

January 8, 2004

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Nancy L. McClintock  
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P.O. Box 1088  
Austin, Texas 78767

Dear Ms. McClintock,  
The Pavement Coating Technology Center (PCTC) is a joint enterprise of industry and the University of Nevada, Reno. The mission of the center is to provide opportunities for dialogue, education, advancement, and improvement of all aspects of the pavement coating industry through meetings, research and development, training, seminars, communications, publications, and other programs and activities. For information about our organization please contact Dr. Peter Sebaaly at the Pavement Coating Technology Center, Department of Civil Engineering, University of Nevada at Reno, Reno, NV 89557.

Our membership includes companies that are represented and/or doing business in Texas including Austin.

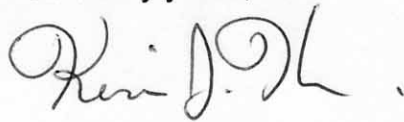
PCTC has retained environmental assessment services from Dr. Robert DeMott and ENVIRON International to review and evaluate coal tar emulsion sealers and their potential contribution of PAHs to the environment specifically relating to Barton Creek. The resulting report is attached.

We are submitting this report and comments in conjunction with the meeting scheduled by your department on January 14, 2004 for the voluntary elimination of coal tar sealers in Austin. Based on our understanding of coal tar sealers and other PAH containing materials and this report by Dr. DeMott, the PCTC does not agree with the Watershed Protection Departments conclusion that the elimination of coal tar sealer would eliminate PAH input into the Barton Springs/Creek watershed. We also feel that coal tar

sealers are being inappropriately singled out as the main source of PAH's in the springs, which is contrary to the scientific consensus that the activities of urbanization (vehicle exhaust, rubber tires, asphalt roads, etc.) are the primary source of PAH's, not any single material.

We look forward to meeting with you to discuss the issues relating to Barton Creek and the relevance of coal tar sealers specifically.

Sincerely yours,

A handwritten signature in cursive script, appearing to read "Kevin J. Hardin".

Kevin J. Hardin  
Chairman  
Pavement Coating Technology Center

ENVIRON

**Review and Evaluation of Coal Tar Emulsion  
Sealers and Potential Runoff Transport of  
Polycyclic Aromatic Hydrocarbons**

*Prepared for:*

**Pavement Coating Technology Center**

*Prepared by:*

Robert P. DeMott, Ph.D., DABT  
Principal  
ENVIRON International Corporation  
Tampa, Florida

**January 2004**

## Letter of Transmittal

January, 8 2004

Pavement Coating Technology Center  
Department of Civil Engineering/258  
College of Engineering  
Reno, NV 89557-0152

ATTN : Peter Sebaaly, Director and Kevin Hardin, Chairman

Dear Messrs. Sebaaly and Hardin,

I am pleased to submit to you this report pertaining to your interest in evaluating coal tar emulsion sealers and their potential to contribute to concerns related to polycyclic aromatic hydrocarbons (PAHs) in the Barton Creek Watershed in Austin, Texas.

The conclusions presented in this report are reached on the basis of the materials that you have provided to me, including other reports, and my experience and expertise as a board-certified toxicologist evaluating exposure to PAHs from environmental sources.

In transmitting this report to you, I would like to note that work on this report was initiated while I was affiliated with Exponent, Inc. and substantial contributions to the initial components of this report were made by several former colleagues at Exponent.

Thank you for requesting my evaluation in this regard.

Sincerely yours,



Robert P. DeMott  
Managing Principal

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## Executive Summary

This report evaluates information developed for the City of Austin, Texas (COA) regarding concentrations of polycyclic aromatic hydrocarbons (PAHs) and potential sources near an unnamed tributary upstream from Barton Springs pool and an adjacent park, Zilker Park.

PAHs are a large class of chemicals ubiquitous in the environment due to both natural and human-influenced processes. PAHs are derived primarily during combustion (burning in the presence of oxygen) and are formed during the burning of any organic material, including coal, petroleum, wood, garbage, and plant or animal-derived materials. Typical environmental sources include forest fires, volcanoes, and human-related activities such as agricultural burning, asphalt road construction and motor vehicle use. Routine human exposure sources to PAHs include the diet, particularly food cooked over an open flame, tobacco smoke and motor vehicle exhaust.

Following up on the recognition that PAHs are present in roadway construction materials, attention has been directed toward coal tar emulsion (CTE) sealers as one specific source of the PAHs initially identified in the subject area. This report addresses the scientific strength of information available for identifying particular sources by reviewing and evaluating the testing protocol, comparing the contributions of various sources to roadway runoff and reviewing the characteristics of CTE sealers.

