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Contributions of Common Sources of Polycyclic Aromatic Hydrocarbons to Soil Contamination

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Asphalt products, particularly sealants, are prepared using petroleum products that contain a complex mixture of aliphatic and aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs). Clearly, these products are ubiquitous in urban environments, which raises an issue regarding the potential for PAHs to be transported from parking lots to underlying or adjacent soil, surface-water bodies, or groundwater. Based on a literature review, there are limited studies focusing on this issue; however, the studies that have been published have fascinating conclusions. The literature shows, as expected, that asphalt-based products contain PAHs. The highest PAH concentrations are present in asphalt sealants, particularly those manufactured using coal tar. Furthermore, due to the low solubility and high partition coefficients of PAHs, the potential for PAHs to leach from asphalt surfaces is negligible, which has been confirmed by leachability studies. Thus, there is little risk that PAHs will be present in stormwater runoff or leach into groundwater from asphalt-paved areas in a dissolved form. However, asphalt pavement and sealants produce particulate matter that can contain concentrations of PAHs in the sub-percent range (100s to 1,000s mg/kg total PAHs) that is transported in stormwater runoff. Some studies show that this can cause soil and sediment contamination with total PAH concentrations in the range of 1 to 10 mg/kg. From a remediation perspective, many site cleanups are conducted to remediate the presence of PAHs to cleanup goals below 1 mg/kg or, in some cases, 0.1 mg/kg or lower. From a total risk perspective, remediating sites to low PAH cleanup goals may be unwarranted in light of the risk of transportable PAHs produced from paved parking surfaces. In other words, is it reasonable to conduct a cleanup to remediate low PAH concentrations and then redevelop the area with asphalt pavement and sealant, which may pose a greater PAH-related risk? © 2006 Wiley Periodicals, Inc.

INTRODUCTION

One of the most common contaminant classes at hazardous sites is polycyclic aromatic hydrocarbons (PAHs). A significant amount of research has been devoted to the toxicity of PAHs (Agency for Toxic Substances and Disease Registry [ASTDR], 1995), and many PAHs are considered known or suspected carcinogens or otherwise exhibit acute or chronic toxicity characteristics. This has prompted many states to develop cleanup standards for PAHs in soil and groundwater. Fortunately, most PAHs are relatively immobile, and cleanup is generally only triggered for soil or when the presence of undissolved petroleum-type products are present as nonaqueous phase liquids (commonly referred to as NAPLs). However, there is an interesting paradox related to remediating PAHs present in soil in that these same chemicals are present in asphalt products and other building products, such as roofing tar. It is not unusual for significant remediation,

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generally in the form of excavation, to be conducted, only to be followed by the placement of sealed asphalt pavement containing the same general PAHs as the excavated soil. Based on this concern, the authors conducted a literature search on the presence of PAHs in asphalt, asphalt sealers, and other building products. In addition, the research included the potential for PAHs to leach through asphalt or migrate in stormwater runoff, thereby effectively contaminating the same sites that recently were remediated. The literature search findings support that remediating sites to remove low concentrations of PAHs may not be beneficial from a risk perspective, because the site conditions would not be measurably improved if the site is paved in the future due to the presence of PAHs in asphalt and asphalt sealants.

Globally, the largest source of PAHs in surface water and soil is from the deposition of airborne PAHs from combustion sources.

Although this article is not intended to provide an exhaustive analysis of the chemical properties and toxicity of PAHs, it begins with a basic overview of PAH properties, since an understanding of the properties, particularly those related to the fate and transport of PAHs, is important relative to the subject. This is followed by a review of remediation goals and technologies commonly employed at sites with PAH contamination. Then, a literature review of studies researching the content and leachability of PAHs in asphalt and related sealants is presented. The article culminates with a summary and recommendations for further research.

OVERVIEW OF PAH SOURCES AND PROPERTIES

PAHs, also known as polynuclear aromatics (PNAs), are a group of over 100 organic compounds composed of carbon and hydrogen in different fused-ring structures. By definition, PAHs contain two or more benzene rings (six-sided rings with three double carbon bonds), but may also contain additional fused rings that are not six-sided. PAHs are found naturally in coal and crude oil. PAHs generally occur as complex mixtures rather than single compounds; however, some PAHs are manufactured as individual compounds for research purposes or for use in medicines, dyes, plastics, and pesticides (ATSDR, 1995).

