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November 12, 2007

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Project AL-07-04857

Ms. Amy Hulett
City of White Bear Lake
4701 Highway 61
White Bear Lake, MN 55110

Re: Pond Evaluation
Varney Pond and Lily Lake Pond
White Bear Lake, Minnesota

Dear Ms. Hulett:

Braun Intertec has completed the evaluation of Lily Lake Pond and Varney Pond, as verbally authorized and in accordance with the authorized scope of services described in our proposal dated November 8, 2007. The objective of the evaluation was to measure sediment thickness at various locations in the ponds and evaluate whether the pond sediments would require special management and disposal.

Introduction

The City of White Bear Lake (City) is proposing to improve several stormwater ponds. The ponds are part of the City's stormwater control system. Improvements will likely include dredging the sediment(s) that have accumulated over the years in order to improve water quality and to restore pond capacities. Two ponds were selected for improvements in the near future, Lily Lake Pond and Varney Pond.

In preparation for pond improvements, the City retained Braun Intertec to evaluate the pond sediments for the presence, if any, of environmental contaminants.

Location

Lily Lake Pond and Varney Pond are located within the City of White Bear Lake. Lily Lake Pond is a generally rectangularly shaped pond located between South Shore Boulevard and Joy Avenue. Several single-family residences border the pond. Varney Pond is an irregularly shaped pond located in the northwest quadrant of Van Dyke Street and Orchard Lane.

Scope of Work

Sediment characterization for this evaluation was performed in general conformance with the guidelines outlined in *Managing Dredged Materials in the State of Minnesota* (October 2007) for Municipal Separate Stormwater System (MS4) projects. The following tasks were conducted at the site as part of this evaluation.

- Collected three (3) sediment samples from the Lily Lake Pond for laboratory analysis.
- Collected three (3) sediment samples from the Varney Pond for laboratory analysis.
- Submitted the sediment samples collected from each pond for laboratory analysis for the presence and concentrations of the following parameters:

- Polynuclear aromatic hydrocarbons (PAHs)
 - Total arsenic
 - Total copper
- Measured water depth and sediment thickness at various locations within the ponds.
 - Evaluated the data and prepared this evaluation report.

Sampling Locations

Sampling locations were based on site characteristics and were generally taken at or near the storm sewer inlets to the ponds. The field work relating to the evaluation was conducted by Ms. Amy Hulett, City of White Bear Lake, and Mr. Paul Gionfriddo, Braun Intertec, on October 15, 2007 and October 17, 2007. Sampling location maps are attached. The sampling location maps were generated by Ms. Amy Hulett.

Six (6) sediment probes were advanced at Lily Lake Pond and Varney Pond to obtain pond sediments for evaluation. Three (3) sediment probes were advanced at each pond location (designated Lily Lake Pond 1 through Lily Lake Pond 3 and Varney Pond 1 through Varney Pond 3).

Methods and Procedures

Water Levels and Pond Sediment Probing Methods

Water levels within the ponds were measured using a metal tape measure. The tape was inserted into the water until contact with the apparent sediment surface. Due to the generally soft nature of the sediments, the water levels should be considered approximate. We used a PVC pipe, 1 1/2 inches in diameter, fitted with a plastic sleeve to collect the sediment samples and measure sediment thickness. The PVC pipe was pushed through the sediment into the underlying pond bottom and then retrieved. The inner sleeve was removed and the sediment measured using a tape measure.

In some cases, particularly in Lily Lake Pond, there was not a distinct stratification between the pond sediment and underlying pond bottom. In these situations, we assumed the pond bottom to be the point at which we could no longer advance the sampler manually.

Soil Classification

The sediments encountered in the pond sediment probes were visually and manually classified in the field by a geotechnical engineer, in general accordance with ASTM procedures.

Sediment Sampling Procedures

Sediment samples were collected from each pond for laboratory analysis. The sediment samples were placed in clean, laboratory supplied containers, labeled, and transported to the Braun Intertec laboratory under refrigerated conditions using chain-of-custody procedures.

The sediment samples were submitted for laboratory chemical analyses for the presence and concentrations of the following chemical parameters:

- PAHs using EPA Method 8270.
- Total arsenic using EPA 6000/7000 Series Method.
- Total copper using EPA 6000/7000 Series Method.

All analyses were performed using EPA or other recognized standard procedures. Data were reviewed prior to release and all quality control guidelines were met. Specific information on standard operating procedures, detection limits, and quality control measures is available upon request.

Results – Environmental

The results of field observations and laboratory analysis conducted as part of the scope of work for this assessment are provided in the following sections.

Results of Pond Sediment Sampling

A summary of the analytical results for the soil samples is provided in Table 1. Chemical components detected in the sediment samples are compared with their respective MPCA Dredge Material Level 1 and Level 2 Soil Reference Values (SRVs). The SRVs are derived by the MPCA using risk assessment methodology, modeling, and risk management policy. The SRVs are expressed as a concentration in milligrams per kilogram (mg/kg).

The results of the laboratory analysis indicate that:

- Several PAH compounds were detected at concentrations that exceed the laboratory reporting limits. None of the individual PAH compounds exceed their respective Level 1 SRV, if established. However, the calculated Benzo(a)Pyrene equivalent (BaP) for two pond sediment samples from Varney Pond exceed the Level 2 SRV of 3 mg/kg. The pond samples from Varney Pond 1 and Varney Pond 2 had a calculated BaP equivalent of 9.97 mg/kg and 3.2 mg/kg, respectively. The calculated BaP equivalent concentrations for the three Lily Lake Pond samples were below the Level 1 SRV.
- Arsenic was detected in the sediment samples from the two ponds at concentrations that ranged from 1.5 mg/kg to 7.7 mg/kg. The Level 1 SRV for arsenic is 5 mg/kg. Only the Lily Lake Pond 1 sediment sample had a concentration of 7.7 mg/kg, which exceeds the Level 1 SRV. The Level 2 SRV for arsenic is 20 mg/kg.
- Copper was detected in the sediment samples from the two ponds at concentrations that ranged from 8.2 mg/kg to 98 mg/kg. The Level 1 SRV for copper is 11 mg/kg. All of the sediment samples collected from the two ponds exceed the Level 1 SRV for copper, with the exception of the Lily Lake Pond 2 sediment sample. Sample Lily Lake Pond 2 had a copper concentration of 8.2 mg/kg, which is below the Level 1 SRV.

The complete laboratory report is attached.

Results – Geotechnical

The water level measurements and sediment thickness measurements are plotted on the plan sheets attached. The plan sheets were generated using aerial photographs of the ponds. The approximate location at which water levels and sediment thickness were measured are marked with an "X" on the plan sheets. The associated water depth and sediment thickness is shown near the "X".

Lily Lake Pond

The water levels in Lily Lake Pond ranged from about 40 inches deep near the storm sewer inlet near the southwest corner of the pond to about 72 inches toward the middle and east end of the pond. However, on average, the water was about 60 to 72 inches (5 to 6 feet) deep throughout much of the pond.

Sediment thickness in Lily Lake Pond ranged from about 12 inches at the east end of the pond to about 33 inches near the middle of the pond. We estimate an average thickness of about 30 inches. Sediment thickness was difficult to accurately measure in Lily Lake Pond. There was not a distinct layer change between the sediment and the pond bottom. The pond bottom appeared to be composed of organic clays that appeared to gradually transition to peat. We understand that Lily Lake Pond was not entirely "man-made". Based on conversations with Ms. Amy Hulett, we understand the current shape of the pond has been influenced by development of the area. Apparently, the area previously existed as a low-land/wetland that was much larger in size and has been reduced to its current size as the area was developed.

Varney Pond

Water levels in Varney Pond ranged from about 7 inches deep near the storm sewer inlet at the northeast corner of the pond to about 51 inches deep near the overflow outlet in the southwest corner of the pond. We estimate the average water depth to be about 36 inches.

Sediment thickness ranged from about 5 inches near the center portion of the pond to about 20 inches near the northeast corner of the pond.

Deltas or islands comprised of sand and gravel were encountered near the inlets at the northwest and northeast corners of the pond. The thickness of the sediments (sand and gravel) in these areas was not determined. The sand and gravel prohibited advancing the sampler through the sediment. Attempts to bore into the sediment with a hand auger also proved unsuccessful. The borehole caved-in due to the water in the pond.

We anticipated that the sediment (sand and gravel) near the storm sewer inlets would be about 1 1/2 to 2 feet. This is based on an average water depth of about 36 inches (3 feet) and an average sediment thickness of about 20 inches (about 1 1/2 feet).

Conclusions and Recommendations

Based on the results of this evaluation, we provide the following recommendations:

Environmental

Dredged material is defined as a "waste" and "other waste material" by Minn. Statute 115.01 as stated in the Minnesota Pollution Control Agency's (MPCA) guidance document titled: *Managed Dredged Materials*, dated October 2007. In accordance with the previously mentioned document, except for specific situations, a permit is required for the management of dredged material in the State of Minnesota.

To address the environmental issues associated with the management of the dredge material and discharges from the dredge project and/or management areas, the MPCA utilizes the regulatory controls of the National Pollutant Discharge Elimination System (NPDES) and/or the State Disposal System (SDS) permitting program. The NPDES/SDS Program is structured to provide two types of permit coverage for regulated activities. The "general" permit covers common pollutants and issues that create a

similar discharge at a number of facilities. The "individual" permit covers specific activities and types of pollutants managed and/or discharged from a project.

We recommend that either a "general" or "individual" permit be sought to provide management options for dredge material, including temporary storage, rehandling, off-loading, transportation, treatment, disposal, and/or reuse. Based on this evaluation, the dredged material may be disposed at a permitted solid waste facility, through permitted on-site disposal, or through use or reuse for beneficial purpose, including backfill.

If the dredged material is disposed of at a permitted solid waste facility, additional laboratory testing will be required. The laboratory analysis required will vary depending on the facility selected for disposal.

If the dredged material is permitted to be disposed of on-site or for off-site reuse, additional analytical sampling would be required and MPCA reuse criteria would need to be followed including providing adequate separation distance and clean cover.

Geotechnical

In general, the sediment thickness were greatest near the storm sewer inlets to the ponds. In addition, the sediment near the storm sewer inlets was composed mainly of sand and gravel. Sediment thickness at these locations was not determined. The sampling probe could not be advanced through the material manually, especially in Varney Pond. However, we estimate that the sediment thickness near the storm sewer inlets in Lily Lake Pond to be about 30 inches (2 1/2 feet) and the sediment thickness near the storm sewer inlets in Varney Pond to be about 1 1/2 to 2 feet.

