated for each PAH compound in the calibration standards by dividing the relative area of the compound to internal standard by the relative concentration of the internal standard to the compound [Equation 3.1].

[Eq. 3.1]
$$RRF_{std} = \left(\frac{Area_{cmpd}}{Area_{IS}}\right) \div \left(\frac{Conc_{IS}}{Conc_{cmpd}}\right)$$

External standards were included for every ten samples and RRF values before and after each set of samples were averaged to account for any differences in the signal over the course of the sample analysis. The mass of each compound in the samples was then calculated by multiplying the signal area in the sample by the RRF and the mass to area ratio of the internal standard in each sample [Equation 3.2].

[Eq. 3.2]
$$Mass_{cmpd} = Area_{cmpd} \times RRF_{std} \times \left(\frac{Mass_{IS}}{Area_{IS}}\right)$$

Laboratory blanks of the XAD-2 resin and GF/F filters were also analyzed and any mass found was subtracted out of each sample. Surrogate recoveries (SR) were calculated to quantify the compound loss during processing by dividing the mass measured by the mass added at the beginning of the laboratory procedure [Equation 3.3].

[Eq. 3.3]
$$SR = \frac{(Mass_{SS})_{measured}}{(Mass_{SS})_{initial}}$$

The resulting mass of each compound was corrected for surrogate recoveries for low (phenanthrene and anthracene), mid- (fluoranthene and pyrene) and high molecular weight (MW) (benzo[*e*]pyrene and benzo[*a*]pyrene) compounds by dividing its mass by the corresponding surrogate recovery [Equation 3.4].

[Eq. 3.4]
$$(Mass_{cmpd})_{corrected} = (Mass_{cmpd})_{non-corrected} \div SR$$

3.2.5 Quality Assurance/Quality Control

Lab blanks were processed for each matrix (water, TSS and sediment) through all steps from extraction to analysis along with the samples. The mass of any compound found in the blanks was subtracted out of each corresponding sample mass within the same group of samples. Surrogate recoveries (\pm standard deviation) for D₁₀-anthracene, D₁₀-fluoranthene and D₁₂-benzo[*e*]pyrene, respectively, were 54% \pm 22%, 70% \pm 20%, and 76% \pm 21% in water; 48% \pm 20%, 62% \pm 25%, and 65% \pm 24% in TSS; and 71% \pm 10%, 82% \pm 10%, and 73% \pm 15% in sediment. The surrogate recoveries were used to correct the PAH masses that were measured in samples due to losses during processing. Detection limits for all PAH congeners were less than 0.0086 ng/L for the water and TSS samples and 0.039 ng/g for sediment samples.

3.3 Results

3.3.1 Water and TSS

3.3.1.1 Spatial Variation

The November 2008 and May 2009 samplings showed the variation of PAHs in the Tacony-Frankford Creek at different locations in the tidal portion. In both sets of data, the Σ PAH increased upstream from the Delaware River (Site1), as shown in Figure 3.2.



Figure 3.2 PAH concentration in the Delaware River and at various locations in the Tacony-Frankford Creek.

In the 2008 sampling, the highest concentrations were found near Site 3, which were 2.0 to 3.6 times higher than the downstream locations (Sites 1 and 2) and 2.8 times higher



PAH Concentration in Water Phase

PAH Concentration in gas phase at Camden, NJ (Gigliotti et al. 2005)



Figure 3.3 Comparison of water-phase PAH in Tacony-Frankford Creek with gaseous-phase PAH in Camden, NJ.

PAH Concentration in TSS



PAH Concentration Wet and Dry Particle Deposition (Gigliotti et al. 2005)



Figure 3.4 Comparison of PAH in TSS fraction of Tacony-Frankford Creek with atmospheric particles in Camden, NJ.

than the Site 4. The 2009 data mirrored the 2008 data by increasing from the Delaware River upstream to the Site 3 samples, but continued to increase upstream to Site 4. The 2009 concentrations were also less variable, increasing by a factor of 1.55 to 1.56 at each subsequent site upstream. Both sampling events took place under similar weather and flow conditions, so it is unlikely that these results are due to the combined sewer outfall upstream of the sampling site. These data do show that in this small stream, the concentrations of PAHs upstream can vary significantly even when the downstream concentrations are similar from one sampling to the next.

Within these results, the concentration of smaller, more volatile PAHs increases upstream, but the larger, less volatile compounds do not show this pattern as strongly. This might indicate that the major source of PAH to the stream is atmospheric. The PAH fingerprint in the aqueous fraction from both sampling events had high levels of phenanthrene, pyrene, fluoranthene and fluorene. This is similar to the gaseous phase PAHs measured across the Delaware in Camden, NJ (Gigliotti et al. 2005), as seen in Figure 3.3. In addition, the sorbed fraction (TSS) samples had high levels of fluoranthene, pyrene, benzo[b+k]fluoranthene and indeno[1,2,3-cd]pyrene, and exhibit a similar fingerprint to the wet and dry deposition as shown in Figure 3.4.

3.3.1.2 Temporal Variation

Samples taken at Site 2 between November, 2008 and June, 2011 show that the Σ PAH concentration remained relatively stable over time. The Σ PAH concentration ranged from 140 ng/L to 520 ng/L and a correlation matrix of the aqueous and sorbed fractions reveals that the PAH fingerprint is the same ($R^2 > 0.83$) for these samples. The

concentration of Σ PAHs at Site 2 went from 240 ng/L in November 2008 and May 2009 to 520 ng/L in October 2009 and then gradually decreased to 140 ng/L in June 2011. (See chapter 4 for details of the June, 2011 sampling.) Once again, phenanthrene, fluoranthene and pyrene were present in the highest concentration in the aqueous phase and fluoranthene and pyrene in the sorbed phase. In addition to the long-term sampling, weekly samples were collected in October and November 2009 to investigate short-term variability at one location. All aqueous PAH compounds were unchanged from week to week with exception of first week, which had concentrations of many compounds two to four times higher than in subsequent weekly samples. The sorbed fraction remained stable throughout the four-week period with concentrations varying by less than a factor of 2. In addition to the weekly samples, PAHs were also measured a three points in a tidal cycle in April 2010. The PAH compounds were variable over the course of the tide, and the rising tide had lower concentrations than falling and low tide. This is strongly correlates with the data from 2008-09 in which the PAH concentrations were lower in the Delaware River than in the Tacony-Frankford Creek. The samples taken from November, 2008 until June 2011 at Site 2 show that although there was variability in the concentration of individual congeners (up to a factor of four), there was no clearly defined temporal trend (Figure 3.5).

Comparing the PAH concentrations found in this study to those found for the NY/NJ harbor (Litten 2003), the averaged aqueous-phase fingerprint in the stream showed a stronger correlation (81%, 87%) to the aqueous-phase fingerprint in the 2003 Arthur Kill samples than any other location (1%-71%). This correlation to the Arthur Kill

fingerprint is strongest (90%, 94%) when compared to the samples collected in the Tacony-Frankford Creek during October and November 2009. Positive matrix



Figure 3.5 Concentrations of select PAH compounds in the Tacony-Frankford Creek at various sampling times.

factorization performed on the data NY/NJ harbor data (Rodenburg et al. 2008) indicates the 2003 Arthur Kill samples are unique and point to a possible petroleum spill, which could be possible for the Fall 2009 samples in this study also.

3.3.2 Sediment Bed

The total organic carbon content for the sediment samples is presented in Table 3.1. It is well documented that PAHs partition more readily to organic carbon than inorganic carbon (Moeckel et al. 2013; Countway, Dickhut, and Canuel 2003; Agarwal and Bucheli 2011). Therefore, the PAH concentrations can be expected to follow a similar pattern as the TOC concentrations if all of the sediments have been exposed to similar aqueous concentrations of each compound. However, regression analysis shows no correlation between TOC and PAH concentrations at the different locations, with R² ranging from 0.00 to 0.27 for all compounds except retene, which had an R² of 0.79. Since the PAH compounds are not strictly correlated to the organic carbon content in the associated sediments, it can be concluded that the PAH concentrations are variable at different locations in the stream.

Site	% Organic Carbon
1	1.74%
2	1.80%
3	0.65%
4	0.82%
5	1.23%
6	0.62%

Table 3.1 Organic carbon content of sediment samples from 6 sites on the Tacony-Frankford Creek in Philadelphia, PA.

The study stream is known to be flashy and sediments may be scoured periodically during above average precipitation events. The sediment sampling on November 19, 2008 took place during average flow conditions when recent scouring of the bed should not be an issue. The concentrations of the 28 PAHs at six sites from this sampling event are shown in Table 3.2, along with the effects range low (ERL) and effects range median (ERM) standards for the compounds that have established values. The ERL standards were exceeded in at least one sample at each site for fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, benzo[*a*]pyrene, and Σ PAH. All compounds were measured above the ERM standard in one of the samples taken at Site 4 (4A). The ERM standards were also exceeded for phenanthrene and pyrene at Site 1 and benz[*a*]anthracene at Sites 1 and 2.

A correlation matrix performed on the data shows that the congener pattern is strongly correlated ($\mathbb{R}^2 > 0.86$) for all samples except for one sample at Site 4 (4A), which was moderately correlated to the other samples ($0.76 < \mathbb{R}^2 < 0.91$). In addition to having slightly different fingerprint, sample Site 4 (4A) had a total concentration of PAHs that was three times higher than Site 1 and an order of magnitude higher than Sites 3 and 6. The elevated PAH concentration might be related to the multiple factories and bridges in that section of the stream. The rest of the samples are variable, showing no well-defined pattern either with distance downstream or with tidal vs. non-tidal reaches of the Tacony-Frankford Creek. However, the PAH concentrations in the Delaware River sediments is higher than for all other sites besides Site 4. The PAH fingerprint for the sediment samples from the Tacony-Frankford Creek were compared to the data collected and compared with a correlation matrix with the NY/NJ harbor CARP data (Litten 2003). All six sites on the Tacony-Frankford Creek show a high correlation (74%-86%) to sediments collected in the Raritan River. The correlation to other sites in the CARP study ranged from 0%-68%, with a median of 49%. According to the report, factor 1 was the primary source in the Raritan River samples and is comprised of mostly mid- to high-molecular weight compounds that point to pyrogenic sources (Rodenburg et al. 2008). This agrees with the source apportionment ratio for anthracene/phenanthrene and benzo[*a*]pyrene/benzo[*g*,*h*,*i*]perylene in the Tacony-Frankford samples. Both streams flow through urban and industrialized areas with high amounts of traffic emissions, so the similarity is not surprising.

3.3.3 Fish Tissue

The five species of fish that were collected and analyzed were channel catfish (*Ictalurus punctatus*), carp (*Cyprinus carpio*), striped bass (*Morone saxatilis*), white perch (*Morone americana*) and white sucker (*Catostomus commersoni*). Channel catfish, carp, and white sucker are resident species in the Tacony-Frankford Creek and can be found almost any time of year. The white perch are semi-migratory, spending much of the growing season in the study stream and the rest of the year in the Delaware Estuary (Stanley et al. 1983). Striped bass are an anadromous species, born in freshwater and migrating out to the Atlantic Ocean for several years until sexual maturity, returning to freshwater to spawn (Fay et al. 1983). Young striped bass may remain in smaller

			0										٥		
		Site 1	Site 1	Site 2	Site 2	Site 3	Site 3	Site 4	Site 4	Site 5	Site 5	Site 6	Site 6		
	det limits	Sediment	ERL	ERM											
	Conc. (na/a)														
Fluorene	0.0071	211	18	34	<mark>77</mark>	<mark>20</mark>	33	545	22	49	28	15	15	19	540
Phenanthrene	0.0044	1546	1732	378	1018	288	400	9063	752	775	937	434	202	240	1500
Anthracene	0.0048	343	404	20	179	38	60	1402	126	130	167	81	29	85	1100
1 Methylfluorene	0.011	32	45	12	18	9.6	10	38	16	14	÷	12	4.3		
Dibenzothiophene	0.0045	79	80	19	24	13	21	433	36	31	43	21	8.7		
4,5Methylenephenanthrene	0.0063	228	293	96	173	50	68	641	119	113	134	140	33		
Fluoranthene	0.0053	3048	2849	1275	2492	807	1029	10548	1436	1585	2068	1063	414	600	5100
Pyrene	0.0054	2531	2696	1084	2079	678	848	8350	1339	1358	1711	1114	356	670	2600
3,6-Dimethylphenanthrene	0.016	n.d.	n.d.	n.d.	4.4	n.d.	2.2	n.d.	n.d.	n.d.	0.92	n.d.	n.d.		
Benzo[a]fluorene	0.012	824	970	356	502	207	245	1085	297	379	442	355	104		
Benzo[b]fluorene	0.015	514	592	203	291	112	133	288	49	206	220	165	53		
Retene	0.022	46	38	52	38	20	17	5.8	7.9	6.3	9.5	9.1	13		
Benzo[b]naptho[2,1-d]thiophene	0.016	566	538	256	442	151	188	1429	236	283	358	234	79		
Cyclopenta[cd]pyrene	0.039	2423	2616	906	1650	480	622	6107	1083	963	1262	542	234		
Benz[a]anthracene	0.010	2271	2233	839	1602	454	571	6134	1026	928	1189	514	214	261	1600
Chrysene/Triphenylene	0.0067	1845	1733	811	1386	495	636	4566	797	1015	1198	758	294		
Naphthacene	0.019	369	309	176	340	86	103	584	86	203	246	151	55		
Benzo[b+k]fluoranthene	0.0050	2169	1969	952	1520	509	750	4742	768	1066	1249	474	261		
Benzo[e]pyrene	0.0080	929	916	459	790	278	423	2656	400	618	717	347	169		
Benzo[a]pyrene	0.0091	1278	1354	615	1044	346	525	3985	572	803	949	510	197	430	1600
Perylene	0.0086	374	353	175	297	<u>8</u> 3	147	1076	147	223	271	139	57		
Indeno[1,2,3-cd]pyrene	0.022	2057	2035	1022	1601	567	866	5674	858	1236	1240	465	276		
Benzo[g,h,i]perylene	0.0092	760	795	364	466	210	233	2131	319	574	520	259	148		
Dibenzo[a,h+a,c]anthracene	0.0072	121	116	47	82	29	36	257	39	59	52	20	÷		
Coronene	0.013	103	165	18	16	9.6	8.0	303	32	68	52	22	12		
SumPAHs	0.29	24668	24847	10220	18133	5949	7974	72043	10561	12707	15105	7845	3238	4000	45000

Concentrations in red exceed the Effects Range – Medium (ERM). Concentrations in yellow exceed the Effects Range – Low (ERL). Table 3.2 Concentrations of PAH compounds in sediments of Delaware River and various locations in the Tacony-Frankford Creek.

freshwater tributaries to the Delaware Estuary, using these areas are "nursery" areas, where they can escape larger predators and feed on smaller fishes. The striped bass are a top predator in this stream, feeding on white perch, carp and white suckers (Fay et al. 1983).

Adult channel catfish will eat plant matter and insects when necessary, but they prefer animal matter and will prey on the perch, carp and suckers in the Tacony-Frankford Creek (Starostka, Nelson, and U.S. Fish and Wildlife Service. 1974). While adult white perch are piscivores, their trophic class is size-dependent (Stanley et al. 1983) and the small size of individuals collected for this study suggests they are mostly a prey species. Carp are considered generalist bottom feeders and primarily eat plant matter by bottom sucking and are in frequent contact with the sediments and benthos (Benson and U.S. Fish and Wildlife Service. 1968). This, coupled with the fact that humans commonly consume this species, makes them an excellent choice for contaminant analysis. Small and immature carp can also serve as a prey species for the catfish and bass in the stream. The white suckers are at the bottom of this hierarchy, and are exclusively considered a prey species (Schneberger et al. 1977). They mostly feed on the bottom, like carp, but are not studied as often since they are not typically used for human consumption.

The muscle tissue (fillet) and non-liver organs were analyzed for all species and the livers were analyzed for the channel catfish and white suckers. The highest concentrations of PAHs in all species were found to be in the non-liver organs. Table 3.3 shows the concentrations of PAHs found in the various fractions for all five species. The two compounds that stand out are phenanthrene and fluoranthene, comprising an average of 23% and 14% in all samples, respectively. This agrees with previous studies that describe elevated concentrations of phenanthrene, fluoranthene and pyrene in the fish organs, specifically the liver (Pointet and Milliet 2000; Deb, Araki, and Fukushima 2000). Indeed, if only the two liver samples are taken into account, then the relative percent of phananthrene, fluoranthene and pyrene are 35%, 35% and 17%, respectively.