Sources of PAHs Released to the Environment

Most PAHs released to the environment are emitted to the atmosphere. Anthropogenic sources release significantly more PAHs than natural sources and include the burning of common fuels, such as coal, oil, gas, and wood, and other organic materials, such as garbage, tobacco, and grilled meat. The residential burning of wood is the single largest source of atmospheric PAHs (ATSDR, 1995). Forest fires and volcanoes are the largest natural sources. Most PAHs present in the atmosphere are sorbed to solid particulates with a lesser amount present in the vapor phase. Emissions from stationary sources, such as industrial power generators, incinerators, and the production of coal tar, coke, and asphalt, account for approximately 80 percent of total PAH emissions. Mobile sources, predominantly exhaust from gas- and diesel-powered vehicles, account for the remaining 20 percent. The composition of PAH emissions varies significantly depending on the combustion source (ATSDR, 1995).

Globally, the largest source of PAHs in surface water and soil is from the deposition of airborne PAHs from combustion sources (ATSDR, 1995); however, in local environments, the largest contribution of PAHs may come from stormwater runoff from sealed roads and parking areas. In addition to the combustion products listed above, PAHs are

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found in significant concentrations in materials associated with parking lots and roadways, including asphalt, asphalt sealants, new and used motor oil, tire dust, and brake-lining particles. As presented in this article, recent research has also shown stormwater runoff from sealed asphalt surfaces to be a significant source of PAHs to surface waters and soils, and subsequently sediments. With approximately 61,000 square miles of roads and parking lots in the United States, the potential impacts to local environments surrounding roads and parking lots are substantial (http://www.grist.org/news/maindish/2001/03/01/rice/).

Physical and Chemical Properties

The fate and transport of PAHs released to the environment are largely dependent on the physical and chemical properties of the individual PAHs, such as water solubility, vapor pressure, Henry's Law constants, the octanol-water partitioning coefficient (K_{ow}), and the organic carbon partitioning coefficient (K_{oc}). Vapor pressure and Henry's Law constants indicate the chemical's potential to volatilize when in its pure form or dissolved in water. The K_{ow} value provides an indication of the potential for the organic compound to partition from water into lipids and provides a correlation for bioconcentration in aquatic organisms. The K_{oc} value indicates a compound's potential to bind to organic carbon in soils and sediments. Generally, as a group, PAHs have relatively low water solubilities, vapor pressures, and Henry's Law constants and high K_{ow} and K_{oc} values. Exhibit 1 summarizes these properties for the 17 PAHs profiled in the landmark study completed by the ATSDR in 1995. These PAHs were selected for the ATSDR study because they have relatively high levels of toxicity and exposure and, as a group, are generally representative of the harmful effects of PAHs. Seven of the PAHs, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene, are classified by the US EPA as probable human carcinogens (ATSDR, 1995).

With approximately 61,000 square miles of roads and parking lots in the United States, the potential impacts to local environments surrounding roads and parking lots are substantial.

Environmental Fate and Transport

As shown in Exhibit 1, the properties that primarily control fate and transport in the environment roughly correlate to the molecular weights of the PAH compounds. These properties span several orders of magnitude. Based on molecular weight, the PAHs can be categorized into three groups (low, medium, and high), with similar physical and chemical behaviors within each group. The molecular weight categories correspond to two or three benzene rings (low), four benzene rings (medium), and five or more benzene rings (high).

PAHs in the atmosphere are either in the vapor phase or sorbed to particulates. Generally, low molecular weight PAHs are found predominantly in the vapor phase, medium molecular weight PAHs are found in both the vapor phase and bound to particulates, and high molecular weight PAHs are found predominantly bound to particulates (ATSDR, 1995). Atmospheric residence time, transport distance, and wet and dry deposition largely depend on the distribution of particle sizes to which the PAHs are sorbed.

