

**PAHs in Lakes** 



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We encourage the submission of abstracts for papers or posters on any of the topics listed below, or abstracts that address topics of broad interest to the lake and reservoir management community.

- Reservoir Management
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- Mixing and Aeration Systems
- National Lakes Assessment
- Alum treatment
- Harmful Algal Blooms
- Drinking Water Treatment
- Arid West Issues
- Invasive Species
- Inter-basin Water Transfers
- Western Water Law
- Watershed Management, including Wildfire Impacts and Acid Mine Drainage
- Water Quality Monitoring
- Climate Change Impacts
- Citizen Science
- Storm Water Impacts
- Agricultural Uses
- National Park Lakes and Reservoirs
- Data Analysis and Innovative Visualization Techniques
- Model Applications
- Regulatory Framework
- Communicating Lake Issues to Users and Other Stakeholders
- African Lakes
- Central and South American Lakes
- Beersheds and Brewing

## **Important Dates**

May 31, 2017 Abstracts due.

Late Spring Registration opens.

August 25, 2017

Registration and payment from presenters of accepted abstracts due.

**September 15, 2017** Early-bird registration deadline.

**October 27, 2017** Regular registration deadline.

Visit www.nalms.org/nalms2017 for more information and to submit your abstract.

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# From the Editor

Sometimes, however, projects that address an issue in one area can have unintended consequences that can be harmful in another area. The theme of our spring 2017 issue of *LakeLine* focuses on one LakeLine encourages letters to the editor. Do you have a lake-related question? Or, have you read something in LakeLine that stimulates your interest? We'd love to hear from you via e-mail, telephone, or postal letter.

such issue. It is devoted to communicating what we've recently learned about a class of potentially toxic organic contaminants – *polycyclic aromatic hydrocarbons* (*PAHs*) – in urban lakes and streams.

## Q) What are polycyclic aromatic hydrocarbons (PAHs)?

A) PAHs are a large group of organic compounds created by heating or burning materials that contain carbon. They are an environmental concern because many have been shown to cause cancer, birth defects, or death in fish, invertebrates, and other wildlife. The U.S. Environmental Protection Agency (EPA) has classified seven PAHs as probable human carcinogens (Class B2) and 16 PAHs as Priority Pollutants. Environmental and health effects depend on which PAHs are present and their concentrations. Exposure to sunlight greatly intensifies the adverse effects of several PAHs. In the urban environment, PAHs almost always occur as mixtures, reflecting their many different sources. Most PAHs are insoluble in water. Thus, in the environment, they tend to accumulate in soils and sediments (Figure 1).



*Figure 1. Several common PAH compounds showing different arrangement of benzene rings.* (*Peter Van Metre, U.S. Geological Survey*).

Monitoring and research during the past 20 years by the U.S. Geological Survey has shown unexpected and alarming increases in concentrations of PAHs – in sediments of urban lakes across the United States while concentrations of other contaminants of concern, such as DDT and PCBs, were flat or decreasing (Figure 2).

Additional work done by state and federal agencies and universities has found that coal-tar sealcoat, applied to restore and protect asphalt driveways, parking lots, playgrounds, and hiking trails, is one of the largest sources of PAHs to urban streams and lakes. Over time, sealcoat wears off asphalt due to the abrasive action of vehicle tires and foot traffic. Small particles of sealcoat attach and mix with the dust on the pavement and wash off with stormwater where it may be transported directly to streams and lakes or may accumulate in the sediment of stormwater detention ponds. The accumulation in sediment ponds can result in considerable expense to communities that are responsible for the disposal of the contaminated sediment.

Spring is the season most commonly recommended for repairing and restoring asphalt surfaces through the application of sealcoat. So, in addition to describing the science that has been done on the trends, sources of these contaminants in urban watersheds, and their potential effects to humans and aquatic ecosystems, information about what local and State agencies are doing to successfully address some of the concerns related to coal-tar sealcoat and key best practices for use by homeowners in repairing and restoring asphalt pavement surfaces is provided.

We begin this issue with an article by **Peter Van Metre** and **Barbara Mahler** of the U.S. Geological Survey,

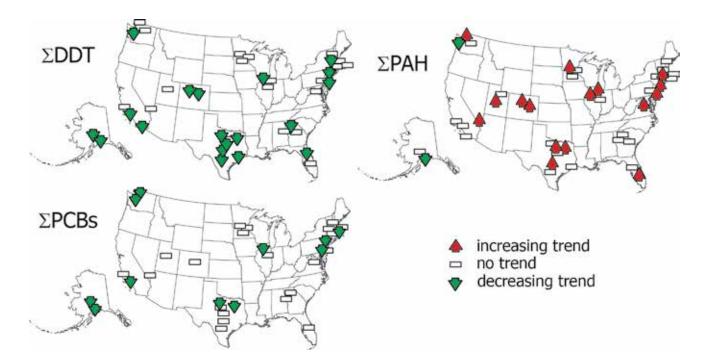


Figure 2. Map of U.S. showing trends in concentrations of PCBs, DDT, and PAHs in urban and reference lakes from 1970 to 2001.

## Q) What is coal tar?

A) Coal tar is a thick, black or brown liquid that is a byproduct of the coking of coal for the steel industry or the gasification of coal to make coal gas. Coal-tar pitch is the residue that remains after various light oils are distilled from crude coal tar for commercial use. Coal-tar pitch is separated (refined) into 12 different viscosities, RT-1 (the most fluid) through RT-12 (the most viscous, and the viscosity used in coal-tar-based pavement sealcoat). Coal-tar emulsion pavement sealants contain either crude coal tar (Chemical Abstracts Service [CAS] Registry Number 8007-45-2) or coal-tar pitch (CAS Registry Number 65996-93-2). Coal tar and coal-tar pitch are known human carcinogens.

that presents findings from studies of 38 urban and reference lakes from across the nation that were sampled to determine how concentrations of contaminants in the environment were changing with time. The results of these studies showed improvements in water quality for some contaminants that have historically been of concern; but, unexpectedly, also showed that concentrations of PAHs were increasing in and around urban areas raising concerns that PAHs were becoming a threat to aquatic biota in urban streams and lakes. Research findings from work done to determine the relative contributions of PAHs from different sources in the urban environment is also presented.

In the second article, **Barbara Mahler** and **Peter Van Metre** summarize findings from field studies comparing PAH levels in soils, dust, runoff, and air on or near sealcoated pavement and pavement without sealcoat that provides additional lines of evidence about the potency of coal-tar-based sealcoat as a major source of PAH contamination in urban and suburban areas.

In the third article, **Spencer Williams**, formerly a research assistant professor at Baylor University's Environmental Health Science Program, summarizes findings from several studies that provide insights about the potential human health effects from exposures to PAHs associated with coal-tar-sealed pavement.

Jenifer K. McIntyre, authored the fourth article that summarizes what has been learned from studies examining the potential health effects to aquatic life from PAHs in stormwater runoff associated with sealcoat. Jenifer is currently an assistant professor for the School of the Environment at the Research and Extension Center for Washington State University (WSU). She is also the lead on collaborative research projects between NOAA-Fisheries, the U.S. Fish and Wildlife Service, and the WSU Puyallup Research and Extension Center on the biological effectiveness of green stormwater infrastructure (GSI) for pollution reduction.

The fifth article in this issue is authored by Al Innes, an environmental planner and pollution prevention and green chemistry specialist with the Minnesota Pollution Control Agency. Al's article shares the history and lessons learned from applying Minnesota's Toxic Pollution Prevention Program to the release of PAHs from coal-tar-based sealcoats in Minnesota and elsewhere around the Great Lakes. Minnesota's approach - addressing environmental issues where they originate and before there is an impact has helped improve the net profits of the business community, while helping to improve the health, environment, and sustainability of the State's natural resources.

The final section of the PAHthemed articles includes a few additional Frequently Asked Questions that are intended to be helpful to those that may be considering a project that involves the application of sealcoat or know of others

(From the Editor, continued on p. 7...)

# From the President

elcome to the spring issue of LakeLine. By the time you read this, hopefully there are signs of spring and renewal where you live, because as I write the column a new four inches of snow has accumulated overnight after we were teased with green grass and warm temperatures across the Pacific Northwest (PNW). It looks like winter will hang on for a bit more, and it's not quite time to hang up the shovel just yet. While I, and I'm sure many others, don't particularly like heaving snow around to get out of the house and driveway, I realize that precipitation in flake form as opposed to rain these days builds the mountain snow pack, a vital source of water for later in the year here in the west. Not only does a healthy mountain snowpack bode well for a good summer white water rafting season, it also maintains abundant and cold stream and river flows for our fish, not to mention a steady summer supply to lakes and reservoirs, the latter of which serve a variety of purposes - one of them being for irrigated agriculture in areas where this would not be possible otherwise. Here in the West, a healthy snow pack is vital to make the world go around as usual or "normal" given the systems and culture that have come to rely on it. However, we best start thinking about a "new" normal.

Having just poked around some longterm climate data for the PNW with a graduate student to examine the frequency of rain-on-snow (ROS) events – as these relate to flooding and the movement of heavy metal laden sediments from legacy mining in the Coeur D'Alene area, it was alarming to see the general trends across the West reported in the peer-reviewed scientific literature: (l) less precipitation overall, (2) warming winter air temperatures, and thus a rise in elevation at which precipitation falls and accumulates as snow, and (3) declines in the ratio of snow/rain precipitation meaning less precipitation as snow and more as rain. A disappearing snow pack across the West does not bode well for reliance on water from a "normal" snow pack. We know that life depends on access to water, as do farms that grow food, so if the normal life-giving flow from mountain snow packs will diminish in the future, we had best come together collectively to figure out the "new" normal. This will not be easy by any means, and we'll need to decide on trade-offs as we establish a new norm for our water supplies.

Similarly, we live in a world that relies extensively on hydrocarbons and their byproducts. While there are obvious conveniences such as the freedoms afforded by individual automobiles and the availability of new materials, these conveniences come with trade-offs that significantly affect our natural and aquatic environment as you'll read in this issue. Again, it is through collective dialog that

we will establish what is, and what is not acceptable – don't expect everyone to be happy at the end of the process.

It is the norming of what is and what is not acceptable that has me very concerned at the moment as we learn what is "normal" or to be expected of the new administration in D.C. Regulations for our environment via the Environmental Protection Agency (EPA) were born out of a collective will by U.S. citizens for a healthy environment capable of supporting us, and recovering what has been polluted. You read the editor's column last month about the re-authorized but unfunded section 314 Clean Lakes Program of the Clean Water Act and what is and what is not happening around the nation with regards to our lakes. I am disappointed to see that H.R. 681 "To terminate the Environmental Protection Agency" (https://www.congress.gov/ bill/115th-congress/house-bill/861) aimed to terminate the EPA by December 2018, was introduced by Rep. Matt Gaetz, [R-FL-1] on Feb 3rd, 2017. In addition,



As we have done every other summer for the past six years, our next issue focuses on Harmful Algal Blooms (HABs). The NALMS Inland HAB Program leaders, Angela Shambaugh and Shane Bradt, have contacted leading HAB researchers in the field to present the latest findings and information for this issue. H.R. 637, "Stopping EPA overreach Act of 2017" (https://www.congress. gov/bill/115th-congress/house-bill/637), aimed to stop the EPA from taking actions not originally intended by Congress, "incorrectly" labeling greenhouse gasses as air pollutants, and identifying no regulation of climate change, etc., was introduced by Rep. Gary, J. Palmer, [R-AL-6] on Jan 24th, 2017 with 121 co-sponsors. The ramifications of these bills should give collective pause for thought - who will mind the proverbial store? In the face of an expanding human population that relies on water and its environment for survival now is not the time to abandon the EPA, or we might as well be drinking with a straw from our own diaper. As a citizen, it is your responsibility to inform yourself and participate in our democratic process.

To end on a positive note, check out the current George Barley Water Prize competition hosted by the Everglades Foundation (<u>http://www.barleyprize</u>. <u>com/</u>), a four-year, stepped competition with a \$10-million prize to the team who develops the most cost-effective, scalable technology that thoroughly removes and recovers phosphorus from freshwater bodies. The final phase will be a fully functioning operations plant. Now that's exciting for renewal and a new norm – think of the possibilities for our waters!

Frank Wilhelm is an associate professor of limnology at the University of Idaho in Moscow, Idaho, where he teaches courses in limnology and in the introductory sequence of natural resources



course. He has an active research program focused broadly on limnology including cyanobacteria, invasive species, nutrient cycling, and foodweb dynamics. He has been an active member of NALMS, having served on various committees and as Region 10 director previously.

## $(\ldots$ from the Editor, continued from p.5)

planning such a project. Information is provided on: How to determine whether a particular sealant product contains coal tar; How to determine whether the existing sealant on your driveway contains coal tar; Alternative products to coal-tar sealcoat; and Best practices for maintaining and applying sealcoat.

In our "Student Corner," **Andrew Labaj** and **Branaavan Sivarajah**, students in the Paleoecological Environmental Assessment and Research Laboratory (PEARL) at Queen's University in Ontario describe their research into using lake sediments to assess the long-term ecological consequences of mining in Canada.