The total PAH concentration ranged from 73 ng/g to 310 ng/g in the fillet samples and from 100 ng/g to 1,300 ng/g in the organ samples. These ranges are in agreement with with previously published studies of fish tissue and organs in similar river ecosystems (Arias et al. 2009; White and Triplett 2002; Binelli and Provini 2004). In addition, the distribution of PAH concentration in the fish was similar to many previous studies, showing that low molecular weight PAHs are more commonly detected, while the high molecular weight compounds (benzo[*a*]pyrene, indeno[*1,2,3-cd*]pyrene, and benzo[*g,h,i*]perylene) are not detected in most samples (Zhao et al. 2014; Malik, Ojha, and Singh 2008). White perch had the highest concentrations of PAHs, with total PAH ranging from one to four times the fillet concentration and two to thirteen times the organ concentration of the other species. This might be due to the fact that perch of this size primarily feast on fish eggs, which have been shown to be a bioaccumulation factor for PAHs in some species (Meador et al. 1995).

Since the perch, carp and suckers are the prey species in this stream, it is informative to compare the PAH concentration in each to their predators, catfish and bass. Comparison of the perch fillets shows that the PAH concentrations are not strongly correlated to either catfish or bass ($R^2 = 0.46$ and 0.67, respectively). The catfish and bass

)	Carp		Bass	P	erch		White Sucker			Catfish	
		Organs (no		Organs (no		Organs (no		Organs (no	;		Organs (no	;
РАН	Fillet	liver)	Fillet	liver)	Fillet	liver)	Fillet	liver)	Liver	Fillet	liver)	Liver
	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(g/gn)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(ng/g)	(g/g)	(ng/g)
ACY	5.8	4.3	0.22	0.72	5.8	2.2	0.81	0.88	5.3	17	3.1	0.23
ACE	8.1	9.8	0.91	1.8	12	3.8	2.0	1.7	6.8	31	8.6	0.36
F	17	17	17	6.2	31	31	4.7	4.8	18	52	21	1.4
Ρ	28	190	36	78	67	180	24	36	34	64	56	15
Α	15	15	9.3	n.d.	22	38	11	n.d.	16	43	20	n.d.
FL	20	26	19	45	33	160	18	40	21	28	66	11
ΡΥ	8.3	8.8	9.2	23	10	39	n.d.	19	14	13	22	5.8
BAA	n.d.	13	n.d.	n.d.	16	100	2.6	n.d.	n.d.	11	52	3.6
C	3.7	23	3.4	7.7	32	240	2.4	3.0	17	19	93	4.4
BBFL	2.0	17	n.d.	n.d.	36	170	n.d.	n.d.	n.d.	n.d.	80	n.d.
BKFL	9.8	15	n.d.	n.d.	8.6	130	6.4	n.d.	7.8	n.d.	49	n.d.
BAP	n.d.	0.6	n.d.	n.d.	17	28	n.d.	n.d.	n.d.	n.d.	35	n.d.
IP	n.d.	11	n.d.	n.d.	12	85	n.d.	n.d.	n.d.	n.d.	37	n.d.
DBA	n.d.	2.8	n.d.	n.d.	2.9	24	n.d.	n.d.	n.d.	n.d.	12	n.d.
BPE	n.d.	9.9	n.d.	n.d.	11	43	n.d.	n.d.	n.d.	n.d.	33	n.d.
ΣPAHs	120	380	95	160	310	1300	73	100	140	280	590	43

Table 3.3 PAH Concentration in the fish tissue of various species in Tacony-Frankford Creek in Philadelphia, PA.

are larger and mobile, so the low correlation could mean that they are not preying on the perch, or that their time spent preying on fish outside of this stream has more of an influence on the concentration of PAHs in their diet. Additionally, the catfish/sucker coupling does not have a strong correlation ($R^2 = 0.53$). However, the same comparison for the other predator/prey couplings yield much stronger correlations. Bass/carp and bass/sucker PAH concentrations had correlation factors of $R^2 > 0.85$ and $R^2 > 0.83$, respectively while catfish/carp had a factor of $R^2 > 0.76$. These correlations indicate a more important predator/prey relationship for the respective species. The fact that the catfish were slightly less strongly correlated to the three prey species may be due in part to the fact that they may eat more insects and plant matter during the times of year when bass are present and outcompeting the catfish for prey.

3.4 Discussion

PAHs can be found in most urban areas, and the Tacony-Frankford Creek is no exception. In the whole water samples comprising the dissolved and suspended portions, the PAH concentration varies in concentration but the compound fingerprint does not change with time. The same samples show an overall increasing PAH concentration from the mouth of the stream to upstream of the tidal portion. The increase of total PAH concentration in water samples at upstream locations is driven primarily by the low molecular weight compounds, which exhibit the steepest gradient. One possible reason for this is that the larger population and combustion activities upstream add low molecular weight PAHs to the atmosphere and atmospheric deposition could be a major mechanism for PAH introduction to the stream. As these low molecular weight PAHs flow downstream, some may volatilize away before reaching the Delaware River.

The sediment bed exhibits the opposite trend, with average PAH concentrations highest in the Delaware River and lower in the upstream reaches of the Tacony-Frankford Creek. As expected, the main driver of this trend is the high molecular weight compounds sorbed to the sediments. The trend might be due to the stream widening and changing direction as it approaches the Delaware River. At slower velocity, large sediment particles with high PAH concentrations may fall out of suspension and be deposited at the confluence. Another explanation is that the Delaware samples suffer more frequent contamination from boating activity and spills. However, source apportionment analysis (Table 3.4) conducted on the sediment and TSS results point to pyrogenic sources for the PAHs found in this study, based on the phananthrene and anthracene ratios (Budzinski et al. 1997). Therefore, the former explanation is more supported than the latter. The specific pyrogenic source was a little less straightforward, with the benzo[a] pyrene to benzo[g,h,i] pervlene ratio in all samples pointing toward motor vehicle emissions as the main source (Katsoyiannis, Terzi, and Cai 2007), while the fluoranthene and pyrene ratio indicates coal combustion (Budzinski et al. 1997). Since the stream is located in an area that has both industry and multiple heavily travelled roadways, it makes sense that these sources could affect the stream to varying degrees based on sampling location.

Ratio	Value	Source	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6
P/A	4-10	pyrogenic	4.39	5.61	6.97	6.42	5.77	5.76
FL/P	>1	coal	1.13	1.19	1.20	1.24	1.19	1.00
BAP/ BPE	>0.6	traffic emissions	1.69	2.00	1.97	1.86	1.60	1.74

Table 3.4 Selected PAH source apportionment ratios

Understanding the fate of PAHs by finding the temporal and spatial distribution is not enough to understand the stream dynamics unless we take into account their transport behavior in the stream. As hydrophobic compounds, they are predominantly associated with sediments (suspended or bed) and biota living in the stream, but a measurable amount can also be found dissolved in the water. The relative concentrations of compounds in each of these media can only tell us so much, as the structure of each



Figure 3.6 $\log(K_D)$ (squares) and $\log(K_{OC})$ (diamonds) vs. $\log(K_{OW})$ for the sediments in Tacony-Frankford Creek in Philadelphia, PA

compound affects its affinity and kinetics of moving from one medium to another.

Partitioning coefficients were calculated for the water and sediments (K_D) and sediment organic carbon (K_{OC}) . Since a stream is not a static system, the compounds might not be at equilibrium but we can compare the partitioning coefficients calculated for the stream to known values such as the octanol-water partitioning constant (K_{OW}) . Figure 3.6 shows the calculated sediment partitioning coefficients plotted against the log (K_{OW}) . The regression coefficients for the sets of data are 0.73 and 0.69 for the log (K_D) and log (K_{OC}) , respectively. Both of the calculated coefficients are well correlated to the known values and therefore it is likely that the compounds are close to equilibrium in these samples. This conclusion, coupled with the knowledge that there was no correlation between the TOC and PAH concentrations (as discussed previously), point to chronic differences in the PAH concentrations at different locations within the stream.

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Chapter 4: Tidal Variation of PAH and PCB Concentrations in the Tacony-Frankford Creek

Abstract

Grab water samples were taken from a tidal, non-saline stream in Philadelphia, PA in June 2011 and filtered to separate suspended particles from the aqueous samples. Both fractions were analyzed for polycyclic aromatic hydrocarbon (PAH) and polychlorinated biphenyl (PCB) concentrations. The sum of 16 PAH compounds ranged from 74 to 160 ng/L and 41 PCB compounds ranged from 2.7 to 7.9 ng/L in the whole water samples. The purpose of the study was to determine whether sampling depth and time impact the PAH or PCB concentrations in a tidal stream. Sampling depth impacts both classes of compounds, with concentrations found to be higher near the sediment bed than near the surface, driven mostly by the portion that was associated with particles. However, the tidal timing had a much larger impact on the concentration of PAHs than PCBs due in part to the continuous release of PAH compounds in urban settings. The findings of this study are important considerations when designing sampling plans to determine pollution levels in small streams for purposes of environmental impact assessment and remediation.

4.1 Introduction

Due to the importance of marine transport throughout history, many urban environments occur in coastal areas in which local streams can be influenced by the tidal flow of an adjacent estuary or ocean. There are numerous examples of rivers that are both tidally influenced and also located in or near urban development, such as the Anacostia River (Hwang and Foster 2006), Caloosahatchee River (Fernandez, Marot, and Holmes 1999), Elbe River (Götz et al. 1998), Hudson River (Butcher and Garvey 2004; Farley, Wands, and Cooney III 2014), Hugli River (Guzzella et al. 2005), and Pearl River (Chen et al. 2013). These river systems are distinct from upland systems due to the fact that tidal forces impact the fate and transport of contaminants in the stream. The main goal of this study is to determine how hydrophobic organic compound (HOC) concentrations vary in tidal streams. To that end, the study looks at the aqueous and sorbed fraction concentrations of two classes of HOCs at different times in the tidal cycle and examines variations due to depth and time differences. The data presented in the previous chapter show that the water and suspended sediments of the Tacony-Frankford Creek have measurable concentrations of HOCs and thus are well suited to a study of this type. The study was conducted in the industrial section of the Philadelphia watershed, in a stream that is a tributary to the Delaware River. The depth at this location varies as much as 2.5 m with the semi-diurnal tide.

The first hypothesis for this study was that tides affect sorption and desorption of HOCs in urban streams. The objective was to determine whether HOC concentrations vary with tide. Tides introduce increased turbulence and hydrodynamic forces that can affect the partitioning of pollutants between water and sediments at the streambed interface. If the stream is located close enough to an ocean, the salinity of the water column might vary also (Kuivikko et al. 2010). In these tidal streams, the flow of water can carry HOCs in both the dissolved and particulate phases either upstream or downstream at different points in the tide. This complicates the typical downstream-only transport regime that is a basic assumption of pollutant modeling in non-tidal streams. In
addition, changes in salinity and water chemistry affect the partitioning behavior of HOCs and heavy metals, causing variation in their concentrations in different phases (Kuivikko et al. 2010; Tremblay et al. 2005; Spencer and MacLeod 1999). Each of these factors affects the spatial and temporal distribution of HOCs in a particular river and therefore could impact the availability and accumulation of these compounds in the biota living in the system.

The second hypothesis of the study was that the depth of sampling in the water column influences the concentration of HOCs. The objective for this part of the study was to determine whether differences in concentration are present between samples taken near the surface or samples taken near the sediment bed. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are two classes of HOCs that are suspected carcinogens, mutagens and teratogens (Jennings 2012; Ohe, Watanabe, and Wakabayashi 2004; Mayer, Mayer, and Witt 1985; Hyötyläinen and Olkari 1999). Many PAH compounds are by-products of petroleum industry and fuel combustion and as such, are commonly found in urban settings (O'Sullivan and Sandau 2013). PCBs are manufactured compounds that were banned in the US during the 1970s. Unfortunately, due to their recalcitrant nature, they are still ubiquitous in the environment (Bogdal et al. 2013). Once released to the aquatic environment, most PCBs and PAHs quickly become associated with sediment particles due to their low solubility and high hydrophobicity. There are slight variations in solubility within each class of compound, with larger-ring PAHs and more chlorinated PCBs exhibiting reduced solubility. For this reason, in a riverine system some of the smaller, low molecular weight compounds may be desorbed from sediments and become mobilized in the dissolved phase. Even so, the major

mechanism of transport occurs in the sorbed phase when the flow is great enough to carry suspended sediments (TSS) downstream. The variations in concentrations provide insight into how urban tidal streams differ from non-tidal streams and how time and depth of sampling can affect the resultant concentrations of PAHs and PCBs found in the water column.

4.2 Method and Materials

4.2.1 Sample Collection

The site selected for this study was Site 2 the Tacony-Frankford Creek in Philadelphia, PA as shown in Figure 3.1. Samples were collected on June 8, 2011 at a site located approximately 3 m downstream of the bridge at Hedley Street, approximately 300 m upstream of the mouth of the Tacony-Frankford Creek. The tidal water that flows in from the Delaware River influences this site twice daily, with the specific conductance also showing a spike twice a day at low tide. At this section, the stream is approximately 42 m wide and varies between 1-3.25 m deep. Samples were taken from a rowboat, as close to the middle of the stream as possible (Figure 4.1). The sampling occurred during average to dry conditions, with less than 0.3 cm of precipitation occurring in the prior two weeks (Weather Underground 2015). For the week previous to sampling, the stream had a flow that was at or below the mean daily discharge statistic compiled by USGS (Station 01467087) and had not recently been influenced by scouring (USGS 2015).



Figure 4.1 Schematic of tidal sampling setup

Water samples were collected in 20 liter stainless steel Pepsi cans following the techniques described in Rowe et al. (2007). At high, falling, and rising tide, water samples were collected at 0.3 m above the sediment bed (near-bed) and approximately 0.3 m below the water surface (near-surface). At low tide, samples were only collected at 0.3 m above the sediment bed because the stream was only about 1 m deep. Sampling near the surface was done by submerging the Pepsi can completely in the stream water and capping underwater to ensure no headspace. Sampling near the sediment bed involved deploying a pole into the water column with tubing secured exactly 0.3 m up from the bottom of the pole. The tubing ran to the stream bank, through a peristaltic pump and into the stainless steel canister. Due to this set up, the near-bed samples were not necessarily triplicates, since it took approximately 15-20 minutes to collect each sample and therefore they represent a natural variation between the first and last sample collected at any given tide.

Triplicate samples were taken at high tide and low tide. Duplicate samples were taken at the mid-falling tide and near the sediments only at the mid-rising tide. Only one sample was collected near the surface at mid-rising tide due to a structural failure in a steel tank. All samples were taken back to the laboratory and processed through extraction within two days after the sampling following the procedure described below.

In addition, at each sampling time and location, a 500 ml sample and a 3.8 liter sample were taken. The 500 ml sample was filtered onsite using Whatman GF/F filters (0.45 μ m), transported back to the laboratory, and stored at 4°C before analysis of TOC and DOC. Samples designated for TOC/DOC analysis were analyzed using a Shimadzu TOC-5000 using the USEPA Standard Method 5310-B TOC Analysis by Combustion-Infrared Method. The 3.8 liter sample was taken back to the laboratory and filtered through pre-weighed 0.7 μ m GF/F filters and dried completely in a 70°C oven and weighed again to determine total suspended sediment concentration in water.

4.2.2 Chemicals and Materials

The chemicals and materials used in this study have been outlined in the last chapter with the exceptions to follow. A sixteen PAH calibration mix #6 for EPA Method 610 was purchased from Restek Chromatography (Bellefonte, PA) and included naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[*1,2,3-cd*]pyrene, benzo[*g,h,i*]perylene and dibenz[*a,h*]anthracene. PCB 14, PCB 30, PCB 65 and PCB 166 were purchased as surrogate standards and PCB 23 and PCB 204 were purchased as internal standards from Cambridge Isotope (Andover, MA). The Quebec Ministry of Environment Congener Mix (QME) containing forty-one PCB congeners was purchased from Accustandard (New Haven, CT) and included PCBs 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 187, 191, 194, 195, 199, 205, 206, 208, and 209.

