Trends and Sources of PAHs to Urban Lakes & Streams

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Over the past few decades, concentrations of polycyclic aromatic hydrocarbons (PAHs) have been increasing in the sediments of many U.S. urban lakes and streams. These upward trends contrast those of legacy pollutants, such as lead, PCBs, and DDT, which were restricted or banned in the 1970s. Trends of these legacy pollutants have been downward since they were banned (Figures 1 and 2).

Understanding the causes of trends in PAHs is complicated by their many natural and anthropogenic sources. PAHs are contained in fossil fuels and also are produced when materials that contain carbon, including oil, coal, gasoline, and diesel fuel, are heated or burned. Although many studies have considered vehicle emissions as a potential source of urban PAHs, estimated emissions of PAHs from vehicles in the United States declined almost ten-fold from 1971 (32,000 metric tons, or Mg) to 2000 (3,500 Mg), and this decline continues. Vehicle emissions therefore cannot account for the upward trend found in urban lake sediments – there must be some other primary source or sources of the upward trend in PAHs.

Discovery of Sealcoat as a PAH Source

A breakthrough in identifying urban PAH sources occurred in 2003, when scientists with the City of Austin (COA), TX, measured PAHs in sediment samples from very small streams in Austin. The PAH concentrations in some samples were extremely elevated – in the 1000s of milligrams per kilogram (mg/kg), on par with concentrations measured in some Superfund site soils. A COA scientist noted that the sites with the elevated PAH concentrations were immediately downstream from parking lots that had a black sealer on the surface. The sealer was coal-tar-based pavement sealcoat. Coal tar and coal-tar pitch, which are used in coal-tar sealcoat, consist of about 50 percent or more PAHs and are known human carcinogens (Figure 3).

In collaboration with the COA, U.S. Geological Survey (USGS) researchers carried out a series of tests to measure concentrations and yields (the amount leaving the pavement per unit area) of PAHs in runoff from sealed and unsealed pavement. The study was the first to document coal-tar sealcoat as a potentially major source of PAHs in urban runoff (Mahler et al. 2005).

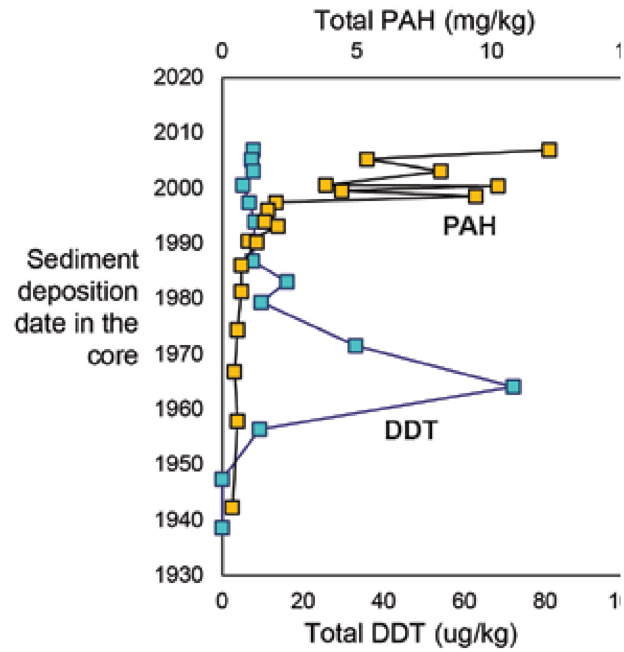

Figure 1. Contaminant profiles from Lake in the Hills, suburban Chicago, IL, indicate contrasting trends for (total) DDT and (total) PAHs.

