Spatial and Temporal Distribution of Polycyclic Aromatic Hydrocarbons within Sediments and Fish Tissues of the Lower Chesapeake Bay Basin

COLEMAN, Katherine L.[1], ODHIAMBO, Ben K.[1], SHARPLESS, Charles M.[2], COXON, Taylor M.[1], WIELAND, Werner[3], BUNCH, Aaron J.[4]
University of Mary Washington, Departments of Earth and Environmental Sciences[1], Chemistry[2], and Biological Sciences[3], Fredericksburg, VA, USA, kcolema2@mail.umw.edu
Virginia Department of Game and Inland Fisheries, Charles City, VA, USA[4]

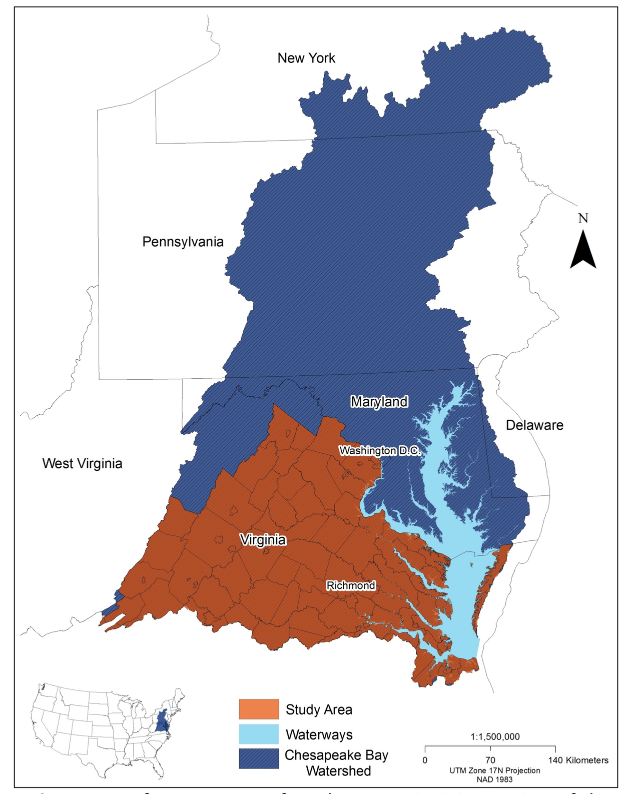

Figure 1: Reference map of study area; Virginia portion of the Chesapeake Bay Basin.

Introduction:

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic persistent organic pollutants that pose serious environmental risks to aquatic ecosystems. The presence of PAHs is related to various anthropogenic activities, predominantly fossil fuel combustion and the resurfacing of roads with tar-based pavement. PAHs are re-suspended into the water column or into the atmosphere, making their remediation extremely difficult; as each molecule is continually in motion between hosts, their containment and isolation is increasingly challenging (Countway et al., 2003). Gaining an understanding of the sources of PAHs, their distribution and monitoring the severity of their effluence is important in remediation planning and management. Measuring PAHs in aquatic abiotic and biotic media allows for an understanding of PAH transport mechanisms. PAH's mutagenic and carcinogenic behavior not only poses serious and potentially lethal implications for the natural ecosystem but also the human population.

Over four centuries of settlement and landscape alterations have lead the aquatic systems of the Chesapeake Bay basin to display disrupted sedimentation patterns, declining water quality, and inexorably altered ecologies (Walker et al., 2004). We report an ongoing analysis of the spatial and temporal distribution of PAHs in the fluvial and lacustrine systems within the Virginia portion of the Chesapeake Bay basin. Monitoring PAHs on a large scale enables analysis of both point and atmospheric sources, and how they may be reclassified based on scale. PAH analysis is being done on surficial sediment grab samples and dated sediment cores as well as on muscle and liver tissues of largemouth bass (*Micropterus salmoides)*, bluegill (*Lepomis macrochirus*), and blue catfish (*Ictalurus furcatus*). The analysis employs accelerated solvent extraction and gas chromatography mass spectrometry (GCMS) with selected ion monitoring. The data will be combined with currently available surface PAH data compiled by the Virginia Department of Environmental Quality to provide a clear picture on both the historical and spatial variation of PAH in the surface waters. The residents of the basin are continually exposed to PAH contamination through ingestion of contaminated foods, dermal contact, and through breathing in contaminated air. These subtle pollutants, produced by yet harmful to humans, impact areas beyond their point sources, traveling kilometers through the atmosphere (Environmental Protection Agency, 2013). Analyzing the movement of PAHs across trophic levels reveals how vulnerable this community is to contamination.

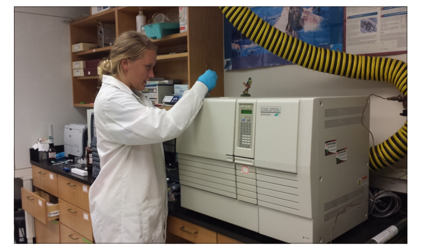

Plate 1: Injecting a standard on the GCMS.

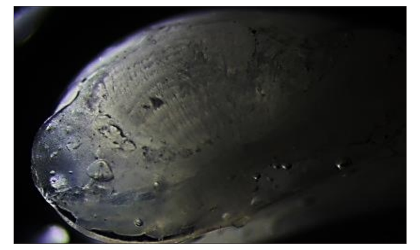

Plate 2: Otolith of 12 year old blue catfish.

Plate 3: Morgantown Generation Station.

Background:

With a human population of over 6.8 million, the southern portion of the Chesapeake Bay basin dominates the landscape of Virginia (Figure 1).

The temperate and humid climate of the region, with annual precipitation of approximately 100 cm, facilitates an ecosystem built on densely vegetated terrain. Four major basins drain a total land area of 5.6x 104 km2: In descending order of land area James, Potomac-Shenandoah, Rappahannock, and York (Figure 2). Flowing through the metamorphic and igneous bedrock of the Blue Ridge and Piedmont and the more recent sedimentary deposits of the Coastal Plain, each of these fluvial systems interacts with the varied geologic assemblies that define the physiographic provinces of Virginia (McFarland and Bruce, 2006). Annual sedimentation rates into the Bay range largely between 0.1 to 1cm/yr, considerably higher than those characteristic of estuaries around the world (National Climatic Data Center, 2014). Sediments tend to be the main conveyor of contaminants, including PAHs, to surface water bodies and thus their flux rates and distribution tend to be associated with contaminants dispersal and hotspots.

