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**POLYCYCLIC AROMATIC HYDROCARBON CONTAMINATION IN AND
AROUND THE ARTHUR KILL, STATEN ISLAND, NEW YORK**

By

GERALD THOMAS RUSTIC

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ABSTRACT OF THE THESIS

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Thesis Director:

Lisa Rodenburg

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants. PAHs are often found in industrialized and urbanized areas as a result of industrial processes, combustion of carbon-bearing compounds, and urban runoff. The area surrounding the Arthur Kill in Staten Island, New York, is an area with a long history of industrial activity, pollution, and anthropogenic contamination. The area is known to have elevated levels of metal pollution which has impacted the benthic infaunal community dynamics. The purpose of this study is to determine the levels of PAHs present in sediments in and around the Arthur Kill, and to determine if the levels of PAHs present have affected benthic macroinfaunal community structure. Sediment PAH concentrations were measured using isotope dilution mass spectrometry, and the effects of that contamination on community structure were determined using linear regression,

Principal Component Analysis (PCA), and Canonical Correspondence Analysis (CCA). Organic carbon normalized PAH concentrations ranged from 45 to 211 ug/g organic carbon, below concentrations considered dangerous. No significant relationship was found between benthic macrofauna biomass or abundance using the various statistical methods, suggesting that PAH contamination is not a driving factor in the community composition in and around the Arthur Kill.

Dedication

To my mother, who taught me to look things up in the Encyclopedia when I was five.

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Introduction

The Arthur Kill is a highly industrialized waterway between Staten Island, New York and Raritan Bay, New Jersey. This waterway has a long history of pollution from various sources, including industrial outflow, landfill leachate, urban runoff, metal smelting, shipping, oil spills and sewage outflow (Berger, 1994). Previous studies (Adams et al., 1998; Farley et al., 1999) investigated the levels of various pollutants in the area, including Polycyclic Aromatic Hydrocarbons (PAHs), metals (Cd, Hg, Zn, Pb, Cu) and Polychlorinated Biphenyls (PCBs). Metal contamination and the effects of that contamination on the community structure have been studied by a research group from the College of Staten Island (CUNY) (Seebaugh and Wallace, 2009; Perez and Wallace, 2004; Goto and Wallace, 2009; Khoury et al., 2008). These recent studies have not included a determination of the sediment concentration of PAHs, nor have the studies examined the possible impact of PAH contamination on the same benthic communities. This study aims to fill that knowledge gap by examining the PAH concentrations at the same study sites used by previous researchers to study sediment metal contamination (Seebaugh and Wallace, 2009, Perez and Wallace, 2004, Goto and Wallace, 2010). These measurements are presented in Chapter 1 of this thesis. In addition, in Chapter 2, the measured PAH sediment concentrations are used to investigate the possible effects of chronic, sub-lethal PAH contamination on the benthic macroinfaunal communities.

PAHs are both naturally occurring and anthropogenic compounds, largely produced from the burning of carbon-containing materials (fossil fuels, plant material, etc.) (Shor et al., 2003). PAHs are a class of organic compounds composed of several fused aromatic rings. The number of rings (from three to six) and the orientation of the rings determine various properties of the compounds and the name of the individual compounds. In the environment, these compounds tend to sorb tightly to organic carbon or black carbon, and may exhibit limited bioavailability to organisms, especially when contamination is long-term and weathering has been allowed to occur (Shor et al., 2004).

Some PAHs (notably benzo[a]pyrene) are known carcinogens, while many other PAHs are considered probably carcinogens by the EPA (U.S. EPA, 2010). The most toxic PAHs have been labeled “Chemicals of Concern” by the EPA, and for many of these, toxic threshold values have been determined. In addition, NOAA (1993) has determined the Effects Range – Low and Effects Range – Median concentrations for various PAH compounds. Because PAHs sorb quickly and very strongly to organic carbon in sediments (Shor et al., 2003), sediment concentrations are often expressed in terms of the amount of PAHs per gram of organic carbon (Swartz, 2009). This normalization accounts for the binding effects the organic carbon and the potential reduction of bioavailability of the PAHs to benthic infauna (Shor et al., 2003). This normalization does not account for the effects of black carbon, which may further reduce bioavailability of PAHs in sediments (Shor et al., 2004).

PAH contamination has been shown to have deleterious effects on biota at various sediment concentrations (Aas et al., 2000; Shor et al., 2004; Erstfeld and Snow-Ashbrook, 1999). Both acute exposure and chronic exposure to PAHs can disrupt cellular activity and cause toxicity to organisms. Acute exposure causes cell damage and cell death by disrupting normal cellular processes, such as membrane transport and respiration, and can also cause energy-balance changes in cells, causing cell death (Varanasi, 1989). Long term exposure can cause DNA adduct formation, genotoxicity, and tumor formation via biochemical pathways involving the cytochrome P450 enzyme family (Varanasi, 1989, Marston et al., 2001, Mallakin et al., 1999, McConkey et al., 1997).

Previous studies have found elevated levels of PAHs in both the water and sediments of the Arthur Kill, and in the surrounding area (Huntley et al., 1995; Adams et al., 1998; Farley et al., 1999). In studies along the Arthur Kill, Huntley et al. (1995) found dry-weight sediment concentrations of 37 ± 81.9 ug/g for a suite of 19 PAHs, while Adams et al. (1998) reported calculated dry-weight sediment concentrations between 4 ug/g and 11 ug/g for a suite of 16 PAHs. Adams et al. (1998) grouped data into large geographic features (Raritan Bay, Upper New York Bay), while Huntley et al. (1995) were much more specific, showing sites along the Arthur Kill, and focused on sites to the north and west (New Jersey side) of the Arthur Kill.

In recent work assessing the levels of metal contamination in and around the Arthur Kill, a specific set of sites has been repeatedly used to measure both the sediment concentrations and the benthic infaunal community species

diversity and abundance (Seebaugh and Wallace, 2009; Perez and Wallace, 2004; Goto and Wallace, 2009; Khoury et al., 2008). These studies have determined that Hg contamination is the dominant factor in driving community structure, as determined by Canonical Correspondence Analysis (Goto and Wallace, 2010). None of these previous studies of metal contamination measured the concentration of PAHs in the sediment. Furthermore, in previous studies of PAHs, the locations were not the same as those used in the metals studies. Measurement of PAHs at the metals sites would therefore be useful, since PAHs can have effects on the biota in sediment (Shor et al., 2004; Erstfeld and Snow-Ashbrook, 1999), depending on the concentrations found and the sorption of PAHs to organic carbon and black carbon. PAHs can also interact with some metals, notably Cd, to increase the effects of Cd on organisms (Roesijadi et al., 2009).

The intent of this study was therefore to determine the sediment concentrations of PAHs at the study sites previously used to determine the effects of metals on benthic infaunal communities in and around the Arthur Kill. Sediment samples were collected from the various study sites and analyzed using Accelerated Solvent Extraction and Gas Chromatography/Mass Spectrometry (GC/MS) to determine the concentrations of a suite of 26 PAHs in the sediment samples. Using these sediment PAH concentrations, benthic infaunal community data was analyzed to determine if the concentrations of PAHs found at the study sites were correlated with various measures of species diversity, total biomass and total abundance. This study is both a survey of the

sediment concentration of PAHs in and around the Arthur Kill, and an analysis of the effects those PAHs have on the benthic community.

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Chapter 1. Determination of the Concentration of Polycyclic Aromatic Hydrocarbons in sediment around the Arthur Kill, New York.

Abstract

Previous studies of sediments from the salt marshes around Staten Island have found elevated levels of various metals, including Cd, Hg, Cu and Ag. Aside from metal contamination, this area also has a history of Polycyclic Aromatic Hydrocarbon (PAH) contamination. The concentrations in sediment at various study sites in and near the Arthur Kill in Staten Island were determined for 26 PAHs using isotope dilution mass spectrometry. Sediment concentrations of PAHs at all study sites ranged from 4000 to 11400 ng/g dry sediment, below critical thresholds for observed biotic effects, but similar to sediment concentrations found in previous studies of the New York Bight and Raritan Bay estuary. Organic Carbon normalized PAH concentrations were calculated to be from 45 to 211 ug/g organic carbon, below levels considered dangerous. Concentrations of PAHs in sediments were below EPA's sediment benchmarks based on component toxicity (0.5) for both acute and chronic effects levels.

Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous environmental pollutants, found in sediment, air, and water. The main sources of PAHs are the

incomplete combustion of organic materials, petroleum residues and petroleum product spills, industrial waste, and urban runoff (Varanasi, 1989). Elevated levels of many PAHs have been found in the New York/New Jersey area (Huntley et al., 1995). The Hudson River Estuary and New York/New Jersey Harbor have long been used for shipping, receive outflow from industrial sites and sewage treatment facilities, and are the ultimate destination of urban runoff from the industrialized and heavily urban areas of Northern New Jersey and New York City (Burger, 1993). One of the waterways in this area is the Arthur Kill, a heavily industrialized and highly impacted (Huntley et al., 1995), tidally influenced waterway separating Staten Island from New Jersey (Figure 1.1). Aside from industry, shipping, and runoff, the Arthur Kill has been subjected to numerous oil spills, including a large 550,000+ gallon spill in 1990 and numerous smaller spills (Burger, 1993).

PAHs can cause toxicity to aquatic organisms from both acute exposure and chronic exposure. Acute exposure causes cell damage and cell death by the disruption of necessary cellular processes (transport across membranes and through the cell; cellular respiration). Acute exposure can also cause an overload of the xenotoxic removal systems in the cells, resulting in large numbers of reactive oxidative compounds, which interfere with cell processes and which change the energy balance in cells (Varanasi, 1989). Long term exposure causes DNA adduct formation, genotoxicity and tumor formation along a biochemical pathway involving the cytochrome P450 enzyme family (Varanasi, 1989, Marston et al., 2001, Lee and Anderson, 2005, Mallakin et al., 1999).

Species exposed to PAHs can show effects ranging from acute toxicity to necrosis, lesions, DNA adduct formations, elevated enzyme activity levels, or little effect at all, depending on the species, length of exposure, the concentration of PAHs and the bioavailability of the PAHs (Shor et al., 2003; Aas et al., 1999; Paine et al., 1996).

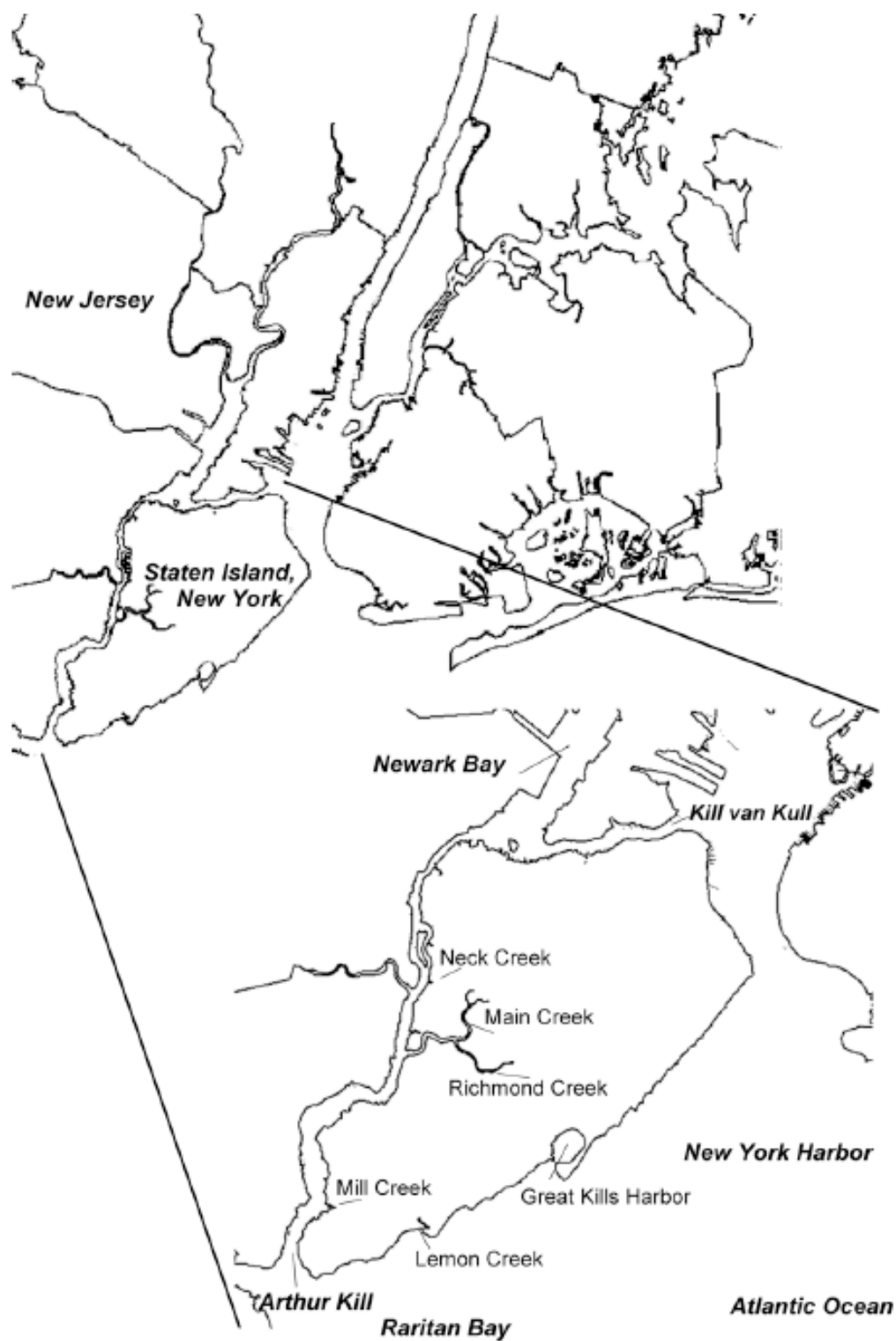
The U.S. Environmental Protection Agency (EPA) considers PAHs to be tumorigenic agents capable of causing genotoxicity (U.S. EPA, 2007). In the environment, PAHs are generally found as complex mixtures of various component PAHs (U.S. EPA, 2007). The EPA lists fourteen individual PAHs as priority chemicals, and seven are singled out as Chemicals of Concern (CCs), indicating a higher potential health hazard for these compounds. These seven CCs are Benzo[a]anthracene (BaA), Benzo[a]pyrene (BaP), Benzo[b+k]fluoranthene (B(b+k)F), Chrysene (Chr), Indeno[1,2,3-cd]pyrene (Indeno), and Dibenzo[a,h]anthracene and Dibenzo[a,c]anthracene, which co-eluted in this work, and are grouped together as Dibenzo[a,h+a,c]anthracene (DBA) (U.S. EPA, 2010).