An East-West Divide

One straightforward line of evidence is to compare PAH concentrations in areas where coal-tar sealcoat is used to concentrations in areas where it is not used. In the United States, there is a general east-west difference in the type of pavement sealant product used: high-PAH coal-tar-based sealants are predominantly used east of the Continental Divide, and low-PAH asphalt-based sealants are predominantly used in the West. This difference in use is reflected in PAH concentrations in urban lakes (Mahler et al. 2012). Lakes in the central and eastern U.S. tend to have higher PAH concentrations in sediment than lakes in the western U.S. for a similar level of urban development. A comparison of Lake Anne in Reston, VA, and Decker Lake in Salt Lake City, UT, illustrates this east-west difference. Both are small lakes with fully developed watersheds, and both have a population of about 2,100 people per square kilometer. Yet PAH levels in Lake Anne sediment are about 20 times higher than in Decker Lake sediment, with mean concentrations of PAH of 17 and 0.76 mg/kg, respectively, for sediment deposited in the 1990s (Van Metre and Mahler 2010). PAH concentrations in dust samples collected from sealed pavement in the two watersheds point to a likely explanation: 3,200 mg/kg for pavement dust in the Lake Anne watershed and 2.1 mg/kg in the Decker Lake watershed. This thousand-fold difference is consistent with the difference in PAH concentrations between the coal tar and asphalt products

Figure 2. A break during sediment core sampling at Lake in the Hills, IL.

Figure 3. Freshly applied coal-tar sealcoat gives this parking lot a new look.

(Mahler et al. 2012). The fact that PAH concentrations in western urban lakes are relatively low indicates that commercial and residential development – and even interstate highways – do not necessarily lead to high "urban background" levels of PAHs.

Quantifying the PAH Contribution of Coal-Tar Sealcoat

Just how important is coal-tar sealcoat as a source of PAHs to urban waterbodies? In other words, what percentage of the PAHs in urban lakes and streams is coming from coal-tar-sealed pavement compared with other PAH sources? Several research groups have used multiple lines of evidence to address this question. The consensus that has emerged is that coal-tar sealcoat use accounts for roughly 50 percent to as much as 90 percent of the PAHs in urban streams, lakes, and stormwater ponds studied in the central and eastern United States (Mahler et al. 2012; Pavlowsky 2013; Crane 2014; Baldwin et al. 2016).

Coal-tar-sealed pavement was demonstrated to be the dominant source of PAHs to urban streams and ponds in Springfield, MO, contributing more than 80 percent of the PAHs (Pavlowsky 2013). This study found a strong relation between PAH concentrations in stream sediments and the area of the watershed upstream from the sampling point that was sealed pavement. PAH concentrations increased as the amount of sealed pavement in the watershed increased, but did not show a relation to total impervious cover, thus indicating sealcoat as the source. Samples of dust from coal-tar-sealed parking lots and the sediment from stream sites draining those lots were enriched in PAHs at concentrations considered toxic to aquatic life based on comparison to widely used sediment quality guidelines.

In the environment, PAHs always occur in complex mixtures of many compounds. PAH sources tend to have a characteristic mixtures of PAHs, which can be thought of as PAH "fingerprints." This is useful, because the fingerprints provide a "forensic" approach for determining the PAH sources to stream or lake sediment. Statistical "source-receptor" models have been developed that use chemical fingerprints to estimate the contribution of each PAH potential source (such as tire particles, used motor oil, and wood burning) to a receptor (such as stream or lake sediment). We applied a source-receptor model (the U.S. Environmental Protection Agency's Contaminant Mass Balance (CMB) model) to PAH concentrations in the upper layer of sediment collected from 40 lakes from across the United States (35 medium and small urban lakes and 5 large lakes with a mixture of land uses). The results of the model indicated that, overall, coal-tar sealcoat was the largest source of PAHs to the lakes, accounting for, on average, about one-half of the PAHs in recent sediments (Figure 4) (Van Metre and Mahler 2010). Many of the lakes in the central and eastern U.S. had PAH concentrations that exceeded the probable effect concentration (PEC), indicating PAH concentrations that are expected to be toxic to some types of aquatic life.

