# Environmental Issues Associated with the Use of Coal Tar-based Sealants: A Minnesota Perspective

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# Recent Newspaper Headlines

- New doubts cast on safety of common driveway sealant. *Extremely high levels of toxic chemical in coal tar found in booming suburb* (Jan. 16, 2011 Chicago Tribune, http://www.chicagotribune.com/health/ct-met-toxic-coal-tar-sealant-20110115,0,2601922.story?page=1)

- American urban lake pollution traced to parking lot seal coat (Dec. 5, 2010, McClatchy Washington Bureau, http://www.mcclatchydc.com/2010/12/05/v-print/104742/american-urban-lake-pollution.html)

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# Overview

- How coal tar-based sealcoat products contribute polycyclic aromatic hydrocarbons (PAHs) to urban waterways and why this is of concern;

- How the Minnesota Pollution Control Agency (MPCA) and MN State Legislature are addressing this issue; and

- What the preliminary results of a stormwater pond sediment study of the Minneapolis-St. Paul, MN metropolitan area reveal about the distribution of PAHs, the effects of land use practices, and likely sources of PAHs to the study sites.
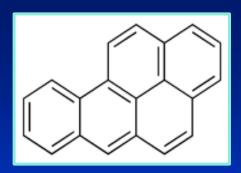


LeVander Pond (SWP09-02) in South St. Paul, MN

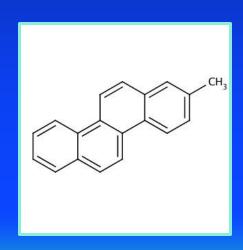**Minnesota Pollution Control Agency**

# Properties of PAHs

- Are persistent organic pollutants and include hundreds of individual compounds. These compounds usually occur as mixtures with a range of physical/chemical characteristics.

- PAHs are found everywhere.

- Parent PAHs consist of only benzene rings fused together.

- Alkylated PAHs have alkyl substitutions added to the fused ring.



Benzo[a]pyrene (parent PAH)



2-methyl chrysene (alkylated PAH)

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# Why Are We Concerned About PAHs?

- Seven PAHs are classified as probable human carcinogens (Group B2);

- Other PAHs are known for their carcinogenic, mutagenic, and teratogenic properties;

- PAHs can cause skin tumors and other effects in fish; and

- Most bottom-dwelling aquatic invertebrates can't metabolize PAHs and are susceptible to a number of adverse effects.

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Mouth tumor in brown bullhead.

# Problem: Stormwater ponds in the Twin Cities are filling up with sediment, some of which are contaminated with PAHs.





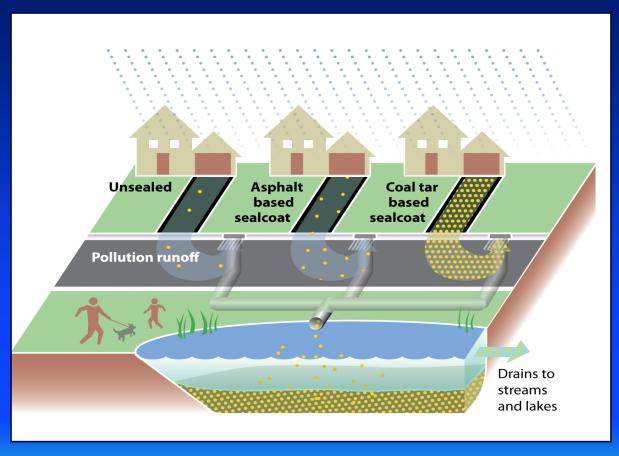Nonfunctioning stormwater ponds in Woodbury, MN

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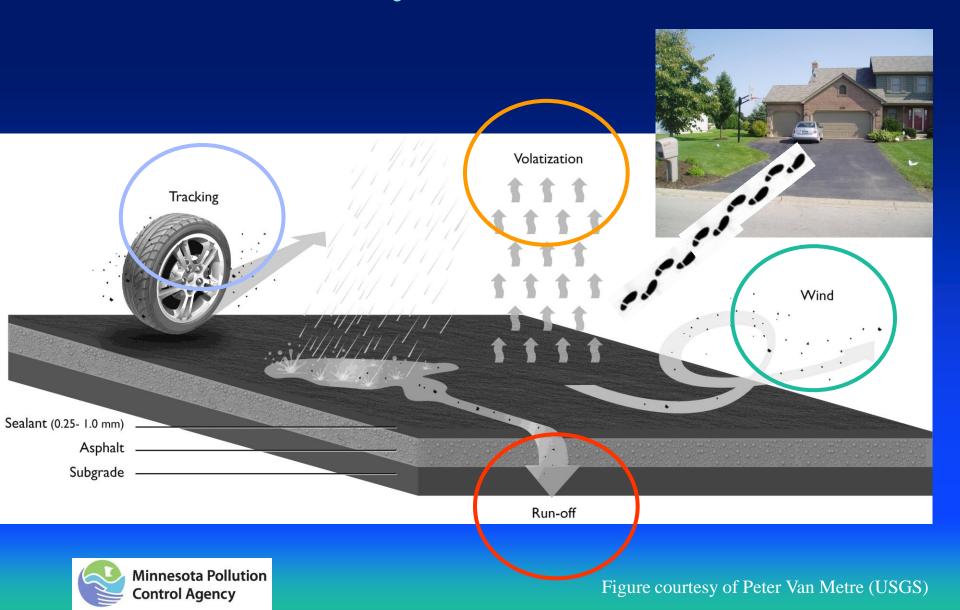
# Coal Tar-based Sealcoats have Emerged as a Source of PAHs to Stormwater Ponds