Because of their low water solubility and high affinity for organic carbon (high K_{oc} values), PAHs in surface waters are typically found sorbed to particles either settled at the bottom (sediments) or suspended in the water. Studies have estimated that

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Exhibit 1. Physical and chemical properties of PAHs

Compound	Molecular Weight	Solubility (μg/L)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m^3/mol)	Log K_{ow}	Log K_{oc}
Low MW (2–3 Rings)						
Acenaphthylene	152.20	3,930	2.9E-02	1.45E-03	4.07	1.40
Acenaphthene	154.21	1,930	4.5E-03	7.91E-05	3.98	3.66
Fluorene	166.20	1,680–1,980	3.2E-04	1.00E-04	4.18	3.86
Anthracene	178.20	76	1.7E-05	1.77E-05	4.45	4.15
Phenanthrene	178.20	1,200	6.8E-04	2.56E-05	4.45	4.15
Medium MW (4 Rings)						
Fluoranthene	202.26	200–260	5.0E-06	6.50E-06	4.90	4.58
Pyrene	202.30	77	2.5E-06	1.14E-05	4.88	4.58
Benzo(a)anthracene*	228.29	10	2.2E-08	1.00E-06	5.61	5.30
Chrysene*	228.30	2.8	6.3E-07	1.05E-06	5.16	5.30
High MW (≥ 5 Rings)						
Benzo(a)pyrene*	252.30	2.3	5.6E-09	4.90E-07	6.06	6.74
Benzo(b)fluoranthene*	252.30	1.2	5.0E-07	1.22E-05	6.04	5.74
Benzo(e)pyrene	252.30	6.3	5.7E-09	NA	NA	NA
Benzo(k)fluoranthene*	252.30	0.76	9.6E-11	3.87E-05	6.06	5.74
Benzo(j)fluoranthene	252.32	6.76	1.5E-08	1.00E-06	6.12	4.7–4.8
Indeno(1,2,3-c,d)pyrene*	276.30	62	1.0E-11–1.0E-06	6.95E-08	6.58	6.20
Benzo(g,h,i)perylene	276.34	0.26	1.0E-10	1.44E-07	6.50	6.20
Dibenz(a,h)anthracene*	278.35	0.5	1.0E-10	7.30E-08	6.84	6.52

MW = molecular weight; NA = no data available.

* Classified by the US EPA as a probable human carcinogen.

Note: Table adapted from Table 3-2 of the 1995 ATSDR study.

roughly two-thirds of PAHs in surface waters are bound to particles, with the remaining one-third dissolved in water (Eisler, 1987). Previous estuary studies have demonstrated that volatilization and biodegradation are the primary removal mechanisms for low molecular weight PAHs, while volatilization and adsorption to sediments are the primary removal mechanism for medium and high molecular weight PAHs (Readman et al., 1982).

In subsurface soils, PAHs are relatively immobile due to their low water solubility and high affinity for organic carbon. Limited leaching and migration in groundwater can be attributed to movement of the dissolved fraction in water and the sorption of PAHs onto mobile colloidal particles. PAHs sorbed to surface soil particles are subject to significant transport via stormwater runoff and erosion.

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REMEDIAL GOALS AND CLEANUP TECHNOLOGIES FOR PAH CONTAMINATION

Exhibit 2 presents the soil US EPA Region 9 Preliminary Remediation Goals (PRGs) and soil cleanup criteria from the states of Connecticut, Michigan, and New York for the most commonly regulated PAHs. These criteria were selected as examples of typical standards and demonstrate the variance in cleanup criteria across different jurisdictions. The values shown for US EPA Region 9 PRGs, Connecticut, and Michigan include both residential direct contact criteria and protection of groundwater criteria. In Technical and Administrative Guidance Memorandum 4046, New York State presents one recommended soil cleanup goal that takes into account both direct contact exposure and protection of groundwater. Exhibit 3 presents groundwater and protection of surface-water criteria from the same regulatory agencies, as well as the federal EPA maximum contaminant levels (commonly referred to as MCLs).

As shown in Exhibit 2, direct contact criteria are higher than protection of groundwater criteria for most PAHs, with differences of up to four orders of magnitude. Considerable variance also exists in cleanup criteria across the different jurisdictions, with Michigan having significantly higher standards for most compounds. Interestingly, protection of groundwater criteria has not been established for many of the higher molecular weight PAHs, likely because of their limited potential to leach due to a high affinity for organic carbon in soils and low water solubilities.