The following conclusions are reached:

- PAHs associated with the subject parking lot/roadway area do not pose a health risk for users of Barton Springs Pool.
- In comparison to normal dietary intake of PAHs, consistent exposure to sediments containing the highest measured levels of PAHs (unlikely in any event given the concentrations were actually identified within a limited area of a drainage ditch) would represent an insignificant increase in average daily intake. For context, the PAHs associated with one grilled 6-ounce pork chop amounts to 65 times the average daily intake associated with the highest sample results reported.
- Samples of soil and roadway runoff materials, even those with the highest detected PAH concentrations, are consistent with typical urban background levels.

- Crankcase oil and vehicle emissions, not asphalt debris, are consistently identified as the primary source of PAHs transported in the environment from roadway runoff.
- Elevated PAH levels identified in the area were restricted to samples that contained visible asphaltic materials, expected to contain PAHs, and were apparently not being transported substantially.
- While CTE sealers and asphalt are expected to contribute PAHs in deposited roadway debris, the physical forms of these materials have low potential for leaching and are poorly taken up by biological organisms.
- Appropriate prioritization of particular sources of PAHs would require chemical analyses for additional PAHs. The set of PAHs included in the COA-commissioned study were not sufficient to distinguish the potential contribution of CTE-based sealers from asphalt roadway material itself, typical parking lots debris (including tire particles, dust with adherent combustion byproducts, and motor oil) and discarded asphalt roofing materials.
- Prior to developing any source control or management strategies, it would be necessary for the COA to complete a characterization adequate to identify significant contributions from particular sources in order to ensure that management efforts could have an impact.





## 1. Introduction

This memorandum presents an evaluation of the information and data regarding coal tar emulsion (CTE) sealers and the potential contribution of these sealers to transport of associated polycyclic aromatic hydrocarbons (PAHs) to Barton Springs pool in Austin, Texas via runoff from sealed surfaces.

PAHs are ubiquitous and occur naturally in the environment. They are a group of chemicals formed during the burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and flame grilled meat. Sources of PAHs in the environment include volcanoes, forest fires, cigarette smoke, vehicle exhausts, asphalt roads, coal, coal tar, agricultural burning, residential wood burning, municipal and industrial waste incineration, and hazardous waste sites (ATSDR, 1995).

The overall context for this evaluation relates to questions in Austin over potential human health concerns from PAHs in recreational water bodies. This issue emerged from reports on the results from soil and sediment sampling conducted by the COA in an unnamed tributary to Barton Creek. Analytical results from the COA sampling showing apparent elevations in PAHs indicated the need to further characterize the material that was sampled and to evaluate the source of PAHs to area surface water. Prior to the COA's completion of a comprehensive analysis of the results, media attention, based on simplified comparisons of the preliminary results to generic environmental screening criteria, promoted the perception that there were unusual PAH exposures around recreational water bodies and speculation about CTE sealers as a source of exposure. Concerns regarding the recreational threat appear to have been exacerbated by the perception of a time-critical issue based on media coverage and generally limited public understanding of these facts: 1) PAHs are ubiquitous in the environment, especially in urban areas and drainage features receiving road runoff; 2) PAH concentrations in samples containing actual roadway materials are expected to be relatively high based on their composition, and 3) environmental criteria used for comparison are derived for hypothetical lifetime cancer risks including assumptions about long-term exposure to chemicals that are not relevant to the issue at hand.

The COA further evaluated the Barton Springs area and received an assessment by Geomatrix Consultants, Inc. (March 27, 2003) concluding that PAHs detected at the unnamed tributary were due to isolated accumulation of roadway-derived materials associated with stormwater discharge points. A finding by Geomatrix that there were no generalized ambient surface water impacts (i.e., only isolated areas of roadway impacts were identified) is consistent with the findings of the Texas Commission on Environmental Quality (April 17, 2003) that there is no health threat to recreators at Barton Springs Pool due to the minimal waterborne transport of PAHs and limited potential for contact with impacted sediments. While the Geomatrix report

provides qualitative speculation about asphalt paving materials, CTE sealer used on pavement, and discarded roofing materials as potential sources of PAH-containing particles in sediment, no scientific analysis of contributions from various sources, or prioritization of sources, was presented. Such analysis is necessary in order to target any source reduction initiative effectively due to the number of readily identified possible contributors. Absent such analysis, media reports characterizing the Geomatrix report as having identified only pavement sealers as a potential source of PAHs may be misleading to city officials and the public.