4.2.3 Analysis

The procedures for analyzing the water samples are described in the previous chapter with slight variation in the procedure to include PCB analysis. In addition to the three deuterated PAH compounds (D_{10} -anthracene, D_{10} -fluoranthene and D_{12} -benzo[*e*]pyrene), added as surrogate standards prior to Soxhlet extraction, four PCBs (PCB 14, PCB 23, PCB 65 and PCB 166) were also added. After liquid/liquid extraction and volume reduction using ultra high purity nitrogen, alumina was used to purify and fractionate the samples into two fractions. The columns were set up as described previously, but the PCBs were first eluted with 15 ml of hexane before the PAH compounds were eluted with 15 mL of a 2:1 dichloromethane:hexane mixture. After being concentrated to a volume of 0.5 ml, internal standards including D_{10} -phenanthrene, D_{10} -pyrene and D_{12} -benzo[*a*]pyrene and PCB 30 and PCB 204 were added.

4.2.4 Quantification

All samples were analyzed on a Hewlett-Packard 6890N gas chromatograph with a Hewlett-Packard 5973 mass spectrometer detector with a 60 m x 0.25 mm internal diameter DB-XLB capillary column and a 0.25 µm film thickness. The GC-MS method for PAH analysis was as follows: 1 µL splitless injection at 280°C and 27psi, oven temperature held at 80°C for 1 min, then increased by 15°C/min to 180°C, then increased by 4°C/min to 240°C, and finally increased by 8°C/min to 310°C and held for 16 min. The GC-MS method for PCB analysis was as follows: 3µL pulsed splitless injection at 280°C and 26 psi, oven temperature held at 70°C for 2 min, then increased by 15°C/min to 190°C, then increased by 5°C/min to 220°C and held for 1min, then increased by 2.5°C/min to 260°C and held for 1min, then increased by 5°C/min to 280°C and held for 5min, and finally increased by 3.5°C/min to 300°C and held for 15 min. Chromatograms were integrated using Agilent MSD Chemstation software. For PAHs, a five point calibration curve using varied concentrations of the deuterium-labeled surrogate standards and the Method 610 PAH Mix and deuterated internal standards was constructed. For PCBs, a five point calibration curve was constructed using varying concentrations of the PCB internal standards and QME mixture.

Relative response factors (RRFs), surrogate recoveries and sample concentrations were calculated for each PAH and PCB compound as described previously.

4.2.5 Quality Assurance/Quality Control

Two lab blanks and two matrix spikes (one each for XAD and GFF) were processed through all steps from extraction to analysis along with the samples. The mass of any compound found in the blanks was subtracted out of each sample mass. Surrogate recoveries (\pm standard deviation) for D₁₀-anthracene, D₁₀-fluoranthene and D₁₂benzo[*e*]pyrene were 68% \pm 12%, 66% \pm 9%, and 52% \pm 6%, respectively. Surrogate recoveries for PCB 14, PCB 23, PCB 65 and PCB 166 were 67% \pm 16%, 72% \pm 18%, 78% \pm 20%, and 71% \pm 19%, respectively. The surrogate recoveries were used to correct the PAH and PCB masses that were measured in samples due to losses during processing. Detection limits for PAH congeners were found to be 0.001 ng with concentrations in all samples at least 100 times above this limit. Likewise, the detection limits for PCB congeners ranged from 0.02 ng to 0.05 ng and the concentrations in all samples were at least 5 times above the limit. The coefficient of determination was above 98% for all PAHs and above 99% for all PCBs in the calibration curves, showing excellent linearity over the analyzed range of concentrations.

The relative standard deviations among the triplicate samples taken near the surface at each tide ranged from 2% to 22% for PCBs and 12% to 17% for PAHs. These percentages show excellent reproducibility and compare favorably with other studies (Cam et. al., 2000) where reproducibility was on the order of 13-28%. There was much more variation in the near-bed samples due to the fact that each sample took 15 minutes to fill and so the near bed samples are not true duplicates and triplicates, but time-lapsed samples taken over a 30-45 minute period during the tide. Conversely, near-surface samples could be drawn within minutes of one another. For this reason, uncertainties in the tables and graphs in the results section represent one standard deviation of the duplicate or triplicate samples for the near-surface samples and represent the minimum and maximum sample concentration near the bed.

4.3 Results and Discussion

In general, the highest concentrations of PAH and PCB compounds were the low to mid-molecular weight compounds, near the sediment bed at low tide. Concentrations in the whole water samples were dominated by the fraction associated with suspended matter. In concert with this finding, the concentrations of each class of compounds were elevated and more variable near the sediment bed than near the surface. In addition, the near-bed samples included more high molecular weight compounds than were present in the surface samples, which were almost completely comprised of low to mid- molecular weight compounds. PCB concentrations were low overall and exhibited very little variation with tide, especially when compared to PAH concentrations, whose occasional large variations were driven by a few of the lighter compounds. The variations in the concentrations between tides or sampling depths do not seem to be driven by dissolved organic carbon or total suspended sediment concentrations.

4.3 1 Total Organic Carbon

Both near-bed and near-surface measurements of dissolved organic carbon (DOC), shown in Table 4.1, were relatively stable and similar ranging from 2.6 to 2.9 mg/L for the high, falling and low tides. Near the surface, the rising tide DOC was slightly higher (2.9 mg/L) than at the other tides (2.6 mg/L) and was similar to the concentrations near the bed (2.5 - 2.8 mg/L). The DOC concentrations found in this stream are relatively low compared to streams in similar climates (Thurman 1985; Meybeck 1982), but matches previously reported data from the Delaware River (Tian et al. 2013). The higher DOC near the surface during the rising tide might indicate that the incoming tide resuspends the sediments, mixing the suspended load and associated DOC throughout the water column. Since the DOC concentrations were not very high and also relatively stable, it is probable that most of the PCB and PAH compounds analyzed in the water fraction are fully dissolved and not affected by the organic carbon content at a given time and location in the water column.

4.3.2 PAH Compounds

The concentration of each PAH compound in the water fraction, the TSS fraction, and whole water samples is displayed in Table 4.2, Table 4.3 and Table 4.4, respectively. All compounds in the water fraction, the TSS fraction, and whole water samples have a measurable concentration and show slight variation with time and location, but phenanthrene, fluoranthene and pyrene concentrations are much higher than

	Near-Surface	Near-Bed
	(mg/L)	(mg/L)
High Tide	2.55 ± 0.02	2.74 ± 0.03
Mid-Falling Tide	2.62 ± 0.02	2.75 ± 0.08
Low Tide		2.48 ± 0.03
Mid-Rising Tide	2.85 ± 0.01	2.80 ± 0.004

Table 4.1 Dissolved organic carbon concentrations in water taken near the surface and near the sediment of Tacony-Frankford Creek.

concentrations of the other compounds. Acenaphthene concentrations were relatively stable, except for the water samples taken near the bed at low tide, in which the concentration was up to 39 times larger than at other tides. This may indicate a flux from the sediments to the water fraction that is enhanced when the overlying water is shallow enough to disturb the sediment bed.

Table 4.2 Concentrations of all PAH compounds in water fraction near the sediment bed and near the surface at varying tides.

PAH Concentration in Water (ng/L)		Near-Se	diment		Ne	ar-Surface	
	High	Falling	Low	Rising	High	Falling	Rising
Naphthalene	0.68 ± 0.09	0.43 ± 0.05	0.27 ± 0.17	0.22 ± 0.10	0.95 ± 1.22	0.19 ± 0.06	0.72
Acenaphthylene	0.10 ± 0.01	0.17 ± 0.06	0.42 ± 0.20	0.20 ± 0.06	0.11 ± 0.05	0.06 ± 0.06	0.10
Acenaphthene	0.39 ± 0.10	0.74 ± 0.13	15.6 ± 5.46	1.26 ± 0.79	0.63 ± 0.36	0.41 ± 0.10	0.40
Fluorene	2.77 ± 0.33	4.42 ± 2.40	20.1 ± 8.82	5.48 ± 2.38	4.24 ± 1.24	3.29 ± 0.18	2.99
Phenanthrene	24.4 ± 9.67	38.2 ± 32.6	46.0 ± 9.73	54.2 ± 19.3	56.0 ± 23.8	31.0 ± 6.90	23.4
Anthracene	1.83 ± 0.27	2.07 ± 0.23	3.32 ± 0.14	2.02 ± 0.03	1.76 ± 0.24	1.76 ± 0.02	1.95
Fluoranthene	12.3 ± 3.65	15.4 ± 0.52	27.2 ± 3.22	15.2 ± 2.75	10.6 ± 2.19	12.3 ± 0.15	13.2
Pyrene	11.7 ± 3.36	12.7 ± 0.74	25.4 ± 9.26	14.9 ± 6.32	10.0 ± 1.97	11.0 ± 0.33	20.6
Benz[a]anthracene	3.22 ± 1.20	2.81 ± 1.03	3.14 ± 0.80	3.06 ± 1.82	1.71 ± 0.19	1.97 ± 0.39	1.90
Chrysene	3.15 ± 1.03	2.92 ± 0.93	3.42 ± 0.62	2.98 ± 1.55	1.87 ± 0.15	2.19 ± 0.39	2.07
Benzo[b]fluoranthene	3.92 ± 1.81	2.94 ± 1.72	2.93 ± 1.47	4.00 ± 3.28	1.72 ± 0.33	1.93 ± 0.69	2.15
Benzo[k]fluoranthene	2.49 ± 0.58	2.22 ± 0.27	2.05 ± 0.46	2.44 ± 0.84	1.92 ± 0.19	1.81 ± 0.24	1.94
Benzo[a]pyrene	2.85 ± 0.88	2.42 ± 0.74	2.13 ± 0.73	2.96 ± 1.75	1.83 ± 0.21	1.82 ± 0.33	1.92
Dibenz[a,h]anthracene	1.40 ± 0.10	1.37 ± 0.10	1.20 ± 0.10	1.30 ± 0.08	0.96 ± 0.83	1.27 ± 0.07	1.27
Indeno[1,2,3,-cd]pyrene	2.70 ± 0.68	2.34 ± 0.44	2.09 ± 0.59	2.67 ± 1.16	1.98 ± 0.20	1.89 ± 0.25	1.93
Benzo[g,h,i]perylene	2.31 ± 0.81	1.89 ± 0.71	1.71 ± 0.70	2.37 ± 1.54	1.38 ± 0.17	1.38 ± 0.29	1.45
ΣΡΑΗ	76.15 ± 24.56	93.06 ± 42.67	157.0 ± 42.48	115.2 ± 43.80	97.7 ± 33.33	74.3 ± 10.45	77.9

PAH Concentration in TSS	(ng/g)	Near-Sec	liment		Ne	ear-Surface	
	High	Falling	Low	Rising	High	Falling	Rising
Naphthalene	14.8 ± 17.8	ND	14.6 ± n/a	5.03 ± 3.05	197 ± 92.8	90.8 ± n/a	63.5
Acenaphthylene	30.7 ± 0.17	28.4 ± 36.2	25.3 ± 22.7	14.2 ± 8.76	26.8 ± 2.52	21.1 ± 3.63	31.4
Acenaphthene	2.63 ± 1.51	6.06 ± n/a	6.96 ± 2.6	3.94 ± 1.14	14.9 ± 6.24	12.8 ± 8.09	13.1
Fluorene	39.2 ± 23.9	43.9 ± 38.1	48.1 ± 30.4	28.6 ± 13.2	90.8 ± 74.0	52.5 ± 7.64	23.1
Phenanthrene	418 ± 388	1084 ± 38.8	732 ± 287	395 ± 2.47	5417 ± 4255	1943 ± 1024	ND
Anthracene	116 ± 65.1	215 ± 226	135 ± 85.6	62.2 ± 44.4	155 ± 7.47	127 ± 11.7	108
Fluoranthene	1076 ± 821	1567 ± 1911	1413 ± 1082	501 ± 500	491 ± 165	415 ± 76.2	326
Pyrene	923 ± 694	1341 ± 1621	1247 ± 866	449 ± 445	459 ± 151	400 ± 49.6	363
Benz[a]anthracene	720 ± 549	1055 ± 1294	939 ± 706	313 ± 312	295 ± 77.4	282 ± 38.9	207
Chrysene	587 ± 437	873 ± 1047	761 ± 545	262 ± 253	290 ± 64.3	281 ± 29.7	206
Benzo[b]fluoranthene	1059 ± 800	1546 ± 1861	1401 ± 1026	466 ± 435	490 ± 175	457 ± 97.3	345
Benzo[k]fluoranthene	364 ± 246	513 ± 552	467 ± 311	165 ± 134	289 ± 38.9	258 ± 6.17	203
Benzo[a]pyrene	661 ± 477	969 ± 1127	861 ± 621	292 ± 260	386 ± 75.5	341 ± 33.3	263
Dibenz[a,h]anthracene	142 ± 75.1	184 ± 148	179 ± 99.5	66.0 ± 38.8	200 ± 2.42	175 ± 15.6	134
Indeno[1,2,3,-cd]pyrene	566 ± 394	831 ± 928	758 ± 526	249 ± 207	389 ± 56.8	348 ± 26.0	260
Benzo[g,h,i]perylene	594 ± 433	874 ± 1016	802 ± 566	259 ± 227	338 ± 82.5	312 ± 45.9	226
ΣΡΑΗ	7,313 ± 5,425	11,130 ± 11,843	9,793 ± 6,776	3,530 ± 2,885	9,528 ± 5,327	5,517 ± 1,474	2,772

Table 4.3 Concentrations of all PAH compounds in sorbed fraction near the sediment bed and near the surface at varying tides.

Table 4.4 Concentrations of all PAH compounds in whole water samples near the sediment bed and near the surface at varying tides.

PAH Concentration in Whole Sample (ng/l		Near-See	diment		Ne	ear-Surface	
	High	Falling	Low	Rising	High	Falling	Rising
Naphthalene	1.00 ± 0.38	0.43 ± 0.05	0.38 ± 0.31	0.42 ± 0.01	2.33 ± 0.58	0.58 ± 0.61	1.88
Acenaphthylene	0.53 ± 0.39	0.70 ± 0.62	0.98 ± 0.54	0.75 ± 0.28	0.30 ± 0.06	0.24 ± 0.02	0.68
Acenaphthene	0.45 ± 0.09	0.80 ± 0.21	15.7 ± 5.40	1.41 ± 0.75	0.74 ± 0.37	0.52 ± 0.03	0.65
Fluorene	3.60 ± 0.82	5.25 ± 1.68	21.2 ± 8.63	6.58 ± 1.87	4.87 ± 0.73	3.74 ± 0.25	3.42
Phenanthrene	30.3 ± 16.4	58.6 ± 33.3	62.1 ± 7.64	69.4 ± 19.4	81.2 ± 12.0	47.6 ± 1.82	23.4
Anthracene	4.30 ± 1.65	6.13 ± 4.02	6.30 ± 1.79	4.42 ± 1.68	2.84 ± 0.22	2.85 ± 0.12	3.93
Fluoranthene	35.1 ± 21.1	44.9 ± 35.5	58.4 ± 21.5	34.5 ± 22.0	14.1 ± 1.93	15.9 ± 0.80	19.2
Pyrene	31.3 ± 18.1	37.9 ± 31.3	52.9 ± 12.0	32.1 ± 23.4	13.2 ± 2.24	14.4 ± 0.09	27.2
Benz[a]anthracene	18.5 ± 12.9	22.7 ± 25.4	23.8 ± 16.0	15.1 ± 13.8	3.77 ± 0.35	4.38 ± 0.71	5.70
Chrysene	15.6 ± 10.3	19.4 ± 20.6	20.2 ± 12.3	13.1 ± 11.3	3.90 ± 0.31	4.59 ± 0.64	5.85
Benzo[b]fluoranthene	26.4 ± 18.8	32.0 ± 36.8	33.8 ± 23.4	21.9 ± 20.0	5.14 ± 0.90	5.84 ± 1.52	8.47
Benzo[k]fluoranthene	10.2 ± 5.81	11.9 ± 10.7	12.3 ± 7.15	8.78 ± 6.00	3.94 ± 0.14	4.01 ± 0.29	5.66
Benzo[a]pyrene	16.9 ± 11.0	20.7 ± 22.0	21.1 ± 14.2	14.2 ± 11.8	4.53 ± 0.38	4.74 ± 0.61	6.75
Dibenz[a,h]anthracene	4.42 ± 1.69	4.84 ± 2.69	5.15 ± 2.29	3.84 ± 1.57	2.36 ± 0.84	2.76 ± 0.07	3.73
Indeno[1,2,3,-cd]pyrene	14.7 ± 9.05	18.0 ± 17.9	18.8 ± 12.0	12.3 ± 9.12	4.69 ± 0.34	4.87 ± 0.46	6.70
Benzo[g,h,i]perylene	14.9 ± 10.0	18.3 ± 19.8	19.4 ± 12.9	12.3 ± 10.3	3.73 ± 0.46	4.05 ± 0.68	5.59
ΣΡΑΗ	228 ± 138	302 ± 262	372 ± 158	251 ± 153	152 ± 21.9	121 ± 8.7	129

Concentrations of phenanthrene, fluoranthene and pyrene were about an order of magnitude higher concentrations than the other PAHs. Indeed, Gigliotti et al. (2005) reported that these three compounds had concentrations that were higher than most of the other PAHs in both the aerosol phase and in precipitation in the Delaware River basin. Figure 4.2 demonstrates the strong similarities between the aqueous and sorbed concentrations in this study and the wet and dry deposition fluxes reported by Gigliotti et

al. (2005). Since the source apportionment results from last chapter indicate that the dominant source of PAHs is motor vehicle emissions, it makes sense that particles in the atmosphere as well as in the stream have comparable signatures.