For comparison, Exhibit 2 also presents the ranges of PAH concentrations detected in commercially available parking lot sealants. These concentrations were measured during a study conducted by the City of Austin and the U.S. Geologic Survey (USGS) that included six coal tar–based sealants and three asphalt-based sealants (City of Austin, 2005). This study is summarized in more detail below. Generally, the coal tar–based sealants contained significantly higher concentrations of PAHs compared to the asphalt-based sealants. Both types of sealants, however, contained PAH concentrations above the soil cleanup criteria shown. For many of the PAHs, the concentrations detected in both types of sealants were many orders of magnitude higher than the soil criteria. For example, benzo(a)pyrene, a probable human carcinogen, was detected at maximum concentrations of 347 mg/kg in the asphalt-based sealants and 11,100 mg/kg in the coal tar–based sealants. In comparison, the presented cleanup criteria for benzo(a)pyrene ranged from 0.06 to 8 mg/kg. The lowest cleanup criterion (0.06 mg/kg) is six orders of magnitude lower than the highest detected concentration in the sealants (11,100 mg/kg). This illustrative example demonstrates the nonsensical situation that often develops in the environmental field, where regulatory agencies require soil remediation of PAHs under and around active parking lots coated with these types of sealants.

Common remedial technologies for PAHs in soils include bioremediation, stabilization, steam and thermal heating, and excavation and offsite disposal.

Common remedial technologies for PAHs in soils include bioremediation, stabilization, steam and thermal heating, and excavation and offsite disposal. Of these, excavation and offsite disposal as nonhazardous waste is by far the most common approach. In some instances, the excavated soil may be recycled for use in asphalt batch plants. The wide variance in physical and chemical properties, coupled with the tendency for the PAHs to be present in complex mixtures, prohibits the application of many *in situ* remedial technologies. For groundwater remediation of PAHs, common technologies include *in situ* bioremediation, *in situ* chemical oxidation, containment, groundwater extraction

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Exhibit 2. Example soil cleanup criteria and PAH concentrations in parking lot sealants

	US EPA Region 9 PRGs[a]		Connecticut[b]		Michigan[c]		New York[d]	Austin Study[e]	
Compound	**Residential Direct Contact**	**Migration to Groundwater**	**Residential Direct Contact**	**Groundwater GA, GAA Mobility**	**Residential Direct Contact**	**Drinking Water Protection**	**Recommended Soil Cleanup Objective**	**Coal Tar–Based Sealants**	**Asphalt-Based Sealants**
Low MW (2–3 Rings)									
Acenaphthylene	NE	NE	1,000	8.4	1,600	5.9	41	ND	ND–0.23
Acenaphthene	3,682	570	NE	NE	41,000	300	50	1,590–9,230	12.1–222
Fluorene	2,747	560	1,000	5.6	27,000	390	50	1,340–7,860	13–266
Anthracene	21,896	12,000	1,000	40	230,000	41	50	2,020–11,800	17–364
Phenanthrene	NE	NE	1,000	4	1,600	56	50	8,420–49,600	60.7–1,700
Medium MW (4 Rings)									
Fluoranthene	2,294	4,300	1,000	5.6	46,000	73	50	6,830–41,300	50.4– 1,510
Pyrene	2,316	4,200	1,000	4	29,000	48	50	5,240–32,200	49.6–1,100
Benzo(a)anthracene*	0.62	2.0	1	1	20	NE	0.224	1,710–9,950	13–422
Chrysene*	62.1	160	NE	NE	2,000	NE	0.4	1,710–10,100	22.2–427
High MW (≥ 5 Rings)									
Benzo(a)pyrene*	0.06	8.0	1	1	2	NE	0.061	1,840–11,100	16.2–347
Benzo(b)fluoranthene*	0.62	5.0	1	1	20	NE	1.1	1,650–9,260	35.2–314
Benzo(e)pyrene	NE	NE	NE	NE	NE	NE	NE	NA	NA
Benzo(k)fluoranthene*	6.2	49	8.4	1	200	NE	1.1	1,120–6,880	ND–297
Benzo(j)fluoranthene	NE	NE	NE	NE	NE	NE	NE	NA	NA
Indeno(1,2,3-c,d)pyrene*	0.62	14	NE	NE	20	NE	3.2	1,000–5,920	ND–135
Benzo(g,h,i)perylene	NE	NE	NE	NE	2,500	NE	50	1,280–7,660	ND–140
Dibenz(a,h)anthracene*	0.06	2.0	NE	NE	2	NE	0.014	ND– 670	ND

Note: All criteria shown in units of mg/kg.

MW = molecular weight; NA = not available; ND = not detected above reporting limit; NE = criterion not established.

* Classified by the US EPA as a probable human carcinogen.

[a] EPA Region 9 Preliminary Remediation Goals. Migration to groundwater criteria shown for a dilution attenuation factor of 20.