Unsealed

Asphalt based sealcoat

Coal tar based sealcoat

Pollution runoff

Drains to streams and lakes

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MPCA graphic by Scott Andre

# PAH Pathways from Sealed Areas



Tracking

Volatization

Wind

Sealant (0.25- 1.0 mm)

Asphalt

Subgrade

Run-off

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Figure courtesy of Peter Van Metre (USGS)
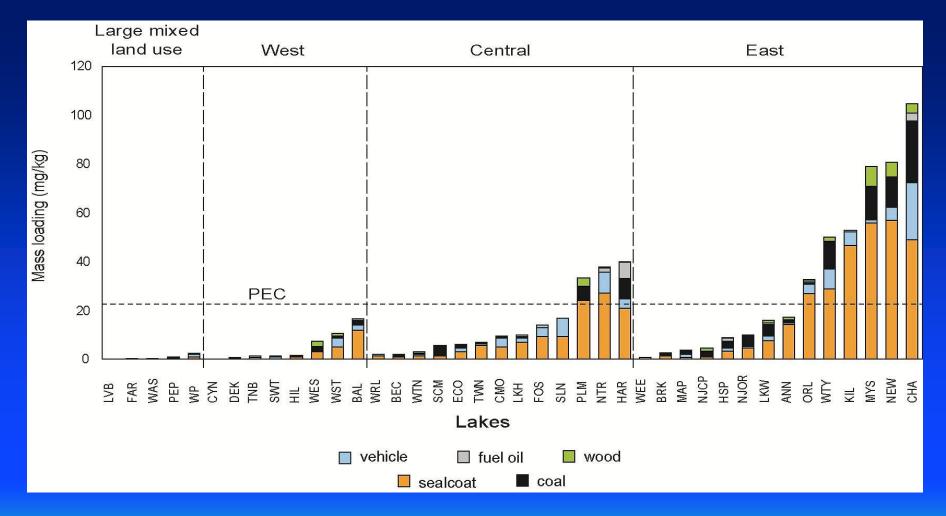
# PAH Sources to 40 U.S. Lakes (Van Metre and Mahler, 2010)



Coal tar sealcoat contributes about one-half of PAHs in sediment, followed by vehicle-related sources, and coal combustion.
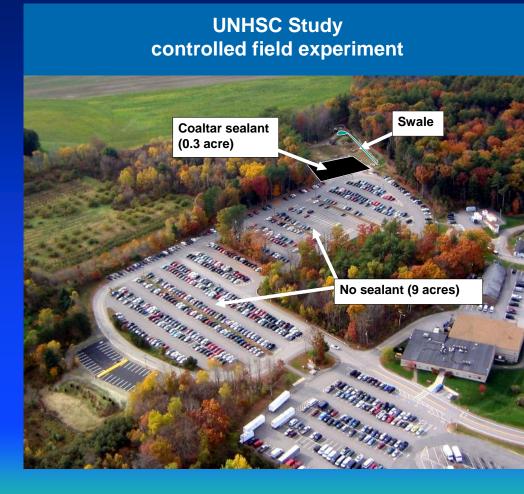
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# University of New Hampshire (UNH) Study of PAHs in Stormwater Runoff from Sealcoated Pavements

- Watts *et al*. (2010) study published Nov. 2010 in *Environmental Science & Technology*.

- Study measured a 2-year release of PAHs in parking lot runoff.

- Determined coal tar-based parking lot sealcoat was a significant source of PAHs in stormwater runoff, and the presence of coal tar sealant increased the mass of PAHs released in runoff by over an order of magnitude.
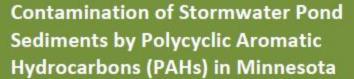
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# UNH Study (continued)

- The study also found that even partial coverage of a drainage area by coal tar sealant resulted in measurable increases in PAH concentrations in sediment.



