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POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) PILOT STUDY IN CONODOGUINET CREEK, SOUTHCENTRAL PENNSYLVANIA

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a large group of chemicals commonly detected in the environment. These compounds occur naturally in gasoline, coal, and crude oil, as well as combustion byproducts of coal, wood, gas, oil, and other substances (Centers for Disease Control and Prevention (CDC) 2009). PAHs enter the environment in many ways, including wastewater treatment plants, surface runoff from parking lots and roadways, spills, and landfill leachate. PAHs are frequently detected in air pollution and bind to sediment and soil particles in the environment. They do not break down quickly and are very persistent in nature (Perrin 2012). Because of their tendency to attach to sediment and not dissolve in water, sediment concentrations are expected to be substantially higher than instream water concentrations.

There are at least fifteen PAHs that are anticipated to be human carcinogens (National Toxicology Program (NTC) 2011). In addition, PAHs have been shown to be toxic to aquatic organisms. A study of the effect of specific PAHs on a crustacean, *Diporeia sp.*, established LC_{50} values – the concentration found to kill half of the test organisms – between 1,757 µg/L for naphthalene and 79.1 µg/L for pyrene (Landrum et al. 2003). Threshold effect concentrations (TECs) – concentrations below which it is unlikely that harmful effects will occur – have ranged from 10 to 750 µg/kg in a number of studies for a variety of PAHs (MacDonald et al. 2000). A study on the aquatic worm *Lumriculus variegatus* showed rapid pyrene accumulation from sediment and avoidance of sediment at high pyrene concentrations (i.e., 64,000, 132,000, 206,000, and 269,000 µg/kg sediment pyrene), likely due to sediment avoidance at the higher concentrations. At concentrations of 206,000 and 269,000 µg/kg, worms were mainly on the surface of the sediment, but burrowed into the sediment at the lower treatment concentrations (Kukkonen & Landrum et al. 1994).

The Pennsylvania Department of Environmental Protection (DEP) initially became aware of high levels of PAHs in stream sediment due to a study conducted by staff of Dickinson College in Carlisle, Pennsylvania. In May 2010, staff from Dickinson College sampled sediment at 35 sites for various PAHs in the main stem of Conodoguinet Creek in Cumberland County, a tributary to the Susquehanna River. Samples were collected from the headwaters to the mouth. Sites were determined by dividing the main stem into 35 5-km segments and collecting a sample from each segment. The Dickinson study found PAHs across the 35 sites ranging from 44 to 26,200 μ g/kg with a mean of 4,100 μ g/kg and median of 2,280 μ g/kg. Urban sediments collected from the eastern end of the watershed had PAH concentrations approximately three times greater than sediment from the rural west end (Witter et al. 2014).

Based on previous research, PAHs may be harmful to benthic macroinvertebrate and fish communities. In addition, PAHs have the potential to be resuspended during high flow events and become contaminants in the water column. PAH standards for the medium of sediment have not been developed by DEP and very little sediment is collected routinely during DEP stream surveys. Freshwater sediment screening benchmarks have been published by the United States Environmental Protection Agency (USEPA 2006) for many PAHs in this study. DEP performs aquatic life assessments primarily using macroinvertebrate surveys (Shull and Pulket 2018). Aquatic life use assessments, in addition to other uses, are reported through a biannual integrated water quality monitoring and assessment report as required by Sections 303(d) and 305(b) of the federal Clean Water Act. Although DEP does not currently assess water uses based on sediment quality, sediment is a potentially useful tool that could be used to determine probable cause of certain water use impairments. As such, the goal of this study was to characterize PAH sediment levels in the Conodoguinet Creek watershed to determine if sediment may be a useful tool for informing future assessments.

METHODS AND MATERIALS

The watershed of Conodoguinet Creek drains 1,313 km² of predominately agricultural and urban land in southcentral Pennsylvania (Figure 1). The Conodoguinet Creek headwaters begin in State Game Lands No. 235 in Franklin County and the main stem of the creek winds through Cumberland County to its confluence with the Susquehanna River at Wormleysburg, Pennsylvania. Land use is predominantly forested in the headwaters but becomes progressively more agricultural and urban/suburban towards the mouth. To examine the concentrations of PAHs in sediment, eight sites within the main stem of Conodoguinet Creek were selected. Although 35 sites were sampled in the Witter et al. (2014) study, DEP decided to sample less sites for this initial DEP pilot study. Six of the eight locations sampled by DEP were initially sampled by Witter et al. (2014). The eight sites were chosen by DEP to represent a distribution of locations from the upstream headwaters downstream towards the mouth, encompassing agricultural/rural and urban/suburban areas of the creek (Table 1). Sites CONO 1, CONO 2, CONO 3, CONO 5, CONO 6, and CONO 7 were sites sampled by Witter et al. (2014). CONO_4 was chosen to gather more information in the urban area between sites CONO 3 and CONO 5, and CONO 8 was a braid in the creek, adjacent to CONO 7. CONO 7 and CONO 8 were selected to distinguish any differences between the opposite shores of the braid.