This analysis provides an interpretation of the source-related information reported and characterized in the Geomatrix report. Section 2, below, provides a review and evaluation of the City of Austin's (COA's) testing protocols, test results and conclusions from the analysis performed by Geomatrix. Section 3 provides an assessment of CTE sealers as a protective coating for pavements and their potential contribution to PAH levels in the environment relative to other roadway-related sources. Section 4 reviews the known regulations regarding PAH-containing runoff.

## **2. Review of City of Austin's Current Testing Protocol**

The primary goal of this section is to provide technical review of the testing protocols, test results, and conclusions reached by Geomatrix and the COA regarding the assessment of the Barton Springs area. In January 2003, Geomatrix undertook an investigation of an area south and west of Barton Springs pool in an attempt to characterize the source(s) of certain elevated chemical constituents previously found in sediments in an unnamed tributary to Barton Creek.

In summary, results were presented for 24 samples collected at 15 locations including soil samples at depths ranging from 0 to 22.5 feet below ground surface (bgs), as well as samples of material accumulated on a parking lot and scrapings of the parking lot surface. This included several soil samples in and around a portion of Zilker Park referred to as the "area of primary concern."

### **Sampling Strategies**

For soil borings, the sampling protocols implemented by Geomatrix appear to be generally consistent with those typically performed when doing a site investigation. One exception is categorizing boring B-1 as a "soil boring" and grouping it with the other borings. This boring is reported to be "in the immediate area of the asphalt debris within the tributary," raising questions about the characterization of the associated samples.

Clearly identifiable debris is normally removed from the land surface prior to collecting a "soil" sample in order to ensure that results pertain to the environmental substrate, i.e., soil, rather than surficial debris. Further, classifying samples as soil versus sediment is uncertain in

areas that may be inundated and within a drainage feature. In this case, boring B-1 most closely reflects depositional materials from runoff collected in the tributary. The boring log for this boring indicates a substantially different surficial profile than the other definitive soil borings, with 60-80% gravel and the remainder listed as silty, loose clay in the first 1' bgs. These characteristics, along with the observed asphaltic debris nearby, suggest that the 0-0.5 foot depth sample from this location would have been more properly characterized as deposited roadway-associated materials than soil. The significance, as pointed out in the Geomatrix report, is that chemicals bound up in roadway materials are relatively non-mobile compared to many chemicals in soil. Also, environmental criteria derived for soil and/or sediment are not relevant for roadway gravel.

The Geomatrix report specifies that a goal of sampling this location was to characterize surficial debris and discusses the difference between asphaltic debris as a potential source versus impacted soil. However, the distinction between soil samples and eroded roadway debris samples is not sufficiently described to preclude non-specialist readers from assuming incorrect analogies between the B-1 samples versus B-2 through B-10 soil samples. Also, it was not appropriate to compare analytical results from the surficial B-1 sample to the Texas Risk Reduction Program Soil Protective Concentration Limits (PCLs). Samples containing 60-80% gravel present a substantially different potential for exposure than actual soil, primarily because of reduced adherence to skin. There are no risk-based PCLs derived for deposited roadway gravel (TRRP 2003). If such criteria had been derived, the concentrations would be substantially higher than the soil PCLs, reflecting the reduced exposure potential because the gravel material would not readily adhere to skin. Thus, the exposure contact would be reduced, resulting in less of the PAHs associated with the gravel material passing through the skin barrier. The end result would be that a PCL developed for this material would allow higher concentrations of PAHs than the PCL developed for soils.

The single composite soil sample (S-2) collected from multiple, unspecified, non-random locations and depths is appropriate for preliminary screening purposes to identify areas where there are not notable levels of chemicals, as it was apparently used by Geomatrix in reaching their conclusions. But, this type of sample would not be appropriate for characterizing the extent or degree of any environmental impacts.

The collection of accumulated material on top of a roadway/parking lot (S-1, S-3) and scrapings from such surfaces (S-4, S-5) is not typically included in environmental site investigations and there are not standardized protocols for collecting/analyzing this type of sample. The description provided by Geomatrix suggests that these samples were collected in an appropriate manner for addressing the specialized question of determining PAH and metals levels in roadway-associated materials. However, the report does not make clear that samples from these substrates are not relevant for comparisons to environmental screening or target levels

derived for soil or sediment. Also, by labeling samples S-1 and S-3 as “sediment,” the report could be misunderstood to suggest that this material is analogous to the sediment from water bodies typically considered in environmental site investigation. These samples are not “sediment” as the term is relevant to environmental assessments and compliance with specific chemical criteria.

