Polycyclic Aromatic Hydrocarbons
And Coal Tar Sealants

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Why Pavement Sealcoats?

Sprayed or brushed onto asphalt pavement
• Improve appearance (black, shiny coating)
• Done to increase pavement longevity (??)

Asphalt or Coal-Tar based sealcoats
• similar in appearance, however...
• Polycyclic Aromatic Hydrocarbons concentrations ~1000x higher in Coal Tar-based sealants

Polycyclic aromatic hydrocarbons are group of organic compounds (>200) containing only carbon and hydrogen atoms arranged around two or more aromatic (benzene - C₆H₆) rings.
Where do PAHs come from?

- Naturally occur in oil, coal, tar.
- Form during incomplete combustion of carbon-based materials or fossil fuels (petroleum, coal, wood, diesel, gasoline).
- There are two distinct categories of PAHs.
  - Petrogenic
  - Pyrogenic
What are the differences between the two categories of PAHs?

**Petrogenic:**
- Formed at low temperatures, lower molecular weight
- Formed over geologic time scale
- Found in fossil fuels
  - Coal, crude, refined petroleum products, lubricants, asphalt, etc.

**Pyrogenic**
- Formed at high temperatures, higher molecular weight
- Natural = forest & grass fires, volcanic eruption, etc.
- Manmade = engine exhaust, coal fired power plant emissions, creosote, *coal tar sealants*, etc.
Why Should We Care About PAHs?

* Many PAHs are toxic, carcinogenic, or mutagenic to aquatic life and humans.
* These environmental effects can be additive.
* Prenatal exposure to PAHs linked to later developmental problems.
* 17 PAHs have been identified as being of greatest concern with regard to potential exposure and adverse health effects on humans (Agency for Toxic Substances and Disease Registry).
* 16 PAHs are on USEPA’s priority pollutant list.
* Costly to remediate.
**What are the urban sources of PAHs?**

All concentrations in mg/kg, sums of 12 PAHs (means of as many as 6 studies)

<table>
<thead>
<tr>
<th>Source</th>
<th>Concentration</th>
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<tbody>
<tr>
<td>Fresh asphalt</td>
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<tr>
<td>Weathered asphalt</td>
<td>3</td>
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<td>Fresh motor oil</td>
<td>4</td>
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<td>Brake particles</td>
<td>16</td>
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<td>Road/tunnel dust</td>
<td>24</td>
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<tr>
<td>Tire particles</td>
<td>86</td>
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<tr>
<td>Diesel engine</td>
<td>102</td>
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<tr>
<td>Gasoline engine</td>
<td>370</td>
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<tr>
<td>Used motor oil</td>
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**Pavement Sealcoat**

Asphalt-based ~ 50
Coal-tar-based ~ 70,000

*from B. Mahler SETAC presentation 2014*
Once applied, how do PAHs in Coal-tar sealants move through the environment?

Source: USGS - Mahler et al. 2012
Example of pavement sealcoat weathering

- Abraded by vehicle traffic, tires, snow plows, etc.
- Weathered particles are carried and dispersed by the wind or are washed into storm drains by rain or snow melt, ultimately reaching waterways.
USGS study highlights coal-tar sealant use and human health risks.

PAH concentrations 25 time higher indoors where coal-tar sealants are used outdoors.

PAH-contaminated dust on coal-tar-sealcoated pavement (right) is tracked indoors. Concentrations shown are median values for the sum of the 16 Priority Pollutant PAHs, in units of milligrams per kilogram, in house dust and parking lot dust.
Exposure to Coal-Tar Sealants pose risk of developing cancer.

The excess cancer risk for people living adjacent to coal-tar sealcoated pavement (1.1 cancer incidences for every 10,000 individuals exposed) was 38 times higher, on average (central tendency), than for people living adjacent to unsealed pavement.
Cells exposed to the coal-tar-sealcoat runoff have damaged DNA and reduced capacity to perform repair.

- The combination of DNA damage and impaired repair capacity intensifies the potential for long-term damage to cell health.
- DNA damage has many possible consequences, including aging, cell death, and mutations.
- Mutations can affect the function of genes and can potentially lead to cancer.
So.... are PAHs of concern for the Milwaukee Region and SE Wisconsin?
## Sediment Results

<table>
<thead>
<tr>
<th>Sites (least to most urban, top to bottom)</th>
<th>Antioxidants</th>
<th>Dyes/pigments</th>
<th>Fire retardants</th>
<th>Polycyclic aromatic hydrocarbons</th>
<th>Plasticizers</th>
<th>Fuels</th>
<th>Solvents</th>
<th>Herbicides</th>
<th>Insecticides</th>
<th>Antimicrobial disinfectants</th>
<th>Detergent metabolites</th>
<th>Flavors and fragrances</th>
<th>Human drugs, nonprescription</th>
<th>Sterols</th>
<th>Miscellaneous</th>
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### EXPLANATION

**Maximum concentration, in micrograms per kilogram**
- <100
- 100–999
- 1,000–9,999
- ≥1,000

**Detection frequency, in percent**
- 0
- 20–39
- 40–59
- 60–79
- 80–100
PAH’s potential for toxicity in sediments
A Second MMSD and USGS Study

Identify Sources and Toxicity of PAHs in Milwaukee Area Streams

* Collect ~40 samples from streambeds and determine source areas.

* Identify source(s) of PAHs to streams
  * Contributions from various sources, use multiple lines of evidence to identify greatest sources (i.e. coal-tar based sealants).