Interconnected by over 1,400 km of major interstate, this region of Virginia has been greatly influenced by anthropogenic activity. Active petroleum power plants, paper mills, and military and commercial airports abound within the region, and retired creosote factories have left a chemical signature upon the landscape that has yet to be discerned. These identified sources of PAHs are located mostly along the I-95 transportation corridor, connecting Washington D.C. to Petersburg (Figure 3). While development is highest in the Potomac basin with over 27% urban land use, concentrated around the Capital Beltway of Washington D.C., nearly half of the population resides in the James basin, dominating the Richmond and Hampton Roads metropolitan areas (Virginia Department of Environmental Quality, 2012). The Rappahannock and York basins are characteristically rural with no major population centers. Western portions of the region are dominated by agricultural land use; however, these areas are susceptible to atmospheric fallout from West Virginia's coal mining and combustion (Clark et al., 2013). With endangered and vulnerable fish populations occupying an area of nearly 4,400 km2, the implications of this variation in anthropogenic activities necessitate critical analysis and insight into how PAH dynamics can impact the health of the Chesapeake Bay, an economically important estuarine ecosystem that hosts a $3 billion dollar fishing industry (Dickhut et al 2000, Fernaindez, 1999).

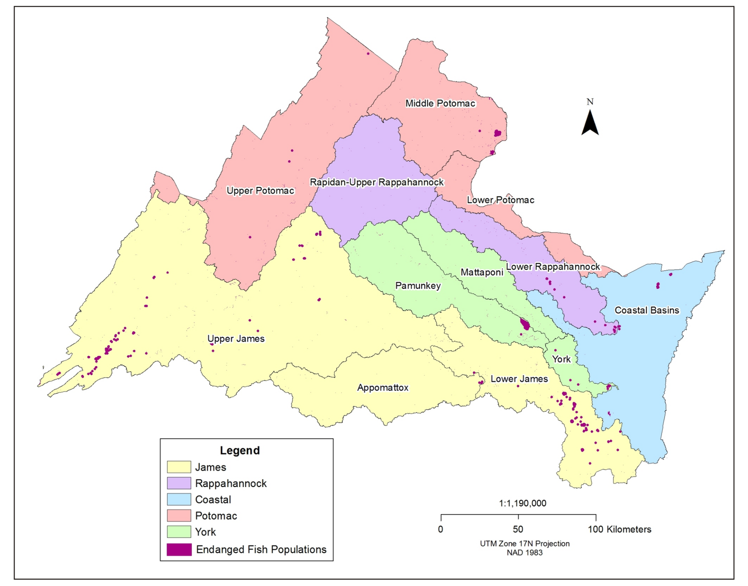

Figure 2: Major basins within the study area; Fish sampling areas. A minimum of three collection sites within each area, at each site 3 individuals of each target species were collected.

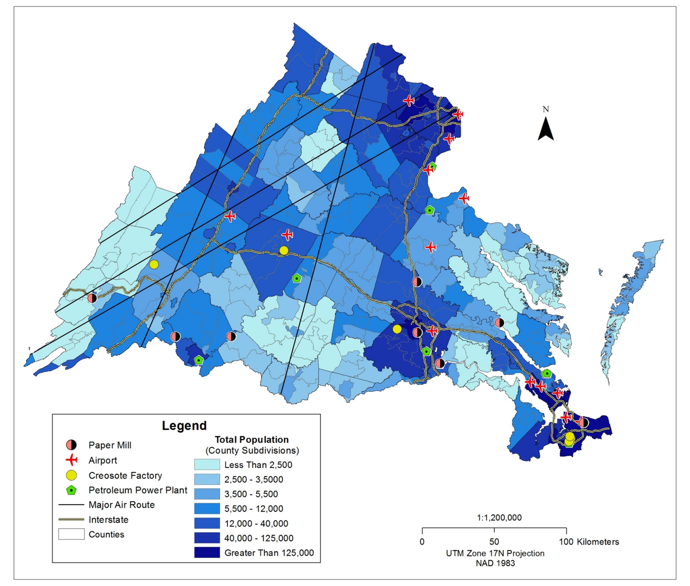

Figure 3: Identified sources of PAHs and the distribution of human population.

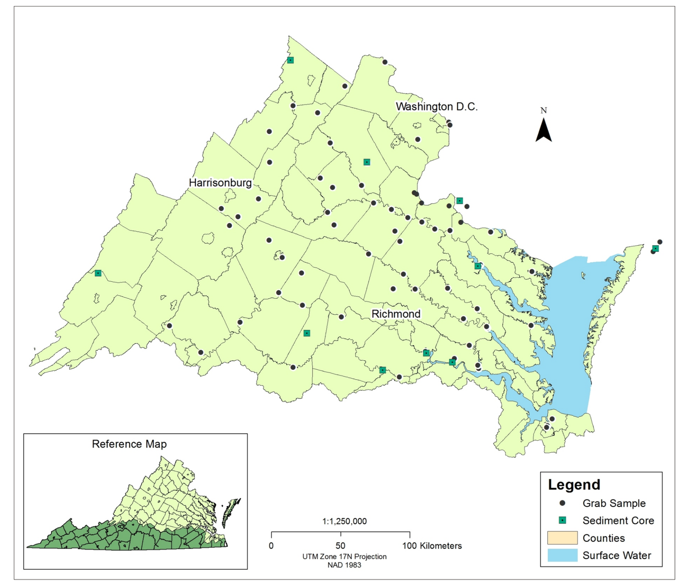

Figure 4: Surficial sediment and sediment core sampling sites.