Due to the high concentrations of phenanthrene, fluoranthene and pyrene compounds, the overall 3- and 4-ring PAH concentrations in the water fraction were much higher than the 5-ring concentrations, which were in turn higher than the 6-ring concentrations. No single compound dominates the 5- and 6-ring PAH groups throughout the different locations and tides. The only exception to this trend in the water fraction is during the high and falling tides, when the 2- and 3-ring groups have a higher concentration than the 4-ring group. In all aqueous samples, benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[*1,2,3-cd*]pyrene, and dibenz[*a,h*]anthracene concentrations were below the water quality standards set by the Delaware River Basin Commission (DRBC 2014). The phenanthrene concentration in water is highest near the surface at high tide, indicating that atmospheric deposition may be an important source of phenanthrene. Rodenburg et al. (2010) found that atmospheric deposition was the dominant source of phenanthrene in the nearby New York/New Jersey Harbor.

In almost all samples, phenanthrene dominated the 2, 3-ring compounds, comprising 51-90% of this group in the aqueous samples and 37-95% of this group in the sorbed fraction. Additionally, phenanthrene showed a wide range of variability in the individual samples of both the aqueous fraction and the sorbed fraction over the course of the tide, ranging from 15-68 ng/L near the streambed and 23-81 ng/L near the surface in the water samples. In the sorbed fraction, the phenanthrene concentration in the





Figure 4.2 Comparison of a.) aqueous and wet deposition fractions, and b.) sorbed and dry deposition fractions of select PAHs in Tacony-Frankford Creek. (Constant deposition velocity was assumed; flux is proportional to concentration.)

individual samples varied from 140-1,100 ng/g in near-bed samples and 1,200-8,400 ng/g in near-surface samples. In the 4-ring group, fluoranthene and pyrene are the dominant compounds in the aqueous fraction, each comprising 35-55% of the total 4-ring concentration and together comprising 78-91%, while in the sorbed fraction they each only comprise 28-33% of the concentration of the 4-ring group. The fluoranthene and pyrene lack the wide variability of phenanthrene in the aqueous and near-surface sorbed fractions, but the individual near-bed sorbed samples range from 130-2,900 ng/g for fluoranthene and from 120-2,500 ng/g for pyrene as shown in Table 4.3. A closer examination of the low tide near-bed aqueous fraction showed the total concentration of acenaphthene, fluorene, phenanthrene, fluoranthene, and pyrene was higher by a factor of 1.5 to 2.6 as compared to other tides. The high concentrations would indicate that these compounds have a source near the bed at low tide and their variability indicates that they either redeposit into the bed at other times in the tide or that they degrade rapidly once suspended in the water column. One study showed that when acenaphthene, fluorene, phenanthrene and pyrene are present together in the sediments, the biodegradation rate can triple vs. each compound alone (Yuan, Shiung, and Chang 2002), but was still on the order of days, not hours. Therefore, the variation is most likely due to settling and not degradation.

4.3.3 PCB Congeners

The concentrations for all PCB congeners in whole samples are shown in Table 4.5. The near-surface and near-bed whole water sample PCB concentrations for the tri, tetra, penta, hexa and hepta groups were similar, with more variation among groups nearer to the sediment bed. In the near-bed samples, the octa, nona and deca homolog

groups had concentrations that were on average an order of magnitude lower than the

other homolog groups, while the near-surface samples had no detectable concentrations

of these more chlorinated compounds.

Table 4.5 Concentrations of all PCB congeners in whole water samples near the sediment bed and near the surface at varying tides.

Whol	e Samj	ole (ng/L)	Near Sediment			Near Surface		
		High	Falling	Low	Rising	High	Falling	Rising
PCB	17	0.066 ± 0.019	0.071 ± 0.036	0.13 ± 0.011	0.11 ± 0.019	0.069 ± 0.030	0.057 ± 0.002	0.089
PCB	18	0.11 ± 0.022	0.15 ± 0.036	0.25 ± 0.027	0.18 ± 0.017	0.10 ± 0.024	0.13 ± 0.003	0.15
PCB	28	0.16 ± 0.063	0.21 ± 0.057	0.26 ± 0.051	0.23 ± 0.012	0.13 ± 0.034	0.12 ± 0.019	0.15
PCB	31	0.13 ± 0.054	0.16 ± 0.043	0.21 ± 0.044	0.17 ± 0.002	0.11 ± 0.037	0.097 ± 0.013	0.13
PCB	33	0.071 ± 0.032	0.092 ± 0.003	0.13 ± 0.025	0.11 ± 0.004	0.067 ± 0.022	0.046 ± 0.005	0.095
PCB	44	0.14 ± 0.059	0.19 ± 0.021	0.20 ± 0.051	0.22 ± 0.013	0.11 ± 0.032	0.10 ± 0.011	0.13
PCB	49	0.13 ± 0.056	0.18 ± 0.042	0.18 ± 0.057	0.19 ± 0.023	0.099 ± 0.021	0.090 ± 0.002	0.12
PCB	52	0.20 ± 0.087	0.27 ± 0.014	0.28 ± 0.066	0.29 ± 0.003	0.18 ± 0.034	0.15 ± 0.012	0.19
PCB	70	0.15 ± 0.079	0.21 ± 0.005	0.19 ± 0.058	0.22 ± 0.012	0.13 ± 0.040	0.089 ± 0.008	0.12
PCB	74	0.074 ± 0.035	0.10 ± 0.030	0.096 ± 0.032	0.099 ± 0.009	0.058 ± 0.017	0.047 ± 0.007	0.058
PCB	82	0.071 ± 0.031	0.082 ± 0.020	0.079 ± 0.029	0.078 ± 0.016	0.055 ± 0.006	0.038 ± 0.001	0.040
PCB	87	0.10 ± 0.049	0.14 ± 0.005	0.14 ± 0.035	0.14 ± 0.010	0.098 ± 0.026	0.068 ± 0.006	0.068
PCB	95	0.16 ± 0.079	0.22 ± 0.041	0.22 ± 0.070	0.21 ± 0.004	0.13 ± 0.029	0.11 ± 0.019	0.13
PCB	99	0.071 ± 0.036	0.092 ± 0.009	0.086 ± 0.029	0.094 ± 0.001	0.064 ± 0.018	0.042 ± 0.004	0.056
PCB	101	0.22 ± 0.12	0.31 ± 0.062	0.30 ± 0.11	0.29 ± 0.010	0.19 ± 0.050	0.13 ± 0.028	0.16
PCB	105	0.089 ± 0.039	0.12 ± 0.026	0.11 ± 0.041	0.11 ± 0.023	0.075 ± 0.026	0.055 ± 0.011	0.058
PCB	110	0.23 ± 0.11	0.31 ± 0.045	0.29 ± 0.11	0.29 ± 0.002	0.20 ± 0.056	0.14 ± 0.025	0.16
PCB	118	0.18 ± 0.097	0.25 ± 0.052	0.23 ± 0.089	0.23 ± 0.005	0.15 ± 0.045	0.098 ± 0.018	0.12
PCB	128	0.048 ± 0.039	0.053 ± 0.032	0.058 ± 0.028	0.047 ± 0.011	0.019 ± 0.009	0.011 ± 0.002	0.019
PCB	132	0.12 ± 0.061	0.16 ± 0.076	0.17 ± 0.073	0.13 ± 0.045	0.064 ± 0.015	0.058 ± 0.013	0.069
PCB	138	0.31 ± 0.18	0.43 ± 0.19	0.46 ± 0.19	0.34 ± 0.121	0.16 ± 0.055	0.15 ± 0.023	0.17
PCB	149	0.32 ± 0.18	0.41 ± 0.24	0.48 ± 0.23	0.36 ± 0.14	0.16 ± 0.038	0.15 ± 0.034	0.19
PCB	151	0.095 ± 0.055	0.13 ± 0.092	0.16 ± 0.078	0.11 ± 0.052	0.044 ± 0.009	0.045 ± 0.008	0.060
PCB	153	0.38 ± 0.220	0.49 ± 0.324	0.58 ± 0.29	0.41 ± 0.16	0.16 ± 0.037	0.17 ± 0.032	0.21
PCB	156	0.037 ± 0.028	0.050 ± 0.042	0.058 ± 0.029	0.043 ± 0.019	0.013 ± 0.005	0.010 ± 0.002	0.018
PCB	158	0.061 ± 0.031	0.076 ± 0.032	0.088 ± 0.037	0.071 ± 0.008	0.037 ± 0.006	0.032 ± 0.004	0.031
PCB	169	ND	ND	ND	ND	ND	ND	ND
PCB	170	0.47 ± 0.29	0.28 ± 0.13	0.67 ± 0.72	0.16 ± 0.23	0.20 ± 0.104	0.24 ± 0.184	0.091
PCB	171	ND	0.006 ± 0.008	0.037 ± 0.061	ND	ND	ND	ND
PCB	177	0.10 ± 0.077	0.14 ± 0.096	0.16 ± 0.054	0.12 ± 0.044	0.031 ± 0.007	0.037 ± 0.008	0.066
PCB	180	0.33 ± 0.25	0.48 ± 0.53	0.62 ± 0.28	0.34 ± 0.27	0.079 ± 0.030	0.12 ± 0.010	0.20
PCB	183	0.084 ± 0.070	0.11 ± 0.10	0.13 ± 0.071	0.098 ± 0.079	0.023 ± 0.005	0.033 ± 0.004	0.053
PCB	187	0.16 ± 0.11	0.21 ± 0.21	0.27 ± 0.13	0.16 ± 0.12	0.043 ± 0.011	0.057 ± 0.012	0.098
PCB	191	0.008 ± 0.014	0.008 ± 0.011	ND	0.014 ± 0.019	0.001 ± 0.001	0.005 ± 0.007	0.002
PCB	194	0.088 ± 0.077	0.10 ± 0.14	0.17 ± 0.15	0.11 ± 0.008	ND	ND	ND
PCB	195	ND	0.031 ± 0.044	0.074 ± 0.065	ND	ND	ND	ND
PCB	199	0.078 ± 0.068	0.11 ± 0.16	0.16 ± 0.062	0.094 ± 0.019	ND	ND	ND
PCB	205	ND	ND	0.066 ± 0.11	ND	ND	ND	ND
PCB	206	0.15 ± 0.11	0.053 ± 0.075	0.044 ± 0.077	0.11 ± 0.050	ND	ND	ND
PCB	208	0.029 ± 0.021	0.012 ± 0.017	0.011 ± 0.019	0.005 ± 0.007	ND	ND	ND
PCB	209	0.042 ± 0.009	0.031 ± 0.044	0.038 ± 0.035	0.030 ± 0.028	ND	ND	ND
ΣΡCΒ	s	5.2 ± 2.6	6.5 ± 3.1	7.9 ± 3.4	6.0 ± 1.4	3.0 ± 0.67	2.7 ± 0.064	3.3

The aqueous fraction of the near-surface samples had concentrations of tri, tetra, penta and hexa-PCBs ranging from 0.26-0.68 ng/L, and hepta, octa, nona and deca concentrations were below detection limits, except for the sample corresponding to rising tide, which had five of the seven hepta-PCB congeners present in detectable concentrations. In every aqueous sample, the sum of total PCBs was above the water quality standard of 0.016 ng/L set by the DRBC (2014). The sorbed fraction of the nearsurface samples showed increasing concentrations from tri- through hepta-PCB at all times during the tide, but still the octa, nona, and deca homolog concentrations were not detected. In the near-bed aqueous fraction, the concentrations of tri, tetra, penta and hexa-PCBs were similar the near-surface concentrations, except for the rising tide, which has higher concentrations near the bed. Additionally, hepta-PCB concentrations were detected at all tides near the bed (as opposed to only during the rising tide near the surface), and octa, nona and deca concentrations were detected at high tide only, albeit at concentrations near the detection limit (>0.1 ng/L). Similar to the aqueous fraction, the sorbed fraction had comparable concentrations of tri through hepta homologs through the water column. For the tri and tetra groups, average values were between 9.2 and 16 ng/g, while the penta, hexa and hepta groups ranged from 31 to 49 ng/g throughout the water column. This is contrasted by the octa, nona and deca-PCBs, which were not detected near the surface, but had an average concentration of 12 ng/g, 3.0 ng/g and 1.4 ng/g, respectively near the sediment bed.