In his column, NALMS President **Frank Wilhelm** shares his concerns for the future of water resources and some hope. Although the successful Banff Symposium is still on our minds, it is time to make plans for the NALMS Denver Symposium, November 6-9, 2017. We include the Call for Papers in this issue. We also include announcements for the annual Lakes Appreciation Month and NALMS Photo Contest.

We conclude this issue with "Literature Search." Enjoy!

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## Large Lake Aeration System Engineering



## Trends and Sources of PAHs to Urban Lakes & Streams

Peter Van Metre and Barbara Mahler

ver 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).

## 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

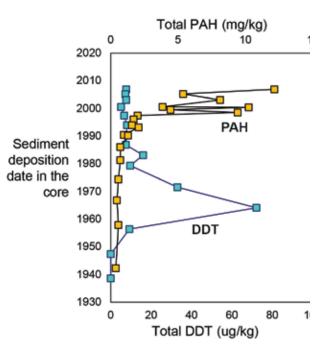


Figure 1. Contaminant profiles from Lake in the Hills, suburban Chicago, IL, indicate contrasting trends for (total) DDT and (total) PAHs.

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-tarsealed 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-tarsealed 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 "sourcereceptor" 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

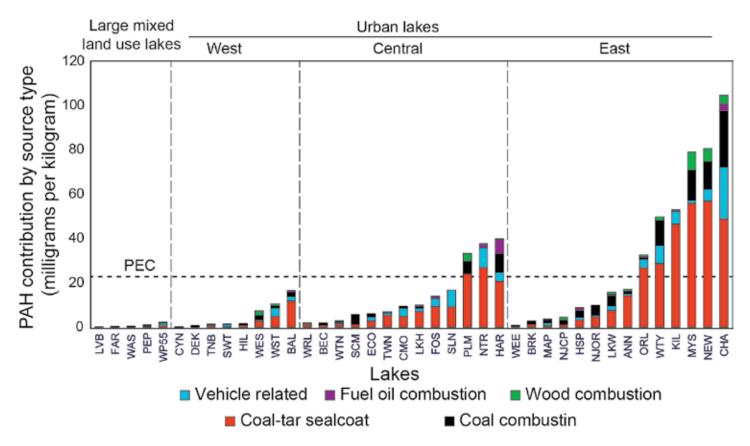


Figure 4. Coal-tar sealcoat was the largest source of PAHs to 40 lakes studied by the USGS (Van Metre and Mahler 2010).

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-ofevidence 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 coaltar 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 coaltar 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 coaltar-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

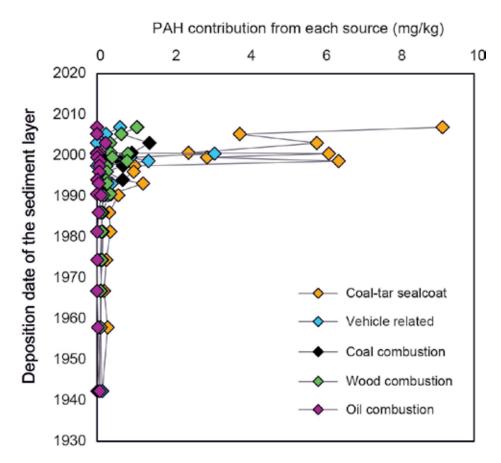
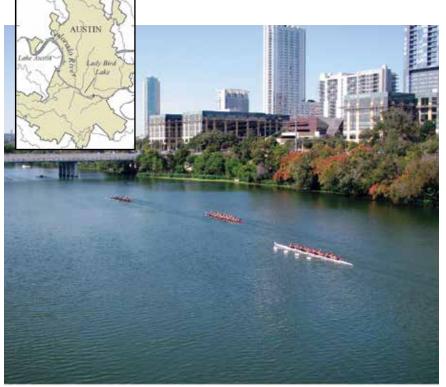


Figure 5. The rapid increase in PAH concentrations in recent years at Lake in the Hills, IL, was primarily from coal-tar sealcoat, which contributed ~70 percent of the PAHs in post-2000 sediment (Van Metre and Mahler 2010).



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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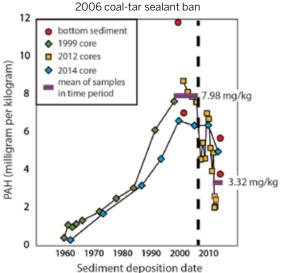


Figure 6. PAH concentrations increased for about 40 years in Lady Bird Lake in Austin, TX, until a ban on coal-tar sealcoat was instituted in 2006. In the eight years following the ban, average concentrations have decreased about 58 percent (Van Metre and Mahler 2014).

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## Coal-tar-based Pavement Sealants – A Potent Source of PAHs

Barbara J. Mahler and Peter C. Van Metre

avement sealants are applied to the asphalt pavement of many parking lots, driveways, and even playgrounds in North America (Figure 1), where, when first applied, they render the pavement glossy black and looking like new. Sealant products used commercially in the central, eastern, and northern United States typically are coal-tarbased, whereas those used in the western United States typically are asphalt-based. Although the products look similar, they are chemically different. Coal-tarbased pavement sealants typically are 25-35 percent (by weight) coal tar or coal-tar pitch, materials that are known human carcinogens and that contain high concentrations of polycyclic aromatic hydrocarbons (PAHs) and related chemicals (unless otherwise noted, all

data in this article are from Mahler et al. 2012 and references therein).

PAHs are a large group of organic chemicals created by heating or burning material that contains carbon; 16 PAHs are classified as U.S. Environmental Protection Agency Priority Pollutants, six are classified as probable human carcinogens, and one (benzo[a]pyrene) is classified as a known human carcinogen. The many sources of PAHs to the urban environment span a wide range of PAH concentrations and include tire particles, used motor oil, and diesel and gasoline engine exhaust (Figure 2). Of known urban PAH sources, coal tar and the related compound creosote have the highest PAH concentrations. Coaltar-based pavement sealant products contain, on average, about 70,000 mg/

kg polycyclic aromatic hydrocarbons (PAHs), on the order of 1,000 times higher than asphalt-based products, which typically contain about 50 mg/kg PAHs.

Pavement sealant is not permanent - the sealant must be reapplied every few years, because it is removed from the pavement by wear and tear from traffic, weathering, and chemical processes. There are at least three ways that pavement sealant (and the PAHs and other chemicals it contains) can leave the pavement surface and enter the surrounding environment: by eroding into small, mobile particles; by dissolving into water; and by volatilizing into air. Where do PAHs derived from sealant go? The answer depends on the process involved. Pavement sealant is worn by vehicle tires into a fine powder that



*Figure 1. Pavement sealant is commonly used to seal parking lots, playgrounds, and driveways throughout the United States. Sealants used in the central, northern, eastern, and southern United States typically contain coal tar or coal-tar pitch, both of which are known human carcinogens.* Photos by the U.S. Geological Survey.

## **Urban PAH Sources by the Numbers Fresh asphalt** 1.5 Weathered asphalt 3 **Fresh motor oil** 4 **Brake particles** 16 **Road dust** 24 **Tire particles** 86 **Diesel engine exhaust** 102 **Gasoline engine exhaust** 370 Used motor oil 440 Asphalt-based sealant 50 Coal-tar-based sealant 70,000 All concentrations in mg/kg. See tx.usgs.gov/sealcoat.html for references.

Figure 2. PAH concentrations in typical urban sources. The concentrations shown are a mean or median from as many as six studies.

is transported by stormwater runoff to streams or lakes, or by wind to adjacent soils or other impervious surfaces. Eroded sealant particles can also stick to shoes and be transported indoors. Some PAHs can dissolve into stormwater, especially just after application, and be transported, along with eroded sealcoat particles, to nearby streams and lakes. PAHs also can be released directly into the atmosphere (volatilization). The high PAH concentrations in coal-tar-based sealant can result in high concentrations of PAHs in a number of environmental settings, with potential adverse effects for human and ecosystem health (see other articles on health and ecosystem effects in this issue).

How can we evaluate whether coal-tar-based sealants are an important source of PAH contamination to the environment? One straightforward way is to compare PAH concentrations in pavement dust, runoff, soil, sediment, house dust, and air on or near coal-tarsealed pavement with PAH concentrations in those same media on or near unsealed asphalt pavement or asphalt-sealed asphalt-based sealant (Figure 3).

## **Pavement Dust and Runoff**

The abrasive action of vehicle tires and snowplows grinds dried sealant on the pavement surface into small particles that mix with other dust on the pavement. In southern, central, and eastern U.S. cities, where coal-tar-based sealant use dominates, dust on sealed pavement has about 1,000 times higher concentrations of PAHs than dust on sealed pavement in western U.S. cities, where asphaltbased sealant use dominates (Figure 4). Concentrations of PAHs on pavement with coal-tar-based sealant generally are in the thousands of mg/kg, comparable to concentrations in soils at some Superfund sites. Further, PAH levels in dust on sealed parking lots in the eastern U.S. can be hundreds of times higher than concentrations in dust on unsealed parking lots in the same watersheds. All of these parking lots, sealed and unsealed, share other sources of urban PAHs vehicle exhaust, leaking motor oil, tire

particles, atmospheric deposition – the only difference is the presence or absence of coal-tar-based sealant.

Pavement dust is mobile – it collects on the pavement surface and at curbs and is readily transported by runoff down storm sewers (Figure 4). When researchers measured PAH concentrations in particles transported by simulated runoff from six coal-tar-sealed parking lots, the mean concentration was 3,500 mg/kg, whereas the mean PAH concentration of particles in runoff from unsealed parking lots (asphalt or concrete) was 54 mg/kg (Mahler et al. 2005). For context, the concentration at which PAH concentrations are expected to harm bottom-dwelling aquatic life is 23 mg/kg.

PAH concentrations in stormwater runoff are highest in the months following sealant application and decrease with time, but even years after application PAH concentrations remain much higher than those in runoff from unsealed pavement, as demonstrated by studies in Wisconsin and New Hampshire. In Madison, WI, the median PAH concentration in unfiltered runoff six years after application of coaltar sealcoat to a commercial parking lot was 52  $\mu$ g/L, about 20-1000 times higher than concentrations in runoff collected from a minor arterial street, a commercial rooftop, and a residential street (0.05-2.4  $\mu$ g/L). During the three months following application of coal-tar-based sealant to a parking lot at the University of New Hampshire, the mean PAH concentration in unfiltered runoff measured by the University of New Hampshire Stormwater Center (UNHSC) was 1,357  $\mu$ g/L, and decreased over the next two years to a three-month mean of  $17-116 \,\mu g/L$ (Figure 5). PAH-contaminated runoff can be acutely and chronically toxic to fish and other aquatic biota, as described in "Toxicity of Coal Tar Pavement Sealant to Aquatic Animals," page 23 this issue.

In some cases, runoff is collected in a stormwater management device, such as a retention pond, to improve water quality by retaining suspended particles. A study by the UNHSC demonstrated that sediment collected in a stormwater management device draining a coal-tarsealed parking lot contained 393-1,180 mg/kg PAHs, and sediment collected in a device draining an adjacent unsealed lot contained about 2 mg/kg PAHs. The

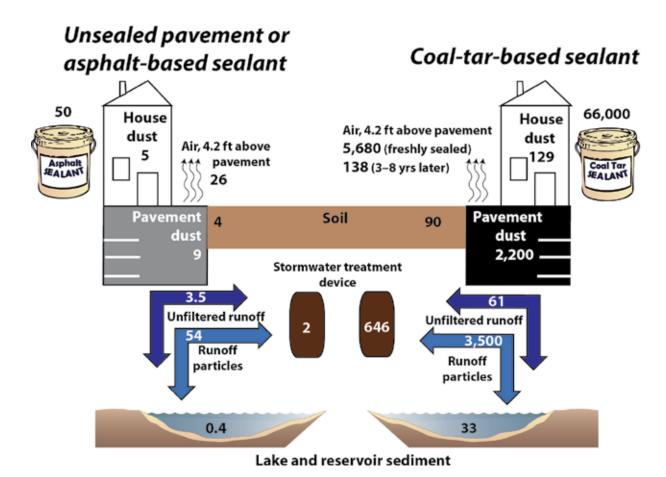


Figure 3. Concentrations of PAHs associated with unsealed or asphalt-sealed pavement (left) are many times lower than those associated with coaltar-sealed pavement (right). PAHs from sealed pavement are transported to the environment by a variety of pathways, including stormwater runoff to stormwater treatment devices, lakes, and streams; windblown transport to soils; tracking of dried particles indoors; and release by volatilization into air. Humans are exposed to PAHs in pavement dust, soil, house dust, and air; aquatic biota are exposed to PAHs in aquatic sediment, such as in lakes and reservoirs. Concentrations shown are in units of milligrams per kilogram (mg/kg), with the exception of unfiltered runoff ( $\mu$ g/L) and air (ng/m<sup>3</sup>). Concentration data are from Mahler et al. (2012) (and references therein) or studies cited in this article, and in many cases are the median

efficient collection of PAH-contaminated sediment in stormwater retention ponds or other devices can have unintended consequences for a municipality because elevated concentrations of PAHs and other contaminants can greatly increase the cost for sediment disposal. Costs for disposing of PAH-contaminated sediment in stormwater ponds in the Minneapolis-St. Paul area are estimated to be \$40-50 per cubic yard, or about \$125,000 per pond, depending on pond size (Judy Crane, Minnesota Pollution Control Agency, written communication, 2015). That translates to an estimated cost of as much as \$1 billion if just ten percent of the ponds in Minnesota contain PAH concentrations that exceed the state's Level 2 human-health risk-based value (Donald Berger, Minnesota Pollution Control Agency, written communication, 2011).

of multiple studies.