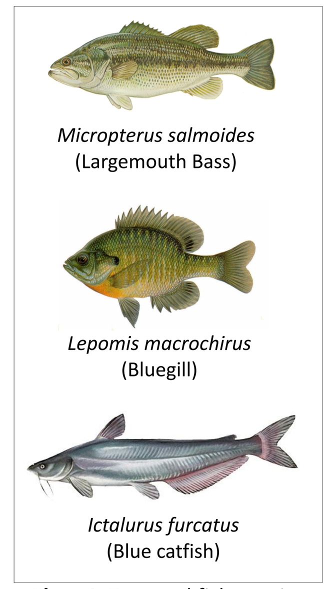

Plate 4: Targeted fish species.

Methods:

Field Sampling:

A manual push core device with 75cm plastic liners was used to collect sediment cores for temporal PAH analysis. Sediment cores were taken in fluvial depositional areas in the lower reaches of the four major river systems (James, Shenandoah-Potomac, Rappahannock, and York Rivers) and in lacustrine systems in the upper portions of these basins (Figure 4). A Wildco Petite Ponar Bottom Grab Sampler was used to retrieve surficial sediment samples (top 5 cm) at various locations throughout the study site for a spatial analysis (Figure 4). Sampling sites were also chosen based on distance to potential identified PAH source locations, i.e. power plants and population concentration centers, as well as known sedimentation characteristics of fluvial system reaches and lacustrine environments.

Fish samples were collected in conjunction with the Virginia Department of Game and Inland Fisheries (VDGIF), Charles City, Virginia, USA (Figure 2) following the methods of Nickum et al. (2003). Sampling was done using electroboating direct current techniques. Adult individuals of *Micropterus salmoides* (largemouth bass), a top predator, and *Lepomis macrochirus* (bluegill), an omnivore, were targeted (Plate 4). Juveniles of *Ictalurus furcatus* (blue catfish), a benthic feeder, were also targeted because blue catfish mature to top predators through an autogenetic switch nearly two years after birth.

Laboratory Methods:

Sediment samples were subsampled for measure of organic matter content via loss on ignition as described in Clark et al. (2013) and Heiri et al. (2001). Additional wet core subsamples were sent to CORE International Research Labs (Winnipeg, Canada) for isotopic analysis. Lacustrial subsamples at 2cm increments were analyzed for ^{210}Po via alpha spectrometry and fluvial subsamples at 5cm increments for ^{137}Cs via gamma emissions following the methods of United States Department of Energy (1997).

The concentrations of 24 known PAHs were analyzed (Table 1). Extractions were completed on thawed, wet, homogenized samples through an accelerated solvent extraction method in a 1:1 ratio of acetone: hexane using a Thermo Scientific Dionex™ ASE™ 350 Accelerated Solvent Extractor system. Each extract was dried via exposure to activated sodium sulfate anhydrous and concentrated using the Biotage TurboVap II. Concentrated solutions were run through selection ion monitoring on the Shimadzu QP5050 GCMS after addition of four internal standards: fluorine d10, pyrene d10, benzo(a)anthracene d12, and perylene d12 (Plate 1). Resultant chromatograms were analyzed based on species specific PAH peaks via retention times and m/z ratios; a linear model was applied to each PAH species reliant of a series of standard calibrations. Quality assurance was provided by analyzing every 10^{th} sample in duplicate, utilization of laboratory blanks, and periodic use of a recovery standard, chrysene d-12 (Thermo Scientific Dionex, 2011).

Chronology:

This historical analysis of PAH variations in the sediments is being analyzed via lacustrine and fluvial sediment cores dated with ^{210}Pb and ^{137}Cs isotopic chronology respectively. The ^{210}Pb chronology is based on the CRS model detailed in Odhiambo et. al (2013), Applyby and Oldfield (1985), and Applyby (2008).; whereas the ^{137}Cs method relies on the 1963 peak typical of sediments in this region (Corcho-Alvaradoa et al., 2014). In addition to chronology, the isotopic data will provide sediment accumulation rates estimates thus providing a framework for PAH flux estimates in sediments. Fish ages, critical in analyzing length of exposure to PAHs, was determined by otolith analysis method detailed in Campana and Thorrold (2011), Sakaris and Irwin (2007) and Secor and Dean (1992). Utricular otoliths (lapilli) were removed from blue catfish, while saccular otoliths (sagittae) were removed from bluegill and largemouth bass. The otolith was ground until the central core was exposed; each observed ring was considered as one growth season (Plate 2). Scale annuli were analyzed as described in Frie (1982) where otolith analysis was insufficient.

