

5-23-2010

Analysis of Polycyclic Aromatic Hydrocarbons (PAHS) and Oxygenated PAHS in Stream Sediments Along an Increasingly Urbanized Land-Use Gradient: Conodoguinet Creek Watershed, Cumberland County, PA

Minh Huu Nguyen
Dickinson College

Follow this and additional works at: http://scholar.dickinson.edu/student_honors

 Part of the [Chemistry Commons](#)

Recommended Citation

Nguyen, Minh Huu, "Analysis of Polycyclic Aromatic Hydrocarbons (PAHS) and Oxygenated PAHS in Stream Sediments Along an Increasingly Urbanized Land-Use Gradient: Conodoguinet Creek Watershed, Cumberland County, PA" (2010). *Dickinson College Honors Theses*. Paper 105.

This Honors Thesis is brought to you for free and open access by Dickinson Scholar. It has been accepted for inclusion by an authorized administrator. For more information, please contact scholar@dickinson.edu.

**Analysis of Polycyclic Aromatic Hydrocarbons (PAHs)
and Oxygenated PAHs in Stream Sediments Along an
Increasingly Urbanized Land-Use Gradient**

Conodoguinet Creek Watershed, Cumberland County, PA

By
Minh H. Nguyen

Submitted in partial fulfillment of Honors Requirements for the Department of
Chemistry

Dr. Amy E. Witter, Supervisor
Dr. Michael S. Holden, Reader
Dr. Cindy Samet, Reader
Dr. Kristi J. Humphreys, Reader
Dr. Sarah K. St. Angelo, Reader
Dr. Rebecca E. Connor, Reader
Dr. John R. Seiders, Reader

December 9, 2010

| Contents | page # |
|-----------------------------|--------|
| Abstract..... | 3 |
| Introduction..... | 3 |
| Experimental..... | 6 |
| Results and Discussion..... | 10 |
| Conclusions..... | 20 |
| Acknowledgements..... | 20 |
| References..... | 21 |
| Appendices..... | 22 |

Abstract

The concentrations and distributions of polycyclic aromatic hydrocarbons (PAHs) and oxygenated PAHs (oxy-PAHs) in stream sediments collected from thirty-four sites along the Conodoguinet Creek were measured and analyzed. The sites are well-characterized in terms of adjacent land-use features as determined using Geographic Information Systems (GIS) data. It was found that urban areas are characterized by elevated concentrations of PAHs and oxy-PAHs representative of pyrogenic processes. A combination of GIS data and principal component analysis (PCA) were employed to interpret the concentration data, and the results demonstrate that oxy-PAHs show a higher potential than PAHs to distinguish among different pollutant sources in an urbanizing watershed. This work is, to our knowledge, the first study to propose oxy-PAHs as unique chemical markers that can serve as proxies for various land-use practices, and may aid in identifying pollutant sources that contribute to ecosystem decline.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common environmental pollutants, and are frequently found at various sites as a result of anthropogenic contamination and/or natural processes.¹ Structurally, they are organic molecules composed of carbon and hydrogen atoms built from two or more fused benzene rings. Some examples of common PAHs in the environment are shown in Figure 1. Historically, PAHs have become one of the most monitored groups of chemicals since they are known to be toxic, mutagenic, and carcinogenic.²⁻⁴

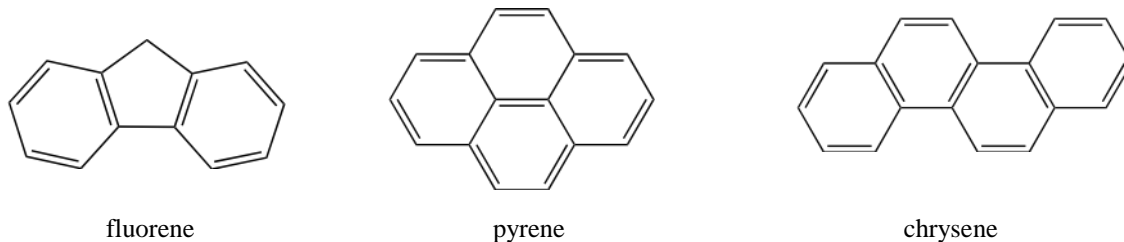


Figure 1. Some examples of common PAHs that are frequently found in environmental samples.

While the occurrence of PAHs in the environment has been widely studied, much less attention has been focused on their oxygenated analogues, referred to as oxy-PAHs. Structures of common oxy-PAHs detected in environmental samples are included in Figure 2. Together with PAHs, oxy-PAHs have been found in contaminated soil,^{5,6} diesel exhaust,⁷ fly ash,⁸ urban aerosols,^{9,10} sediments,¹¹ and sewage sludge.¹² Recent studies have shown that oxy-PAHs may have an important toxicological significance. Oxy-PAH quinones formed *in vivo* by mammalian metabolism are capable of generating reactive oxygen species associated with oxidative stress, as well as arylating cellular proteins that results in disruption of signal transduction pathways and DNA damage.^{13,14} Moreover, bioassays of environmental samples classified oxy-PAHs as extremely toxic, and potentially more harmful than PAHs.^{15,16}

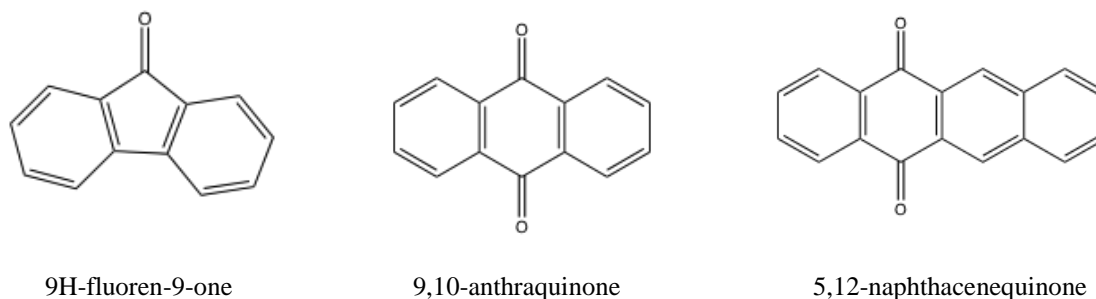


Figure 2. Structures of common oxy-PAHs detected in environmental samples.

Unambiguous quantitative data is difficult to obtain for oxy-PAHs due to their semi-polar nature, diversified ring structure, and the lack of standard reference materials. As a consequence, knowledge concerning the concentration, distribution, and fate of these

compounds in the environment remains enigmatic.⁹ Furthermore, while several studies measuring oxy-PAHs in soils and air have been carried out, analysis of oxy-PAHs in other environmental media is largely underrepresented. Given the few studies that exist concerning the concentration and distribution of oxy-PAHs in the environment, the major goal of this work is to measure the concentrations of oxy-PAHs, in addition to PAHs, in stream sediments collected from thirty-four well-characterized sites within the Conodoguinet Creek watershed (Figure 3). The data have been interpreted using principal component analysis (PCA) and correlated against GIS data to identify potential sources, and to assess trends of PAHs and oxy-PAHs in sediments in relation to urbanization. By examining the variations in concentrations and distributions of oxy-PAHs, this study demonstrates the utility of these compounds as unique chemical markers that can help delineate various land-use practices that negatively impact stream health in urbanizing watersheds.

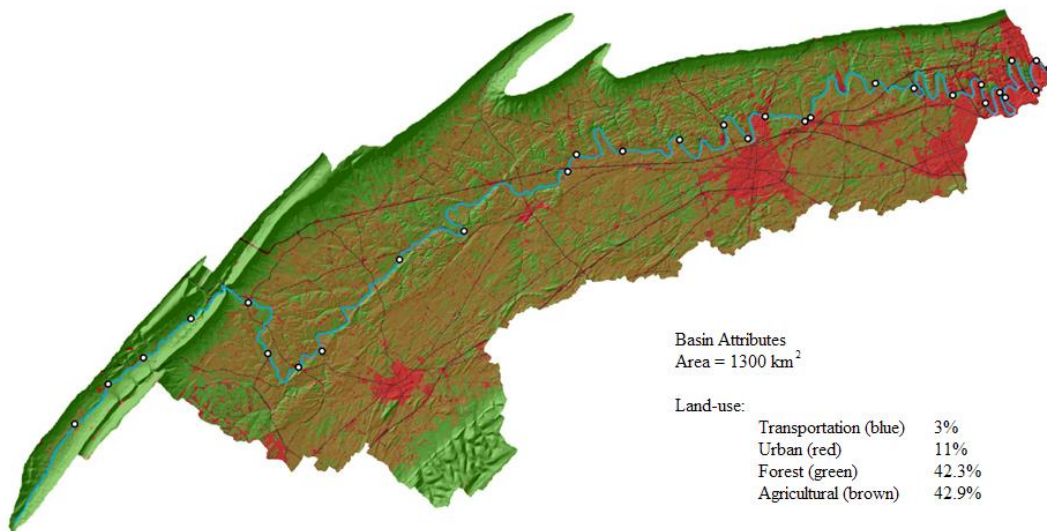


Figure 3. Study area showing different land-use categories and location of sampling sites (white dots). (Figure provided courtesy of Professor Peter B. Sak, Department of Earth Sciences, Dickinson College).

