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Determining the Impact of Coal Tar Based Driveway Sealant on Polycyclic Aromatic Hydrocarbon Concentrations in NH Waterbodies

Alison Watts
University of New Hampshire, alison.watts@unh.edu

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NH WRRC Final Report

Determining the Impact of Coal Tar Based Driveway Sealant on Polycyclic Aromatic Hydrocarbon Concentrations in NH Waterbodies.

Alison Watts and Thomas Ballestero, University of New Hampshire, Dept of Civil Engineering

Problem

Recent studies have found that coal-tar-based pavement is a major source of polycyclic aromatic hydrocarbons (PAHs) to the environment (Mahler et al., 2005; Selbig et al., 2009; Mahler et al., 2010; Watts et al., 2010, UNHSC 2010). The US EPA identifies 16 PAHs as priority pollutants, one of which, benzo(a)pyrene, is also listed as a Persistent Bioaccumulative and Toxic Chemical. PAHs are ubiquitous in the environment, and are one of the compounds most likely to be associated with Tier 1 impacted aquatic sediments. PAHs are released to the environment by many sources, including automotive exhaust, industrial activity and fires. Driveway sealant is applied to the surface of driveways and parking lots as a thin black layer, which wears off and is reapplied every few years. Two types of sealant are commonly used in the US; refined coal-tar-pitch emulsion and asphalt-based emulsion. Although the two sealcoat product types are similar in appearance, PAH concentrations in coal-tar-based sealcoat are about 1,000 times higher than those in asphalt-based sealcoat (Scoggins et al., 2009).

Studies by the University of New Hampshire Stormwater Center (UNHSC), and the United States Geological Service (USGS) have found that stormwater runoff from coal-tar-based sealant contains PAH concentrations one to two orders of magnitude higher than concentrations measured in stormwater runoff from adjacent, unsealed surfaces (Mahler et al., 2005; Watts et al., 2010). Additional work by USGS researchers found that up to 50% of the total PAH load in sediment samples collected from 40 lakes across the country were attributable to the use of coal-tar-based sealant (Van Metre and Mahler, 2010). None of the lakes sampled in this study were located in NH, but coal-tar-based sealant is frequently used in this region, and it is reasonable to conclude that a similar trend may be present. The Piscataqua Region Estuaries Program (PREP) State of the Estuaries 2009 Report identified PAHs as the contaminant which most commonly exceeded threshold values in Great Bay sediments, and noted that concentrations in the Great Bay mussel tissue are increasing. PAH contamination in portions of the Great Bay is partially associated with legacy contamination from former manufactured gas plants (MGPs) (Figure 1), but may also reflect runoff from increasing urbanization, and associated sealant use, in the region.

Figure 1. Silver colored sheen associated with PAH contamination from coal tar in the Cocheco River, Dover, NH.

This project will evaluate existing and data sets and methods as a first step towards determining whether the use of coal-tar-based sealant is impacting aquatic sediments in New Hampshire. PAH compounds are a class of hydrocarbon compounds composed of 2 or more benzene rings. PAHs analyses most commonly report the 16 compounds identified as priority pollutants by EPA, however extended analyses can identify over 60 parent PAH compounds and alkyl homologs, and the distribution of the compound suite can be used to infer the source process. PAH compound profiles have been used extensively to identify PAH sources in sediments, most commonly associated with allocation of responsibility for industrial contaminants (e.g. Stout et al., 2005, Costa, H. J.; Yunker et al., 2002). These methods have also been used to identify sediments contaminated by PAHs released from coal-tar-based sealant (Mahler and Van Metre, 2005, Watts 2010, Van Metre and Mahler 2010).

Objectives

To validate the use of existing data and statistical methods as effective tools to distinguish PAH sources in Great Bay sediments, and determine the impact of coal-tar-based sealcoat in urban and suburban sediments in New Hampshire by:

- Developing a consistent database of PAH compounds in sediments in the Great Bay region, using both existing and new data.
- Developing and testing a contaminant mass balance model, and applying the method to each sample set to determine the most probable source of PAHs, and identify shifts in PAH source.