* Relate sediment PAH concentrations to toxicity to aquatic organisms (bioassays).
2013-2015 Study Overview

Streambed sediment at 40 stream sites
- Targeted fine, depositional sediment, 0-4cm depth
- Sieved to remove particles > 2mm

Parking lot dust at 6 sites using vacuum
- Sealed pavement (3)
- Unsealed pavement (2)
- Concrete (1)

QA/QC: 4 samples
- 2 Spikes, 2 duplicates
Multiple lines of evidence approach:

1. Land Use Analysis

2. Elimination of some sources based on stream concentrations (Mass Fraction Analysis)

3. Summation of parent to alkyl PAHs

4. Summation of high molecular weight to low molecular weight PAHs

5. Diagnostic compound ratios and double ratios\(^a-d\)

6. Proportional concentration source profiles\(^c,d\)

7. EPA’s Chemical Mass Balance (CMB) model\(^c,e,f\)

8. Principal Component Analysis

\(^{a, Yunker et al. 2002; b, Ahrens and Depree 2010; c, Crane et al. 2014; d, Van Metre et al. 2009; e, Van Metre and Mahler 2010; f, Li et al. 2003}\)
Examples of sampling locations:
Lincoln Cr at 76th St
PAH Concentrations

Coal tar-sealed lot (old DMV)

Unsealed Concrete lot

Lincoln Creek at 76th

20,774 mg/kg
Lot dust

17.3 mg/kg
Parking lot dust

208 mg/kg
Stream sediment

Preliminary Information-Subject to Revision. Not for Citation or Distribution
Double ratio plot

(Source ratios from Yunker et al. 2002; CT dust from Van Meter et al. 2008; Asphalt dust from Mahler et al. 2004)
Milwaukee stream sed.

Milwaukee parking lots

(Source ratios from Yunker et al. 2002; CT dust from Van Meter et al. 2008; Asphalt dust from Mahler et al. 2004)
Source Contributions of PAHs to Milwaukee Streambed Sediments

Estimated using the US EPA Contaminant Mass Balance Model
Toxicity to aquatic organisms
• PAH concentrations exceed Sediment Quality Guidelines at many sites
  • Sites exceeding Threshold Effect Concentration: 37/40
  • Sites exceeding Probable Effect Concentration: 13/37

• Bioassays demonstrate increasing PAH concentrations were associated with decreasing *Hyalella* survival

Source apportionment
• 8 methods indicate that coal tar-based sealcoat is the primary source of PAHs to Milwaukee streams.
  • EPA CMB Model: *On average 77% of PAHs are from coal tar sealcoat dust.*
What are the economic impacts of coal-tar sealant derived PAHs?

- Sediment contamination with PAHs from coal-tar sealants are costly to remove because special handling and disposal methods are required.

- Estimates for sediment disposal costs in Minneapolis-St Paul area are up to $1 billion if 10% of stormwater detentions facilities have PAH concentrations above the Minnesota’s human-health risk-base Soil Reference Value.

- Minnesota banned the uses of coal-tar sealants to eliminate the human health risks and costs associated with removal of sediments contaminated with coal-tar sealants.
Alternatives for Management of Coal-tar Sealants

Hierarchy of Alternatives

- Outright Ban
- Public Restricted Use
- Government Agency Bans
- Institutional Use Bans
- Voluntary Supplier/Contractor Agreements
- Voluntary Market Place Controls
- Public Education / Awareness
Coal-Tar Sealant Bans are Effective!  
PAH Source Reductions  

Austin, Tx  
Source: Van Metre et al. 2014
Successful Local Bans

- **Cities**
  - Austin, Bee Cave, TX
  - Des Plaines, Winnetka, and South Barrington, IL
  - Springfield, MO
  - Greenfield, SC
  - Winfield, KS
  - Ann Arbor, MI

- **Counties**
  - Dane County, WI
  - Montgomery County, MD
  - Prince Georges County, MD
  - Suffolk County, NY
  - Edwards Aquifer, Comal and Hays Counties, TX
  - Multiple Counties in Minnesota before statewide ban

- **Districts**
  - Washington D.C.
80.08 REGULATION OF THE APPLICATION AND SALE OF SEALCOAT PRODUCTS CONTAINING COAL TAR.

(1) No person shall apply any sealcoat product within Dane County that is labeled as containing coal tar.

(2) No person shall sell, offer to sell, or display for sale any sealcoat product within Dane County that is labeled as containing coal tar.

(3) Any person who sells pavement sealcoat products shall prominently display, in the area where such pavement sealcoat products are sold, a notice that contains the following language: “The application of coal tar sealcoat products on driveways, parking lots and all other paved surfaces in Dane County is prohibited by section 80.08 of the Dane County Code of Ordinances.

Coal tar is a significant source of polycyclic aromatic hydrocarbons (PAHs), a group of organic chemicals that can be carried by stormwater and other runoff into Dane County’s lakes and streams. PAHs are an environmental concern because they are toxic to aquatic life.”

Why should we take action on coal-tar sealants now?

- Excessive PAHs in coal-tar sealants are known to be detrimental to the environment and human health.
- Most studies find coal-tar sealants are a primary source of PAHs in areas where used, including the MILWAUKEE REGION!
- Arguments for policy action can be made on multiple grounds:
  - Human health
  - Environmental health
  - Economics
- Coal-tar sealants are a CONTROLLABLE source with REASONABLE alternatives available.
Reasonable Alternatives Available

Prices advertised on internet 10/12/2015

- Coal-tar Based
- Asphalt Emulsions
- Acrylic

Cost Comparison
A Regional or Statewide Coal-Tar Sealant Policy would do the following:

1. Protect human health.
   - By reducing exposure to potential carcinogens.

2. Protect aquatic ecosystems from harm.
   - By reducing lethal and sublethal effects.

3. Reduce municipal costs for hazardous/contaminated sediment disposal.

4. Determine if a regional or statewide phase-out or ban on coal-tar sealants is necessary.