More recent studies that have used the CMB model and other forensic techniques separately or in combination also have concluded that coal-tar sealcoat is a major PAH source to urban

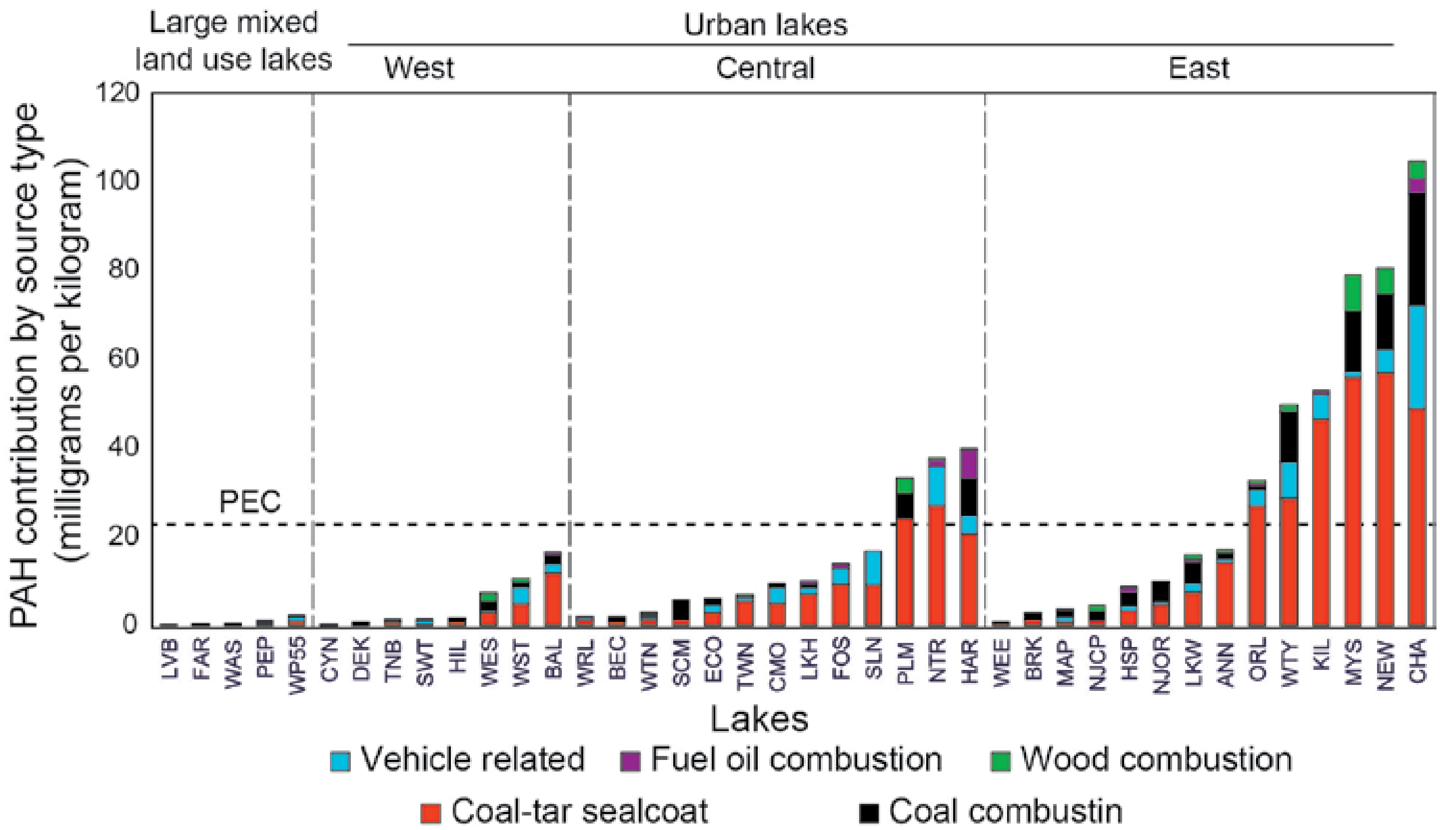

Figure 4. Coal-tar sealcoat was the largest source of PAHs to 40 lakes studied by the USGS (Van Metre and Mahler 2010).