## Soil

Contaminated pavement dust can be washed by runoff or blown by wind onto nearby soils. PAH concentrations in soil adjacent to sealcoated pavement in a Chicago, IL, suburb were 23 and 140 mg/kg, 2.3 to 14 times higher than in soil adjacent to unsealed pavement (10 mg/ kg) (Van Metre et al. 2009). Composite soil samples from two commercial districts in Fort Worth, TX, where coal-tar sealants were present on some parking lots, had a mean total PAH concentration of about 90 mg/kg, whereas composite soil samples from nearby residential areas, where sealants were not observed, had a mean concentration of about 4 mg/kg (Wilson et al. 2006). Similarly, PAH concentrations in soil adjacent to a coal-tar-sealed parking lot studied by the UNHSC were as high as 411 mg/kg, and decreased with distance from the parking

lot to less than 10 mg/kg. The highest PAH concentrations were measured in soil in areas where snowplows had piled snow containing pavement dust and sealant particles scraped off with the snow during the winter.

#### Lake and Stream Sediment

PAH-contaminated sediment that is not trapped by stormwater ponds can be transported to streams and lakes. The contribution of coal-tar-based sealant to PAHs in lake sediment can be evaluated by a variety of approaches, including "environmental forensics" (the application of statistical methods to evaluate the chemical content of the source and the sediment), microscopic identification of particles, and land-use analysis. An example of environmental forensics is a comparison of the relative proportions of different PAHs – the "fingerprint"



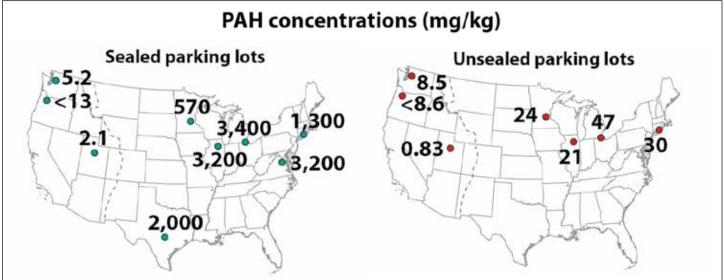


Figure 4. Parking lot "dust" contains abraded sealant (black particles, top). The dust collects on the parking lot surface and along curbs, where it can be carried by runoff down storm drains. PAH concentrations in dust swept from sealed parking lots in the eastern United States, where coal-tarbased sealant is predominantly used, were about 1,000 times higher than in dust from sealed parking lots in the west, where asphalt-based sealant is predominantly used. PAH concentrations in dust on sealed lots in the eastern U.S. also were as much as 100s of times higher than concentrations in dust on unsealed lots in the same watersheds, indicating that the sealant is the principal source of the elevated PAH concentrations (Van Metre et al. 2009). Photo by the U.S. Geological Survey.



Figure 5. Researchers at the University of New Hampshire Stormwater Center simulate runoff on coal-tar-sealed pavement for measurement of polycyclic aromatic hydrocarbons (PAHs). Photo by the University of New Hampshire Stormwater Center.

- in dust collected from parking lots in U.S. cities to fingerprints in sediments from lakes in the same watersheds. For central and eastern U.S. watersheds, the fingerprints of sealed pavement dust and lake sediment were similar, and were different from those in western U.S. watersheds, where the asphalt-based product is used. A more quantitative approach - a statistical method known as source-apportionment modeling estimated that coal-tar-based sealant contributed about one-half of the PAHs to 40 U.S. urban lakes studied by the U.S. Geological Survey; the other major contributors were vehicles and coal combustion. The topic of PAH sources to lakes and streams is further discussed in "Trends and Sources of PAHs to Urban Lakes & Streams," page 8 this issue.

## **House Dust**

Coal-tar-based sealant can cause indoor as well as outdoor contamination. Abraded sealant particles can stick to the bottoms of shoes and be tracked indoors, where they become incorporated into house dust. In a study of 23 ground-floor apartments in Austin, TX, apartments with coal-tar-sealed parking lots had house dust with PAH concentrations that were 25 times higher on average than apartments with parking lots that were unsealed or that were sealed with an asphalt-based product (Figure 3). The study found no relation between PAH concentrations in house dust and other factors such as tobacco smoking, barbecue and fireplace use, and candle and incense-burning.

These results are of concern because ingestion of house dust is well recognized as a pathway for human exposure to chemicals, especially for toddlers, who play on the floor and put their hands and objects into their mouths. This topic is discussed in more detail in "Human Health Concerns Associated with Exposure to PAHs & Coal-Tar-Sealed Pavement," page 19 this issue.

#### Air

Some of the PAHs in coal-tar-based sealant are released into air during and after application (Figure 3) through a

process called volatilization. Many PAHs, including the seven classified as probable or known human carcinogens, are volatile to some degree. Airborne PAHs are of concern because inhalation is another important pathway for human exposure. Although unseen, airborne releases of PAHs from freshly applied coal-tarbased sealant are on the order of 45,000  $\mu$ g/m<sup>2</sup>/hr, which is tens of thousands of times higher than releases from unsealed asphalt. Taken across the entire United States, emissions of PAHs to air from newly applied coal-tar-based sealant are estimated to exceed those from motor vehicles.

The concentrations of PAHs in air above freshly coal-tar-sealcoated pavement decrease rapidly during the weeks following application, but even years later remain several times higher than in air over unsealed pavement (Figure 3). Air at approximate breathing height above coal-tar-sealed pavement (4.2 feet, or 1.28 meters) even in suburban areas contains PAH concentrations that rival or exceed those in highly industrialized areas. For example, in a study that measured volatilization of PAHs from parking lots that had been treated with coal-tar-based sealant years previously, the mean concentration of the PAH pyrene was about 2-19 times higher than pyrene concentrations measured in air samples from urban industrial sites from New Jersey and Chicago, USA (Van Metre et al. 2012).

## **A Scientific Consensus**

Independent research by scientists and engineers from academic institutions and government agencies demonstrates that coal-tar-based sealant is a potent source of PAHs to water, dust, soil, stream and lake sediment, and air. The comparison of PAH concentrations in settings where coal-tar-based sealant is or is not applied provides an unambiguous picture of the importance of coal-tar-based sealants as a source of PAHs to our urban and suburban environments.

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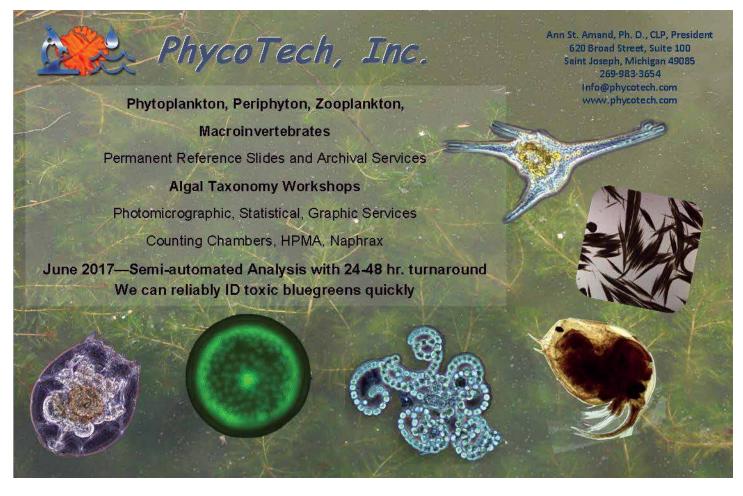
and suspended and streambed sediment, Lake Como and Fosdic Lake watersheds, Fort Worth, Texas, 2004. U.S. Geological Survey Data Series 211, 24 p.

Additional information is available at USGS Research: PAHs and Coal-Tar-Based Pavement Sealcoat, <u>http://tx.usgs.</u> gov/sealcoat.html.

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## Human Health Concerns Associated with Exposure to PAHs & Coal-Tar-Sealed Pavement

hether polycyclic aromatic hydrocarbons (PAHs) and other chemicals in the environment pose a risk to human health depends on the extent to which people are exposed to them. Paracelsus, the 16<sup>th</sup> century Swiss scientist and founder of modern toxicology was the first to expound on the concept of dose response and its importance in determining whether chemicals pose a risk to human health: "Poison is in everything and no thing is without poison. The dosage makes it either a poison or a remedy."

#### Assessing the Risks of Cancer

Exposure to PAHs has been linked to increased risk for lung, bladder, and skin cancers. Coal-tar-based pavement sealants are 15-35 percent coal-tar pitch. Coal tar and coal-tar pitch are listed as Group 1 carcinogens (carcinogenic to humans). PAHs are the major constituents of coaltar pitch, and commercially available coaltar-based sealants contain on the order of 50,000-100,000 mg/kg PAHs (sum of the 16 U.S. Environmental Protection Agency [USEPA] priority pollutant PAHs). The USEPA currently classifies the following seven PAH compounds as probable human carcinogens (Group B2): benz[a]anthracene, benzo[a] pyrene, benzo[b]fluoranthene, benzo[k] fluoranthene, chrysene, dibenz[a,h] anthracene, and indeno[1,2,3-cd]pyrene. Coal tar itself is a powerful mutagen; having a mutagenicity index that is about 1,000 times that of asphalt cements.

The way the risk of cancer is assessed for these PAHs is still evolving. While confirming that benzo[a]pyrene is carcinogenic to humans, the USEPA recently revised a number that describes the relationship between exposure and the risk of developing cancer (i.e., the

Spencer Williams and William G. WIlber

cancer slope factor). Scientists are also re-evaluating the potency of numerous PAHs. The proposed Relative Potency Factor (RPF) for dibenz[a,h]anthracene is 10, whereas its previous value was 1. Also, several more PAHs may be added to the list of substances that are considered carcinogenic: two of these have proposed RPFs of 20 and 60. Without a doubt. these efforts will change our assessment of the risk posed by people living in environments contaminated with coal-tarbased pavement sealants. Considering the number of sites and situations in which people come into contact with PAHs, our understanding of risk and potency of various PAHs will continue to evolve.

## **Potential Avenues of Exposure**

There are numerous potential avenues for exposure to the PAHs in coal-tar-based sealants. These pathways include direct skin contact with the sealant; incidental ingestion of abraded particles from driveways, parking lots, and playgrounds where coal tar sealcoat has been used; from nearby soils; household dust inside homes adjacent to sealed pavement; and inhalation of PAHs that emanate from asphalt surfaces after sealcoat has been applied (Figure 1).

Although coal-tar-based sealcoat has been on the market since at least 1960, there are few published studies about the contribution of sealcoat to PAH exposures



Figure 1. Incidental ingestion of abraded particles and skin contact are two ways humans can be exposed to PAHs. Parking lots and driveways with coal-tar-based sealcoat have concentrations of PAHs hundreds to thousands of times higher than those with asphalt based sealcoat or no sealcoat. Photo: ©HalfPoint; used under license from Shutterstock®.

and the associated potential for adverse human-health outcomes. Most of the information that is available to evaluate the potential for human health effects consists of data on the concentrations of specific PAH compounds and laboratory toxicity studies.

## Exposure to PAHs in Soils and House Dust

In 2008, a study of 23 apartments in Austin, Texas, found that house dust adjacent to coal-tar-sealed parking lots contain concentrations of PAHs 25 times higher on average than house dust collected from apartments near unsealed or asphalt-sealed parking lots. The presence or absence of coal-tarbased sealcoat on the parking lot of the apartment complex was strongly correlated with PAH concentrations in house dust. Although tobacco smoking, candle burning, and barbecue and fireplace use are also potential sources of PAHs in house dust, the research scientists could not attribute the PAH concentrations in the house dust to any of these other sources. The potential for exposure to high concentrations of PAHs in soils and house dust is particularly important for young children who typically spend more time crawling and playing on floors and are prone to hand-to-mouth behaviors that make them more likely to be exposed than older children and adults. This is a similar pathway that makes children susceptible to contact with lead in their environments, either from deteriorating lead-based paint or contaminated soil (Figure 2).

There are no U.S. health-based guidelines for exposure to PAHs in house dust. The only existing guideline is for a single PAH - benzo[a]pyrene - issued by the German Federal Environment Agency Indoor Air Hygiene Commission. The guideline advises minimizing exposure to concentrations of benzo[a]pyrene greater than 10 milligrams per kilogram in dust to avoid adverse health effects. In the Austin, TX study, that guideline was exceeded for 4 of the 11 apartments adjacent to parking lots covered with coal-tar sealcoat and for one of the 12 apartments with a parking lot with a different surface type. Also possibly of concern is contact with sealcoated pavement surfaces themselves through play activities. Dust on some of the parking lots covered with coal-tar sealcoat



Figure 2. The potential for exposure to high concentrations of PAHs in soils and house dust is particularly important for young children, who spend more time crawling and playing on floors and are prone to hand-to-mouth behaviors that make them more likely to be exposed than older children and adults. Photo: ©Marko Poplasen; used under license from Shutterstock®.

had a concentration of benzo[a]pyrene that was more than 50 times higher than the German guideline.