We understand the City desires to keep the quantity of dredged material to practical minimums. To achieve their goals, the City may wish to focus dredging activities near the storm sewer inlet pipes. We estimate that about 1 1/2 to 2 1/2 feet of sediment will be removed near the storm sewer inlets.

Based on conversations with Ms. Amy Hulett, we understand the residents bordering Lily Lake Pond have expressed a desire for the City to dredge the pond to a depth of about 10 to 11 feet. We understand the current shape of Lily Lake Pond was influenced by development of the area. The organic clay and peat encountered in the probes are relatively low-strength soils. Sloughing of the adjacent soils into or toward the dredged areas will likely occur if the pond is dredged to the proposed depths of 10 to 11 feet. Docks, retaining walls, and landscaping along the perimeter of the pond could be impacted. If this option is considered, we recommend soil borings and a geotechnical evaluation to characterize site conditions. The geotechnical evaluation should include an analysis of slope and soil stability.

Assessment Limitations

The analyses and conclusions submitted in this report are based on our field observations and the results of laboratory chemical analyses of soil samples collected from Lily Lake Pond and Varney Pond.

In performing its services, Braun Intertec used that degree of care and skill ordinarily exercised under similar circumstances by reputable members of its profession currently practicing in the same locality. No warranty, expressed or implied, is made.

General

This evaluation was prepared on behalf of and for use by the City of White Bear Lake ("Client"). No other party has a right to rely on the contents of this evaluation without the written authorization of Braun Intertec Corporation. All authorized parties are entitled to rely on the attached report according to our contract with Client and under the same terms, conditions, and circumstances. Please note that our contract with Client may contain a limitation of our total liability. If so, such limitation also applies to all those receiving this permission.

We appreciate the opportunity to provide our professional services to you for this project. If you have any questions or comments regarding this report, please call Paul Gionfriddo at 763-497-4159 or Mike Bratrud at 952-995-2430.

Sincerely,

BRAUN INTERTEC CORPORATION



Paul S. Gionfriddo, P.E.
Senior Engineer



Michael L. Bratrud, P.G.
Principal

Attachments:

Sampling Location Maps – Lily Lake Pond and Varney Pond
Soil Analytical Results (Table 1)
Laboratory Reports

c: Mr. Brent Thompson, Assistant City Engineer, City of White Bear Lake

Table 1
Soil Analytical Results
Varney Pond and Lily Lake Pond
White Bear Lake
Project AL-07-04857

Compound/Parameter	CAS No.	Sample Identifier						Level 1 Soil Reference Value (mg/kg)	Level 2 Soil Reference Value (mg/kg)
		Varney Pond #1 10/17/2007	Varney Pond #2 10/17/2007	Varney Pond #3 10/17/2007	Lily Lake Pd #1 10/15/2007	Lily Lake Pd #2 10/15/2007	Lily Lake Pd #3 10/15/2007		
Semivolatile Organic Compounds (mg/kg)									
2-Methylnaphthalene	91-57-6	<(0.87) ^d	<(0.16)	<(0.094)	<(0.71)	<(0.098)	<(0.12)	100	369
Acenaphthene	83-32-9	<(0.87) ^d	0.42	<(0.094)	<(0.71)	0.18	<(0.12)	1200	5260
Acenaphthylene	208-96-8	<(0.87) ^d	<(0.16)	<(0.094)	<(0.71)	<(0.098)	<(0.12)	NE	NE
Anthracene	120-12-7	1.9 ^d	1.4	0.27	<(0.71)	0.19	<(0.12)	7880	45400
Benz(a)anthracene	56-55-3	6.3 ^d	2.1	0.88	<(0.71)	0.15	<(0.12)	***	***
Benz(e)pyrene	50-32-8	7.1 ^d	2.3	1	<(0.71)	0.17	0.14	***	***
Benzo(b)fluoranthene	205-99-2	7.5 ^d	2.8	1.5	<(0.71)	0.16	0.15	***	***
Benzo(a,h)perylene	191-24-2	1.8 ^d	0.17	0.12	<(0.71)	<(0.098)	<(0.12)	NE	NE
Benzo(k)fluoranthene	207-08-9	6.9 ^d	2.7	1.2	<(0.71)	0.17	0.14	***	***
Carbazole	86-74-8	1.8 ^d	0.76	0.14	<(0.71)	<(0.098)	<(0.12)	700	1310
Chrysene	218-01-9	8.1 ^d	2.5	1.2	<(0.71)	0.2	0.13	***	***
Dibenz(a,h)anthracene	53-70-3	<(0.87) ^d	<(0.16)	<(0.094)	<(0.71)	<(0.098)	<(0.12)	***	***
Dibenzofuran	132-64-9	<(0.87) ^d	0.24	<(0.094)	<(0.71)	0.13	<(0.12)	104	810
Fluoranthene	206-44-0	23 ^d	8.4 ^d	3.2	<(0.71)	0.67	0.32	1080	6800
Fluorene	86-73-7	<(0.87) ^d	0.59	0.14	<(0.71)	0.21	<(0.12)	850	4120
Indeno(1,2,3-cd)pyrene	193-39-5	2.3 ^d	0.23	0.16	<(0.71)	<(0.098)	<(0.12)	***	***
Naphthalene	91-20-3	<(0.87) ^d	<(0.16)	<(0.094)	<(0.71)	0.13	<(0.12)	10	28
Phenanthrene	85-01-8	12 ^d	6.9	1.6	<(0.71)	0.93	0.14	NE	NE
Pyrene	129-00-0	14 ^d	5.3	2	<(0.71)	0.4	0.21	890	5800
BaP Equivalent**	NA	9.97	3.20	1.44	1.40	0.28	0.26	2	3
Metals (mg/kg)									
Arsenic, Total	7440-38-2	1.5	4.5	2.4	7.7	2	4.7	5	20
Copper, Total	7440-50-8	17	27	22	98	8.2	12	11	9000
Other Parameters									
% Solids (% Wt)	NA	76	86	70	47	69	56	NA	NA

Notes:
^d The method reporting limit (MRL) was raised for one or more analytes; a dilution of the sample was necessary due to high analyte levels and/or matrix interferences.

mg/kg = Milligrams per Kilogram.

< = Less than the reporting limit indicated in parentheses.

NE = Not Established

** = Benzo(e)pyrene (BaP) equivalent is calculated based on the concentration and weighted toxicity of carcinogenic PAHs (cPAH), Minnesota Pollution Control Agency, 2002.

*** = cPAH. Individual SRV not established. Included in BaP equivalent calculation.

NA = Not applicable

Concentration exceeds the MPCA Level 2 SRV

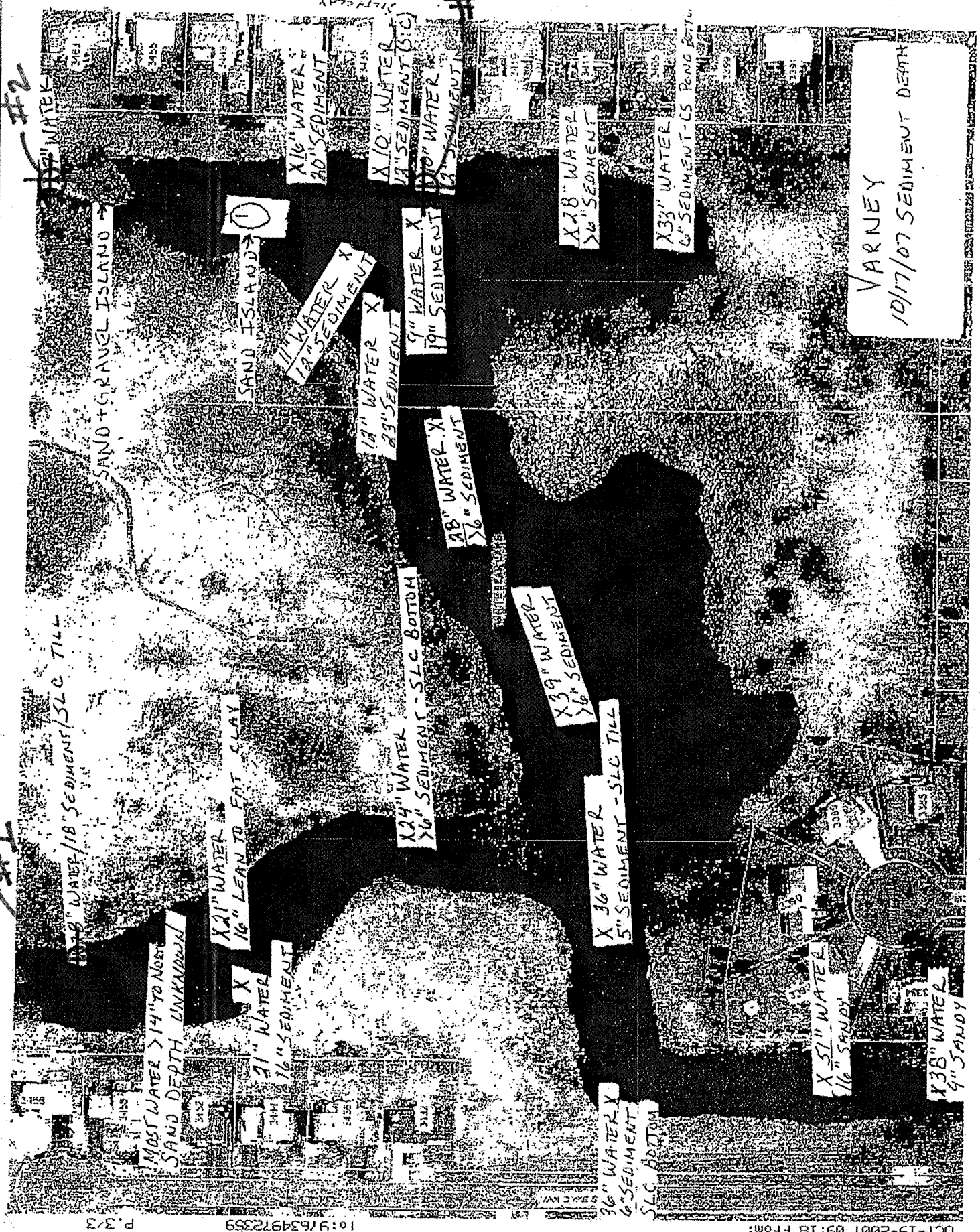
Concentration exceeds the MPCA Level 1 SRV

LILY
10/15/79 SEDIMENT DEPTHS



#2

#3



VARNEY
10/17/07 SEDIMENT DEPTH

X 18" WATER / 18" SEDIMENT - SLC TILL

MOST WATER > 14" TO NOSE
SAND DEATH UNKNOWN

X 21" WATER
16" LEAN TO FAT CLAY
X 21" WATER
16" SEDIMENT

SAND ISLAND
X 11" WATER
17" SEDIMENT

X 19" WATER
23" SEDIMENT

X 14" WATER
X 14" SEDIMENT - SLC BOTTOM

X 28" WATER
X 28" SEDIMENT

X 39" WATER
X 39" SEDIMENT

X 36" WATER
5" SEDIMENT - SLC TILL

X 36" WATER
6" SEDIMENT
SLC BOTTOM

X 51" WATER
16" SANDY

X 38" WATER
4" SANDY

X 16" WATER
20" SEDIMENT

X 10" WATER
12" SEDIMENT (S.C.)

