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USGS-NIWR Project Title:

Determining the Fate and Toxicity of Polycyclic Aromatic Hydrocarbons Associated with Coal-Tar and Other Carbonaceous Material Particles in Urban Lakes

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Problem and Research Objectives:

Particle associated contaminants (PACs) have resulted in the impairment of thousands of streams, lakes, and reservoirs; PACs were responsible for fish-consumption advisories for 39 percent of total river mileage and 43 percent of total lake acreage in the United States in 2008. Results from recent water quality surveys indicate that metal, polychlorinated biphenyl, and DDT concentrations in freshwater sediments have generally decreased since their peak in the mid 1970's, consistent with their use and regulatory histories. However, total concentrations of polycyclic aromatic hydrocarbons (SPAHs) have increased, and generally with increasing urbanization. PAHs are toxic to aquatic life, and many are probable or suspected carcinogens. This is of special concern because many urban surface waters are used for human recreation (e.g., fishing, swimming) and/or drinking water.

Sources of particle-associated PAHs in urban lake sediments are located both within and outside the watershed. They include point (e.g., industrial emissions) and nonpoint (e.g., automobiles) combustion sources, asphalt from roads and parking lots, vulcanized rubber products such as automobile tires, and coal-tar and asphalt based sealcoats on parking lots and driveway pavement and roofs. Results from a number of our recent studies indicate that coal-tar pavement sealcoat is fluviually transported into urban streams and lakes with runoff, and can be the dominant source of PAHs in urban streams and lakes.

The overall goal of this study is to determine the fate and toxicity of PAHs associated with coal-tar particles in urban lake sediments. The specific objectives of this study are listed below.

- 1) Determine the sorption equilibrium and desorption kinetics of PAHs in coal-tar and other carbonaceous material particles that comprise urban lake sediments. We hypothesize that sorption capacities are low and release rates are high for PAHs in coal-tar and other less condensed carbonaceous materials (CMs) compared to highly condensed CMs like black carbon char and soot.

- 2) Determine PAH losses and redistribution associated with coal-tar particles in urban lake sediments. We hypothesize that lower molecular weight PAHs are released from coal-tar particles soon after burial (weeks to months) and taken up by more strongly sorbing black carbon, and that higher molecular weight PAHs are only lost to black carbon over much longer time scales (i.e., years) as phenolic and heterocyclic compounds that comprise coal-tar degrade. As a result, we hypothesize that PAHs are largely conserved in lake sediments and are not significantly released to the water column, and that sediment pore-water concentrations of PAHs decrease with aging.
- 3) Determine the toxicity of PAHs associated with coal-tar and other carbonaceous material particles in urban lake sediments. We hypothesize that toxicity of pore water in sediments decreases with time as PAHs and other organic pollutants redistribute from less strongly sorbing CMs like coal-tar to more strongly sorbing black carbon, and as less recalcitrant pollutants are biologically degraded over time. Such information is important because these lakes are sources of recreation and/or drinking water for large populations, and understanding coal-tar contributions to toxicity is an important step in protecting the environment and public health.

Methodology:

The proposed work combines bench scale laboratory experiments, field experiments, and laboratory analysis of field samples. It is divided into four tasks that cover 1) lake core retrieval, analysis, treatment, and in situ placement, 2) sorption isotherm and desorption kinetic profile measurement, 3) PAH and CM analysis of in situ cores, and 4) toxicity analysis of in situ cores.

Task 1: Lake core retrieval, analysis, treatment, and in situ placement

The deployment and retrieval of all field samples has been completed. The field study was deployed on 5/30/13, and samples were collected 11/2/13, 5/20/14, 10/22/14, and 7/3/15. Details on Task 1 are outlined in previous reports. Briefly, in situ cores were amended with carbonaceous materials (CMs) spiked with deuterated PAHs and placed into the top layer of sediment at Whitnall Park Pond. Images of the in situ cores as well as the four types of CMs are shown below in Figures 1 and 2.