Building on the findings from the 2008 household dust study in Austin, Texas, researchers examined the potential human health effects from incidental ingestion of the PAHs from household dust and soil under several scenarios. One scenario estimated the risks of exposure over the first six years of a child's life, and another examined risks associated with a lifetime of exposure to that environment. In 2012, the authors reported that children living in homes adjacent to pavement with coal-tar-based sealcoat are likely to be exposed to doses of PAHs that are about 14-fold higher than children living in residences adjacent to unsealed pavement, through ingestion of house dust. The scientists concluded that the presence of coal-tar-based pavement sealants is associated with an increase in estimated excess lifetime cancer risk for nearby residents and that much of this calculated excess risk was attributed to exposures to PAHs in early childhood, up to six years of age.

While many of the choices made by the authors in the risk assessment result in conservative (lower) estimates of risk; given the inherent uncertainty associated with doing risk analysis with relatively small data sets, the authors point to a need for biomonitoring and/or other additional research to better characterize exposure patterns to children and adults.

In 2016, researchers at Oregon State University (OSU) published results from new laboratory analytical procedures that enabled them to analyze for a larger number of PAH compounds in sealcoat. The authors detected several substances in coal-tar sealants that have not previously been analyzed in this product, one of which is projected to be 30 times more potently carcinogenic than benzo[a] pyrene. The OSU study also showed that including new PAH compounds found in coal-tar sealcoats increased the equivalent dose of carcinogenic PAHs by 4 percent to 40 percent, using the proposed RPFs. By contrast, the study showed that compounds from asphalt-based sealcoat (more commonly used in the Western U.S.) were far less hazardous than coaltar-based sealcoat.

## Exposure to PAHs in Urban Streams and Lakes

Research has shown that coal-tar sealcoat use accounts for as much as one-

half to 90 percent of the PAHs in urban streams, lakes, and stormwater ponds. Exposure to PAHs from swimming and other contact recreation in streams and lakes is generally not considered to pose a human health risk because most of the compounds of concern usually associate with sediment where the exposure is typically low and infrequent. Potential risks associated with other forms of dermal contact, for example, when children are playing on sealed surfaces or in soil has not been investigated.

## Exposure to Volatile PAHs from Asphalt Surfaces

In addition to exposure of PAHs from particles and dust that abrades from pavement coated with sealcoat, individuals can be exposed to several lower molecular weight PAHs in coaltar-based sealcoat that are volatile and emanate from asphalt surfaces after sealcoat is applied. The volatile characteristics of these compounds, including naphthalene (the key ingredient in mothballs) is why freshly sealed parking lots and driveways frequently give off a strong smell (Figures 3). A recent study that compared measured concentrations of PAHs in the air above parking lots with and without coal-tar based sealcoat found that concentrations of eight PAHs were, on average, 60 times higher than concentrations above unsealed pavement, even though the sealants were applied 3 to >8 years before the study. A second study found that the total amount of eight PAH compounds in air just after sealcoat application was about 5,000 times higher than the amount above unsealed parking lots and that one quarter to one half of the PAHs in the applied sealcoat volatilized during the first 16 days following application. The amounts suggest that PAH emissions from new applications of coal-tar based sealant each year are larger than vehicle emissions of PAHs for the United States. Risks associated with exposures to these compounds has yet to be studied, though any such contact would be expected to be greatest for professional applicators of sealcoat products and relatively low for others).



Figure 3. Individuals can be exposed to several lower molecular weight PAHs in coal-tar-based sealcoat that are volatile and emanate from asphalt surfaces after sealcoat is applied. Risks associated with exposures to these compounds has yet to be studied, though any such contact would be expected to be greatest for professional applicators of sealcoat products and relatively low for others. Photo: Peter Van Metre.

## **Restrictions on Use of Coal-Tar Sealants**

Based on the numerous scientific publications that detail environmental contamination and the potential for adverse health effects, two states and several counties and cities have banned the use of coal-tar based sealants in their jurisdictions. These jurisdictions are listed in the frequently asked questions later in this issue. In summer 2016, EPA proposed a rule that industrial facilities that use coal-tar-based pavement sealants will not be able to register for a stormwater permit. In November 2016, the American Medical Association adopted a new policy aimed at reducing or ending the use of common coal-tar-based sealcoats that are used and applied on pavement and playgrounds across the country. The new policy advocates for legislation either to ban the use of pavement sealcoats containing polycyclic aromatic hydrocarbons (PAH) or to mandate the use of sealcoat products with minimal PAH concentrations.

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## Dr. E. Spencer Williams

was formerly a research sssistant professor at Baylor University, Waco, Texas. His research interests include risk assessment, toxicology, occupational health, and regulatory policy.

William G. "Bill" Wilber, Ph.D. (retired). For most of his 37-year career with the U.S. Geological Survey (USGS), Bill was part of a team of scientists that developed and managed the National



Water Quality Assessment (NAWQA) Program. The NAWQA Program is the largest and most ambitious water-quality program ever undertaken by USGS, with the goals to assess water quality conditions in the nation's streams and aquifers, evaluate how water quality is changing over time, determine how natural factors and human activities affect status and trends, and forecast future water-quality conditions.

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Send your entry to: Bill Jones, Editor, *LakeLine* joneswi@indiana.edu

## Toxicity of Coal-Tar Pavement Sealant to Aquatic Animals

## Jenifer McIntyre

n 2010, residents of Boone, North Carolina, called their fire department to report the unusual smell of mothballs in the air. Nearby, officials found that dead crayfish and trout littered Hodges Creek. Naphthalene is the volatile chemical that gives mothballs their particular smell; it belongs to a group of chemicals called polycyclic aromatic hydrocarbons (PAH). What was the sudden source of the naphthalene and was it tied to the fish kill? It turns out that a parking lot with a storm drain to Hodges Creek had been treated with coal-tar sealant just prior to a large rainstorm, which had flushed much of the sealant into Hodges Creek. This creek is located in a highly urbanized area with multiple potential sources of toxic chemical inputs. However, the sudden and complete die-off of resident fish and invertebrates for 1.5 miles downstream of the parking lot following the rain event does not leave much doubt as to the cause. Applicators avoid applying sealcoat prior to rain, but this unfortunate event highlights the toxic potential of coal-tar sealcoats to aquatic animals.

#### What is Coal Tar?

As described in earlier articles of this volume, coal tar is a byproduct from processing coal, mainly for the steel industry. Coal-tar pitch is the sludge left over after further refinement of coal tar by distillation. These coal products have many uses in industry and manufacturing. Coal tar is sometimes used topically to treat skin conditions such as psoriasis and dandruff, and was the original source of the analgesic drug acetaminophen! Coal tar or coal-tar pitch is the main ingredient in most coal-tar-based pavement sealants. Chemically, coal tar and coal-tar pitches are a complex mixture of hydrocarbons - many of which are PAHs and related compounds. Coal-tar-based sealants are predominantly used in the central, eastern, northern, and southern U.S. Asphalt-based pavement sealants – used predominantly in the western U.S. – contain many of the same chemicals, but at much lower concentrations (approximately 1,000 times less). Coal tar and its distillates are known human carcinogens.

#### **Toxicity of PAHs**

Many of the aromatic hydrocarbons in coal tar and coal-tar pitch are carcinogenic, and can cause mutations, birth defects, and even death. Additionally, many PAHs are phototoxic – that is, toxicity is substantially increased when exposed to the ultraviolet radiation (UV) in sunlight. In humans, this is relevant to topical applications such as treatment for skin conditions, and unintentional skin exposure – for example, workers at foundries and coal tar or tar roofing applicators.

In addition to being toxic to humans, many of the PAHs and related compounds that leach from coal-tar sealcoat are also toxic to aquatic animals, including fish and aquatic invertebrates. Scientists describe toxicity in a number of different ways. One way is to determine whether the toxic effect occurs after a brief exposure (hours to days = acute) or after a longer exposure (weeks/months/years = chronic). The 2010 fish kill in Hodges Creek after the accidental wash-off of coal-tar sealant is an example of an acute effect because the mortality occurred after just a few hours. Cancer is an example of a toxic effect resulting from chronic exposure. This is because the cellular injuries that ultimately cause cancer take time to build up.

Another way to assess toxicity is whether the effects are lethal or sublethal. Lethal effects are those that result in mortality (death) of the organism. Sublethal effects impair or harm the organism in some measurable way, but do not directly kill it. For example, fish embryos exposed to low levels of the PAH phenanthrene develop eyes with shorter retinas and smaller lenses, which impairs their vision. Importantly, sublethal effects can indirectly cause mortality. For example, impaired vision is a sublethal effect, but it can hinder important behaviors like feeding and predator avoidance – indirectly leading to the death of the fish in the wild.

PAHs also include many chemicals that are "cardiotoxic" – affecting heart development and/or function. For example, fish embryos exposed to PAH mixtures develop subtly misshaped hearts that cannot pump as much blood as normal hearts. This in turn results in poorer swimming performance that affects the ability of fish to survive and thrive in the wild. Further, through all developmental stages, some PAHs can directly impair heart function by blocking potassium channels in heart muscle cells, which causes arrhythmia. A final important concept of toxicology is that "the dose makes the poison." Typically, stronger effects occur at higher concentrations and/or longer exposure durations. Therefore, a compound that causes sublethal effects at one concentration may be lethal at a higher concentration and/or longer exposure time. For example, if the PAH exposure continues for hours, the cardiac arrhythmias from blocked potassium channels in cardiac muscle cells can be fatal.

## PAHs in Coal-Tar Sealcoat

The PAHs and similar contaminants in coal-tar sealant can come into contact with aquatic animals through a number of exposure routes. They can be dissolved directly from the sealant surface or from tiny eroded particles of sealant. This means that water simply passing over a coal-tar-sealed surface will pick up toxic contaminants. Larger particles - often "flakes" - of sealcoat that are worn from the sealcoated surface wash into streams and lakes where they are incorporated into the sediment. Aquatic animals can ingest those particles, in which case the contaminants are released and become 'bio-available' inside the animal's gut. The larger particles also provide a longterm source of contaminants that can be leached off of the particle. Coal-tar-sealed pavements are the largest source of PAHs to streams in areas that commonly use this type of sealant. Several studies, using a variety of methods, have demonstrated the link between use of coal-tar-based pavement sealants and PAHs in aquatic sediments. This topic is further discussed in "Trends and Sources of PAHs to Urban Lake & Streams," page 8 in this issue.

Environmental scientists have documented toxicity to aquatic animals from different types of exposure to coaltar sealant. In some studies, water is applied to a sealcoated surface to simulate stormwater runoff (Figure 1) and the runoff is tested immediately for toxicity to aquatic animals. In these studies, the test organisms (fish or aquatic invertebrates) typically are exposed to the water for a short duration (days). These exposures measure "acute" impacts. Many of the studies have investigated how the toxicity of runoff changes as the sealant ages, or "weathers," over months to years. In other studies. flakes of dried sealcoat are added to water or to clean stream sediment prior to adding aquatic animals. In these studies, the test organisms are typically exposed to the water or sediment for a longer duration (weeks), measuring impacts from "chronic" exposure.

## Toxicity to Aquatic Animals from Acute Exposure

Runoff water collected within hours of coal-tar sealcoat drying is consistently lethal to fish and aquatic invertebrates (Table 1). This is because of the high



Figure 1. Coal-tar sealant application (A) and a sprinkler system to simulate rain on coal-tarsealed pavement at Washington State University (B).

concentrations of contaminants that dissolve into runoff water after the sealcoat is first applied. Concentrations of some contaminants (e.g., the PAH phenanthrene; Figure 2) decrease rapidly over the first few days following application, but runoff waters continue to be toxic for a surprisingly long time. A study in Texas collected water from parking spaces with coal-tar sealcoat applied. Runoff water was generated at intervals between 5 hours and 111 days after sealant application. Daphnia – tiny hard-shelled aquatic invertebrates – and juvenile fathead minnows were placed in these waters and their survival monitored for 48 hours. The researchers saw 100 percent mortality even 36 days after the sealant was applied. For coal-tar-sealed plots 36 to 111 days old, the daphnia

Table 1. Studies of the Toxicity of Coal-Tar Sealant to Aquatic Animals.