X 9" WATER
19" SEDIMENT

X 18" WATER
X 18" SEDIMENT

X 33" WATER
6" SEDIMENT - CS PANG BATH

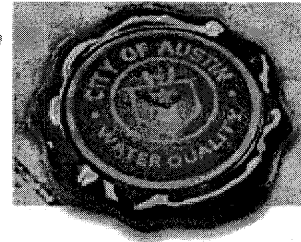
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Stormwater

FEATURES

PARKING LOT SEALANTS

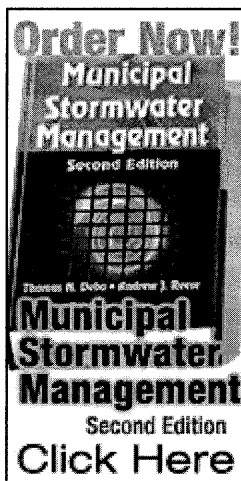


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On the trail of urban PAHs

By David C. Richardson

StormCon

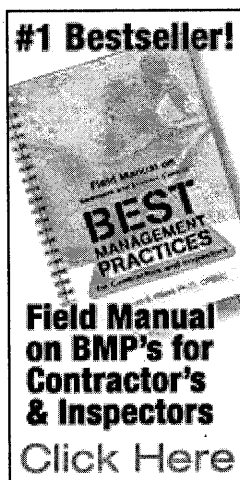


Parking lot sealcoating is a national obsession. On any fair-weather day, dozens of work crews in cities throughout the nation can be seen spreading gooey black tars over acres of parking lot pavements and driveways—spraying, mopping, or brushing a few years' shine onto their fading surfaces, dutifully following applicators' recommendations that the practice be repeated every couple of years. But few people pause to consider what may have become of the previous years' coatings, abraded away by tire treads, wind, and rain. As the spring paving season heats up, however, the people of Austin, TX, will be regarding shiny new parking lots with a new sense of discernment.

There are two major types of parking lot sealants widely in use throughout the United States; one is based on asphalt, and the other has a coal-tar base. Refined coal-tar sealants are used in some regions of the country, while asphalt sealants are favored in other regions. As of January 1, 2006, coal-tar-based sealants were banned for use in Austin.

Coal tars contain a high concentration of polycyclic aromatic hydrocarbons (PAHs)—environmental pollutants that have been the subject of scrutiny for a number of years. In recent studies researchers have noted increases in sediment PAH concentrations in urban ponds and lakes over time.

Tom Ennis, director of the Spills Response Division of the Watershed Protection and Development Review Department



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(WPDRD), estimates that “in Austin, 600,000 gallons of parking lot sealcoat is laid down each year.” He says that applicators recommend the sealants be applied every two to three years to maintain the shiny new appearance and integrity of the parking lot surfaces. Ennis adds that the vast majority of sealant “traditionally used in Austin has been coal-tar based, but now using a coal-tar sealant in Austin can net you a \$2,000 fine.”

How do you tell the difference between two gooey black substances intended to seal and coat parking lot surfaces to protect them from weathering and wear? For Ennis, this became an important question. “We developed a simple screening test, which we demonstrated on a local newscast to help inform the public of the new policy. The test involves a black light, some vegetable oil, a swab, and the wheel well of the investigator’s vehicle. We know that coal tar leaves a residue that fluoresces yellow under certain wavelengths of black light. We also know from experience that when people who worked in the industry needed to remove the residue from their skin, they would first wipe down with vegetable oil and then look at the stained area under black light. If it glowed yellow, that meant there was still coal-tar residue left behind.”

On the morning of January 4, 2006, the test would undergo its first real-life enforcement application as the WPDRD received its first call for a potential violation of the coal-tar ban. A concerned citizen had observed a contractor applying a substance he suspected might have been one of the banned sealants onto a parking lot surface. The WPDRD Spills Response Division responded to the caller by dispatching a team to investigate. Ennis was confident that by the end of the day he would have the answer. But answers have not always been that easy to come by.

Routine Studies Uncover Problems

It all began innocently enough when in 1993, with the help of an EPA grant, the WPDRD began a comprehensive environmental survey of Austin’s creeks. Nancy McClintock, assistant director for Watershed Protection at the WPDRD, provides a rationale for the project: “In a state like Texas, we don’t have as much water as some places have, and we’ve always been really focused on protecting it. People in Austin always wanted to know that their resources were going to be protected.” The WPDRD planned to test all of the 50 creeks in its jurisdiction for numerous parameters, from physical characteristics to biodiversity to chemical and flow characteristics.

McClintock says the idea “was to get an overall assessment of stream health that could help us in development planning and resource management.” One of the chemicals they tested for

was PAH.

A Big Family

PAHs comprise a family of chemical compounds composed of the two elements carbon and hydrogen, arranged in a lattice of interconnecting hexagonal rings, similar in structure to the benzene ring. Like carbon monoxide, they do exist in nature, but they are also created from the incomplete combustion of hydrocarbons. There are about 100 distinct PAHs, and they can be categorized in 17 families. Within each branch of the PAH family of molecules, the benzene-like rings bear distinctive patterns of connections with one another. Some forms of these molecules stretch out as chains, others coalesce into complex polygons, some are a combination of both, and occasionally some PAHs may include traces of elements other than carbon and hydrogen among their constituents. PAH molecules of varying shapes and sizes display distinctive, and sometimes divergent, chemical and physical properties.

PAHs tend to adhere to surfaces. They are hydrophobic and don't dissolve readily in water, and those derived from coal tar also have a high resistance to petroleum products. Many of the PAH compounds are remarkably chemically stable. All of these are qualities that would make them potentially useful as sealants. Coal-tar-based sealants contain the highest concentration of PAHs—between 20% and 35%—whereas asphalt-based sealants contain about 5% PAHs. But the same characteristics that make sealants containing high levels of PAHs so effective also might make exposure to them hazardous. Once PAHs adhere to an object, they are hard to remove, whether that object is a pebble, a grain of sand, or (if inhaled, ingested, or in contact with) living tissue. Historically, PAHs have been associated with many negative biological impacts, ranging from reproductive effects in wildlife to cancers in humans. In 1775, Dr. Percival Pott traced an epidemic of scrotal cancer in English chimney sweeps to coal-tar residues in soot. Subsequently, the Danish Chimney Sweepers' Guild and other occupational authorities in many European nations recommended frequent bathing for chimney sweeps, reducing dermatologic exposure levels and illness in those countries (*Nature*, August 2004, Vol. 4). At least 13 branches of this suite of chemicals have been designated to be of environmental concern or hazardous by the EPA.

Paradoxically, as dangerous as they sound, with sophisticated and sensitive detection methods, PAHs can be found virtually everywhere it is possible to look. Astronomers have even detected them in traces on meteorites and in interstellar space. PAHs can be found among natural sources—spouting from volcanic flows, in the ashes of forest fires—from manmade

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sources such as vehicle exhaust and coal furnaces, and as a byproduct of the coking processes used in the manufacture of aluminum and steel. They can even be detected on meats grilled over an open flame.


The majority of PAHs in the environment are believed to arise from two primary sources: petrochemical and combustion processes. These are scientifically termed, respectively, petrogenic and pyrogenic. However, they are usually found in low concentrations in the ambient environment and are seldom concentrated enough to be a health concern. But recent studies are in fact showing increasing concentrations of PAHs in the sediments of lakes and reservoirs in the urban environment over time. This became a growing concern for Leila Gosselink, an engineer working with data analysis for the WPCRD. She and her team, as part of their study of Austin's streambed ecology, had found widely divergent concentrations of PAHs in sediments in certain hot spots along the city's creeks.

“When we started sampling, there was not a lot of data on PAH levels in small creeks and tributaries of urban watersheds,” Gosselink recalls. She says their sampling had disclosed PAH concentrations varying from “undetectable levels in some creeks to levels of hundreds to thousands of parts per million in others”—a discrepancy, she says, large enough to warrant further scrutiny. “We had these data that showed widely these varying concentrations. At that time there were no guidelines for PAHs in creek sediments. We checked with our colleagues in other cities, and no one had done any studies like this on creek sediments. So we needed someone to help us interpret our data.”

They contacted Peter Van Metre of the US Geological Survey's (USGS's) National Water-Quality Assessment Program, who had been working on a study investigating rising PAH concentrations in sediments of 38 lakes nationwide.

“When we informed him of some of the high PAH readings we were getting, he told us our data couldn't be right, that we must have a problem with our study, or that we must have misplaced our decimals.” But Gosselink was sure of her data.

She and her team agreed to split samples with Van Metre and also did some side-by-side sampling with USGS researchers in the field. When Van Metre sent his samples to USGS labs to have them perform an independent analysis, along with the lab reports, he also received a complaint. “They wanted to know what the heck was in the stuff. They said it gummed up the equipment and the PAH levels were off the charts.”