Figure 1. DEP sediment PAH sampling sites in Conodoguinet Creek, 2014 and 2016.

Site ID	Location Description	Latitude	Longitude
CONO_1	Mouth of Conodoguinet Creek	40.27181	-76.91442
CONO_2	Creek Road under bridge	40.25550	-76.92748
CONO_3	Erb's Bridge Road	40.24545	-76.97307
CONO_4	Lamb's Gap Road	40.25337	-77.00304
CONO_5	Willow Mill Park off 114	40.25569	-77.03975
CONO_6	Behind Knight Transport	40.23680	-77.13792
CONO_7	Bridge outside Roxbury	40.10910	-77.66226
CONO_8	At 2nd braid of bridge outside Roxbury	40.10748	-77.66246

Table 1. DEP sediment PAH sampling sites in Conodoguinet Creek, 2014 and 2016.

Summer was chosen as the sampling period because this mirrored the sampling time of the Witter et al. (2014) study. In addition, some activities that can produce PAH runoff, such as sealcoating and paving, occur mainly in the summer.

Samples were collected according to the DEP's streambed sediment sampling data collection protocols found in Chapter 4 of Shull and Lookenbill (2018). Samples were sent to DEP's Bureau of Laboratories (BOL) in Harrisburg, Pennsylvania. In 2014, PAHs in sediment were analyzed by USEPA method 8270D (USEPA 2014). In 2016, samples were collected again and analyzed using the same method but followed the selected ion monitoring (SIM) technique (USEPA 2014). This variation in EPA method 8270D allowed for quantitation limits that were below the normal electron impact mass spectrometry range (USEPA 2014); however, the SIM technique only allows for specific compounds to be observed. In 2014, 109 compounds were analyzed and in 2016, with the SIM technique, 22 compounds were analyzed (Appendix A).

Land cover of the upstream watershed was calculated for each site. Watershed polygons were created using the ArcGIS Online watershed tool (Scopel 2014). Watershed polygons, including watershed area data, and the 2011 National Land Cover Database (NLCD, Homer et al. 2015) were then imported into R, version 3.3.2 software (R Core Team 2016) to calculate land use percentages. Watershed percentages of the NLCD land cover categories "Developed, Open Space", "Developed, Low Intensity", "Developed, Medium Intensity", and "Developed, High Intensity" were summed into a total percent developed score for each watershed.

Slope of the land around each site was also calculated using ArcMap 10.4.1 to determine if PAHs were more likely to be at high concentrations in lower gradient reaches. This analysis was done with the Slope Tool in the Spatial Analysis extension for ArcMap 10.4.1. A 50-meter raster layer created by the United States Geological Survey (USGS) and Pennsylvania Department of Conservation and Natural Resources Bureau of Topographic and Geologic Survey, based on the USGS National Elevation Dataset (1999), was used to produce a raster layer of slope degrees. A 200-m buffer was placed around each site and slope was clipped to each buffer using Image Analysis in ArcMap 10.4.1. Slope statistics (i.e., maximum slope and average slope) were determined for the buffered area around each sampling site.

RESULTS

In 2014, there were only 8 total compound detections (Appendix B). Most detections in 2014 were close to the mouth of Conodoguinet Creek, in suburban/urbanized areas. Detections included diethylphthalate at CONO_1, CONO_4, and CONO_7; pyrene at CONO_2 and CONO_3; and benzo(b)fluoranthene, chrysene, and fluoranthene at CONO_2.

In 2016, there were 142 total compound detections using the lower detection limits (Table 2, Appendix A, Appendix B, Appendix C). All PAH compounds tested were detected at least once, except for 7,12-dimethylbenz(a)-anthracene and 3-methylcholanthrene, which were not detected. USEPA has freshwater sediment screening benchmarks recommended for all but 5 of the 22 PAHs tested in 2016 (USEPA 2006). Four compounds exceeded USEPA benchmarks at sites in 2014, with CONO_2 having the most detects above USEPA benchmarks. Twelve compounds exceeded USEPA benchmarks that were above USEPA benchmarks (Table 3).

	Average Concentration
Test Description	of Detects – 2016 (ug/kg)
1-Methylnaphthalene	10.4
2-Methylnaphthalene	14.9
Acenaphthene	15.9
Acenaphthylene	31.5
Anthracene	52.8
Benz(a)anthracene	207.5
Benzo(a)pyrene	233.3
Benzo(b&j)fluoranthenes	296.8
Benzo(e)pyrene	176.1
Benzo(g,h,i)perylene	180.4
Benzo(k)fluoranthene	104.7
Chrysene	282.2
Dibenzo(a,h)anthracene	35.7
Dibenzofuran	13.4
Fluoranthene	490.9
Fluorene	18.3
Indeno[1,2,3-cd]pyrene	196.3
Naphthalene	16.8
Phenanthrene	167.8
Pyrene	446.6

Table 2. Average concentration of detected PAHs, 2016.

