Study of Polycyclic Aromatic Hydrocarbons in Pike River Sediment

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) are organic compounds constructed with two or more aromatic rings. Many of these compounds are considered probable carcinogens by the EPA and can cause adverse health effects in aquatic organisms. They are a byproduct of the incomplete combustion of carbon and are released by the burning of fossil fuels. Significant anthropogenic sources of PAHs include the dissolution of coal-tar sealants or large spills of oil-based products. As a result, industrial sites and other sources such as sealed pavement can cause problematic concentrations in the environment.

The Pike River flows through southeast Wisconsin into Lake Michigan. The North Pike and Pike River are listed as impaired by the DNR, which has raised concern within the community and prompted remediation efforts. The history of industrial activity in this region suggests the potential for PAH contamination, but no previous data had been collected. In this study, sediment samples were collected from 5 sites in the Pike River. Each sample was extracted, cleaned, and analyzed for 16 EPA priority pollutant PAHs using a GC-MS. The results provide a baseline for future monitoring through the Root-Pike Watershed Initiative.

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Introduction

Despite our efforts of preservation, the history of pollution is far and deep. Dichlorodiphenyltrichloroethane (DDT), is one of the most well-known examples for a chemical compound causing havoc in our ecosystems, and it appropriately increased our level of awareness for these toxins. In more recent years researchers detected a parallel compound structure known as Polycyclic Aromatic Hydrocarbon (PAH). There are more than 100 different PAHs (ASTR 1995). The ubiquitous compounds are created by the incomplete combustion of carbon, which includes the burning of fossil fuels to simply burning your toast in the toaster. There are many sources, but coal-tar sealants have been proven to release a dangerously high level of these toxins. Certain PAH compounds are carcinogenic and may cause negative health effects in large quantities such as cancer, mutations, and other genetic altering complications. Besides having a negative consequence on human health, they can largely impact the aquatic species. While individual compounds either volatilize, degrade, or become embedded in the sediments of our water bodies, cumulatively PAH compounds can persist in the environment for a long amount of time .

Cycle and Persistence

Each compound consists of two or more condensed aromatic rings rarely found in nature individually, but rather as complex mixtures of varying PAHs (EPA). PAHs with two to three rings are present in the air as a vapor while those with four rings exist in both vapor and particulate phases, and five or more rings remain in the particulate phase. Types with 3 rings include: naphthalene, acenaphthene, acenaphthylene, anthracene, fluorene, phenanthrene; 4 rings: fluoranthene, pyrene, chrysene, benz[a]anthracene; 5 or more rings:

benzo[a] pyrene, benzo [g,h,i] perylene (Neff 1979). The higher molecular weight PAHs
(e.g., fluoranthene, benzo[a]pyrene) are products of combustion, whereas the lower
molecular weight PAHs (e.g., naphthalene, fluorene) are generally derived from unburned
petroleum sources and alkylated PAHs (Orane 2010). The more rings the compound has the
higher its molecular weight will be, which influences the behavior of the molecule in the
environment.

Figure 1: Chemical Structure of the 16 Priority PAH compounds listed by the EPA (Fähnrich
2002).
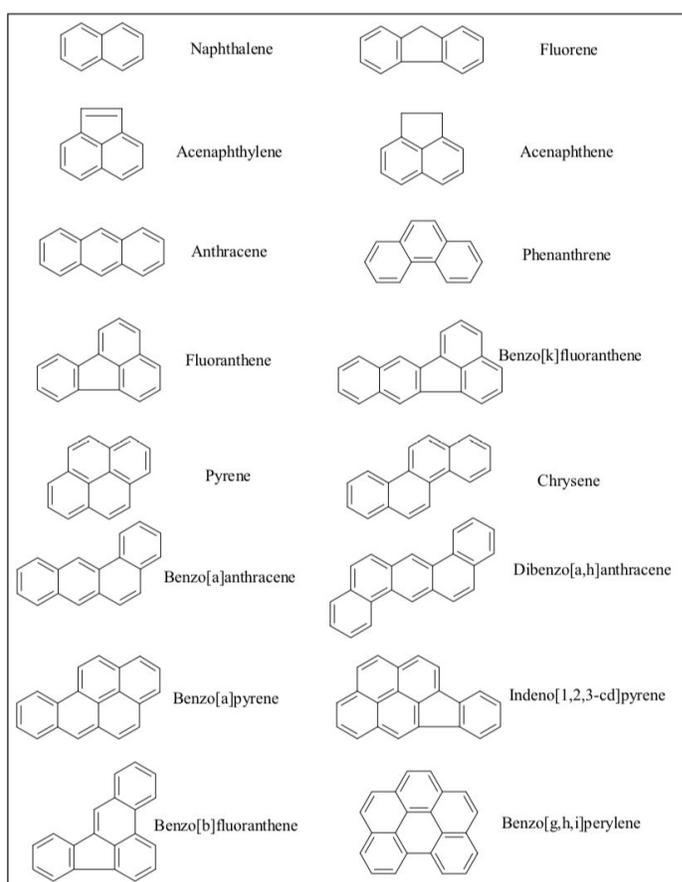
Atmosphere