No one had ever seen PAH readings like this from ambient sources. So Gosselink began the meticulous task of source tracing. Because of the expense of laboratory analysis for PAH, she first did some research to find an inexpensive screening method. Her colleague, Mateo Scoggins, an aquatic biologist with the WPDRD, describes the process. "We used the enzyme-based ELISA method and were able to do the analysis on samples in-house at a cost of between \$25 and \$50, compared to the usual \$150 or more for lab analysis." They sampled sediments from the creeks and tributaries starting at their mouth at Town Lake on the Colorado River, all the way up the creeks, looking for the source of the PAH contamination. "We tracked sediments up the creek until PAH concentrations started dropping again. So we knew it wasn't continuing from the main stem. Then we started looking at the small drainages immediately upstream of the area where we were getting the high readings. We got a couple of readings that showed increasingly large concentrations the farther we went up the channel." Following the trail of the increasing levels, he says, "led us right up to the parking lots. One of our people in the Spills Response Division who had experience in the building trades observed that these were in fact sealed lots." A picture was beginning to emerge.

But all sealed parking lots were not equal. Some parking lots had PAH runoff levels many times higher than others. Another variable had to be involved. McClintock recalls what she calls the "Aha!" moment. "Tom Bashara from our Spills Division was doing some research and stopped by at a local hardware dealer while puzzling over the question of where these high concentrations might be coming from. He examined containers of two types of parking lot sealcoat and suddenly it struck him—one type of sealant contained coal tars, and coal tars are heavy in PAHs." All that would be necessary now was to confirm that coal-tar sealants had in fact been applied to the parking lots in question, and the WPDRD would have its answer and could begin looking for a remedy. But things were not going to be that simple.

The Puzzle of Barton Springs

Nestled not far from downtown Austin is a spring-fed pond surrounded by rolling parklands. With waters a temperate 70 degrees year-round, it had become a favorite summertime escape from the sweltering city. The park is well regarded by Austin residents. In fact, Scoggins says, "There are indications the site was visited by humans as far back as prehistoric times, although more recently in the early 1900s, the pond was dammed and the banks reinforced with concrete to convert it to a public swimming hole called Barton Springs Pool."

McClintock adds that it is special for another reason. "Along with a few other related springs in the area, it's the only habitat for the endangered Barton Springs salamander." For her, "The Barton Springs Pool is the heart and soul of the city."

In January 2003, staff from the WPDRD prepared to announce their conclusions that coal-tar-based sealants were a major contributor to elevated PAH levels in Austin's creeks, when suddenly a dramatic story hit the media. The *Austin American-Statesman*, a local daily, citing some of the WPDRD's data, reported that traces of potentially cancer-causing PAH residues had been detected in the vicinity of Austin's favorite swimming destination, Barton Springs Pool. The paper's reports discussed the hazardous nature of PAHs and developed a position contrary to what the WPDRD believed the data would demonstrate. The *Statesman* made the association between PAH concentrations and toxic waste sites such as retired coal gasification plants, which had heretofore been the only widely discussed source for elevated PAH concentrations. The paper developed a theory that the PAHs in and around Barton Springs Pool were constituents of wastes from one of these plants. It was theorized that wastes containing coal tar had in the past been disposed of on a hillside adjacent to the park and were contributing contaminants to the groundwater, eventually making their way to the pool. Immediately public attention was galvanized. Austin clamored over PAHs and the history and fate of Barton Springs Pool.

McClintock remembers the shock and disappointment that rippled through the community. "It was a difficult time for everyone—people were saddened at the notion that one of their cherished parks was being compared to a toxic site."

For the community, the question of human health effects from PAHs in the pool was the first priority. From McClintock's point of view, however, there was never any real human health threat. "Because PAHs tend to cling to sediments and don't dissolve readily, they are usually there left behind by the water, and therefore they seldom become a drinking-water or a groundwater problem." Furthermore, "The contaminated sediments in the pool were generally under 15 to 17 feet of water, so the risk of significant contact with them was practically nonexistent. Also, she suspected that "the concentrations of PAHs in those and other contaminated sediments in the area, while above the screening limits for our study, were far below those at which one would expect adverse health impacts." She was right. In the toxicological report that was made in the aftermath of the incident, one toxicologist who concurred with McClintock's view is Dr. Richard Beauchamp of Texas Department of Health. Beauchamp was quoted in a press

release from the Austin City Council announcing the reopening of the pool, indicating that concentrations were so low that a child playing in the mud, with the most contaminated sediments found covering his hands, arms, and legs for an hour at a stretch, would face no significant health risks. He added, "There is really no risk for a child playing with sediment."

According to McClintock, "The whole question is exposure."

Nevertheless, researchers and staff from the WPDRD joined with city, state, and federal officials as they took steps to ensure public safety at the park. The pool was closed to bathers for three months while efforts were made to isolate the source of the contaminants. Core samples were taken along the hillside in question. The Texas Council on Environmental Quality, along with the WPDRD, assessed the results. Samples of sediment from various locations in the nearby creeks and the pool were analyzed. A constellation of factors was to be considered: the historical record, the hydrology of the area, the topography. One factor after another seemed to militate against the possibility of a toxic waste issue at Barton Springs, and together these analyses seemed to indicate a source other than a toxic waste deposit. And once again, sediment sampling in the nearby creeks revealed that the highest concentrations of PAHs were not to be found buried in the core samples taken from the suspected toxic dump on the hillside, but in runoff from the freshly sealcoated parking lot of an apartment complex at the crest of the hill.

Seasonal flooding that sometimes caused the creeks near the springs to top their banks had probably carried residues from the parking lot along with the flow. "The indications were that in this case, what we were dealing with was in fact a surface runoff issue from those parking lots," says McClintock.

Comparing Risks to Create Policy

While the Barton Springs incident did not endanger public health or safety, it did raise the consciousness of the community to the risks from this ubiquitous contaminant. And it helped confirm the WPDRD's position that much of the PAHs were coming from parking lots. Nonetheless, the WPDRD needed more information to evaluate the implications of its developing knowledge base. For instance, Van Metre says, "No one had ever identified sealant as a problem; no data existed describing how quickly PAHs washed off of them into sediments. There had been no side-by-side comparisons of sealant products."

The WPDRD, along with Van Metre, designed a study to answer some of these questions. They would compare PAH

yields from parking lots of several different types including sealed, unsealed, and concrete—13 parking lots in all, throughout the city. They had several broad questions they hoped to address: Did freshly applied sealants yield higher concentrations of PAHs than aged or worn coatings? Did parking lot use patterns have any significant impact on PAH yields? What was the prospective PAH yield over time of the various types of sealants?

Another component of their study called for the application of fresh coats of sealants on test plots at the retired airport. These test plots would provide a direct comparison between PAH levels from asphalt sealants and coal-tar sealants. The results of their research were published in the journal *Environmental Science & Technology* in 2005 (Vol. 39, No. 15).

Van Metre summarizes their methodology. “We contacted several businesses and got permission to sample on their lots. The University of Texas and the city gave us permission to sample on their lots. We went out on Saturdays or Sundays when there weren’t a lot of people driving in and out and marked off an area of about 50 square meters for the study. We took 100-liter jugs of distilled water, clean tubing, and clean pumps and used a light spray through a watering nozzle and just moved gradually down the lot until the water would run down to the spill berms we had set up. This would simulate about one-tenth of an inch of rain. Then we pumped the runoff up into containers as we were doing the washoff. By the time we got to the end of that process, we hadn’t completely cleaned the lot, but we were getting a lot clearer water than when we started, which indicated we were getting most of the loose dirt and particles. Then we did the filtering through Teflon filters, which let us trap the particles in a real fine mesh. This allowed us to separate the water and get the mud right back off so we could measure the chemistry of the sediments directly.” When the sediments were isolated, they had the appearance of a dark brown mud the color of coffee grounds, including particulates of varying sizes from fine dusts to granules the size of a grain of sand and larger.

When tested, the particles in runoff from parking lots with coal-tar-emulsion sealcoat had mean concentrations of PAHs 65 times higher than the mean concentration from unsealed asphalt and cement lots. In fact, PAH yields from the sealed parking lots were “100 times higher than from used motor oil,” which Van Metre says “is the next-most-contaminated stuff out there for PAHs.”

By way of comparison, Van Metre recalled another study of urban PAH levels with which he had been involved. This one

focused on PAH runoff from asphalt-shingled rooftops. "One might have expected the asphalt rooftops to be a large source of PAH, but runoff we collected in that study right here in Austin was 200 times lower in PAH yield per area than the sealed lots."

The test plots where Van Metre had applied fresh coats of the sealants revealed more conclusive data; coal-tar sealants yielded more PAHs by an order of magnitude over the asphalt-sealed plots. According to Van Metre, "An ongoing study in Fort Worth is looking at particles swept off of parking lots and streets. Their findings seem to support what we have seen: much higher concentrations of PAHs coming from the sealed parking lots and much lower concentrations from the roadways, which are generally not sealed, and from unsealed parking lots." This information gave Van Metre added confidence. "I think it shows it wasn't just some kind of weird anomaly we were picking up here in Austin."

The joint study concluded that when all the other sources of urban PAHs that parking lots receive—such as vehicle exhaust, tire particles, leaking motor oil, and atmospheric fallout—are accounted for, the average yield from sealed parking lots is 50 times greater than from unsealed lots. Based on this, statistical projections generated from their study data, and an analysis of four local watersheds in the Austin area, the researchers estimated that the total PAH load from parking lots in those watersheds would be reduced to 5% to 11% of the current loading if all the parking lots were unsealed.

Important Little Bugs

Mateo Scoggins, the aquatic biologist for the WPDRD, undertook a separate line of inquiry that began to look into the biological impacts of PAH exposure on the typical stream ecology. He looked at indicator organisms under several concentrations of PAH exposure. As a benchmark, he used the consensus-based probable effect concentration, the level at which biological impacts are considered likely. He exposed creek-dwelling macroinvertebrate species to low, medium, and high concentrations of PAHs derived from parking lot sealants.

His group conducted three major studies. The three studies involved looking at the effects of PAH exposure under laboratory conditions, in microcosms, and in the field. In the lab study, test organisms were exposed to water dosed with sample scrapings from either asphalt-based sealants or coal-tar-based sealants in low, medium, and high concentrations for a one-month period. In the microcosm study, test samples of creek organisms were seeded in waters spiked at the same three treatment levels. In the field study, communities of

organisms were evaluated at various locations in five urban creeks.

Effects were evident at all levels of PAH concentration tested, but at moderate and high concentrations, the negative impacts of PAH toxicity were pronounced. Scoggins says the results of the studies “showed the coal-tar-based sealants to be significantly more toxic to these organisms than the asphalt-based products. When ultraviolet light was added to more closely simulate the aquatic environment in the streambeds, the effects were profound.” Under moderate PAH exposure levels, the samples exposed to coal-tar-based sealants showed zero survivability when dosed with UV light, while those in the asphalt-exposure group survived at a rate of 70% under the same UV dosing. The control groups were not affected by the addition of UV exposure and showed 100% survival. It appeared that coal-tar-based PAHs could be expected to become significantly more toxic when exposed to sunlight, which is unavoidable in the urban aquatic environment.