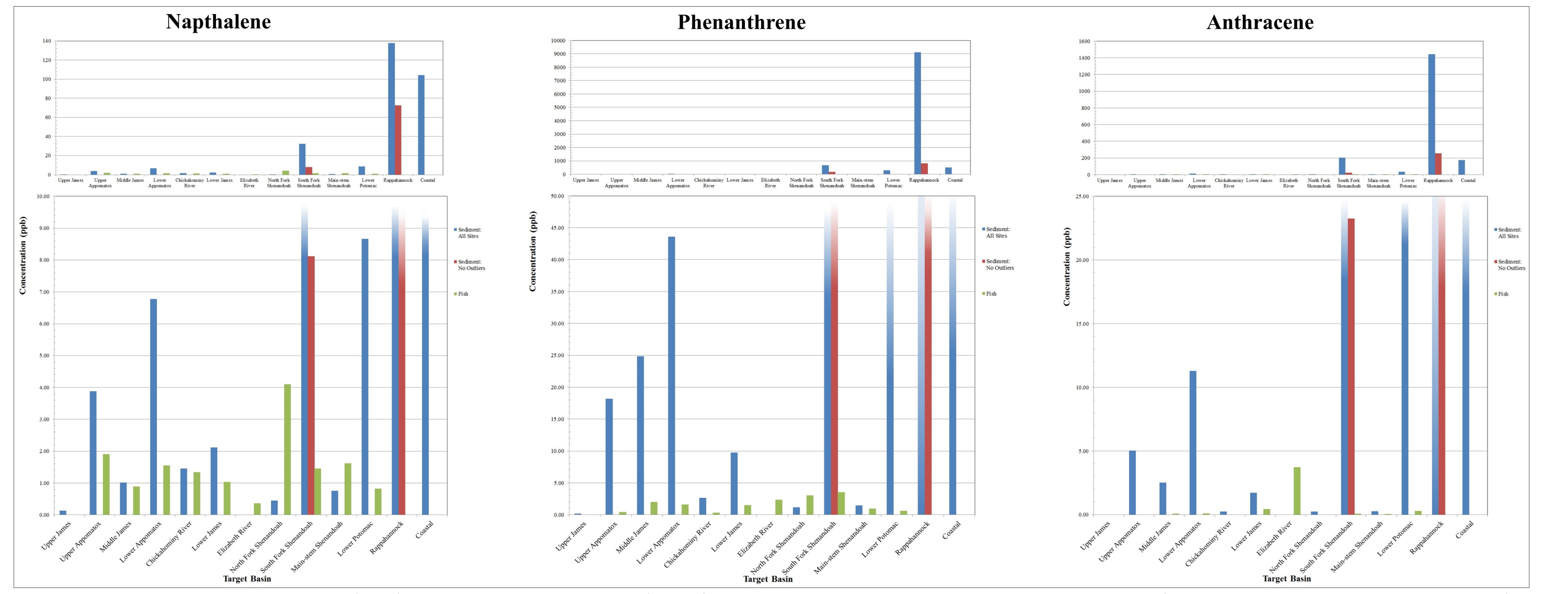

Figure 5: Average concentrations (ppb) of low molecular weight (LMW) PAHs by basin of all surficial sediment samples (with and without two outlying sites) and of all fish samples. Preliminary data excluded samples from the Elizabeth River (blue) and the Upper James, Rappahannock, or Coastal basins (green).

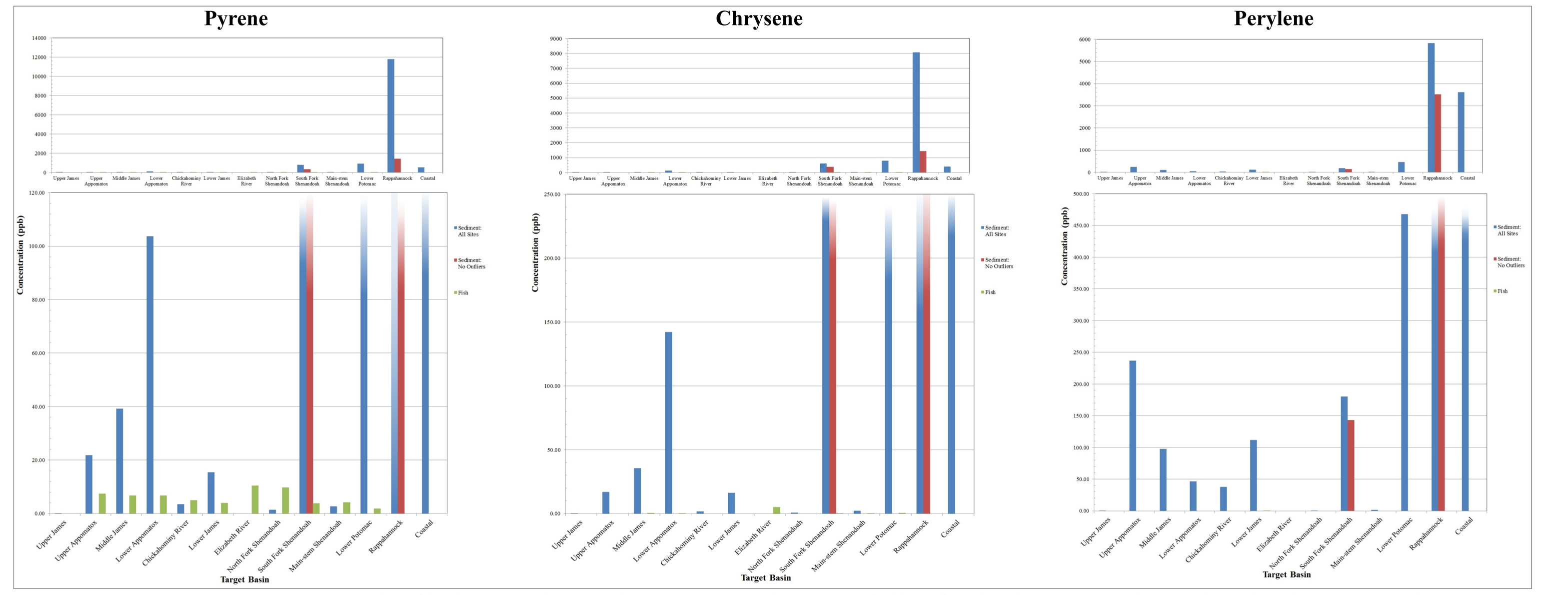

Figure 6: Average concentrations (ppb) of high molecular weight (HMW) PAHs by basin of all surficial sediment samples (with and without two outlying sites) and of all fish samples. Preliminary data excluded samples from the Elizabeth River (blue) and the Upper James, Rappahannock, or Coastal basins (green).

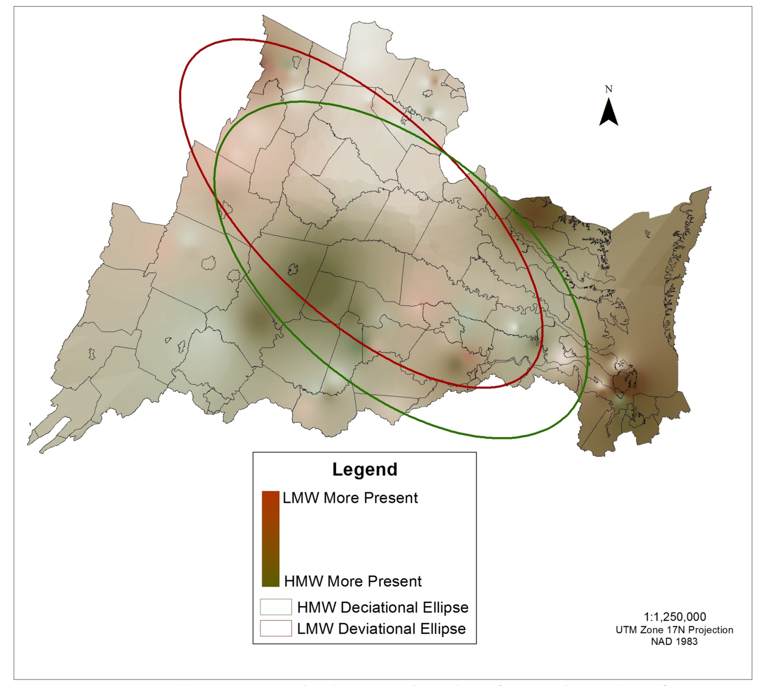

Figure 7: Fish tissue overlaid interpolated surfaces: the red surface showing the concentration gradient of LMW PAHs and the green surface of HMW PAHs.