As the molecular weight of the compound decreases the vapor pressure increases, which means that it will volatilize more easily into the atmosphere (Neff 1979). The lowest molecular weight PAH such as Naphthalene and Pyrene (2-3 Benzene rings) are more abundant in the gas phase and are transported worldwide, preferentially to the poles (Orane 2010). Atmospheric fallout of airborne PAHs occurs during rain, dry fall out, or vapor phase deposition (Neff 1979). In contrast, high molecular weight PAHs are characterized by higher temperatures of condensation and are attached to airborne particles. While this usually means more rapid deposition close to the source, ultimately the size of particulate that the PAH is adsorbed to is a primary determinant of particulate PAH residence time and dispersal distance (Rivandra 2008).

Land and Aquatics

Relative concentrations of PAH in aquatic ecosystems are generally highest in the sediments, intermediate in aquatic biota, and lowest in the water column. Rainwater may contain significant concentrations of volatile PAH and represent an important route to land and water contamination from airborne PAH. Large sources of PAHs; i.e asphalt sealants are broken into smaller particles due to weathering and abrasion from vehicles and other activities which are washed away with stormwater. The higher molecular weight PAHs will not persist in the water column for long, and sink toward the bottom of waterways (Orane 2010). Once deposited in sediments, PAH is less prone to photochemical or biological oxidation (Neff 1979). The PAHs either will eventually be buried in depositional sediment

zones while some will be resuspended due to current, waves, bioturbation, or recreational activities (Ravindra 2008).

Figure 2: Fate of PAHs in Sediments (Orane 2010).
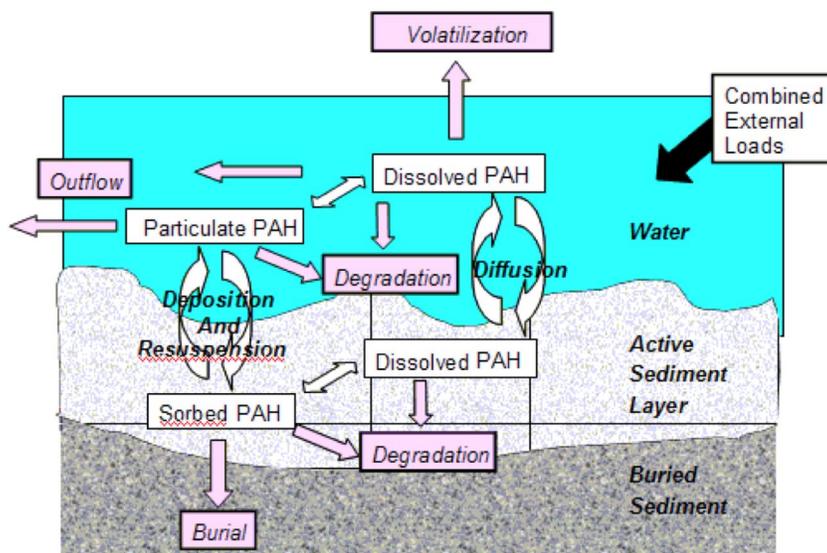
Objectives:

(1)Due to the toxicity of PAH for the aquatic life of the stream and to the residents in the area, they would share a similar interest in the results of the analysis. The data could be used for the education of municipalities, private landowners, citizens of the basin, other nonprofit groups, and governmental agencies. Therefore, The Root Pike Watershed Initiative was consulted when deciding the locations of the sample sites. The sample sites were selected due to previous restoration efforts, potential polluters, and to generate a baseline for areas that expect land-use changes in the following years. (2) There has not been any documented work on analyzing the concentration of PAHs in the Pike River. Therefore, the

basis of this study will be exploratory in nature, to determine if there are in fact any PAHs found in the sediment.

Literature Review

Sources

The tremendous amount of sources for PAH naturally and anthropogenically make it difficult to verify the sources of pollution. PAH are nonpolar, organic compounds that are created by heating or burning of material that contains carbon (Sivram 2018). Any natural, industrial or domestic process where organic carbon is subjected to high temperatures will result in the production of PAHs(1). Low hydrocarbons form PAHs by pyrosynthesis. As the temperature exceeds 500 °C the carbon to hydrogen and carbon to carbon bonds are broken to form free radicals. These radicals combine to acetylene which further condenses with aromatic ring structures (Ravindra 2008). While natural events such as fires and volcanic activity produce significant levels of these compounds, they are mainly from anthropogenic sources such as direct, large spillages of oil or oil-based products; along with the non-direct dissolution of products covered in coal-tar sealants, i.e asphalt parking lots, drinking water pipes, and creosote coating on riverbanks (Fähnrich 2002). Specifically the industrial sources of PAHs include water effluents from oil refineries, electrical and heating facilities, and many more which burn fossil fuels (Neff 1979).