Experimental

Sample Collection

Thirty-four sediment samples were collected from sites within the Conodoguinet Creek watershed during Summer 2010. These sites were all well-characterized in terms of commonly defined land-use features (i.e. vehicle miles travelled, impervious surface area, % forest, % agriculture, etc.) impacting the stream, which allow close correlation between the chemical results and land-use activities that contribute to stream chemistry. The 150 km creek was roughly divided into thirty, 5 km segments from which sediment samples were collected. In general, from west to east along the creek (from Site 1 to Site 35), the degree of urbanization increased. The sampling protocol targeted depositional zones with organic carbon-rich soil where possible, and avoided areas directly adjacent to roadways. At each sampling site, 5 samples were collected with a stainless steel scoop from depositional zones along a 25-m length of stream, and combined together in a stainless steel bowl to make up a composite sample. Then, a 50 g portion of the composite sample was removed and placed in a solvent-rinsed glass jar with Teflon cap. Based on the sample collection depth (1-2 cm), as well as sediment accumulation rates, the sediments are expected to represent modern inputs. All samples were transported on ice to the laboratory, and freeze dried to remove residual water. After drying, the samples were sieved through a 1-mm sieve (ASTM No. 18) to obtain a consistent particle size for extraction. Visible debris such as sticks or stones was removed before sieving. The sieved samples were returned to the collection jars and stored frozen at -20°C until analysis, which occurred within three months of collection. Field blanks were not included as part of this study because earlier studies had shown no PAH contamination during sample collection.

Chemicals

All chemicals measured in this study are presented in Appendix I. The oxy-PAHs measured in this study include 9H-fluoren-9-one, 9,10-anthraquinone, 7H-benz[de]anthracen-7-one, and 5,12-naphthacenequinone. These four analytes were chosen because there are commercial sources of these chemicals available: Alfa Aesar (9H-fluoren-9-one, 7H-benz[de]anthracen-7-one), Aldrich (5,12-naphthacenequinone), and Chem Service (9,10-anthraquinone). The PAHs were quantified using a standard reference mixture (Restek Corp. Bellefonte, PA.) containing 17 EPA analytes, including naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[ghi]perylene. The following perdeuterated compounds were used as surrogate standards: d₈-naphthalene, d₁₀-pyrene, d₁₀-anthracene, and d₁₂-chrysene (Supelco Analytical). The following perdeuterated compounds were used as recovery internal standards: d₁₀-phenanthrene and d₁₂-perylene (Supelco Analytical). Solvents were Optima grade or better (Fisher Scientific).

Soxhlet Extraction

For each sediment, approximately 20 g of homogenized, freeze-dried sample was placed in a Soxhlet thimble (Whatman), spiked with 50 µL of 100 ng/µL of perdeuterated surrogate internal standards, and extracted overnight (~ 20 hours) with 250 mL of dichloromethane. Extracts were reduced in volume via rotary evaporation to approximately 1 mL.

Crude Extract Clean-Up

Each crude extract was transferred to a pre-conditioned aminopropyl solid-phase extraction (SPE) cartridge (Thermo Scientific) that had been previously rinsed with 20 mL of 20% dichloromethane in hexane. The cartridge was eluted with 40 mL of 20% dichloromethane in hexane, and the eluent was percolated through an activated copper column prepared daily in order to remove elemental sulfur. The extract was reduced to 1 mL in volume, followed by addition of 5000 ng of perdeuterated recovery internal standards to give a final concentration of 5 ng/ μ L each.

GC-MS Analysis

The extracts were analyzed using a gas chromatograph (GC, Agilent 7890A) coupled to an electron impact mass spectrometer (MS, Agilent 5975C) using a 30 m RTX-5SiMS capillary column (0.25 mm I.D., 0.25 μ m film) and helium (1.2 mL/min) as carrier. Aliquots of 1 μ L were injected into the GC by an autoinjector. The GC was operated in splitless mode with a single taper liner and no glass wool under the following conditions: injector temperature 275°C, transfer line temperature 280°C, source temperature 230°C, MS Quad temperature 150°C. The GC oven temperature was programmed from 40°C (1 min) to 310°C (5°C/min), and held at 310°C for 10 min. Full scan mass spectra were acquired over m/z range 45 to 450. The MS was operated in single ion monitoring (SIM) mode for quantification. The target compounds were identified by comparison of their mass spectra and retention times with those of authentic reference standards. Six calibration standards containing 4 oxy-PAH analytes (25 - 1000 pg/ μ L) and 17 PAH analytes (0.1 - 10 ng/ μ L) were prepared for quantitative analysis. A total of 21 target analytes were measured in each sediment sample.

Quality Control

All sample concentrations obtained from GC-MS analysis were calculated using relative response factors based on internal standards. Four deuterated surrogate standards were added to all samples to quantify PAH recoveries. Surrogate recoveries in sediment samples are as follows: d₈-naphthalene, 54.9 ± 9.6%; d₁₀-anthracene, 76.5 ± 14.6%; d₁₀-pyrene, 86.3 ± 6.4%; and d₁₂-chrysene, 58.4 ± 5.3%. Oxy-PAH recoveries were quantified by spike-recovery experiments because deuterated oxy-PAH standards were not commercially available. Recoveries of oxy-PAHs are as follows: 9H-fluorene-9-one, 93.9 ± 3.3%; 9,10-anthraquinone, 38.6 ± 1.5%; 7H-benz[de]anthracene-7-one, 97.6 ± 4.9%; and 5,12-naphthacenequinone, 102.5 ± 6.0%. The PAH and oxy-PAH concentrations reported in this study were corrected based on the recoveries determined above. Detection limits of PAHs and oxy-PAHs were determined to be 0.17 ng/μL and 84 pg/μL, respectively.

Principal Component Analysis

Principal component analysis (PCA, Eigenvector Solo, v.4.2.1, Eigenvector Research, Inc.) was conducted by Professor Witter on the PAH and oxy-PAH datasets in order to aid in understanding the common distributions and/or trends among the various PAHs and oxy-PAHs observed in these sediments. PCA is a mathematical method that transforms a number of possibly correlated variables into a number of uncorrelated variables called principal components (PCs) that best describe the variations in the data. Prior to PCA, the PAH and oxy-PAH input data were normalized to remove the effect of widely varying concentrations between samples. The results of the PCA analysis are presented and discussed using score and loading plots below.

Results and Discussion

Total PAH Concentrations

Total PAH concentrations ranged from 1634 ng/g to 9244 ng/g, as presented in Appendix II. Comparison of total PAH concentrations among sampling sites showed a trend of increasing PAH concentrations with increasing urbanization, when measured as decreasing distance from confluence of the Conodoguinet Creek with the Susquehanna river (Figure 4). As expected, concentrations of each individual PAH and total PAHs increase from forested and rural areas to urban areas. The only exception to this trend is the significantly high concentration of PAHs at site 5, which is a relatively pristine rural area. Given the proximity of this site to a local gas station, we hypothesize that this aberrant value is due to a probable leak from an underground storage tank at this nearby gas station (data not shown).

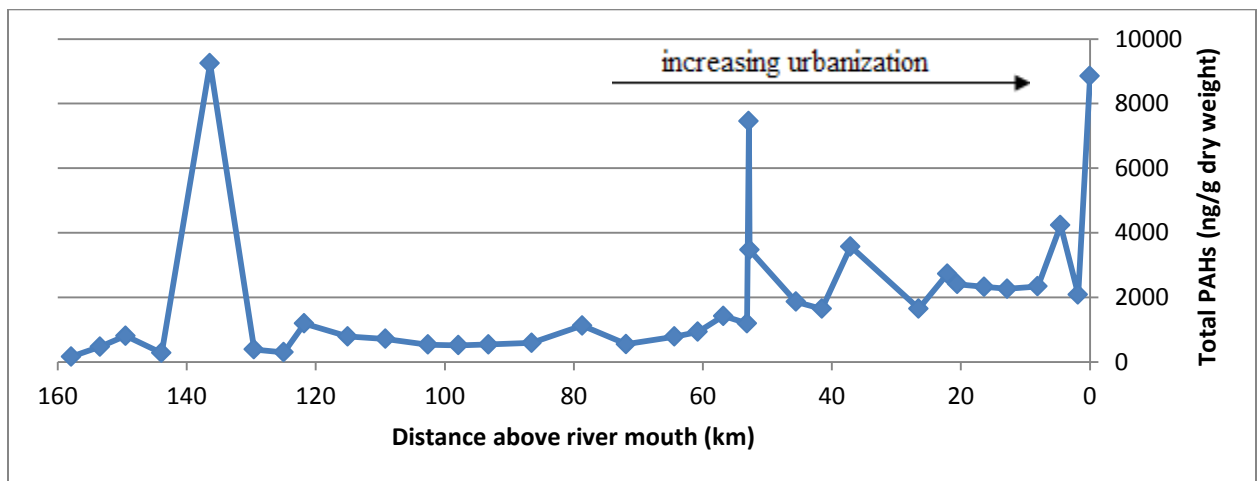


Figure 4. Total PAHs versus distance above river mouth collected from sites within the Conodoguinet Creek watershed.