Several methods of determining sediment toxicity from PAHs are in use. In the older literature, total PAH concentrations, in terms of ng/g or mg/kg in dry sediment, were used to characterize toxicity (Wolfe et al., 1996). NOAA **Effect Range-Low** (ER-L) and **Effect Range-Median** (ER-M) sediment concentrations for constituent PAHs are based on this bulk sediment concentration (NOAA 1999). Recent work frequently normalizes sediment PAH levels to the levels of organic carbon found in sediment (Swartz, 1999). This method accounts for the binding

of PAHs to organic carbon and the reduced bioavailability to organisms as a result of sorption to organic carbon (Shor et al., 2003). In addition to these methods, the EPA has created Equilibrium Partitioning Sediment Benchmarks (ESBs), which account for the variable toxicity of component PAHs in mixtures (Hansen et al., 2003).

The purpose of this study was to measure the levels of PAHs in the various locales in the Arthur Kill and to determine whether the patterns of metal contamination of sediments are also observed for PAHs. Previous studies in the same study sites have determined that contamination levels are highest at sites inside the Arthur Kill, and are reduced outside of the Arthur Kill. Furthermore, sites further away from the entrances to the Arthur Kill are generally more contaminated, and show decreased levels of dissolved oxygen and evidence of stressed benthic communities as a result of the contamination (Goto and Wallace, 2010a, Perez and Wallace, 2004, Khoury et al., 2008). However, previous studies at these sites did not measure PAH contamination. The PAH concentrations presented here provide additional data and can be used to determine whether PAH levels have an impact on the benthic community structures.

Figure 1.1. Map of study sites on Staten Island, including Neck Creek, Main Creek, Mill Creek, Lemon Creek and Great Kills Harbor. From Goto and Wallace (2010a)



Materials and Methods

Study Sites

The Arthur Kill is a tidally influenced waterway roughly 10 km in length between Staten Island, New York, and New Jersey (Figure 1.1). The Arthur Kill is bound by Kill van Kull and Newark Bay in the north and by Raritan Bay (on the New Jersey side), Great Kills Harbor (on the Staten Island side) and New York Harbor to the south. The geography of the Arthur Kill leads to limited tidal flushing, as tides enter from both the north and south, increasing the entrapment of pollutants in the sediments (Goto and Wallace, 2010b). The Arthur Kill has suffered from various forms of pollution for more than a century, including oil spills, industrial discharge, sewage treatment, landfill leachate and urban runoff (Berger, 1994; Farley et al., 1999; Wolfe et al., 1996). High levels of metal contamination and low levels of dissolved oxygen are found in the Arthur Kill and the tributaries feeding into it from Staten Island, and the ecosystems in this area have been adversely affected, with effects on individual species, food webs and entire ecosystems, as measured by diversity and abundance (Seebaugh and Wallace, 2009, Goto and Wallace, 2009, Koury et al., 2007, Goto and Wallace, 2010a, Goto and Wallace, 2010b).

Five study sites previously used to study metal contamination (Seebaugh and Wallace, 2009, Goto and Wallace, 2010b) were chosen as locations for sediment sampling. Great Kills Harbor is considered the cleanest of the study sites. It is on the southeastern side of Staten Island, outside of the Arthur Kill,

and has open circulation to New York Harbor. Sources of contamination at this location include a marina and a sewage treatment plant. The Lemon Creek site also faces the New York Harbor, roughly 4 km from the Arthur Kill. Urban runoff, a marina, and residual contamination from a dental tool plant are possible sources of contamination here. Mill Creek is the southernmost site in the Arthur Kill, roughly 1 km north of the southern end of the Arthur Kill. A metal smelting facility was present here from the 1930s to the 1970s. Main Creek is one fork of a creek that terminates at the Fresh Kills landfill. Leachate from the landfill is a major source of metal (Seebaugh and Wallace, 2009). Neck Creek is at the northernmost end of the Arthur Kill. Waterborne pollutants from the Arthur Kill are considered a major source of contamination for the Neck Creek site (Seebaugh and Wallace, 2009, from Ward, 2002).

The study area encompasses an environmental gradient, with relatively clean sediments, low levels of metal pollutants, and vigorous flushing and exchange with New York Harbor at Great Kills Harbor, and with levels of contamination increasing and levels of flushing decreasing as one gets closer to the Arthur Kill (Seebaugh and Wallace, 2009). The most contaminated sites, with regards to levels of metals in sediments and low dissolved oxygen levels, are the sites farther in to the Arthur Kill (Neck Creek and Mill Creek) (Goto and Wallace, 2010b). Main Creek, in the middle of the Arthur Kill, is the sampling site furthest from sources of tidal flushing, and also the sampling site furthest from the confluence with the Arthur Kill and closest to the Great Kills landfill. The general

pattern observed is that sites in the middle of the Arthur Kill are the most contaminated, with higher levels of metals in sediments and lower levels of dissolved oxygen. As the distance increases from the middle of the Arthur Kill, dissolved oxygen increases, metal concentrations decrease, and communities show less stress.

Sampling

Sediment samples were retrieved from the five study sites on December 14, 2009, during low tide, between 11:30AM and 1PM. At each study site, three samples were taken between the visible low tide and high tide lines, from seven to ten meters apart. Approximately 1cm of surface sediment was collected with a disposable plastic spoon. Approximately 100 g (wet weight) of sediment were collected from each location within each site. Locations selected for sampling were free of surface organic debris and plant or animal material. Samples were placed in Ziploc polyethylene freezer bags, labeled, and placed in a 4°C cooler, then placed in a -10°C freezer. Samples remained frozen until analysis in January and February 2010.

Sample Preparation

Individual sample bags were slightly thawed on the bench top until the freezer bags could be safely opened and samples could be broken into smaller pieces. Sub-samples of roughly 12-15 g wet weight were measured into hexane/acetone washed aluminum trays and placed in a fume hood to thaw and dry for 48-72 hours. Wet weight and weight after drying were measured to

determine percentage water content in sediments. Spatulas and scoops used to separate sub-samples from the larger samples were wiped with Kim-wipes, and rinsed with hexane, then with acetone before re-use to prevent cross contamination.

After drying for 48-72 hours, samples were weighed (dry weight) and then ground in a mortar and pestle. Both mortar and pestle were wiped with Kim-wipes, and rinsed with acetone then hexane between samples. The ground samples were placed in cleaned and rinsed glass jars, sealed with aluminum foil and screw top lids. Samples were then kept frozen until extraction. Extraction was performed using 3.5 g to 6 g of ground sample. Each sample was added to a hexane-rinsed Accelerated Solvent Extraction (ASE) tube, spiked with deuterium-labeled surrogate solution of d10-Anthracene, d10-Pyrene and d12-Benzo[e]pyrene, packed with cleaned and baked sand (500°C for 12+ hours) and double-filtered using baked cellulose filters. Extraction was performed using 60 mL dichloromethane on a Dionex ASE 200. Each run of up to twelve samples included a lab blank and matrix spike.

Sample Cleanup and Analysis

The volume of each extract was reduced to 10 mL via blowdown with purified nitrogen. Sample cleanup used baked alumina (500°C, 24 h) packed into extraction bulbs stopped with glass wool. The cleanup columns were preconditioned with 30 mL hexane. After preconditioning, the sample was added to the column and allowed to elute until nearly dry. 15 mL of 2:1

dichloromethane:hexane mix was added to the column, which was followed by 30 mL hexane. The resulting eluant was reduced in volume by rotary evaporation to less than 10 mL and transferred to cleaned, baked 10 mL vials. Sample volumes were then further reduced to 1 mL via blowdown with purified nitrogen. 5 mL hexane was added for solvent exchange, and subsequently reduced by purified nitrogen blowdown to 1 mL volume. The resulting liquid was transferred to hexane-rinsed baked autosampler vials, and hexane was added to bring the volume to 2 mL. Samples were then spiked with deuterium-labeled PAH internal standard solution of d10-Phenanthrene, d10-Pyrene and d12-Benzo[a]pyrene. These vials were then used for analysis on an Agilent 5973 Gas Chromatograph/Mass Spectrometer (GC/MS). Concentrations were determined using a single point calibration using PAH standards and deuterium-labeled PAH standards versus the response of prepared performance standards. Sediment concentrations were standardized to percent recovery and sample dry-weight sediment mass for three groups of PAHs (MW 168-198, MW 202-252, MW 252-300). PAH compounds measured were Fluorene (166 g/mol), Phenanthrene (178), Anthracene (178), 1-Methylfluorene (180), Dibenzothiophene (184), 4,5-Methylenephene (190), co-eluting Methylphenanthrenes (192), Fluoranthene (202), Pyrene (202), 3,6-Dimethylphenanthrene (206), Benzo[a]fluorene (216), Benzo[b]fluorene (216), Retene (219), Benzo[b]naphtho[2,1-d]thiophene (234), Cyclopenta[cd]pyrene (226), Benz[a]anthracene (228), Chrysene/Triphenylene (228), Naphthacene (228),

Benzo[b+k]fluoranthene (252), Benzo[e]pyrene (252), Benzo[a]pyrene (252), Perylene (252), Indeno[1,2,3-cd]pyrene (276), Benzo[g,h,i]perylene (276), Dibenzo[a+c,a+h]anthracene (278), and Coronene (300).

Dibenzo[a+c,a+h]anthracene are two co-eluting compounds, Dibenzo[a,h]anthracene and Dibenzo[a,c]anthracene. In EPA analyses, these are treated as separate compounds, but these co-elute in this analysis and are treated as a single compound (abbreviated as DBA). Calculations to determine GC/MS response and sediment concentrations were performed in MS Excel. Response for each PAH compound is normalized to internal standard response and multiplied by the mass of the internal standard to determine the mass of the compound in the sample. This mass is divided by the sediment mass to determine the sample concentration. These results were corrected to percent recoveries, and calculated based on sediment dry weight.

Quality Assurance/Quality Control

Laboratory blanks and matrix spike samples were run in each sample set to ensure recovery and to test for contamination. All PAHs were below detection limit in laboratory blanks. Matrix spikes showed recovery comparable to environmental samples and no additional PAH contamination.

Environmental Data

Percent organic carbon, metal concentrations, and other environmental data for the study sites were taken from Goto and Wallace (2010b). The same study sites as in Goto and Wallace (2010a) were used in this study, facilitating re-

use of the data (Wallace, pers. comm. 2010). Organic-carbon normalized levels of total sediment PAH concentrations ($\Sigma_{OC}PAH$) were calculated using organic carbon values from Goto and Wallace (2010) (see Table 1.1) using the following calculation:

$$\Sigma_{oc} PAH = \frac{\Sigma_{26} PAH}{\%OC} \quad (1)$$

Where %OC is the percentage of organic carbon.

EPA ESB levels for acute and chronic responses based on the measured PAH concentration were determined using values from (Mount, 2003) and the method as outlined by Mount (2010):

$$\sum \frac{\left(\frac{\text{conc. PAH}_i}{\%OC} \right) (\text{alkylation factor}_i)}{\text{potency factor}_i} \quad (2)$$

The alkylation factor and potency factor are for each compound and are listed for each compound in Table 1.4 (for acute potency) and Table 1.5 (for chronic potency). All statistical analyses were performed using MATLAB v 7.10. One-way analysis of variance (ANOVA) of sediment concentrations for the sum of PAHs (ΣPAH) and the 6 EPA CCs was used to determine differences between sediment samples. Standard error was calculated as the standard deviation divided by the square root of the number of samples (in all cases, 3).

Significance was defined at the 95th percentile confidence interval (i.e. $p < 0.05$)

Results

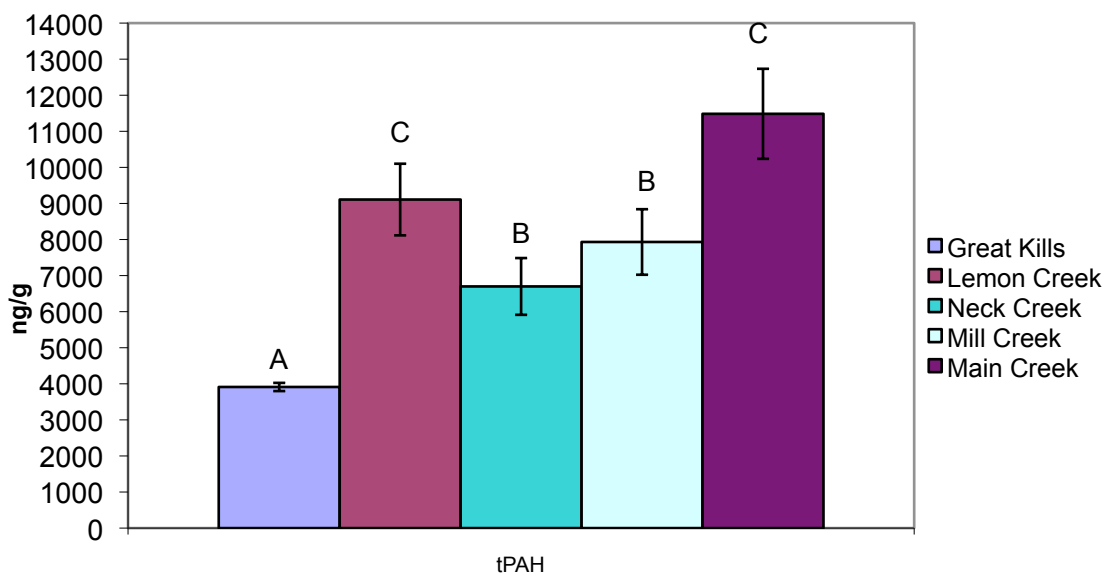
Full results for all 26 measured PAHs across all sites can be found in Appendix A, as well as the calculations for determining concentration and recovery. Average recoveries of surrogates were 64.5%, 91.5%, and 78.9% for d10-Anthracene, d10-Fluoranthene and d12-Benzo[e]pyrene, respectively.

Total PAH Sediment Concentrations

Table 1.1. Σ_{26} PAH Sediment Concentration (ng/g) for the five study sites

Location	Σ_{26} PAH Sediment Concentration \pm standard error (ng/g)
Great Kills	3912 \pm 113
Neck Creek	6699 \pm 787
Lemon Creek	9108 \pm 993
Mill Creek	7932 \pm 908
Main Creek	11484 \pm 1248

Figure 1.2. Σ_{26} PAH Sediment Concentrations showing within site variability.