[b] Connecticut Remediation Standard Regulation.

[c] Michigan Part 201 Generic Cleanup Criteria and Screening Levels.

[d] New York Technical and Administrative Guidance Memorandum (TAGM) 4046

[e] Range of concentrations in commercially available sealants: six coal tar–based and three asphalt-based (City of Austin, 2005).

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and treatment, and thermally enhanced groundwater extraction and treatment (Federal Remediation Technologies Roundtable [FRTR], 2006).

THE PRESENCE OF PAHS IN ASPHALT PRODUCTS

Asphalt binder is produced from the fractional distillation of crude oil. It contains a mixture of aliphatic hydrocarbons, substituted benzenes, and PAHs. Asphalt binder is used to bind aggregate materials to form pavement. In most pavement formulations, the asphalt only comprises 4.5 to 12 percent of the pavement, with the remainder consisting of stone aggregate and mineral filler. Unsealed asphalt pavement is prone to degradation when it is exposed to petroleum products, such as gasoline, diesel fuel, and motor oil, and also other common materials, such as salts. This poses a greater problem in areas with low traffic, such as parking lots, where these materials tend to accumulate without the heavy traffic to disburse them. In the 1950s, the asphalt industry determined that pavement could be preserved by placing a protective sealant on top of the asphalt. This sealant was produced from coal tar and was less susceptible to dissolution because it is composed predominately of closed-ring compounds (PAHs) instead of the aliphatic hydrocarbons present in gasoline, diesel fuel, and motor oil. Recently, another type of sealant with an asphalt base has been introduced. These sealants have an asphalt emulsion formulation that incorporates a soap emulsion or clay-stabilized emulsions. The asphalt-based sealants are easier to handle than coal tar–based sealants because they are relatively odorless and do not irritate the skin upon contact. An excellent, yet brief, description of asphalt and asphalt sealants is available at www.pavementpro.org/understanding.htm.

City of Austin, Texas, and U.S. Geological Survey Studies

The City of Austin has been working closely with the USGS for several years in evaluating the contribution of PAHs to surface-water bodies (City of Austin, 2005). Part of this research involved collecting samples of sealants and asphalt pavement to ascertain the concentration of PAHs in various paving scenarios. In the studies, three types of samples were collected related to measuring the concentration of PAHs in pavement:

1. Different types of coal tar–based and asphalt-based sealant products;
2. Dried material samples of sealants; and
3. Samples of scrapings from used and unused parking lots, including parking lots sealed with asphalt-based and coal tar–based sealants, and unsealed lots.

The asphalt-based sealants are easier to handle than coal tar–based emulsion because they are relatively odorless and do not irritate the skin upon contact.

The above testing showed that the majority of the PAH content is related more to the sealant than the asphalt itself. Furthermore, the coal tar–based sealants had PAH concentrations three orders of magnitude higher than the asphalt-based sealants (average concentrations of greater than 50,000 mg/kg for the coal tar–based sealants compared to approximately 50 mg/kg for the asphalt sealants). This result was expected based on the higher concentrations of closed-ring compounds in coal tar than asphalt.

Test results for the samples of asphalt pavement scrapings showed somewhat lower concentrations of PAHs than the product samples, indicating that some of the PAHs were likely lost to volatilization during application; however, the total PAH concentrations are still notable (a median of approximately 18,000 mg/kg for the coal tar–based

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Exhibit 3. Example groundwater cleanup criteria for PAHs