Figure 1: In situ core design and field deployment (credit: Victoria Boyd, UIUC and Peter Van Metre, USGS)

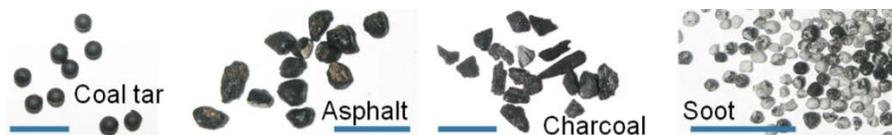


Figure 2: Carbonaceous materials, the scale bar is 1 cm (credit: Victoria Boyd, UIUC)

Each type of CM was spiked with three unique deuterated PAHs in a range of molecular weights. This allows for the transport of PAHs from each CM to be measured. Using a range of molecular weights in the spike makes it possible to determine the effects of PAH molecular weight on transport.

Task 2: Sorption isotherm and desorption kinetic profile measurement

A series of lab experiments will be conducted to supplement the field study using a similar setup. However, the lab experiments will be scaled down and conducted in a controlled, well mixed environment. The purpose of these lab experiments will be to quantify rates of intra-particle exchange, and to extend the field experiments past the two-year sampling period to equilibrium. All CM particles have been prepared and the experiments will begin October 2015.

Task 3: PAH and CM analysis of in situ cores

Retrieval of in situ cores was completed with the help of divers as shown in Figure 3. Analysis of the in situ cores has started. During field deployment the samples were divided into different layers in order to determine if sediment depth had an impact on PAH transport. Mesh screens were added at that time to separate the different layers of sediment. This allowed for the samples to be divided back into the same depths after retrieval. Samples retrieved from the lake were frozen in order to preserve the layering of the sediment and cut open (Figure 4).



Figure 3: Divers retrieved in situ samples (credit: Victoria Boyd, UIUC)

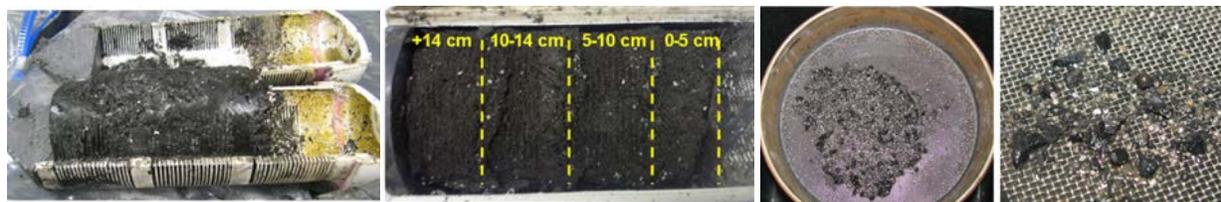


Figure 4: Samples retrieved from the lake were frozen and cut open. Then divided into the original depths, and sieved to separate the particles from the sediment. The particles were separated by hand and analyzed along with the sediment that was sieved away from the particles (credit: Victoria Boyd, UIUC)

The sediment and particles are currently being analyzed for PAHs. Sediment samples and soot and charcoal particles are dried using a Labconco Freeze Dry System prior to analysis.

All samples except coal tar are extracted using EPA method 3534 for pressurized fluid extraction using a Dionex Accelerated Solvent Extractor. Coal tar particles are extracted using a microextraction method in which samples are extracted three consecutive times with 1 mL of 50% acetone and 50% dichloromethane, and sonicated for 3 minutes at 50 °C. The resulting extract is cleaned following EPA method 3630c for silica gel clean up. Finally, sample extracts are analyzed by gas chromatography/mass spectrometry with an Agilent 7890B GC with a DB5-MS capillary column and 5977A inert MSD (EPA method 8270d). All samples will be analyzed for EPA priority 16 PAHs as well as all deuterated PAHs used to spike the particles. Quality assurance will be provided by using three surrogates (fluorene-d10, p-terphenyl-d14, and benzo[a]pyrene-d12) as well as an internal standard (naphthalene-d8). The surrogate standards will be used to correct for PAH losses accrued during extraction and cleanup. The internal standard will be added prior to GC/MS analysis to account for instrument errors.