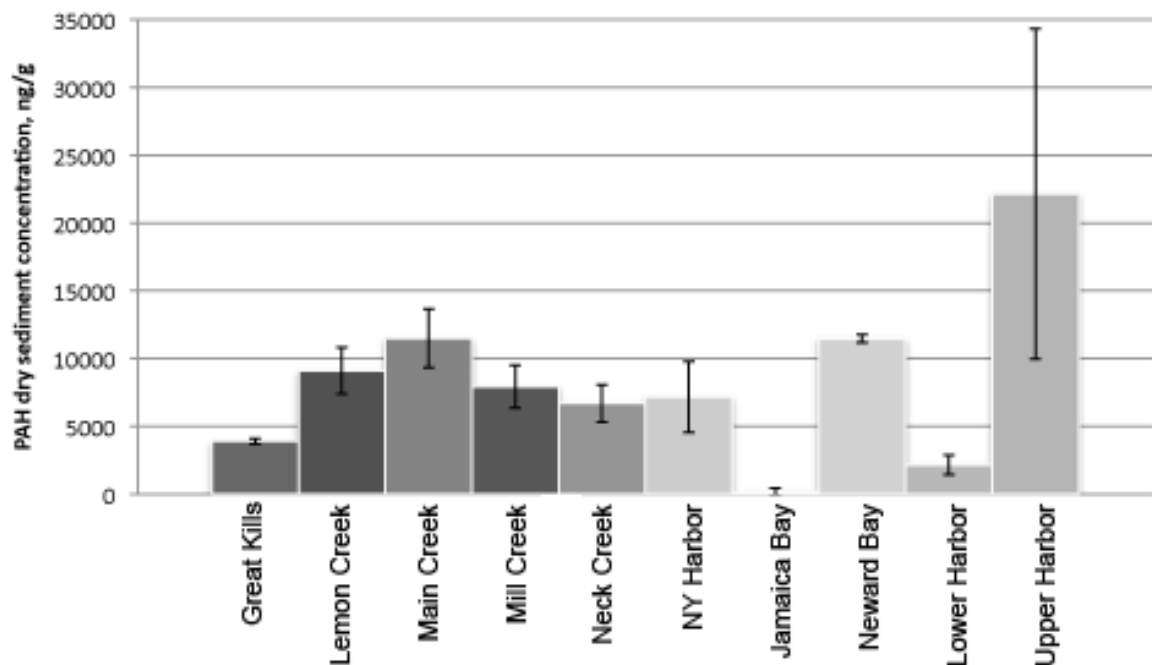
Analysis of Variance (one-way ANOVA) indicates that Σ_{26} PAH concentrations at the various sampling locations (Table 1.1; Figure 1.2) are significantly different from each other. Tukey's honestly significant different test indicates that Σ_{26} PAH sediment concentration at Great Kills is significantly different from that at Lemon Creek and Main Creek. However, Σ_{26} PAH is not significantly different at Neck Creek vs. Lemon Creek using Tukey's test. For the EPA CCs, one-way ANOVA indicates that levels of each component are significantly different for all six compounds at all five sites with the exception of Chrysene ($p < 0.06$).

Levels of Σ_{26} PAHs were highest at Main Creek and lowest at Great Kills. Dry sediment Σ_{26} PAHs sediment concentrations were similar for the sites at the ends of the Arthur Kill (Mill Creek and Neck Creek). The concentrations at these locations were elevated above Great Kills, but below the levels found at Main

Creek in the center of the Arthur Kill. Lemon Creek was the surprising site, with levels elevated above those found in Neck Creek or Mill Creek, despite the sampling site being outside of the Arthur Kill and on the south shore of Staten Island with exposure to New York Harbor.

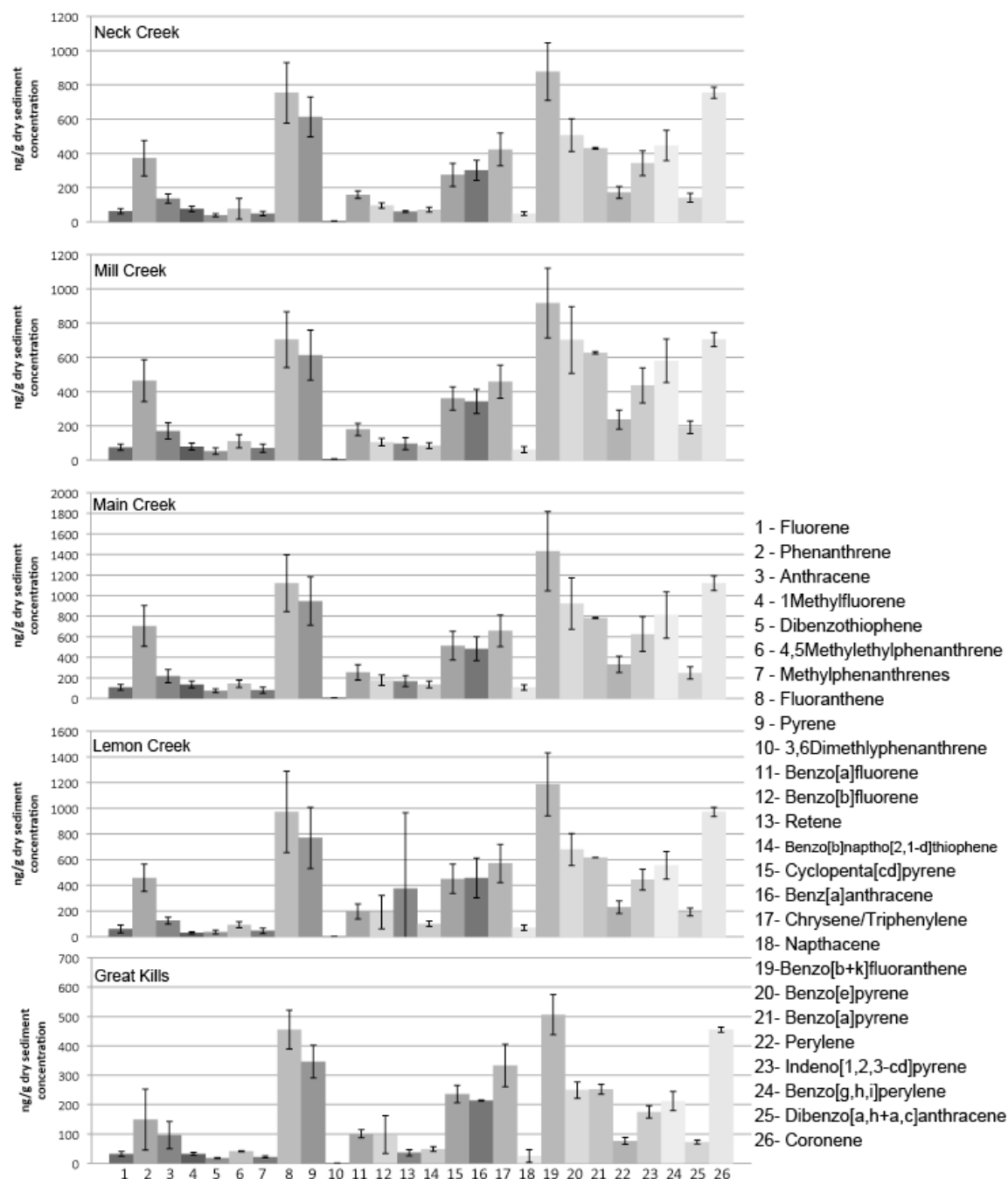
Σ_{26} PAH concentrations were within the range found by Adams et al. (1998). The highest dry-sediment concentrations (Main Creek) were similar to those found by Adams et al. in Newark Bay, and the lowest concentrations (Great Kills) were similar to those found in the Lower Harbor in the Adams study (see Figure 1.3).

Figure 1.3. Dry Sediment PAH concentrations, compared with Adams et al (1998). Concentrations measured in this study are in darker gray. Values from Adams et al. are in lighter gray.



Component PAH Concentrations

Figure 1.4. Concentrations of component PAHs for each site.



Concentrations of each of the 26 component PAHs are seen in Figure 1.4.

The relative concentrations of the various component PAHs do not appear to

vary from site to site. Levels of Fluoranthene, Pyrene, Chrysene/Triphenylene, Benzo[b+k]fluoranthene, Benzo[e]pyrene and Benzo[a]pyrene are relatively similar across the five sites, and are the dominant signals at each of the study sites.

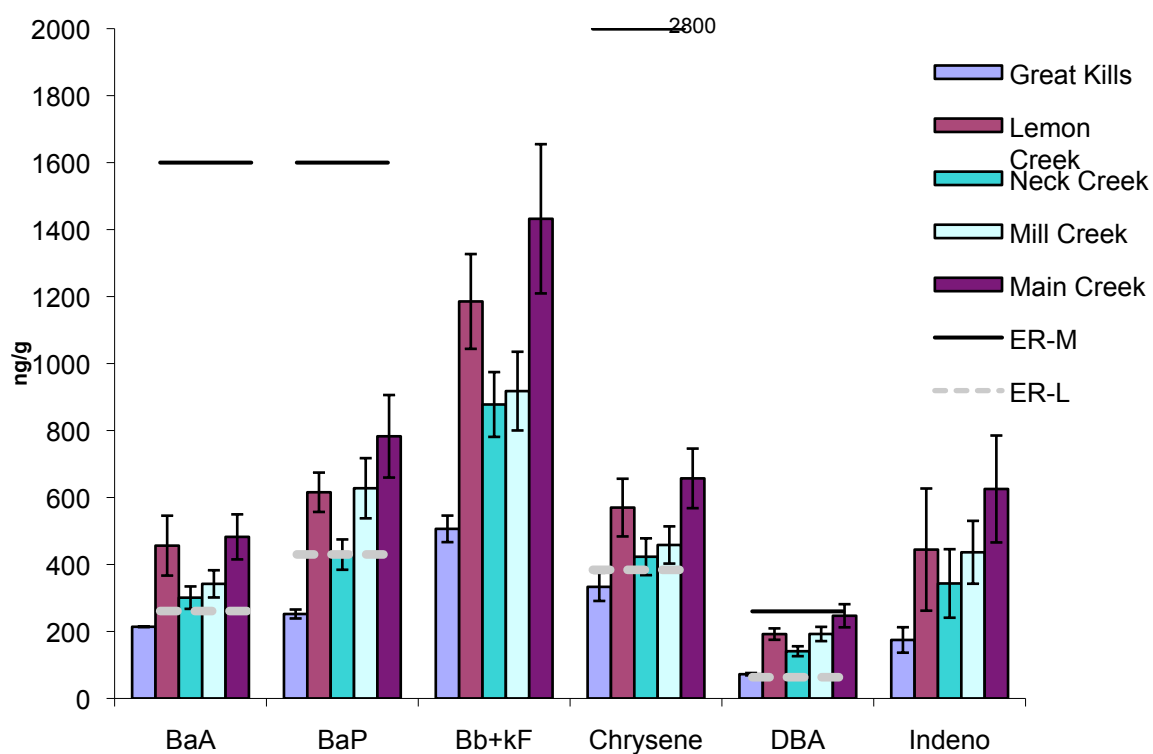
The six component PAHs listed as CCs by the EPA showed variable levels between sites (Figure 1.5), but the levels of each component were positively associated with the Σ_{26} PAHs sediment concentration. The percentage of Σ_{26} PAHs represented by each component changed very little across sites for the six CCs, representing $70 \pm 3\%$ of Σ_{26} PAHs. For the co-eluting DBA compounds, sediment concentrations were above NOAA ER-L levels for all sites. ER-L levels were exceeded for 4 of 6 CCs at the Main Creek and Lemon Creek sites (BaA, BaP, Chr, DBA). Mill Creek was also above ER-L levels for BaA, BaP, Chr and DBA. Neck Creek showed sediment concentrations above ER-L levels for Chr and DBA. Great Kills only exceeded ER-L for DBA. No ER-L or ER-M values were found for Indeno and Bb+kF. No sites were found to have sediment concentrations of any component PAH in excess of NOAA ER-M levels aside from the co-eluting DBA compounds.

Table 1.2. Concentrations of PAHs (ng/g) at the five sampling locations. PAH concentrations exceeding ER-L levels are in bold italics.

	ER-L ^a	ER-M ^a	Great Kills	Neck Creek	Mill Creek	Lemon Creek	Main Creek
BaA	261	1600	214	301	342	456	482
BaP	430	1600	252	430	628	616	783
Bb+kF	--	--	506	878	918	1185	1432
Chr	384	2800	333	423	<i>458</i>	560	657
DBA	63.4	260	72	141	192	192	247
Indeno	--	--	175	343	436	444	625
Σ24PAH	--	--	3912	6699	7932	9108	11485

^a from NOAA (1999).

Figure 1.5. Sediment concentrations (ng/g dry weight) of PAHs listed as EPA CCs. ER-L levels are shown as dashed lines, ER-M levels are shown as solid lines.



Organic Carbon-Normalized PAH Concentrations

PAHs sorb quickly and strongly to organic carbon (Shor et al., 2003) and to black carbon (Shor et al., 2004), and levels of organic carbon in sediment can greatly affect the toxicity of the PAHs. Sorption to the organic and black carbon reduces the bioavailability of the PAHs, thereby reducing the effective toxicity of a given sediment concentration (Shor et al., 2003). For this reason, sediment concentrations of PAHs are often normalized to organic carbon content (Farley et al., 1999; Weston et al., 2010; Paine et al., 1996; Erstfeld and Snow-Ashbrook, 1999) to account for the sorption effect. General benchmarks for sediments are given by Swartz (2009) where organic carbon-normalized PAH concentrations are used to determine the probable effects level. Organic carbon-normalized PAH sediment concentrations for all measured PAHs, Σ PAH, of 290 ug/g_{oc} is considered the threshold effect concentration (TEC). This level can be considered a guideline, as there is no canonical list of PAHs to be measured. The inclusion or exclusion of lighter, two and three ring PAHs (especially) may affect the concentrations (Mount, 2010). The median effect concentration (MEC) is 1,800 ug/g_{oc} and the extreme effects concentration (EEC) is >10,000 ug/g_{oc}. For the five sites studied, Σ_{26} PAH ranged from 44 to 211 ug/g_{oc}, below the TEC. These levels are in line with organic carbon-normalized PAH concentrations reported by Farley, et al.(1999) for both the New York Bight (5-90 ug/g_{oc}) and for Raritan Bay (60-300 ug/g_{oc}) sediments.

One-way ANOVA for organic carbon-normalized Σ_{26} PAH showed significant differences between the sites. Tukey's honestly significant difference test indicates that organic carbon-normalized Σ_{26} PAH concentrations are in two groups. The first group contains Great Kills and Neck Creek. The second contains Mill Creek, Lemon Creek and Main Creek. This differs from the groups created using in the non-organic carbon normalized case, where three groups (Great Kills by itself, Neck Creek and Mill Creek, and Lemon Creek/MainCreek) were suggested. Organic carbon lowers the PAH concentrations at the Neck Creek site, relative to the other sites, and raises the concentrations at Mill Creek, creating fewer groups. This can largely be attributed to the higher levels of organic carbon at Neck Creek.

Table 1.3. Total PAH values normalized for Organic Carbon. % Organic Carbon from Goto and Wallace (2010a).

Location	% Organic Carbon	Σ_{OC}PAH ug/g_{organic carbon}
Great Kills	8.70 ± 0.14	44.97 ± 2.4
Neck Creek	12.5 ± 0.36	53.59 ± 11.0
Mill Creek	4.92 ± 1.60	161.22 ± 61.4
Lemon Creek	5.95 ± 0.03	153.08 ± 28.9
Main Creek	5.43 ± 0.44	211.37 ± 43.4

EPA Equilibrium Partitioning Sediment Benchmarks

The EPA ESB is a calculation of the total danger represented by the concentrations of all of the PAHs in a given sediment sample, based on the

toxicity of the component compound and the organic carbon content (Hansen et al., 2003). The EPA method, outlined in Mount (2010), uses the 6 CCs PAHs used above as well as some 2-and 3-ring compounds not analyzed in this study. Sediment concentrations for individual PAHs are normalized to organic carbon concentrations and divided by Potency Factors that are unique to the compound and differ for chronic and acute effects levels (see Table 1.4 and Table 1.5). The values for all individual PAHs are summed to give the ESB value for either chronic or acute effects, depending on the potency factor applied. An ESB of 1 or greater indicates potential danger for either acute or chronic effects.