Health Studies

Animal studies have shown that PAH can cause harmful effects on the skin, body fluids, and ability to fight disease after short and long term exposure. People who have breathed or touched a mixture of PAH for long periods of time in the workplace have

developed cancer (ToxFAQ 1996). The EPA classified PAHs with B[a]P indicator species as a B-2 pollutant, which means it is a probable human carcinogen with sufficient evidence from animal studies, but insufficient evidence from human studies (Ravindra 2008). The Occupational Safety and Health Administration (OSHA) has set a limit of 0.2 milligrams of PAHs per cubic meter of air mg/m^3. OSHA permissible exposure limit is 5 mg/m^3 averaged over an 8 hour exposure period. The institute recommends levels not exceed 0.1 mg/m^3 per 10 hr workday and 40 hours workweek (ToxFAQs 1996).

Case Study

In a Milwaukee study of PAH in varying stream sediment, they measured the values of concentrations with respect to varying land usages. The results determined out of 5 primary urban land-use categories (residential, roads and streets, parking, commercial, and industrial) that the parking lot coverage in the drainage area and commercial land use were the only two related to significant PAH concentrations in the river sediment. The Parking lots of land use was most strongly correlated with significant PAH concentrations with a correlation coefficient of 0.75. Additionally, the study observed that the dust samples taken from coal-tar sealant pavements had the closest similarities to the ratios of PAH compounds in the sediment of the streams. Therefore their results suggested that the PAH concentrations found were all of a common source, being the coal-tar sealants on the pavements of parking lots (Baldwin 2016) .

Coal-Tar

Coal-tar is produced from high temperature treatments of coal. Coal-tar contains PAH that could be derived from PAH indigenous to the coal or from pyrolysis of coal

hydrocarbons. PAH in coal tar is approximately 44.4 percent PAH by weight (Neff 1979). Subsequently, coal-tar sealants are the largest source of pollution for PAHs. Coal-tar has been manufactured into the black, liquid sealants. These sealants contain 20-35 percent coal-tar and somewhere between 35,000 to 200,000 mg/kg of PAHs. This amount is 100 times greater than the amount of PAHs found in motor oil (Mahler 2016). According to Geoff Crenson, chairman of the Pavement Coating Technology Center, approximately 85 million gallons of coal tar-based seal coat products are sold each year in the United States (Orane 2010). These sealants are then sprayed onto asphalt pavement of residential driveways, parking lots, and playgrounds (Watershed Council). The Pavement Coating Technology Council, an industry group representing sealant producers, is considering pursuing research that would determine whether it actually expands the lifespan of asphalt (Orane 2010).

Kenosha History

While it is important to be able to predict the presence or the absence of toxicity in samples, it is equally desirable to identify the factors that are causing or contributing to the sediment toxicity. Kenosha and Racine have been known for historically being industrial sites. In 1968, the industrial complex of Kenosha included 118 firms producing a vast range of production for worldwide distribution worth more than 1, 250,000,000 US dollars. Over 75 percent of all the citizens earned their living wage from one of the many manufacturing facilities within the town (1968). The downtown harbor area used to be a mattress factory from 1870-1960, and then was converted to an American Motors operation until 1988 (1968).

Racine History

Additionally, Racine faces a similar problem along the shoreline, formerly known as the "Machinery Row" where there are over 300 brownfield sites left from past industrial activity. A brownfield is characterized by the DNR as Abandoned, Idled, or under-used industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination (Public Health and Brownfields). In 2011, the EPA granted The City of Racine 200,000 dollars specifically for petroleum contamination related clean-up and more recently 300,000 dollars in grants to clean up the 20 acres of contaminated soil (EPA). Kenosha and Racine are still facing the persistence of contamination from their historically industrially active sites. If there are any PAHs in the soil, it could possibly be from persisting chemicals from these sites that were not managed and restored properly. Understanding the historical and current land uses in the watershed basin can help identify potential sources of PAHs.