Furthermore, the study recorded almost complete mortality for some organisms at levels of PAH exposure below some of those actually recorded in the most contaminated streams.

Observations recorded in the actual aquatic environment of the streams supported these findings. One consistent finding was a loss of taxa, a classic measure of ecosystem impairment, in the most severely impacted streams. Scoggins was surprised “that with all the other urban stressors affecting these creeks, the effects of PAH exposure would be so pronounced. Some of these creeks had only a seasonal flow and were so severely impacted by the urban environment that they would not appear in any way to be inviting aquatic environments.” Nevertheless, Scoggins says, “The simple factor of being downstream of one of these sealed lots caused a significant loss of taxa relative to locations on the same creek just upstream of the parking lots.” Among the five streams studied, he says, “The two most highly impacted showed a 21% to 42% loss of taxa. This could have major implications for overall watershed health.”

Scoggins adds, “The organisms that I look at as indicators of stream health, worms and invertebrates who inhabit streams, are definitely being degraded by these PAHs. Though we just look at them as indicators of stream health, if you’re dropping out large percentages of the food base and the food web, obviously you’re going to be influencing other organisms. I feel that the small critters are extremely important from a wide range of perspectives. I’m sure the problem with the bugs in the streams will be passed on further up the food chain—the fishery is probably being influenced by it indirectly.” He notes that “if

people could grasp the magnitude of this, it is kind of a big deal.”

The results of these studies, along with a review of policy and federal regulations, led the WPDRD first to suggest a voluntary ban on coal-tar-based sealants and finally to propose legislation to the city council for a mandatory ban on coal-tar-based sealants—the first in the nation. The ban, enacted by the City of Austin in November 2005, went into effect on January 1, 2006. McClintock says response has been mostly positive so far from the community. In fact, during the period of the voluntary ban, she says, one of the major local sealant applicators, Wheeler Coatings, indicated its intention to switch over to using an asphalt-based product. “They committed that they would not apply the coal-tar-based product any longer in the Barton Creek watershed.” Also, her staff members tell her that they’re no longer seeing the product on the shelves in local hardware stores. McClintock also says the department will be “developing a communication plan for working with the other cities that are adjacent to Austin whose runoff may be affecting our watershed to help them understand our new policy.”

Closing the Loop

On the afternoon of Friday, January 7, 2006, Ennis met with Sharon Cooper, manager of the Spills Response investigative team; they discussed the progress of the enforcement effort after one week of implementation. With one investigation concluded, Ennis was able to say, “So far, so good.” The investigative team from the Spills Division was able to report the satisfactory result that the sealant sample taken from the complaint site sample did not fluoresce under black light, confirming that it was not the banned coal-tar sealant, and the contractors were allowed to proceed with their work. Ennis was pleased to see the department’s outreach efforts had been effective: “Even though it turned out not to be a violation, the citizen knew enough about the ban from our media coverage to pick up the phone and ask us to find out what was going on out there. We tested, talked with the contractor, and verified that they were using an asphalt sealant and not one of the banned products. I understand that the citizen was happy to see us respond so quickly and to learn that the appropriate product was being placed.”

Ennis doesn’t think the coal-tar sealants will be missed and sees big opportunities for using less-toxic alternatives on the hundreds of acres of parking lots previously sealed with coal tar that may come in need of repair the future. “As those pavements need resealing, repair, and rehabilitation, we’ll be looking at putting down less-toxic alternatives. Those with the need to seal will still have the option of using asphalt sealants.

And then," Ennis adds, "there's the option of not sealing at all. The preferred option would be to just have a concrete pavement, which would have the added benefit of reducing the urban heat island effect. There are pavers. There's even a technique called 'white-topping' in which a 1- or 2-inch layer of high-strength concrete is laid over asphalt." With all these options to consider, this year's spring paving season in Austin could be one of the most interesting and environmentally innovative ever.

David C. Richardson is a journalist based in Baltimore, MD.

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Parking Lot Sealcoat: An Unrecognized Source of Urban Polycyclic Aromatic Hydrocarbons

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Abstract:

Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous contaminant in urban environments. Although numerous sources of PAHs to urban runoff have been identified, their relative importance remains uncertain. We show that a previously unidentified source of urban PAHs, parking lot sealcoat, may dominate loading of PAHs to urban water bodies in the United States. Particles in runoff from parking lots with coal-tar emulsion sealcoat had mean concentrations of PAHs of 3500 mg/kg, 65 times higher than the mean concentration from unsealed asphalt and cement lots. Diagnostic ratios of individual PAHs indicating sources are similar for particles from coal-tar emulsion sealed lots and suspended sediment from four urban streams. Contaminant yields projected to the watershed scale for the four associated watersheds indicate that runoff from sealed parking lots could account for the majority of stream PAH loads.

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Parking Lot Sealcoat: An Unrecognized Source of Urban Polycyclic Aromatic Hydrocarbons

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Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous contaminant in urban environments. Although numerous sources of PAHs to urban runoff have been identified, their relative importance remains uncertain. We show that a previously unidentified source of urban PAHs, parking lot sealcoat, may dominate loading of PAHs to urban water bodies in the United States. Particles in runoff from parking lots with coal-tar emulsion sealcoat had mean concentrations of PAHs of 3500 mg/kg, 65 times higher than the mean concentration from unsealed asphalt and cement lots. Diagnostic ratios of individual PAHs indicating sources are similar for particles from coal-tar emulsion sealed lots and suspended sediment from four urban streams. Contaminant yields projected to the watershed scale for the four associated watersheds indicate that runoff from sealed parking lots could account for the majority of stream PAH loads.

Introduction

Concentrations of polycyclic aromatic hydrocarbons (PAHs)—a group of widely recognized aquatic contaminants (1) comprising numerous carcinogens (2)—have been increasing in recent decades in many urban lakes, particularly in areas undergoing rapid urban growth (3). PAHs adversely affect mammals (including humans), birds, fish, amphibians, invertebrates, and plants; in the aquatic environment, the effects of PAHs on invertebrates include inhibited reproduction, delayed emergence, sediment avoidance, and mortality, and the effects on fish include fin erosion, liver abnormalities, cataracts, and immune system impairments (4). Numerous sources of PAHs to urban runoff have been identified, including automobile exhaust, lubricating oils, gasoline, tire particles, erosion of street material, and atmospheric deposition (5–8), but uncertainty remains as to their relative importance. Investigations of urban sources of PAHs have thus far overlooked a potentially major source: parking lot sealants, also called “sealcoat”. Our objective in this study was to evaluate the contribution of PAHs from sealed parking lots to urban streams.

In the United States and Canada, sealcoat is applied to many parking lots and driveways in an effort to protect the

underlying asphalt pavement and enhance appearance. The two primary sealcoat materials on the market are refined coal-tar-pitch-based emulsion and asphalt-based emulsion. Although similar in appearance (glossy black), coal tar and asphalt have different molecular structures stemming from their origins: coal tar is a byproduct of the production of coke from coal, whereas asphalt is derived from the refining of crude petroleum. Coal tar, a known human carcinogen, is 50% or more PAHs by weight (2); the predominant constituents of asphalt are bitumens, complex mixtures of hydrocarbons that include asphaltenes, saturates, aromatics, and resins (9). Coal-tar-emulsion- and asphalt-emulsion-based sealcoats typically contain 20–35% of the emulsion.

Parking lot sealants are used extensively in the United States and Canada. Although national use figures are not available, the *Blue Book of Building and Construction* (10), a directory for the construction industry, lists over 3300 pavement sealant companies in 28 U.S. states. One company advertises the application of 1.7 billion liters to date worldwide (11), and another reports having sealed over 33 million square meters (12). The City of Austin, population 650000 (2000 census), estimates that about 2.5 million liters of sealcoat is used annually in this city (13).

Sealcoat abrades from the parking lot surface relatively rapidly, and reapplication is recommended every two to three years (14). In 2003, the City of Austin identified abraded parking lot sealcoat as a possible source of high concentrations of PAHs in streambed sediment (15). Here we present evidence suggesting that parking lot sealcoat could indeed be the dominant source of PAHs to watersheds with residential and commercial development.

Experimental Section

Sample Collection. We compared concentrations and yields of particulate PAHs in simulated runoff from parking lots sealed with coal-tar-based sealcoat, from lots sealed with asphalt-based sealcoat, and from unsealed asphalt and cement lots. Thirteen urban parking lots, representing a range of sealant types that are currently in use in Austin, TX, were sampled (Table 1). In addition, four test plots, each about 120 m², were sampled. Three of the test plots were sealed just prior to testing, and one was left unsealed (asphalt surface). The test plots are at the Robert Mueller Municipal Airport, Austin, TX, which has been closed since 1999. A full description of the sampling is given in ref 16. In brief, 50 m² areas of each parking lot and the test plots were sprinkled with 2 mm of distilled water (100 L over a 50 m² area) to simulate a light rain, and concentrations of PAHs were analyzed in particles filtered from the runoff. The study focused on the particulate fraction, as PAHs in urban runoff, particularly those of higher molecular weight, are mostly associated with particulates (7, 17); for selected samples (test plots and seven parking lots), the dissolved phase also was analyzed. The testing followed a minimum of 5 days with no rainfall. The parking lots were sampled once, and the test plots were sampled three times over a 6 week period. Water was sprayed from a plastic hand-held sprayer at a rate of about 7 L/min from a height of about 0.75 to 1 m. Spill berms were used at the down-slope end of the delineated area to gather water, which was then pumped into high-density polyethylene (HDPE) containers (Figure S1, Supporting Information). Recovery of water and observations about losses of water to wetting and leakage under the berms were noted. The water was returned to the laboratory, poured into a 50 L churn to keep the sample well mixed, and filtered through 0.45 μm pore size PTFE filters. The filters were