Wate	r Fract	ion (ng/L)	Near Se	diment		Ne	ar Surface	
		High	Falling	Low	Rising	High	Falling	Rising
PCB	17	0.050 ± 0.0092	0.048 ± 0.0091	0.091 ± 0.012	0.091 ± 0.026	0.062 ± 0.030	0.052 ± 0.0001	0.079
PCB	18	0.088 ± 0.012	0.11 ± 0.0006	0.19 ± 0.013	0.15 ± 0.025	0.091 ± 0.023	0.12 ± 0.0013	0.13
PCB	28	0.096 ± 0.026	0.13 ± 0.031	0.14 ± 0.017	0.16 ± 0.023	0.11 ± 0.043	0.094 ± 0.016	0.11
PCB	31	0.079 ± 0.023	0.10 ± 0.024	0.12 ± 0.020	0.13 ± 0.017	0.093 ± 0.046	0.078 ± 0.0091	0.10
PCB	33	0.046 ± 0.017	0.066 ± 0.033	0.074 ± 0.017	0.082 ± 0.013	0.056 ± 0.028	0.041 ± 0.0052	0.062
PCB	44	0.080 ± 0.027	0.11 ± 0.044	0.093 ± 0.015	0.13 ± 0.022	0.088 ± 0.035	0.080 ± 0.012	0.094
PCB	49	0.073 ± 0.021	0.094 ± 0.034	0.079 ± 0.011	0.11 ± 0.012	0.075 ± 0.024	0.068 ± 0.0038	0.085
PCB	52	0.12 ± 0.040	0.16 ± 0.077	0.14 ± 0.020	0.20 ± 0.040	0.14 ± 0.052	0.12 ± 0.012	0.15
PCB	70	0.077 ± 0.031	0.11 ± 0.075	0.074 ± 0.017	0.13 ± 0.043	0.099 ± 0.051	0.065 ± 0.0085	0.079
PCB	74	0.035 ± 0.013	0.050 ± 0.024	0.034 ± 0.009	0.058 ± 0.012	0.043 ± 0.022	0.031 ± 0.0007	0.039
PCB	82	0.020 ± 0.0085	0.028 ± 0.013	0.020 ± 0.012	0.031 ± 0.002	0.030 ± 0.009	0.016 ± 0.0032	0.015
PCB	87	0.049 ± 0.019	0.072 ± 0.046	0.048 ± 0.014	0.086 ± 0.030	0.073 ± 0.036	0.040 ± 0.0074	0.043
PCB	95	0.079 ± 0.029	0.10 ± 0.046	0.083 ± 0.015	0.13 ± 0.031	0.098 ± 0.043	0.076 ± 0.0140	0.085
PCB	99	0.035 ± 0.015	0.043 ± 0.026	0.030 ± 0.008	0.056 ± 0.016	0.045 ± 0.022	0.028 ± 0.0022	0.033
PCB	101	0.099 ± 0.041	0.14 ± 0.078	0.097 ± 0.026	0.17 ± 0.044	0.14 ± 0.066	0.087 ± 0.019	0.096
PCB	105	0.035 ± 0.011	0.046 ± 0.030	0.028 ± 0.009	0.057 ± 0.004	0.049 ± 0.027	0.029 ± 0.0056	0.032
PCB	110	0.107 ± 0.037	0.14 ± 0.085	0.099 ± 0.027	0.17 ± 0.045	0.14 ± 0.069	0.094 ± 0.016	0.098
PCB	118	0.076 ± 0.033	0.11 ± 0.070	0.069 ± 0.021	0.13 ± 0.038	0.11 ± 0.056	0.062 ± 0.012	0.069
PCB	128	0.010 ± 0.011	0.009 ± 0.0065	0.009 ± 0.004	0.020 ± 0.005	0.010 ± 0.009	0.002 ± 0.0023	0.010
PCB	132	0.035 ± 0.011	0.052 ± 0.020	0.036 ± 0.014	0.056 ± 0.003	0.038 ± 0.018	0.026 ± 0.0058	0.033
PCB	138	0.083 ± 0.041	0.12 ± 0.071	0.085 ± 0.031	0.13 ± 0.007	0.086 ± 0.041	0.063 ± 0.012	0.070
PCB	149	0.092 ± 0.035	0.12 ± 0.039	0.095 ± 0.035	0.14 ± 0.007	0.095 ± 0.042	0.072 ± 0.017	0.088
PCB	151	0.028 ± 0.012	0.035 ± 0.0021	0.031 ± 0.013	0.041 ± 0.008	0.026 ± 0.009	0.019 ± 0.0031	0.026
PCB	153	0.099 ± 0.040	0.12 ± 0.042	0.095 ± 0.043	0.14 ± 0.007	0.085 ± 0.038	0.068 ± 0.013	0.087
PCB	156	0.003 ± 0.0056	0.005 ± 0.0069	0.004 ± 0.006	0.012 ± 0.001	0.006 ± 0.005	ND	0.007
PCB	158	0.019 ± 0.0035	0.026 ± 0.0085	0.015 ± 0.005	0.030 ± 0.007	0.023 ± 0.006	0.012 ± 0.0005	0.013
PCB	169	ND	ND	ND	ND	ND	ND	ND
PCB	170	ND	ND	ND	0.031 + 0.043	ND	ND	0.024
PCB	171	ND	ND	ND	ND	ND	ND	ND
PCB	177	ND	ND	0.005 +, 0.009	0.016 + 0.022	ND	ND	0.031
PCB	180	0.027 + 0.047	0.051 + 0.072	0.014 + 0.025	0.053 + 0.074	ND	ND	0.071
PCB	183	0.004 + 0.0078	0.007 + 0.010	0.005 +, 0.009	0.013 + 0.019	ND	ND	0.021
PCB	187	0.011 + 0.018	0.016 + 0.022	0.009 +,0.016	0.023 + 0.033	ND	ND	0.033
PCB	191	ND	ND	ND	ND	ND	ND	ND
PCB	194	ND	ND	ND	ND	ND	ND	ND
PCB	195	ND	ND	ND	ND	ND	ND	ND
PCB	199	0.012 + 0.0207	ND	ND	ND	ND	ND	ND
PCB	205	ND	ND	ND	ND	ND	ND	ND
PCB	206	0.093 + 0.1617	ND	ND	ND	ND	ND	ND
PCB	208	0.018 + 0.0305	ND	ND	ND	ND	ND	ND
PCB	209	0.012 + 0.0201	ND	ND	ND	ND	ND	ND
ΣΡCΒ	s	1.8 + 0.53	2.2 + 0.82	1.9 + 0.42	2.8 + 0.24	1.9 + 0.84	1.4 + 0.14	1.9

Table 4.6 Concentrations of all PCB congeners in aqueous fraction near the sediment bed and near the surface at varying tides.

TSS F	TSS Fraction(ng/g) Near Sediment			ediment		Ne	ar Surface	
		High	Falling	Low	Rising	High	Falling	Rising
PCB	17	0.73 ± 0.49	1.2 ± 1.4	1.5 ± 0.58	0.61 ± 0.16	0.94 ± 0.82	0.64 ± 0.22	0.55
PCB	18	1.1 ± 0.52	2.0 ± 1.9	2.6 ± 1.5	0.93 ± 0.21	1.5 ± 1.1	1.3 ± 0.18	1.1
PCB	28	3.0 ± 1.8	4.3 ± 4.7	4.8 ± 2.5	1.8 ± 0.89	3.4 ± 1.8	2.8 ± 0.34	1.8
PCB	31	2.4 ± 1.5	3.1 ± 3.6	3.5 ± 2.0	1.2 ± 0.50	2.8 ± 2.1	2.3 ± 0.43	1.3
PCB	33	1.2 ± 0.68	1.4 ± 1.6	2.0 ± 1.1	0.69 ± 0.23	1.5 ± 0.91	0.63 ± 0.02	1.8
PCB	44	2.6 ± 1.6	4.2 ± 3.5	4.4 ± 2.6	2.2 ± 0.92	3.8 ± 1.5	2.6 ± 0.20	1.8
PCB	49	2.7 ± 1.6	4.5 ± 4.1	4.3 ± 2.6	1.9 ± 0.91	3.4 ± 1.1	2.5 ± 0.16	2.2
PCB	52	3.7 ± 2.3	5.6 ± 4.8	5.9 ± 3.4	2.3 ± 0.96	5.1 ± 2.9	3.3 ± 0.05	2.5
PCB	70	3.4 ± 2.3	5.1 ± 4.2	5.0 ± 3.0	2.1 ± 0.80	4.5 ± 1.6	2.9 ± 0.01	2.2
PCB	74	1.8 ± 1.1	2.7 ± 2.9	2.7 ± 1.7	1.1 ± 0.56	2.1 ± 0.66	1.8 ± 0.76	1.1
PCB	82	2.4 ± 1.2	2.9 ± 1.8	2.5 ± 1.1	1.2 ± 0.47	3.6 ± 1.2	2.6 ± 0.23	1.3
PCB	87	2.4 ± 1.4	3.7 ± 2.2	3.5 ± 1.7	1.4 ± 0.53	3.6 ± 1.6	3.2 ± 0.18	1.4
PCB	95	3.7 ± 2.5	6.0 ± 4.6	5.8 ± 3.3	2.1 ± 0.92	4.8 ± 2.1	3.5 ± 0.56	2.2
PCB	99	1.7 ± 1.1	2.6 ± 1.9	2.3 ± 1.4	0.98 ± 0.40	2.7 ± 0.53	1.7 ± 0.22	1.2
PCB	101	5.5 ± 3.8	8.8 ± 7.4	8.7 ± 5.3	3.2 ± 1.4	7.1 ± 2.7	5.1 ± 1.1	3.5
PCB	105	2.5 ± 1.3	3.8 ± 2.9	3.3 ± 2.0	1.4 ± 0.70	3.8 ± 0.84	3.0 ± 0.68	1.4
PCB	110	5.7 ± 3.7	8.7 ± 6.9	8.1 ± 4.9	3.2 ± 1.2	7.6 ± 2.4	5.3 ± 1.1	3.5
PCB	118	4.7 ± 3.1	7.4 ± 6.5	6.7 ± 4.1	2.5 ± 1.1	5.8 ± 1.8	4.2 ± 0.80	2.8
PCB	128	1.8 ± 1.4	2.4 ± 2.0	2.1 ± 1.2	0.70 ± 0.42	1.4 ± 0.89	1.1 ± 0.07	0.51
PCB	132	3.8 ± 2.4	5.6 ± 5.1	5.8 ± 3.2	2.0 ± 1.3	3.8 ± 0.71	3.7 ± 0.88	2.0
PCB	138	11 ± 6.9	16 ± 14	17 ± 8.1	5.6 ± 3.0	11 ± 3.6	9.7 ± 1.3	5.5
PCB	149	11 ± 6.8	16 ± 15	17 ± 10	5.7 ± 3.4	9.4 ± 2.6	9.1 ± 2.0	5.6
PCB	151	3.2 ± 2.1	5.0 ± 5.0	5.8 ± 3.4	1.8 ± 1.1	2.6 ± 0.83	3.0 ± 0.57	1.9
PCB	153	13 ± 8.6	20 ± 19	21 ± 12	6.9 ± 4.1	11 ± 3.4	11 ± 2.3	6.9
PCB	156	1.6 ± 1.2	2.4 ± 2.6	2.3 ± 1.5	0.80 ± 0.46	0.92 ± 0.81	1.2 ± 0.23	0.56
PCB	158	1.9 ± 1.3	2.7 ± 2.2	3.2 ± 1.7	1.1 ± 0.39	2.1 ± 0.43	2.2 ± 0.41	1.0
PCB	169	ND	ND	ND	ND	ND	ND	ND
PCB	170	22 ± 14	15 ± 6.7	30 ± 33	3.4 ± 4.8	29 ± 15	28 ± 22	3.7
PCB	171	ND	0.3 ± 0.4	1.7 ± 2.8	ND	ND	ND	ND
PCB	177	4.7 ± 3.6	7.2 ± 5.1	6.9 ± 2.7	2.6 ± 0.57	4.5 ± 0.97	4.4 ± 0.95	1.9
PCB	180	14 ± 11	23 ± 25	27 ± 13	7.6 ± 5.1	11 ± 4.3	14 ± 1.2	7.0
PCB	183	3.8 ± 3.0	5.3 ± 4.8	5.4 ± 3.5	2.2 ± 1.6	3.4 ± 0.70	3.9 ± 0.46	1.8
PCB	187	6.9 ± 4.8	10 ± 10	12 ± 6.1	3.5 ± 2.3	6.2 ± 1.6	6.7 ± 1.4	3.6
PCB	191	0.39 ± 0.67	0.4 ± 0.6	ND	0.35 ± 0.50	0.11 ± 0.19	0.57 ± 0.81	0.14
PCB	194	4.2 ± 3.6	5.4 ± 7.7	7.6 ± 6.9	2.8 ± 0.20	ND	ND	ND
PCB	195	ND	1.7 ± 2.4	3.3 ± 3.0	ND	ND	ND	ND
PCB	199	3.1 ± 2.9	6.0 ± 8.5	7.4 ± 2.8	2.4 ± 0.49	ND	ND	ND
PCB	205	ND	ND	3.0 + 5.2	ND	ND	ND	ND
PCB	206	2.6 ± 2.3	2.8 ± 4.0	2.0 ± 3.5	2.8 ± 1.3	ND	ND	ND
PCB	208	0.52 ± 0.46	0.6 ± 0.9	0.5 ± 0.88	0.14 ± 0.19	ND	ND	ND
PCB	209	1.4 ± 1.3	1.6 ± 2.3	1.7 ± 1.6	0.79 ± 0.73	ND	ND	ND
ΣΡСΒ	s	161 ± 106	227 ± 210	260 ± 158	84 ± 42	164 ± 31	147 ± 8.8	76

Table 4.7 Concentrations of all PCB congeners in sorbed fraction near the sediment bed and near the surface at varying tides.

In summary, both classes of compounds showed variation of certain compounds. Near the bed, larger PAHs (>4-ring) fluctuate the most and 2,3-ring compounds showed less variation among samples taken at the same tide. This variation can be explained as variation due the lengthy sampling times described above. Near the surface, the PAH variation between samples was minimal, but the penta-, hexa-, and hepta-PCBs fluctuated both near the surface and near the bed. The exception to this was the rising tide near bed, for which the penta-, hexa-, and hepta-PCBs did not vary as much as at other tides. In terms of individual compounds, the biggest contributors to total PAH concentration in this stream were three low molecular weight compounds (phenanthrene, fluoranthene, and pyrene). The largest individual contributors to PCB concentrations were PCB 101, 138, 149, 153, 170 and 180.

4.3.4 Tidal Variation

The concentrations of 4-, 5- and 6- ring PAHs in the whole water samples (comprised of the aqueous and sorbed fractions together) were relatively stable in the near-surface samples across the tide (Figure 4.3), ranging from 31-58 ng/L, 15-25 ng/L and 7.5-12 ng/L, respectively. The 2- and 3-ring PAH concentrations in the near-surface samples showed more variation with the tide (33.9-104 ng/L) than the other groups, with a threefold increase in the concentration at the high tide over the rising tide. In the near-bed samples, 2- and 3-ring PAHs range from 29-130 ng/L, the 4-ring PAHs range from 29-220 ng/L, 5-ring from 15-120 ng/L and 6-ring from 7.7-63 ng/L. All ring groups in the whole samples show a similar pattern during the course of the tides, with the 4-ring, followed by 2-, 3- and 5- ring and lastly, 6-ring as the lowest concentration in near-bed samples. The trend was similar near the surface during rising tide, but during the high and falling tide, the 2- and 3-ring PAHs were present in higher concentrations than the 4-ring PAHs.



Figure 4.3 Concentration of PAHs in whole water samples taken from the Tacony-Frankford Creek.

In the water fraction, most of the variability in the data was seen in the 2- and 3ring group, owing to the phenanthrene. Figure 4.5 shows a comparison of the total PAH concentrations near the bed and near the surface with and without phenanthrene. When phenanthrene is removed, the tidal effects diminish as well as much of the variation with depth. The near-bed samples ranged from 21-110 ng/L and the near-surface samples ranged from 30-90 ng/L for 2- and 3-ring PAHs. The 4-ring group had slightly less variability, ranging from 20-56 ng/L near the bed and 21-38 ng/L near the surface. The 5and 6-ring PAH groups were relatively stable with 6.5-15 ng/L and 2.9-6.2 ng/L, respectively near the bed and 4.7-7.8 ng/L and 2.9-3.7 ng/L, respectively near the surface. Figure 4.4 shows that the 5- and 6-ring compounds were stable in both the near-surface and near-sediment samples with the 2-, 3- and 4-ring compounds showing the most variation over the course of the tide. Near the bed, the aqueous concentrations of 2-, 3-, and 4-ring PAHs increased as the tide went out and decreased as the tide came back. An increasing trend was also seen in the 4-ring compounds near the surface as the tide went from high to falling to rising, but the opposite was true for the 2- and 3-ring compounds, which decreased during the same time. Within the specific 2- and 3-ring PAH group, the near-surface concentration found in the aqueous fraction at high tide was higher than at any other time in the tide. Furthermore, this concentration was surpassed only by the 2and 3-ring concentration found in the near-bed samples at low tide (Figure 4.4a). The 2-, 3- and 4-ring PAH near-bed concentrations show a decreasing trend as the tide goes out, peaking at low tide and decreasing again as the tide rises. In the near-surface water samples, the 4-ring PAH concentration follows the same increasing trend as tide goes out, but the 2- and 3-ring group has the opposite trend (Figure 4.4b). Both the near-surface

and near-bed concentrations of 5- and 6-ring PAHs in the aqueous fraction were relatively low and stable when compared to the rest of the congeners.



Figure 4.4 Concentration of PAHs in aqueous fraction of samples taken from the Tacony-Frankford Creek



Figure 4.5 The sum of PAHs at various tides including and excluding phenanthrene in aqueous samples.

The near-surface and near-bed sorbed fraction samples showed divergent behavior, as shown in Figure 4.6. In the sorbed fraction samples near the surface, all compounds decreased in concentration as the tide went from high to falling to rising. Near the streambed, however, all compound groups had low concentrations at the rising tide and increased with the high and falling tide before decreasing slightly at the low tide. The sorbed fraction near-bed samples show much more variation over the tides than the water samples do. The near-bed samples range from 64-1,600 ng/g for 2- and 3-ring, from 420-9,000 ng/g for 4-ring, from 38-5,800 ng/g for 5-ring and from 200-3,100 ng/g for 6-ring. Likewise, the near-surface samples vary from 240-8,900 ng/g for 2- and 3-ring, but the 4-, 5- and 6-ring groups have much less variation, with 1,100-2,000 ng/g, 950-1,400 ng/g and 490-830 ng/g, respectively.



Figure 4.6 Concentration of PAHs on sorbed fraction of samples taken from the Tacony-Frankford Creek.

The whole water PCBs, as seen in Figure 4.7, showed less tidal variation than the PAHs both near the surface and near the sediment bed. Near the bed, there a considerable amount of variability in the individual samples taken at each point in the tide, but the

overall concentration of PCBs did not show much variation over the course of the tide. The whole water samples near the bed showed a slight overall trend of increasing PCB concentration as tide fell, peaking at low tide, and decreasing concentration with the rising tide. This closely resembled the trend seen in the sorbed fraction concentrations (Figure 4.8).