Guidelines

The PAH results from the Pike River can be compared to the concentrations of the Standard Quality Guidelines (SQGs). Multiple approaches have been developed to support the derivation of numerical SQGs for the protection of sediment dwelling organisms in the United States and Canada (Macdonald 2000). These specific guidelines were drafted in a consensus based style from previous toxicity publications and are a unifying synthesis of current SQGs. The levels of toxicity for sediment-dwelling organisms include 28 common

freshwater polluting chemicals. Two SQGs were created for each chemical, which are distinguished as Threshold Effect Concentrations (TEC) and Probable Effect Concentrations (PEC). The TEC is the level at which contamination is not expected to be harmful to the sediment-dwelling organisms, whereas the PEC is the level at which adverse health effects on these benthic dwelling organisms will occur frequently. Approximately, 1,610 mg/kg and 22,800mg/kg PAH concentrations for dry weight sediment samples are the TEC and PEC levels respectively. The consensus-based SQG provides a reliable basis for assessing sediment quality conditions in the freshwater ecosystem and will be used for interpreting the concentrations of PAHs in the Pike River (Macdonald 2000).

Priority PAHs Regulations

The complex mixture of similar molecules makes it difficult to conduct detailed analysis(Fähnrich 2002). To practically identify and regulate these compounds, the EPA has classified 16 distinct compounds and given chemical names to each which makes up the Priority Pollutant List (Toxic). These PAHs have been chosen because (1) there is more information available than the others;(2) these are suspected to be the more harmful than others, and exhibit harmful effects that represent PAHs in general;(3) There is a greater chance for exposure to these PAHs;(4) of all the these PAHs analyzed are the highest concern (Orane 2010). Environmental organizations use this list of the compounds to regulate and monitor them. Currently, these compounds are regulated by the Clean Water Effluent Guidelines in Title 40, Sections 400-475, of the Code of Federal Regulation (George 1995);In the 1990 US Clean Air act amendment added PAHs to the list of hazardous air pollutants (Orane 2010). Additionally, the Resource Conservation and Recovery Act has

several PAHs listed as hazardous wastes when they are discarded commercial chemical products, off-specification species, container residues, and spill residue (George 1995).

Pike Statistics

The basin of the Pike watershed is about 56 square miles on the eastern side of Kenosha and Racine counties. The Pike has 2 branches that feed into it, meeting at Petrified Springs Park and flowing east towards Lake Michigan. The Northern branch is located in the residential area of Mt. Pleasant, near the junction of highway C on 90th street. The river flows approximately 1 mile before turning south and continues the rest of its total 6.9 mile stretch towards Petrified Spring (Wisconsin). Waxdale creek is one of the main streams which feeds into this branch. The south branch is a drainage pathway from highway 50 in Kenosha County. It flows 7.8 miles parallel to the Union Pacific Railroad, draining the agriculture tiles and tributaries including the airport and Somer branches. The North and

Fig. 3: Pike River and Direct Drainage Watershed
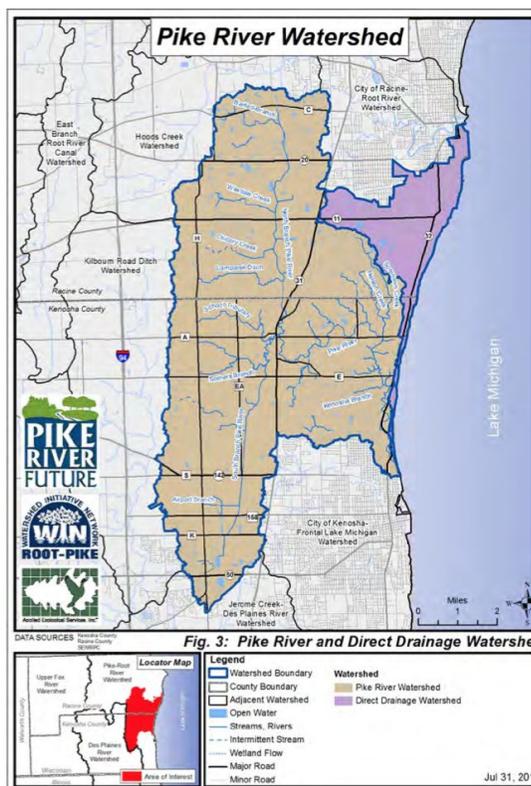
South branches converge to form the Pike River at Petrified Springs park which runs about 9.6 miles before draining into Lake Michigan.

Figure 2: The Pike River Watershed Basin (Pike River Plan).

Pike Characteristics

The Pike River is becoming more channelized due to its flashy properties which can reduce the likelihood of capturing accurate representations of PAH. The "flashy" nature of the river simply means that when there is a large rainfall, the river elevates and increases in speed quickly. Conversely, when a dry spell occurs the river slows and stagnates. This variation between low energy and high energy results in heightened erosion rates. Currently, the bank heights range from 9-22 feet which means that there is a high degree of erosion in parts of the watershed (Wisconsin). Streams that are prone to scouring from one event to the next can make it challenging to determine the total PAH concentration (Bryer 2006). Erosion of the banks in the headwaters may increase the levels of PAHs downstream of the river because the suspended solids carry pollutants such as nitrogen, phosphorus, and hydrocarbons (Pike). The increase in runoff and stormwater drainage from development, within this particular site of the watershed, contributes to the higher total suspended solids (Wisconsin). Currently, the North branch and main branch of the Pike River are listed as impaired by the DNR because of the degraded habitat.