Total oxy-PAH Concentrations

Total oxy-PAH concentrations ranged from 21 ng/g to 748 ng/g, as presented in Appendix III. The concentration of oxy-PAHs varies from site to site, and is approximately an order of magnitude lower than that of PAHs. It is notable that the trend obtained by comparison of total oxy-PAH concentrations between sampling sites follow the same general pattern as that of PAHs (Figure 5).

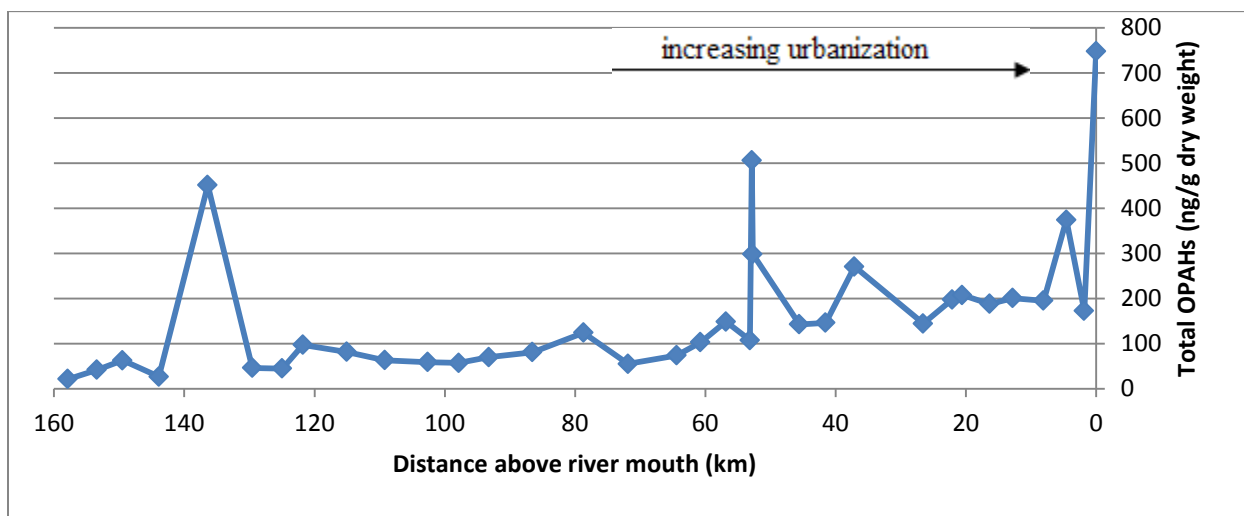


Figure 5. Total oxy-PAHs versus distance above river mouth collected from sites along the Conodoguinet Creek watershed.

Although PAHs are common environmental pollutants, and they are frequently detected at various sites as a result of anthropogenic contamination, their usefulness as molecular markers for pollution monitoring is limited because there are many sources of these molecules in the environment.¹⁷ Incomplete combustion of biomass and fossil fuels can produce pyrogenic (meaning: combustion-derived) PAHs, and is in fact the main source of PAHs in the environment. Petrogenic PAHs are present in unburned petroleum that can be released to the environment through human activities (oil spills) or natural processes (oil

seepage). Furthermore, there is some evidence suggesting that PAHs can be generated by modern biological processes or by diagenetic processes (biogenic sources),¹⁸⁻²⁰ making it even more difficult to identify the sources of PAH at contaminated sites. The formation of oxy-PAHs in high concentration, on the other hand, occurs mainly through direct combustion.²¹ Thus the fact that very similar patterns of PAHs and oxy-PAHs were observed along the Conodoguinet Creek watershed is indicative of pyrogenic processes as the main source of the PAHs found in stream sediments, especially in the urbanized and highly-urbanized areas.

PAH Analysis

An assemblage showing the concentration and distribution of individual PAH components can provide insight into the sources of PAHs in sediments, and is often referred to as a PAH source “fingerprint”. It has been shown that assemblages of PAHs emitted by different sources vary widely.²² As illustrated in Figure 6, while PAHs derived from petrogenic sources are richer in lower molecular weight 2- to 3-ring components; pyrogenic sources are dominated by higher molecular weight 4- to 6- ring PAHs. In order to better understand the pollutant sources that contribute to the decline of water and sediment quality in the stream, the PAH assemblage of each sediment was analyzed. It was found that PAH fingerprints from all sampling sites in this study show a predominance of high-molecular weight PAHs (HMW PAHs). Furthermore, significantly higher abundance of HMW PAHs was encountered closer to urban centers versus forested sites, once again suggesting that combustion processes are responsible for the elevated concentrations of PAHs in the stream (Figure 7).

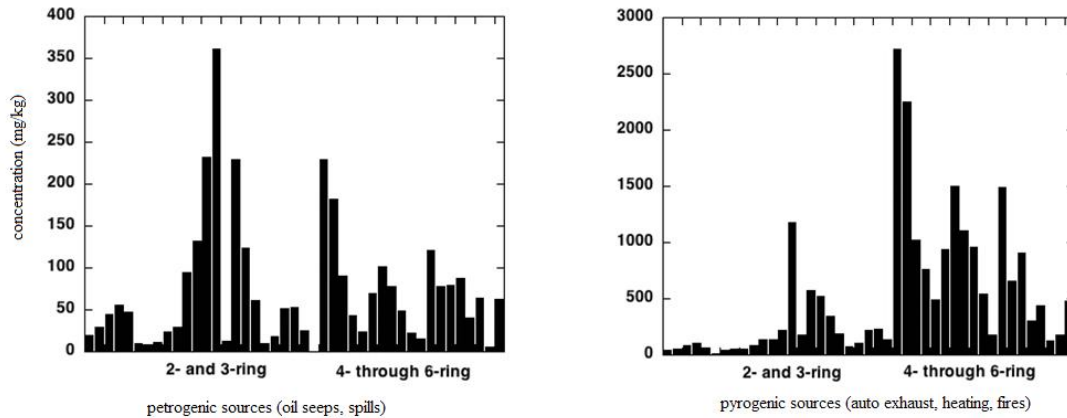


Figure 6. PAH assemblages showing the different distributions and concentrations of PAHs in petrogenic and pyrogenic sources. (Figure provided courtesy of Professor Amy E. Witter, Department of Chemistry, Dickinson College).

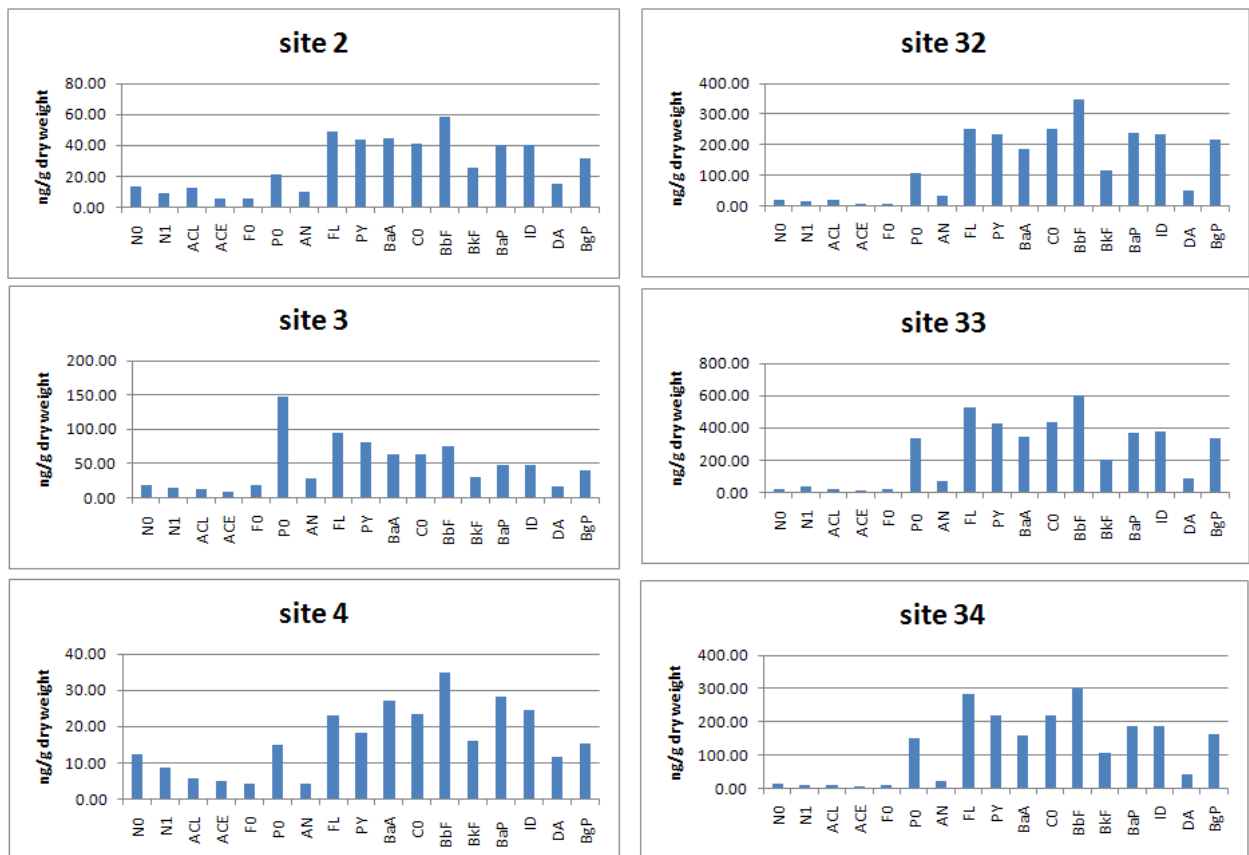


Figure 7. PAH assemblages showing individual PAH concentrations and distributions in forested (left, Sites 2, 3, 4) and urban (right, Sites 32, 33, and 34) sediments collected from sites within the Conodoguinet Creek watershed. Abbreviation used to indicate the individual PAH is given in Appendix I.