The Σ PCBs concentrations in near-bed whole water samples (Figure 4.7b) were $6.0 \pm 1.4 \text{ ng/L}$, $5.2\pm 2.6 \text{ ng/L}$, $6.5\pm 3.1 \text{ ng/L}$, and $7.9\pm 3.4 \text{ ng/L}$ during the rising, high, falling and low tides, respectively. Similarly, the $\Sigma PCBs$ concentrations on the near-bed sorbed fraction (Figure 4.8b) were $84\pm42 \text{ ng/g}$, $161\pm106 \text{ ng/g}$, $227\pm210 \text{ ng/g}$ and 260 ± 158 ng/g during the rising, high, falling and low tides, respectively. However, the near surface whole water samples exhibited the opposite trend with PCB concentration being elevated at rising and high tides, and lower with the falling tide. This trend was again seemingly driven by the sorbed fraction, but was evidenced to a much smaller extent in the aqueous fraction as well. The Σ PCBs concentrations in near-surface whole water samples (Figure 4.7a) were 3.3 ng/L and 3.0±0.67 ng/L, respectively at the rising and high tide and 2.7 ± 0.064 ng/L at falling tide. Similarly, the $\Sigma PCBs$ concentrations on the near-surface sorbed fraction (Figure 4.8a) were 76 ng/g and 164 ± 31 ng/g at rising and high tide, respectively, and 147±8.8 ng/g during the falling tide. The majority of the tidal variation in the sorbed and aqueous fractions (Figure 4.8 and Figure 4.9) occurs in the trithrough octa-PCB groups, regardless of position in the water column, with the exception of the nona-PCB group in the near-bed aqueous fraction that was much higher at high tide than at any other time in the cycle.



Figure 4.7 Concentration of PCBs in whole water samples taken from the Tacony-Frankford Creek.



Figure 4.8 Concentration of PCBs in sorbed fraction of samples taken from Tacony-Frankford Creek.



Figure 4.9 Concentration of PCBs in aqueous fraction of samples taken from Tacony-Frankford Creek.

As the tide goes out, the PCB concentration near the bed increases, peaking at low tide, and then decreases as the tide comes back in from the Delaware. Conversely, near the surface, the sum PCBs decreases as the tide falls and increases when the tide comes back in from the Delaware. It does not appear that this is due to resuspension of sediments from the sediment bed, because the concentration of PCBs sorbed to sediments is much higher near the surface than near the bed at high and falling tides. The water velocity is greatest near the surface, so instead it could point to particles advancing into the stream carried with the faster moving water near the surface in the middle of the channel, rather than being distributed up though the column. This could be evidence of Delaware water adding PCBs to Tacony, which then sink to the bottom when the tides shift and do not make their way back out to the Delaware. This theory is supported by the similarity of this study's homolog signature to that of PCBs in sediment samples on the Delaware near Philadelphia taken by the DRBC (2014). In both sets of data, the tetra through hepta homolog groups comprise the largest portion of the sum of PCBs sorbed to sediments.

Assuming the rising and falling concentrations are representative of each tidal cycle, the average flow measured at the upstream USGS gage (1.2 m³/s) can be used to derive a very rough estimate of flux for PAHs and PCB. The estimation indicates that based on tidal cycling only, the Tacony-Frankford Creek is a source of PAHs to the Delaware, adding approximately 0.07 kg/year and a sink for PCBs, receiving approximately 0.005 kg/year. These limitations of this type of estimate is that is based on a single set of tidal measurements, includes only the PCB and PAH compounds present in the water column, whether in the dissolved phase or sorbed to suspended sediments, and does not take into account any air/water interactions. More importantly, these fluxes represent typical dry-weather conditions. Under wet-weather flow, there is likely a large efflux of both classes of compounds out of the creek and into the river. A report on PCB loading to the Delaware lists Tacony-Frankford as a source of PCBs at loading of 0.12 kg/yr. but the study did not consider the tidal nature of this stream (Yagecic, J. et al.

2003). The USGS gauge used to derive these values is well upstream of the tidal range and only downstream flow was considered.

4.3.5 Fractions

The sum of PAHs in the whole samples ranged from 120-150 ng/L near the surface and 230-370 ng/L near the bed. The water fraction was much less variable (74-160 ng/L) across all samples than the sorbed fraction (2,800-11,000 ng/g). On a whole water basis, reported in ng/L (see Figure 4.7), the fraction of PAHs in the dissolved fraction was much higher than the sorbed fraction for 2- and 3-ring PAHs, on the order of 200%-700% and 200%-400% higher, near the surface and bed, respectively. The 4-ring PAH concentration in water was approximately 200% higher in near-surface samples, but 30%-60% lower in the near-bed samples, when compared to the sorbed fraction. For both 5- and 6-ring PAHs, the sorbed fraction dominated, being nearly 200% higher than the dissolved fraction near the surface and from 400%-800% the dissolved fraction near the surface whole sample concentration for 4-, 5- and 6-ring groups, while near the surface whole sample concentrations were slightly more equally distributed, but still showed differences between 2-, 3- and 4-ring groups and 5- and 6-ring PAH groups.

As expected, the mass of TSS per volume of water in the near-bed samples was much higher than in the near-surface samples (Table 4.8). Overall, the 4-, 5- and 6-ring PAH concentrations were higher in the suspended sediments near streambed on a per gram basis (Table 4.4) when compared to the suspended solids near the surface. The near-surface sorbed samples had higher concentrations of 2- and 3-ring PAHs, while the near-sediment sorbed samples had much higher concentrations of 4-, 5- and 6-ring PAHs, except during the rising tide (Figure 4.6). At the rising tide, the 5- and 6-ring PAH concentrations in the sorbed fraction were found to be the same for both the near-bed and near-surface samples, but for the 2-, 3- and 4-ring PAHs, the near-surface sample concentration was half to three-quarters of the near-bed concentration. For the 2- and 3- ring PAHs, the opposite pattern was evident at the high and falling tides, with the near-surface concentration found to be 8.7 and 1.6 times higher than near the bed, respectively.

	Near-Surface	Near-Bed
	(mg/L)	(mg/L)
High Tide	6.98	21.27
Mid-Falling Tide	8.54	18.81
Low Tide		22.04
Mid-Rising Tide	18.35	38.50

Table 4.8 Concentration of total suspended solids (TSS) over the course of a tide in the Tacony-Frankford Creek.

In the near-surface water fraction, the tri through hexa PCB homolog groups are predominant, with concentrations of each group ranging from 0.26 to 0.68 ng/L. The only the near-surface sample to have hepta-PCB is the rising tide sample at 0.18 ng/L. This more closely resembles the near-bed samples, which had tri through hepta groups present during the all tides in concentrations ranging from 0.03 to 0.83 ng/L. During the high tide, all homolog groups (tri through deca) were present in the near-bed samples, although the lower weight homolog groups, tri through hexa, still dominate the total aqueous concentration.

In the sorbed fraction, tri through hepta-PCBs are present in all samples taken near the surface and bed. The near-bed samples also have concentrations of octa through deca PCBs, though in much lower concentrations than the other homolog groups. The near surface samples range from 6.6 to 10 ng/L for the tri-PCBs up to 18 to 57 ng/L for hepta-PCBs. Near the bed, the PCB concentrations are higher, ranging from 5.2 to 14 ng/L for the tri-PCBs and from 20 to 83 ng/L for hexa-PCBs. At both depths, the penta, hexa and hepta homolog groups dominate the PCBs on the sorbed fraction. The octa through deca groups are absent in the near-surface sorbed samples and detected in much smaller concentrations than other groups (except tri) on the near-bed samples.

The sorbed Σ PCB concentration was about 65% of the whole water Σ PCB concentration near the bed and 42% near the surface. However, the near-surface whole water samples show less variation among homolog groups and varying tides than either the aqueous or sorbed samples, with concentrations of tri through hepta groups range from 0.45 to 0.95 ng/L for all tides. The near-bed samples also exhibit little variation with tide, with each individual homolog group having no statistical deviation over the course of the tide. The near-bed samples do show some variability with homolog group though, with penta, hexa and hepta groups highest at concentrations ranging from 1.1 to 2.0 ng/L, followed closely by the tri and tetra groups ranging from 0.54 to 1.0 ng/L and the lowest concentrations in the octa to deca group at 0.02 to 0.47 ng/L.

As shown in Table 4.1, the dissolved organic carbon (DOC) concentration was constant for all tides and depths $(2.4 \pm 0.1 \text{ mg/L})$. Due to the lack of DOC variation, high concentrations of PAH compounds on the sorbed fraction of the near-surface samples might indicate either deposition of particles rich in these compounds to the top of the

stream, or possible degradation of these compounds in the streambed. The proximity of heavily traveled roadways near the sampling site could point to the deposition of particles as the more likely candidate for PAHs, but the higher concentration of 4-ring compounds as opposed to 5- and 6-ring compounds could point to degradation or aging of the PAHs before or after deposition in the stream. For most of the samples, the sorbed fraction of PAHs largely determines the water column concentration at a given location and tide. As stated previously, the near-surface sorbed fraction samples have a lower relative concentration of 4-, 5- and 6- ring PAHs, which contributes to the lower overall water column concentration found near the surface. At low tide, the concentration of DOC near bed is lowest of all tides, but both PAH and PCB concentrations are highest in whole water and highest (PCB) and second highest (PAH) in sorbed fraction. The sediment concentration is also lowest at low tide, so perhaps only small particles with relatively large surface area to volume ratios and high concentrations of organics sorbed to them are present.

A comparison of water-suspended sediment partitioning coefficients (K_D) for each sample and location is presented in Figure 4.10. These graphs show an almost linear relationship for PCB partitioning to sediments (log K_D) compared to PCB partitioning to octanol (log K_{OW}). It is important to note that only the tri- through hexa-PCBs were used to determine log K_D because they were present above detection limits in both fractions of the samples this study. For PAHs, the plot of log K_D vs. log K_{OW} exhibits a leveling off trend toward the higher molecular weight compounds. This can be explained by the fact that their larger ring structures inhibit the sorption of these compounds in the macropores of sediments. Therefore, even with their high hydrophobicity, their ability to partition to



Figure 4.10 Comparison of partitioning coefficients for sediments in Tacony-Frankford Creek to octanol-water coefficients for a.) PAHs and b.) PCBs.

the sorbed phase is inhibited relative to their ability to partition into an organic solvent like octanol.

4.4 Discussion

Overall, there are two aspects of this study – one is the variation of HOC concentrations with depth, and the other is the variation of concentrations with tidal cycle. For the PAHs, both depth and tide impact the concentration, but the depth in water column is more influential parameter than tidal timing when considering sampling methodology. There are tidal effects for PAHs, but removal of phenanthrene eliminates much of the variation with tide. Even after eliminating phenanthrene, low tide still has a much different distribution of PAHs than at other tides. The most abundant compounds in the low tide samples are biodegradable (Verrhiest et al. 2002; Heitkamp, Franklin, and Cerniglia 1988) so the spike in concentration can be partially attributed to underlying sediments that have not been exposed to degradation being stirred up through the water column. Tide does not appear to greatly impact the PCB partitioning between the suspended sediments and the water phase in this stream, likely due to the fact that PCBs are an historic pollution that is not currently being generated in large quantities and released to the environment. The effects of depth on PCB concentration are present but much less pronounced, especially in the water fraction.

The tidal influence on both classes of compounds showed some similarities. The rising tide had the lowest normalized concentrations of both PAH and PCB on the suspended matter, so it is possible that either the sediments were cleaner overall or that the individual particles were larger. A possible reason for this is that the incoming tide suspends throughout the water column larger particles that have lower normalized

concentrations and those particles re-deposit during the high and falling tides. The hydrodynamic forces present during the ebb and flow of the tide can expose sediment as well as pore water and the tides in this stream seem to act to cycle the HOCs between the two phases, creating concentrations that are in a constant state of flux between the water and sediment phases. The overall effect of tides in this urban stream is that the HOC concentration in the water column is in a constant state of flux and does not come to equilibrium with the sediment concentration.

Sampling depth is also important for analysis in tidal systems, as the chemical analysis can fluctuate greatly due to physical variations in the stream. In a tidal system, the rising tide represents a different regime from the largely one-directional flow of inland streams. Since most of the PAH and PCB concentration in a whole water sample is associated with suspended matter, the stagnation and reversal of flow has a large impact on the size of particles and compounds that are transported within the stream. Depth of sample has large effect on PAH concentration in the whole water samples, which was mostly due to the contribution of the sorbed fraction. Once again, removal of phenanthrene eliminates the variation with depth in aqueous samples, but has almost no effect on the sorbed fraction. PCB concentrations are much higher near the bed for the whole water and sorbed fraction, but dissolved concentrations show no appreciable difference with depth. No one PCB congener was the obvious source of any variation as all congeners had been present in the system with no known source for decades. Individual compounds from both classes can vary in similar samples, depending on small differences in sample location, tidal influence and micro eddies. Near-bed sampling is

even more variable than near-surface sampling due to bed perturbations caused by fish and tidal fluctuations.

The final take-home message of this study is that smaller urban tidal streams can be more complex systems with unique concerns (relating to planning and design, sampling, and fate and transport of pollutants) when compared to inland streams. Even in a well-mixed system such as a tidal stream in an urban area that is prone to flooding events that scour the sediment bed, the concentration of organics can vary with depth and fluctuate over the course of a tide. Depending on the source and level of contamination, pollutants can be rapidly redistributed between the different phases during transport downstream. Compounds that are weakly sorbed (via physisorption) or that have lower hydrophobicity can be redistributed, but strongly sorbed, highly hydrophobic compounds can not because their rates of desorption are so low. Due to this, much care must be taken to ensure that the samples taken are representative for the study design. If the experiment seeks to determine the concentrations of organics that bottom feeding fish are exposed to, then grab samples near the surface would tend to under estimate the concentration and variability of PAHs and PCBs in the water. Likewise, if the study objective is to determine the average concentration of PAHs and PCBs in the water column of a tidal stream, then care should be taken to collect grab samples at different times in the tidal cycle or use of passive sampling techniques should be considered.
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Chapter 5: Application of Polyoxymethylene Film to Monitor Small Urban Streams

Abstract

Small and tide-influenced streams can be a challenge to sample because they are highly dynamic systems that can exhibit a high degree of variability. In addition, inputs to the system are not as readily diluted as inputs to larger rivers. Polyoxymethylene (POM) was investigated as a material that could be used to collect passive samples in small aquatic systems. In the laboratory, 76 μ m thick POM sheets exhibited fast sorption, coming to equilibrium with aqueous-phase phenanthrene within 2 weeks at 23°C and 5 weeks at 4°C. Partitioning coefficients log(K_{POM}) were developed for 16 PAHs and 41 PCBs and ranged from 3.1 to 6.4, and 4.1 to 6.1, respectively. The log(K_{POM}) values were used with collected POM concentrations to predict PAH and PCB concentrations in the aqueous phase of the Tacony-Frankford Creek in Philadelphia, PA and were found to underpredict the aqueous phase for most compounds. Correlations between POM films and sediments and biota were not very strong, except for samples of white sucker fish and catfish livers.

5.1 Introduction

The first two chapters of this work demonstrate the large degree of variability in concentrations of hydrophobic organic contaminants (HOCs) that exists in small urban streams. The timing and location of the sampling can impact the results and either underor over-predict the longer-term average concentration of a pollutant in the system. In addition, the processing and analysis times can make the cost of collecting multiple samples prohibitive to local government and organizations concerned with the health of small streams. One way to reduce the variability of single point sampling and processing time for whole water analysis is to use passive sampling techniques. Passive samplers are useful because they are not disruptive and non-degrading to the environment. In addition, a passive sampler that requires time to attain equilibrium is less likely to show short-term variability. Therefore, they can provide a better assessment of the long-term exposure of aquatic organisms to HOCs.

In recent years, there has been interest in finding different materials that are suitable for passive sampling of environmental media (Muijs and Jonker 2012; Monteyne, Roose, and Janssen 2013; Lohmann et al. 2012). Polyoxymethylene (POM), also called polyacetyl, is a polymer that has been used for years as a replacement for metal in industrial applications and is available in various shapes and thicknesses (Herbst and Hunger 2006). POM films have been used in aqueous systems in order to determine the presence of and to quantify hydrophobic organic compounds (Beckingham and Ghosh 2013; Hawthorne et al. 2011; Hong and Luthy 2008). Laboratory studies have been published using POM films to determine various organic compound concentrations in water (Hawthorne, Miller, and Grabanski 2009). There are also a number of studies that have used POM films in the environment to measure organic compounds in both water column and sediment pore water of estuaries (Jonker and Koelmans 2001).