				-				
Organisms	Tissue	Exposure Duration	Time since sealcoat application	Coal-tar sealant source	Sediment ΣPAH (mg/kg) <sup>a</sup>	Water ΣΡΑΗ (μg/L)	Toxic Effect	UV <sup>b</sup> or other treatment
Daphnia magna and fathead minnow ( <i>Pimepheles</i> promelas)	Whole	48 h	5 h – 36 d	Runoff water	n.a.	167-367	100% dead	UV: 100% dead
Daphnia magna and fathead minnow ( <i>Pimepheles</i> promelas)	Whole	48 h	68 - 111 d	Runoff water	n.a.	167-367	<20% dead	UV: 100% dead
Zebrafish embryos ( <i>Danio rerio</i> )	Whole	48 h	2 h	Runoff water	n.a.	1040	100% dead	
Zebrafish embryos (D. rerio)	Whole	48 h	7 - 207 d	Runoff water	n.a.	137-164	>60% hearts abnormal	Unsealed: no effect
Rainbow trout (Oncorhynchus mykiss)	Liver cells	48 h	5 h – 36 d	Runoff water	n.a.	1.7-36	1%, 10% runoff: no DNA damage	UV: 1%, 10% runoff: DNA damage
Juvenile salmon ( <i>Oncorhynchus kistuch</i> )	Whole	96 h	2 h	Runoff water	n.a.	1040	100% dead	
Juvenile salmon ( <i>O. kisutch</i> )	Whole	96 h	7 - 207 d	Runoff water	n.a.	137-164	10-55% dead	° Unsealed: no effect
Medaka embryos ( <i>Oryzias</i> latipes)	Whole	9 d	1-2.5 years	Runoff water <sup>d</sup>	n.a.	n.m.	23% dead, DNA damage	UV: No additional DNA damage
Frog embryo (Xenopus laevis)	Whole	10 d	n.a.	Dried flakes in water	n.a.	1310 mg flake/L	100% dead	Not tested
Midge (Chironomus dilutes)	Whole	10 d	unknown	Parking lots	0.6-208° median: 33	n.m.	Reduced mass	
Newt (Noptophthalmus viridescens)	Whole	28 d	n.a.	Dried flakes in sediment	8-1149 median: 57	160-1464	Liver damage, impaired righting behavior	Asphalt sealcoat flakes: no effect
Salamander (Ambystomas maculatus)	Whole	28 d	n.a.	Dried flakes in sediment	48-1360	66-263	Impaired swimming	UV: blood cell changes
Amphipod (Hyallela Azteca)	Whole	28 d	unknown	Parking lots	0.6-208° median: 33	n.m.	Reduced mass	UV: 31% sites increased death, 69% sites immobility
Benthic macroinvertebrates	Community	24 d	n.a.	Dried flakes in sediment	5.8-324 median:11		Altered	
Benthic macroinvertebrates	Community	Field	unknown	Parking lots	0.7-32 <sup>f</sup> median: 7	n.m.	Less richness and density as sediment PAHs increased	
Frog embryo (Xenopus laevis)	Whole	52 d	n.a.	Dried flakes in water	n.a.	15,131 mg flake/L	Developmental delay	

<sup>a</sup> dried sediment weight

<sup>b</sup>UV following water exposure

° exposure to runoff from a sealed pavement <sup>d</sup> runoff in retention pond at least 7 days old

<sup>e</sup> sediments from 33 streams <sup>f</sup> downstream of input from parking lots at 5 sites

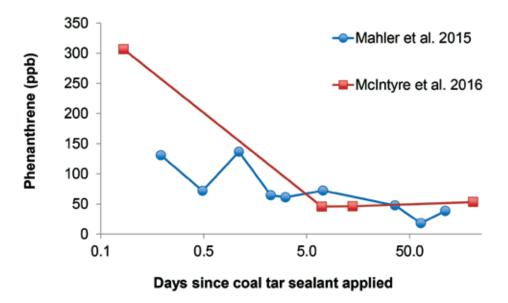


Figure 2. Decrease in the PAH phenanthrene in runoff water over time after coal-tar sealcoat application. Data from Mahler et al. 2015 and McIntyre et al. 2016.

and minnows placed in runoff water survived – unless they were exposed briefly to UV radiation at the end of the 48-hour monitoring period, in which case they all died. This was true even for runoff water diluted 1:10. In contrast, runoff from a mixed coal-tar and asphalt-based sealcoat was toxic to the animals only if they also got a dose of UV. In daphnia, runoff from the asphalt-based sealant was phototoxic for 36 days after sealant application, but for minnows the phototoxicity of the coal tar + asphalt sealant lasted less than one week after sealcoat application.

A study in Washington tested runoff water from pavement sealed with coal tar on juvenile salmon (Oncorhynchus kisutch) and the developing embryos of zebrafish (Danio rerio). Toxicity remained high enough seven months after sealant application for runoff to kill 55 percent of juvenile salmon within 96 hours. The bile of surviving salmon was black instead of a healthy pale green (Figure 3), indicating that the fish were actively metabolizing the coal-tar chemicals. Runoff from the sevenmonth-old sealcoat also caused cardiovascular abnormalities in more than 60 percent of developing zebrafish embryos within 48 h (Figure 4). In contrast, unsealed pavement from an adjacent plot did not cause any mortality or sublethal toxicity in either species over the exposure time. Acute toxic effects were also seen in frog embryos (Xenopus laevis) reared in water containing coal-tar sealant flakes. All of the embryos exposed to the highest dose of flakes (1,301 mg/L) died within ten days (Table 1), even though the contaminated water was replaced with fresh water daily.

Finally, a study with Japanese killifish embryos (*Oryzias latipes*) tested water sampled from a detention pond receiving runoff from a parking lot sealed with coal tar. Approximately one year after the sealcoat was applied, the pond water killed 17 percent of killifish embryos within 9 d of exposure. Approximately 2.5 years after the sealcoat was applied, embryos exposed to the pond water showed significant damage to their

DNA. It is important to note that many of the contaminants in coal-tar sealant, including PAHs, are "organic" chemicals. This refers to the fact that they are made up of carbon and hydrogen and as such can be degraded by bacteria. The result is that, typically, these chemicals will lose potency over time once they are dissolved in natural waters. This is an important study not only because the sealcoat itself was older, but also because the water used in these experiments was collected from the retention pond more than one week after the most recent rainfall. As such, there would have been significant degradation of the chemicals carried from the parking lot into the pond.

## Toxicity to Aquatic Animals from Longer Exposures

Several studies have added flakes of coal-tar sealant into clean water or

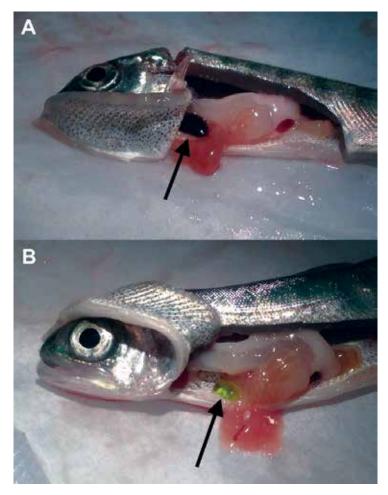


Figure 3. Bile from the liver is excreted into the intestines for removal from the body. Gallbladder containing bile is indicated by a black arrow. (A) The bile of salmon surviving exposure to runoff from coal-tar sealcoat was black. (B) The bile of control salmon and salmon exposed to runoff from unsealed pavement was a healthy pale green.

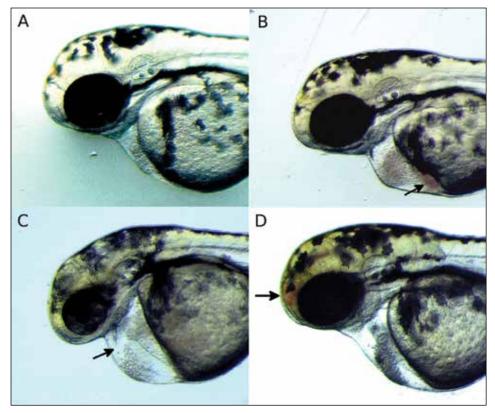


Figure 4. Zebrafish embryos following exposure to (A) control water or (B-D) runoff from coal tar sealcoated pavement showing various cardiovascular abnormalties. (A) Normally developed embryo. (B) Blood pooling in the common cardinal vein. (C) Pericardial edema – fluid accumulation around the heart. (D) Cranial hemorrhaging from broken blood vessels in the head.

sediments and studied the chronic (weeks) toxicity to aquatic vertebrates including frogs, newts, and salamanders (Table 1). Frog embryos exposed to dried coal-tar sealant flakes in water at medium (131 mg/L) and low (15 mg/L) doses survived the full exposure of 52 days, but by 14 days, the embryos had significant developmental delay. By 52 days, 66 percent of the control tadpoles had metamorphosed into frogs, but none of those exposed to either the low or medium doses reached metamorphosis. Eastern newts (Notophthalmus viridescens) showed evidence of liver damage after 28 days associated with sediments containing coal-tar sealant flakes. The amount of liver damage was related to the amount of PAHs that dissolved in the water. Similarly, salamanders (Ambystoma maculatum) exposed to sediment with coal-tar sealant flakes had impaired swimming ability. However, exposure to flakes of asphalt-based sealcoat produced much lower levels of dissolved PAHs and did not cause measurable impairment.

Many aquatic invertebrates are closely associated with sediments. These "benthic" invertebrates include families like amphipods that spend their whole lives in or near the sediments, while others like midges or mayflies eventually emerge from water and metamorphose into flying insects. During their benthic phase, these invertebrates are especially vulnerable to particles from coal-tar sealant. Changes in entire benthic invertebrate community composition have been observed when exposed to clean sediments with added flakes of coal-tar sealcoat. Furthermore, in streams receiving runoff from parking lots with coal-tar sealant scientists have observed a clear negative relationship between concentration of PAHs in sediments and the number and diversity of aquatic invertebrates. The most recent study on the toxicity of coal-tar sealant to aquatic invertebrates used sediment collected from streambeds at 33 sites around Milwaukee, WI. A midge species (Chironomus dilutus) was reared with the Milwaukee sediments for 10 days and an amphipod (Hyallela azteca) for 28

days. There was no significant mortality for either species, but the animals lost weight when exposed to sediments from 19 percent of the sites. Following a fourhour UV exposure, *H. azteca* survival was reduced at 1/3 (31 percent) of sites, and mobility was impaired at 2/3 (69 percent) of sites. PAH concentrations at nearly all of these sites (91 percent) had PAH concentrations above the sediment quality guideline (probable effect concentration) of 22.8 mg PAH/kg sediment, the concentration at which negative effects to benthic animals are likely.

## Is Phototoxicity Relevant to Aquatic Animals?

Some have argued that UV-induced phototoxicity of PAHs is not relevant to animals living underwater, because UV radiation dissipates with depth. However, many of the streams where animals are exposed to sediments with elevated PAHs are shallow and the water is typically clear – making the laboratory exposures similar to actual conditions in the wild. Additionally, many aquatic animals and/ or their embryos are translucent or clear, which increases their vulnerability to phototoxic PAHs.

### Summary

Healthy ecosystems provide economic and health benefits to humans. Ecosystems made unhealthy by chemical pollution do more than deny us these benefits - they are mirrors that link our welfare to that of other animals. Numerous research studies show that toxic chemicals from coal-tar sealcoats can cause a suite of toxic injuries in a variety of invertebrates, amphibians, and fish. These injuries include mortality as well as sublethal effects such as DNA damage, cardiotoxicity, developmental delay, and alterations of critical behaviors. In contrast there appears to be relatively little toxicity associated with unsealed pavements or pavements sealed with asphalt-based products. Finally, sunlight can exacerbate the toxic effects of exposure to PAHs, particularly for animals living in shallow water. In response to the 2010 fish kill on Hodges Creek mentioned in the introduction to this article, council members of Boone, North Carolina, passed strict regulations to discourage the use of coal-tar-based products as

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Dr. Jenifer McIntyre is an assistant professor of aquatic toxicology at Washington State University in Puyallup, WA. Her major research goals include understanding the impacts to

aquatic animals of contaminants present in urban stormwater runoff, and the biological effectiveness of green stormwater infrastructure to prevent those impacts.



## (Student Corner, continued from p. 39 ...)

Andrew Labaj, M.Sc., is currently pursuing a Ph.D. in biology at Queen's University, Ontario, Canada in the Paleoecological Environmental Assessment and Research Laboratory



(PEARL). His M.Sc. work used paleolimnology to assess the biological recovery of lakes surrounding Sudbury, Ontario. Andrew's current research uses paleolimnology to examine the impacts of climate change in the high-elevation lakes of the South American Andes.

Branaavan Sivarajah,

M.Sc., is currently pursuing his doctoral research with PEARL at Queen's University, Ontario, Canada. For his M.Sc. project, Branaavan used paleolimnological



techniques to examine the cumulative effects of multiple stressors on aquatic ecosystems around Georgian Bay, Lake Huron, including acidified lakes in Killarney Provincial Park near Sudbury, Ontario. Branaavan's current research focuses on assessing the long-term biological consequences of arsenic contamination in subarctic lakes from Yellowknife, Northwest Territories.



The Host Committee is busy working on the details for the 37th annual Symposium. Potential highlights include nature photography workshop, new aeration/ oxygenation workshop, field trip to Lake Dillon, factory tours for local probe manufactures, and a visit to the USGS ice core laboratory.

## Protecting Urban Waters & Sediments in Minnesota & the Great Lakes Region

Al Innes\*

## Recent action to reduce PAHs from coal-tar sealcoats to protect urban waters and sediments in Minnesota and the Great Lakes region

## Background

Since its establishment in 1990, Minnesota's Toxic Pollution Prevention Program approach has been applied broadly to an array of existing and emerging environmental issues in addition to toxic waste including inefficiencies in energy and water use. Addressing environmental issues where they originate, before there is an impact, has helped improve companies' net profits, while helping to improve health, environment, and sustainability of natural resources.

In recent years, environmental monitoring and research has detected the presence of existing as well as new and emerging contaminants in people and the environment that are released during or after the use of a product, including plastics monomers, plasticizers, surfactants, flame retardants, fragrances, corrosion inhibitors, pigments, pharmaceuticals, and polycyclic aromatic hydrocarbons (PAHs). In response, the Minnesota Pollution Control Agency (MPCA) has used the prevention approach to promote green and safer chemistry and engineering of products.