**UNHSC Study controlled field experiment**

Coaltar sealant (0.3 acre)

Swale

No sealant (9 acres)

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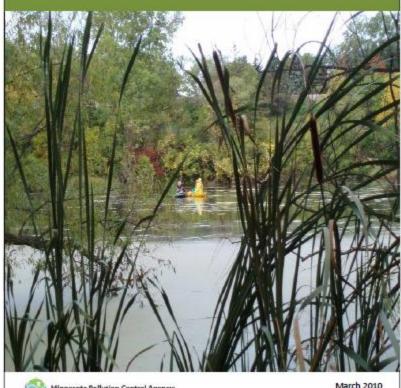
PAH White Paper available at: http://www.pca.state.mn.us/publications/tdr-g1-07.pdf



**Contamination of Stormwater Pond Sediments by Polycyclic Aromatic Hydrocarbons (PAHs) in Minnesota**
The Role of Coal Tar-based Sealcoat Products as a Source of PAHs

Minnesota Pollution Control Agency

March 2010

Minnesota Pollution Control Agency

# MPCA Approach

- The MPCA is using education and outreach to increase awareness of the PAH contamination problem in stormwater pond sediments;

- Agency staff recognize there are several sources of PAHs in urban environments that can contribute to the load of PAHs in stormwater ponds;

- In the MPCA's education efforts, the selection of sealcoat products is presented as a P2 (pollution prevention) decision that property owners and local units of government need to make.

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# Legislative Response to Issue

- The 2009 Minnesota Legislature provided the MPCA with funding to study this issue on July 1, 2009.

- Part of the funding related to developing best management practices. This included evaluating sampling and screening methods for good, cost-effective techniques through a study of stormwater pond sediments in different land use categories (residential, commercial, and industrial areas) for PAHs and other contaminants of potential concern.

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# Study Objectives

- Determine the influence of urban watershed land uses on PAHs (and other contaminants) in stormwater pond sediments;

- Determine the applicability of an analytical screening technique (laser induced fluorescence—LIF), as well as simple chemical modeling, for conducting sediment assessments of stormwater ponds;



Tahoe Rd. North Pond (SWP09-11) in Woodbury,MN. Photo by Tim Nelson (Minnesota Public Radio)

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# Study Objectives

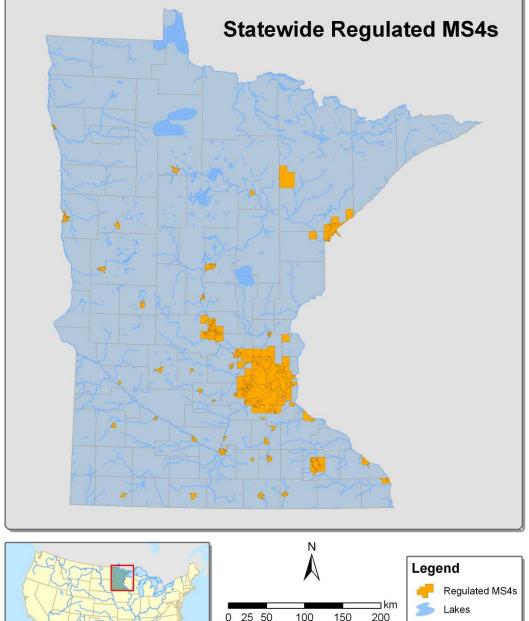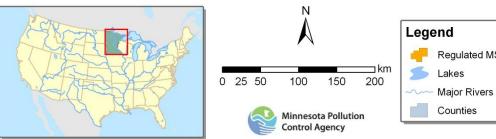- Determine whether some emerging contaminants are present at detectable concentrations;

- Compare data to MPCA soil reference values (SRVs) and sediment quality targets (SQTs);

- Determine contaminants of concern; and

- Modify, if needed, sampling and dredge disposal recommendations for stormwater permittees.

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ConAgra Foods Pond (SWP09-03) in Lakeville, MN.