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TABLE 1. Sampling Site Characteristics

site name	surface type	date of sealant application	sampling date	study component
CT _{TP1}	coal-tar emulsion sealant	Aug 5-6, 2003	8/21/2003	test plot
CT _{TP2}	coal-tar emulsion sealant	Aug 5-6, 2003	8/21/2003	test plot
AS _{TP}	asphalt emulsion sealant	Aug 5-6, 2003	8/21/2003	test plot
UNAS _{TP}	unsealed asphalt pavement	Aug 5-6, 2003	8/21/2003	test plot
CT _{TP1}	coal-tar emulsion sealant		9/9/2003	test plot
CT _{TP2}	coal-tar emulsion sealant		9/9/2003	test plot
AS _{TP}	asphalt emulsion sealant		9/9/2003	test plot
UNAS _{TP}	unsealed asphalt pavement		9/9/2003	test plot
CT _{TP1}	coal-tar emulsion sealant		9/26/2003	test plot
CT _{TP2}	coal-tar emulsion sealant		9/26/2003	test plot
AS _{TP}	asphalt emulsion sealant		9/26/2003	test plot
UNAS _{TP}	unsealed asphalt pavement		9/26/2003	test plot
AS _{PL1}	asphalt emulsion sealant	June 2003	9/7/2003	parking lot
AS _{PL2}	asphalt emulsion sealant	June 2003	9/7/2003	parking lot
AS _{PL3}	asphalt emulsion sealant	July 2003	9/28/2003	parking lot
CT _{PL1}	coal-tar emulsion sealant	March 2003	9/7/2003	parking lot
CT _{PL2}	coal-tar emulsion sealant	July 2003	9/28/2003	parking lot
CT _{PL3}	coal-tar emulsion sealant	July 2003	9/28/2003	parking lot
CT _{PL4}	coal-tar emulsion sealant	July 2003	9/30/2003	parking lot
CT _{PL5}	coal-tar emulsion sealant	July 1999	9/30/2003	parking lot
CT _{PL6}	coal-tar emulsion sealant	Nov 2000	9/30/2003	parking lot
UNAS _{PL1}	unsealed asphalt pavement		9/8/2003	parking lot
UNAS _{PL2}	unsealed asphalt pavement		9/30/2003	parking lot
UNSCON _{PL1}	unsealed concrete pavement		9/8/2003	parking lot
UNSCON _{PL2}	unsealed concrete pavement		9/8/2003	parking lot

massaged inside locking bags to remove retained particles, as described in ref 18, and the recovered particulates were submitted as chilled slurries in clean glass vials to the U.S. Geological Survey National Water Quality Laboratory (NWQL) for analysis. In some cases the filtrate also was shipped, in chilled and clean amber glass bottles, to the NWQL for analysis of dissolved PAH. One or more samples of unfiltered water were collected from the churn for measurement of suspended sediment concentration (SSC), used to determine the mass of sediment recovered during each test. Although the 2 mm of simulated rain was not enough to wash off all of the mobile sediment, the recovered water was visibly clearer toward the end of each application. In samples from the five sites in which SSC was measured in the first 50 L and final 50 L of water, SSC decreased by a mean of 65% (range of 39-84%). We therefore assumed that the tests recovered most of the sediment that would be mobilized from the parking lot surfaces by a rain event, regardless of magnitude. Large, intense storms, however, likely would generate a higher yield of sediment.

The test plot and parking lot scrapings were obtained by scraping a small area (less than 0.25 m²) with a metal paint scraper. The particulates removed were brushed onto a piece of new cardstock and then into a cleaned glass jar. The paint scraper was cleaned between sites, and a new brush was used at each site. Scrapings were examined by light and electron microscopy (Figure S2, Supporting Information), and submitted to the NWQL for PAH analysis.

Computation of Yields. Losses of water to wetting and losses of water and sediment leaking under the berms were estimated. Recovery of water ranged from 19 to 85 L with a median of 58 L. The lowest recoveries were from flat, unsealed asphalt lots, and the highest recoveries were from sealed lots and cement lots with gentle slopes. On the basis of recoveries and field observations, it was concluded that about 18 L of water was retained on the surface of sealed lots and cement lots and that the remainder of the water loss was a result of leakage past the berms. It was assumed that no yield of

particles was associated with the water volume lost to surface wetting and that water leaking past the berms had the same SSC and contaminant levels as recovered water. For unsealed asphalt lots, the loss to wetting was estimated as 36 L for a maximum potential recovery of 64 L. Thus, to estimate the total yield of sediment from each lot, SSC was multiplied by the assumed maximum recovery (82 L for sealed and cement lots and 64 L for unsealed asphalt lots) to account for recovered water and leakage past the berms. Yields of PAH were estimated by multiplying the total yield of sediment times particle concentrations.

Chemical Analysis. Samples were prepared by extracting about 0.5 g dry weight of sample using pressurized solvent extraction at 120 and 200 °C with a mixture of water and isopropyl alcohol. The samples were extracted at each temperature at a pressure of 13800 kPa. Surrogate compounds were added to the sample prior to extraction to verify method recoveries. The extract was cleaned up using polystyrene divinylbenzene and Florisil solid-phase extraction cartridges. The extract was concentrated, solvent exchanged to ethyl acetate, and diluted to 10 mL. An internal standard mixture was added to an aliquot of the extract, and the extract was analyzed by full-scan gas chromatography/mass spectrometry (GC/MS). Difficult sample matrices were diluted before the full-scan analysis, and diluted surrogates were estimated in the samples.

Compound identifications were based on comparison of peak retention times and mass spectra to those of authentic standard compounds for the target compounds. Response factors were calculated for each compound from a set of calibration standards. Quantitation was carried out following the methods of Olson et al. (19). For PAHs in the particulate phase, the estimated method reporting limit (MRL) is 5 µg/kg for a 25 g sample. As less than 25 g was extracted, the MRL was raised accordingly, on a sample-by-sample basis. In some cases, MRLs were raised because of background interferences.

Dissolved-phase samples were analyzed following the method described by Fishman and Friedman (20), with the

difference that continuous liquid-liquid extraction was substituted for use of the separatory funnel. In brief, 1 L samples fortified with surrogate compounds were extracted by continuous liquid-liquid extraction for 6 h under acidic and then basic conditions. Internal standards were added and sample extracts concentrated to 1 mL. Samples were analyzed by GC/MS in electron impact mode. Sample identifications were made by matching retention times and mass spectra with those of standard compounds. Quantitation involved use of internal standards and calibration curves generated by standard compounds of known amounts.

Quality control (QC) consisted of environmental and internal laboratory samples. Two duplicate environmental samples for particulate analysis of PAH were collected. For one of the sets of duplicates, Σ PAH differed by 8%; for the second (which had Σ PAH > 4000 mg/kg), Σ PAH differed by 54%. In the equipment blank analyzed for dissolved PAH, three parent PAHs were detected at concentrations about half that of the environmental sample with the lowest concentrations, and less than 1% that of the environmental sample with the highest concentrations.

Laboratory QC samples for particulate PAH analyses consisted of analysis of spiked samples, blanks, and samples of certified reference material (CRM). The median recovery for the six spiked samples was 76%. For the six laboratory blanks, an analyte was detected in 85 of 336 possible cases. The detected concentrations ranged from 0.1% to 3.5% of that in the environmental sample with the lowest concentration for that analyte. For the two analyses of CRM, the recoveries were within the NWQL-established acceptable range for 83% of the cases.

Three commercially available asphalt-based emulsion sealcoat products and six coal-tar-based emulsion sealcoat products were analyzed at DHL Analytical, Round Rock, TX, using EPA method SW 8270 (21). In each case, the product sample was taken directly from the container. Concentrations of 16 parent PAHs were determined. The sealants analyzed were not necessarily the same as those applied to the test plots or on the parking lots in use, although there was some overlap (product AS_{PA} was used on test plot AS_{TP}; product CT_{PF} was used on test plot CT_{TP2}) (Table 2).

Results

Concentrations and yields of total particulate PAH and total dissolved PAH in the runoff and total PAH in the scrapings were computed and compared between parking lot surface types (Table 2). The total particulate PAH (Σ PAH) concentration was computed for each sample as the sum of naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[a]pyrene, and dibenz[ah]anthracene, which are the same as those used for the consensus-based sediment quality guidelines of MacDonald et al. (22). For unsealed parking lots (asphalt pavement and concrete combined), the mean Σ PAH was 54 mg/kg (range of 7.2–75 mg/kg), more than twice the probable effect concentration sediment quality guideline of 22.8 mg/kg (22) (Table 2), and in the range of those found by others in urban and roadway runoff (e.g. refs 23–25). However, the mean Σ PAH concentration from the asphalt-sealed parking lots was more than 10 times higher (mean of 620 mg/kg, range of 250–830 mg/kg) than that from unsealed parking lots, and the mean Σ PAH concentration from the coal-tar-sealed parking lots was 65 times higher (mean of 3500 mg/kg, range of 520–9000 mg/kg) (Table 2; complete concentration data are given in ref 16). Σ PAH concentrations in runoff from coal-tar-sealed lots were significantly higher than in runoff from other surface types (Kruskal-Wallis test of comparisons, hypothesis of no difference between groups rejected for $p < 0.05$). PAH concentrations from coal-tar-

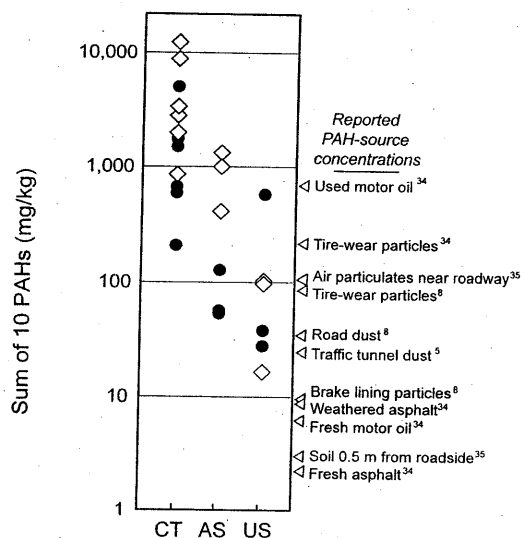


FIGURE 1. Sum of 10 PAHs (fluoranthene, pyrene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[ghi]perylene) in particles in runoff from simulated rainfall on coal-tar emulsion sealcoat (CT), asphalt emulsion sealcoat (AS), and unsealed cement and asphalt (US) parking lots (◇) and test plots (●). Parking lots were sampled once, and test plots were sampled three times. Concentrations for other PAH sources reported in the literature also are indicated. These 10 PAHs were summed for this graph to facilitate comparison between experimental and reported concentrations.

sealed lots also were much higher, in most cases by orders of magnitude, than PAH concentrations in other urban sources such as tire particles, motor oil, and weathered asphalt (Figure 1; note that this figure uses a different summation of PAH). Σ PAH concentrations in runoff from the sealed test plots were generally lower than those from the sealed parking lots, but the difference was not statistically significant, and concentrations from unsealed surfaces, with the exception of one outlier, were similar for test plots and parking lots.