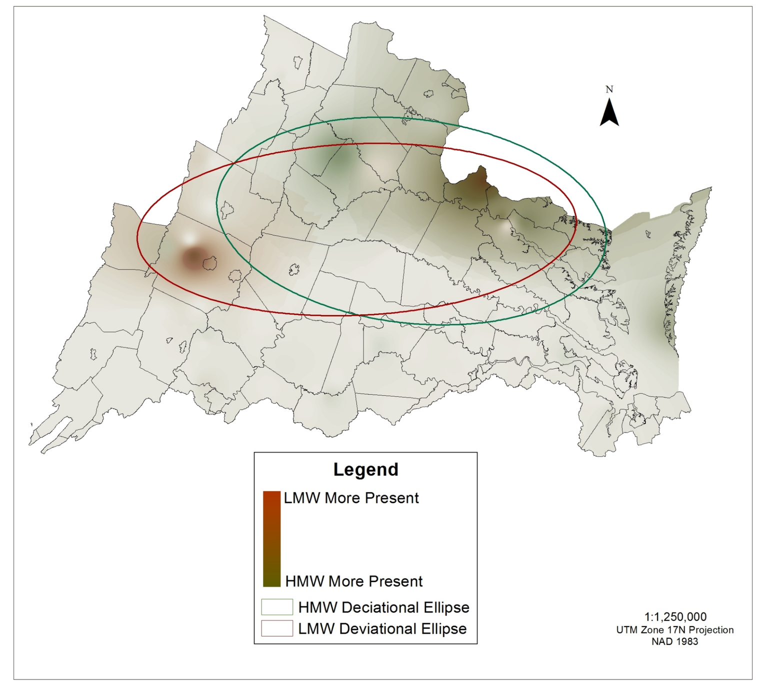

Figure 8: Surficial sediment overlaid interpolated surfaces: the red surface showing the concentration gradient of LMW PAHs and the green surface of HMW PAHs.

PAH Species	Retention Time	Base Peak
Naphthalene*	4.36	128
Acenaphthalene*	5.44	152
Acenaphthene	5.6	153
Fluorene*	6.11	166
Phenanthrene*	7.55	178
Anthracene*	7.65	178
Fluoranthene*	10.82	202
Pyrene*	11.66	202
Benzo(c)phenanthrene	16.73	228
Benz(a)anthracene*	17.91	228
Chrysene*	18.15	228
Benzo(b)fluoranthene*	23.8	252
Benzo(k)fluoranthene*	24.69	252
Benzo(j)fluoranthene	24.72	252
7,12-Dimethylbenz(a)anthracene	24.87	256
Benzo(e)pyrene	26.18	252
Benzo(a)pyrene*	26.46	252
3-Methylcholanthrene	28.93	268
Indeno(1,2,3-cd)pyrene*	32.41	276
Dibenz(a,h)anthracene*	32.64	278
Benzo(g,h,i)perylene*	33.45	276
Dibenzo(a,l)pyrene	37.5	302
Dibenzo(a,i)pyrene	38.95	302
Dibenzo(a,h)pyrene	39.17	302

Table 1: Targetted PAH species. The * indicates this species is an EPA priority pollutant.

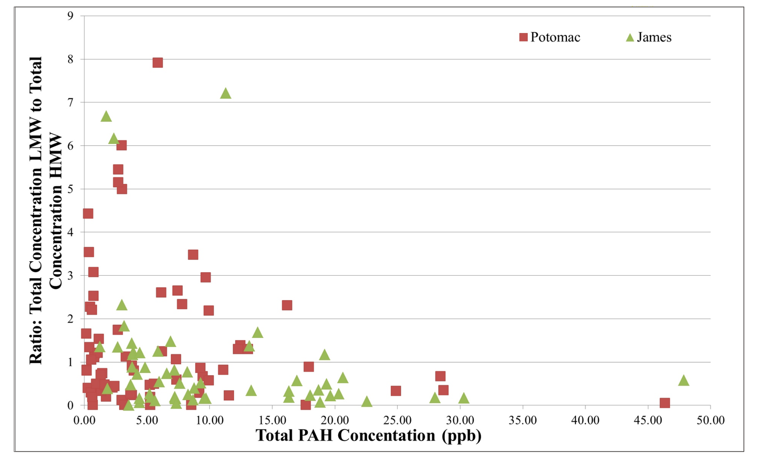

Figure 9: Fish tissue total PAH concentration versus the ratio of total LMW to HMW PAHs revealing degree of source similarity - includes sites with detectable PAH concentrations and excludes outlier (5.36, 59.25).