The Geomatrix report makes clear the distinction between “PAH-containing materials” and “PAH-contaminated sediments” in discussing the previous sampling of Barton Creek sediments by the COA. The same distinction is relevant for the samples that Geomatrix collected. Materials accumulated on a roadway and particularly road surface scrapings would be expected to contain PAHs characteristic of roadway construction materials and this is not an indication of actual or potential “contamination.”

### **Analytical Strategies**

The chemical analyses of the samples performed by DHL Analytical were generally appropriate for evaluating the compounds that were considered. The analytical methods and reported limits of detection appear to be appropriate for the compounds considered.

While standardized laboratory protocols do not pertain specifically for the handling, extraction, and analysis of samples scraped from roadways (S-4, S-5), the use of the standard soil protocol is probably sufficient for general identification of PAH compounds in known PAH-containing materials. Any quantitative comparisons between results from these samples and results from standard soil samples should take into account the uncertainty associated comparing samples from distinctly dissimilar matrices.

The notable analytical limitation for this investigation is the lack of analytical results for a broader set of PAH compounds. The chemicals included in the laboratory analyses include only a small subset of PAHs. While the analyzed compounds are standard for generic environmental investigations, an investigation looking for specific PAH sources could have included an expanded set of analyses to help differentiate among potential sources. Different materials and original sources of PAHs produce distinct patterns (profiles) of PAH compounds, many of which are identifiable using expanded sets of PAH analyses. Most notably, the absence of results for methylated forms of PAHs precludes using a straightforward profiling approach to distinguish between the contribution from coal tar-derived materials (e.g., CTE sealers) versus petroleum-derived materials (e.g., asphalt). Laboratories handling environmental samples can provide analyses for methylated PAHs.

### **Reported Results**

The results of the analyses completed showed detectable levels of PAHs in 12 samples from 10 of the locations (i.e., B-1, B-2, B-4, B-8, B-9A, B-10, S-1, S-3, S-4, and S-5). PAH levels

were below detection limits in all samples from borings B-3, B-5, B-6, and B-7 and in the composite soil sample S-2 taken from various locations in the Zilker park “area of primary concern.”

Boring B1 was located within the “area of primary concern” and the highest overall PAH concentrations (138.54 mg/kg – sum of reported PAHs) found were reported for the 0 to 0.5 foot bgs sample at this location. As noted in the Geomatrix report, this sample was clearly associated with visible asphaltic particles and was downhill from where asphalt-roofing materials were observed in the embankment. Regardless of the observable presence of PAH-containing asphaltic roadway/roofing materials, the total PAH and individual compound concentrations in this sample were generally consistent with levels reported for urban soil (ATSDR 1995) and for urban sediment (Talley et al. 2002). This suggests that the deposited roadway debris at this location is not substantially different in PAH content than typical urban environmental sources.

As described above, PCL values derived for soil and sediment are not relevant as risk-based criteria for gravel matrices because the exposure potential is reduced. Since these values serve as a frame of reference to Texas regulations, particularly for media representations, however, comparisons are informative. Concentrations of five compounds [benzo(a,h)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene] were higher than the corresponding Tier 1 residential PCLs in the 0-0.5 foot bgs sample at B-1. Concentrations for two compounds (benzo(a)pyrene, dibenz(a,h)anthracene) were higher than Tier 1 commercial/industrial and sediment PCLs. Exceedance of these non-applicable criteria is not an indication of a significant or actionable health risk from deposited roadway debris and the consistency of the results for this sample with reported urban levels reinforces that normal urban exposure levels can routinely exceed the cited PCLs.

In the deeper samples at B-1 (1.5 to 2 feet, 5.5-6 feet bgs) PAH concentrations were significantly lower. Based on the boring logs, these deeper samples appear to represent soil rather than deposited roadway debris and all compound-specific concentrations were below their respective Tier 1 Residential Soil PCLs (TRRP 2003). In the 5.5-6 foot bgs sample from B-1, no PAHs were detectable.

Because PAHs are naturally occurring and ubiquitous in the environment and in food through both environmental inputs and food processing, there is a normal dietary intake of PAHs that has been characterized. According to ATSDR (1995), the average intake of carcinogenic PAHs in the American diet is 1-5 µg (micrograms) per day. Exposure to the deposited materials at the surface at boring B-1 (the Geomatrix sampling location with the highest concentration of PAHs) for children playing in the outfall area would not significantly increase PAH intake beyond normal dietary intakes. Playing in this specific location over 6 years with the associated incidental ingestion of surficial particles would result in an increase of average daily intake by 0.04 µg per day over a lifetime. This value is based on a standard USEPA approach to

characterizing incidental soil ingestion and the 90<sup>th</sup> percentile estimate for the amount of time per day 5-11 year-old children play in gravel or sand (i.e., 2 hrs) (USEPA 1997).