	USEPA Freshwater	
	Sediment Benchmark	USEPA-Indicated as
PAH	(µg/kg)	Bioaccumulative?
2-Methylnaphthalene	20.2	
Acenaphthene*	6.7	Y
Acenaphthylene*	5.9	Y
Anthracene*	57.2	Y
Benz(a)anthracene*	108	Y
Benzo(a)pyrene*	150	Y
Benzo(g,h,i)perylene*	170	Y
Benzo(k)fluoranthene	240	Y
Chrysene*	166	Y
Dibenzo(a,h)anthracene*	33	Y
Dibenzofuran	415	
Diethylphthalate*	603	
Fluoranthene*	423	Y
Fluorene	77.4	Y
Indeno-1,2,3-cd-pyrene*	17	Y
Naphthalene	176	
Phenanthrene*	204	Y
Pyrene*	195	Y

Table 3. USEPA freshwater sediment benchmarks for PAHs tested in the Conodoguinet Creek study.

*Detected above EPA benchmark in 2014 or 2016

CONO_4 and CONO_5 had the fewest number of detections in 2016, although those two sites are not in minimally developed areas (Figure 2). The number of detections in 2016 ranged from 12 to 20 per site. The site at the mouth of Conodoguinet Creek (CONO_1) had the highest number of PAH detections in 2016. The second highest number of detections was at the Erb's Bridge Road location (CONO_3). Generally, urban and agricultural land uses increased through the watershed from headwaters to the mouth (Table 4).



Figure 2. Number of sediment PAH detections at eight Conodoguinet Creek sites in 2016 (CONO_7 also had a duplicate collected on the same date/time, included in the figure above).

		Land Use (%)												
Sito ID		C)eveloped				Cultivated							
One ib	Open Space	Low Intensity	Medium Intensity	High Intensity	Total	Deciduous	Evergreen	Mixed	Crops					
CONO_1	8.6	6.4	2	0.9	17.9	31.2	1	1.1	21.4					
CONO_2	8.6	6.2	2	0.9	17.7	31.3	1	1.1	21.6					
CONO_3	8.2	5.6	1.9	0.9	16.6	31.3	1	1.1	22.2					
CONO_4	8.1	5.4	1.9	0.9	16.3	31.5	1	1.1	22.3					
CONO_5	7.5	4.6	1.4	0.6	14.1	33.4	1.1	1.2	22					
CONO_6	7.2	4.5	1.5	0.7	13.9	33.3	1.1	1.3	22.5					
CONO_7	3.8	0.1	0	0	3.9	84.8	3.9	4.6	0.2					
CONO_8	3.8	0.1	0	NA	3.9	84.9	3.9	4.6	0.2					

Table 4. Selected land use characteristics of sediment sites (%)

In 2016, concentrations of PAHs generally increased from the headwaters to the mouth (Figure 3). The site with the highest total concentrations of PAHs was CONO_1, located at the mouth. However, the lowest concentrations were at CONO_5 and CONO_4, which are relatively low in the watershed and contain higher urban/suburban development compared to the headwater sites.



Figure 3. Concentrations of sediment PAHs at eight Conodoguinet Creek sites in 2016 (CONO_7 also had a duplicate collected on the same date/time, included in the figure above) from upstream to downstream.

Maximum and average slope were highest at CONO_4, CONO_1, and CONO_5 and lowest at CONO_3 (Table 5). Normality testing revealed data is not normally distributed and base-10 log transformation of the data did not normalize it. Non-parametric Spearman rank correlation analyses were run between maximum slope versus total PAH concentration (ρ (rho) = -0.3682041) and maximum slope versus number of PAH

detections (ρ (rho) = -0.4705882). Total number of detections and total PAH concentration versus maximum slope were also graphed (Figure 4).

	Slope (D	egrees)
Site ID	Maximum	Average
CONO_1	45.1	18.7
CONO_2	29.5	15.0
CONO_3	17.5	8.4
CONO_4	50.0	23.2
CONO_5	44.4	15.5
CONO_6	38.5	15.2
CONO_7	26.9	13.5
CONO 8	32.6	16.8

Table 5. Slope statistics at each site using a 200 m buffer.



Figure 4. Total number of detections versus maximum slope (degrees). Total PAH concentration (μ g/kg) indicated by size of the bubble.

Witter et al. (2014) individual PAH results were compared with PAH results from this study (Figure 5). Normality testing and transformation of the data did not result in normal distributions. A non-parametric Wilcoxon signed-rank test was conducted on paired samples and found that the samples were significantly different, i.e. not from the same population (p-value = 3.726e-16). In general, concentrations detected in the Witter et al. (2014) study were higher than those detected at sites also sampled in this study.



DEP Result DEP Result

Figure 5. Box-and-whisker plot of compounds sampled in Witter et al. (2014) and DEP study. Top of box: 75th percentile, bottom of box: 25th percentile, "x": median.