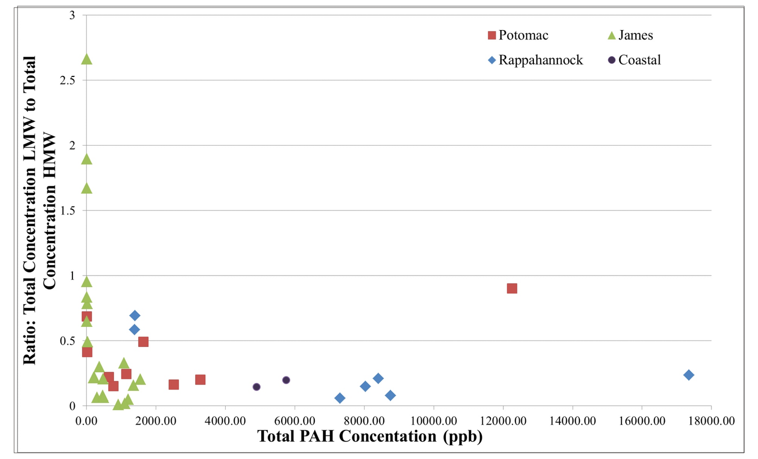

Figure 10: Surficial sediment total PAH concentration versus the ratio of total LMW to HMW PAHs revealing degree of source similarity - includes sites with detectable PAH concentrations and excludes outlier (238,401.23, 0.48).

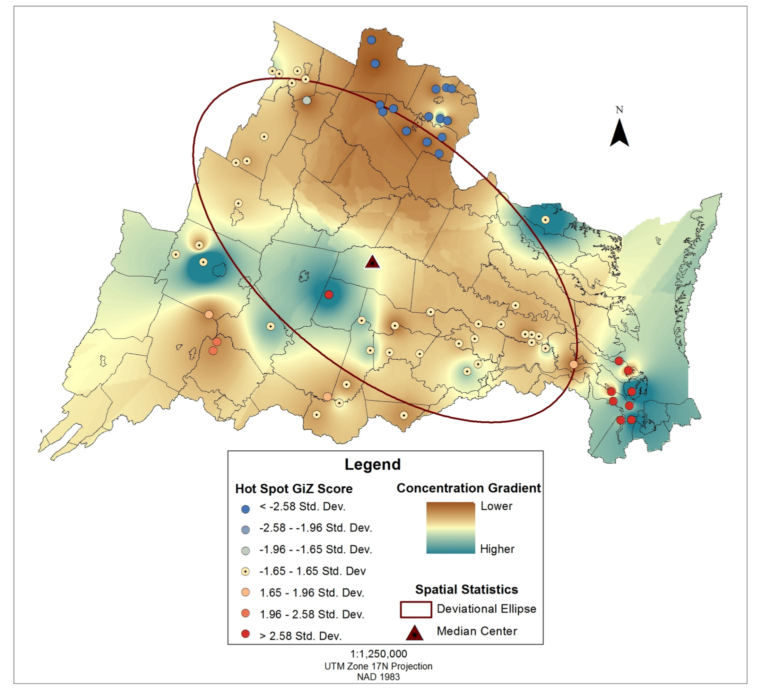

Figure 11: Interpolated surface via inverse weighted distance function of fish tissue sampling sites' total PAH concentration.

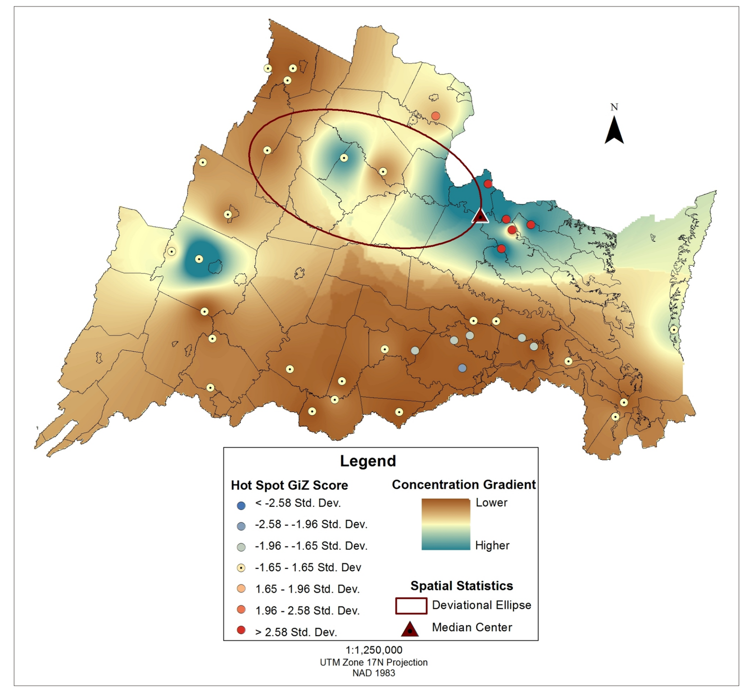

Figure 12: Interpolated surface via inverse weighted distance function of surficial sediment sampling sites' total PAH concentration.

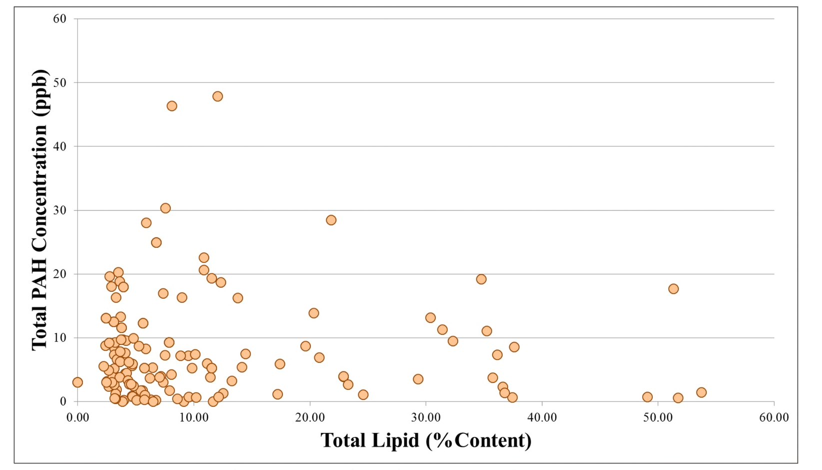

Figure 13: Fish tissue total lipid versus total PAH concentration.