Table 1.4. EPA ESB levels - Acute potency. Values greater than 1 indicate potential for effects.

PAH	Alkylation factor	Potency (Acute)	Great Kills	Neck Creek	Mill Creek	Lemon Creek	Main Creek
BaA	1	3500000	0.0007	0.0007	0.0020	0.0025	0.0025
BaP	1	4020000	0.0007	0.0009	0.0032	0.0036	0.0034
Bb+kF	1	4075000	0.0014	0.0017	0.0046	0.0065	0.0065
Chrysene	5	3510000	0.0055	0.0048	0.0133	0.0172	0.0171
DBA	1	4660000	0.0002	0.0002	0.0008	0.0010	0.0010
Fluoroanthene	1	2940000	0.0018	0.0021	0.0049	0.0070	0.0071
Indeno	1	4620000	0.0004	0.0006	0.0019	0.0025	0.0024
Pyrene	2.1	2900000	0.0029	0.0036	0.0090	0.0126	0.0125
Fluorene	14	2240000	0.0023	0.0032	0.0096	0.0025	0.0113
Phenanthrene	6.8	2480000	0.0047	0.0082	0.0259	0.0036	0.0319
Perylene	1	4020000	0.0002	0.0003	0.0012	0.0065	0.0014
Benzo[e]pyrene	1	4020000	0.0007	0.0010	0.0035	0.0172	0.0040
Benzo[g,h,i]-perylene	1	4540000	0.0005	0.0008	0.0026	0.0010	0.0031
EPA ESB Level - Total			0.0221	0.0280	0.0824	0.0737	0.1101

Table 1.5. EPA ESB levels - Chronic potency

PAH	Alkylation factor	Potency (Chronic)	Great Kills	Neck Creek	Mill Creek	Lemon Creek	Main Creek
BaA	1	841000	0.0029	0.0029	0.0083	0.0091	0.0106
BaP	1	965000	0.0030	0.0036	0.0132	0.0107	0.0149
Bb+kF	1	980000	0.0059	0.0072	0.0190	0.0203	0.0269
Chrysene	5	844000	0.0227	0.0201	0.0552	0.0567	0.0717
DBA	1	1120000	0.0007	0.0010	0.0035	0.0029	0.0041
Fluoroanthene	1	707000	0.0074	0.0085	0.0202	0.0231	0.0292
Indeno	1	1110000	0.0018	0.0025	0.0080	0.0067	0.0104
Pyrene	2.1	697000	0.0120	0.0148	0.0375	0.0389	0.0525
Fluorene	14	538000	0.0096	0.0132	0.0399	0.0260	0.0520
Phenanthrene	6.8	596000	0.0195	0.0339	0.1076	0.0878	0.1481
Perylene	1	967000	0.0009	0.0014	0.0050	0.0040	0.0063
Benzo[e]pyrene	1	967000	0.0030	0.0042	0.0148	0.0118	0.0176
Benzo[g,h,i]-perylene	1	1090000	0.0022	0.0033	0.0108	0.0086	0.0137
EPA ESB Level - Total			0.0918	0.1164	0.3430	0.3067	0.4580

Sediment concentrations at the various study sites were corrected using the procedure outlined by the EPA using both acute and chronic potency divisors. Using this method, the levels of PAHs at the study sites did not exceed the acute or chronic benchmarks set by the EPA for total PAH contamination (see Table 1.4 and Table 1.5). This sediment benchmark should quantify the total toxicity, and hence the total biotic effect, of a suite of PAHs. No locale is close to 1 for either the acute potency values or chronic values, although several sites exceed 0.3 for the chronic potency values.

Source Apportionment

Ratios of certain PAHs components in field mixtures of PAH contamination can be used to determine the source of the contamination (Yunker et al., 2002). Ratios of Anthracene/[Anthracene + Phenanthrene] (An/178), Fluorene/[Fluorene + Pyrene] (Fl/Fl+Py), Benzo[a]Anthracene/[Benzo[a]Anthracene + Chrysene/Triphenylene] (BaA/228) and Indeno[1,2,3-cd]pyrene/[Indeno[1,2,3-cd]pyrene + Benzo[g,h,i]perylene] (IP/IP+Bghi) were calculated. An/178 ratios were most variable, largely due to the large variation in measured anthracene concentrations at Great Kills. An/178 ratios of >0.10 are indicative of combustion. Despite the large variation among sites, all are above this ratio, suggesting combustion rather than petroleum as the dominant source. Fl/Fl+Py ratios are considered less reliable than An/178 ratios as pyrene levels can be affected by weathering (Yunker et al., 2002). Fl/Fl+Py ratios are below the threshold of 0.4-0.5 for combustion, suggesting the possibility of petroleum as a PAH source. BaA/228 ratios of greater than 0.35 are combustion signals, and all of the sites are above this value. IP/IP+Bghi ratios of less than 0.20 are signals of petroleum, while 0.2-0.5 are indicative of liquid fossil fuel combustion. The ratios for PAHs at all five sites are within this range, indicating liquid petroleum combustion (Yunker et al., 2002). All of the ratios, aside from An/178 are fairly consistent across the sites for each ratio. This suggests similar sources for all of the sites.

Table 1.6. Source-apportionment diagnostic ratios values.

	An/178	Fl/Fl+Py	BaA/228	IP/IP + Bghi
Great Kills	0.39	0.09	0.39	0.45
Mill Creek	0.27	0.11	0.43	0.43
Lemon Creek	0.21	0.07	0.44	0.44
Neck Creek	0.27	0.09	0.42	0.44
Main Creek	0.24	0.10	0.42	0.44

Discussion

Σ_{26} PAH concentrations ranged from 3900 ng/g (dry weight sediment) at Great Kills to over 11480 ng/g (dry weight sediment) at Main Creek. On a dry weight basis, the Σ_{26} PAH levels at Great Kills are significantly lower than the other four sites. Of the component PAHs, only DBA shows sediment concentrations in excess of ER-L levels. However, DBA analysis is suspect as DBA is actually two co-eluting compounds using this analytical method. Leaving DBA aside, none of the other individual PAHs listed as CCs show concentrations near the ER-M level. The Main Creek site shows the highest levels of PAH sediment contamination on a dry weight basis, followed by Lemon Creek. That Main Creek would show high levels of PAHs in the sediment is not surprising. This site is both in the middle of the Arthur Kill, where flushing is lowest (Goto and Wallace, 2010b), and closest to Fresh Kills landfill, where leachate may have the greatest effect. This site also has levels of Ag, Cd, Hg, Ni and Zn that are the highest or very near the highest levels, and Specific Diversity and Richness

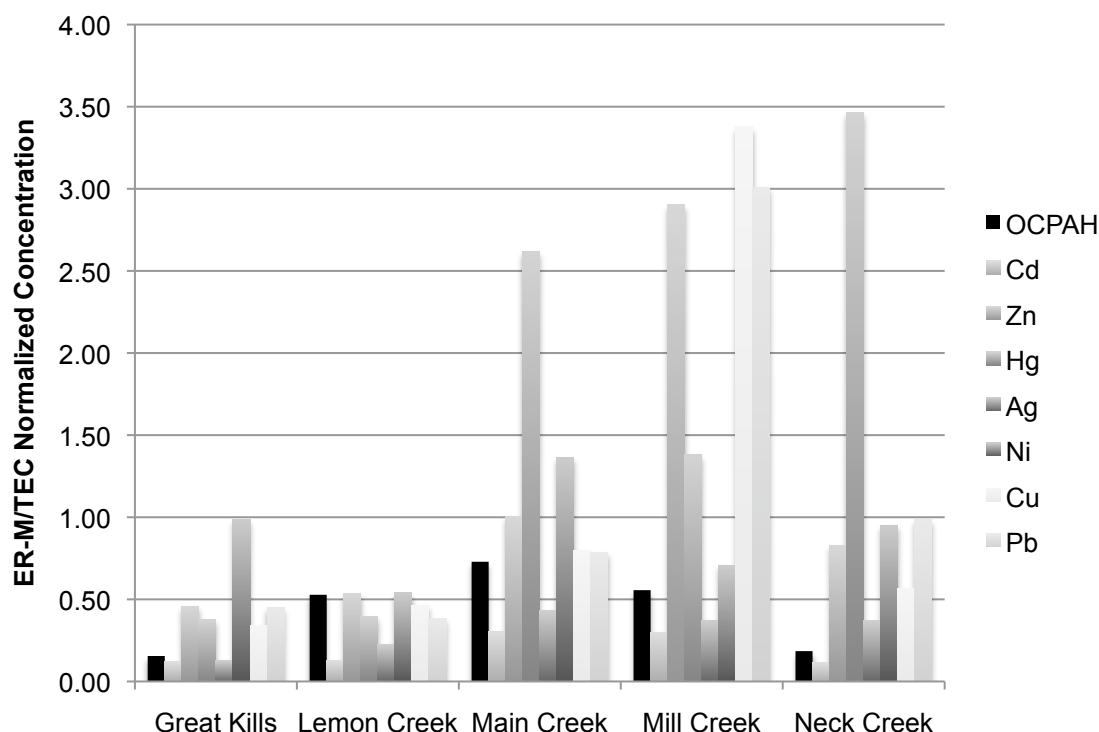
levels that are among the lowest (Goto and Wallace, 2010b). Main Creek, by these definitions, would be the most contaminated, and this analysis suggests that this description extends to PAH sediment levels. The sediment concentrations at Neck Creek and Mill Creek, both within the Arthur Kill, are intermediate, showing concentrations in excess of ER-L levels for BaA, BaP (at Mill Creek, and very close at Neck Creek) and Chrysene, but levels below ER-L levels for other individual PAHs.

The most surprising finding was the Σ_{26} PAH dry weight sediment concentrations at Lemon Creek. Metal concentrations at Lemon Creek are low, and PAH concentrations may be expected to follow this pattern. However, Lemon Creek levels were higher than expected for all PAHs and rivaled those of Main Creek in many instances. Using Tukey's honestly significant difference test, the organic carbon normalized Σ_{26} PAH concentration in Lemon Creek is in the same group as Main Creek, the most contaminated site, and with Mill Creek, a site within the Arthur Kill. While ANOVA shows a significant difference between the sites, the more sensitive Tukey's test indicates that Lemon Creek and Main Creek are comparable with regard to organic-carbon normalized PAH concentrations. Lemon Creek does have a history of a dental instrument factory, which, if using techniques similar to an aluminum smelter, may explain the high levels (Aas et al., 2001, Paine et al., 1996), as may the presence of an active marina nearby, as marinas can be sources of PAH contamination (Callier et al., 2009). Source analysis does not indicate a difference in diagnostic ratios

between Lemon Creek and the other sites with the exception of Great Kills, for one diagnostic ratio. Combustion sources are indicated from the diagnostic ratios (Yunker et al., 2002).

Organic carbon normalized Σ_{26} PAH concentrations at Lemon Creek are comparable to those at Mill Creek, owing to the higher organic carbon levels at Lemon Creek. However, as indicated above, Tukey's test indicates that Lemon Creek, Mill Creek and Main Creek form a group of high organic carbon normalized Σ_{26} PAH concentrations. Organic carbon normalized Σ_{26} PAH concentrations at Neck Creek are low, due to the high organic carbon content at that site, and bring the organic carbon normalized Σ_{26} PAH values in line with those found at the cleanest site (Great Kills). Tukey's test indicates that two statistically significant groups exist. The first is Great Kills and Neck Creek with low concentrations (<60 ug/g). The second includes Mill Creek and Lemon Creek (~160 ug/g), as well as Main Creek (>211 ug/g). While Main Creek appears to have higher concentrations of PAHs than Mill Creek and Lemon Creek according to ANOVA values, Tukey's test places these three sites in the same group. The same pattern holds for EPA ESB indices, with a low group, intermediate group, and Main Creek representing the highest levels.

Figure 1.6. ER-M normalized sediment metal concentrations and Organic-Carbon Normalized PAH concentrations. Values for metals are normalized to ER-M levels, with 1 representing the ER-M value for that metal. PAH concentrations were first normalized to the TEC value of 290 ug/g_{organic carbon} from Swartz, 2009.



The study sites represent an environmental gradient of contamination (Seebaugh and Wallace, 2009). Based on metal contamination and biotic indicators, the least impacted site appears to be the Great Kills location (Figure 1.4). Lemon Creek is the next least contaminated site, with Neck Creek and Mill Creek more contaminated, and the most contamination present at Main Creek. This pattern does not completely apply to levels of PAH contamination. First, the Neck Creek site appears to have lower Σ_{OC} PAHs and ESB levels than would be expected purely from correlating metals contamination to PAHs. This is largely attributable to the high levels of organic carbon at the site (>12%), which is more than double that found at any other site. The more surprising finding is the levels of PAH contamination at Lemon Creek. The levels at Lemon Creek for Σ_{26} PAHs,

Σ_{OC} PAHs and ESB levels are much higher than would be expected if the metal-contaminant gradient pattern were to hold, with Lemon Creek among the highest (comparable to Main Creek, a known polluted site), rather than being comparable with Great Kills, the site assumed to be cleanest.

The relative proportion of each component PAHs was quite similar across the sites. This suggests a similar origin of contamination, but more investigation is necessary, including Principal Component Analysis or Positive Matrix Factorization to determine the relative importance of various sources and to further determine the exact source mixture (Larsen and Baker, 2003).

Conclusion

Despite the contamination history of the Arthur Kill and the surrounding area, the sediments in this area are not contaminated at levels that are considered dangerous, or even above the threshold level for which biotic effects would be visible. Organic carbon-normalized PAH concentrations are near levels previously found in sediments in the area. The pattern of contamination found in studies of other contaminants is different when applied to PAH contamination, and when applied to different measures of PAH contamination. For all measures, Great Kills harbor was the cleanest site, and Main Creek was the most contaminated, consistent with the findings from other contaminants. The relative levels of the other sites are dependent on the measure chosen for comparison, due to varying levels of organic carbon at the sites. For non-organic carbon corrected measures, Lemon Creek exceeds levels at Mill Creek and Neck Creek,

a confounding finding possibly explained by the presence of a marina near Lemon Creek. However, when normalized to organic carbon, Lemon Creek and Mill Creek become comparable (for Σ_{OC} PAHs and ESB levels), and Neck Creek becomes comparable to the cleanest site at Great Kills.

Normalizing sediment concentrations to organic carbon amounts provides values for Σ_{OC} PAHs amounts below the TEC levels in all study sites. Likewise, sediment concentrations, when corrected for the varying toxic effects of various PAHs using EPA ESB values, are not above the level at which effects would be observed.