Furthermore, diagnostic ratios can also be utilized to examine source inputs of PAHs to the stream. Here, the ratio of 2- and 3-ring PAHs to 4- through 6-ring PAHs found in sediments along the stream was examined. As seen in Figure 8, this ratio remains relatively constant across more urban areas with an average value of 0.14 ± 0.02 (approximately 100 km upstream the river mouth), which suggests a single PAH source, a single transport mechanism, or both, are responsible for the PAH assemblage measured in this part of the stream. The fact that the PAH ratio varies widely (range: 0.14-0.75) among the more forested, upstream areas, suggests that there are other possible PAH sources or transport mechanisms that control PAH assemblages in forested versus urbanized areas.

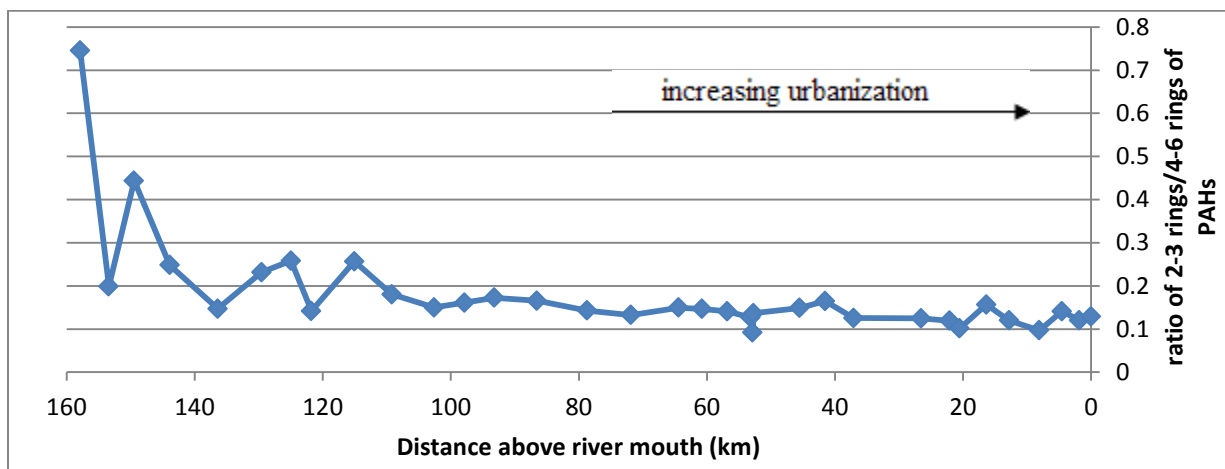


Figure 8. PAH ratios of lower to higher molecular weight PAHs versus distance above river mouth from sediments collected from sites along the Conodoguinet Creek watershed.

Oxy-PAH Analysis

While PAH assemblages and PAH ratios have been widely used to detect and identify sources of environmental pollution, the use of oxy-PAH for these purposes has been until recently, overlooked. Here, we take an unprecedented opportunity to analyze the pattern and distribution of oxy-PAHs along an increasingly urbanized gradient to investigate the

potential utility of these molecules to distinguish between different pollutant sources within a single drainage basin. The oxy-PAH profile of each sediment along the stream was analyzed. It was found that there is a significant difference between the patterns of the oxy-PAH assemblages from pristine, forested sites and those from urbanized and highly urbanized sites. As illustrated in Figure 9, the concentration of 5, 12-naphthacenequinone is consistently lower than that of 9H-fluoren-9-one in pristine, forested sites. However, the reverse trend is observed for urban sites. Furthermore, when the concentration ratio of 5, 12-naphthacenequinone (NQ) to 9H-fluoren-9-one (FO) was plotted, the result obtained is fascinating. According to Figure 10, in conjunction with land-use data in Appendix IV, this ratio is repeatedly less than one for pristine, forested sites ($\geq 85\%$ forest land-use); higher than one for urbanized and highly urbanized sites ($\leq 50\%$ forest land-use); and approximately equal to one for moderately urbanized sites (between 50% and 85% forest land-use). Thus we find the use of oxy-PAH assemblages and oxy-PAH ratios to be a far more effective and sensitive indicator than PAH diagnostic ratios to distinguish between pyrogenic and petrogenic sources, and potentially between natural and anthropogenic sources.

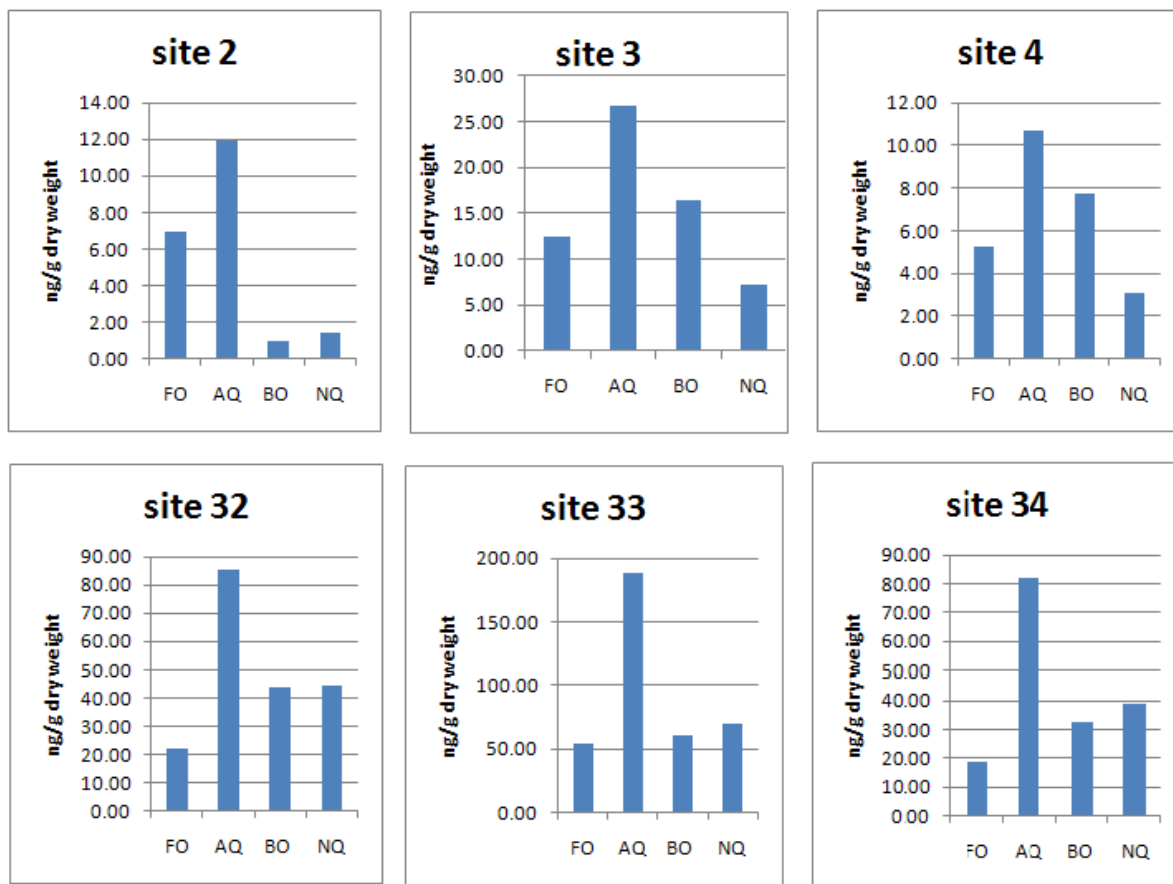


Figure 9. Oxy-PAH assemblages showing different concentrations and distributions of oxy-PAHs in remote (top) and urban (bottom) sediments collected from sites along the Conodoguinet Creek watershed. Abbreviation used to indicate the individual oxy-PAH is given in Appendix I.