# Municipal Separate Storm Sewer System (MS4) Areas Regulated by the MPCA



**Statewide Regulated MS4s**

**Legend**
- Regulated MS4s
- Lakes
- Major Rivers
- Counties

0 25 50 100 150 200 km

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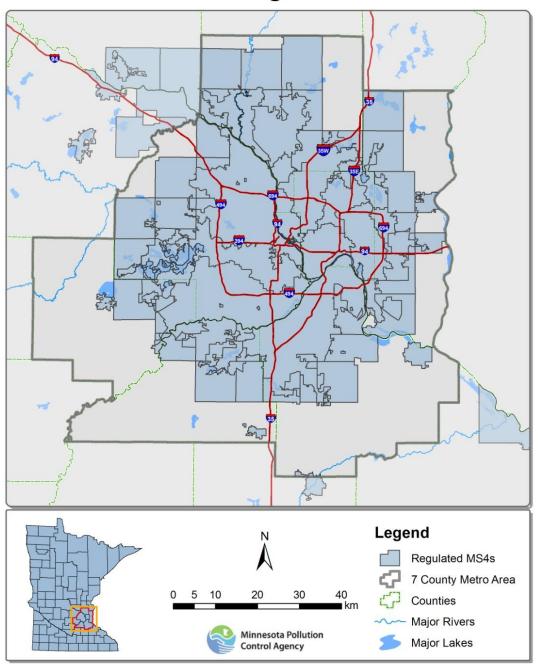
# Metro MS4 Areas Regulated by the MPCA



**Metro Area Regulated MS4s**

Legend
- Regulated MS4s
- 7 County Metro Area
- Counties
- Major Rivers
- Major Lakes

0  5  10    20    30    40 km

N

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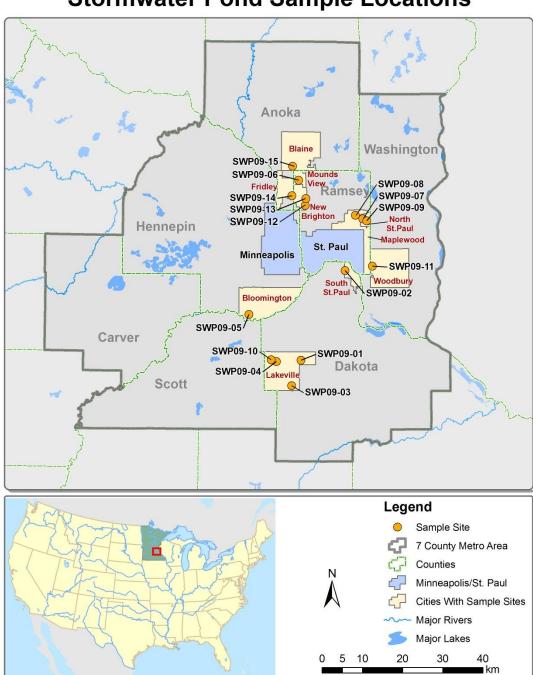
Residential Land Use



Commercial (up); Industrial (down)



# Stormwater Pond Sample Locations



Anoka

Washington

Blaine

SWP09-15

SWP09-06

Mounds View

Fridley

SWP09-08

SWP09-07

Ramsey

SWP09-14

SWP09-13

New Brighton

SWP09-09

Hennepin

SWP09-12

North St.Paul

Maplewood

Minneapolis

St. Paul

SWP09-11

South St.Paul

Woodbury

SWP09-02

Bloomington

SWP09-05

Carver

SWP09-10

SWP09-01

SWP09-04

Dakota

Lakeville

Scott

SWP09-03

## Legend

- 🟠 Sample Site
- 7 County Metro Area
- Counties
- Minneapolis/St. Paul
- Cities With Sample Sites
- Major Rivers
- Major Lakes

N

0  5  10   20     30     40
km

# Field Sampling During October 2009



Photo by Anna Kerr (MPCA)



Photo by Judy Crane (MPCA)



Photo by Tim Nelson (Minnesota Public Radio)

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# PAH-Related Analyses

- Parent and carcinogenic PAHs were analyzed on all samples by Pace Analytical Services, Inc. using EPA 8270 by GC/MS-SIM;

- Semivolatile organic compounds (SVOCs) were analyzed on composite samples by Pace Analytical Services, Inc. using EPA 8270 by GC/MS;

- Parent and alkylated PAHs were analyzed on composite samples by Battelle using modified EPA methods (SW-846 3550 and EPA 8270) by GC/MS-SIM; and