Figure 3: USGS Gauge at the Pike River, displaying the "flashy" nature of water levels

fluctuating 3 up to 3 feet over a two day time frame (USGS .)

Root Pike Watershed

The Root Pike Watershed Initiative is a nonprofit organization that has been working

for over two decades to remediate the Pike River. The goals include trying to educate their

residents about the health of the waterways and implement action designated for restoring the

Root and Pike River. Restoring the waterways includes slowing down the velocity of the

stream, reducing the number of sediment loads from erosion, and increasing habitat (Pike).

They are focusing on key issues that can potentially impact the introduction of PAHs to the

sediment such as channelization, man-made impediments and suspended solids from runoff.

Since the conceptualization of their 9 step key plan, they have done extensive research and

monitoring of the branches and tributaries of the Pike River. Dave Giordano, the director of

the organization was contacted to help determine areas of concern for PAHs as well as sites

that would be ideal monitoring areas. If PAH concentrations are found they would be able to mobilize a plan in order to remediate said areas.

Remediation

Remediation of these toxins is an ongoing issue and there are varying degrees of action happening to clean-up and prevent exposure. In fact, PAHs have been found in at least 600 of the 1,430 national priorities list sites identified by the EPA (Fact sheet). In the Great Lakes region, more than 50 million dollars has been spent at 19 different sites to clean up sediment contaminated with PAHs (Baldwin 2017). Cities have begun to ban products that contain coal-tar, and certain stores have placed restrictions on products that contain these chemicals. Although there is no evidence that it is a problem in the river, there have been efforts to clean up the Root-Pike watershed due to its recognition as an impaired stream.
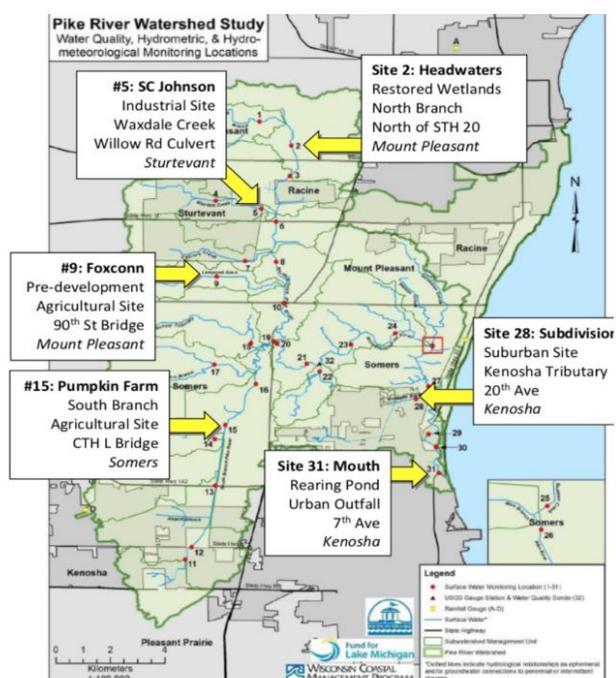
Location:
Figure 4: Suggested Sample Sites Provided by the Director of the Root-Pike Watershed Initiative- Dave Giordano.

Table 1: Sample Sites Details and Observations

Sample Sites	Description of location and area	Disrupting land-uses/ pollution sources
S.C Johnson 'Culvert'	Surrounded by subdivisions and farming. Not far from the commercial center and busy road. High amount of organic litter in the stream.	Industrial waste
Foxconn	90th St. Bridge right next to a bus road and residential housing.	Construction of nearby site
Subdivisions	Within a Park, noticeable mesh to stabilize shore bank. Closer to the lake with sandy soils.	Next to a golf course and residential areas.
Pumpkin Farm	High Erosion of stream, with quick stream velocity.	Agriculture
Headwaters	Surrounded by suburbs Restored land	Residential runoff potential

Methodology

Sampling

Each sample was extracted using an Eckmann Ponar dredge. The Dredge was used above bridges and on occasion from the edge of the bank. Prior to collection, the glass mason jars were cleaned with a hexane:acetone solution and allowed to dry. The observed turbidity and velocity of the sample area was recorded in a field notebook for later discussion and speculation. After the samples were placed in the mason jars, they would be wrapped in aluminum foil and placed in a cooler with ice packs for transportation back to the lab. All the

samples were measured for their wet weights prior to being dried in the fume hoods; then

measuring the dry weight.

The samples were crushed with a mortar and pestle and then frozen for later analysis.

Sediment Extraction

The sediment was thawed and weighed out to ~5g, then the exact mass was recorded.