For example, from a typical dietary intake range of 1-5 µg/day, adding in routine exposure at the sampled location would yield a range of 1.04 –5.04 µg/day for overall intake of the corresponding PAHs. By way of contrast, the carcinogenic PAHs associated with one 6-ounce grilled pork chop amount to approximately 1.3 µg (ATSDR 1995). These comparisons point out the limited change in normal PAH intake that could correspond to exposure in the area with the highest PAH levels measured in the Geomatrix report (i.e., location B-1). Obviously, routine incidental ingestion of materials from this limited area is highly unlikely in any case.

The only other soil boring results with concentrations higher than PCLs related to boring B-9a in the 5-5.4 feet bgs sample. Concentrations of benzo(a)pyrene and dibenz(a,h)anthracene were higher than the corresponding Tier 1 residential PCLs, but below all other criteria. Just as with the B-1 boring, there were asphaltic materials, presumably roadway particles that may have had associated CTE sealers, noted in this sample and it is therefore not unexpected to find detectable PAHs. The concentrations are again consistent with routine urban levels and the limitation of these detected PAHs in the 5-5.4 foot depth interval indicates that risk-based criteria relevant for exposures at the ground surface are not directly applicable.

While detectable, concentrations of PAHs in soils from boring numbers B-2, B-4, B-8 and B-10 were below the most protective criteria, Tier 1 Residential PCLs, and are low relative to urban background levels.

The other samples evaluated in the Geomatrix report reflect sampling of the material accumulated on a parking lot surface (S-1 and S-3) and scrapings of the parking lot surface (S-4 and S-5). As expected for roadways constructed and sealed with PAH-containing materials, PAH concentrations were reported above detection limits in all of these samples and were higher than those found in environmental (i.e., soil or sediment) samples.

Samples S-1 and S-3 were noted to include a “high” percentage of abraded parking lot particles assumed to be surface sealant. Presumably, other normal parking lot debris containing PAHs (e.g., asphalt, motor oil, tire particulate) were present as well, and without definitive analyses of PAH profiles, the proportionate amount of total PAHs from the various sources cannot be established. Also, distinguishing between abraded tire particles and surface sealer particles is highly uncertain on normal visual inspection.

Samples taken at S-4 and S-5 were obtained by scraping the asphalt surface, and as such consisted of asphalt and seal coating material. As expected, the analytical results for these samples showed relatively high levels of PAHs consistent with the concentrations of PAHs found in asphalt treated with CTE sealers.



## Interpretations

The results of the Geomatrix report indicate clearly that elevated PAHs are only found where observable roadway-associated, asphaltic materials were located. The report concludes that there is no active migration of PAHs to subsurface soils or groundwater. This conclusion is consistent with studies of PAH leachability from asphaltic materials that demonstrate there is very low potential for PAH transport via leaching from roadway materials (Kriech 2003; Townsend 1998). The design and protocol of the investigation is appropriate for reaching this type of conclusion about the potential for PAH transport and impacts on environmental matrices. The limitation of detectable PAH levels to samples containing visible roadway materials in the parking lot and lack of a complete transport pathway is also consistent with the analysis of PAH levels downstream in the Barton Springs Pool area. An analysis conducted by the Agency for Toxic Substances and Disease Registry also provided a quantitative evaluation of potential health risks (ATSDR 2003). The ATSDR report concluded that PAHs found in the sediments of the Pool would contribute at most an excess lifetime cancer risk probability of 2.6 in one hundred million, well below the risk probability the USEPA uses to determine the need for comprehensive site-specific considerations, i.e., one in one million excess lifetime risk. The ATSDR report was peer-reviewed by the Texas Commission of Environmental Quality, the USEPA, and the Texas Department of Health. All three agencies concurred with the ATSDR's conclusion that the water and sediments of Barton Springs Pool did not pose a health risk to people swimming and playing in the pool.