Compound	MCL[a]	US EPA Region 9 PRGs Tap Water[b]	Connecticut[c] Groundwater Protection	Connecticut[c] Surface-Water Protection	Michigan[d] Groundwater Protection	Michigan[d] GSI Protection	New York[e] Groundwater Protection
Low MW (2–3 Rings)							
Acenaphthylene	NE	NE	420	0.3	52	NE	20
Acenaphthene	NE	365	NE	NE	1,300	19	20
Fluorene	NE	243	280	140,000	880	12	50
Anthracene	NE	1,825	2,000	1,100,000	43	NE	50
Phenanthrene	NE	NE	200	0.077	52	2.4	50
Medium MW (4 Rings)							
Fluoranthene	NE	1,460	280	3,700	210	1.6	50
Pyrene	NE	183	200	110,000	140	NE	50
Benzo(a)anthracene*	NE	0.09	0.06	0.30	2.1	NE	0.002
Chrysene*	NE	9.2	NE	NE	1.6	NE	0.002
High MW (≥ 5 Rings)							
Benzo(a)pyrene*	0.2	0.009	0.2	0.3	5.0	NE	0.002
Benzo(b)fluoranthene*	NE	0.09	0.08	0.3	1.5	NE	0.002
Benzo(e)pyrene	NE	NE	NE	NE	NE	NE	NE
Benzo(k)fluoranthene*	NE	0.9	0.5	0.3	0.8	NE	0.002
Benzo(j)fluoranthene	NE	NE	NE	NE	NE	NE	NE
Indeno(1,2,3-c,d)pyrene*	NE	0.09	NE	NE	0.022	NE	0.002
Benzo(g,h,i)perylene	NE	NE	NE	NE	0.26	NE	5
Dibenz(a,h)anthracene*	NE	0.01	NE	NE	0.21	NE	50

Note: All criteria shown in units of μg/L.

NE = criterion not established

* Classified by the US EPA as a probable human carcinogen.

[a] Federal US EPA drinking water maximum contaminant level.

[b] US EPA Region 9 Preliminary Remediation Goals.

[c] Connecticut Remediation Standard Regulation.

[d] Michigan Part 201 Generic Cleanup Criteria and Screening Levels; GSI = groundwater-surface water interface.

[e] New York Division of Water Technical and Operational Guidance Series (TOGS) 1.1.1.

sealants versus approximately 2 mg/kg for the asphalt-based sealants). The sealed lots had higher concentrations than the unsealed lots. Furthermore, the used lots had higher PAH concentrations than the unused lots, indicating that materials from vehicles, such as oils and greases, contribute to the PAH content of the asphalt.

In general, the individual PAHs in the City of Austin tests of both product and scraping samples were fluoranthene, phenanthrene, pyrene, chrysene, and benzo(b)fluoranthene. Two of these PAHs, chrysene and benzo(b)fluoranthene, are suspected carcinogens (ATSDR, 1995).

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Heritage Research Group Study

The Heritage Research Group (Indianapolis, Indiana) performed a study to determine the PAH content of asphalt pavement and roofing products (Kriech et al., 2002). This study did not include any sealant analysis. The study involved testing six samples of pavement and four samples of roofing products for total and leachable PAHs. The test results showed total PAH results for asphalt pavement products ranging from 1.6 to 66 mg/kg and roofing products ranging from 4.0 to 23 mg/kg (29 individual PAHs were quantified in the tests). These data confirm the results of the City of Austin study, which concluded that the greatest contribution of PAHs in asphalt pavement is from the sealant, not the asphalt. The leachability testing demonstrated that the PAHs contained in the asphalt and roofing products are not readily leachable, with only 2 of 10 samples containing detectable PAH concentrations. One asphalt paving sample contained 0.18 μg/l of naphthalene and another contained 0.1 μg/l of phenanthrene. These concentrations are quite low and, based on the negligible transport properties of PAHs, would not pose a significant risk to groundwater at most sites.

Another study conducted by The Heritage Group for the Asphalt Institute (Lexington, Kentucky) confirms the influence the presence of coal tar has on the PAH concentrations in asphalt products (Kriech et al., 1999). In this study, the mastic and pulver layers were separated from cores of asphalt taken from streets in Copenhagen, Denmark. The two layers were then analyzed for 16 individual PAHs and the presence of phenolics, which are an indicator of coal tar. The sample results indicate that the total PAH concentrations of samples that are not coal tar–based had a maximum PAH concentration of 233 mg/kg, whereas the cores of coal tar–based asphalt contained up to 10,340 mg/kg of total PAHs. These results also confirm those of the City of Austin study relative to the contribution of coal tar to the PAH concentrations in asphalt-related products.

PAHS IN RUNOFF FROM ASPHALT SURFACES

It is reasonable to expect that PAH-containing particles migrating in stormwater can contaminate adjacent soil and surface-water bodies.