DISCUSSION

In 2014, there were only 8 total compound detections, likely due to the high detection limits. With lower detection limits, the 2016 samples had many more detects. There were lower concentrations and numbers of detections of sediment PAHs in the upper parts of the watershed and higher concentrations and detections closer to the mouth. This pattern is expected – the greater the extent of impervious and urban areas, the higher likelihood that PAHs will run off into surrounding waterbodies. However, CONO 4 and CONO 5 did not appear to fit this pattern. These sites were lower in the watershed and had high urban land use but had very low PAH concentrations and detections. Slope estimations were steeper at these locations, so this may have factored into the lower concentrations - contaminants may not have been able to run into the stream as easily or the steeper slopes may have facilitated flushing the sediments through more thoroughly. However, there could also be lower amounts of PAH usage at CONO 4 and CONO 5. The site with the highest PAH concentrations, CONO 3, did have the lowest average slope in the surrounding 200 m. While CONO 1 had a high average and maximum slope around it, it was also located at the mouth, which could have impacted the levels of PAHs. Slope did not appear to affect total PAH concentration, but lower slopes did have higher numbers of PAH detections (Figure 4). However, maximum slope and total concentration/total number of detections were not significantly correlated (p-values = 0.3296 and 0.2011, respectively), suggesting that although slope may have an impact on sediment contaminant accumulation, there are also other factors at play. PAHs may travel downstream with sediment fluxes, but concentrations indicate that under certain conditions, the deposition of PAHs in sediment may be more local in nature.

PAH results were significantly different between the Witter et. al. (2014) study and the DEP study. However, samples were collected different years. This does demonstrate that concentrations of PAHs in sediment likely fluctuate over the years. Stream flows were markedly different between the Witter sampling period (May 2010) and the current study (July/August 2014 and 2016). Stream flows as measured on Conodoguinet Creek at Hogestown (USGS Gage 01570000) demonstrated that May 2010 was a very flashy month, with flows from 400 cubic feet per second (cfs) to 4,000 cfs over the course of the month (Figure 6). In contrast, flows during July/August 2014 (Figure 7) and July/August 2016 (Figure 8) were much lower and less flashy. A discharge spike was seen in late July 2014, but this was after most samples had been collected. In July/August 2016, flows were much lower overall, remaining between <100 to <500 cfs. The higher flows in May 2010 may have increased the scouring of the creek and surrounding soil, increasing the PAH concentrations. In addition, precipitation facilitating runoff from the surrounding area may have also caused the increase in concentrations.



Figure 6. Conodoguinet Creek at Hogestown discharge (cfs), May 2010 (USGS 2019).



USGS 01570000 Conodoguinet Creek near Hogestown, PA

Figure 7. Conodoguinet Creek at Hogestown discharge (cfs), July/August 2014 (USGS 2019).



Figure 8. Conodoguinet Creek at Hogestown discharge (cfs), July/August 2016 (USGS 2019).

An aquatic life assessment of Conodoguinet Creek was last conducted in 2018, and the creek was assessed as impaired from Newburg to the mouth. The cause of this impairment was organic enrichment/low dissolved oxygen. The 2018 aquatic life assessment, unlike most DEP aquatic life assessments, was based on continuous instream monitoring (CIM) data and discrete readings that indicated low oxygen levels in the water. Previously, an aquatic life assessment occurred in 2006 and assessed the entire mainstem of the Conodoguinet Creek as attaining. Conodoguinet Creek is only attaining aquatic life use now from the headwaters to Newburg. Conodoguinet Creek is also impaired for recreational use based on fecal coliform samples in the mainstem between Shippensburg and Newville, and again around Carlisle. Conodoguinet Creek is attaining potable water use at the mouth, a reach around Mechanicsburg, a reach around Carlisle, and a reach in the upstream portion in Franklin County. It is attaining recreational use from the headwaters to around Orrstown and sections from Carlisle to the mouth. Fish consumption is attaining from the confluence of Letort Spring Run to the mouth.

Macroinvertebrates collected in November 2016 in conjunction with the CIM work supported the aquatic life impairment of Conodoguinet Creek. Although not directly tied to the aquatic life impairment, PAHs are present in the sediment of Conodoguinet Creek at concentrations that could harm aquatic life, as suggested by USEPA's sediment quality benchmarks. Although sediment standards have not been established in Pennsylvania, sediment contamination could be used as supplemental data for stream surveys.

Sediment PAH samples, as well as other contaminants in sediments, could be collected in conjunction with macroinvertebrate samples while conducting aquatic life assessments to assist in determining causes of impairment. Because many macroinvertebrates live in direct contact with sediment, they have the potential of being highly impacted by a variety of sediment contaminants. In many cases, contaminants, including PAHs, could have an affinity for adhering to sediment and may not be found in a routine water sample. Sediment sampling could be particularly useful in cases where sources and causes of impairment to macroinvertebrates are unknown.

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APPENDIX A: COMPOUNDS ANALYZED

 Table A-1. Compounds analyzed in 2014.