The sediment was placed into a 50 mL beaker, a 40 mL volumetric 1:1 hexane/acetone

solvent was added to the beaker ; two to three scoops of anhydrous sodium sulfate was added

to the beaker. The Sonicator probe was rinsed three times with hexane/acetone (H:A) before

placing the beaker underneath; about 1-2 cm above the sediment line. It pulsed for 6 minutes

in 15 second intervals and was allowed to settle. The liquid contents were decanted into a

125 mL Erlenmeyer flask through filter paper with anhydrous sodium sulfate. This process

was repeated twice. For the final filter, the sediment was poured into the filter paper, and the

glass funnel was rinsed with more (H:A). The flask was moved to the nitrogen evaporator to

exchange the solvent to hexane; the liquid was decanted into 40 mL vial and concentrated to

~5mL. The vial wrapped in parafilm and placed into a refrigerator if the cleanup stage did not

follow immediately.

Cleanup

The Manifold is vacuum sealed with two waste beakers and the 15 mL Centrifuge

Tubes. The 5g alumina cartridges are inserted into the spigots of the manifold and

conditioned with 10 mL of 2:1 and 10:1 Hexane:Dichloromethane (H:D) sequentially. The

waste from the conditioning rinse drips into a waste beaker; and the rinse from the sample

will be collected in 15 mL centrifuge tubes. The sample is added to the cartridge and then the

40 mL vial is rinsed with ~2ml of 5mL of 10:1 (H:D); then the rest of the solvent is poured into the cartridge. The final 5mL poured is the 2:1 (H:D) which then is drained completely.

Concentration and Derivatization

The solution in the centrifuge vial was further concentrated from 10mL to 200 µL using the nitrogen evaporator. During the concentration, 1-2mL of hexane was added three times around the 7-8 mark on the conical section and then evaporated to the 2nd mark. The sample was extracted with a syringe and 200uL and transferred into a gas-chromatography (GC) vial for analysis using a gas chromatograph-mass spectrometer (GC/MS). Prior to analysis, 10 µL of the internal standard was added to the GC vial.

Data Analysis

Gas Chromatography-Mass Spectrometry

The analyses of the samples were done by using Agilent Technologies 7890B/5977A GC/MSD instrument. It worked in two parts: the gas chromatograph volatilized a small liquid sample; the gaseous sample traveled through a capillary column carried by helium. The different phases separated heavier compounds from lighter ones . The result was different compounds separated in the capillary column at varying retention times. At the end of the column, the molecules passed through a transfer line into the mass spectrometer. The molecules entered a quadrupole in which electron ionization occurred, splitting the molecules in a unique manner to which the detector can assign a mass to charge ratio (m/z), creating a fingerprint of the molecules present. To get an accurate reading, samples were run with a full-range m/z scan and a selected-ion monitoring (SIM) scan.

Calibration Curves

16 calibration curves of different magnitudes (0.1µg/L, 1µg/L, 10µg/L, 100µg/L) were created. The calibration curves corresponded to different standards of PAHs, and these curves were used to determine the concentrations of derivatized PAHs in each sample.

Results:

16 Priority PAHs	% Recovery	Sample 1 (µg/kg)	Sample 2 (µg/kg)	Sample 3 (µg/kg)
Naphthalene	24±10	-7	-27	2
Acenaphthylene	48±10	61	25	13
Acenaphthene	51±9.7	10	10	-8
Fluorene	61±9.7	84	89	3
Anthracene	142±14	1186	1073	18
Phenanthrene	74±4	242	336	0
Fluoranthene	82±2	1762	1437	53
Pyrene	90±2	1254	1118	40
Benz[a]anthracene	166±10	1150	973	29
Chrysene	196±28	1429	1101	49
Benzo[b+k]fluoran	138±21	1639	1268	75
Benzo[a]pyrene	61±8	236	15	-4
Indeno[1,2,3-cd] p	190±20	718	447	50
Benzo[g,h,i]peryle	123±13	693	446	50
Dibenz[a,h] anthra	70±6	182	122	68

Table 2: Culvert Sample Spike Recovery and Dry Weight concentration in sediment

Spike Recoveries

The percent recoveries for the larger PAHs are fairly high with Chysene having an average close to 200 percent and a large degree of variation of 30 percent. This would mean that the spiked sample reported having twice as much Chrysene than originally injected into the sample. The lowest spike recovery was Naphthalene which is the lightest molecular weight and most easily volatilized chemical. Generally, the higher spike recoveries corresponded to the larger concentrations of the chemicals found in the sediment.

Sediment concentrations

The averages of the three samples were taken and displayed on the graph below, Graph 1. The PAHs are ordered in descending molecular weights with Dibenz[a,h] anthracene as the highest and Naphthalene as the lowest molecular weight. The concentrations formed a bell shaped curve, where there were the highest concentrations found in PAHs from the mid-ranges of molecular weight. Naphthalene reported a negative mass which can be ignored and considered a value of zero because you cannot have a negative concentration. The units µg/kg were chosen in order to easily compare to the SQG concentrations of the individual chemicals.