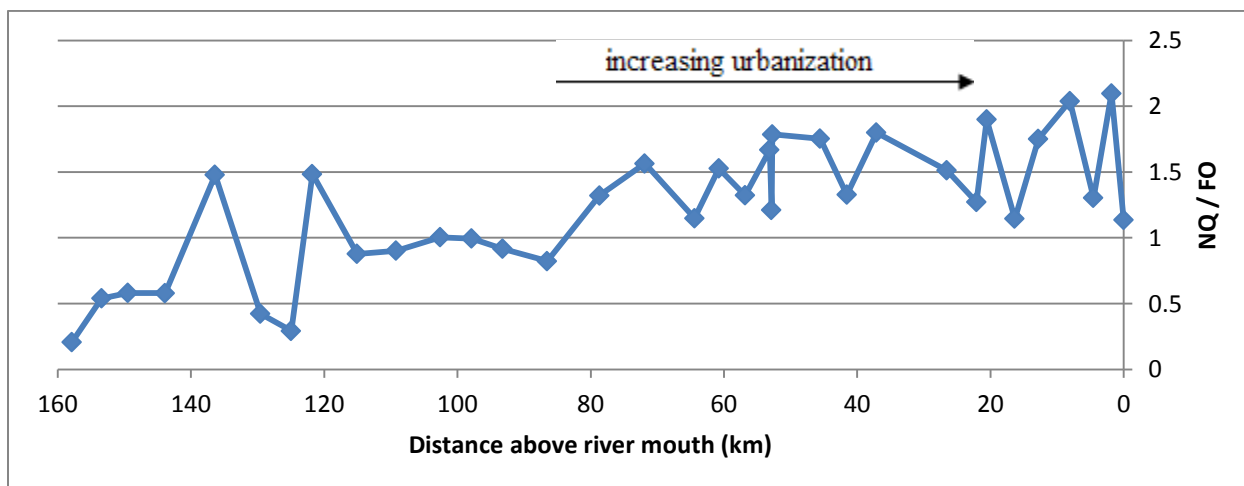


Figure 10. Ratio of 5, 12-naphthacenequinone to 9H-fluoren-9-one obtained from sediments collected from sites along the Conodoguinet Creek watershed.

Principal Component Analysis

In addition to diagnostic ratios and assemblages, PCA was conducted on the PAH and oxy-PAH datasets in order to determine common distributions and/or trends among the sediments obtained (Figure 11). The first two principal components (PCs) account for 79.89% of the total variance for the PAH dataset. Scores plot for PAHs clearly show a cluster of samples collected at sites closer to the urbanized centers. Comparison of scores and loadings plots lead to the conclusion that urbanized and highly urbanized samples are distinguished by the increasing contribution of HMW PAHs. On the other hand, the first two PCs account for 90.69% of the total variance for the oxy-PAH dataset. While highly urbanized sites are distinguished by the contribution of 5, 12-naphthacenequinone, clean and remote sites are characterized by the contribution of 9H-fluoren-9-one. It is noteworthy that each of the four oxy-PAHs displays a unique pattern, as observed in the loadings plot, suggesting the potential use of these compounds in identifying different pollutant sources. Overall, the results obtained from PCA are in agreement with previous analyses.

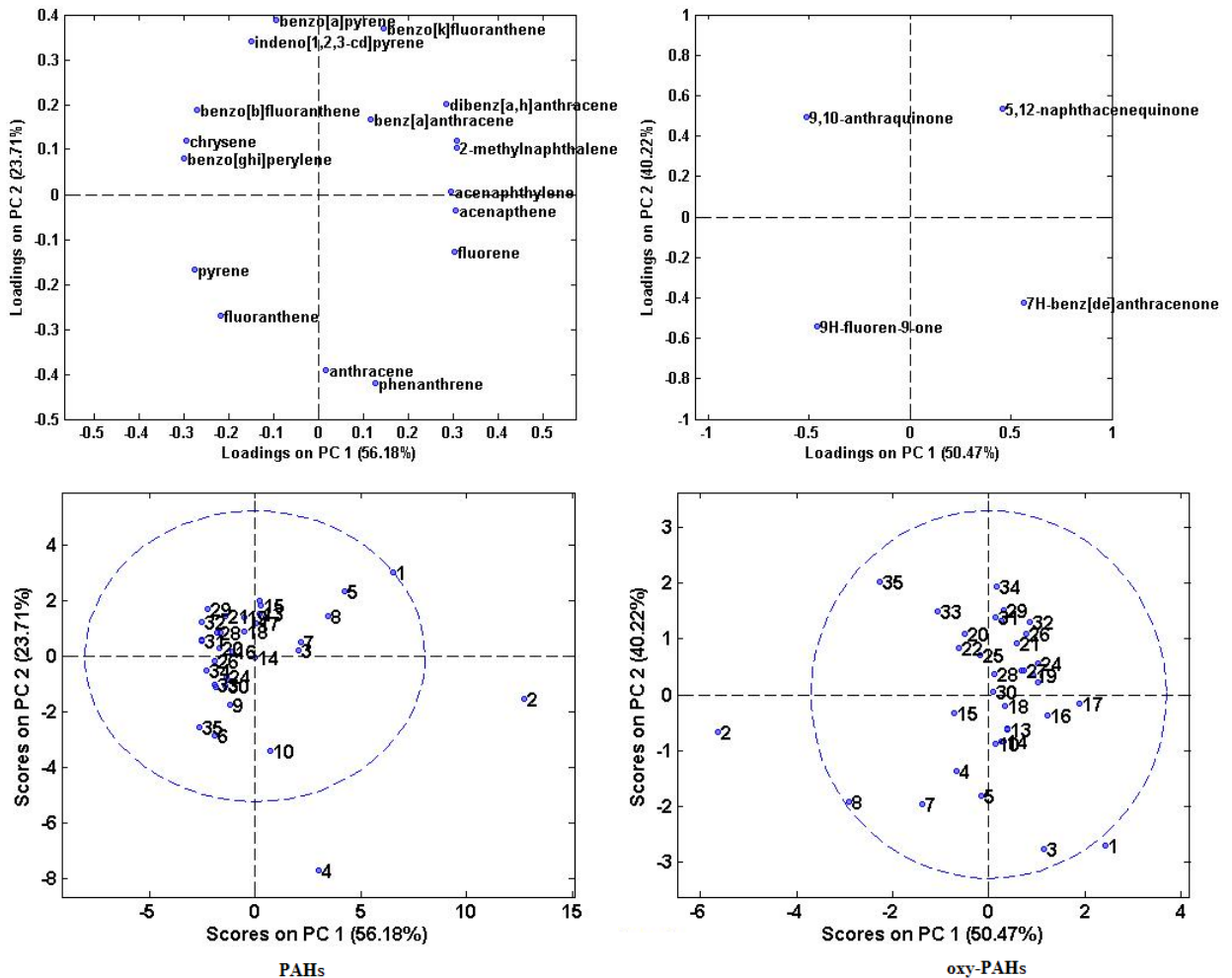


Figure 11. Loadings (top) and scores (bottom) plots of PAHs and oxy-PAHs from sites along the Conodoguinet Creek watershed. Scores plots provide information about how the sites differ from each other in terms of their chemical behavior; loadings plots provide information about what specific chemicals are responsible for that variation.

The Correlation between the Urban Land-Use Gradient and PAH and oxy-PAH concentrations

Previous study has indicated that concentration of PAHs is strongly correlated with urbanization, with the strongest relations to percentage commercial, industrial, and transportation land-uses.²³ Given the nature of the Conodoguinet Creek that drains along an increasingly urbanized land-use gradient and the above characteristics observed for oxy-PAHs, it would be interesting to compare the occurrences of PAHs and oxy-PAHs with

specific land-use activities. To this end, the total concentration of PAHs and oxy-PAHs obtained at sites along the stream were correlated with specific land-uses determined via geographic information systems (GIS) data (Appendix IV). A matrix of Pearson’s correlation coefficients that summarizes the strength of the linear relationship between the sediment data and the GIS data is presented in Table 1. Typically, the absolute value of Pearson’s correlation coefficients varies from 0 to 1, with higher values indicating a stronger correlation. Notably, the total oxy-PAHs showed higher correlations with all land-use categories than the total PAHs by a factor ranging from 1.4 to 2.4, indicating the potential use of oxy-PAH as a more specific indicator of urbanization, consequently allowing us to better predict the types of land-use activities that result in impaired ecosystem health.

Table 1. Correlation coefficients of comparisons between the different land-use categories to total PAHs and total oxy-PAHs from sites along the Conodoguinet Creek watershed

| Land-use | Total PAH concentrations | Total oxy-PAH concentrations | Ratio^a |
|-----------------------------------|---------------------------------|-------------------------------------|--------------------------|
| Distance above river mouth | -0.36 | -0.51 | 1.4 |
| Area (km²) | 0.32 | 0.46 | 1.4 |
| % Hi_Urban | 0.33 | 0.46 | 1.4 |
| % Lo_Area | 0.23 | 0.38 | 1.7 |
| % Trans | 0.26 | 0.40 | 1.5 |
| % Urban | 0.33 | 0.48 | 1.5 |
| % Ag | 0.10 | 0.25 | 2.4 |
| % Forest | -0.15 | -0.30 | 2.0 |
| % Imprev | 0.33 | 0.47 | 1.4 |
| 60m_% Tran | 0.25 | 0.38 | 1.5 |
| 60m_%Lo Urban | 0.16 | 0.31 | 1.9 |
| 60m_% Hi Urban | 0.35 | 0.49 | 1.4 |

^a Values represent ratio of correlation coefficients obtained from oxy-PAH and PAH datasets. For complete descriptions of different land-use categories, please refer to Appendix IV.