	Analyte (Test) Description	
1,2,4,5-Tetrachlorobenzene	7,12-Dimethylbenz(a)anthracene	Hexachlorobutadiene
1,2,4-Trichlorobenzene	Acenaphthene	Hexachlorocyclopentadiene
1,2-Dichlorobenzene	Acenaphthylene	Hexachloroethane
1,3-Dichlorobenzene	Acetophenone	Hexachloropropene
1,3-Dinitrobenzene	Aniline	Indeno[1,2,3-cd]pyrene
1,4-Dichlorobenzene	Anthracene	Isodrin
1,4-Naphthoquinone	Aramite	Isophorone
2,2'-oxybis(1-Chloropropane)	a-Terpineol	Isosafrole
2,3,4,6-Tetrachlorophenol	Benz(a)anthracene	Methyl Methanesulfonate
2,4,5-Trichlorophenol	Benzo(a)pyrene	Methyl Parathion
2,4-Dichlorophenol	Benzo(b)fluoranthene	Naphthalene
2,4-Dimethylphenol	Benzo(g,h,i)perylene	Nitrobenzene
2,4-Dinitrophenol	Benzo(k)fluoranthene	n-Nitrosodibutylamine
2,4-Dinitrotoluene	Benzyl alcohol	n-Nitrosodiethylamine
2,6-Dichlorophenol	bis(2-Chloroethoxy)methane	N-Nitrosodimethylamine
2,6-Dinitrotoluene	bis(2-Chloroethyl)ether	N-Nitrosodi-n-propylamine
2-Acetylaminofluorene	bis(2-Ethylhexyl)phthalate	N-Nitrosomethylethylamine
2-Chloronaphthalene	Butylbenzylphthalate	N-Nitrosomorpholine
2-Chlorophenol	Chlorobenzilate	N-Nitrosopiperidine
2-Methylnaphthalene	Chrysene	N-Nitrosopyrrolidine
2-Methylphenol	Diallate (cis or trans)	o,o,o-Triethylphosphorothioate
2-Nitroaniline	Dibenzo(a,h)anthracene	o-Toluidine
2-Nitrophenol	Dibenzofuran	Pentachlorobenzene
2-Picoline (2-Methylpyridine)	Diethylphthalate	Pentachloroethane
3&4-Methylphenol	Dimethoate	Pentachloronitrobenzene
3,3'-Dichlorobenzidine	Dimethylaminoazobenzene	Pentachlorophenol
3-Methylcholanthrene	Dimethylphthalate	Phenanthrene
3-Nitroaniline	Di-n-butylphthalate	Phenol
4,6-Dinitro-2-Methylphenol	Di-n-octylphthalate	Phorate
4-Aminobiphenyl	Dinoseb	Pronamide
4-Bromophenyl-phenyl ether	Diphenylamine	Pyrene
4-Chloro-3-methylphenol	Disulfoton	Pyridine
4-Chloroaniline	Ethyl methanesulfonate	Safrole
4-Chlorophenyl-phenyl ether	Ethyl Parathion	Tetraethyl Dithiopyrophosphate
4-Nitroaniline	Fluoranthene	Thionazine
4-Nitrophenol	Fluorene	
5-Nitro-o-toluidine	Hexachlorobenzene	

Table A-2. Compounds analyzed in 2016.

Analyte (Test) Description

1-Methylnaphthalene 2-Methylnaphthalene 3-Methylcholanthrene 7,12-Dimethylbenz(a)-anthracene Acenaphthene Acenaphthylene Anthracene Benz(a)anthracene Benzo(a)pyrene Benzo(b&j)fluoranthenes Benzo(e)pyrene Benzo(g,h,i)perylene Benzo(k)fluoranthene Chrysene Dibenzo(a,h)anthracene Dibenzofuran Fluoranthene Fluorene Indeno-1,2,3-cd-pyrene Naphthalene Phenanthrene Pyrene