Results and Discussion

Data compilation: Existing data from EPAs National Coastal Assessment (NCA) program, the GulfWatch mussel program, and individual research projects conducted by researchers at UNH was identified and collated. The data was reviewed for consistency and merged into a single, comprehensive database for the statistical analysis and modeling. PAH source profile data was drawn from an extensive database complied by the USGS (Van Metre and Mahler, 2010) augmented with sealant and other coal tar source data collected in NH (Watts et al, 2010, Watts unpublished data). These sample data and source data were evaluated to identify a set of compounds consistently present in all analysis. These compounds were used to develop the CMB model. The compounds selected for the CMB model were; anthracene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene, chrysene, fluoranthene, indeno(1,2,3-cd)pyrene, phenanthrene and pyrene.

Coastal Assessment sediment data: NCA data is collected every 1-5 years from the top layer of sediment in 71 locations in the Great Bay. The samples are analyzed for 22 PAH compounds. Conventional compound ratio analysis was used to screen the data and determine if there were any significant difference in compound assemblage based on location (Figure 2). No correlation was found with location, but there is a shift in the 2006 data driven primarily by the flouranthene/pyrene ratio (Figure 2). A higher Fl/Py ratio is consistent with inputs of coal tar compounds released during dredging operations in the Cocheco River in 2004-2005.

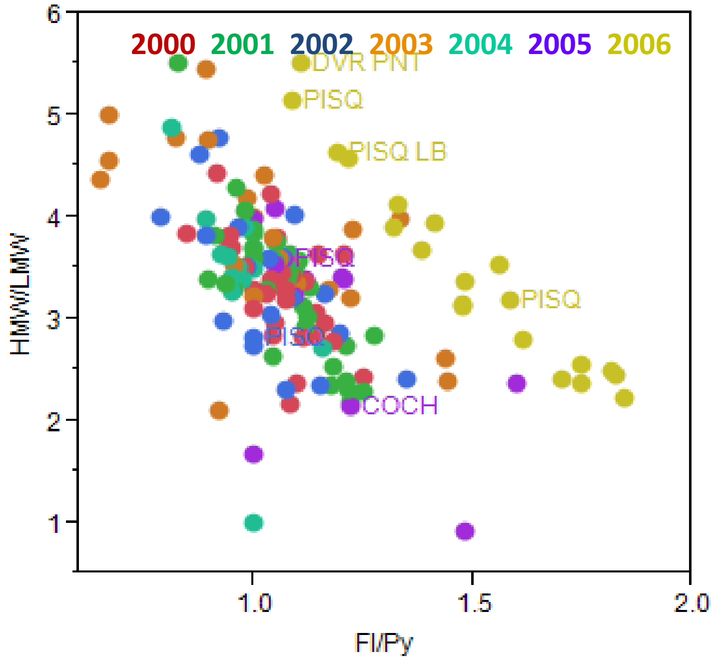


Figure 2. Double ratio plot of flouranthene (Fl)/Pyrene (Py) and high molucular/low molecular weight PAH compounds. Samples were collected at Dover Point (DVR PNT), Pisqcataqua river (PISQ), Little Bay (LB), and the Cocheco River (COCH).

Samples collected from within the Cocheco River before and after dredging show an increase in concentrations (Figure 3), but not a change in source (Figure 4), indicating that erosion of coal tar laden sediments was the primary source of PAHs in the river both prior to, and following, dredging.

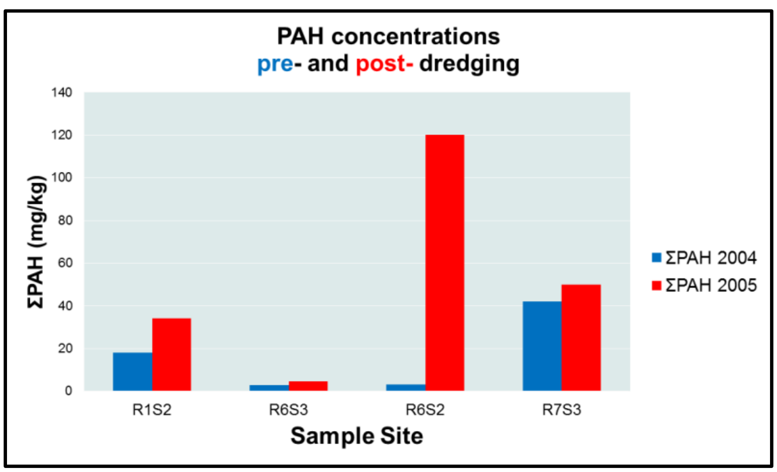


Figure 3. PAH concentrations increased in surface sediment samples collected before and after dredging PAH-contaminated sediments in the Cocheco River.