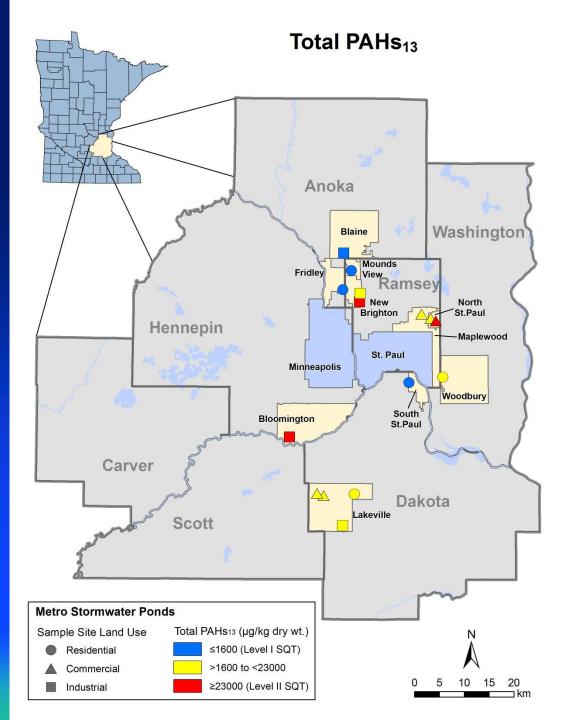- All sediment samples were screened using multiple LIF techniques by Dakota Technologies.

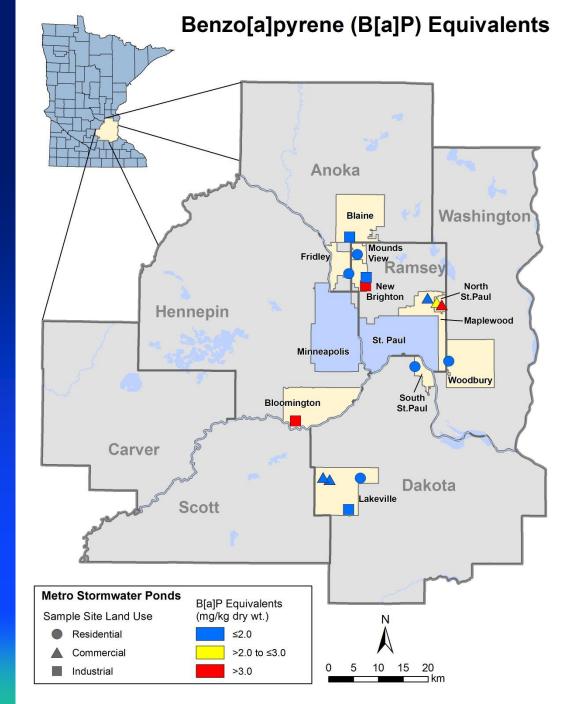Minnesota Pollution Control Agency

# Results

Two industrial sites and one commercial site exceeded the Level II sediment quality target (SQT) value for total $PAHs_{13}$.

No significant differences ($p = 0.085$) between land uses due to one low industrial site concentration.



**Total $PAHs_{13}$**

Anoka

Blaine

Washington

Fridley

Mounds View

Ramsey

New Brighton

North St.Paul

Maplewood

Hennepin

St. Paul

Minneapolis

Woodbury

Bloomington

South St.Paul

Carver

Dakota

Scott

Lakeville

**Metro Stormwater Ponds**

| Sample Site Land Use | Total $PAHs_{13}$ (µg/kg dry wt.) |
|---|---|
| ● Residential | ■ ≤1600 (Level I SQT) |
| ▲ Commercial | ■ >1600 to <23000 |
| ■ Industrial | ■ ≥23000 (Level II SQT) |

N

0  5  10  15  20
km

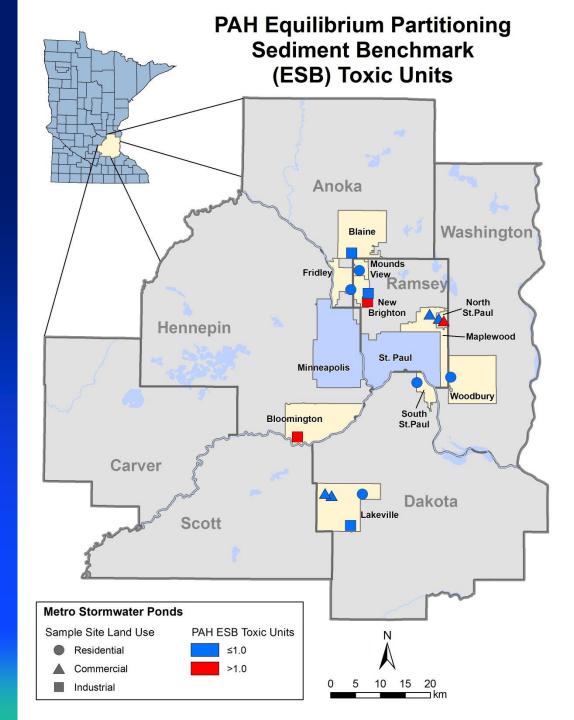**Minnesota Pollution Control Agency**

One commercial site exceeded the MPCA's Level 1 (residential) soil reference value (SRV) limit of >2.0 to ≤3.0 B[a]P equivalents.
Three sites exceeded the MPCA's Level 2 (industrial) SRV limit of >3.0 B[a]P equivalents.