waterbodies (Crane 2014; Witter et al. 2014; Baldwin et al. 2016). In one of the most comprehensive studies of PAH sources to date, researchers from the USGS and the City of Milwaukee, WI, applied six different forensic approaches to assess sources of PAHs in Milwaukee stream sediment (Baldwin et al. 2016). On the basis of this multiple-lines-of-evidence approach, the researchers concluded that coal-tar sealcoat was the primary source of PAHs to the streams, contributing an estimated 77 percent of total PAHs to stream sediment sampled. They also reported that 75 percent of the samples were toxic to standard toxicity test organisms, and that PAHs were the cause of the toxicity.

Other studies have taken different tacks to evaluate the importance of coal-tar sealcoat as a source of PAHs to urban waterbodies. In one study, a research team from the University of Illinois used microscopic analysis to identify the different types of carbonaceous material (CM) present in samples of pavement dust, soils, streambed sediment, and lake (reservoir) sediment collected in Fort Worth, TX (Yang et al. 2010). Carbonaceous materials, such as soot, coal tar, and asphalt, are of interest because they are the primary vectors (carriers) that transport PAHs into urban waters. The researchers characterized PAH concentrations associated with the CM and concluded that coal-tar pitch (used in coal-tar sealcoat) contributed as much as 99 percent of the PAHs in sealed parking lot dust, 92 percent in unsealed parking lot dust, 88 percent in a composite soil sample from a commercial area with some sealed parking lots, 71 percent in streambed sediment, and 84 percent in lake sediment. The identification of coal-tar sealcoat as the main source of PAHs in unsealed parking lot dust and commercial soils demonstrates the potential for these contaminants to move to neighboring areas by wind and tracking on tires.

PAH Trends in Lakes Linked to Coal-Tar Sealcoat Use

Returning to our original question, is coal-tar sealcoat responsible for the upward trends in PAHs measured in some urban lakes? To address this question, we applied the CMB model to the whole sediment-core record for eight urban lakes from across the United States. In the six lakes that had statistically significant upward trends in PAHs since 1970, coal-tar sealcoat was identified by the CMB model as the primary source of the increase in concentrations (Figure 5).

Given the importance of coal-tar sealcoat as a source of PAHs to urban lakes, what happens when its use is curtailed? In January 2006, Austin, TX, became the first jurisdiction in the United States to ban use of coal-tar sealcoat, providing a unique opportunity to address this question. Much of the runoff from the City of Austin flows into Lady Bird Lake, a 9-km-long impoundment on the Colorado River. PAH concentrations in Lady Bird Lake sediment increased for the four decades prior to the ban. We collected sediment cores and surficial bottom sediment samples from the lake in 2012 and 2014, which were six and eight years after implementation of the coal-tar-sealcoat ban (Van Metre and Mahler 2014). PAH concentrations in that period after the ban was imposed had decreased by about 58 percent relative to the 1998–2005 mean (Figure 6). This rate of decrease is consistent with those measured