Conclusion

The overall objective of this study was to assess the concentrations and distributions of oxy-PAHs, in addition to PAHs, in stream sediments collected from well-characterized sites within the Conodoguinet Creek watershed, along an urbanized land-use gradient. It was found that urban centers are characterized by elevated concentrations of PAHs and oxy-PAHs due to pyrogenic processes. Even though the trend obtained by comparison of total oxy-PAHs along the stream follows the same pattern as that of PAHs, a closer examination indicate that oxy-PAHs assemblages and ratios exhibit higher potential than those of PAHs to distinguish between pyrogenic and petrogenic sources, and potentially between natural and anthropogenic sources. Thus this class of compounds displays unique characteristics that can serve as proxies for various land-use practices, and may aid in identifying pollutant sources that contribute to ecosystem decline.

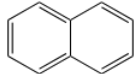
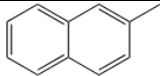
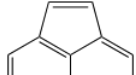
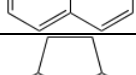
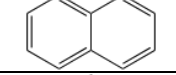
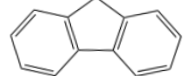
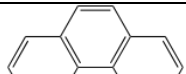
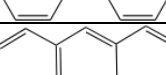
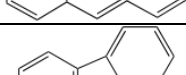
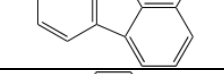
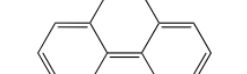
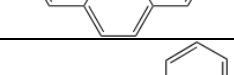
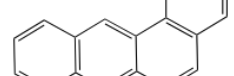
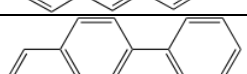
Acknowledgements

PCA was performed by Professor Amy Witter, and GIS data was provided by Professor Peter Sak. The author is indebted to Professor Amy Witter for her guidance during this work. This research was supported by Dickinson College Research and Development Grant.

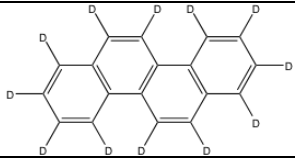
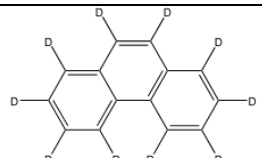
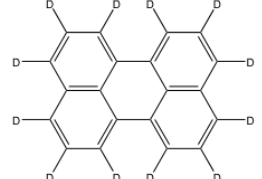
References

- (1) Howsam, M.; Jones, K. C. In *Anthropogenic Compounds. PAH and Related Compounds*; Neilson, A. H., Ed.; Springer: Berlin, Germany, 1998; pp 137-174.
- (2) Lee, M. L.; Novotny, M V.; Bartle, K. D. *Analytical Chemistry of Polycyclic Aromatic Compounds*; Academic Press: New York, 1981.
- (3) *Handbook of Polycyclic Aromatic Hydrocarbons*; Bjorseth, A. Ed.; Marcel Dekker: New York, 1983.
- (4) *Handbook of Polycyclic Aromatic Hydrocarbons*; Bjorseth, A., Ramdahl, T., Eds.; Marcel Dekker: New York, 1985; Vol. 2.
- (5) Lundstedt, S., Haglund, P., Oberg, L. G. *Environ. Toxicol. Chem.* **2003**, *22*, 1413-1420.
- (6) Meyer, S., Cartellieri, S., Steinhart, H. *Anal. Chem.* **1999**, *71*, 4023-4029.
- (7) Leotz-Gartziandia, E., Tetry, V., Carlier, P. *Polycyclic. Aromat. Compd.* **2000**, *20*, 245-258.
- (8) Akimoto, Y., Aoki, T., Nito, S., Inouye, Y. *Chemosphere* **1997**, *34*, 263-273.
- (9) Allen, J. O., Dookeran, N. M., Taghizadeh, K., Lafleur, A. L., Smith, K. A., Sarofim, A. F. *Environ. Sci. Technol.* **1997**, *31*, 2064-2070.
- (10) Moyano, E., Galceran, M. T. *Quim. Anal. (Barcelona)* **1997**, *16*, 159-164.
- (11) Fernandez, P., Grifoll, M., Solanas, A. M., Bayona, J. M., Albaiges, J. *Environ. Sci. Technol.* **1992**, *26*, 817-829.
- (12) Bodzek, D., Janoszka, B., Dobosz, C. Warsecha, L., Bodzek, M. J. *Chromatogr., A* **1997**, *774*, 177-192.
- (13) Bolton, J. L., Trush, M. A., Penning, T. M., Dryhurst, G., Monks, T. J. *Chem. Res. Toxicol.* **2000**, *13*, 135-160.
- (14) Kumagai, Y. *J. Health Sci.* **2009**, *55*, 887-894.
- (15) WHO *Air Quality Guidelines for Europe*, World Health Organization: Copenhagen, 2001.
- (16) Cavalieri, E. L., Rogan, E. G., Higginbotham, S., Cremonesi, P., Salmasi, S. *J. Cancer Res. Clin. Oncol.* **1989**, *115*, 67-72.
- (17) Luo, X., Chen, S., Mai, B., Sheng, G. *Arch. Environ. Contam. Toxicol.* **2008**, *55*, 11-20.
- (18) Laflamme, R. E., Hites, R. A. *Geochim. Cosmochim. Ac.* **1978**, *42*, 289-303.
- (19) Tan, Y. L., Heit, M. *Geochim. Cosmochim. Ac.* **1981**, *45*, 2267-2279.
- (20) Wakeham, S., Schaffner, C., Giger, W. *Geochim. Cosmochim. Ac.* **1980**, *44*, 415-429.
- (21) Konig, J., Balfanz, E., Funcke, W., Romanowski, T. *Anal. Chem.* **1983**, *55*, 599-603.
- (22) Stout, S. A., Uhler, A. D., Emsbo-Mattingly, S. D. *Environ. Sci. Technol.* **2004**, *38*, 2987-2994.
- (23) Chalmers, A. T., Metre, P. C., Callender, E. J. *Contam. Hydrol.* **2007**, *91*, 4-25.

Appendix I. Target compounds of PAH & oxy-PAH study.

| Compounds | Abbr | RT (min) | M ⁺ /Z ions | IS ref | SS ref | Structure |
|----------------------|------|----------|------------------------|--------|--------|---|
| PAHs | | | | | | |
| naphthalene | N0 | 14.720 | 128.1 | A | 1 |  |
| 2-methylnaphthalene | N1 | 17.837 | 142.1 | A | 1 |  |
| acenaphthylene | ACL | 21.814 | 152.1 | A | 2 |  |
| acenaphthene | ACE | 22.653 | 153.1 | A | 2 |  |
| fluorene | F0 | 25.072 | 166.1 | A | 2 |  |
| phenanthrene | P0 | 29.448 | 178.1 | A | 2 |  |
| anthracene | AN | 29.691 | 178.1 | A | 2 |  |
| fluoranthene | FL | 34.990 | 202.1 | B | 3 |  |
| pyrene | PY | 35.964 | 202.1 | B | 3 |  |
| benz[a]anthracene | BaA | 41.638 | 228.2 | B | 4 |  |
| chrysene | C0 | 41.805 | 228.2 | B | 4 |  |
| benzo[b]fluoranthene | BbF | 46.334 | 252.1 | B | 4 |  |
| benzo[k]fluoranthene | BkF | 46.453 | 252.1 | B | 4 |  |
| benzo[a]pyrene | BaP | 47.576 | 252.1 | B | 4 |  |

| | | | | | | |
|-----------------------------|-----|--------|---------------------------|---|---|--|
| indeno[1,2,3-cd]pyrene | ID | 51.678 | 276.1 | B | 4 | |
| dibenz[a,h]anthracene | DA | 51.821 | 278.2 | B | 4 | |
| benzo[ghi]perylene | BgP | 52.502 | 276.1 | B | 4 | |
| Oxy-PAHs | | | | | | |
| 9H-fluoren-9-one | FO | 28.487 | 180.1, 152.1, 126.0 | A | - | |
| 9, 10-anthraquinone | AQ | 33.256 | 208.1, 180.1, 152.1 | A | - | |
| 7H-benz[de]anthracene-7-one | BO | 42.302 | 230.1, 202.1, 175.1 | B | - | |
| 5, 12-naphthacenequinone | NQ | 45.005 | 258.1, 230.1, 202.1 | B | - | |
| Surrogates | | | | | | |
| d ₈ -naphthalene | 1 | 14.631 | 136.1 | A | - | |
| d ₁₀ -anthracene | 2 | 29.603 | 188.2 | A | - | |
| d ₁₀ -pyrene | 3 | 35.861 | 212.2 | A | - | |

| | | | | | | |
|-------------------------------|---|--------|-------|---|---|---|
| d ₁₂ -chrysene | 4 | 41.685 | 240.2 | B | - |  |
| Internal Standards | | | | | | |
| d ₁₀ -phenanthrene | A | 29.339 | 188.1 | - | - |  |
| d ₁₂ -perylene | B | 47.793 | 264.2 | - | - |  |