**Benzo[a]pyrene (B[a]P) Equivalents**
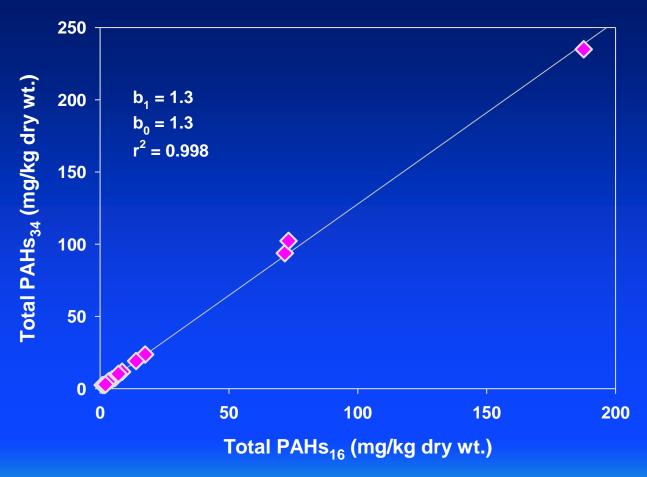
**Metro Stormwater Ponds**

Sample Site Land Use
- ● Residential
- ▲ Commercial
- ■ Industrial

B[a]P Equivalents
(mg/kg dry wt.)
- ≤2.0 (blue)
- >2.0 to ≤3.0 (yellow)
- >3.0 (red)

0 5 10 15 20 km

N

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Two industrial sites and one commercial site had PAH ESB toxic units exceeding 1.0.



## PAH Equilibrium Partitioning Sediment Benchmark (ESB) Toxic Units

**Metro Stormwater Ponds**

Sample Site Land Use
- ● Residential
- ▲ Commercial
- ■ Industrial

PAH ESB Toxic Units
- ■ ≤1.0 (blue)
- ■ >1.0 (red)

0 5 10 15 20 km

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# Total PAHs$_{16}$ Can Be Used To Predict Total PAHs$_{34}$



$b_1 = 1.3$
$b_0 = 1.3$
$r^2 = 0.998$

Total PAHs$_{34}$ (mg/kg dry wt.)

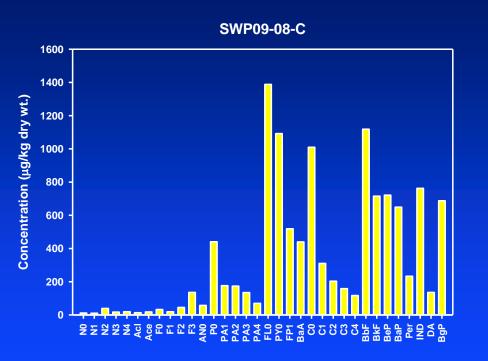Total PAHs$_{16}$ (mg/kg dry wt.)

# Identifying Sources of PAHs with Environmental Forensic Techniques
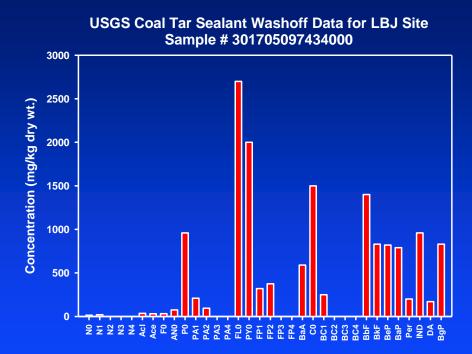
Solving Mysteries
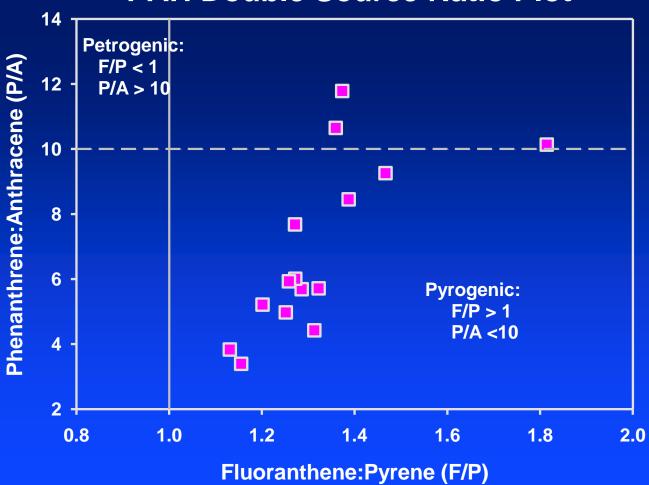
# Comparison of Histogram Plots of PAHs