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Chapter 2. The Effect of Polycyclic Aromatic Hydrocarbons on Benthic Infaunal Communities

Abstract

Sediment contamination can affect the benthic macrofauna of the affected area. The Arthur Kill and surrounding areas of Staten Island have a long history of sediment contamination with metals. In the first chapter of this Thesis, Polycyclic Aromatic Hydrocarbon (PAH) contamination was measured in and around the Arthur Kill. In this work, Principal Component Analysis (PCA) and Canonical Correlation Analysis (CCA) were applied to organic-carbon normalized PAH sediment concentrations to determine the relationship between PAH levels and measures of diversity and abundance of benthic macrofauna at the various study sites. Previous analysis suggested that Hg was a major contaminant controlling diversity and abundance of benthic macrofauna. With PAHs included in the analyses, Hg remains the most important factor. Organic-carbon normalized PAH levels do not appear to be well-correlated with changes in diversity or biomass for any of the classes of benthic macroinvertebrates surveyed in previous studies.

Introduction

The Arthur Kill is a relatively small, tidally influenced waterway between Staten Island, New York and New Jersey. It is relatively short (12 km), bounded

on the north by Kill van Kull and on the South by the Great Kills Harbor and New York Harbor. The tidal range in the area is on the order of 3-4 feet (1.2 m), but the Arthur Kill has rather constrained circulation, as tides come in from both the north and south, and sources of fresh water are generally small and heavily industrialized. Much of the New Jersey side of the river is bulwarked with metal or wood, and many docks and piers are present. The Staten Island side of the Arthur Kill, while slightly less industrialized, has some anthropogenic bulwarks and piers. However, salt marshes and tidal creeks can be found on the Staten Island side, in which sea birds, mussel beds, clams, fiddler crabs, mummichogs and many species of invertebrates can be found (Berger, 1994; Perez and Wallace, 2004; Khoury, et al., 2007; Goto and Wallace, 2009).

The communities of benthic macrofauna residing in and around the Arthur Kill on Staten Island have shown various ill effects from long-term pollution in the area (Goto and Wallace, 2010). Metal contamination in the Arthur Kill has been measured in several assays of the study sites (Perez and Wallace, 2004; Seebaugh and Wallace, 2009, Goto and Wallace, 2009 from Ward 2002; see Table 2.3). Elevated levels of Cd and Hg have been found in mummichogs (*Fundulus herteroclidus*) (Goto and Wallace, 2009), polychaetes (*Nereis acuminata*), and shrimp (*Palaemonetes pugio*) from these study sites (Perez and Wallace, 2004). Benthic macroinvertebrate assemblages varied according to levels of metal contamination among the sites, particularly in response to Hg levels (Goto and Wallace, 2010). Perez and Wallace (2004) found that, for grass

shrimp (*P. pugio*), feeding behavior was adversely affected by the elevated levels of metals in study site sediments. Fiddler crabs (*Uca pugnax*) likewise exhibited reduced feeding activities when subject to contaminated sediment from Merideth Marsh (synonymous with Neck Creek) (Khoury et al., 2007). Goto and Wallace (2010) found that various measures of diversity and abundance of macroinvertebrates were most strongly correlated with elevated Hg levels. While many environmental variables were accounted for in their correlative analysis, Polycyclic Aromatic Hydrocarbon (PAH) levels were not considered.

In Chapter 1, PAHs were measured in sediments in and around Arthur Kill, at the same study sites where Goto and Wallace (2010) determined levels of metals. Organic carbon-normalized PAH levels (expressed in ng/g_{oc}, rather than ng/g_{dry sediment}) were reported. The threshold effects concentration (TEC) is the lowest concentration where effects would be expected to be seen from PAH contamination. By convention, this value is 290 ng/g_{oc} (Swartz, 2009). The levels found in and around the Arthur Kill are below this level, ranging from 45 ng/g_{oc} at the Great Kills Harbor site, to 211 ng/g_{oc} at Main Creek. Nevertheless, these PAHs could influence the ecology of the Arthur Kill. Berger (1994) and Klepper et al. (1998) have demonstrated that persistent pollution, as that found in historically heavily industrialized areas, such as the Arthur Kill and New York Bight, can produce subtle effects on organisms.

PAH contamination is generally a complex mixture of various PAHs in varying amounts. Depending on the mix of individual PAHs and the amount of organic carbon in the sediment, the total toxicity of given suite of PAHs can be

determined. The toxicity of PAHs is assumed to be additive - that is, the toxic effect of each individual compound adds to the toxic effect or risk posed by every other (Hansen, 2003). In addition to toxicity and genotoxicity of PAHs and their metabolites, Roesijadi et al. (2009) found that the presence of benzo[a]pyrene, a known carcinogen, greatly increased the rate of induction of metallothionein mRNA in the intestines of fish in response to Cd ingestion. The nearly doubling of metallothionein expression in the presence of benzo[a]pyrene indicates that combined exposure enhances the toxicity of Cd in a non-linear way. The mechanism for enhancing toxic effect per unit dose may involve increased absorption of Cd through the intestinal walls in the presence of benzo[a]pyrene (Roesijadi et al., 2009).

Sediment pollution, even at low levels, can change community structure, especially among the benthic macrofauna (Warwick et al., 1987, Rakocinski et al., 2000). In the Arthur Kill, changes in benthic macrofauna have been well documented (Goto and Wallace, 2010; Koury et al., 2007; Perez and Wallace, 2004). However, the changes to community structure, as measured by changes in diversity and abundance, are not often simple linear relationships, especially when multiple sources of contamination are present (Callier et al., 2009). For contamination levels above standard effect levels, a weak linear relationship between contamination and diversity or abundance measures may be present (Callier et al., 2009). For entire communities, the response to pollutants may be complex, with some species increasing in abundance while other decrease (Gray, 1979). The increase may be a result of tolerance to the pollutant, or a

result of decreased competition as other species are adversely affected by the pollutant (Gray, 1979). Mixtures of pollutants create further contingencies and interrelationships. Because of this, linear relationships between levels of pollutants and diversity or abundance measures are not expected. Multi-variate regression methods, such as Principal Component Analysis (PCA) and Canonical Correlation Analysis (CCA), are better suited for determining the influence of multiple contaminants across multiple species (Terr Braak, 1987, Rakocinski et al., 2000, Archimbault et al., 2010, Bioechi et al., 2009). CCA, in particular, has been used by Callier et al. (2009) in an attempt to relate the abundance of species in a marina to multiple environmental parameters. Goto and Wallace (2010) used CCA to determine the relative importance of various environmental parameters, including metal pollution, dissolved oxygen, salinity, and other measures, on both diversity and abundance of benthic macroinvertebrates in and around the Arthur Kill. The purpose of this study was to determine the relationship between concentrations of PAHs in the sediments and measures of species diversity and abundance at the various study sites in the Arthur Kill via the use of PCA and CCA.

Materials and Methods

Study Sites

The study site and measured PAH concentrations were presented in Chapter 1. Sediment was sampled from five sites on Staten Island near and

within the Arthur Kill (Figure 1.1). These sites have previously been assayed for metal pollution, as well as various environmental factors including % Organic Carbon, salinity, and dissolved oxygen. In general, sites outside the Arthur Kill (Great Kills, Lemon Creek) are less contaminated and have higher dissolved oxygen than sites within the Arthur Kill (Main Creek, Neck Creek and Mill Creek). However, organic-carbon normalized PAH sediment concentrations ($\Sigma_{OC}PAH$) are comparable at Lemon Creek and Mill Creek (outside and inside the Arthur Kill, respectively) and Great Kills and Mill Creek (also outside and inside the Arthur Kill, respectively).

For the present analysis, measures of benthic macroinvertebrate infauna were provided by Daisuke Goto (pers. comm.). These included biomass at each site (measured in g/m^2) and number of individuals at each site (per m^2), summarized in class-level groups. Summary measures of diversity are from Goto and Wallace (2010) for each study site. Diversity measures include Margalef's index, Shannon-Wiener index, and Heip's index. Margalef's index and the Shannon-Wiener index use the total number of individuals and the number of species present to generate a measure of diversity present in a given ecological assemblage. Heip's index calculates the evenness of distribution among species based on the number of species and their distribution. Diversity indices generally range from 0-3.5, with higher values indicating higher diversity (Heip & Engels, 1974). Sediment concentrations of metals, organic carbon, dissolved oxygen and salinity at each site are from Goto and Wallace (2010).

Table 2.1. Benthic Macrofauna Biomass (g/m²)

Class	Lemon Creek	Great Kills	Mill Creek	Main Creek	Neck Creek
Polychaeta	4.18	5.63	3.50	24.55	9.09
Insecta	0.02	0.00	0.00	0.02	0.00
Crustacea	0.09	0.04	0.06	1.47	0.19
Bivalvia	1.65	0.17	0.35	0.00	0.03
Oligochaeta	0.06	0.12	0.41	0.38	0.29
Gastropoda	1.80	6.91	12.90	0.00	0.00
Nemertinea	0.00	0.00	0.00	0.00	0.03
Sipunculodea	0.00	0.00	0.00	0.00	0.01
Anthozoa	0.00	0.00	0.00	0.00	0.01

Table 2.2. Benthic Macrofauna Abundance (individuals/m²)

Class	Lemon Creek	Great Kills	Mill Creek	Main Creek	Neck Creek
Polychaeta	173	753	396	700	615
Insecta	1	0.4	0.4	2	0.6
Crustacea	9.8	3	4.2	30.8	10.2
Bivalvia	9.2	6.4	11.4	0	0.8
Oligochaeta	62.4	78.6	269	293	277
Gastropoda	0.2	1.8	2.8	0	0.2
Nemertinea	0	0	0	0	5.4
Sipunculodea	0	0	0	0	1.8
Anthozoa	0	0	0	0	1.4

Table 2.3. Metal concentrations at study sites (From Goto and Wallace, 2010). Bold Italics indicate levels of metal concentrations above NOAA ER-M levels.

Metal (ug/g)	ER-M	Lemon Creek	Great Kills	Mill Creek	Main Creek	Neck Creek
Ag	3.7	0.83	0.48	1.38	1.59	1.37
Cd	9.6	1.2	1.14	2.88	2.9	1.08
Cu	270	125	92.2	912	216	153
Hg	0.71	0.28	0.27	0.98	1.86	2.46
Ni	51.6	27.9	50.9	36.5	70.3	49
Pb	218	83.9	98.7	656	171	215
Zn	410	220	188	1190	411	339

Numerical Analysis

Linear regression of Σ_{OC} PAH versus various environmental variables was performed using MS Excel. R^2 values were determined using simple linear trend lines. Correlation analysis using Spearman's rank (ρ) was performed using XLstat-ADA (2010 Addinsoft). Spearman's rank correlation determines whether a monotonic function can represent the relationship between the data points. A p-value of less than 0.05 indicates that the relationship between variables is significant. Principal Component Analysis (PCA) and Canonical Correspondence Analysis (CCA) were performed using XLStat-ADA (2010 Addinsoft). PCA results were analyzed to determine relationships between environmental variables. In PCA, correlated variables are reduced by creating artificial variables that account for most of the variance between the variables. Multi-dimensional data can then be projected on to these variables for visual analysis (Schlens 2005). CCA is intended to visualize the pattern of community variation and also visualize the main features of community distribution in relation to changing environmental variables (Terr Braak, 1987). The axes of a CCA plot represent the solutions to eigenvalue equations that maximize the distribution of entities along the environmental variables (Terr Braak, 1987). Similar to PCA, the axes of the resulting biplot from CCA are artificial variables representing variation in the system. Results generated from CCA (using XLStat) include the eigenvalues representing the correlation between environmental and biological variables; inertia along the axes, which is effectively the variance of the system; a biplot of

results, which allows for visual determination of correspondence and relative importance; and a summary of p-values, hypotheses and null hypotheses. CCA was run with 1000 permutations, and a p-value of 0.05 was selected for significance.

Results

Linear Regression versus Ecological Indices

Σ_{OC} PAH levels at each site were regressed against various ecological variables to identify any potential variables with a simple linear relationship to Σ_{OC} PAH. Biomass (g/m^3), Total Diversity, Richness and Specific Diversity values from Goto and Wallace (2010) showed no significant linear relationship with Σ_{OC} PAH levels. R^2 values were highest for biomass ($r^2=0.43$; Figure 2.1), and all other measures showed r^2 values <0.13 . Regression against % biomass for polychaetes and oligochaetes was performed to determine if class-specific relationships exist. R^2 values were all <0.3 , and were not well correlated (based on Callier et al., 2009).

Figure 2.1. Biomass v $\Sigma_{oc}PAH$ concentration.

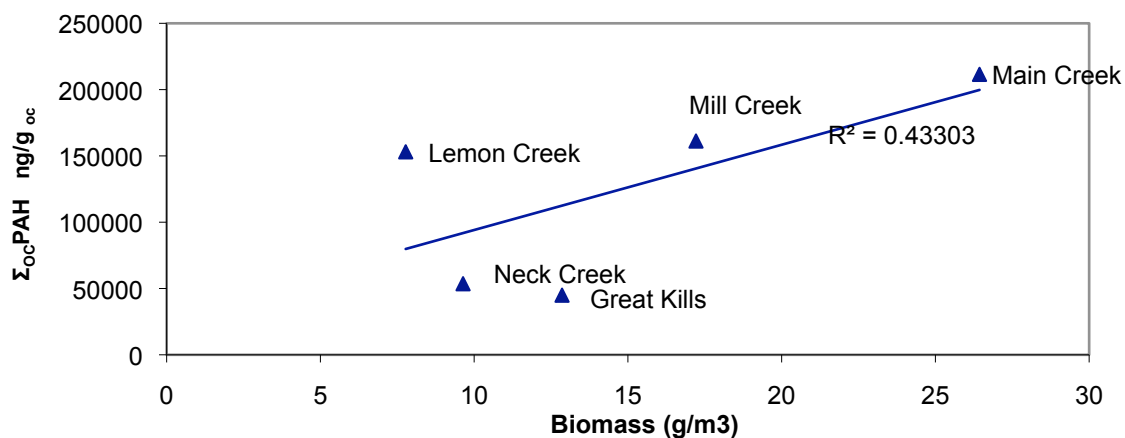


Figure 2.2. $\Sigma_{oc}PAH$ levels versus Total diversity from Goto and Wallace (2010).

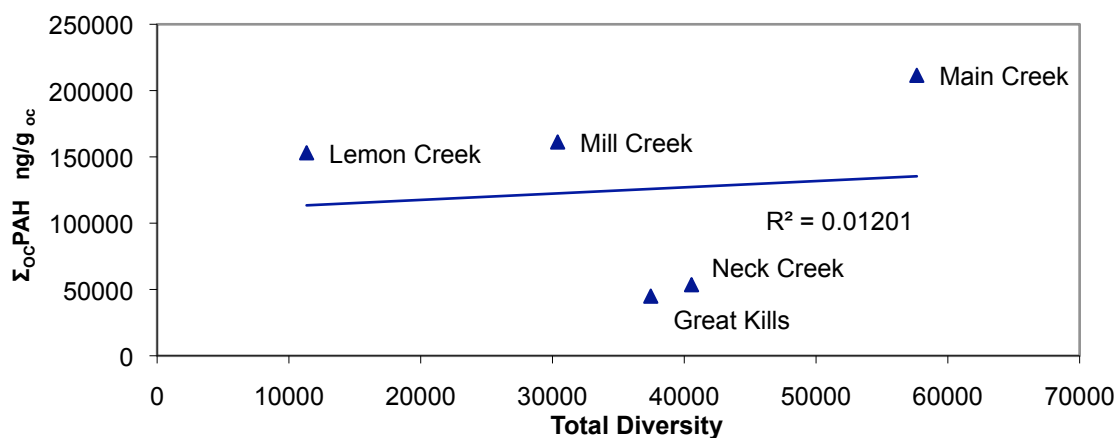


Figure 2.3. Richness and Species Diversity Indices for the study sites, plotted against $\Sigma_{oc}PAH$. Diversity indices from Goto and Wallace (2010).