This article reviews the application of this approach to the release of polycyclic aromatic hydrocarbon compounds (PAHs) from coal-tar-based sealcoats in Minnesota and elsewhere around the Great Lakes.

## Why Coal-Tar Sealcoat Became a Priority in Minnesota

As described in other articles in this issue, research findings reported in the early 2000s revealed increasing PAH contamination in sediments collected from urban lakes, linking a significant proportion of that contamination to stormwater runoff from asphalt surfaces covered with coal-tar sealcoat. These findings were of immediate interest in Minnesota, where lakes and rivers have high social, cultural, recreational, and commercial value, and therefore have a strong history of protection through policies and programs.

Local governments have long provided the foundation of the state's stormwater management infrastructure. However, after 20 or more years of service, the stormwater catchments in many Minnesota cities are filling with sediment, particularly near stormwater entry points, reducing their ability to capture both runoff volume and pollutants. At the same time, the state has developed its municipal separate storm sewer system (MS4) program, which requires cities to monitor and clean out stormwater ponds.

Finally, Minnesota applies standards for cleaning up and managing contaminated sediments that can be quite stringent for high levels of individual and/ or total PAHs in sediments due to their carcinogenic potential and persistence. Sediments that have high concentrations of PAHs must be transported to and disposed of at a permitted landfill with a liner sufficient to prevent the escape of contaminants. The transport and disposal of sediment with high concentrations of PAHs can cost cities as much as \$50 per cubic yard, up to three times the cost of on-site management such as berming. With 5,000 yards<sup>3</sup> or more of highly contaminated sediment built up in some areas in ponds, the costs for cleaning out such ponds mount quickly. In 2010, MPCA estimated that if 10 percent of sediments in 20,000 Minnesota ponds exceeded the most stringent PAH standard, the total cost of clean up to Minnesota cities could exceed \$1 billion (Figure 1).

Minnesota promotes reductions of other active sources of PAH contamination such as wood fires and vehicle emissions. However, by 2009 the weight of evidence from research identified coal-tar sealcoat as a substantial source, and one of the more readily preventable ones. The specter of the enormous cost for sediment clean up therefore led cities to approach the Minnesota Legislature for remedies. In 2009, a statewide ban on coal-tar sealcoat use was proposed. However, instead of a statewide ban, the Legislature:

- 1. enacted a ban on state agency use;
- 2. required that cities inventory and assess their stormwater ponds;
- 3. directed the development of a model ordinance for local bans of coal tar;
- 4. provided grants to underwrite the cities' costs of sediment clean-up if they enacted a local ban.

Local bans would not solve current contamination issues. However, they would slow the rate of future contamination, reducing the future costs of clean up. Minnesota cities began enacting local bans in 2010 and within

<sup>\*</sup>with contributions from Cheryl Kallio, Freshwater Future



Figure 1: Excavation of sediment from Varney Pond, White Bear Lake, Minnesota; left, before; right, in process.

three years, 29 were in place, primarily in the Twin Cities suburbs but with others sprinkled around the state.

## Genesis of a Pollution Prevention Project

Because of these developments, by 2011 an environment of heightened awareness existed, accompanied by pressure on municipalities and the sealcoat supply chain. However, with most state waters not yet protected by bans, the MPCA decided to promote a voluntary phase-out of coal-tar sealcoat on a statewide basis. Since research around the Great Lakes Basin was finding coal-tar-sealcoat-based PAHs at significant levels at all study sites, MPCA teamed with the University of Wisconsin-Extension Solid & Hazardous Waste Education Center and the Michigan Department of Environmental Quality to propose a more far-reaching project.

MPCA was awarded a grant from U.S. EPA's Great Lakes Restoration Initiative (GLRI) program to support a coal-tar sealcoat pollution prevention project first in Minnesota, and then spreading education and effective prevention tools across the Great Lakes region (Figure 2).

Based on 21 years of experience in pollution prevention programs, MPCA had concluded that many conditions necessary for success were in place in Minnesota:

- Heightened awareness and concern over the cost of coal-tar PAH impacts

   strengthened by sediment research in Minnesota showing local occurrences of high PAH levels with more than 50 percent contributed by coal tar;
- Pressure on retailers, distributors, and contractors from the accelerating pace of local bans;
- Availability of safer and affordable sealcoat alternatives. Pollution prevention outreach is more effective when the promoter is able to make referrals to feasible alternatives;
- Endorsement of the performance of asphalt based alternatives by the Minnesota DOT and other pavement experts. This was important because pavement preservation is a shared goal, for both economic and environmental reasons.

## Implementation in Minnesota and Wisconsin

In the early stages of the project, MPCA and the University of Wisconsin-Extension worked with others to develop:

• Educational materials including guidance to assist pavement owners transition away from the use of coaltar sealcoat. Guidance was prepared considering all alternative technologies (asphalt-based, acrylic, gilsonite, plant oil) but featured asphalt-based as the most proven and price-competitive. • An inventory of providers (retailers, suppliers, contractors) of safer alternatives. Preparing the inventory was a significant effort that involved mining multiple data sets to locate the names and addresses of providers; crafting messages that would be compelling to busy owners of (mostly) small businesses; and following up with them by mail or e-mail. In response, and spurred by awareness of local concerns, 77 contractors and suppliers, or about 25 percent of those thought to be active in Minnesota at the time, signed a pledge not to apply coat-tar sealcoat.

Telephone surveys conducted later in the project resulted in ten completed interviews with contractors and suppliers in this pledged group. That group of ten reported eliminating 93,500 gallons of coal-tar sealcoat use per year. The PAH reduction associated with that amount is difficult to pinpoint, since sealcoat PAH concentrations may vary by batch, by company, or by varying methods of estimating concentrations found in the literature or in product data sheets. MPCA therefore presents reductions estimates for the group of ten respondents as a range, anywhere from 28 to 50 tons per year. Minus outliers, the average coal tar volume per contractor per year for this group was about 5,000 gallons.



Figure 2: Great Lakes Basin research.

In Wisconsin, 311 applicators were contacted: 26 (8 percent) signed a commitment not to apply coal-tar sealcoat. MPCA attributes this response to the fact that many western Wisconsin providers serve the Twin Cities, Duluth, or other border markets; the presence of a ban in Dane County (Madison), Wisconsin; and published findings from sediment PAH research conducted in the Milwaukee area.

As a resource to support pavement owners seeking providers of safer alternatives, MPCA staff produced an on-line map and listing of the applicators and suppliers in the Great Lakes area who signed a certification that they would not to apply coal-tar sealcoat (<u>https://www.pca.state.mn.</u> <u>us/water/find-contractors-applying</u> <u>-safer-sealcoat</u>). The map was later enhanced to include points where restrictions are in place.

 With supporting conditions and resources in place, project partners focused on educating owners and managers of properties that typically require the maintenance of asphalt pavement. The target audience included school districts, shopping center and other commercial property owners and managers, hospital associations, industrial stormwater permittees, and faith-based organizations. Assistance in multiplying the message was accomplished by working with business assistance providers involved with environmental compliance and pollution prevention; the League of Minnesota Cities and city networks and other organizations in the Great Lakes area involved with resource sustainability or environmental protection; stormwater professionals, extension service networks; Parent Teacher Associations, and pavement engineers and associations. Information distribution was accomplished using web pages, e-mail blasts, targeted mail, phone calls, webinars, and press releases and interviews.

In all, MPCA estimates the project partners contacted over 31,000 organizations and individuals with indirect messaging (through facilitators), 7,550 of these with messages generated directly by the partners.

## Implementation in Michigan and Eastward

While outreach efforts in Minnesota and Wisconsin progressed well and produced reasonable results, the Michigan Department of Environmental Quality (DEQ) did not have the resources necessary to replicate the same level of outreach. Instead, Michigan focused its efforts on educating their pollution prevention and sustainability networks and on assessing the possibility of developing contaminated sediment clean-up standards and municipal separate storm sewer system (MS4) permits, which were already present in Minnesota and provide the necessary foundation for regulation.

Because some of the lack of response in Michigan and other Great Lakes states and provinces may have been due to the fact that the outreach was coming from an unfamiliar source, MPCA decided in fall 2013 to package the remainder of its GLRI funds as a grant to an organization outside Minnesota or Wisconsin that could undertake a coordinated outreach effort to pavement owners and sealcoat providers in their geographic area. Freshwater Future, the Michigan water protection network and service provider, was awarded the grant and developed the outreach effort through the rest of 2014.

Freshwater Future is a very different originating organization than MPCA or Wisconsin-Extension: nongovernmental, activist, grassroots, and locally oriented, with a readymade network of Michigan municipalities and community-based watershed and public health protection organizations. In addition to organizations located in Michigan, Freshwater Future's membership also includes networks of organizations outside the state, across the Great Lakes Basin. The core of their work plan was to educate these networks on coal tar PAH issues, recruit partners from among those networks, and with those partners, implement local pollution prevention and regulatory initiatives that would protect community members and their waters.

At MPCA's direction, and with its technical assistance. Freshwater Future first carried out statewide contractor outreach, generating a list of 740 companies and contacts (many of which turned out not to be active), and seeking a pledge to reduce or eliminate coal-tar sealcoat applications. However, there was little response to this effort from Michigan suppliers and contractors. Michigan has nine pledged companies now, and most of those responded to independent local efforts in the Grand Rapids area in western Michigan and the Huron River watershed area in the southeast. Only two in Michigan and four in Ontario responded to Freshwater Future. This led Freshwater Future and MPCA to conclude that additional local awareness and impetus from the user/owner/community end of the supply chain was necessary and might lead eventually to greater response by providers.

Freshwater Future ramped up outreach to local organizations and municipalities to build awareness of coal-tar PAH impacts. Ten organizations around the Great Lakes signed on to assist, and 11 others agreed to educate their stakeholders. Freshwater Future found that whenever they approached a new audience with information on coal-tar PAH hazards, there were questions as to why the purpose of the outreach was not aimed primarily at regulatory bans. It took nuanced explanation to show that bans were difficult to accomplish politically, may not be a tool available in charter to all municipalities, and might only be applicable to public property (not private) or to use (not sales).

Nevertheless, some 40 of the 77 Michigan cities and townships Freshwater Future approached considered ordinances or resolutions banning coal tar use on publicly owned property, sometimes on private property (citywide), or if not bans, then education and promotion of safer alternatives with their citizens. Thirteen municipalities adopted resolutions during the project.

In conjunction with these efforts focused on local government, Freshwater Future approached two types of entities not previously targeted in Minnesota and Wisconsin: one on the user/owner end of the supply chain (168 universities and colleges), and the other on the supply end (205 distributors and local hardware stores in the targeted geographic jurisdictions). Five U.S. and two Canadian universities committed to eliminate or reduce coal tar use, while among retailers, 36 stores considered not selling coal-tar sealcoat; ultimately, nine made that commitment.

In the course of the project, Freshwater Future's outreach energized the Huron River Watershed Council (HRWC) in southeast Michigan on the coal tar issue. HWRC's subsequent education of local governments in the watershed led to four new restrictions on coal tar use, and in a couple of those cases, to limits on the concentrations (either 0.1 percent or 1 percent by weight) of total PAHs present in sealcoat. A group of governments west of Chicago also adopted this approach of limiting total PAH content.

MPCA estimates that 62 organizations outside Minnesota and Wisconsin and on the user or purchaser end of the supply chain made decisions to eliminate or reduce coal-tar sealcoat in response to the project's outreach.

Imposing limits to total PAH content as a different approach to regulation was

spurred by the industry's introduction in 2015 of a non-coal-tar sealcoat based on steam-cracked petroleum residues (CAS 64742-90-1). While not as high as coal tar in total PAHs or the heavier molecular weight PAHs that end up in sediments, this material can contain up to 3 percent (30,000 parts per million) total PAHs. In addition, it has high levels of lighter, more volatile PAHs that are an inhalation concern (such as naphthalene, which was clearly connected to carcinogenic activity in animals by the National Toxicology Program in 2001), or medium-weight PAH molecules which can be an aquatic toxicity concern. By comparison, asphaltbased sealcoats contain 0.005 - 0.1 percent total PAHs.

Back in Minnesota, cities renewed their call for a statewide sales and use ban at the 2013 legislative session. That proposal was enacted in May 2013 and has been in effect since January 2014. The numerous local bans, looming sediment clean-up costs, and the 77 contractor commitments indicating willingness within the industry to use alternative sealcoat products – all played a role in the passage of the statewide ban.

### Conclusion

While reductions in Minnesota documented by and attributable to the project are relatively small (93,500 gallons per year), one should remember that they are only those reported voluntarily by ten responding contractors, resulting in anywhere from 28 to 50 tons of PAH reductions in those ten contractors' service areas. This may suggest that investing in developing local conditions to drive supply chain change has good potential for significant local PAH reductions.

MPCA concludes that, given conducive supporting conditions, voluntary pollution prevention initiatives can produce real pollutant reductions and build the case for wider-scale (e.g., statewide) restrictions on sales and use. If there is little local awareness, education can spur local government and retailer action to eliminate use, particularly where stakeholders are motivated to protect a local natural resource perceived to hold high value.