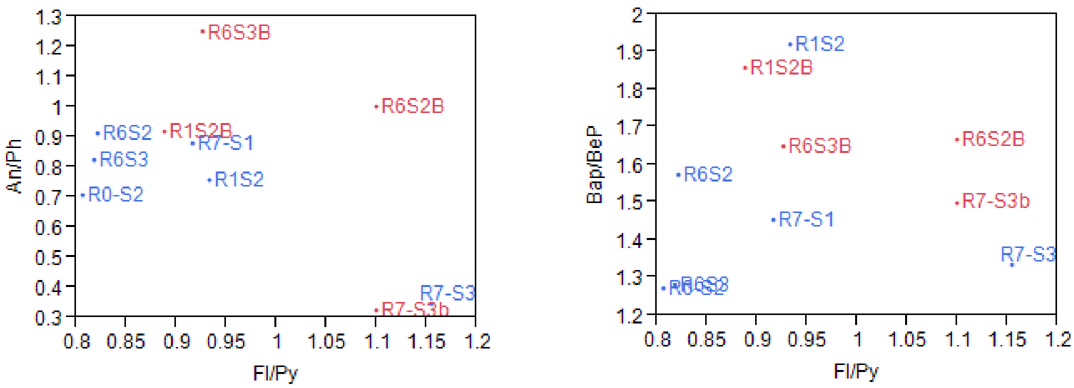


Figure 4. Compounds ratios in pre-and post dredging sediment samples in the Cocheco are similar, indicating that the PAH source did not change.

Regions outside the Cocheco; in the Piscataqua and Little Bay did not experience a measurable rise in concentration (based on the limited data available), but the dominant signature shifted, at least temporarily, from petroleum related sources such as fuel spills, to combustion related sources including coal tar.

Mussel tissue data; Tissue samples are collected by the Gulfwatch program at 21 stations in the Great Bay region, and analyzed for 24 PAH compounds.   Compound ratio analysis indicate distinctly different sources of PAH compounds in mussels collected from with Great Bay, Hampton Harbor and South Mill Pond in Portsmouth.

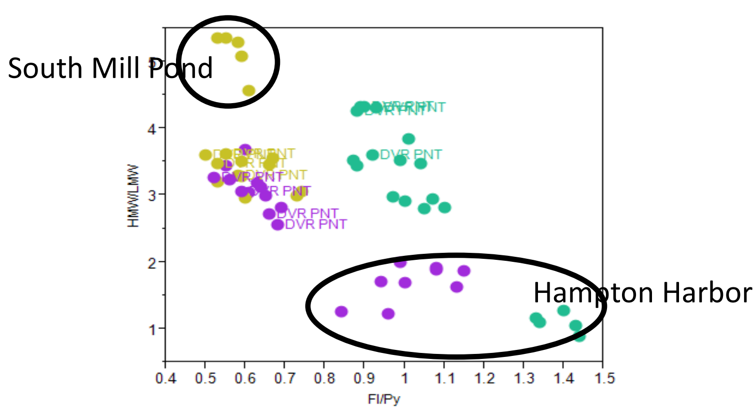
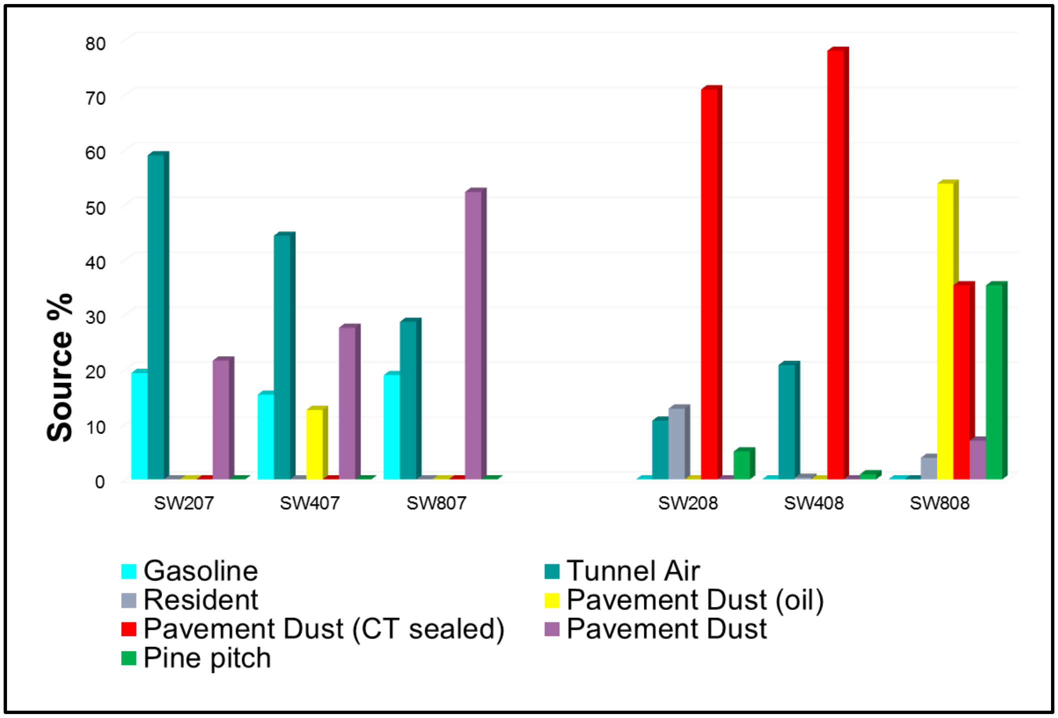