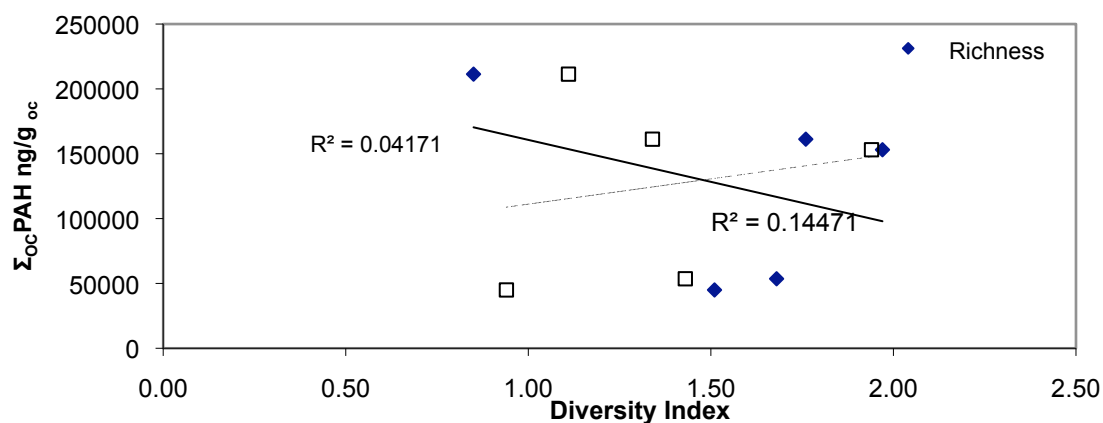
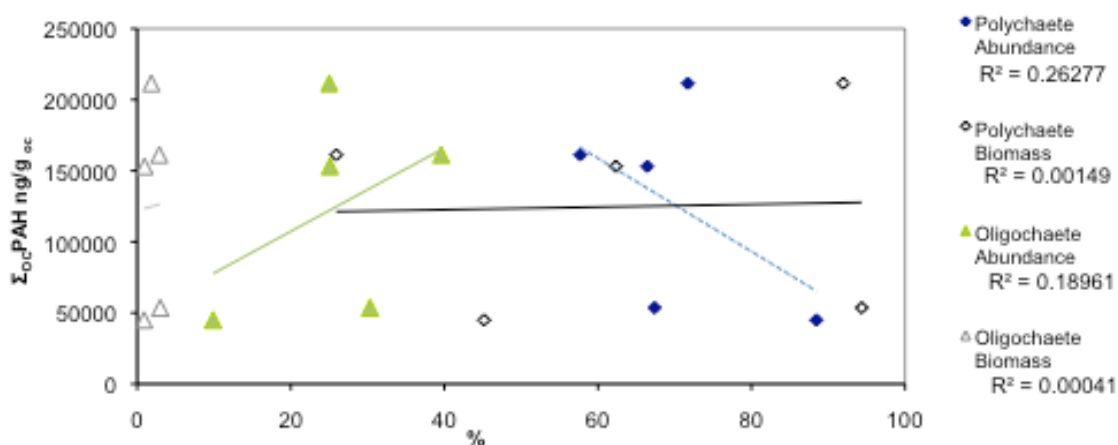


Figure 2.4. Percent Polychaetes and Oligochaetes as a fraction of Total Biomass and as a fraction of Total Abundance (number of individuals). Data from Goto (pers. comm).



Spearman Rank Correlation

Table 2.4. Spearman rank p-value results. Values in bold are significant ($p < 0.05$).

Variables	$\Sigma_{OC}PAH$	Cd	Zn	Hg	Ag	Ni	Cu	Pb	Salinity	DO
$\Sigma_{OC}PAH$	0	0.083	0.133	0.517	0.083	0.950	0.133	0.683	0.233	0.450
Cd	0.083	0	0.350	1.000	0.233	0.783	0.350	0.950	0.450	0.233
Zn	0.133	0.350	0	0.350	0.083	1.000	0.017	0.133	0.683	0.950
Hg	0.517	1.000	0.350	0	0.233	0.783	0.350	0.350	0.450	0.683
Ag	0.083	0.233	0.083	0.233	0	0.683	0.083	0.350	0.350	0.783
Ni	0.950	0.783	1.000	0.783	0.683	0	1.000	0.950	0.950	0.683
Cu	0.133	0.350	0.017	0.350	0.083	1.000	0	0.133	0.683	0.950
Pb	0.683	0.950	0.133	0.350	0.350	0.950	0.133	0	0.783	0.350
Salinity	0.233	0.450	0.683	0.450	0.350	0.950	0.683	0.783	0	0.350
DO	0.450	0.233	0.950	0.683	0.783	0.683	0.950	0.350	0.350	0
Poly	0.950	1.000	0.950	0.450	0.683	0.133	0.950	0.950	0.450	0.683
Insecta	0.683	0.517	0.683	0.950	0.950	0.517	0.683	0.233	0.233	0.083
Crust	0.350	0.683	0.517	0.133	0.233	0.683	0.517	0.950	0.083	0.683
Bivalvia	0.783	0.950	0.783	0.350	0.450	0.083	0.783	0.683	0.683	0.950
Oligo	0.350	0.450	0.083	0.450	0.133	0.683	0.083	0.083	1.000	0.783
Gastro	0.683	0.950	1.000	0.350	0.517	0.450	1.000	0.783	0.133	0.517
Nemer	0.517	0.133	1.000	0.233	1.000	1.000	1.000	0.517	1.000	0.233
Sipun	0.517	0.133	1.000	0.233	1.000	1.000	1.000	0.517	1.000	0.233
Anth	0.517	0.133	1.000	0.233	1.000	1.000	1.000	0.517	1.000	0.233

Spearman's rank correlation likewise revealed little or no significant correlations between species abundance and contaminant concentrations (Table 2.4). Correlation was attempted using class-level biomass values for benthic

macrofauna and environmental indicators (metal contamination, salinity, dissolved oxygen) from Goto and Wallace (2010). $\Sigma_{OC}PAH$ values were not significantly correlated with any of the environmental variables.

Principal Component Analysis

Principal component analysis (PCA) was performed for both class-level biomass measures and diversity (total abundance) levels. The results of both analyses are similar. In both cases, over 64% of the variability in the environmental data is explained by the first two principal components. The results are presented in the form of biplots (Figures 2.5 and 2.6). In these plots, the red vectors are the projection of the data points from multi-dimensional space into two dimensional space, where the axes are the principal components (artificial variables which explain the variability of the system). The sites are plotted as blue circles, representing the position of the sites relative to the principal components. The environmental variables for each site (diversity/abundance or contaminant concentration) are plotted as the red vectors. Grouping of vectors or points indicate which items are more closely related. Items close together can be explained by the same sets of principal components, and may therefore be related. However, the exact nature of the relationship is not defined by PCA, as the axes do not represent real environmental variables, but artificial variables that explain variance in the data. The grouping of all site points near one contaminant vector would indicate a strong influence of that contaminant on the variation between the sites. Likewise,

grouping of all of the sites in one quadrant would suggest a common set of factors explaining the variability in the data. . For both abundance and biomass, the sites are widely distributed, with different environmental factors near each site. $\Sigma_{OC}PAH$ is not plotted closely to any of the study sites in the biplots for both abundance and biomass (Figure 2.5 and Figure 2.6). This lack of proximity indicates there may be no relationship between elevated levels of PAHs at the site and high biomass/low diversity.

The points for the study sites are widely distributed on the plots. This lack of a grouping among all of the sites suggests that different variables are contributing to the variation at each site. Great Kills and Lemon Creek reside in the same quadrant, suggesting that similar factors are affecting these sites. Main Creek and Mill Creek occupy completely separate halves of the plot, above the second axis, as the other sites, suggesting that the factors affecting Main Creek and Mill Creek are different than those affecting the Great Kills/Lemon Creek group. Neck Creek is in a group by itself, suggesting a completely different set of influences for that site. The relatively wide distribution among all of the sites suggests that a variety of factors is influencing variability at each location. Additionally, that only 64% of the variability in the data is described with two principal components indicates that other, unmeasured factors are probably influencing the biomass and diversity.

Figure 2.5. Principal Component Analysis using class-level abundance.

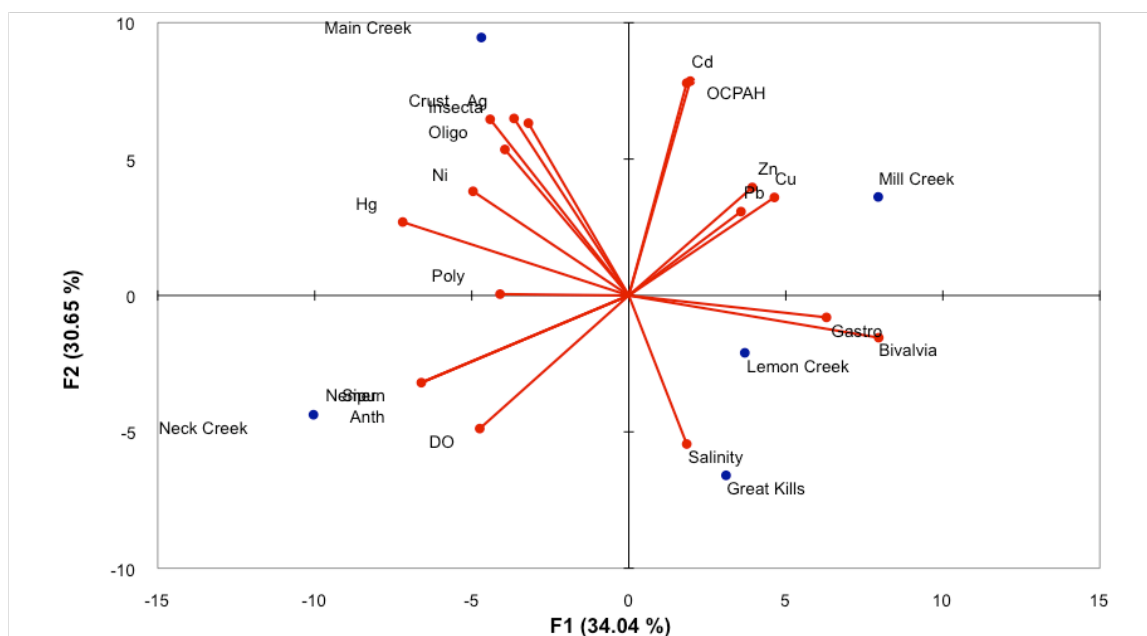
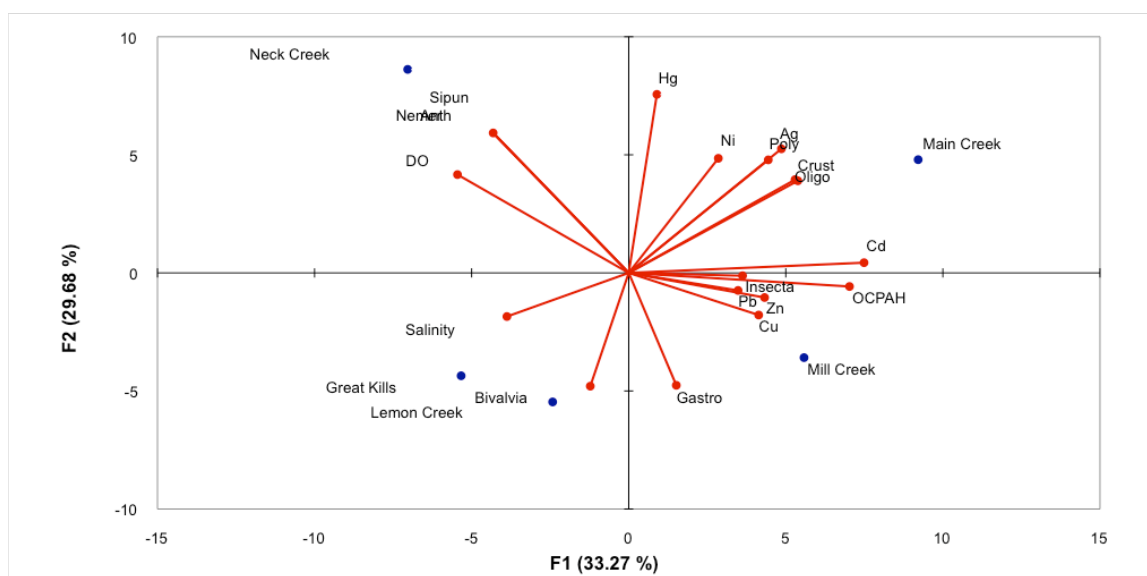
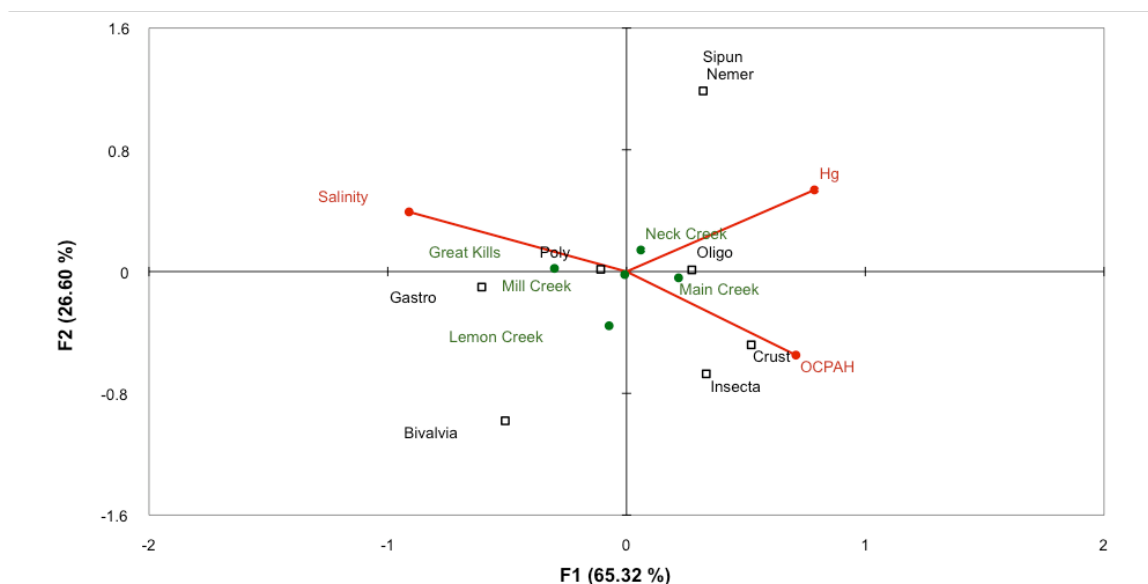