MPCA's Pollution Prevention Program has committed to maintaining the dynamic page at <u>https://www.pca.</u> <u>state.mn.us/water/</u>

find-contractors-applying-safer-sealcoat. This will involve continuing to post forms for contractors, suppliers, retailers, municipalities, and universities to use to make commitments to eliminate coal-tar sealcoat use, to accept completed forms and to post their commitments on the map and list on that page. The other pages linked there are more static, so their maintenance should also be feasible.

MPCA will also monitor research to assess sediment coal tar PAH levels in areas where prevention projects or bans have been implemented. One such study suggests that reductions may begin to show up in sediment in as little as eight years. Planning and securing resources for a 2024 follow-up at Minnesota sites studied 15 years earlier might demonstrate the value of reduction efforts.

## **Possible Future Efforts**

1. Expand partnerships with hospitals, other care facilities, medical organizations and schools. A number of those that MPCA and partners contacted suggested that health care and educational institutions would be interested in acting on coal-tar sealcoat use - the medical facilities for public health purposes, and the schools to protect their students. MPCA conducted some outreach to hospital and health care associations, but did not invest resources in a full partnership and direct outreach. This could be a productive approach, and yield subsequent support from health facilities and associations as a public health improvement opportunity.

2. Consider developing and offering applicator trainings. MPCA worked with a local provider to develop training for winter maintenance (road salt reduction) providers to address increasing chloride contamination in urban lakes and streams. Much of the early resistance by sealcoat contractors to the use of coal tar alternatives was due to early formulations that did not perform well and have since been improved, and to the use of application methods suited to coal tar but not for the alternatives. Training would help to alleviate contractors' concerns, elevate professionalism, and improve the performance of alternatives.

3. Support the development and acceptance of cost-competitive, zero-PAH sealcoats. As suggested earlier, one response from the sealcoat industry to pressure on coal tar was to introduce another high-PAH alternative in 2015. Technically legal in areas with a coal tar ban, this option nevertheless releases carcinogenic and toxic PAHs that can be harmful to people and animals. In addition, this alternative product smells and reacts to other screening tests exactly like coal tar when applied, making compliance with sealcoat restrictions more difficult and costly to assess.

The MPCA and its partners would prefer an eventual option that is cost competitive and contains zero PAHs. MPCA has encouraged makers of newer, zero-PAH sealants or rejuvenators to work with transportation departments and other experts to test the pavement preservation performance of their products to standards, and to submit their formulations to EPA's Safer Choice program, Green Seal, or other confidential, third-party certifiers to establish them as clearly safer alternatives.

4. Leverage sustainability efforts. There is a growing number of sustainability initiatives within cities, companies, colleges, and community and regional organizations. Developing and acting on information on the use of fertilizers, coal tar sealcoats, or other potentially toxic chemicals in products used by organizations in their business or on their properties would broaden the scope of many organizations' sustainability programs,

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- University of Wisconsin-Extension Solid & Hazardous Waste Education Center (fact sheets) <u>http://shwec.engr.wisc.edu/</u> <u>publications</u>
  - Coal Tar-Based Asphalt Sealcoats A Health and Environmental Hazard
  - Non-Coal Tar applicators
  - Avoiding High Costs from Stormwater Sediment Contaminated by Coal Tar-Based Asphalt Sealcoats

For the past 7 of his 22 years at the Minnesota Pollution Control Agency, **Al Innes** has been leading the agency's initiatives to support safer product chemistries that reduce environmental loadings



of hazards. Prior to this work, Al led several MPCA initiatives using pollution prevention and environmental management systems approaches in permitting, inspections, self- and third-party auditing, and performance-based incentive programs. He has delivered pollution prevention assistance through grants, outreach, and training, both at MPCA and in the non-profit sector previously. You may contact Al Innes (alister.innes@state.mn.us) for further details and lessons learned from the project.

# Frequently Asked Questions:

## Polycyclic Aromatic Hydrocarbons (PAHs)

## **Q)** Aren't polycyclic aromatic hydrocarbons (PAHs) also in some foods, medicines, and shampoos? Are the risks to human health comparable?

A) PAHs are present in some foods, medicines, and shampoos. However, the risks from food-derived sources of PAHs and medicinal uses of coal tar are not comparable since these exposures are a matter of consumer choice and the concentrations of those PAH compounds of concern to human health are not the same. The choice to use a product containing coal tar as a treatment for a medical condition is weighed against the potential benefits of the exposure. Generally, medical treatments are limited to those suffering a disease. Consumption of food containing PAHs (such as charcoal-grilled meat) is also a matter of choice. While food exposures may be the greatest exposure to PAHs for most people, typically carcinogenic PAH concentrations in contaminated sediment and soil are two or more orders of magnitude greater than carcinogenic PAH concentrations in food. Because environmental exposures to PAHs can be significant for some people, homeowners and businesses alike are encouraged to ask retailers and commercial applicators for products that are not coal-tar based.

## Q) How can I tell if a sealcoat product contains coal tar?

A) To determine if the product has a coal-tar base, look for the Chemical Abstracts Service (CAS) number 65996-93-2, 65996-89-6 or 8007-45-2 on the product Material Safety Data Sheet (MSDS). The words "coal tar," "refined coal tar," "refined tar," refined coal-tar pitch," RT-12, tar or other similar terms may be listed on the MSDS or on the product container.

## **Q)** How can I tell if the existing sealant on my driveway contains coal tar?

A) The most accurate way to determine whether sealant contains coal tar is to request analysis of the sealant by a laboratory experienced in testing for PAHs. Two inexpensive field tests may be used to help screen for the presence of coal tar. First, coal-tar-based sealcoats typically have a strong mothball-like odor indicative of the presence of napthalene, whereas, asphalt and acrylic sealcoats do not. Second, the City of Austin, Texas, developed a qualitative screening test to check for the presence of coal tar. The screening test involves collection of pea-sized samples of the top layer of sealcoat, which are combined in a small glass container with a small amount of a paint thinner containing mineral spirits, or aliphatic petroleum distillates. The sample-solvent mixture is gently agitated for up to 30 minutes and evaluated for color change. A translucent amber/yellow color with no significant degradation of the particles is usually indicative of coal-tar sealants. A translucent red/brown color with no significant degradation to the sample is indicative of blended coal tar and asphalt materials. An opaque brown/black color and degradation of the sample material is indicative of asphalt sealant. Steam-cracked petroleum residue sealcoat, a recently introduced product, has been found to have high concentrations of naphthalene. So, new applications of this product will smell similar to coal-tar sealcoat. Steam-cracked petroleum residue

sealcoat will also produce the same result in the solvent test as coal-tar sealcoat. So, the aforementioned screening tests will not discriminate this new product from coal tar sealcoat.

## Q) Is the use of coal-tar-based sealant regulated?

A) Coal-tar sealant is banned in several jurisdictions, including the states of Washington and Minnesota; the counties of Dane, Wisconsin; Montgomery, Prince George's, and Anne Arundel, Maryland and Suffolk, New York; the Cities of Austin and San Antonio, Texas, and Washington, D.C.

## **Q)** What "best practices" should be followed in the application of sealcoat?

A) The following best practices should be considered for maintaining asphalt and applying sealcoat.

- Monitor your pavement's condition and invest in treatments before significant deterioration occurs. When fully cured, sealcoat covered pavement should have uniform coverage and appearance. All aggregate (small stones) should be covered without spaces, gaps or pinholes. Watch for the formation of cracks, gaps in the aggregate, and loss of the aggregate itself. While a sealcoat is a less-expensive, short-term treatment option, it may not be the most protective and cost-effective in the long run for your pavement's condition. If your pavement is older or has already deteriorated, a different treatment or total replacement with asphalt or other materials may be the best option. Consult with paving engineers or contractors about the history of damage and what future threats you need to protect against. Consider also whether your primary concern is the visual appearance versus preservation.
- Avoid the use of products containing coal tar. If sealcoat treatment is determined to be the best option, speak with two or more sealcoat or pavement contractors with experience using safer alternatives to coal tar like petroleum asphalt-based products.
  - Review Product Data Sheets. Work only with providers who can show you complete product data sheets to avoid those that contain coal tar. It is the buyer's responsibility to review the data sheets and speak with providers about key ingredients for pavement protection and manufacturer's recommendations for optimal application.
  - Avoid the use of products that have labels containing the words "coal tar," "refined coal tar," "refined tar," "refined coal tar pitch," "coal tar pitch volatiles," "RT-12," "tar" or similar terms or have safety data sheets, container labels, or technical bulletins listing Chemical Abstracts Service (CAS) numbers 65996–93–2, 65996-89-6, or 8007-45-2. Coal tar/asphalt blends with as low as 10 percent coal tar content may be offered. But even at this reduced level, PAH content is about 100 times higher than other alternative products such as asphalt-based sealcoat.

#### · Consider alternatives to coal tar sealants.

- Petroleum asphalt-emulsion (CAS number 8052-42-4) is the most common non-coal-tar sealcoat on existing asphalt pavement. Asphalt sealcoats contain PAHs, but at as little as 1/1000th the PAH level of coal-tar sealcoat products. Good asphalt sealcoat emulsions are affordable, provide a black appearance, can provide protection for two to four years if properly applied, and can be used in locations that ban coal tar.
- Gilsonite<sup>®</sup> and acrylic and agricultural oil-based sealants contain few or no PAHs, but they tend to be higher-priced and do not have as much of a performance track record as asphalt sealants. Even so, these products should be considered as research and market conditions evolve.
- Repair and prepare the asphalt surface prior to applying sealcoat
  - Cracks in the asphalt one inch wide or less should be cleaned thoroughly and filled with a durable and flexible rubberized sealant that will adhere tightly to the asphalt. Cracks wider than one inch wide should be filled with new asphalt pavement.
  - Clean the asphalt surface of any loose material to ensure effective bonding of the sealcoat
- Follow the manufacturer's recommendations for mixing, application rate, and number of coats of sealant
- Apply sealcoat only under the right weather and temperature conditions
  - Application of asphalt sealcoat should take place only if the air temperature is at least 55° F and rising (typically May through September).
  - Asphalt and other sealcoats should not be applied at night or when rain is expected in less than three hours, in foggy conditions, or when the pavement surface has standing water. Turn off or cover all sprinkler irrigation systems.

#### Q) Can coal-tar sealcoat be removed from pavement?

A) Safe removal of sealcoats and top layers from asphalt pavement is typically done by grinding or shot blasting. Removal is not

recommended for asphalt in poor condition or with significant cracking, since the blasting or grinding process may break the pavement into pieces. Safe removal of sealants or top layers of asphalt should include enclosing the grinding or blasting process, vacuumcollection of the debris (with HEPA filtration of the exhaust), and containing it for disposal. This includes providing the employees doing the removal with proper hearing, respiratory, and skin protection. Even with high-efficiency containment and collection, these protective measures are a necessary precaution given the health risks of working with coal tar and asphalt dust.

Property owners should ensure that their contractor is properly licensed and bonded and will use proper removal and disposal methods. Contacting neighboring property owners in advance is also encouraged so they may close windows and air intakes and take additional precautions to reduce exposure.

Coal-tar sealcoat and other removal debris should be disposed of properly. No matter the location, pavement owners and contractors must be aware of, and comply with, applicable local, state, or provincial requirements for management and disposal. For example, in Minnesota, coal-tar sealcoat removal debris should be disposed of in a solid waste landfill, with the approval of the landfill operator.

Removal costs around the U.S. have ranged from \$0.60 per square foot for larger surfaces to \$1.25 per square foot for small areas. However, experience is limited so there may be significant variation.

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## The NALMS Board of Directors is soliciting letters of interest from individuals who would be interested in serving as Editor for the society's peer-reviewed publication, *Lake and Reservoir Management*.

Interested individuals should have experience with the journal as an author, reviewer or associate editor, and have familiarity with the ScholarOne manuscript management system and with the wide range of topics that come under the umbrella of lake and reservoir management. Candidates for this position should have:

- Tact and diplomacy
- Excellent project management skills, attention to detail and demanding review timelines
- Excellent English writing and editing skills
- Lake or reservoir management experience

Interested individuals should send a letter of interest to Frank Wilhelm, NALMS President, expressing their interest in the position and briefly outlining their qualifications. Letters will be reviewed by the Publications Committee and further information will be requested if necessary. Materials will then be advanced to the *Lake and Reservoir Management* Editorial Board and the NALMS Board of Directors for further review and approval.

LAKE AND RESERVOIR

## North American Lake Management Society Achievement Awards Call for Nominations

"You may delay, but time will not." –Benjamin Franklin

Start preparing your North American Lake Management Society Award nominations! Do not delay to put into words the actions and outcomes of an individual, organization, program, or corporation having notable impact in lake and reservoir management.

#### Award nominations are due August 15, 2017

## NALMS AWARDS AND NOMINATION INFORMATION

#### Leadership and Service Awards

Nominations should detail how individuals or teams demonstrate leadership, service, and practice of lake and reservoir management. Selection criteria for Leadership and Service Awards include level of involvement, measurable impact, sustainability of action(s), and innovation in lake and reservoir management.

#### Volunteer

Nomination should address the significance of an individual or team's volunteer efforts devoted to lake and reservoir management. Professionals (i.e., anyone paid to work on the project) are ineligible.