Stream Characteristics

The Culvert had the quickest velocity as well as a high amount of suspended solids. The section of the stream that had a meandering path was slowest moving and clearest of all the sites. This was located in the subdivisions where there was also evidence of bank stabilization efforts.

Site	Velocity (ft/s)	Turbidity
Culvert	1.22	turbid
Foxconn	0.60	clear
Subdivisions	0.27	clear
Pumpkin Farm	0.50	turbid
Headwaters	0.48	slightly turbid

Table 3: The characteristics of the sample site such as average velocity and turbidity on the day that the sample was taken.
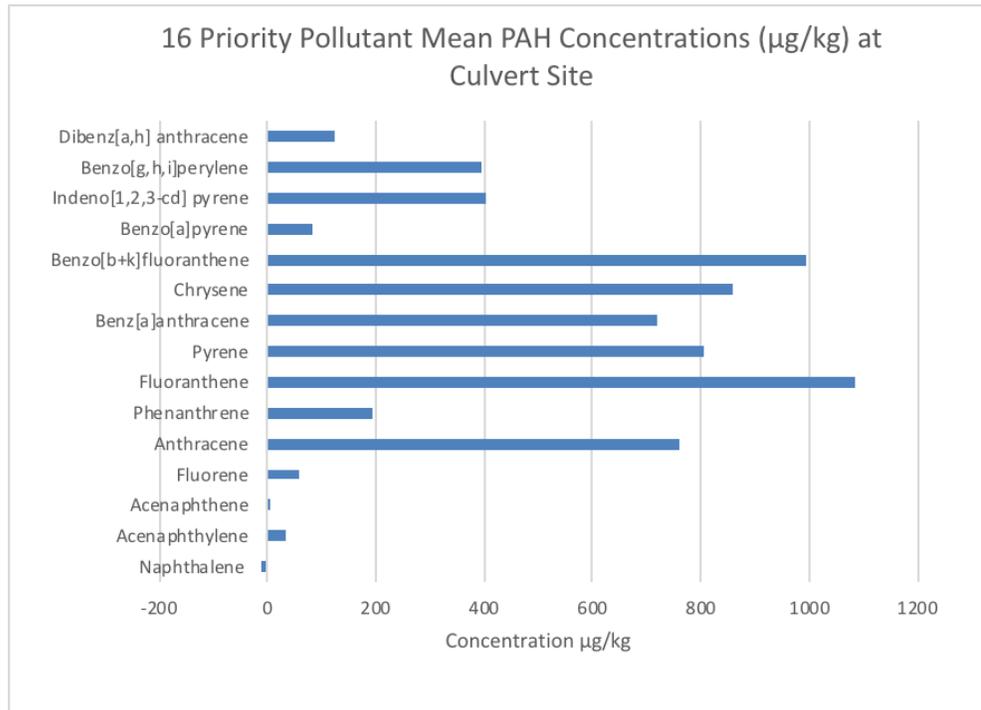
Graph 1: The Averages of PAH Concentrations Compared to Show The Range of Presence within the Sample at the Culvert Site.

Discussion:

The bell shaped curve shows the higher molecular weight PAHs with similar concentrations to the lower molecular weight PAHs which is perplexing. The partitioning coefficients of PAHs in the air to soil decrease respectively with increasing molecular weights. The low concentrations for the highly volatile and low molecular weight PAH is reasonable, but one would have presumed there to be a direct relationship with the increasing molecular weight to an increase in soil concentrations. To further speculate, the samples were taken from the biologically active 5 cm of the river sediment which means that the heavier

PAHs may have sunk and been buried further in the sediment. In which case, taking a core sample instead of using a ponar dredge should be considered for future sampling procedures.

Analysis efficiency:

There are a few negative concentrations of PAHs because the sample response factor was lower than my lowest standard 1μg/L. What happened is that the y-intercept for the calibration curve is higher than the sample response factor, shifting the assumed concentration value to the negative side of the graph. I could correct this by creating even more diluted standards, or just acknowledge that the amount is small enough to be considered irrelevant. Also, the three smallest concentration values Naphthalene, Acenaphthene, and Acenaphthylene were also the lowest molecular weight PAHs. There may have been higher amounts present in the soil, but my process of drying the samples was not ideal for preserving these highly volatile compounds. While other studies had freeze-dried the samples, these samples were placed under a fume hood for about a week before grinding and putting them in the freezer. This was not a major concern since finding these smaller ring compounds in high concentrations was unexpected, however this may have caused our data to be a misrepresentation of the actual concentrations of the low molecular weight PAHs in the sediment. Future monitoring of all Priority Pollutants would benefit from taking preemptive measures using a freeze-drying method.