APPENDIX B: PAH RESULTS all results in µg/kg

Test Description	CONO_1 7/22/14	CONO_1 7/22/16	CONO_2 7/22/14	CONO_2 7/22/16	CONO_3 8/25/14	CONO_3 7/22/16	CONO_4 7/22/14	CONO_4 7/22/16	CONO_5 7/22/14	CONO_5 7/22/16	CONO_6 7/22/14	CONO_6 8/16/16	CONO_7 7/22/14	CONO_7 8/09/16	CONO_7 DUP 8/09/16	CONO_8 7/22/14	CONO_8 8/09/16
1,2,4,5-Tetra-																	
chlorobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
1,2,4-Trichlorobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
1,2-Dichlorobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
1,3-Dichlorobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
1,3-Dinitrobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
1,4-Dichlorobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
1,4-Naphthoquinone	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
1-Methylnaphthalene		10.4		<12		<8.16		<6.68		<7.86		<6.64		<6.45	<6.31		<6.42
2,2'-oxybis (1-Chloropropane) 2,3,4,6-	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Tetrachlorophenol	<1620		<1040		<2710 a		<1570		<1130		<671		<672			<645	
2,4,5-Trichlorophenol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2,4-Dichlorophenol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2,4-Dimethylphenol	<1620		<1040		<2710 g		<1570		<1130		<671		<672			<645	
2,4-Dinitrophenol	<6460 g		<4150 g		<2710 b		<6300 g		<4540 g		<2680 g		<2690 g			<2580 g	
2,4-Dinitrotoluene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2,6-Dichlorophenol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2,6-Dinitrotoluene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2-Acetylaminofluorene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2-Chloronaphthalene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2-Chlorophenol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2-Methylnaphthalene	<1620	14.9 c	<1040	<12	<2710	14.9	<1570	<6.68	<1130	<7.86	<671	<6.64	<672	<6.45	<6.31	<645	<6.42
2-Methylphenol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2-Nitroaniline	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
2-Nitrophenol	<1620		<1040		<2710 a		<1570		<1130		<671		<672			<645	
2-Picoline (2-Methylpyridine)	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
3&4-Methylphenol	<3230		<2070		<5410		<3150		<2270		<1340		<1340			<1290	
3,3'-Dichlorobenzidine	<808		<518		<1350		<787		<567		<335		<336			<322	
3-Methylcholanthrene	<808	<14.9	<518	<24	<1350 a	<16.3	<787	<13.4	<567	<15.7	<335	<13.3	<336	<12.9	<12.6	<322	<12.8
3-Nitroaniline 4,6-Dinitro-2-	<3230		<2070		<2710		<3150		<2270		<1340		<1340			<1290	
	<323U		<2070		~2710 D		<3150		<zz td="" u<=""><td></td><td><134U <674</td><td></td><td><1340 <670</td><td></td><td></td><td><1290 <645</td><td></td></zz>		<134U <674		<1340 <670			<1290 <645	
	×1020		<1040		~2710		\$1570		×1130		5071		5072			<u><u></u> </u>	
4-Bromophenyl- phenyl ether	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
4-Chloro-3-methylphenol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	

															CONO_7		
Test Description	CONO_1 7/22/14	CONO_1 7/22/16	CONO_2 7/22/14	CONO_2 7/22/16	CONO_3 8/25/14	CONO_3 7/22/16	CONO_4 7/22/14	CONO_4 7/22/16	CONO_5 7/22/14	CONO_5 7/22/16	CONO_6 7/22/14	CONO_6 8/16/16	CONO_7 7/22/14	CONO_7 8/09/16	DUP 8/09/16	CONO_8 7/22/14	CONO_8 8/09/16
4-Chloroaniline	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
4-Chlorophenyl- phenyl ether	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
4-Nitroaniline	<3230		<2070		<2710		<3150		<2270		<1340		<1340			<1290	
4-Nitrophenol	<16200 h		<10400 b		<2710 g		<15700 h		<11300 h		<6710 g		<6720 g			<6450 g	
5-Nitro-o-toluidine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
7.12-Dimethvlbenz(a)																	
anthracene	<808	<7.44 n	<518	<12 n	<1350	<8.16 j	<787	<6.68 n	<567	<7.86 n	<335	<6.64 n	<336	<6.45 n	<6.31 n	<322	<6.42 o
Acenaphthene	<1620	28.4 c	<1040	<12	<2710	9.54	<1570	<6.68	<1130	<7.86	<671	<6.64	<672	<6.45	9.83	<645	<6.42
Acenaphthylene	<1620	39	<1040	34.3	<2710	85.7 Q	<1570	<6.68	<1130	16.2	<671	11	<672	11.5	14.8	<645	39.6 i
Acetophenone	<3230		<2070		<5410		<3150		<2270		<1340		<1340			<1290	
Aniline	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Anthracene	<1620	72.9	<1040	37.2	<2710	95.7	<1570	7.27	<1130	14.9	<671	49 Q	<672	67 Q	81.8 Q	<645	49.2 i
Aramite	<6460		<4150		<2710		<6300		<4540		<2680		<2690			<2580	
a-Terpineol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Benz(a)anthracene	<808	303	<518	184 Q	<1350	372	<787	23.9 a	<567	47.2	<335	346	<336	227	196	<322	168
Benzo(a)pyrene	<808	396	<518	212	<1350	433	<787	26.8	<567	59.2	<335	340	<336	234	214	<322	185
Benzo(b&j)fluoranthenes		545		338		550		36.2		77.6		394		294	262		174 k
Benzo(b)fluoranthene	<808		859		<1350		<787		<567		<335		<336			<322	
Benzo(e)pyrene		338 I		192 I		335 I		19.6 I		46.3 I		213 I		157 I	166 I		118 m
Benzo(g,h,i)perylene	<808	324	<518 a	192	<1350 a	325	<787	19.3	<567	46	<335	220	<336	184	185	<322	128 k
Benzo(k)fluoranthene	<808	195	<518	96.8	<1350	162	<787	9.79	<567	20.7	<335	162	<336	112 Q	113 Q d	<322	71.2
Benzyl alcohol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
bis(2-Chloroethoxy) methane	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
bis(2-Chloroethyl)ether	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Ethylhexyl)phthalate	<808		<518		<1350		<787		<567		<335		<336			<322	
Butylbenzylphthalate	<808		<518		<1350		<787		<567		<335		<336			<322	
Chlorobenzilate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Chrysene	<808	488	703	283	<1350	477	<787	28.9	<567	71	<335	428	<336	272	268	<322	224
Diallate (cis or trans)	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Dibenzo(a,h)anthracene	<808	51.7 d	<518 a	30 d	<1350 a	54.8 f	<787	<6.68	<567	9.98	<335	44.9 a	<336	38.6	33 d	<322	22.3 e
Dibenzofuran	<1620	21 c	<1040	<12	<2710	12.4	<1570	<6.68	<1130	<7.86	<671	<6.64	<672	<6.45	6.88	<645	<6.42
Diethylphthalate	2050		<1040		<2710		1850		<1130		<671		798			<645	
Dimethoate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Dimethvl-																	
aminoazobenzene	<808		<518		<1350		<787		<567		<335		<336			<322	
Dimethylphthalate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	