Task 4: Toxicity analysis of in situ cores

Mutagenicity and cytotoxicity (survivorship) experiments were performed using a single colony isolate of *S. typhimurium* TA100 that was grown overnight in 50 mL LB medium plus 100 µL ampicillin stock solution at 37°C with shaking (200 rpm). The following day, the overnight culture of TA100 was used to evaluate an extract of coal-tar for PAH-induced mutagenicity using a plate incorporation assay. For this assay, overlay tubes were prepared with 2 mL of histidine-biotin, supplemented over agar with 100 µL of overnight bacterial culture and ± 500 µL hepatic microsomal activation (S9) mix. The required volume of the test agent was added to the overlay tube, the tube was flamed sterilized and immediately poured onto a VB minimal plate. The plates were incubated at 37 °C for 36-72 h. Histidine revertant colonies were counted by hand or with a New Brunswick Biotran III automatic colony counter. To confirm the genotype of the TA100 cells, 100 µL of the bacterial cell suspension was added to an LB plate, and spread with a flamed glass rod. Flamed tweezers were used to place a crystal violet disk onto the center of the plate, and the disk was tapped lightly in place. Experiments are planned to evaluate the mutagenicity and cytotoxicity of coal tar extract surrogates containing only PAHs (not other components of the extract), and lake sediment extracts.

Principal Finding and Significance:

Background concentrations in sediment were measured in order to have a baseline to compare the initial conditions of the sediment to the in situ field samples. Sediment samples at time zero are presented in triplicate to show the precision of lab techniques in Figure 5. PAHs are stacked in order of molecular weight, heaviest at the bottom. The PAH concentrations decrease with depth; the PAHs in deeper, older sediment has had more time to degrade and diffuse to the water column.

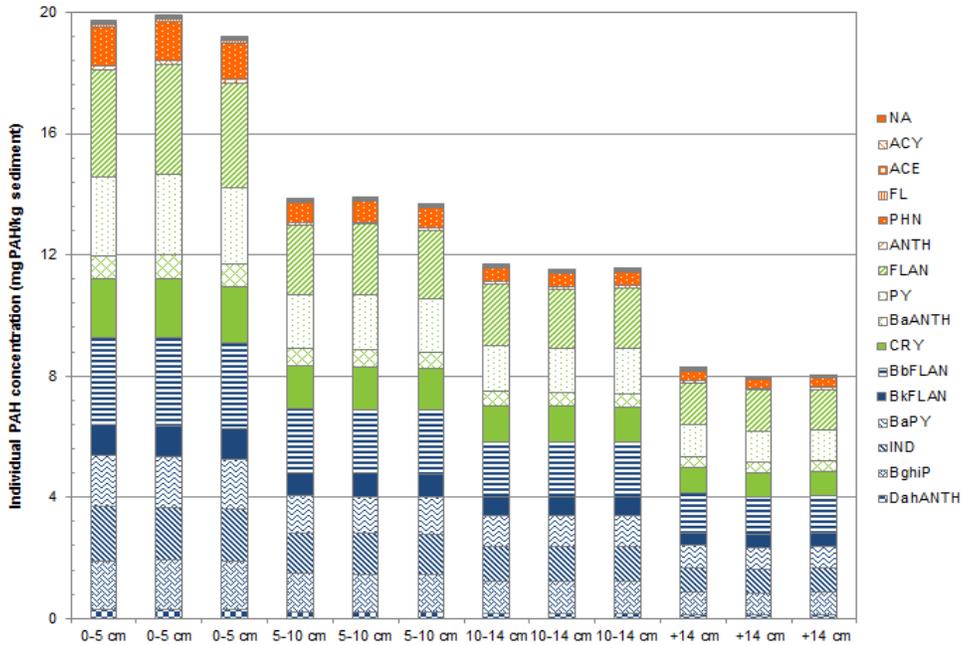


Figure 5: PAH concentrations in original lake sediment (credit: Victoria Boyd, UIUC)

The concentrations of the deuterated PAHs on different CMs and sediment in the sample core after 1.5 years in the lake are presented in Figure 6. The graph is divided into the five material groups along the bottom: sediment, coal tar, asphalt, charcoal, and soot. Each color represents the collection of deuterated PAHs initially spiked onto a specific CM. For example, the green bars represent the deuterated PAHs spiked onto coal tar particles (CT-D). All depths have been averaged in this figure. Notice that concentrations of CT-D are seen in all material types. This means the PAHs initially spiked onto coal tar have transported from the coal tar particles to the other materials while in the lake. All spiked PAHs moved from their original source to other materials. The coal tar (green) and asphalt (red) spikes were the most mobile as they were detected in the highest concentrations in all materials, with coal tar spikes having a significantly larger concentrations in sediment and charcoal particles. PAHs spiked to soot (grey) were the least mobile, and were only seen to move to the charcoal and coal tar particles. These results are consistent with our hypothesis that PAHs associated with coal tar would be more mobile than those with charcoal and soot.