## **Community Education and Outreach**

Nomination should address an individual or team's design, facilitation, or performance of exceptional education and outreach activity facilitating community understanding and appreciation for lake and reservoir management.

#### **Appreciation Awards**

Nominations should address how individuals or teams contribute among a variety of lake and reservoir management areas. Selection criteria for Appreciation Awards include level of involvement, measurable impact, sustainability of action(s), and innovation in lake and reservoir management.

- Secchi Disk Award Nomination should articulate how an individual member is considered to have contributed the most to the achievement of NALMS' goals. Award recipient must be a NALMS member.
- Jim Flynn Award Nomination should recognize how an organizational member is considered to have contributed the most to NALMS' goal. Recipient must be a NALMS corporate member.
- Friends of NALMS Award Nomination should detail major contributions of an individual or team to NALMS. Contributions extend beyond monetary donations.
- Lake Management Success Stories Nomination should demonstrate an individual or team improvement in lake/reservoir condition or watershed management in a cost-effective manner.
- Advancements in Lake Management Technologies Nomination should emphasize process of discovering, developing, or refining innovative methods, technologies, or processes targeting safer, cost-effective, and more effective lake/reservoir/watershed management. Individuals or teams completing research projects within the category that contribute to the science of lake management are eligible. Nominations should include supportive documentation (e.g., journal articles).

#### **Nomination Eligibility**

Secchi Disk Award and Jim Flynn Award nominations must be NALMS members. Current NALMS board members and members of the NALMS Awards Committee are not eligible for nomination.

#### Nominations

Any individual or entity may submit nominations. Nominations must include the following items:

- 1. Nominator contact information (name, title, mailing address, telephone number, and email)
- 2. Nominee contact information (name, title, organization/affiliation, mailing address, telephone number, and email)
- 3. NALMS Award for nomination
- 4. Brief and complete description of achievement(s) to be recognized and statement of how nominee's efforts meet specific award criteria.
- 5. Submit nomination by email to Dana Stephens, NALMS Award Liaison.
- 6. Please contact Dana with any questions or concerns.

### NALMS Award Liaison : Dana Stephens • 100 College Blvd. • Niceville, FL 32578 • Phone: 850-729-6469 • Email: stephed@nwfsc.edu

#### Thank you for your nomination!



Andrew L. Labaj and Branaavan Sivarajah

## Paleolimnology: A Powerful Tool to Understand the Past

atural resource extraction is an integral part of the Canadian economy, adding billions of dollars in revenue annually. Large-scale mining operations for metals began as early as the 19th century in Canada. However, environmental monitoring programs intended to assess the longterm ecological consequences of mining activities were only implemented well into the 20<sup>th</sup> century, often long after environmental impacts - such as acidification and metal pollution - had already occurred. In order to understand the long-term impacts of these industries on the environment, it is necessary to "look back" through time, and understand the environmental conditions that existed before industrial activities began, and the types of changes that occurred as a result of industrialization. A powerful method to accomplish this is through the use of paleolimnology, a discipline of limnology that reconstructs past environmental conditions using the information contained in lake sediments.

Lake sediments act as natural archives for their surrounding environment, preserving material from both inside and outside the lake. Information contained within the sediment record can be used to answer questions about environmental change both natural and anthropogenic - through time (Smol 2008). Paleolimnological studies have been used to answer a number of applied environmental questions, however, some of the most striking examples of its usefulness relate to the assessment of mining impacts. Here, we highlight two examples where paleolimnology was successfully used to track the long-term impacts of

# Student Corner

Looking back to manage the present and predict the future: Using lake sediments to assess the long-term ecological consequences of mining in Canada

regional mining industries on aquatic environments.

## A History of Acidification and Metal Contamination in Sudbury, Ontario

Sudbury, Ontario, has a long history of nickel and copper mining, with the discovery of the nickel deposits occurring in the 1880s. The initial ore roasting beds as well as early smelters released huge quantities of acid rain-causing sulfur dioxide  $(SO_2)$  into the atmosphere, which reached an area of 17,000 km<sup>2</sup> (equivalent to nearly 90 percent of the size of Lake Ontario) around the city (Keller et al. 2007). The large amount of acid rain in the region caused widespread damage to the landscape, killing off vegetation (resulting in a desolate landscape colloquially known as the "moonscape") and acidifying thousands of surrounding lakes. The lakes closest to Sudbury also experienced contamination with nickel and copper particles, which are heavy and do not travel as far as SO<sub>2</sub> in the atmosphere. The combination of these stressors resulted in the loss of many fish species and radically altered food webs in lakes, which had been valued for their recreational use. Although the initial reports of lake acidification were released in the 1960s, the long-term history of damage to the lakes remained unknown - the roasters and smelters had been operating for more than 30 years before the pH scale had even been invented!

Paleolimnology provided a way to determine background conditions and to track the damage that had been done over time. The initial research examined diatoms and chrysophytes – two groups of algae that are sensitive to changes in lake water pH and metal concentrations and leave identifiable fossils in the sediments. Using statistical transfer functions, the

species composition and abundance of diatom and chrysophyte remains was used to reconstruct past pH levels. These methods work by establishing the optimal growth conditions of the species found in the sediments, and using their abundance to calculate the likely pH. A combination of sediment geochemistry and diatom- and chrysophyte-based transfer functions were also used to establish past metal concentrations. The early studies provided the much-needed pre-industrial environmental data and tracked the dramatic shifts in aquatic organisms in response to acidification and metal contamination through time. These studies found that many of the lakes surrounding Sudbury began acidifying and accumulating metals soon after the initial smelting operations commenced in the late 19th century. Furthermore, the pH at the most impacted lakes declined by as much as 2 pH units. Once the extent of the problem had been established, a number of emission reduction methods were put in place, including the installation of exhaust scrubbers to remove SO<sub>2</sub> from the smelter exhaust, as well as governmentlegislated emission controls that became progressively more stringent. Ongoing water quality monitoring programs indicate that these measures were effective, and many lakes in the Sudbury region have returned or are returning to their pre-industrial pH (Keller et al. 2007).

Although the pH of many Sudbury lakes has returned to pre-industrial levels, the biological recovery in these lakes continues to lag behind the chemical recovery (Keller et al. 2007). Just as it was useful for tracking the onset and extent of contamination, paleolimnology is equally well-suited for tracking chemical and biological recovery of the acidified and metal-contaminated

lakes. Recent paleolimnological analysis of several acidified Sudbury lakes has revealed that the Cladocera (a widespread mid-trophic level zooplankton group) and diatoms continue to remain altered from pre-acidification assemblages (Labaj et al. 2015; Sivarajah et al., accepted). The sedimentary cladoceran assemblages in lakes closest to the smelters (Daisy, Middle, and Clearwater) experienced the greatest species shifts as these lakes were exposed to the added stress of nickel and copper contamination (Figure 1). The most recent cladoceran assemblages in these lakes continue to differ from their pre-impact assemblages, likely due to ongoing copper and nickel contamination in sediments and the water column (Labaj et al. 2014; Labaj et al. 2015).

An experimental neutralization and fertilization was conducted in Middle Lake at the peak of acidification, resulting in the significant increase of algal primary production, however similar to the other Sudbury lakes, complete recovery has not occurred in the cladoceran species (Labaj et al. 2014). Copper and nickel contamination are likely inhibiting recovery in many of the lakes surrounding Sudbury (Labaj et al. 2015). Not surprisingly, George and Lumsden lakes (Figure 2) in Killarney Provincial Park - located ~60 km southwest of Sudbury - acidified, but experienced reduced metal contamination compared to the lakes located closer to the smelters in Sudbury. The acidification in these lakes was faithfully tracked by the sedimentary diatom assemblage changes (Sivarajah et al., accepted). Nonetheless, despite pH improvements in the most recent decades, the cladoceran and diatom assemblages of these lakes differ substantially from their pre-acidification states.

In the region as a whole, the recent paleolimnological studies have revealed a new stressor now impacting the lakes: climate warming. Although new industrial contamination has largely been reduced in the Sudbury area, regional air temperatures have increased in recent decades (Figure 3), and the impacts of regional warming are altering the lakes and their biological communities (Labaj et al. 2015; Sivarajah et al. 2016; Sivarajah et al., *accepted*). As climate change continues to impact these lakes, their biological communities will likely never again resemble those of the past.

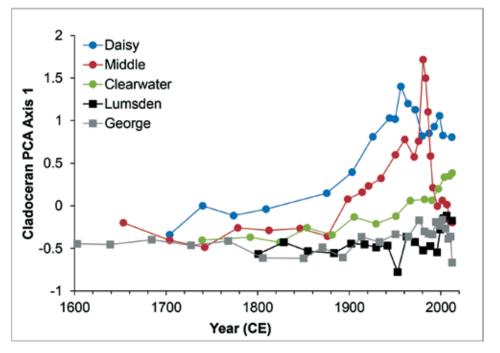


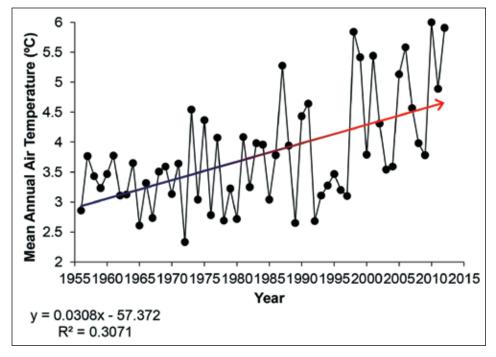
Figure 1. Cladoceran data for each lake (summarized using principal components analysis (PCA)) over time. PCA axis 1, displayed here, accounts for 48.7 percent of the variation in cladoceran assemblages. Circular markers represent the three lakes located closest to Sudbury, while square markers represent the two lakes located approximately 60 km from the city.



Figure 2. View of Lumsden Lake and surrounding landscape, Killarney Provincial Park.

## Gold Mining and Arsenic Contamination in Yellowknife, Northwest Territories

Recently, paleolimnology has been applied in Yellowknife, Northwest Territories, to assess the legacy effects of gold mining on subarctic lakes. During the early 20<sup>th</sup> century, gold deposits were discovered within the ore bodies of arsenopyrite in the Yellowknife greenstone belt. This discovery resulted in the establishment of gold mining operations in the area, and spurred major



*Figure 3. Mean annual air temperature recorded at Sudbury Airport (climate station ID: 71730).* Data from Environment Canada. Trend is indicated by colored linear regression line ( $r^2 = 0.31$ ).

growth of the City of Yellowknife. Giant Mine operated between 1948 and 2004, producing ~220 tons of gold along with  $\sim$ 20,000 tons of toxic arsenic trioxide dust as a by-product, that was released to the environment. The half-century of mining activity at Giant Mine led to the arsenic contamination of many surrounding lakes in Yellowknife. Presently, arsenic levels in many lakes within a 15-km radius of Giant Mine are well above the maximum allowable concentrations for the protection of aquatic life and drinking water (5 and 10  $\mu$ g/L, respectively) (Houben et al. 2016), posing a potential threat to human health, as many of the lakes around the City of Yellowknife are used for recreational purposes. As with the lakes in Sudbury, the lack of longterm monitoring data required the use of indirect methods such as paleolimnology to assess the long-term ecological consequences of arsenic contamination of lakes around Yellowknife.

In one highly impacted lake within the lease boundary of Giant Mine, paleolimnological analyses revealed increases in several pollutants linked to arsenopyrite processing, including arsenic, mercury, antimony, lead, and iron, as operations at Giant Mine progressed. At the same time as these pollutants were increasing, the biological communities of the lake were also changing, including shifts in the diatom species, and a complete elimination of the Cladocera (Thienpont et al. 2016). The striking similarity in the timing of chemical and biological changes clearly indicates that lake sediments are faithfully recording the increases in aquatic contaminant concentrations and the biological shifts occurring as a result of increased pollutants in the lake from Giant Mine operations. The present results have shown that paleolimnology can reliably track the onset and effects of regional gold mining, and have led to ongoing studies in other lakes surrounding Yellowknife, tracking the long-term ecological consequences of arsenic contamination in the region as a whole. The work in this region has provided an important opportunity to combine paleolimnology and ecotoxicology to better understand the impacts of mining, arsenic contamination, climate warming and local land use changes in subarctic lakes.

## Conclusions

Paleolimnology provides the much needed long-term perspective on environmental change that is often not available otherwise. It provides powerful tools to qualitatively and quantitatively gauge the human "footprint" on the environment, a vital first step in providing appropriate context to our past and present environmental issues. In many cases, paleolimnological studies have provided the "smoking gun" necessary to introduce environmental policy and lead to positive change.

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(Student Corner, continued on p. 28...)

# Bill Jones Literature Search

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## Lakes Appreciation Month 2017

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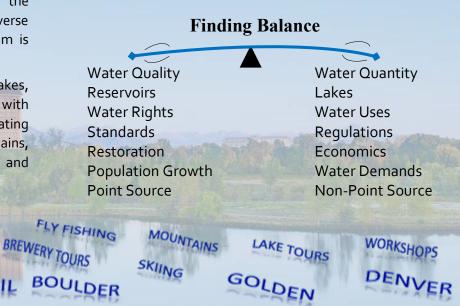
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