The objective of this chapter was to assess the applicability of polyoxymethylene (POM) films for measuring dissolved phase PAHs and PCBs in aquatic environments. Furthermore, the following set of studies investigated whether the partitioning behavior of a suite of PAHs and PCBs changes under varying temperature and salinity conditions. Lastly, a comparison was made between dissolved concentrations predicted from POM measurements and measured dissolved concentrations of HOCs to determine the effectiveness of using POMs to quantitatively assess aqueous phase concentrations.

5.2 Method and Materials

5.2.1 Chemicals and Materials

The chemicals and materials in this chapter were purchased and processed as outlined in the previous two chapters. In addition, spectrophotometric grade (98%) phenanthrene was purchased from Aldrich Chemical Co. (Milwaukee, WI) and HPLC grade methanol and acetonitrile were purchased from VWR International (Radnor, PA). Borosilicate glass vials (200 mL) with Teflon-lined caps and 3.8 L glass jars were also purchased from VWR International. Polyoxymethylene sheets were purchased from McMaster-Carr (Robbinsville, NJ) and steel crab trap cages were purchased from Efinger's Sporting Goods (Bound Brook, NJ).

5.2.2 Laboratory Experiments

The background solution for the laboratory experiments was made by adding 0.4 g of NaN₃ as a biocide, 23 mg of NaHCO₃ and 2.9 g of CaCl₂ to 3.8 liters of ultra-high purity water. All reactors were agitated on an orbital shaker at 125rpm for the duration of the experiment to ensure complete mixing. The room temperature experiments were conducted in a climate-controlled laboratory, which ranged in temperature between 21°C and 23°C and the cold experiments were conducted in a chilled room that was kept at 4°C. All polyoxymethylene films were cleaned before use using soxhlet extraction with

methylene chloride for 24 hr. The films were allowed to dry and then kept in an airtight glass jar until use.

5.2.2.1 Sorption Rate

5.2.2.1.1 Analysis

A phenanthrene stock solution was prepared by dissolving 100 mg of solid phenanthrene into 100 mL of methanol to create a 1,000 ppm solution. The stock solution was then diluted with background solution to prepare initial concentration solutions for the reactors and diluted with aqueous background solution and methanol to prepare the calibration standards. The volume of stock solution added to the initial concentration solutions was less than 0.06% to reduce any cosolvent effects of methanol on the sorption isotherms (Wauchope, Savage, and Koskinen 1983). Reactors were sampled at 1, 3, and 9 hours, 1, 3, and 5 days, and 1, 2, 3, 4, and 5 weeks for the 23°C experiment and at 8 hours, 1 and 4 days, and 1, 2, 3, 4, 5, 6, 7, and 8 weeks for the 4°C experiment. After shaking for the designated length of time, a 1 mL aliquot from each reactor and was transferred to a clean, weighed 2 mL vial and 0.4 mL of methanol was added. The vial was immediately crimp sealed, shaken and stored at 4°C until quantification by HPLC.

5.2.2.1.2 Quantification

Samples were analyzed on an Agilent HPLC (HP-1100) equipped with a 250 x 2.0 mm Hypersil ODS C-18 reverse-phase column (5 μ m, 2.1 x 250 mm, Phenomenex, Torrance, CA), diode array detector (HP-G1315A) and fluorescence detector (HP-G1316A). For low concentrations of phenanthrene (>60 ppb), the fluorescence detector

was used with 250 nm excitation and 364 nm emission wavelengths, and the diode array detector was used with a 250 nm absorption wavelength for higher concentrations. A set of 9 external standards ranging from 1 - 1,000 ppb was used in order to produce two 5-point linear calibration curves, one for the fluorescence detector (1-60 ppb) and one for the diode detector (60-1,000 ppb). A 10 µL sample was injected at 40°C and the carrier fluid was 55% acetonitrile to 45% ultra-pure water at a flow rate of 0.330 mL/min. Chromatograms were integrated using Agilent LC/MS Chemstation software.

The mass of phenanthrene on the POM film was determined using a mass balance of the initial concentration and the aqueous phase concentration. Equation 5.1 shows the calculation of phenanthrene sorbed to the POM film.

[Eq. 5.1]
$$q_{\rm e} = (C_0 - C_{\rm e}) * V/M$$

where q_e is the concentration of phenanthrene on the sorbent (POM), C_0 is the initial aqueous concentration of phenanthrene, C_e is the final aqueous concentration of phenanthrene, V is the volume of aqueous phase in the reactor and M is the mass of the sorbent (POM) in the reactor.

5.2.2.1.3 Quality Assurance/Quality Control

In the lab experiment, control reactors containing the phenanthrene solution without POM film and were analyzed to give a baseline concentration at each sample time and to account for losses from the solution not due to sorption on the tested material. The control reactors showed >0.7% change in the initial concentration, except for the low temperature, high concentration control reactor which exhibited a 5.3% increase in phenanthrene concentration at the end of 8 weeks. Each sample and standard measurement was conducted in duplicate or triplicate and the resulting concentrations were averaged to correct for variations in the signal. The resulting uncertainty in the measurements was calculated to be less than 5%. An R^2 of >0.99 was obtained for all standard calibration curves and all measurements were at least three times higher than the detection limit of 0.5 ppb.

5.2.2.2 Equilibrium Partitioning

5.2.2.2.1 Analysis

Reactors for the partitioning experiment were prepared by filling 3.8 L jars with background solution and spiking 50 µL of 2,000 ng/mL of PAH mix and 2 mL of 5-20 ng/mL of PCB mix. Ultra-high purity nitrogen was used to eliminate the solvent phase from the reactors and pre-weighed POM was added to the jar before it was tightly sealed, shaken vigorously by hand and then placed on the shaker for 4 weeks (23°C) to 6 weeks (4°C). Two water/POM ratios (17 mg/3.8 L and 70 mg/3.8 L) were used to ensure measurable concentrations of all compounds in both phases at equilibrium. Duplicate reactors were created at each water/POM ratio, for a total of four reactors at each temperature and salinity. At the end of the designated time, the POM films were removed from the reactor and immediately soxhlet extracted for 24 hrs. in methylene chloride. The aqueous portion was pumped through pre-cleaned XAD, which was then soxhlet extracted in 50:50 v/v hexane to acetone and processed as described in the previous two chapters.

5.2.2.2 Quality Assurance/Quality Control

Two lab blanks and matrix spikes (one each for XAD and POM) were processed through all steps from extraction to analysis along with the samples. Fluorene, phenanthrene, fluoranthene and pyrene were detected at measurable levels in the XAD and POM blanks and in addition, naphthalene was detected in the POM blanks. The mass of all compounds detected in the blanks was subtracted out of each sample mass. Surrogate recoveries (± standard deviation) for D₁₀-anthracene, D₁₀-fluoranthene and D₁₂benzo[*e*]pyrene were 142%±24%, 152%±23%, and 140%±27%, respectively. Surrogate recoveries for PCB 14, PCB 23, PCB 65 and PCB 166 were 75%±20%, 79%±19%, 82%±21%, and 81%±20%, respectively. The surrogate recoveries were used to correct the PAH and PCB masses that were measured in samples due to losses during processing. Detection limits for PAH congeners were found to be 0.001 ng with concentrations in all samples at least 1,000 times above this limit. Likewise, the detection limits for PCB congeners ranged from 0.02 ng to 0.05 ng and the concentrations in all samples were at least 2 times above the limit.

5.2.3 Field Experiments

5.2.3.1 Sampler Design

POM sheets with a thickness of 76 µm were chosen for this study because of their quick equilibrium time (Endo et al. 2011), but they required a structure in which to be deployed on the streambed. Crab traps were considered as a viable option since the sheets could be strung up inside the trap while still retaining full exposure of the POM to the stream flow. Figure 5.1 shows a sampler cage with six sheets (two samples) attached

inside. Chains were attached to the cages to lower and raise the traps into the water and locks were purchased to ensure that the samplers would not be stolen. Laboratory experiments and previous field data indicated that at typical aquatic concentrations, 9.84 g of POM would provide enough sorption capacity to ensure good analysis of PAHs on the GC-MS.

5.2.3.2 Field Rate Experiment

The sampling location chosen is marked as Site 2 in Figure 3.1. The site is located downstream of the first bridge upstream of the Delaware River. The sediment at this location is mostly small grain size with some leaf litter overlying the bed. The bed has a mostly flat bottom and is well within the tidal portion of the stream. The site was chosen for ease of access and because it has a suitable structure for securing the POM samplers. The exposed metal that runs along the bridge provides a secure bar on which the chains were padlocked to deter tampering with the samplers.

The samplers were assembled and deployed on October 22, 2009. Each week, one cage was surfaced and brought to shore. All field visits were conducted during low tide since the locked chains were submerged at all other times. POM sheets were removed and placed in a clean glass jar filled with river water. The POM sheets were placed into the water as soon as possible after cages were surfaced to reduce any loss of volatile compounds. Two 20-liter water samples were obtained during each of the four sampling events. Prior to sampling, the stainless steel cylinders were washed down with methanol and acetone three times each to remove any residual organics from the containers. Samples were taken from the boat at its location near the deployed samplers.



Figure 5.1 Passive sampler setup with POM sheets

Submerging them in the water on the upstream side of the boat filled the containers. As the canisters filled, they were up-righted in the water to allow all air to escape. Airtight lids were secured onto the canisters while underwater to ensure that there would be no headspace.

Heavy rains took place during the first two weeks of deployment (Weather Underground 2015). The rain and flows during the week between deployment and the first sampler extraction were especially high, causing leaves and debris to partially to full bury the samplers. Each week, the samplers were surfaced, the debris removed and resubmerged. The entire process took less than two minutes for each cage.

5.2.3.3 Field Prediction Experiment

On April 30, 2010, three passive samplers were deployed in the Tacony-Frankford Creek for later retrieval. The area had received little or no rain in the previous week and the temperatures were mild. The first sampler with duplicate samples was deployed near the launch site at the transfer bridge (Figure 3.1, Site 2). Again, the exposed metal that runs along the bridge was used to chain up the samplers. The second site was chosen near the Route 95 Bridge (Figure 3.1, Site 3), also partly due to the structure that the sampler could be secured to. The final site was chosen above the tidal portion, located in Juniata golf club (not shown on map) due to ease of placement. At this location, the sampler was secured to a chain-link fence along the shoreline.

POM samplers were retrieved and water samples taken on June 7, 2010. During retrieval of the third set of samplers from the Juniata Golf Club site, it was observed that the metal sampler had been vandalized and the sample was lost. Therefore, the total number of samples retrieved during this trip was four POM samples and six 20-liter water samples. Four additional POM samplers were deployed on November 4, 2010 at Site 2 (Figure 3.1) and retrieved on December 16, 2010, along with four water samples. The weather during this deployment period was mostly mild with a mean temperature of 50°F and a couple of precipitation events that were 2.5 mm/day or less. All samples were transported back to the lab and processed immediately.

5.2.3.3.1 Analysis

Water samples were transported from the field in 20 L containers and filtered through 0.7 µm filters to capture particulate matter and XAD columns to capture dissolved phase compounds. The procedures for analyzing the water samples are described in the previous chapters. The POM field samples were transported from the field in a sealed glass jar filled with the river water at the time of sampling. In the laboratory, the films were removed from the jars and immediately Soxhlet extracted with dichloromethane for 24 hrs. Three deuterated PAH compounds (D₁₀-anthracene, D₁₀fluoranthene and D₁₂-benzo[*e*]pyrene) and four PCBs (PCB 14, PCB 23, PCB 65 and PCB 166) were added as surrogate standards at the beginning of Soxhlet extraction. Next, rotary evaporation and ultra-high purity N2 gas were used to reduce the volume to ~1ml and each sample was fractionated using a glass column packed with 4 g of prepared alumina and 1 g of sodium sulfate. The PCBs were eluted with 15 ml of hexane and the PAH compounds were eluted with 15 mL of a 2:1 dichloromethane:hexane mixture, and the samples were then concentrated to 0.5 mL under ultra high purity N_2 gas. Finally, a PAH mixture of internal standards (D_{10} -phenanthrene, D_{10} -pyrene and D_{12} benzo[a]pyrene) and a PCB mixture of internal standards (PCB 30 and PCB 204) were added before quantification.

5.2.3.3.2 Quantification

All laboratory and field samples (besides the initial rate experiment) were analyzed on a Hewlett-Packard 6890N gas chromatograph with a Hewlett-Packard 5973 mass spectrometer detector with a 60 m x 0.25 mm internal diameter DB-XLB capillary column and a 0.25 μ m film thickness. The GC-MS methods and data analysis are described in the previous chapter of this dissertation.

5.2.3.3.3 Quality Assurance/Quality Control

Two lab blanks (one each for XAD and POM) were processed through all steps and the mass of any compound found in the blanks was subtracted out of each sample mass. Surrogate recoveries (\pm standard deviation) for D₁₀-anthracene, D₁₀-fluoranthene and D₁₂-benzo[*e*]pyrene were 43% \pm 10%, 73% \pm 12%, and 100% \pm 15%, respectively for the June samples and 33% \pm 1.4%, 53% \pm 1.6%, and 77% \pm 3.7%, respectively for the December samples. Surrogate recoveries for PCB 23, PCB 65 and PCB 166 were 43% \pm 15%, 92% \pm 39%, and 70% \pm 20%, respectively for the June samples and 43% \pm 5.5%, 127% \pm 9.0%, and 75% \pm 9.8%, respectively for the December samples. The surrogate recoveries were used to correct the PAH and PCB masses that were measured in samples due to losses during processing. Detection limits for PAH congeners was 0.001 ng and concentrations in all samples at least 1000 times above this limit. Likewise, the detection limits for PCB congeners ranged from 0.02 ng to 0.05 ng and the concentrations in all samples were at least 7 times above the limit.

5.3 Results and Discussion

5.3.1 Laboratory Rate Experiment

The laboratory rate was determined using phenanthrene because it has a well documented and relatively low $log(K_{ow})$ value (4.46) (Lienig 1980). Therefore, the phenanthrene is expected to have a low activity in the aqueous phase and to reach equilibrium with the solid phase slower than some of the compounds with higher $log(K_{ow})$ values. Figure 5.2 shows the percent of phenanthrene sorbed to the POM film over time. The reactors with a larger POM/water ratio exhibited faster equilibrium times and sorption was more complete (more on the POM phase) than the reactors with a smaller POM/water ratio. The larger POM films sorbed about 90% of the freely dissolved phenanthrene within 2 weeks, regardless of initial concentration or temperature.

The reactors with smaller POM films (Figure 5.2a) reached a lower aqueous equilibrium concentration (<50%) and while the warmer reactors took 2-3 weeks to reach equilibrium, the cold reactors did not achieve this until 5-6 weeks. In all cases, the initial concentration had a very slight impact on the rate, but not the final equilibrium percent concentration in the aqueous phase. Based on these results, it was determined that the compounds of interest (PAHs and PCBs) would come to equilibrium in a stream environment within 4 weeks under typical field conditions.



Figure 5.2 Percent uptake of phenanthrene on 0.076 mm polyoxymethylene film at 4°C and 23°C for a) low POM/water ratio and b) high POM/water ratio at various initial concentrations.

5.3.2 Laboratory Equilibrium Experiment

Partitioning coefficients, $\log(K_{POM})$, for water and POM were calculated for 16 PAHs and 41 PCBs. The resulting values were plotted against $\log(K_{OW})$ values as shown in Figure 5.3. For both PAHs and PCBs, the correlation between $\log(K_{OW})$ and $\log(K_{POM})$ was linear for compounds with $\log(K_{OW})$ less than about 6.5. Above $\log(K_{OW})$ of 6.5, $\log(K_{OW})$ and $\log(K_{POM})$ were negatively correlated. This relationship has been noted in previous studies (Bintein, Devillers, and Karcher 1993; Meylan et al. 1999) and is very similar to the correlation between bioconcentration factor (BCF) and $\log(K_{OW})$ described in Dimitrov *et. al.* (2003), which found that the maximum BCF is observed at an approximate $\log(K_{OW})$ of 6.5.

The log(K_{POM}) values for PCBs (Table 5.1) and PAHs (Table 5.2) are listed by compound for each temperature and salinity (specific conductance). The measured K_{POM} values are significantly different (p<0.02) at different temperatures and salinities (specific conductance) for PCBs, but not significantly different (p>0.05) for PAHs. Cornelissen et. al. (2008) and Jonker and Koelmans (2001) both measured POM/water partitioning coefficients for a smaller set of PAHs and PCBs and the present data are in agreement with the previous findings. The Cornelissen experiment included adding NaCl to the reactors to mimic estuarine field conditions and a comparison to the high salinity, room temperature K_{POM} values in this study indicates better correlation for PCBs (R²=0.81) than PAHs (R²=0.66). The Jonker study did not add ions to their reactors and a comparison with the freshwater data from the present study indicates a much stronger correlation for both PAHs (R²=0.95) and PCBs (R²=0.95). The poor agreement with the Cornelissen



Figure 5.3 Comparison of POM/water and octanol/water partitioning coefficients for a) PAHs and b) PCBs

data for PAHs could point to a difficulty with accurately measuring partitioning coefficients at high salinity.