Figure 2.6. Principal Component Analysis using class-level biomass



Canonical Correspondence Analysis (CCA)

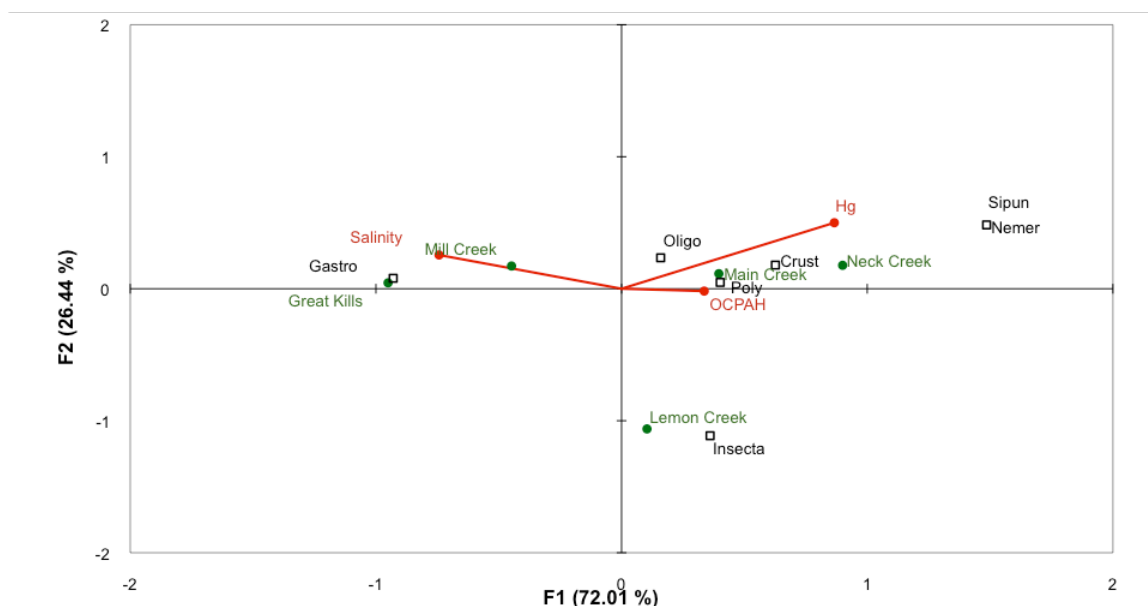
Figure 2.7. CCA biplot for Organic Carbon-Normalized PAH levels, Environmental variables and class-level abundance measures



Canonical Correspondence Analysis (CCA) was performed to determine whether there is a linear relationship between environmental data (salinity, Hg, and $\Sigma_{OC}PAH$ concentrations at each site) and the class-level abundance values. The results are again presented in the form of a biplot (Figures 2.7 and 2.8). In such plots, the red vectors are the environmental variables plotted in multi-dimensional space. The points for the classes and locations are the locations the biological data and sites in multi-dimensional space. By convention, the environmental variables are represented as vectors. The results of the CCA analysis of abundance indicate that the environmental variables (salinity, Hg and PAH levels at each site) and biological variables (abundances at each site) were not linearly correlated (permutation test: $F=0.553$, $P=0.852$). For statistically significant systems, the length of the environmental data vector indicates the

importance of that factor. For systems where the relationship is not linear ($p > 0.05$), the grouping of the environmental data points and the biological and site data may indicate possible relationships. However, this is limited to qualitative analysis, and with high p values, any findings may be suspect. Similar to PCA, the axes of the biplot (see Figure 2.7 and **Error! Reference source not found.**Figure 2.8) represent the variability of the system. In CCA, this term is the inertia of the system. In the case of abundance, most of the inertia is carried by the first axis ($F1 = 65.3\%$). The second axis carries 27% of the inertia, with the two accounting for 92% of the inertia (or variance). This indicates that over 90% of the variance in the system can be represented on a two-dimensional plot using these axes. No clear groupings are seen on the plot. Neither Hg nor $\Sigma_{OC}PAH$ are close to the points representing any of the locations. Great Kills is midway between Hg and $\Sigma_{OC}PAH$. The point for $\Sigma_{OC}PAH$ is in the same quadrant as Crustacean and Insecta abundance, but the p -value of this analysis is so high (0.82) that any association is quite possibly due to chance. The various vectors for the environmental factors (Hg, salinity, $\Sigma_{OC}PAH$) are roughly the same length, indicating no clear difference in relative importance of the factors. Again, because of the high p value, it cannot be determined if this result is because of the influence of PAHs or, more likely, due to chance.

Figure 2.8. CCA biplot for $\Sigma_{OC}PAH$ and class-level biomass.



The CCA biplot results for class level biomass (Figure 2.8) indicate that, as with diversity, the environmental variables (salinity, Hg concentration and $\Sigma_{OC}PAH$) and the class-level biomass values are not linearly related ($F=1.139$, $p=0.63$). Again, most of the inertia (variability) is carried/explained by the first axis ($F1 = 72.01\%$), with the second axis carrying 26.44%. These two axes account for over 98% of the variability in this system. In this plot, Hg is a more important factor (longer vector and more closely associated with other factors). However, the high p value again indicates that there is no linear relationship between the environmental variables and per-class biomass.

Discussion

Simple linear regression of $\Sigma_{OC}PAH$ found no significant relationship between measures of diversity or abundance, in agreement with other analyses (Callier et al., 2009). Multiple contaminants at sub-lethal levels are found at

every location, confounding simple analysis such as linear regression. The failure of linear regression to supply a satisfactory relationship between PAHs and diversity or abundance necessitates the application of multivariate statistical approaches.

PCA does not show evidence for a relationship between $\Sigma_{OC}PAH$ and the abundance and biomass of various benthic invertebrates at the study sites. Mill Creek is the closest site to the $\Sigma_{OC}PAH$, but other environmental variables are much closer than $\Sigma_{OC}PAH$. $\Sigma_{OC}PAH$ does appear to be associated with Cd in both plots. If Cd and $\Sigma_{OC}PAH$ are related, this could increase the potential impact of Cd contamination on the benthic infauna (Bioechi et al., 2010).

Additional analysis using CCA does not show a linear relationship between $\Sigma_{OC}PAH$ and biomass or abundance. CCA also indicates no linear relationship between biomass/abundance and Hg or salinity. This is somewhat surprising since Goto and Wallace (2010) found that these two environmental variables were the strongest indicators of biomass and abundance in this region. This lack of a relationship supports the PCA results of no strong relationship between $\Sigma_{OC}PAH$ levels at the study sites and diversity or abundance.

The $\Sigma_{OC}PAH$ levels at the study sites were all below the TEC levels outlined by Swartz (2009). The highest $\Sigma_{OC}PAH$ concentrations of 211 ng/g_{oc} were measured at Main Creek, and TEC levels are 290 ng/g_{oc}. Klepper et al. (1999) suggest that persistent pollutants, such as PAHs, may have effects without being at levels generally considered the effects level. However, studies

on the effects of PAH contamination on various invertebrate classes by Erstfeld and Snow-Ashbrook (1999) showed that low level contamination had no noticeable effect on many classes, with only some benthic invertebrates showing effects. Paine et al. (1996) found no effect on survival of benthic invertebrates in sediments highly contaminated with PAHs. In both studies, the sorption of PAHs to organic carbon was proposed as a method of reducing the bioavailability of sediment PAHs, reducing their potential effects. This finding is supported by Shor et al. (2003, 2004), who argue for the recalculation of the potential toxicity of contaminated sediment in relation to both the organic carbon and black carbon content in order to correctly characterize the toxicity of a specific sediment. While organic carbon normalization may partially account for this, black carbon may have an additional effect. For the sediments in and around the Arthur Kill, the sediment PAH concentrations are not only below toxic thresholds, but may also exhibit limited bioavailability.

Conclusion

Various statistical methods of correlating ecological properties of the benthic macrofauna communities in the waterways in and around the Arthur Kill with Σ_{OC} PAH sediment concentrations did not reveal any significant relationships. Measures of diversity, biomass and abundance were tested using linear regression, Spearman correlation, PCA and CCA. These analyses suggest that no linear relationship exists between Σ_{OC} PAH and biomass or abundance. The lack of a significant relationship between Σ_{OC} PAH levels and biomass or

abundance could be due to Σ_{OC} PAH concentrations being below standard threshold levels for effects.

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Summary, Limitations and Future Research

Sediment concentrations of PAHs at five study sites in and around the Arthur Kill, Staten Island, New York were determined using isotope dilution mass spectrometry. Sediment concentrations of PAHs at all study sites ranged from 4000 to 11480 ng/g dry sediment. These values are below published thresholds for toxic effects on benthic organisms, but within the range of previously published studies for the New York Bight and Raritan Bay area. Normalized for organic carbon content in the sediments, concentrations ranged from 45 to 211 ng/g_{organic carbon}, which is below the accepted critical threshold for biotic effects. The pattern of PAH contamination was similar to that found for metals, with the least contaminated site (Great Kills) being the site most open to tidal flushing. The site closest to the middle of the Arthur Kill showed the highest concentrations of PAHs among the five sites studied. The Lemon Creek site, which has low levels of metal contamination, has PAH sediment concentrations comparable with the most contaminated site. The source for this elevated PAH contamination was not identified, although a nearby marina is a possible source.

From the PAH concentrations measured in Chapter 1, the effects of PAHs on the benthic infaunal community was analyzed. Using community data from previous studies on the effects of metals at the same sites, the relationship between PAH concentrations and biotic diversity indices, abundance, and biomass were examined. Various statistical analyses did not yield evidence of a relationship between PAH concentrations and diversity or abundance of benthic

infauna. PAH levels do not appear to have an effect on benthic community dynamics. The limited bioavailability of PAHs as a result of sorption to black carbon and organic carbon at the study sites or the low levels of PAHs measured at each site are possible reasons for the lack of a relationship. It is also possible that there are too few data points in this study (five sites, using class-level data) to show more subtle trends in community dynamics as a result of PAH contamination. However, for the scope of this project, PAHs are not a driving factor in determining the community dynamics in and around the Arthur Kill.

Limitations

There are several limitations to the broader application of the results presented in this study. For the determination of PAH concentrations, a limited number of study sites were sampled, sampling was performed only once, and only three replicates per sample were analyzed. In determining biological effects, no sediment toxicity assays were performed on benthic organisms, and the data used to analyze the effect was class-level data. The limited study sites and sampling may hide broader spatial variations in PAH concentrations, and also limited the data set, making some statistical analyses less exact. Seasonal variations in sediment load and runoff may be affecting PAH concentrations, but a single sampling excursion cannot measure this. Using class level data for analysis provides a more limited data set than using genus or species level data, which may have had an impact on results. Sediment toxicity assays would provide direct evidence of toxic effects on organisms of soils with a given PAH

concentration, and could indicate if certain organisms are resistant or particularly at risk to PAH contamination.

Future Research

Based on the results presented here, multiple avenues of future research are possible. Sampling at more sites along the Arthur Kill, and outside the Arthur Kill, may provide a clearer picture of the kinds of contaminant gradients in the area. Sediment studies, indicating the direction of sediment movement, may help in determining the source of PAH contamination. Analyzing the ratios of various PAHs can be used to determine the origin of PAHs, and could be performed using the detailed analytical data. Sediment cores from the study sites would allow analysis of the sediment profile to determine changing in PAH concentrations with depth and over time, providing another dimension for data analysis. The initial results presented here may provide a starting point for multiple future research efforts.