While the report to the COA concludes specifically that the accumulation of asphalt seal coating particles is the source of anomalously high PAH findings for the unnamed tributary, there is no presentation of an analytical approach used to distinguish between various expected sources of PAHs. Further, given the set of PAHs included in the analyses from the laboratories, it is not clear how coal tar-derived PAHs (e.g., CTE sealers) could be readily differentiated from petroleum-derived (e.g., motor oil and road or roofing asphalt) PAHs. It appears that this conclusion was based on observations of the particulate matter in the samples and surrounding area. It would be difficult to distinguish through this method: 1) tire particles from asphalt surface (sealed or unsealed) particles, and 2) particles of asphalt bitumen from sealer particles. Even the description of this particulate matter provided in the Geomatrix report – “observed, or in some instances suspected, to include tiny asphalt and seal coating particles,” reinforces the mixture of roadway materials expected. While the observed site conditions appear to support a conclusion that roadway associated materials, and possibly discarded roofing materials, contributed PAH-containing materials in certain depositional areas, prioritizing asphalt sealers as a source more important than other parking lot sources of PAHs appears premature and is not supported by the COA data analysis.

In summary, the sampling and analysis sponsored by the COA supports the following conclusions:

- Elevated PAHs were only found in samples that contained visible asphaltic materials.
- In general, elevated PAHs were only found on the land (or parking lot) surface in samples with observable roadway (PAH-containing) material.
- Samples of soil and roadway runoff materials contained PAH concentrations consistent with typical urban background soil levels.
- PAHs found from the scraping or sediment samples from the paved parking lot were found at expected concentrations.
- PAHs bound in asphaltic materials have a low potential for leaching.
- PAHs associated with the subject parking lot/roadway area do not pose a health risk for users of Barton Springs Pool.
- An evaluation sufficient to distinguish the contribution of PAHs from CTE-based asphalt sealers, asphalt roadway material itself, typical parking lot debris (including tire particles, dust with adherent combustion byproducts, and motor oil) and discarded asphalt roofing materials has not been completed and would require chemical analyses for additional PAHs to differentiate the actual source(s).

### **3. Review of Coal Tar Sealers as Potential PAH Sources**

There are several key factors regarding PAHs in the environment relevant to considering and communicating the potential significance of CTE sealers and other PAH-containing materials as sources of environmental chemical exposure. First, while PAHs are ubiquitous chemical compounds in our environment and are released through a wide range of natural and human activities (particularly any combustion-related activities), the general public does not recognize the types of chemical release and exposure resulting from these routine activities. Failure to recognize that some exposure to PAHs in the environment is routine and unavoidable can lead to concerns about particular materials that are disproportionate relative to their actual contributions to environmental PAHs. Failure to recognize that the predominant sources relate to normal modern activities such as operating motor vehicles, burning and energy production can also misdirect concerns. For many, the presence of PAHs reported in particular materials as well on their appearance on listings of chemicals considered in environmental cleanups creates an expectation that such materials are necessarily important to consider in managing environmental exposure. At the same time, expectations frequently differ regarding the importance of controlling environmental releases depending upon the source of the release. Familiarity and



acceptance of the presence of cars and roads, for example, leads many people to differentiate between the importance of regulating roadway construction materials and runoff compared to “combustion byproducts and leachate in the environment” though the same chemicals end up in the environment.

Coal tar contains PAHs. CTE sealers, which take advantage of the properties of coal tar in serving their intended uses, not surprisingly, contain PAHs as an intrinsic part of their composition, i.e., not as a “contaminant” of the desired product. As PAH-containing materials, CTE sealers have the potential to contribute to environmental PAH releases and the relevant question becomes in-depth consideration of the actual amount of transfer of PAHs from CTE sealers to the environment. With regard to CTE sealers, important characteristics to consider and communicate in order to provide relevant environmental information include, 1) understanding predominant PAH sources associated with roadways, 2) understanding the effects of physical-chemical characteristics on transport in the environment, and 3) recognizing the limitations on human exposure associated with uses and the environmental fate of CTE sealers.

### **PAH Sources Associated with Roadways**

Elevated levels of PAHs have long been understood to be associated with runoff from paved areas, such as roads and parking lots (Barrick 1982; Tetra Tech 1988; Eganhouse et al. 1981; Mulliss et al. 1996; Yamane et al. 1990). USEPA recognizes that the source of most PAH compounds in urban runoff is vehicles, including automobile and truck engines that drip oil (USEPA 1993). Another source of PAHs in urban runoff appears to be dust particles that accumulate on roads. It has been hypothesized that these particles are from atmospheric fallout processes and regional air pollutant emissions (Pitt and Barron 1990).