Concentrations of Σ PAH in the scrapings ranged from 9500 to 83000 mg/kg for coal-tar-emulsion-sealed surfaces (including test plots) and from 110 to 2000 mg/kg for asphalt-emulsion-sealed surfaces (Table 2). Scrapings of two unsealed asphalt parking lots had Σ PAH concentrations of 7.1 and 20 mg/kg. Scrapings were observed under light and electron microscopy (Figure S2, Supporting Information).

Concentrations of total dissolved PAH (Σ PAH_{diss}, computed as the sum of the same PAHs as in Σ PAH excluding 2-methylnaphthalene; nondetections treated as zeros) for the test plots were about an order of magnitude greater in samples from the coal-tar-sealed test plots than concentrations in samples from the asphalt-sealed test plot, which in turn were about an order of magnitude greater than those from the unsealed test plot (Table 2). Nine of the 16 PAHs analyzed for were detected (complete data are in ref 16). Higher weight PAHs—benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]perylene, benz[a]anthracene, and dibenz[ah]anthracene—were not detected at laboratory reporting levels ranging from 1.7 to 3.4 μ g/L. Four PAHs (acenaphthylene, acenaphthene, chrysene, and fluorene) were detected only in runoff from the coal-tar-sealed test plots; anthracene was detected in runoff from all the sealed test plots but not from the unsealed site. A similar suite of PAHs were detected at those parking lots for which the filtrate was analyzed (Table 2; complete data are in ref 16).

Concentrations of Σ PAH in the commercially available sealant products and surface scrapings exceeded those of

TABLE 2. Concentrations of PAH in Washoff Samples, Scrapings, and Unapplied Sealcoat Product^a

	washoff samples		scrapings	product	
	Σ PAH, mg/kg	Σ PAH _{diss} , μ g/L	Σ PAH, mg/kg	Σ PAH(dry), mg/kg	
Test Plots					
CT _{TP} 1, 8/12/03		21	83000	CT _P A	34000
CT _{TP} 1, 8/21/03	1700	14		CT _P B	113000
CT _{TP} 1, 9/9/03	530			CT _P C	202000
CT _{TP} 1, 9/26/03	460	6.9		CT _P D	86000
				CT _P E	49000
				CT _P F	61000
CT _{TP} 2, 8/12/03		11	11000		
CT _{TP} 2, 8/21/03	1200	7.3		AS _P A	6600
CT _{TP} 2, 9/9/03	4000			AS _P B	1300
CT _{TP} 2, 9/26/03	140	3.8		AS _P C	300
AS _{TP} , 8/12/03		1.3	110		
AS _{TP} , 8/21/03	96	1.2			
AS _{TP} , 9/9/03	40				
AS _{TP} , 9/26/03	28	0.64			
UNSA _S _{TP} , 8/12/03		0.16			
UNSA _S _{TP} , 8/21/03	410	0.34			
UNSA _S _{TP} , 9/9/03	25				
UNSA _S _{TP} , 9/26/03	14	0.17			
Parking Lots					
CT _{PL} 1	2000	NA	25000		
CT _{PL} 2	9000	5.4	15000		
CT _{PL} 3	2000	7.1	11000		
CT _{PL} 4	1300	12	9500		
CT _{PL} 5	520	2.3	9900		
CT _{PL} 6	5900	16	17000		
AS _{PL} 1	250	NA	340		
AS _{PL} 2	830	NA	2000		
AS _{PL} 3	770	5.1	420		
UNSCON _{PL} 1	75	NA	NA		
UNSCON _{PL} 2	69	NA	NA		
UNSA _S _{PL} 1	64	NA	7.1		
UNSA _S _{PL} 2	7.2	0.24	20		

^aSums are as defined in the text. NA = not analyzed, CT = coal-tar-based emulsion, AS = asphalt-based emulsion, UNSAS = unsealed asphalt pavement, and UNSCON = unsealed concrete pavement.

the particulates in the washoff. Concentrations of Σ PAH in commercially available coal-tar-based sealcoat products ranged from 3.4 to 20 wt %, compared to 0.03 to 0.66 wt % for asphalt-based sealcoat products analyzed (Table 2; complete data in Table S1, Supporting Information).

Yields of Σ PAH (mass of Σ PAH per unit area of parking lot) computed for the simulated rainfall followed patterns similar to those of concentrations. Complete data for yields can be found in Table S2 in the Supporting Information. As with the concentrations, there was a wide range in the yields for a given surface type, in most cases more than an order of magnitude. The mean yield from coal-tar-sealed lots exceeded that from asphalt-sealed lots by more than a factor of 2, although this difference was not statistically significant (Kruskal-Wallis test of comparison, $p < 0.05$). However, the mean yield from sealed lots (asphalt and coal tar combined) exceeded that from unsealed lots by a factor of 50, and the difference was statistically significant.

Discussion

Runoff from parking lots typically is contaminated with PAHs from leaking motor oil, tire particles, vehicle exhaust, and atmospheric fallout, and it is not surprising that the mean concentration of Σ PAH in particles washed off each of the different surface types exceeded the probable effect sediment quality guideline. However, the large differences between

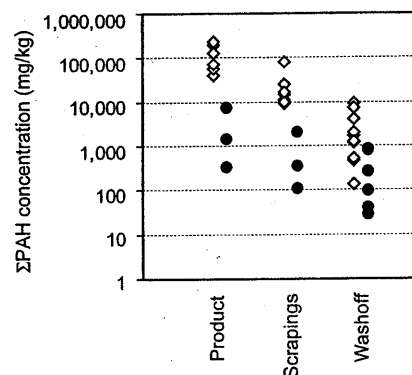


FIGURE 2. Comparison of Σ PAH concentrations in commercially available sealcoat products, scrapings from parking lots, and particles in washoff from parking lots for coal tar (\diamond) and asphalt (\bullet) based sealants.

concentrations for the different surface types suggest that abraded sealant products are a potentially important (and heretofore unrecognized) contributor to PAH contamination in urban and suburban water bodies.

Comparison of Medium, Aging, and Vehicle Use on Concentrations and Yields. For both coal-tar- and asphalt-emulsion-based sealants, the Σ PAH concentration decreased from the unapplied sealant products to the scrapings to the washoff samples, as did the difference in concentration between the coal-tar-based and asphalt-based sealant samples (Figure 2). The difference in the median Σ PAH concentration between the coal-tar-based and asphalt-based sealants was 70-fold for the products analyzed and decreased to 40-fold for the scrapings and to a factor of about 8 for the washoff samples. Although the chemical changes between the product pre- and postapplication were not the focus of this study, the decrease in Σ PAH concentrations from the scrapings to the washoff particulates and the magnitude of the difference between the coal-tar-sealed lots and the asphalt-sealed lots can be attributed to dilution of abraded particles with less contaminated street dust and the greater abrasion of the asphalt-sealed compared to the coal-tar-sealed surfaces. A simple mass balance, assuming dilution of the coal tar scrapings (median Σ PAH concentration of 13000 mg/kg) by street dust (median Σ PAH concentration of 50 mg/kg) at a proportion of 1 part abraded particles to 7 parts street dust, results in the concentration found in the washoff. If the proportion of abraded particles is increased for the asphalt lots on the basis of the increased yields measured for asphalt-sealed lots (assuming that the greater median particle yield of 320 mg/m² from asphalt-sealed lots versus 200 mg/m² from coal-tar-sealed lots results from increased abrasion), the concentration found in the washoff from asphalt-sealed lots is well approximated.

The effect of aging of sealants on concentration over the short term (7 weeks) was evident at the test plots (Figure 3a). Overall, the concentration of Σ PAH and Σ PAH_{diss} in the washoff from each test plot decreased over the 7 week period following application. In one instance (CT_{TP}2, second sampling of washoff) Σ PAH exceeded that previously sampled, but in all cases the concentration at the end of the period was less than that at the beginning. The PAH assemblage changed over the same period as well, as represented by a comparison of higher molecular weight (MW) to lower MW PAHs. In the particulate samples the ratio of higher MW PAHs (represented by benzo[a]pyrene + chrysene) to the lower MW PAHs (represented by fluorene + phenanthrene; these two PAHs were chosen as they were detected in most of the samples) increased at all of the sealed test sites. As the lower MW PAHs are more volatile and soluble than the higher MW PAHs, volatilization and leaching of the lower MW PAHs

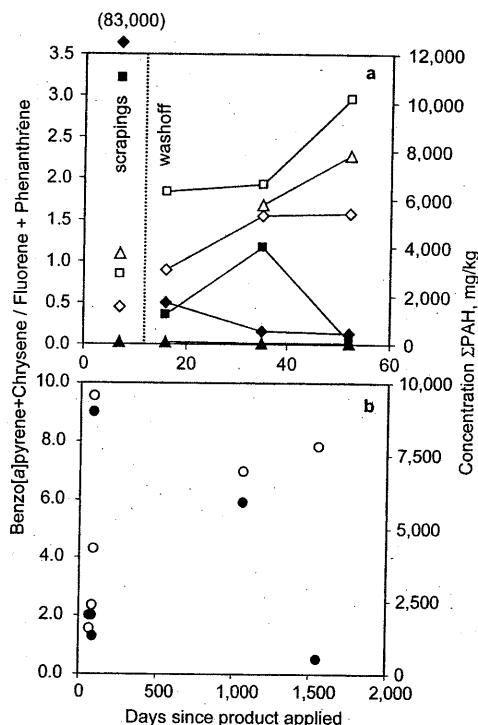


FIGURE 3. ΣPAH concentrations (closed symbols) and PAH ratios of higher and lower molecular weight PAHs (open symbols) (a) in scrapings and particles washed off coal-tar-sealed test plots (□, ◇) and an asphalt-sealed plot (△) and (b) as they relate to the age of coal-tar sealant in samples from parking lots in use.

from the newly applied sealant might be responsible for some of the decrease in concentration. For the parking lots, only coal-tar-sealed lots represented a range of ages, and for these lots there was no relationship between concentration or higher MW to lower MW PAH ratio and age of the sealant (Figure 3b). This might be because the parking lots were each sampled only once; the very wide range in PAH content between products, even those of a similar kind, may mask the effect of aging when time-series data are not available. Although the data are limited, they suggest that lots with older sealant tend to have a higher ratio of higher MW to lower MW PAHs, and that that ratio may reach a plateau after a period of time.