	Sample ID	678.01	678.01	6778.02	6778.02	6778.03	6778.03	6748.04	6748.04	6776.05	6776.05	6771.05	6771.05	6776.06	6776.06
PAH		Mass (ng)	Conc ^a (ng/g)	Mass (ng)	Conc ^a (ng/g)	Mass (ng)	Conc ^a (ng/g)	Mass (ng)	Conc ^a (ng/g)	Mass (ng)	Conc ^a (ng/g)	Mass (ng)	Conc ^a (ng/g)	Mass (ng)	Conc ^a (ng/g)
Fluorene	F	37.79	26.87	1170.40	41.64	92.99	28.17	200.70	58.91	182.04	72.40	195.36	58.91	182.04	72.40
Phenanthrene	Ph	278.52	198.04	853.07	29.71	723.36	219.12	1131.96	393.26	1122.91	488.76	1184.50	393.26	1122.91	488.76
d10-phenanthrene (m1)	d10Ph	100.00	71.10	100.00	3.56	100.00	30.30	100.00	29.57	100.00	29.77	100.00	29.57	100.00	29.77
Acenaphthene	An	100.60	71.53	100.00	1.69	100.00	6.73	100.00	43.41	100.00	43.41	100.00	43.41	100.00	43.41
d10-acenaphthene (Bart)	d10An	70.32	50.00	593.92	21.13	65.34	19.27	61.67	18.10	58.38	23.22	65.10	18.10	58.38	23.22
1-methylfluorene	MFl	39.18	27.86	1030.47	36.66	105.90	32.08	279.32	81.99	245.91	97.80	119.83	81.99	245.91	97.80
Dibenzothiophene	Dt	22.75	16.18	534.47	19.01	63.17	19.14	116.14	34.21	116.14	50.26	151.68	34.21	116.14	50.26
4-methylbenzothiophene	4-Mdt	57.20	40.67	1101.94	39.20	141.16	42.77	249.84	73.33	273.66	108.84	308.36	73.33	273.66	108.84
Methylbenzanthracene	MtBa	25.31	17.99	677.55	24.11	78.34	23.73	207.78	60.99	132.13	52.55	200.93	60.99	132.13	52.55
Methylbenzofluoranthene	MtBF	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Fluoranthene	Fl	851.65	510.01	1508.74	382.18	2151.79	473.57	3024.97	550.93	3260.78	880.67	2280.77	550.93	3260.78	880.67
d10-fluoranthene (Bart)	d10Fl	84.14	49.80	83.68	21.05	89.46	19.69	97.22	18.03	85.65	23.13	111.81	18.03	85.65	23.13
Pyrene	Py	659.86	390.57	1122.88	284.43	1656.22	2485.11	2485.11	460.82	2787.24	752.78	2222.60	460.82	2787.24	752.78
d10-pyrene (m1)	d10Py	100.00	59.19	100.00	25.33	100.00	22.01	100.00	18.54	100.00	27.01	100.00	18.54	100.00	27.01
3,6-dimethylphenanthrene	3,6-DMP	0.76	0.45	0.00	0.00	5.59	1.23	24.45	4.53	18.57	5.01	30.96	4.53	18.57	5.01
Benzofluorene	BuF	158.64	93.90	460.84	116.76	418.83	92.18	737.88	136.85	740.14	199.90	711.72	136.85	740.14	199.90
Benzofluoranthene	BuF	65.27	65.27	676.84	171.45	252.55	55.58	429.58	79.66	452.17	122.12	404.05	79.66	452.17	122.12
Retene	Ret	67.31	59.84	95.68	24.24	201.58	44.36	380.12	66.78	331.38	89.50	478.00	66.78	331.38	89.50
Benzofluoranthene-1-ylchlorophene	BuF-1-Cl	75.24	44.53	228.67	57.92	195.88	43.11	377.88	70.09	384.28	103.79	287.34	70.09	384.28	103.79
Cyclopentadecylpyrene	Cyc15	387.13	219.13	1056.36	267.74	955.07	210.19	1637.14	403.13	1603.60	403.13	1227.04	403.13	1603.60	403.13
Benzo[a]anthracene	BaA	360.18	213.19	852.69	215.99	967.42	214.76	1523.44	383.50	1554.94	419.77	1153.90	383.50	1554.94	419.77
Chrysene/triphenylene	Chrt	523.61	309.92	1638.01	414.92	1248.46	274.76	2065.70	583.05	2098.22	566.69	1511.59	583.05	2098.22	566.69
Naphthalene/triphenylene	NtPh	70.95	41.99	2.35	0.60	139.35	30.71	79.41	54.59	29.45	60.87	110.79	54.59	29.45	60.87
Benzofluoranthene	BuF	960.10	558.28	1707.54	432.53	2355.16	518.33	4188.48	776.68	4261.81	1151.03	2275.74	776.68	4261.81	1151.03
d10-benzofluoranthene (Bart)	d10-BuF	253.87	795.76	1138.15	219.76	1138.15	219.76	2474.75	492.50	2473.18	726.58	2292.36	492.50	2473.18	726.58
d13-benzofluoranthene (Bart)	d13-BuF	80.14	50.30	76.37	21.26	82.36	19.88	88.14	18.51	78.42	23.36	82.46	18.51	78.42	23.36
Benzofluorene	BuF	421.49	264.54	816.34	215.41	1104.13	266.54	2184.88	451.33	2293.24	655.96	1926.78	451.33	2293.24	655.96
d13-benzofluorene (m1)	d13-BuF	100.00	62.76	100.00	27.62	100.00	24.14	100.00	20.66	100.00	29.78	100.00	20.66	100.00	29.78
Pyrene	Py	125.14	79.54	229.59	63.43	361.50	87.27	853.49	176.51	832.06	247.81	740.15	176.51	832.06	247.81
Indeno[1,2,3-cd]pyrene	Ind1P	285.32	179.08	525.53	152.04	798.68	184.40	1318.48	318.84	1638.76	485.09	1312.33	318.84	1638.76	485.09
Dibenz[a,h]pyrene	BbP	218.90	639.05	176.48	594.45	240.06	2117.97	7171.97	1437.51	2095.81	624.19	1762.21	1437.51	2095.81	624.19
Dibenz[a,h]acanthracene	BbA	115.42	72.44	240.11	66.31	324.03	78.44	728.01	150.59	699.25	208.25	598.26	150.59	699.25	208.25
Coronene	Cor	137.13	86.07	280.35	77.42	391.12	94.42	772.12	159.50	787.88	228.69	600.59	159.50	787.88	228.69
Benzo[ghi]perylene	BghiP	-	4059.69	-	3689.11	-	3987.90	-	6133.94	-	9053.98	-	-	-	-
mass of internal acid (mg)		100.00		100.00		100.00		100.00		100.00		100.00		100.00	
mass of sample (g)		2.02		4.78		5.11		5.88		4.35		3.20		100.00	
μ surrogate added		100.00		100.00		100.00		100.00		100.00		100.00		100.00	
μ I.S. added		100.00		100.00		100.00		100.00		100.00		100.00		100.00	
PAH surrogate recoveries (%)															
d13-antanthracene		34.27		28.99		31.80		31.80		30.06		28.45		28.45	
d15-benzofluorene		53.82		53.15		57.22		57.22		62.19		54.77		54.77	
d13-benzofluorene		46.57		44.73		47.87		47.87		51.23		45.58		45.58	
Conc ^a = surrogate corrected concentration (ng/g)															

Samples 1-3 = Great Mills
Sample 4-6 = Mill Creek
Samples 7-9 = Lannon Creek
Samples 10-12 = Neck Creek
Samples 13-15 = Main Creek
Samples_1A = Main Creek samples for Quality assurance
MS = Matrix Spike.

	G75B.07		G72.08		G74D.09		G75.10		G80.11		G77B.12		G82D.1A	
Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	
94.89	194.66	48.82	141.58	34.56	391.24	94.97	174.57	71.35	160.93	46.32	152.54	71.84	342.94	
573.45	2006.55	503.27	1376.57	336.03	2203.91	534.99	1089.25	445.20	880.02	253.31	885.56	417.09	2191.11	
48.42	100.00	25.08	100.00	24.41	100.00	24.27	100.00	40.87	100.00	28.78	100.00	47.10	100.00	
221.30	538.30	94.22	385.98	94.22	596.72	144.85	366.98	149.99	363.07	104.51	322.46	151.88	633.78	
31.56	73.48	18.43	72.72	17.75	77.05	18.70	66.79	27.30	73.25	21.09	67.01	31.56	72.34	
58.01	81.38	20.41	141.77	34.61	139.22	33.79	186.06	76.05	207.65	59.77	192.65	90.74	421.80	
73.44	127.82	32.06	95.93	32.42	213.71	51.88	112.49	46.98	97.65	28.68	91.32	43.01	235.86	
149.31	397.32	99.65	266.02	65.43	459.23	111.48	260.02	106.28	22.65	6.52	248.30	116.95	439.74	
97.29	152.93	38.36	121.85	29.74	287.90	69.89	133.65	54.63	115.93	33.37	124.33	58.56	238.11	
-	-	-	-	-	-	-	-	-	-	-	-	-	-	
669.38	6988.52	1332.84	4246.86	830.95	4480.76	749.34	2890.80	821.24	2375.24	552.55	2712.66	886.96	4945.47	
31.44	96.26	18.36	90.36	17.68	111.40	18.63	95.71	27.19	90.28	21.00	96.15	31.44	98.18	
624.91	5469.24	1043.11	3338.65	653.25	3650.07	610.42	2336.73	663.84	2065.10	480.40	2128.23	695.87	4162.33	
28.12	100.00	19.07	100.00	19.57	100.00	16.72	100.00	28.41	100.00	23.26	100.00	32.70	100.00	
8.70	11.39	2.36	8.11	1.59	15.40	2.58	22.83	6.49	18.91	4.40	14.11	4.61	27.37	
200.11	1383.12	263.79	812.84	159.04	988.08	164.91	605.69	172.07	571.79	133.02	518.51	169.54	1080.23	
113.60	1789.78	341.34	592.55	115.94	691.14	115.58	340.82	96.82	339.29	78.93	339.63	111.05	764.47	
134.40	188.24	35.90	161.38	31.77	6309.25	1055.13	228.46	64.90	240.08	55.85	195.24	63.84	699.27	
80.79	650.22	124.01	435.18	85.15	539.97	90.30	276.16	78.46	242.23	56.35	242.95	79.44	594.10	
345.00	3039.49	579.69	2082.44	407.45	2171.83	363.21	777.46	220.87	1081.85	251.67	1071.61	350.39	2251.30	
324.26	3311.21	631.70	2038.69	398.89	2022.68	338.26	1157.60	328.86	1007.15	234.29	1039.12	339.76	2208.11	
424.98	3878.59	739.72	2607.19	510.13	2249.95	459.89	1670.13	474.47	1346.47	313.23	1473.12	481.67	3045.88	
48.01	482.33	91.99	330.07	64.58	309.43	51.75	170.28	48.37	165.97	38.61	184.31	60.27	479.75	
825.41	7692.01	1467.20	5457.92	1067.91	6106.04	1021.14	3404.86	967.28	2942.19	684.44	3001.90	981.54	6338.22	
876.45	3465.33	730.02	2589.37	536.35	3422.93	769.08	1872.77	570.33	1607.38	397.57	1459.59	551.56	3588.02	
31.75	88.01	18.54	86.30	17.86	83.74	18.81	90.17	27.46	85.76	21.21	82.29	31.75	85.30	
745.71	3339.15	703.46	2433.71	504.11	2845.64	639.37	1571.15	478.48	1371.01	339.11	1220.83	471.01	3027.68	
38.50	100.00	21.07	100.00	20.71	100.00	22.47	100.00	30.45	100.00	24.73	100.00	38.58	100.00	
284.98	1235.39	260.25	839.61	173.91	1128.97	253.66	652.88	198.83	539.66	133.48	478.52	184.62	1300.99	
505.28	2269.72	478.15	1701.81	352.71	2236.74	502.56	1281.98	390.41	1051.05	259.97	984.01	379.65	2365.12	
678.49	2710.62	571.03	2121.03	439.34	2911.64	654.20	1667.96	507.96	1391.16	344.09	1257.35	485.10	3177.12	
218.79	1015.41	213.91	765.89	158.64	907.77	203.96	519.08	158.08	450.77	111.49	397.80	153.48	976.53	
231.24	1022.03	215.31	854.82	177.06	1102.55	247.72	605.28	184.33	517.55	128.01	482.17	186.03	1246.61	
8608.17	100.00	10703.37	7286.78	9334.90	7381.55	5129.93	100.00	5129.93	100.00	5129.93	100.00	5129.93	100.00	
-	5.48	-	5.69	-	5.40	-	3.70	-	4.79	-	3.20	-	5.81	
-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	
-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	-	100.00	
31.77	-	35.82	-	35.44	-	37.55	-	32.55	-	35.70	-	32.66	-	
71.52	-	61.57	-	57.80	-	71.26	-	61.22	-	57.75	-	61.50	-	
47.93	-	51.15	-	50.10	-	48.67	-	52.40	-	49.84	-	47.83	-	

0788_14		0828_15		084D_1A		071C_1A		074C_1A		082D_1A		074_MS	
Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)	Conc* (ng/g)	Mass (ng)
82.41	214.11	105.28	369.21	137.66	289.09	108.70	288.26	119.98	254.30	94.27	342.94	82.41	0.80
526.52	1364.70	671.08	2460.44	917.52	2296.12	883.40	1872.16	779.23	1663.43	670.07	2191.11	526.52	6.15
24.03	100.00	49.17	100.00	37.29	100.00	37.60	100.00	41.62	100.00	40.23	100.00	24.03	100.00
153.74	443.11	217.94	757.02	282.30	684.75	257.48	534.36	222.41	438.63	200.62	639.78	153.74	0.10
17.38	56.12	27.60	63.58	23.71	59.42	22.35	53.33	22.20	60.64	24.40	72.34	17.38	66.84
101.36	284.01	139.66	445.34	166.07	373.97	140.62	365.11	151.97	103.01	41.45	421.80	101.36	4.22
56.68	156.88	77.14	241.65	90.48	198.30	74.79	196.12	81.63	160.33	64.51	235.86	56.68	0.00
105.67	298.86	146.96	471.48	175.82	260.99	98.14	349.31	145.39	349.55	140.64	439.74	105.67	1.14
57.22	144.48	71.05	303.52	113.18	0.00	0.00	322.11	134.07	218.65	87.97	238.11	57.22	0.62
872.14	3350.76	1418.66	5011.22	1072.45	4569.10	1037.95	3943.02	934.97	3713.82	948.93	4945.47	872.14	7.03
17.31	64.92	27.49	110.35	23.62	97.97	22.26	93.24	22.11	95.10	24.30	98.18	17.31	75.12
734.03	2833.40	1199.62	4226.37	904.48	3939.29	694.88	3284.49	778.82	3159.18	807.21	4162.33	734.03	5.50
17.64	100.00	42.34	100.00	21.40	100.00	22.72	100.00	23.71	100.00	25.55	100.00	17.64	100.00
4.83	16.91	7.16	38.49	8.24	0.00	0.00	57.66	13.67	0.00	0.00	27.37	4.83	0.40
190.50	789.36	334.20	1087.35	232.70	1112.72	232.77	92.63	21.96	891.27	227.73	1080.23	190.50	1.25
134.82	551.02	233.29	754.76	161.52	749.55	170.27	588.75	139.60	572.77	146.35	764.47	134.82	0.77
113.32	538.77	228.11	719.51	153.98	683.88	155.36	566.40	134.30	504.13	128.81	699.27	113.32	2.33
104.77	402.14	170.26	600.10	128.43	531.94	110.84	481.62	114.20	426.52	108.98	594.10	104.77	1.20
397.02	1576.13	667.31	2217.40	474.54	2101.98	477.50	1900.95	450.75	1116.74	285.34	2251.30	397.02	2.06
389.40	1448.00	613.06	2079.06	444.94	2035.04	462.30	1752.79	415.62	1712.19	437.48	2208.11	389.40	1.69
537.15	1962.48	830.88	2819.25	603.34	2745.97	633.80	2479.31	587.89	2318.58	592.42	3045.88	537.15	5.95
84.60	322.46	136.52	453.09	96.96	396.68	90.11	356.14	84.45	238.47	76.26	479.75	84.60	0.00
1117.23	4399.48	1862.67	6151.76	1316.75	5715.77	1298.44	5066.28	1201.32	4854.00	1140.26	6335.22	1117.23	11.86
735.18	2211.75	826.39	3744.48	1205.06	3316.50	1018.29	3081.11	1008.42	3105.19	930.83	3586.02	735.18	4.88
17.49	74.20	27.76	74.11	23.85	73.21	22.48	68.23	22.33	81.87	24.54	85.30	17.49	55.46
620.71	1881.67	703.06	3183.80	1024.62	2805.09	861.52	2821.12	923.33	2633.44	789.41	3027.68	620.71	3.35
20.50	100.00	37.36	100.00	32.18	100.00	30.70	100.00	32.73	100.00	29.98	100.00	20.50	100.00
286.72	820.16	306.44	1305.59	420.17	1195.28	367.00	1151.12	377.08	923.37	276.79	1300.99	286.72	0.00
485.70	1547.11	578.09	2525.05	812.62	2183.89	670.54	2408.95	788.43	2165.86	649.25	2369.12	485.70	6.75
651.35	1916.14	715.94	3321.13	1068.82	2722.65	897.37	3135.56	1026.24	2801.11	839.66	3177.12	651.35	8.73
200.20	605.40	226.20	976.57	314.28	886.71	272.26	927.64	303.61	834.69	250.21	976.53	200.20	0.00
255.57	720.14	269.07	1186.74	382.57	1179.49	362.15	1301.02	425.81	1067.54	320.01	1246.61	255.57	0.00
8988.81	100.00	12756.06	100.00	12709.54	100.00	11376.49	100.00	11365.16	100.00	10355.48	100.00	8988.81	100.00
	3.56		4.26		4.52		4.55		4.14		5.81		100.00
	100.00		100.00		100.00		100.00		100.00		100.00		100.00
	100.00		100.00		100.00		100.00		100.00		100.00		100.00
35.26		27.35		30.99		28.96		25.99		29.55		35.26	
62.80		41.53		70.58		62.67		59.64		60.83		62.80	
49.57		43.18		43.07		42.55		39.65		47.58		49.57	