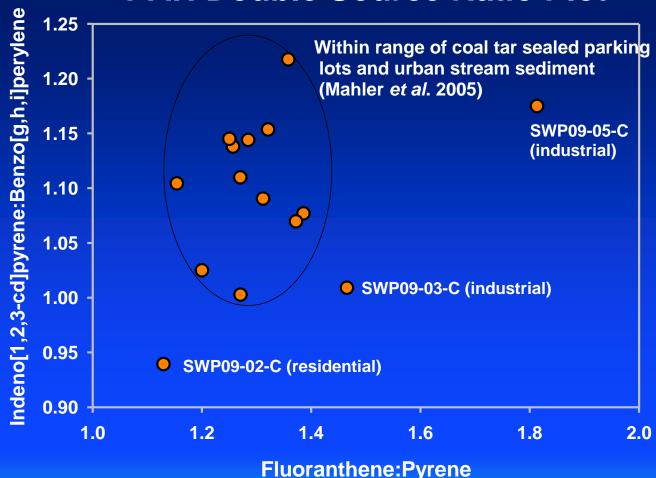SWP09-08-C

USGS Coal Tar Sealant Washoff Data for LBJ Site
Sample # 301705097434000

# PAH Double Source Ratio Plot



**Petrogenic:**
F/P < 1
P/A > 10

**Pyrogenic:**
F/P > 1
P/A <10

Phenanthrene:Anthracene (P/A)

Fluoranthene:Pyrene (F/P)

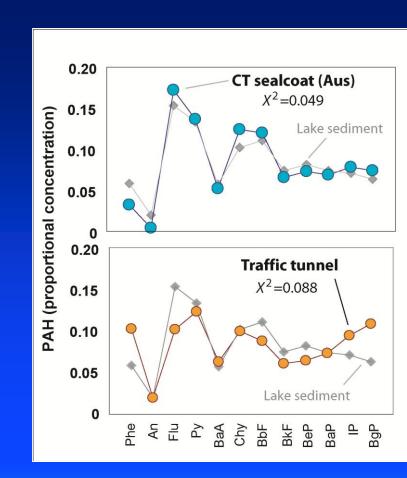Minnesota Pollution
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**Quantitative techniques, like the U.S. EPA's contaminant mass balance model (EPA-CMB8.2), provide a more rigorous method for apportioning sources of PAHs.**

# How does the CMB Model Work?

- Incorporates published source profiles (fingerprints) for 12 PAHs;

- Figures out the best combination of sources to best match the receptor profile (lake sediment) by minimizing Chi-squared ($X^2$);

- Provides estimated mass loading and uncertainty for each source.



**PAH, low to high molecular weight; graphic from Peter Van Metre (USGS).**

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# Assumptions of CMB Model (Li *et al*. 2003)

1. Composition of each source emission is consistent;

2. Chemical species do not react with each other or with the environment;

3. All sources that contribute significantly to the receptor have been identified and their chemical profile is known;

4. The composition of each source is linearly independent of other sources; and

5. Measurement uncertainties are random, uncorrelated, and normally distributed.

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# Summary Statistics of CMB Model Results*

| Summary Statistics | $R^2$ | $CHI^2$ | % MASS |
|---|---|---|---|
| Mean | 0.9801 | 0.2412 | 101.0 |
| SD | 0.00918 | 0.1163 | 1.2 |
| Minimum | 0.9623 | 0.0814 | 99.1 |
| Maximum | 0.9913 | 0.5744 | 103.3 |

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*For Battelle data set of 34 parent and alkylated PAHs.