A report sponsored by the U.S. Department of the Interior and the U.S. Geological Survey (Lopes and Dionne 1998) found that crankcase oil and vehicle emissions were consistently identified as the primary sources of semi-volatile compounds such as PAHs in storm water. It stated further that emission of PAHs from automobiles is directly related to their concentration in gasoline. Naphthalene and alkylated (e.g., methylated) forms of naphthalene comprise 0.5 percent by weight (>5000 mg/l) of gasoline. Thirteen other PAHs occur in gasoline at concentrations ranging from 54 mg/l to less than 0.01 mg/l. A large percentage of PAHs found in automobile emissions is formed during combustion of gasoline with initially low PAH content. In attempting to quantify the potential concentration of PAHs in highway runoff, Lopes and Dionne (1998) concluded that such calculations were not possible because most of the relevant studies have limited ancillary information on PAHs and raw data is rarely reported.

Another study evaluated the likely sources of PAHs found in rivers and estuaries (Zakaria 2002). Using fingerprint analysis of PAH profiles and the ratio of methylphenanthrene to phenanthrene found in sediments, they concluded that the major source of PAHs was petroleum.

The likely source of the PAHs was determined to be crankcase oil that was either spilled or leaking from vehicles onto the road surface. The authors concluded that the fingerprint analysis excluded crude oil, fresh lubricating oil, asphalt, and tire-particles as major contributors to river and estuary sediments. The authors' conclusion is consistent with the limited mobility of roadway-associated particulate matter compared to light, liquid oil and combustion byproducts, for which waterborne and airborne transport is easier. Examining the profile of methylated and non-methylated forms of PAHs represents a straightforward approach for evaluating petroleum versus coal tar sources. Petroleum-derived PAHs can be characterized by concentrations of methylated forms of several PAH types (naphthalenes, anthracenes, phenanthrenes, benz(a)anthracenes) exceeding the concentrations of the parent, non-methylated forms (Stout et al. 2002).

A report by Pawluck and co-workers (2002) points out that PAHs are emitted from practically every combustion source. These PAHs are then deposited either through wet or dry deposition on soil, vegetation and water. PAH residues on land, particularly impervious surfaces, are later transported with storm water runoff to water bodies and depositional areas. The specific traffic-related sources identified by Pawluck and coworkers (2002) were: tire wear, vehicle exhausts, asphalt and asphalt coatings, and lubricating oils and grease.

The Agency for Toxic Substance and Disease Registry's (ATSDR 1995) toxicological profile for PAHs lists the important sources of PAHs in surface water to include deposition of airborne PAHs, municipal waste water discharge, urban storm water runoff, runoff from coal storage areas, effluents from various industries, oil spills, and petroleum processing. ATSDR states further that most of the PAHs in soils are believed to result from atmospheric deposition after local and long-range transport. ATSDR concluded that the principal sources of PAHs in soils along highways and roads are from vehicular exhausts and emissions from wearing of tires and asphalt.

Regardless of the ultimate source, PAHs have been consistently detected in urban runoff from roads and associated with multiple sources. Thus, potentially significant sources of PAHs other than from the CTE materials are well known, and the presence of PAHs are not restricted to runoff from CTE materials.

### **Environmental Transport Characteristics of PAHs and CTE Sealers**

The transport characteristics of PAHs are dependent upon the type of sediment with which they are associated. A study by Ghosh and co-workers (2000) found that PAHs in sediments are concentrated on external surfaces of particles, indicating near surface sorption mechanisms. When comparing a coal/wood derived fraction of sediment with a clay/silt sediment, they found that coal/wood derived sediments constituted only 5% of the sediments by weight but contained 62% of the total PAHs. Measuring PAH desorption indicated that the leachability of PAHs from

the coal/wood fraction (i.e., PAH-containing materials) is low, however, relative to the leachability from the clay/silt fraction (i.e., PAH-impacted matrices). These results indicate that in a mixed sediment with particles of PAH-containing materials (e.g., coal or CTE sealers) and clay/silt, most of the corresponding overall PAH concentration would be expected to relate to the PAH-containing material particles with lower leaching potential (i.e., the PAHs are detected because they have not evaporated or washed away).

Another study investigating the bioavailability (i.e., fraction of chemical available to biological organisms) of PAHs from the same two types of sediments (Talley 2002) confirmed that PAH sorption to coal-related particles in sediments is associated with slow release rates compared to clay/silt particles. This study also found that biodegradation of coal particle-related PAHs is minimal compared to PAHs associated with clay/silt particles, indicating less bioavailability for PAHs associated with the coal derived fraction. This study supports the conclusion that the leachability of PAHs associated with CTE materials is expected to be low and further that the availability for biological uptake and metabolism of PAHs from these types of sources is low.