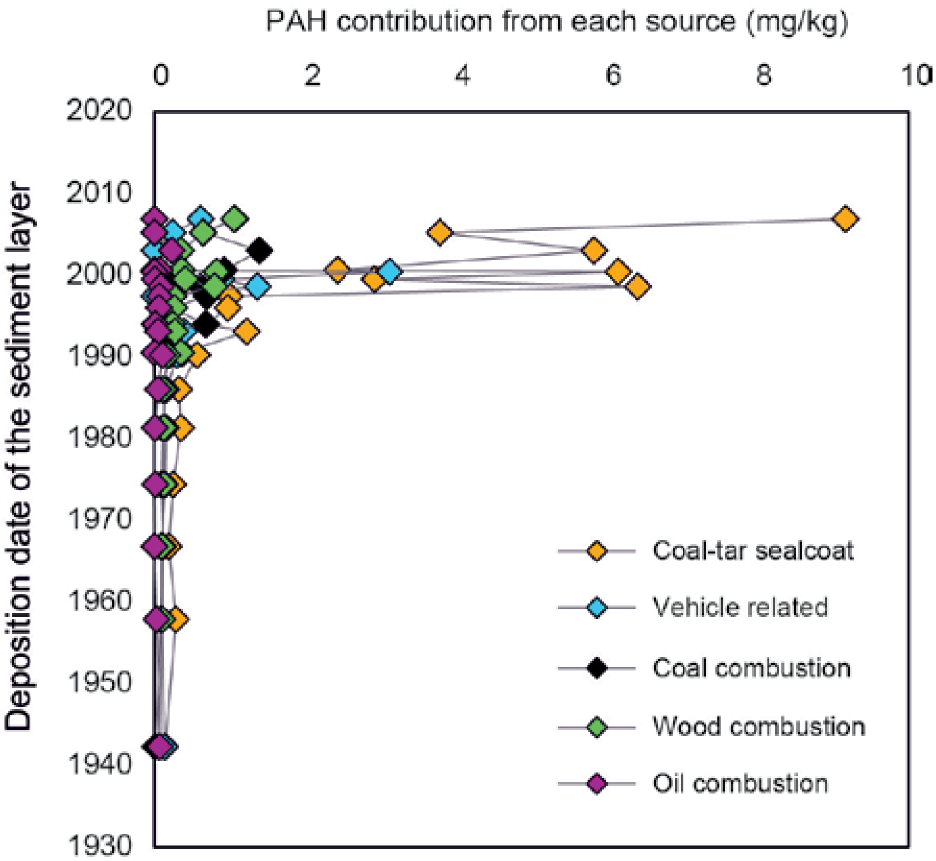

Figure 5. The rapid increase in PAH concentrations in recent years at Lake in the Hills, IL, was primarily from coal-tar sealcoat, which contributed ~70 percent of the PAHs in post-2000 sediment (Van Metre and Mahler 2010).

for other banned chemicals, such as DDT and PCBs. Recently deposited sediment in Lady Bird Lake continues to contain PAHs that, despite their lower concentration, still have a coal-tar signature. This finding implies that PAH concentrations likely will continue to decline as stocks of previously applied sealant gradually become depleted.

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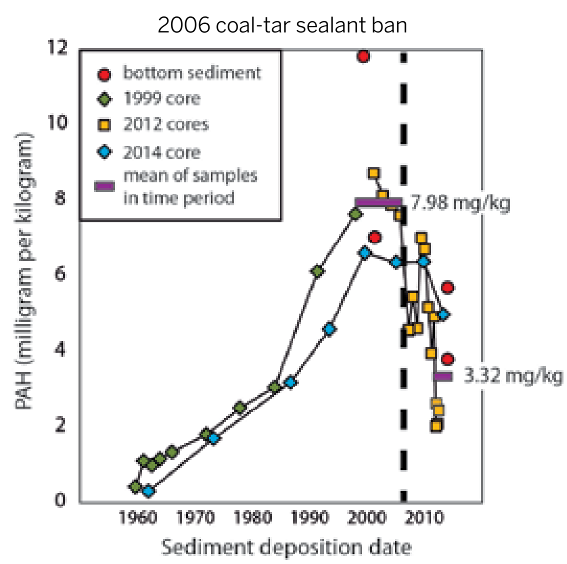

Figure 6. PAH concentrations increased for about 40 years in Lady Bird Lake in Austin, TX, until a ban on coal-tar sealcoat was instituted in 2006. In the eight years following the ban, average concentrations have decreased about 58 percent (Van Metre and Mahler 2014).

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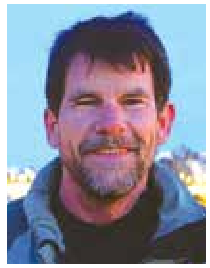

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