Comparison of the yields from the parking lots to those from the test plots, which receive no vehicle traffic, demonstrates the importance of abrasion of sealcoat by vehicles on ΣPAH yield: the mean ΣPAH yield was 20 and 160 times greater for the coal-tar-sealed and asphalt-sealed parking lots, respectively, than for the analogous test plots. This does not appear to be attributable to use patterns, although traffic counts were not made: the coal-tar-sealed lots are a mix of lots in constant use throughout the day (e.g., shopping center) and those with all-day parking (e.g., office), which are assumed to receive less use than those in constant use; all of the asphalt-sealed lots are all-day parking.

Environmental Implications. Given the extremely elevated concentrations of PAHs in particles washed from sealed parking lots, how important is this contribution to the total mass of PAHs in urban streams? To answer this question, we compared the PAH assemblages and estimated PAH loads associated with particulates in parking lot runoff to those associated with suspended sediment collected during storm flow in four streams: Williamson Creek (Austin, TX) (18) and influent streams to Echo Lake, Fosdic Lake, and Lake Como (Fort Worth, TX) (26). These four streams are in highly urbanized watersheds (land use for the Austin watershed is about 65% urban, and for the three Fort Worth

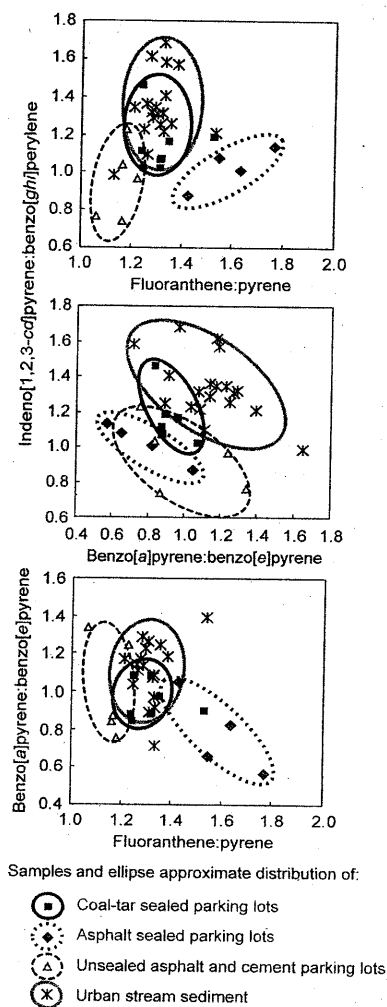


FIGURE 4. Comparison of indicator ratios of PAHs in particles washed from parking lots with coal-tar emulsion sealcoat, asphalt emulsion sealcoat, and unsealed asphalt pavement and concrete pavement, and in suspended sediment collected from four urban streams after storms.

watersheds is more than 90% urban; full land use is given in Table S3, Supporting Information); the streams are ephemeral, and urban runoff is assumed to comprise a large component of storm flow.

PAHs comprise a large group of compounds, and PAH assemblage is often used to infer PAH sources (27). Differences in PAH assemblages can be investigated by computing the ratios of selected PAHs (28, 29). The best indicator ratios of coal tar as a PAH source have been identified as fluoranthene:pyrene, indeno[1,2,3-cd]pyrene:benzo[ghi]perylene, and benzo[a]pyrene:benzo[e]pyrene (30, 31). In graphs that combine these ratios, similarities and differences between parking lot and stream samples are apparent (Figure 4): ratios in the urban stream sediment group match those in runoff from coal-tar-sealed lots more closely than they do those from asphalt-sealed lots and from unsealed lots (asphalt and cement). We found these ratios were far more effective at distinguishing between the different parking lot samples and stream samples than ratios indicative of combustion versus noncombustion sources, or other approaches such as comparison of parent compound distribution (32). Although alkylated PAH homologues were analyzed (including C1-C5 homologues of the MW 128, 178, 202, 228, and 252 PAHs), their interpretation did not assist in discriminating between PAHs from the different parking lot surfaces.

The relative amount of similarity between groups of samples, as defined by the ratios, was quantified through

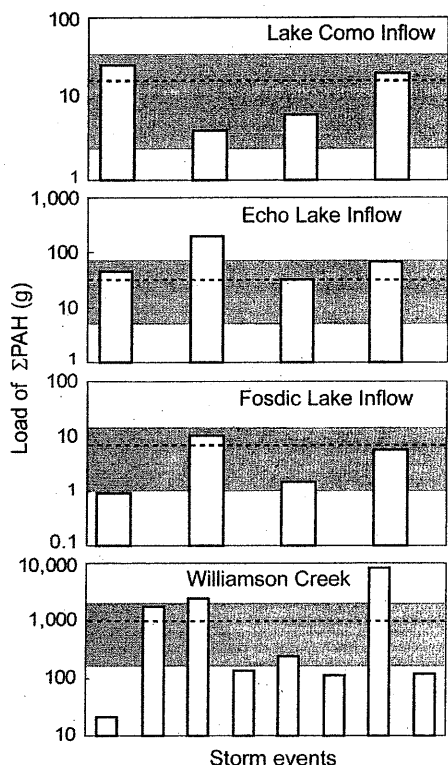


FIGURE 5. Comparison of estimated event loads of Σ PAH from sealed parking lots and measured instream storm-event loads for four urban watersheds. The interquartile range of estimated loads is shown in gray shading, on the basis of 25th and 75th percentile yields computed for sealed parking lots; the mean estimated load is indicated by a dashed line. Measured instream loads for four to eight individual events are shown as bars.

discriminant function analysis. In discriminant function analysis, each significant independent variable adds to discrimination between multiple groups. The three ratios (fluoranthene:pyrene, indeno[1,2,3-*cd*]pyrene:benzo[*ghi*]perylene, and benzo[*a*]pyrene:benzo[*e*]pyrene) were entered into the analysis as the independent variables, with the different types of samples (coal-tar-emulsion-sealed lots, asphalt-emulsion-sealed lots, unsealed lots, and urban stormflow stream sediments) defining four groups of dependent variables. All three variables were shown to contribute significantly to discrimination between the groups ($p < 0.001$). The distances between the centroids of the groups were determined by computing the squared Mahalanobis distance, which is a measure of the distance between two points in the space defined by two or more correlated variables. The centroid of the group defined by the suspended sediment from urban streams is closest to the centroid of the coal-tar-based sealant group, next closest to that of the unsealed lot group, and farthest from that of the asphalt-based sealant group (squared Mahalanobis distances of 5.7, 13.0, and 25.0, respectively). Thus, on the basis of the three ratios diagnostic of coal-tar sources, the PAH assemblage of the suspended sediment from the urban streams most closely resembles that of the coal-tar-based sealant group, supporting the hypothesis that coal-tar-based sealants are an important source of PAHs in urban streams.

Moving to a mass-balance approach at the watershed scale for each of the four urban watersheds, we compared measured storm-event stream loads of Σ PAH to those estimated to be contributed by sealed parking lots. Digital land-use maps that included parking lots were provided by the Cities of Austin and Fort Worth and were updated using recent aerial photography and site inspections. Sealed and

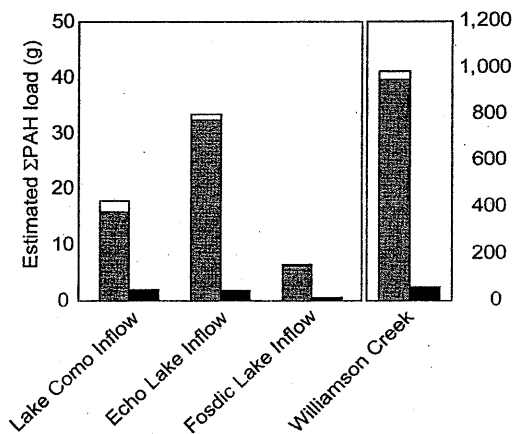


FIGURE 6. Comparison of event loads of Σ PAH for four urban watersheds estimated for parking lots in their current (2004) state (sealed by gray bars and unsealed by white bars) and projected loads if all existing parking lots were unsealed (black bars). Loads were estimated on the basis of the yields from the runoff experiments and the area of parking lots in each watershed.

unsealed lots were identified by site inspection. We computed the hypothetical storm-event load generated by sealed parking lots in each watershed by multiplying the mean yield for sealed parking lots (coal-tar and asphalt emulsion sealcoat combined) determined from the runoff experiments by the sealed parking lot area of each watershed. We assumed that the 2 mm of water applied for the field tests mobilized all available particles, and that all runoff from parking lots entered storm sewers and was delivered to the stream. Although there is substantial variation in event loads for each stream (18, 26), for all four watersheds the estimated Σ PAH loads contributed by sealed parking lots are similar in magnitude to measured stream loads, even though sealed parking lots cover only 1–2% of each watershed (Figure 5). These results might explain why an investigation carried out in Marquette, MI, found that runoff from commercial parking lots contributed 64% of the PAH load to the urban watershed studied (33).

What would be the effect on PAH loading to these watersheds if parking lots were not sealed? For each of the four watersheds, we compared the Σ PAH load contributed by parking lots (computed on the basis of the aerial extent of unsealed and sealed parking lots) to that obtained by applying the average yield for unsealed lots to all parking lots (Figure 6). We estimate that the Σ PAH load from parking lots in these watersheds would be reduced to 5–11% of the current loading if all lots were unsealed.

With the exception of the sealcoat itself, unsealed parking lots receive PAHs from the same urban sources as do sealed parking lots—e.g., tire particles, leaking motor oil, vehicle exhaust, atmospheric fallout—yet the average yield of PAHs from sealed parking lots is 50 times greater than that from unsealed lots. PAH assemblages and estimated loads further suggest that sealed parking lots could be dominating PAH loading in watersheds with commercial and residential land use. The implications of these results extend beyond Texas to the rest of the United States and Canada, where parking lot sealcoat is used extensively, and to other countries where sealcoat is being introduced. Previously identified urban sources of PAHs, such as automobile exhaust and atmospheric deposition, have been difficult to control or even quantify because of their nonpoint nature. In contrast, sealed parking lots are point sources, and use of the sealant is voluntary and controllable.

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Supporting Information Available

Two figures and three tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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