# Source Apportionment of PAHs

| Site ID (SWP09-) | Land Use | Coal Tar Sealant Sum % | tunnel % | coal % | diesel % | oilbrn % | pinept % | gasoline % |
|---|---|---|---|---|---|---|---|---|
| 01-C-alkP | residential | 71.7 | 16.2 | 0 | 0 | 4.8 | 7.3 | 0 |
| 02-C-alkP | residential | 52.0 | 39.5 | 0 | 0 | 7.1 | 0 | 1.4 |
| 06-C-alkP | residential | 81.5 | 11.9 | 0 | 1.3 | 5.3 | 0 | 0 |
| 11-C-alkP | residential | 85.6 | 14.0 | 0 | 0 | 0.4 | 0 | 0 |
| 14-C-alkP | residential | 86.9 | 0 | 0 | 13.1 | 0 | 0 | 0 |
| 04-C-alkP | commercial | 85.0 | 12.1 | 0 | 2.9 | 0 | 0 | 0 |
| 07-C-alkP | commercial | 64.7 | 12.0 | 22.5 | 0 | 0 | 0.8 | 0 |
| 08-C-alkP | commercial | 84.2 | 15.0 | 0 | 0.8 | 0 | 0 | 0 |
| 09-C-alkP | commercial | 48.0 | 17.2 | 27.0 | 0 | 1.8 | 5.9 | 0 |
| 10-C-alkP | commercial | 69.3 | 30.3 | 0 | 0 | 0.3 | 0 | 0 |
| 03-C-alkP | industrial | 82.9 | 10.8 | 0 | 6.3 | 0 | 0 | 0 |
| 05-C-alkP | industrial | 89.3 | 0 | 0 | 10.7 | 0 | 0 | 0 |
| 12-C-alkP | industrial | 85.4 | 5.4 | 0 | 9.2 | 0 | 0 | 0 |
| 13-C-alkP | industrial | 60.6 | 24.0 | 6.7 | 0 | 8.7 | 0 | 0 |
| 15-C-alkP | industrial | 40.9 | 35.5 | 17.7 | 0 | 0.6 | 5.3 | 0 |

Tire particles contributed 0% to this source profile.

# Coal Tar Sealant and Tunnel Air are the Most Prevalent Sources of PAHs in Metro Stormwater Pond Sediments

| Summary Statistics | Coal Tar Sealant Sum % | Tunnel Air % |
|---|---|---|
| Mean | 72.5 | 16.3 |
| SD | 15.9 | 11.7 |
| Minimum | 40.9 | 0 |
| Maximum | 89.3 | 39.5 |

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# Summary

- Three of the 15 stormwater ponds consistently exceeded high benchmark values for PAHs and related indices.

- Subsets of PAHs from the parent/alkylated group of PAHs (total PAHs$_{34}$) were not statistically different based on land use, but additional statistical analyses need to be done to further evaluate any trends (e.g., remove the low industrial site as an outlier).



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Farr Lake study site

# Summary (continued)

- The CMB model provided the most effective technique for apportioning sources of PAHs.
  - A combination of coal tar sealant dust and other weathered coal tar sealant sources were not inconsistent with the PAH profile for about 72% (mean value) of the $PAH_{34}$ data set.
  - Mobile sources of PAHs (represented by tunnel air) was consistent as another important source of PAHs to the $PAH_{34}$ data set.
- Additional analyses need to be done with the parent and carcinogenic PAH data set.

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# For Further Information

- Judy Crane, Ph.D. (MPCA): 651-757-2293 (voice) or judy.crane@state.mn.us.

- MPCA Web page on "Restriction on Coal Tar-based Sealants" at: http://www.pca.state.mn.us/index.php/water/water-types-and-programs/stormwater/municipal-stormwater/restriction-on-coal-tar-based-sealants.html.

- USGS Web page on "PAHs and Coal-Tar-Based Pavement Sealcoat" at: http://tx.usgs.gov/coring/allthingssealcoat.html.

# Acknowledgments

- MPCA Field Sampling Planning and Assistance: Steve Hennes, Harold Wiegner, Alex Levchuk, Mike Anderson, Mary Jean Fenske, Dale Thompson, Anna Kerr, Louise Hotka, Mike Walerak, Steven Weiss, Jordan Donatell, and Jon Janke;

- MS™ Access Sediment Database Updates: Sara Mueller (MPCA);

- GIS Assistance: Kris Parson (MPCA);

- QA/QC Assistance: Sandy McDonald (MPCA);

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- MS4 Municipalities Included in Study:  Cliff Aichinger (City of North St. Paul), Scott Anderson and Steve Segar, P.E. (City of Bloomington), McKenzie Cafferty (City of Lakeville), Sharon Doucette (City of Woodbury), Nick Fleischhacker (City of Mounds View), James Hafner (City of Blaine), James Kosluchar, P.E. (City of Fridley), Michael Thompson, P.E. (City of Maplewood), Kerry Thorne (City of New Brighton), and John Sachi (City of South St. Paul);

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- Pace Analytical Services Inc. Project Manager:  Diane Anderson;
- Dakota Technologies Project Manager:  Randy St. Germain;
- CMB Model Assistance:  Peter Van Metre, Ph.D. and Barbara Mahler, Ph.D., P.G. (U.S. Geological Survey); and
- This project was funded by the Minnesota Legislature in 2009 as part of a bill contained in House File 1231 pertaining to the use of coal tar-based sealants.

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