There were some limitations in the experiment, which were seemingly unavoidable. A couple of compounds act very similar and have the same m/z ratios which meant that their response times were close together. Since it is difficult to differentiate the peak areas in both the standard samples, the Benzo[k]fluoranthene and the Benzo[b]fluoranthene compounds

were analyzed as one compound- Benzo[b+k]Fluoranthene. Although this serves as a viable solution, it is important to note that these are indeed two separate compounds that may be present in significantly different amounts.

Also, in the lower standards (0.1µg/L + 1µg/L) the concentrations of the higher weight PAHs resulted in considerably low peak areas which made it difficult to create reliable estimations. The calibration curve would have benefited from at least one higher concentration standards such as 1000µg/L. Additionally, samples had run through the GC/MS without the column being cleaned prior to loading the standards used to make the calibration curve. In retrospect, the peak areas may have been less noisy for the standards if there had been a hexane run to clean the columns from any leftover sample runs. Therefore the methods could be improved with a higher concentration standard and also by loading a hexane run prior to loading the standards used to create the calibration curves.

16 Priority PAHs	% Recovery	Sample 1 (µg/kg)	Sample 2 (µg/kg)	Sample 3 (µg/kg)	Average	Consensus Based TEC (µg/kg)	Consensus Based PEC (µg/Kg)
Naphthalene	24±10	-7	-27	2	-11	176	561
Acenaphthylene	48±10	61	25	13	33	NA	NA
Acenaphthene	51±9.7	10	10	-8	4	NA	NA
Fluorene	61±9.7	84	89	3	59	77.4	536
Anthracene	142±14	1186	1073	18	759	57.2	845
Phenanthrene	74±4	242	336	0	193	204	1170
Fluoranthene	82±2	1762	1437	53	1084	423	2220
Pyrene	90±2	1254	1118	40	804	195	1520
Benz[a]anthracene	166±10	1150	973	29	717	108	1050
Chrysene	196±28	1429	1101	49	860	166	1290
Benzo[b+k]fluoranthene	138±21	1639	1268	75	994	NA	NA
Benzo[a]pyrene	61±8	236	15	-4	82	150	1450
Indeno[1,2,3-cd] pyrene	190±20	718	447	50	405	NA	1450
Benzo[g,h,i]perylene	123±13	693	446	50	396	NA	NA
Dibenz[a,h] anthracene	70±6	182	122	68	124	33	NA
				Total =	6514	1,610	22,800

Table 2: Consensus based TEC and PEC from Macdonald et al 2000. Compared to the sample concentrations of the culvert site.

Concentration comparison

As mentioned earlier if PAHs were found they would be compared to the consensus based SQGs. These concentrations were compared to hundreds of other studies to determine

which concentration levels were found to be toxic in benthic aquatic organisms therefore reducing the quality of the streams. The total PAH concentration of the Culvert is about four times greater than the Consensus based TEC threshold total concentration. As stated earlier the TEC represents the concentration at which harmful effects are unlikely to be observed on benthic dwelling organisms. Notably, the average concentration of Anthracene from the sample is close to matching the PEC, in which harmful effects are likely to be observed. When comparing the results to the SQGs the levels do not appear to be alarming at the site overall, especially because the spike recoveries showed 100 + percent recovery. The numbers are mostly below the TEC numbers and we can assume that there may have been some over reporting of the values due to over projections which we found in the spike recoveries. Therefore, it doesn't appear that the PAH concentrations at this site would need immediate attention. However, this is only one site, and not representative of the entire watershed basin.

Evaluate hypothesis

The goal of this study was to determine if PAHs existed in the Pike River Sediment. Despite not being able to analyze all the samples, there were detectable concentrations found in the Culvert site. This hypothesis was exploratory and is meant to be answered in a yes/no fashion. The concentrations can be compared to other studies, but there is no previous data in the Pike River to compare results too. The hypothesis can be adjusted to look for areas with higher concentrations than others now, such as evaluating if the concentrations share a correlation with the distance from the headwaters, or the distance from a particular municipality.

Future Direction

   The samples that were not analyzed are still frozen in the lab and could be used for future analysis. The concentrations could be determined for those sites or taken from other areas of the Pike River. Instead of using a Ponar Dredge to collect the sediment, samples could be taken using a soil corer. This would allow one to see if the concentrations for higher molecular weights will in fact be greater in the sediment that has settled. Also, it would be interesting to see if the amount of suspended solids in the areas of the sample sites affect the total concentrations of PAHs found at each site. Since the suspended particles carry hydrocarbons, I would expect there to be greater concentrations in areas where the water is turbid frequently. Both of these suggestions are related to the sampling methods and one would be able to use the same lab analysis methods.

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