															CONO_7		
Test Description	CONO_1 7/22/14	CONO_1 7/22/16	CONO_2 7/22/14	CONO_2 7/22/16	CONO_3 8/25/14	CONO_3 7/22/16	CONO_4 7/22/14	CONO_4 7/22/16	CONO_5 7/22/14	CONO_5 7/22/16	CONO_6 7/22/14	CONO_6 8/16/16	CONO_7 7/22/14	CONO_7 8/09/16	DUP 8/09/16	CONO_8 7/22/14	CONO_8 8/09/16
Di-n-butylphthalate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Di-n-octylphthalate	<808		<518		<1350		<787		<567		<335		<336			<322	
Dinoseb	<1620		<1040		<2710 a		<1570		<1130		<671		<672			<645	
Diphenylamine	<3230		<2070		<5410		<3150		<2270		<1340		<1340			<1290	
Disulfoton	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Ethyl methanesulfonate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Ethyl Parathion	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Fluoranthene	<1620	894	1370	493	<2710	753	<1570	61.4	<1130	113	<671	652	<672	593	506	<645	353
Fluorene	<1620	41.9 c	<1040	14.7	<2710	24.2 k	<1570	<6.68	<1130	<7.86	<671	8.01	<672	10.7	17.4	<645	11.1
Hexachlorobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Hexachlorobutadiene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Hexachloro-																	
cyclopentadiene	<1620 a		<1040 a		<2710 a		<1570 a		<1130 a		<671		<672			<645	
Hexachloroethane	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Hexachloropropene	<1620 a		<1040 a		<2710		<1570 a		<1130 a		<671		<672			<645	
Indeno[1,2,3-cd]pyrene	<808	333	<518 a	208	<1350 a	346	<787	24.6	<567	45.1	<335	259	<336	210	204	<322	137
Isodrin	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Isophorone	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
lsosafrole Methyl	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Methanesulfonate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Methyl Parathion	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Naphthalene	<1620	15.5	<1040	<12	<2710	18	<1570	<6.68	<1130	<7.86	<671	<6.64	<672	<6.45	<6.31	<645	<6.42
Nitrobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
n-Nitrosodibutylamine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
n-Nitrosodiethylamine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
N-Nitrosodimethylamine N-Nitrosodi-n-	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
propylamine N-	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Nitrosomethylethylamine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
N-Nitrosomorpholine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
N-Nitrosopiperidine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
N-Nitrosopyrrolidine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
o,o,o-Triethyl-																	
phosphorothioate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
o-Toluidine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Pentachlorobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Pentachloroethane	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Pentachloronitrobenzene	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	

															CONO_7		
Test Description	CONO_1 7/22/14	CONO_1 7/22/16	CONO_2 7/22/14	CONO_2 7/22/16	CONO_3 8/25/14	CONO_3 7/22/16	CONO_4 7/22/14	CONO_4 7/22/16	CONO_5 7/22/14	CONO_5 7/22/16	CONO_6 7/22/14	CONO_6 8/16/16	CONO_7 7/22/14	CONO_7 8/09/16	DUP 8/09/16	CONO_8 7/22/14	CONO_8 8/09/16
Pentachlorophenol	<3230		<2070		<2710 h		<3150		<2270		<1340		<1340			<1290	
Phenanthrene	<1620	461 c	<1040	162 Q	<2710	228	<1570	28.6	<1130	54.5	<671	74.4 Q	<672	156	180	<645	166
Phenol	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Phorate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Pronamide	<1620 n		<1040 n		<2710		<1570 n		<1130 n		<671 n		<672 n			<645 n	
Pyrene	<808	828	871	375	1830	705	<787	40.3	<567	99.4	<335	596	<336	482	447	<322	447
Pyridine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Safrole	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Tetraethyl																	
Dithiopyrophosphate	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	
Thionazine	<1620		<1040		<2710		<1570		<1130		<671		<672			<645	

Bold indicates analyte was detected.