5.3.3 Field Rate Experiment

Based on the laboratory rate experiment, the POM samplers were deployed for 4 weeks and duplicate samplers withdrawn each week for analysis. The results are shown in Figure 5.4. The concentration on the POM is not steadily increasing as expected. The data instead indicate that the samplers came to equilibrium within the first two weeks of being deployed and the subsequent variation in the data reflects the variable water concentrations at the time of sampler retrieval. Another explanation of the data is that the POM films attained equilibrium within the first week and between Week 1 and Week 2 there was a large and sustained input of PAHs to the stream that increased the concentration from Week 1. This explanation is supported by the fact that there were heavy rains during the first two weeks of deployment. The rain and subsequent high flows could have washed PAHs into the stream from roadways and stirred up underlying sediment and debris that desorbed PAHs into the water.

5.3.4 Field Prediction Experiment

PCBs and PAHs were measured in both the water samples and the POM films taken from the field on October 2009, June 2010 and December 2010. The resulting POM data were used with the $log(K_{POM})$ values measured in the last section to calculate a predicted water value. There were 12 samples total between the three sampling trips and predictions were made for 11 PAHs and 39 PCBs. Comparisons of the predicted vs. measured aqueous concentrations for PAHs and PCBs are displayed in Figure 5.5 and Figure 5.6, respectively.



Figure 5.4 Concentration of total PAHs in water and on POM films after 1 to 4 weeks deployed in Tacony-Frankford Creek.

With the exception of the October, 2009 PAH samples, the modeled data overpredicted the compounds with the lowest molecular weight (and lowest K_{POM}), while underpredicting the majority of compounds. This was true for both PAH and PCBs, although the contrast with the PCBs showed a clear difference between the overprediction of trichlorinated biphenyls versus underprediction of tetra through decachlorinated biphenyls. A logarithmic plot of the ratio of the predicted to measured concentrations (C_{pred}/C_{meas}) as a function of the $\log(K_{OW})$ is shown in Figure 5.7 and gives insight into the degree to which the modeled (predicted) data fit the measured data. While individual congeners vary, the overall average for the $\log(C_{pred}/C_{meas})$ of all the collected data is 0.19 for PAHs and 0.87 for PCBs. These values correspond to a difference factor of 7.3, on average, for PCBs and a factor of 1.5, on average, for PAHs.



Figure 5.5 Comparison of predicted aqueous PAH concentration (calculated using POM concentration and K_{POM}) to the measured aqueous concentration in stream water sampled in a) October 2009 and b) June 2010.





Figure 5.6 Comparison of predicted aqueous PCB concentration (calculated using POM concentration and K_{POM}) to the measured aqueous concentration in stream water sampled in a) June 2010 and b) December 2010.



Figure 5.7 Comparison of predicted to measured aqueous concentration to $log(K_{OW})$ values for a) 11 PAHs and b) 39 PCBs

One explanation for the apparent underprediction of the aqueous phase concentration may be that there is a secondary phase of colloidal particles present in the aqueous samples. These colloidal particles are small enough to pass through the 0.7 μ m filter that is used to capture the suspended particulate phase and some may get trapped in the XAD column used to sorb the dissolved organic compounds. Since both classes of compounds that are addressed in this study are hydrophobic, they will preferentially be adsorbed to the organic particulate phase. Given the high log(K_{ow}) values that define the partitioning behavior of the PAHs and PCBs in this study, even a small amount of colloidal material passing through the filter can have a very large effect on the apparent aqueous concentration. Based on the organic carbon content of the sediments (Table 3.1) and dissolved in the water column (Table 4.1) of the study stream, colloidal organic content can explain the factor of 1.5 to 7.3 difference between the predicted and measured water concentrations.

In addition to comparing POM concentrations to the water concentration, it is informative to look at how well the concentrations of PAHs sorbed onto the POM films represent the PAH concentrations in other environmental media. Using data from the November 2008 sediment sampling and the June 2010 fish sampling, a comparison can be made to determine how well the PAH signature sorbed onto the POM films corresponds to the PAH signature in the sediment bed or biota. The sediment PAH concentrations do not correlate with the POM concentrations as shown by the low regression coefficients ($0.27 < R^2 < 0.49$). Most of the fish tissue gave similarly low regression coefficients, except for the white sucker fillet and organs (R^2 =0.76 and R^2 =0.88, respectively) and the catfish liver (R^2 =0.76). The concentrations and ratios of

phenanthrene, fluoranthene and pyrene heavily influenced the correlations as they were the dominant compounds in both the POM and fish samples.

5.4 Discussion

Passive sampling techniques are increasingly being explored and implemented due to their ease of use and non-degrading impacts on the system in which they are deployed. Thin POM film is useful for measuring PAHs and PCB in small aquatic systems, but there are limitations to how it can be used. First, while POM is more resistant to fouling that other materials that can be used as sorbent passive samplers, it is not completely insusceptible (Arp et al. 2015). If POM is deployed for longer periods of time or in very organic rich environments, biofilms can develop that will interfere with accurate measurement of HOCs in the system.

Second, the sorption rate is short in the environment (on the order of days to a couple weeks, so there is a heightened risk of contamination when deploying and retrieval than with ordinary grab samples. This risk is mitigated by the use of multiple field blanks that are exposed to the same air and conditions that the samples are during transitions into and out of the environmental medium. In order to reduce volatilization losses between time of retrieval and beginning of analysis, POM films were stored in a stream water sample from the time and location of retrieval. There was some evidence that the time delay between retrieval and laboratory analysis was enough for some compounds to begin reaching a new equilibrium with the sampled water, therefore this may pose a problem in some applications where the desired water to be measured is not readily accessible. For these examples it would be recommended to withdraw the film

from the environment and directly into a solvent storage solution that can be analyzed with the rest of the sample.

The concentration on POM correlates to the freely dissolved concentration of PAHs and PCBs, but does not necessarily accurately describe the total water concentrations to which the biota and the stream ecosystem are exposed. This may be a limitation or a benefit, depending on the goal of the research, but it is important to take this factor into consideration in the sampling design. Since POM is measuring only the freely dissolved phase, it might not be an accurate measure of the stream water that the aquatic organisms are ingesting. In addition, it is difficult to validate its use in prediction of water concentrations in systems with high suspended solids and colloidal particles, short of filtering water samples multiple times to eliminate trace particulate phases. POM is better suited to assessing dermal exposures or used in tandem with grab water sampling it can be used to determine the concentration of HOCs in the colloidal phase that would be difficult to remove through conventional treatment. No assumptions can be drawn about the effectiveness of POM to predict biota PAH and PCB loadings as many more data are needed to come to a robust conclusion.

Overall, the development of methods involving POM for passive sampling in small streams is a promising avenue for gathering composite information about HOC loading. Longer deployment times eliminate the temporal variation that is inherent with grab sampling methods. This benefit is greater in tidal systems, where the temporal differences are augmented. The processing times are shorter which should translate to a lower cost for local governments and organizations that monitor smaller streams for water quality. With further development, the method could be used as an alternative to harvesting biota for pollution assessments.

I emperature (*C)	23	23	23	23	4	4	4
Sp. Cond. (uS/cm)	0	300	700	54,000	0	700	54,000
PCB							
17	4.95	4.81	4.94	4.90	4.79	4.86	4.87
18	4.98	4.82	4.88	5.14	4.91	4.96	4.66
28	5.16	5.10	5.21	5.34	5.13	5.20	5.20
31	5.25	5.14	5.29	5.48	5.25	5.30	5.43
33	5.15	5.12	5.17	5.31	5.08	5.12	5.25
44	5.25	5.46	5.30	5.27	5.16	5.23	5.13
49	5.20	5.45	5.27	5.30	5.16	5.25	5.11
52	5.31	5.55	5.37	5.40	5.27	5.35	5.26
70	5.25	5.51	5.32	5.43	5.23	5.35	5.16
74	5.45	5.77	5.56	5.54	5.46	5.56	5.42
82	5.48	5.86	5.63	5.71	5.50	5.62	5.41
87	5.56	5.89	5.66	5.72	5.68	5.79	5.42
95	5.37	5.68	5.48	5.68	5.42	5.49	5.49
99	5.42	5.74	5.55	5.59	5.46	5.55	5.31
101	5.35	5.72	5.48	5.61	5.45	5.56	5.36
105	5.51	5.84	5.61	5.72	5.42	5.54	5.26
110	5.51	5.77	5.56	5.67	5.44	5.61	5.35
118	5.69	5.99	5.75	5.80	5.48	5.57	5.21
128	5.58	5.91	5.67	5.76	5.38	5.52	5.27
132	5.46	5.76	5.57	5.65	5.45	5.55	5.36
138	5.60	5.87	5.59	5.65	5.31	5.31	5.01
149	5.53	5.95	5.69	5.82	5.63	5.74	5.42

Table 5.1 Measured K_{POM} values for select PCBs at two temperatures and three salinities

Table 5.1 (cont.)

Temperature (*C)	23	23	23	23	4	4	4
Sp. Cond. (uS/cm)	0	300	700	54,000	0	700	54,000
PCB							
151	5.70	6.12	5.81	5.81	5.52	5.65	5.17
153	5.66	5.95	5.58	5.42	5.16	5.00	4.53
156	5.65	6.04	5.71	5.86	5.35	5.45	5.08
158	5.61	6.00	5.74	5.78	5.54	5.65	5.23
169	5.75	5.96	5.58	5.46	5.14	4.93	4.63
170	5.74	6.05	5.69	5.66	5.31	5.30	4.93
171	5.73	6.04	5.79	5.70	5.40	5.54	5.06
177	5.56	5.93	5.66	5.52	5.44	5.53	5.23
180	5.71	6.04	5.74	5.84	5.34	5.38	5.02
183	5.64	6.07	5.73	5.94	5.55	5.66	5.25
187	5.61	5.99	5.75	5.80	5.53	5.70	5.28
191	5.71	5.98	5.74	5.74	5.36	5.41	4.97
194	5.73	5.93	5.53	5.59	5.14	5.05	4.75
195	5.68	6.05	5.72	6.01	5.35	5.45	5.44
199	5.72	6.03	5.73	5.73	5.37	5.43	4.99
205	5.66	5.95	5.54	6.09	5.19	5.05	5.24
206	5.69	5.78	5.41	5.36	5.11	4.63	4.50
208	5.56	5.75	5.35	5.18	5.07	4.58	4.30
209	5.46	5.38	4.92	5.48	5.00	4.14	4.86

Temperature (°C)	23	23	23	23	4	4	4
Sp. Cond. (µS/cm)	0	300	700	54,000	0	700	54,000
PAH							
Naphthalene	3.98	3.38	3.42	3.85		3.66	3.57
Acenaphthylene	3.72	3.10	3.36	3.96	3.49	3.56	3.43
Acenaphthene	4.06	3.43	3.65		3.74	3.84	3.82
Fluorene	3.86	3.59	3.52		3.62	3.80	3.85
Phenanthrene	3.89	3.97	3.11		3.65	4.23	3.96
Anthracene	4.40	4.06	4.25	4.48	4.48	4.95	4.95
Fluoranthene	4.59	4.14	4.62	4.31	4.70	4.82	4.61
Pyrene	4.71	4.28	4.74	4.75	4.73	4.82	4.60
Benz[a]anthracene	5.25	4.96	5.39	6.31	5.53	5.51	5.69
Chrysene	5.35	5.01	5.47	5.97	5.48	5.38	5.32
Benzo[b]fluoranthene	5.49	5.10	5.71	6.28	5.78	5.62	5.46
Benzo[k]fluoranthene	5.39	5.14	5.79	5.32	5.93	5.71	5.18
Benzo[a]pyrene	5.64	5.27	5.83	6.44	6.20	6.16	5.38
Indeno[1,2,3,-	5.70	5.44	5.96	5.56	5.68	5.29	4.67
cd]pyrene							
Benzo[g,h,i]perylene	5.55	5.27	5.78	5.42	5.51	5.23	4.78
Dibenzo[a,h]-	5.46	5.36	5.75	6.00	5.46	4.95	4.64
anthracene							

Table 5.2 Measured K_{POM} values for select PAHs at two temperatures and three salinities

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Chapter 6: Conclusions and Further Research

1.1 Conclusions

Samples were collected from the Tacony-Frankford Creek in Philadelphia, PA and analyzed for two classes of hydrophobic compounds: PAHs and PCBs. The result of the PAH analysis shows that concentrations are variable with both time and location and that the two major reservoirs of PAHs in this stream are the sediments and biota (specifically fish organs). In contrast to larger rivers with great volume that can attenuate the impacts of changing inputs, the concentrations in the Tacony-Frankford Creek are subject to great variation based on the sampling location and timing. While the concentrations of PAHs in the water column are variable, the ratios of compounds were less so, indicating that the sources were constant. Signature ratios were compared to and showed a strong correlation to both particulate and gaseous phase compounds measured in the air in Philadelphia. Using source apportionment, the primary source was identified as motor vehicle emissions.

The overall trend based on location was shown as higher PAH concentration upstream for water and downstream for sediments. Since the sediments are a major reservoir of PAHs, their transport downstream is a significant source of loading to the Delaware. In addition to lateral variation, the sampling depth was found to be a very important factor in the determination of PAH and PCB concentrations. PCB concentrations were higher near the surface than the bed, which indicates deposition as a more important source than sediments. Conversely, whole water samples near the sediment bed have higher concentrations of PAHs than samples near the surface, a trend that is enhanced during low tide due to hydrodynamic forces and sediment stirring. Differences in concentration are also evident based on the time of sample collection, but long-term or seasonal trends in this stream are muted by the influence of tidal effects on concentration.

A passive sampling technique was explored to reduce the impact of short-term variability on measured HOC concentrations. The material chosen was polyoxymethylene (POM), which demonstrated the ability to adsorb PAHs and PCBs under both laboratory conditions and in the field. Partitioning coefficients $(\log(K_{POM}))$ for select PAHs and PCBs had previously been published and this work added to that by calculating values for a total of 16 PAHs and 41 PCBs. The $log(K_{POM})$ values from the laboratory studies underestimated the PAH and PCB concentrations determined by simultaneous grab water samples by less than a factor of 10, but this is likely due to difficulty in separating the truly dissolved phase from colloidal particles in grab samples. A comparison of the $\log(K_{POM})$ values to octanol/water partitioning coefficients $\log(K_{OW})$ values revealed a non-linear correlation that was similar to that of bioconcentration factors and $log(K_{OW})$. This would indicate that the POM method could be developed further to predict biota concentration, but few of the fish samples collected in this study were strongly correlated to the aqueous PAH concentration. Overall, POM passive sampling shows potential as a non-invasive method to determine HOC concentrations in small streams.

1.2 Implications

The conclusions drawn from this work have applicability to government and nonprofit organizations concerned with pollutants in small streams and large bodies of water with multiple tributaries. This work shows the variability of HOC concentration in small streams and emphasizes the need for careful planning when designing sampling protocols. Since PCBs and PAHs are ubiquitous, the implications of this work are not limited simply to urban areas.

The expansion of the list of measured $log(K_{POM})$ values has an impact on future use of POM as a passive sampling method. Further development of the method to produce better predictions of water and biota concentrations could change the way monitoring programs are designed. POM sampling is representative of long-term average concentrations, which can be more useful for regulatory agencies. In addition, this work indicates that filtered samples of water might overestimate HOC concentrations and POM is an effective way to eliminate error in the measurement of truly dissolved compounds.

1.3 Future Research

This work lays the foundation for future research on the study stream and other small streams as well as further studies using passive sampling methods. Further research can be undertaken to determine the source of the high upstream concentration of PAHs in the sediments of the Tacony-Frankford Creek and to gather more data on fish to compare to POM. To supplement this work, laboratory studies can be performed using fish and POM films in a single reactor to further determine if POM can be used to predict biota uptake. In addition, HOCs should be measured in other tributaries to the Delaware River in the Philadelphia area to compare the fluxes of HOCs to the results in this work.