As described above, PAHs are relatively insoluble and are not expected to migrate from asphalt surfaces in the dissolved form. However, it is reasonable to expect that PAH-containing particles migrating in stormwater can contaminate adjacent soil and surface-water bodies. Another facet of the above-referenced City of Austin study was collecting particulate samples from asphalt surfaces and analyzing the samples for PAHs. In addition, wash-off samples were collected from unsealed asphalt surfaces (both in use and test lots) and concrete parking lot surfaces (in use only) by applying potable water to the lots, collecting the runoff, filtering the samples to remove the particulates, and analyzing the particulates for PAHs. A total of 18 parking lots were tested. Some of the asphalt surfaces were sealed with either coal tar–based (eight lots) or asphalt-based (five lots) sealants and others were not sealed (three lots). Also, wash-off samples were collected from two concrete parking lot surfaces. The results of portions of this study have also been reported in *Environmental Science & Technology* (Mahler et al., 2005). In addition, the City of Austin collected dry particulate samples at the most down-slope location of used parking lot surfaces for PAH analysis. It was not possible to ascertain whether the used parking lots from which the dry particulate samples were collected had been sealed with asphalt-based or coal tar–based sealants.

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The analytical results for the wash-off samples show that the sealants are the primary contributors of PAHs relative to runoff from asphalt-paved parking surfaces. Again, as with the product samples, the particulate samples collected from parking lots with coal tar–based sealants had higher total PAH concentrations (median of slightly greater than 2,000 mg/kg and maximum of 13,000 mg/kg) than those collected from lots with asphalt-based sealants (median of approximately 100 mg/kg and maximum of 800 mg/kg). The individual PAHs with the highest concentrations were generally fluoranthene, benzo(g,h,i)fluoranthene, chrysene, and phenanthrene. The particulate samples collected from the wash-off from the two unsealed concrete lots contained 69 and 75 mg/kg of total PAHs. These were used lots, indicating that prior vehicular traffic also contributes to the PAH loading from parking surfaces since the concrete is not expected to contain appreciable PAH concentrations. The conclusion that vehicular traffic contributed PAHs is also supported by comparing the data from the used asphalt lots and the newly paved test plots, which showed generally higher PAH concentrations in the wash-off samples than in the used lots.

The data summarized in this article clearly demonstrate that asphalt paving, particularly sealant products, contain PAHs and that these PAHs have the capability to adsorb to particulates, which then are transported with stormwater runoff.

The City of Austin has also conducted several studies of PAH concentrations in sediment samples from Barton Creek and tributaries leading to Barton Springs. The studies included collecting samples from a dry tributary that conveys stormwater runoff into Barton Creek. There is an apartment complex adjacent to the dry tributary that had its parking lot sealed with a coal tar–based sealant before the sampling. Samples collected from this dry tributary adjacent to the apartment complex had PAH concentrations above 1,000 mg/kg. The total PAH concentrations decreased along the tributary but remained greater than 100 mg/kg at the mouth of the tributary, where it discharged into Barton Creek. It is interesting to note that sediment samples collected from Barton Creek upstream of the discharge point of this particular dry tributary did not contain detectable PAH concentrations. Sediments from Barton Creek collected downgradient of the dry tributary discharge point exhibited relatively high concentrations of total PAHs, with a median concentration greater than 10 mg/kg. Sediment samples from a pool located further downstream along Barton Creek and Town Lake that receives the discharge from Barton Creek also had PAH concentrations in the range of 1 to 10 mg/kg. These data demonstrate that runoff from urban areas, particularly sealed parking lots, results in the presence of PAHs in the sediments of surface-water bodies.

The City of Austin also conducted studies of the biological effects in the streams; however, this research is outside the scope of this article.

As a result of the findings from the City of Austin and USGS studies, on November 17, 2005, the City of Austin passed an ordinance (no. 20051117-070) banning the sale and use of coal tar pavement products. The authors are not aware of any other such ordinance passed by a municipality.

SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

The data summarized in this article clearly demonstrate that asphalt paving, particularly sealant products, contain PAHs and that these PAHs have the capability to adsorb to particulates, which then are transported with stormwater runoff. The resulting concentrations in sediments can be significant. From a remediation and risk assessment perspective, this gives rise to an issue relative to the practicability of remediating sites to

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remove low concentrations of PAHs in soil, specifically subsurface soil, that likely poses a nominal risk when compared to the risk posed by the PAHs in asphalt pavement.

Given the significance of the studies summarized in this article, additional research is needed to further elucidate the contribution of PAHs from asphalt parking lots. In addition, the sensibility of conducting soil remediation to remove low concentrations of PAHs from soil, particularly when the area is going to undergo future redevelopment, possibly with the addition of pavement, warrants serious consideration.

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