Appendix II. Concentrations in ng/g dry weight of PAHs from sites collected along the Conodoguinet Creek watershed.

| site # | N0 | N1 | ACL | ACE | F0 | P0 | AN | FL | PY | BaA | CO | BbF | BkF | BaP | ID | DA | BgP | Total PAHs |
|--------|----|----|-----|-----|----|-----|-----|------|------|-----|-----|------|-----|-----|-----|-----|-----|------------|
| 1 | 12 | 8 | 10 | 8 | 7 | 21 | 3 | 9 | 4 | 13 | 8 | 14 | 8 | 13 | 11 | 9 | 4 | 164 |
| 2 | 14 | 9 | 12 | 5 | 6 | 21 | 10 | 49 | 44 | 45 | 42 | 58 | 26 | 40 | 40 | 15 | 32 | 468 |
| 3 | 18 | 16 | 12 | 9 | 18 | 147 | 28 | 94 | 81 | 63 | 63 | 76 | 31 | 48 | 47 | 17 | 39 | 807 |
| 4 | 12 | 9 | 6 | 5 | 4 | 15 | 4 | 23 | 18 | 27 | 23 | 35 | 16 | 28 | 24 | 12 | 15 | 277 |
| 5 | 23 | 14 | 32 | 55 | 70 | 736 | 254 | 1278 | 1042 | 815 | 796 | 1158 | 390 | 893 | 815 | 137 | 736 | 9244 |
| 6 | 14 | 9 | 5 | 3 | 3 | 32 | 6 | 37 | 30 | 37 | 33 | 49 | 20 | 35 | 34 | 14 | 23 | 383 |
| 7 | 15 | 7 | 4 | 4 | 4 | 21 | 4 | 26 | 21 | 28 | 26 | 37 | 15 | 30 | 25 | 11 | 16 | 295 |
| 8 | 11 | 8 | 7 | 5 | 8 | 80 | 28 | 157 | 131 | 111 | 109 | 152 | 54 | 112 | 100 | 27 | 87 | 1187 |
| 9 | 16 | 15 | 14 | 5 | 7 | 85 | 17 | 90 | 82 | 62 | 73 | 102 | 35 | 46 | 63 | 20 | 53 | 788 |
| 10 | 19 | 15 | 10 | 4 | 5 | 44 | 12 | 61 | 61 | 61 | 69 | 98 | 37 | 73 | 66 | 20 | 56 | 710 |
| 11 | 14 | 10 | 7 | 2 | 5 | 25 | 8 | 49 | 48 | 47 | 53 | 73 | 28 | 57 | 50 | 16 | 42 | 535 |
| 12 | 11 | 9 | 7 | 2 | 3 | 31 | 9 | 48 | 44 | 45 | 48 | 71 | 27 | 56 | 49 | 16 | 40 | 516 |
| 13 | 11 | 8 | 9 | 3 | 4 | 34 | 10 | 56 | 54 | 45 | 52 | 71 | 27 | 49 | 48 | 15 | 41 | 537 |
| 14 | 16 | 14 | 8 | 3 | 3 | 29 | 9 | 49 | 51 | 50 | 61 | 82 | 30 | 62 | 55 | 18 | 45 | 586 |
| 15 | 17 | 13 | 13 | 2 | 5 | 68 | 21 | 116 | 113 | 100 | 120 | 154 | 53 | 117 | 99 | 27 | 86 | 1126 |
| 16 | 12 | 8 | 7 | 2 | 4 | 22 | 9 | 57 | 55 | 58 | 55 | 76 | 28 | 56 | 46 | 15 | 36 | 546 |
| 17 | 17 | 12 | 10 | 3 | 4 | 44 | 12 | 80 | 77 | 65 | 75 | 104 | 38 | 83 | 73 | 21 | 63 | 779 |
| 18 | 19 | 16 | 14 | 2 | 5 | 46 | 17 | 82 | 82 | 82 | 92 | 140 | 44 | 99 | 89 | 26 | 77 | 932 |
| 19 | 16 | 15 | 10 | 4 | 7 | 107 | 17 | 162 | 133 | 102 | 145 | 210 | 74 | 121 | 141 | 32 | 125 | 1420 |
| 20 | 18 | 16 | 11 | 3 | 5 | 64 | 17 | 121 | 108 | 94 | 119 | 181 | 59 | 123 | 121 | 31 | 102 | 1192 |
| 21 | 53 | 48 | 86 | 21 | 41 | 243 | 136 | 731 | 709 | 653 | 833 | 1248 | 311 | 748 | 628 | 185 | 782 | 7455 |
| 22 | 25 | 22 | 38 | 12 | 18 | 237 | 65 | 388 | 344 | 296 | 359 | 535 | 147 | 329 | 254 | 79 | 318 | 3466 |
| 23 | 19 | 14 | 20 | 6 | 12 | 132 | 39 | 204 | 196 | 161 | 189 | 245 | 88 | 184 | 164 | 37 | 151 | 1860 |
| 24 | 17 | 16 | 20 | 5 | 11 | 134 | 30 | 177 | 163 | 127 | 168 | 239 | 79 | 142 | 149 | 35 | 133 | 1645 |
| 25 | 24 | 21 | 33 | 11 | 17 | 210 | 82 | 375 | 347 | 315 | 391 | 506 | 168 | 348 | 334 | 77 | 314 | 3573 |
| 26 | 23 | 18 | 15 | 5 | 8 | 89 | 26 | 172 | 162 | 133 | 170 | 237 | 80 | 170 | 158 | 40 | 146 | 1651 |
| 28 | 26 | 21 | 28 | 6 | 12 | 150 | 48 | 262 | 263 | 238 | 286 | 408 | 126 | 283 | 263 | 65 | 241 | 2725 |
| 29 | 20 | 16 | 17 | 6 | 9 | 121 | 33 | 252 | 218 | 186 | 255 | 369 | 128 | 244 | 250 | 57 | 228 | 2409 |
| 30 | 22 | 18 | 31 | 10 | 17 | 168 | 50 | 247 | 241 | 190 | 234 | 320 | 102 | 225 | 208 | 47 | 193 | 2321 |
| 31 | 17 | 13 | 18 | 6 | 11 | 148 | 29 | 240 | 206 | 158 | 237 | 368 | 105 | 204 | 238 | 51 | 214 | 2264 |
| 32 | 19 | 15 | 20 | 4 | 8 | 109 | 32 | 253 | 236 | 188 | 252 | 348 | 117 | 240 | 235 | 49 | 216 | 2338 |
| 33 | 24 | 38 | 18 | 16 | 23 | 335 | 67 | 526 | 429 | 345 | 440 | 601 | 200 | 367 | 377 | 83 | 337 | 4228 |
| 34 | 15 | 12 | 9 | 5 | 8 | 150 | 24 | 284 | 218 | 160 | 219 | 299 | 105 | 187 | 185 | 42 | 162 | 2085 |
| 35 | 35 | 36 | 54 | 34 | 42 | 680 | 130 | 1207 | 999 | 740 | 961 | 1337 | 335 | 746 | 587 | 172 | 754 | 8846 |

Appendix III. Concentrations in ng/g dry weight of oxy-PAHs collected from sites along the Conodoguinet Creek watershed.

| site # | FO | AQ | BO | NQ | Total oxy-PAH |
|--------|-----|-----|-----|-----|---------------|
| 1 | 7 | 12 | 1 | 1 | 21 |
| 2 | 7 | 15 | 16 | 4 | 42 |
| 3 | 12 | 27 | 16 | 7 | 63 |
| 4 | 5 | 11 | 8 | 3 | 27 |
| 5 | 61 | 190 | 110 | 91 | 451 |
| 6 | 11 | 19 | 11 | 5 | 46 |
| 7 | 13 | 20 | 8 | 4 | 45 |
| 8 | 14 | 38 | 24 | 21 | 97 |
| 9 | 17 | 31 | 19 | 15 | 82 |
| 10 | 11 | 25 | 17 | 10 | 63 |
| 11 | 9 | 24 | 16 | 9 | 59 |
| 12 | 10 | 22 | 15 | 10 | 57 |
| 13 | 13 | 28 | 18 | 12 | 70 |
| 14 | 16 | 35 | 17 | 13 | 81 |
| 15 | 18 | 47 | 35 | 24 | 124 |
| 16 | 8 | 19 | 15 | 13 | 55 |
| 17 | 10 | 33 | 21 | 11 | 74 |
| 18 | 14 | 42 | 26 | 21 | 103 |
| 19 | 22 | 70 | 28 | 29 | 149 |
| 20 | 14 | 46 | 24 | 23 | 107 |
| 21 | 72 | 244 | 103 | 87 | 506 |
| 22 | 35 | 138 | 64 | 62 | 298 |
| 23 | 16 | 60 | 37 | 29 | 143 |
| 24 | 19 | 69 | 33 | 25 | 146 |
| 25 | 34 | 115 | 60 | 62 | 271 |
| 26 | 19 | 61 | 36 | 28 | 144 |
| 28 | 28 | 88 | 47 | 35 | 198 |
| 29 | 24 | 96 | 43 | 45 | 207 |
| 30 | 27 | 83 | 47 | 31 | 188 |
| 31 | 24 | 94 | 41 | 42 | 201 |
| 32 | 22 | 85 | 44 | 44 | 195 |
| 33 | 54 | 189 | 61 | 70 | 374 |
| 34 | 19 | 82 | 33 | 39 | 172 |
| 35 | 107 | 425 | 94 | 122 | 748 |