### **Exposure-Related Characteristics of Roadway Materials**

In general, PAH-containing roadway materials, such as those found at sample location B1, are not expected to contribute significantly to overall exposure to PAHs. These materials tend to collect in very localized depositional areas and the exposure potential is quite limited since people generally do not stay in the same localized outside area for long periods of time. Also, these materials have collected in a drainage/retention area that would not likely be intentionally used extensively by individuals from surrounding areas. Zilker Park and Barton Springs, both demonstrated to have relatively low PAH concentrations, and other nearby flatter areas would be used much more heavily than the drainage ditch at the base of a parking lot embankment.

Human exposure is also limited by the particle size and types of the materials described from sample B1. Exposure to the asphaltic and CTE-related PAHs would not be significant since these materials are not associated with the typical media a person is normally exposed to such as surface water, groundwater, or soils. Normally, PAH exposure occurs due to pathways such as the incidental ingestion of surface waters with suspended sediments containing PAHs or incidental ingestion of small soil/sediment particles with adsorbed PAHs that adhere to the skin and are swallowed subsequent to hand-to-mouth activity. Larger, visible particles of asphalt are not readily ingested through this pathway.

In summary, this analysis of sources of PAHs supports the following conclusions:

- There are numerous sources of PAHs that contribute to concentrations detected in the environment.

- PAH content of road run-off is difficult to characterize as to the exact source because of limited raw data.
- Crankcase oil and vehicle emissions, not asphaltic debris, are consistently identified in the literature as the primary sources of PAHs transported in the environment from roadways.
- While CTE sealers are expected to contribute PAHs in deposited roadway debris through the coating on asphalt particles and abraded CTE particles, these physical forms have low potential for leaching and bioavailability and have limited contributions to environmental transport and typical environmental exposure relative to other PAH sources.

#### **4. Review of Regulations for PAH-Containing Runoff**

There are state and federal regulations and screening/cleanup criteria pertaining to PAHs in soil and water. However, as noted above, these criteria are not applicable for samples containing 60-80% gravel. Criteria concentrations specifically derived for these types of samples would be significantly higher because the exposure potential is reduced compared to soils or sediments. For example, the Texas state criteria, PCLs, mentioned previously combine a number of exposure pathways that are not relevant to the potential exposure to PAHs found in the asphaltic materials. These pathways include ingestion, inhalation, and dermal contact with soils, as well as the ingestion of vegetation potentially grown in PAH-impacted soils. Similarly, the risk-based concentrations derived by USEPA Region III and preliminary remediation goals from USEPA Region IX include specific pathways for intake of PAHs from soils that are not relevant to the exposures from the PAH-containing materials found in the Geomatrix study.

Very little information was identified specific to managing PAH-containing runoff. The only relevant federal regulatory information found about runoff was in the USEPA's Management Measures Guidance (USEPA 1993) that were developed for states to incorporate into their coastal nonpoint source (NPS) pollution programs. One specific management measure that may apply is the Management Measure for Road, Highway, and Bridge Runoff Systems.

This runoff measure requires that operation and maintenance systems include the development of retrofit projects, where needed, to collect NPS pollutant loadings from existing highways. It states further that poorly designed or maintained roads can generate significant erosion and pollution loads containing heavy metals, hydrocarbons, sediment, and debris that run off into and threaten the quality of surface waters and their tributaries. The measure states that in areas where such adverse impacts to surface waters can be attributed to adjacent roads, some type of remedial action may be necessary such as the installation of structural or nonstructural pollution controls. Areas with severe erosion and pollution runoff problems may require relocation or reconstruction to mitigate these impacts.

The runoff management systems mentioned are a combination of nonstructural and structural practices selected to reduce NPS pollutant loadings generated from roads or highways. The systems should include structural improvements to existing runoff control structures to protect water quality. Vegetated filter strips, grassed swales, detention basins, constructed wetlands, and infiltration trenches are noted as typical runoff controls.

The Texas Department of Transportation (TxDOT) also has a program for controlling NPS pollutants from highway construction and maintenance (TNRCC 1999). Their approach is to identify opportunities to improve existing urban runoff control structures in priority watersheds. Pollution prevention procedures are incorporated in the operation and maintenance activities for roads to reduce pollutant loading to surface water and sediments. TxDOT also has a program to assess water quality impacts resulting from transportation projects.

No information was found regarding PAH-specific runoff regulations from the COA or Travis County.

In summary, there are few federal, state or city regulations specific to PAH-containing runoff.

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