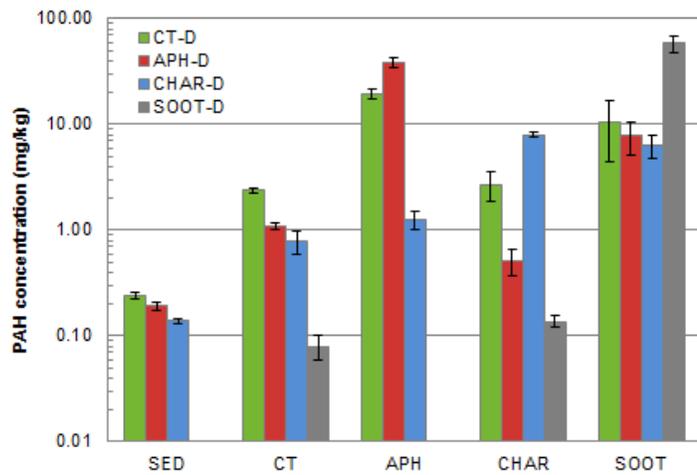


Figure 6: Spiked PAH concentrations in the sample core after 1.5 years in the lake. (credit: Victoria Boyd, UIUC)

A more detailed look at the deuterated PAHs measured in the sediment from the sample core is shown in Figure 7. Triplicate samples from each sampling depth are displayed. The PAHs are divided by the material they were originally loaded onto (same as Figure 6) as well as by molecular weight, the heavier the PAH the darker the color. For example, deuterated PAHs originally spiked onto coal tar particles go from light green (acenaphthene-d at 164 g/mol) to dark green (benzo[b]fluoranthene-d at 264 g/mol). Besides PAHs associated with soot particles, all deuterated PAHs were detected in the sediment, showing transport of a range of molecular weights from each CM. Greater concentrations of heavier PAHs were detected in all samples. This is most likely due to the greater loading of heavier PAHs onto the original CMs due to their lower solubility and greater octanol water partitioning coefficients. Comparison to of the original concentrations of deuterated PAHs on CMs must be completed to determine the extent of transport of spiked PAHs.