Q - Sample held beyond normal holding time.

a - Continuing calibration recoveries high. Results may be biased high.

b - Continuing calibration recoveries low. Results may be biased low. Low-level LFB recovery low. Reporting limit may be biased low.

c - Duplicate values are not within acceptable range.

d - Internal standard recoveries high. Results may be biased

low.

e - Internal standard recoveries high. Results may be biased low. Matrix spike recoveries low. Results and/or reporting limits may be biased low.

f - Internal standard recoveries high. Results may be biased low. Matrix spike recovery high. Results may be biased

high.

g - Low-level LFB recovery low. Reporting limit may be biased

low.

h - Low-level LFB recovery low. Reporting limit may be biased low. Continuing calibration recoveries low. Results may be biased low.

i - Matrix spike recoveries low. Results and/or reporting limits may be biased low.

j - Matrix spike recoveries low. Results and/or reporting limits may be biased low. The second source standard recovery was low. Results and/or reporting limits may be biased low.

k - Matrix spike recovery high. Results may be biased high.

I - Not Covered Under NJ NELAP Accreditation.

m - Not Covered Under NJ NELAP Accreditation. Matrix spike recovery high. Results may be biased high.

n - The second source standard recovery was low. Results and/or reporting limits may be biased low.

o - The second source standard recovery was low. Results and/or reporting limits may be biased low. Matrix spike recoveries low. Results and/or reporting limits may be biased low.

APPENDIX C: PAH RESULTS – DETECTIONS & BENCHMARK COMPARISON all results in µg/kg

													CONO_7	
	CONO_1	CONO_1	CONO_2	CONO_2	CONO_3	CONO_3	CONO_4	CONO_4	CONO_5	CONO_6	CONO_7	CONO_7	DUP	CONO_8
Test Description	7/22/14	7/22/16	7/22/14	7/22/16	8/25/14	7/22/16	7/22/14	7/22/16	7/22/16	8/16/16	7/22/14	8/09/16	8/09/16	8/09/16
1-Methylnaphthalene		10.4												
2-Methylnaphthalene		14.9 N				14.9 N								
Acenaphthene		28.4 Y				9.54 Y							9.83 Y	
Acenaphthylene		39 Y		34.3 Y		85.7 Y Q			16.2 Y	11 Y		11.5 Y	14.8 Y	39.6 Y
Anthracene		72.9 Y		37.2 N		95.7 Y		7.27 N	14.9 N	49 N Q		67 Y Q	81.8 Y Q	49.2 N
Benz(a)anthracene		303 Y		184 Y Q		372 Y		23.9 N	47.2 N	346 Y		227 Y	196 Y	168 Y
Benzo(a)pyrene		396 Y		212 Y		433 Y		26.8 N	59.2 N	340 Y		234 Y	214 Y	185 Y
Benzo(b&j)fluoranthenes		545		338		550		36.2	77.6	394		294	262	174
Benzo(b)fluoranthene			859											
Benzo(e)pyrene		338		192		335		19.6	46.3	213		157	166	118
Benzo(g,h,i)perylene		324 Y		192 Y		325 Y		19.3 N	46 N	220 Y		184 Y	185 Y	128 N
Benzo(k)fluoranthene		195 N		96.8 N		162 N		9.79 N	20.7 N	162 N		112 N Q	113 N Q	71.2 N
Chrysene		488 Y	703 Y	283 Y		477 Y		28.9 N	71 N	428 Y		272 Y	268 Y	224 Y
Dibenzo(a,h)anthracene		51.7 Y		30 N		54.8 Y			9.98 N	44.9 Y		38.6 Y	33 N	22.3 N
Dibenzofuran		21 N				12.4 N							6.88 N	
Diethylphthalate	2050 Y						1850 Y				798 Y			
Fluoranthene		894 Y	1370 Y	493 Y		753 Y		61.4 N	113 N	652 Y		593 Y	506 Y	353 N
Fluorene		41.9 N		14.7 N		24.2 N				8.01 N		10.7 N	17.4 N	11.1 N
Indeno[1,2,3-cd]pyrene		333 Y		208 Y		346 Y		24.6 Y	45.1 Y	259 Y		210 Y	204 Y	137 Y
Naphthalene		15.5 N				18 N								
Phenanthrene		461 Y		162 N Q		228 Y		28.6 N	54.5 N	74.4 NQ		156 N	180 N	166 N
Pyrene		828 Y	871 Y	375 Y	1830 Y	705 Y		40.3 N	99.4 N	596 Y		482 Y	447 Y	447 Y

Y – Above EPA Benchmark N – Not above EPA Benchmark No "Y" or "N" – EPA Benchmark does not exist for this analyte Q – Sample held beyond normal holding time.