Figure 5. Mussel tissue samples indicate different PAH sources in different water bodies in the Great Bay region.

Source-receptor Modeling: EPA's Chemical Mass Balance (CMB) receptor model consists of a solution to linear equations that express each receptor chemical concentration as a linear sum of products of source profile abundances and source contributions. The CMB model starts with the PAH profiles of known sources and determines the fractional contribution required from each source to reproduce the PAH profile measured in the receptor. The model relies on several primary assumptions; 1) that the PAH profile is constant from source to receptor, and 2) that all potential sources have been identified, and a "fingerprint" profile is available. Chi-square and Pearson correlation will be used to quantitatively evaluate the similarity between source and sediment profiles. Chi-square is calculated as the square of the difference in proportional PAH concentrations divided by the mean of the two values, summed for the total number of PAHs; where lower Chi-square indicates greater similarity. The model is run repeatedly, using various combinations of source profiles, fitting parameters, and estimates of uncertainty to identify a model with the best fit for the source mixtures expected in sediments.

Samples collected at the UNH Stormwater center were used to test the model, and determine if it can effectively differentiate sediments contaminated with coal tar-based sealant from samples not associated with sealant. Samples collected in a stormwater swale prior to sealant application in 2007 were compared to samples collected from the same swale a year later, after coal-tar based sealant was applied to an adjacent parking lot. Figure 6 shows the model results. The model identied tunnel air (automotive exhaust), pine pitch (indicative of wood smoke), and pavement dust as the primary sources of PAHs in the swale prior to sealant, and correctly identified pavement dust from coaltar sealed pavement as a primary source in the post-sealant samples. This exercise confirms the potential for this modeling method to identify locations where coal-tar based sealant is a primary source of PAHs.

Figure 6. EPA Chemical Mass Balance Model of PAH sources in a stormwater swale prior to sealant application (SW207, SW407, SW807 and at the same locations after sealant application (SW208, SW408, SW807). The model correctly identifies the addition of coal-tar-based sealant as the predominant source in 2008.



Principal Findings and Significance

This study confirmed the viability of using PAH compound distributions as a method of identifying PAH sources in Great Bay sediments. We found that:

- Existing national data sets can be used to identify large scale shifts in source, such as contaminants released during river dredging. Specifically, the analysis identified a significant release of PAHs associated with dredging of contaminated sediments in the Cocheco River. This operation increased PAH concentrations in the river downstream of the operation, and impacted (at much lower concentrations) sediments in further reaches of Little Bay.
- Compound analysis can effective identify PAH releases associated with the application of coal-tar-based sealant.
- Existing data sets do not have sufficient spatial resolution to identify the impact of specific practices, such as sealant application, on regional sediments.

A second phase of this study is recommended to extend existing data sets and more fully understand the impact of coal-tar-based sealant on aquatic sediments.

Personnel supported

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