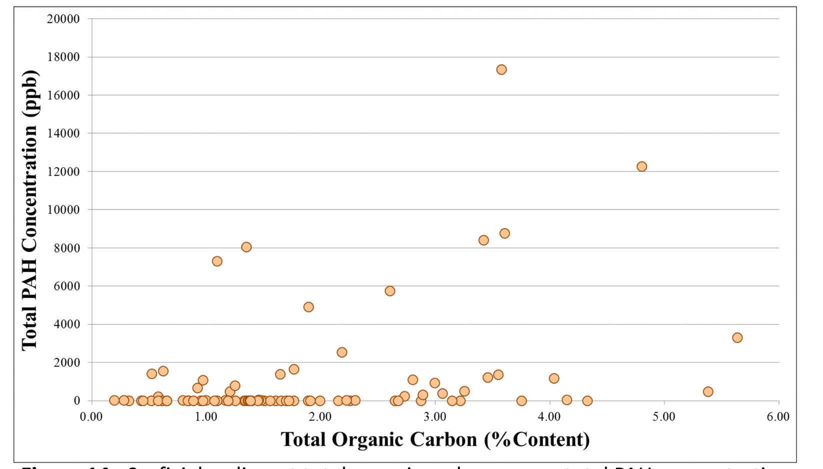

Figure 14: Surficial sediment total organic carbon versus total PAH concentration - excludes outlier (0.46, 238,401.23).

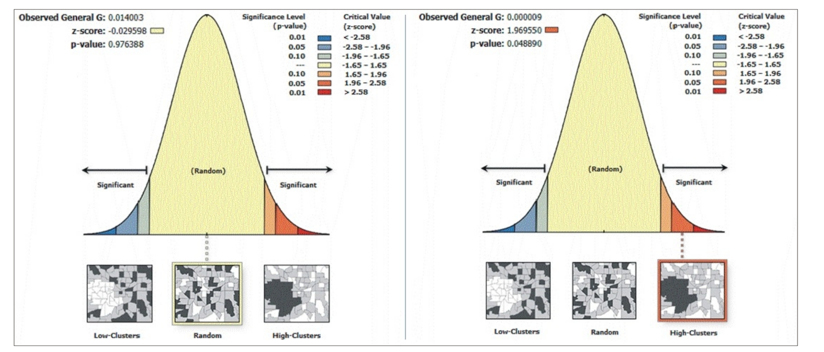

Figure 15: High-low clustering report for fish tissue (left) and surficial sediment (right).

Results and Discussion:

Figure 5 and 6 depict the concentrations of PAHs by basin. Low molecular weight PAHs, associated with atmospheric fallout, exhibit diminishing concentrations towards Chesapeake Bay, indicating atmospheric deposition dominates in the western portions of the region (which experience the highest amounts of precipitation). Overlaid surfaces corroborate the westward dominance of low molecular weight PAHs (Figure 7 and 8). The Shenandoah's southern fork and the Rappahannock consistently yield significant levels of high and low molecular weights. These sites are likely severely impacted by West Virginia coal mining and power generation to the east. The ratio of low molecular weight to high molecular weight PAHs indicates the degree of source similarity at a given site; greater ratios have less similar sources. In both mediums there is a negative relationship between total PAH concentration and this ratio (Figure 9 and 10), supporting the findings of Mai et al. (2003). Surficial sediment PAH levels had a mean value of 3.9x103 ±2.5x104 ppb, while fish tissue PAH levels had a mean value of 8.1 ±8.2 ppb.

Preliminary geospatial analysis of VADEQ surficial sediment and fish tissue concentration data suggests that PAH concentrations are highest in areas with multiple PAH identified sources. The fish and sediment samples have varying distributions (Figure 11 and 12). Areas of high PAH concentrations in sediment and in fish tissues were observed near the King George reach of the Potomac and outside of Staunton (along southern fork of the Shenandoah basin). The Morgantown Power Generation Station is located across the Potomac River from King George and has known environmental implications as studied by Seaman (2010). Hotspots of PAHs in fish tissue are also seen in the Elizabeth River, where shipping and retired paper industries dominate.

PAH levels are sensitive to organic composition. As seen in Figure 13, there is a negative relationship between PAH levels and lipid content. PAHs cling to surfaces of lipids within fish tissues; however, this lipophilic nature increases biological degradation rates (Birkholz et al., 1988). Conversely, there is a positive relationship between PAH levels and total organic carbon in sediment (Figure 14). The low efficiency of bio-concentration, a result of equilibrium partitioning coefficients, may be viewed in the disparity between average PAH levels in sediment and fish (Hawthorne et al., 2006). Apex predator species were shown to have PAH values greater than could be accounted for by the direct exposure experienced by bottom feeding fish. This is indicative of bio-magnification within targeted species (Bierman, 1990). However, high-low clustering spatial statistics shows that fish tissue levels were randomly distributed across the study area (Figure 15). This contrasts the significant high value clustering of surficial sediment samples, perhaps a result of sampling a wide range of both migratory and stationary fish species.

Sediment core analysis will offer insight into how these spatial distributions evolved. These preliminary results have isolated the region's longstanding industrial locales and atmospheric fallout as sources of dominant PAH loading to aquatic environments now considered ecologically vulnerable.

Acknowledgments:

The authors would like to thank the University of Mary Washington for funding this project. We acknowledge the contributions of NSF Summer Interns, Jazmin Andrews and Mikaila Clinkscales, during field work as well as the work of all those at the Virginia Department of Game and Inland Fisheries. Thank you to Elyse Clark for her initial exploration of the topic and consequently inspiring this project.