Appendix IV. Specific land-use activities of sampling sites as determined by GIS data.^a

| Site | Location | Distance (km) | Area (km ²) | % Hi_Urban | % Lo_Area | % Trans | % Urban | % Ag | % Forest | % Imperv | 60m_% Tran | 60m_%Lo Urban | 60m_% Hi Urban |
|------|-------------------------------|---------------|-------------------------|------------|-----------|---------|---------|------|----------|----------|------------|---------------|----------------|
| 1 | Gilbert Rd | 158 | 23.7 | 0.0 | 0.0 | 0.2 | 0.6 | 4.4 | 94.2 | 0.0 | 0.5 | 0.0 | 0.0 |
| 2 | Keefer Rd | 153 | 42.1 | 0.0 | 0.0 | 0.2 | 1.9 | 3.6 | 93.5 | 0.0 | 0.3 | 0.0 | 0.0 |
| 3 | Upper Horse Valley Rd | 149 | 55.4 | 0.0 | 0.0 | 0.5 | 2.1 | 3.2 | 93.5 | 0.0 | 0.8 | 0.0 | 0.0 |
| 4 | State Game Lands #76 | 144 | 72.1 | 0.0 | 0.0 | 0.5 | 1.7 | 2.8 | 94.5 | 0.0 | 0.6 | 0.0 | 0.0 |
| 5 | Bridge Exiting Roxbury | 136 | 109.1 | 0.0 | 0.0 | 0.8 | 1.4 | 2.1 | 95.1 | 0.0 | 1.1 | 0.1 | 0.0 |
| 6 | Creek Rd off 997S | 130 | 120.7 | 0.1 | 0.3 | 1.0 | 2.0 | 5.8 | 90.5 | 0.2 | 1.2 | 0.4 | 0.1 |
| 7 | 433S towards Orrstown | 125 | 136.7 | 0.1 | 0.5 | 1.1 | 2.2 | 11.7 | 84.2 | 0.2 | 1.3 | 0.7 | 0.1 |
| 8 | Mongul Rd off SR 4016 | 122 | 252.7 | 0.6 | 1.2 | 2.0 | 5.8 | 30.2 | 61.4 | 0.4 | 1.9 | 1.8 | 0.4 |
| 9 | outside Southhampton Twn. | 115 | 274.4 | 0.6 | 1.3 | 1.9 | 5.7 | 33.5 | 58.4 | 3.6 | 1.8 | 1.9 | 0.3 |
| 10 | upstream from covered bridge | 109 | 469.1 | 0.8 | 1.4 | 2.1 | 6.5 | 37.6 | 53.3 | 3.6 | 2.6 | 2.0 | 0.6 |
| 11 | Bridgewater St | 103 | 531.4 | 0.7 | 1.3 | 2.2 | 6.2 | 37.1 | 54.0 | 3.3 | 2.6 | 1.9 | 0.6 |
| 12 | Whiskey Run Rd & SR 4006 | 98 | 552.0 | 0.7 | 1.3 | 2.2 | 6.1 | 37.5 | 53.7 | 3.1 | 2.6 | 1.9 | 0.5 |
| 13 | Creek Rd and Bridge St | 89 | 753.0 | 0.6 | 1.4 | 2.3 | 5.9 | 42.5 | 48.8 | 2.6 | 2.8 | 1.9 | 0.5 |
| 14 | Bloserville & Potato Rd | 87 | 765.7 | 0.6 | 1.4 | 2.3 | 5.8 | 42.6 | 48.8 | 2.6 | 2.8 | 1.9 | 0.5 |
| 15 | Creek Rd & Old Mill | 79 | 791.0 | 0.6 | 1.4 | 2.3 | 5.8 | 42.8 | 48.5 | 2.6 | 2.8 | 1.9 | 0.5 |
| 16 | Creek Rd & Meadowbrook | 72 | 895.0 | 0.6 | 1.4 | 2.4 | 5.7 | 44.5 | 46.8 | 2.4 | 2.9 | 1.9 | 0.5 |
| 17 | N. Middleton Park | 64 | 953.9 | 0.6 | 1.4 | 2.5 | 5.9 | 45.5 | 45.5 | 2.5 | 3.1 | 2.0 | 0.5 |
| 18 | Cave Hill Rd | 61 | 982.4 | 0.6 | 1.4 | 2.5 | 5.9 | 45.3 | 45.6 | 2.5 | 3.0 | 2.0 | 0.5 |
| 19 | Clearwater Dr | 57 | 996.6 | 0.7 | 1.5 | 2.6 | 6.3 | 45.1 | 45.4 | 2.7 | 3.1 | 2.0 | 0.5 |
| 20 | N. Middlesex Rd & Clemson | 53 | 1028.5 | 0.7 | 1.5 | 2.5 | 6.4 | 44.7 | 45.8 | 2.7 | 3.1 | 2.0 | 0.5 |
| 21 | behind Knight Transportation | 53 | 1088.8 | 1.1 | 1.7 | 2.7 | 8.1 | 44.4 | 44.1 | 4.1 | 3.2 | 2.1 | 0.9 |
| 22 | Carlisle Country Club | 53 | 1088.9 | 1.1 | 1.7 | 2.7 | 8.1 | 44.4 | 44.1 | 4.1 | 3.2 | 2.1 | 0.9 |
| 23 | Scott Farm (ATC Headquarters) | 46 | 1109.8 | 1.1 | 1.7 | 2.7 | 8.1 | 44.3 | 44.2 | 4.1 | 3.2 | 2.1 | 0.9 |
| 24 | Beechcroft Dr. | 42 | 1124.1 | 1.1 | 1.7 | 2.7 | 8.1 | 44.3 | 44.2 | 4.1 | 3.2 | 2.2 | 0.9 |
| 25 | Willow Mill Park off 114 | 37 | 1141.5 | 1.1 | 1.7 | 2.8 | 8.1 | 44.1 | 44.4 | 4.0 | 3.2 | 2.2 | 0.9 |
| 26 | Trailer Park-Eberly Dr | 24 | 1247.7 | 1.4 | 1.9 | 2.9 | 9.5 | 44.2 | 42.7 | 5.1 | 3.3 | 2.3 | 1.1 |
| 28 | Sporting Hill Rd | 22 | 1252.7 | 1.9 | 1.9 | 2.9 | 9.6 | 44.2 | 42.6 | 5.2 | 3.3 | 2.3 | 1.2 |
| 29 | Erb's Bridge Rd | 21 | 1254.3 | 1.4 | 1.9 | 2.9 | 9.7 | 44.1 | 42.6 | 5.2 | 3.3 | 2.3 | 1.2 |
| 30 | Conodoguinet Youth Park | 16 | 1270.5 | 1.4 | 1.9 | 3.0 | 9.9 | 43.8 | 42.6 | 5.4 | 3.3 | 2.4 | 1.2 |
| 31 | Gale Rd & Little Run Rd | 13 | 1272.6 | 1.4 | 1.9 | 3.0 | 10.1 | 43.7 | 42.6 | 5.5 | 3.3 | 2.4 | 1.1 |
| 32 | Oyster Mill Park | 8 | 1287.6 | 1.4 | 2.0 | 3.0 | 10.4 | 43.3 | 42.6 | 5.7 | 3.4 | 2.4 | 1.1 |
| 33 | Creek Rd | 5 | 1290.7 | 1.4 | 2.0 | 3.0 | 10.6 | 43.2 | 42.5 | 5.8 | 3.3 | 2.4 | 1.1 |
| 34 | Ridley Park | 2 | 1297.9 | 1.4 | 2.0 | 3.0 | 10.9 | 43.0 | 42.3 | 6.0 | 3.3 | 2.4 | 1.2 |
| 35 | Mouth of River | 0 | 1299.4 | 1.4 | 2.0 | 3.0 | 11.0 | 42.9 | 42.3 | 6.0 | 3.4 | 2.4 | 1.2 |

^aTypes of land-use include upstream catchment area (Area), percentage of high urban (% Hi-Urban), percentage of land area classified as low urban development (% Lo-Area), percentage of urban (% Urban), percentage of transportation (% Trans), percentage of agricultural (% Ag), percentage of forest (% Forest), percentage of impervious surface (% Imperv), percentage of transportation within 60 m of the stream channel (60m-% Tran), percentage of low intensity development within 60 m of the stream channel (60m-% Lo Urban), and percentage of high intensity development within 60 m of the stream channel (60m-% Hi Urban) . Distance refers to distance above the river mouth.