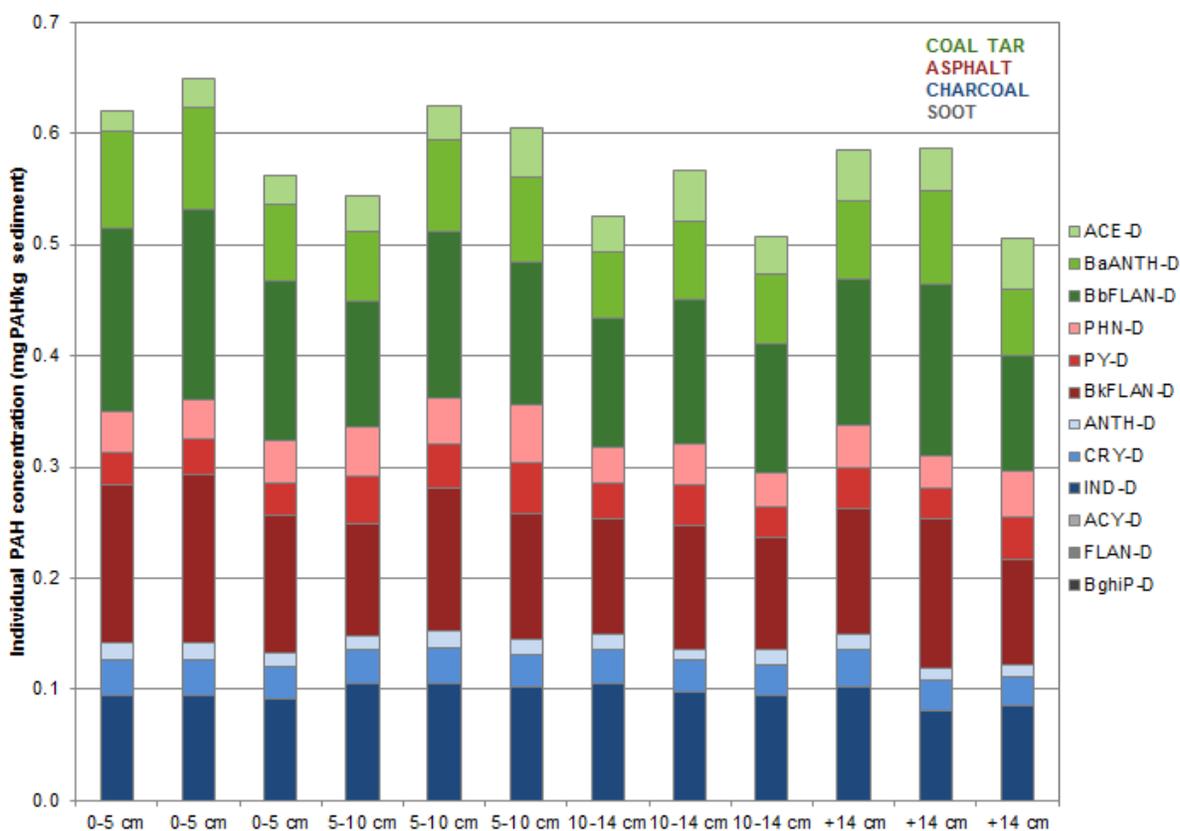


Figure 7: Spiked PAH concentrations in sample core sediment after 1.5 years in the lake (credit: Victoria Boyd, UIUC)

Concentration response curves are shown in Figure 8 for mutagenicity induced by benzo(α)pyrene and coal tar extract containing polyaromatic hydrocarbons in *S. typhimurium*, strain TA100, with and/or without mammalian hepatic microsomal activation. Benzo(α)pyrene with microsomal activation shows a linear increase in histidine revertants with increasing benzo(α)pyrene concentration. Coal tar extract with microsomal activation shows high numbers of histidine revertants as compared to coal tar extract without microsomal activation. Also, the response is nonlinear, showing a plateau at high loadings of extract.

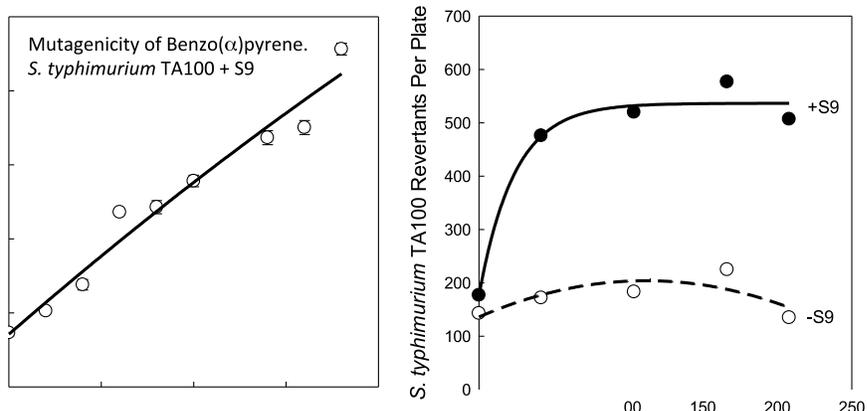


Figure 8: Mutagenic response of *S. typhimurium* to benzo(α)pyrene and a coal tar extract containing PAHs (credit: Azra Dad, UIUC).

Notable Achievements:

The conclusion of the field sampling in July, 2015 was a significant achievement in the project. The analysis of the retrieved field samples shows the movement of spiked PAHs between different CMs and sediment. The most significant trend in this data is the high mobility of spiked PAHs associated with coal tar and asphalt particles compared to those with charcoal and soot.

Students supported with funding:

In the summer of 2012 two graduate students were hired. Ms. Tory Boyd was hired to perform all work except toxicity testing. Ms. Boyd obtained her MS degree at Illinois, and the work in this proposal represents the bulk of her PhD thesis. The other graduate student is Ms. Azra Dad, who is performing the toxicity testing as part of her PhD thesis.

Publications and presentations:

This work was presented at the Environmental Engineering and Science Symposium at the University of Illinois on April 3, 2014 and at the Society of Environmental Toxicology and Chemistry in Vancouver, BC on November 10, 2014.

Photos and figures credited to Boyd, Dad, and Van Metre can be used in IWRC publications.