Works Cited:

Appleby, P. G.. "Three decades of dating recent sediments by fallout radionuclides: a review." *The Holocene* 18 (2006): 83-93. Print.
Appleby, P.G., and F. Oldfield. "The assessment of 210Pb data from sites with varying sediment accumulation rates." *Development of Hydrobiology* 15 (1983): 29-35. Print.
Bierman Jr, Victor J.. "Equilibrium partitioning and biomagnification of organic chemicals in benthic animals." *Environmental Science and Technology* 24.9 (1990): 1407-1412. Print.
Birkholz, Detlef A., Ronald T. Counts, and Steve E. Hrudey. "Determination of polycyclic aromatic compounds in fish tissue." *Journal of Chromatography* 449 (1988): 251-260. Print.
Campana, Steven, and Simon Thorrold. "Otoliths, increments, and elements: keys to a comprehensive understanding of fish populations." *Canadian Journal of Fisheries and Aquatic Sciences* 58.1 (2011): 30-38. Print.
City of Lebo, Kansas. "Welcome to the City of Lebo, Kansas." *Species*. Web. 10 Oct. 2014. <http://www.leboks.org/species.shtml>.
Clark, Elyse , Ben Odhiambo, and Matthew Ricker. "Comparative analysis of metal concentrations and sediment accumulation rates in two Virginian reservoirs, USA: Lakes Moomaw and Pelham." *Water Air Soil Pollution* 225 (2013): 1859-1877. Print.
Corcho-Alvaradoa, J.A., M. Diaz-Asencio, P. Froidevaux, F. Bochud, C.M. Alonso-Hernandez, and J.A. Sanchez-Cabeza. "Dating young Holocene coastal sediments in tropical regions: Use of fallout 239,240Pu as alternative chronostratigraphic marker." *Quaternary Geochronology* 22 (2014): 1-10. Print.
Countway, Rebecca, Rebecca Dickhut, and Elizabeth Canuel. "Polycyclic Aromatic Hydrocarbon (PAH) Distributions and Associations with Organic Matter in Surface Waters of the York River, VA Estuary." *Organic Geochemistry* 34 (2003): 209-224. Print.
Dickhut, R., K. Gustafson, K. Arzayus, G. Edgecombe, E. Macdonald, E. Canuel, K. Liu, S. Walker, and M. Gaylor. "Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the chesapeake bay region." *Environmental Science Technology* 34 (2000): 4635-4640. Print.
Environmental Protection Agency. "Polycyclic aromatic hydrocarbons (PAH) on gulf coastline after the BP spill." Environmental Protection Agency, 14 Feb. 2013. Web. 9 Oct. 2014. <http://www.epa.gov/bpspill/pahs.html>.
Fernaindez, Pilar, Rosa Vilanova, and Joan Grimalt. "Sediment fluxes of polycyclic aromatic hydrocarbons in european high altitude mountain lakes." *Environmental Science and Technology* 33.21 (1999): 3716-3722. Print.
Frie, Richard V.. "Measurement of fish scales and back calculation of body lengths using a digitizing pad and microcomputer." *Fisheries* 7.5 (1982): 1. Print.
Hawthorne, Steven, Carol Grabanski, and David Miller. "Measured partitioning coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments." *Environmental Toxicology and Chemistry* 25.11 (2006): 2901-2911. Print.
Heiri, Oliver, Andrea Lotter, and Gerry Lemcke. "Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results." *Springer Link* 25.1 (2001): 101-110. Print.
Mai, Bixian, Shinua Qi, Eddy Y. Zeng, Qingshu Yang, Gan Zhang, Jiamo Fu, Guoying Sheng, Pingan Peng, and Zhishi Wang. "Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: Assessment of input sources and transport pathways using compositional analysis." *Environmental Science and Technology* 37 (2003): 4855-4863. Print
McFarland, E., and T. Bruce. "The virginia coastal plain hydrogeologic framework." *United States Geological Survey* (2006): 1-120. Print.
National Climatic Data Center. "National Overview - August 2014." *National Climatic Data Center, National Oceanic Atmospheric Administration*. 1 Sept. 2014. Web. 10 Oct. 2014. <https://www.ncdc.noaa.gov/sotc/national/2014/8>.
Nickum, J, H Bart, Jr, J Tomasso, P Bowser, I Greer, C Hubbs, J Jenkins, J MacMillan, J Rachlin, J Rose, and P Sorensen. "Guidelines for the use of fishes in research." *The American Fisheries Society* (2003): 01-53. Print.
Odhiambo, Ben K., Virginia Brown, Gayle Armentrout, Leanna C. Giancarlo, and Chelsea Wegner. "Sediment trace metals and PCB input history in Lake Anna, Virginia, USA." *Environemtnal Earth Science* 69.6 (2013): 2103-2117. Print.
Oklahoma Department of Wildlife Conservation. “Blue Catfish Ictalurs furcatus.” Oklahoma Department of Wildlife Conservation. 2011. Web. 13 Oct. 2014. < https://www.wildlifedepartment.com/fishing/fishid/bluecatfish.htm>. *Administration*. 1 Sept. 2014. Web. 10 Oct. 2014. <https://www.ncdc.noaa.gov/sotc/national/2014/8>.
Sakaris, Peter C., and Elise R. Irwin. "Validation of daily ring deposition in the otoliths of age-0 channel catfish." *North American Journal of Fisheries Management* 28.1 (2007): 212-218. Print.
Seaman, Sean. "Environmental review of the Morgantown coal blending/gypsum loadout project." *Maryland Power Plant Research Program* (2010). *Maryland Department of Natural Resources*. Web. 14 Oct. 2014.
Secor, David H., and John Mark Dean. "Comparison of otolith-based back-calculation methods to determine individual growth histories of larval striped bass, Morone saxatilis." *Canadian Journal of Fisheries and Aquatic Sciences* 49.7 (1992): 1439-1454. Print.
Thermo Scientific, Dionex. "Extraction of PAHs from enbironmental samples by accelerated solvent extraction." *Dionex* 1.1 (2011): 1-5. Print.
United States Department of Energy. "Environmental measurements laboratory." *United States Department of Energy* 28 (1997): Print.
Virginia Department of Environmental Quality. "Individual river basin description and assessments." *Virginia Department of Environmental Quality*. (2012): 62-91. Print.
Walker, Shelby E., Rebecca M. Dickhut, and Catherine Chisholm-Brause. "Polycyclic Aromatic Hydrocarbons in a Highly Industrialized Urban Estuary: Inventories and Trends." *Environmental Toxicology and Chemistry* 23.11 (2004): 2655-2664. Print.
West Virginia Division of Natural Resources. "West Virginia DNR - Sport Fishing Species Identification." *West Virginia DNR - Sport Fishing Species Identification*. West Virginia Division of Natural Resources. Web. 10 Oct. 2014. <Http://www.wvdnr.gov/fishing/sport_fish_image.asp?species=largemouth_bass.jpg>.