PAHs in Austin, Texas
Sediments and Coal-Tar Based Pavement Sealants
Polycyclic Aromatic Hydrocarbons

City of Austin
Watershed Protection and Development Review Department
Environmental Resources Management Division

May 2005 (Revised July 2005)

PAHS IN AUSTIN, TEXAS, SEDIMENTS AND COAL-TAR BASED PAVEMENT SEALANTS POLYCYCLIC AROMATIC HYDROCARBONS

Prepared by
City of Austin
Watershed Protection and Development Review Department
Environmental Resources Management Division

Project Team
Nancy L. McClintock, Assistant Director Watershed Protection
Leila Gosselink, P.E., Engineer
Mateo Scoggins, Environmental Scientist, Surface Water Team Leader

Department Director
Joseph G. Pantalion, P.E., Director

Prepared For
The Austin City Council, Environmental Board, and Austin Community

Acknowledgements

This report was prepared in the Environmental Resources Management Division of the City of Austin's Watershed Protection and Development Review Department under the general supervision of Joe Pantalion, Department Director, and Nancy L. McClintock, Assistant Director

The authors appreciate the assistance in field support, editing, direction, data management and technical support given to them by a number of other City employees. The authors also thank the many agencies, organizations and individuals who have provided valuable input into the development of the Coal Tar Analysis. Contributors and agencies include:

Ed Peacock, P.E., Manager, Environmental Resource Management
Tom Bashara, Environmental Compliance Specialist
Martha Turner, P.E., Watershed Modeling and Analysis Team Leader
David Johns, P.G., Senior Environmental Scientist
Scott Hiers, P.G., Environmental Scientist
Chris Herrington, Analyst
Ellen Geismar, Environmental Scientist
Jo Dee Myatt, Administrative Assistant

Lower Colorado River Authority
Texas Council on Environmental Quality
United Stated Geological Survey

TABLE OF CONTENTS

List of Figures

List of Tables

PAHS IN AUSTIN, TEXAS
SEDIMENTS AND COAL-TAR BASED PAVEMENT SEALANTS
POLYCYCLIC AROMATIC HYDROCARBONS

EXECUTIVE SUMMARY

Investigations in the Austin area have identified parking lot sealants as a concentrated source of particulate Polycyclic Aromatic Hydrocarbons (PAHs) to the stream sediment environment. Historical and current PAH concentrations in Austin stream-bed sediments exceeded biological effects levels in localized areas; 13 percent of creeks showed levels exceeding the Probable Effects Concentration, and 35 percent more exceeded the Threshold Effects Concentration. PAH profiles along a tributary traced the source of elevated PAHs in one sensitive area to a parking lot coated with a coal-tar based sealant. Multiple investigations by the City of Austin and cooperative agencies were initiated to investigate this potential toxic contaminant source.

Using aerial photography, large parking lots with sealant-wear patterns were selected in areas adjacent to creeks. Sediment sampling above and below runoff discharging from these lots showed significant increases in total PAHs. Additional analyses used historical data from small watersheds in the Austin area, aerial photography and GIS analyses to examine the percent parking lot and percent sealed parking lot areas in contributing watersheds. A significant regression with percent parking lot area was found; the correlation coefficient increased dramatically when the percent sealed parking lots was used. A consistent chemical signature for coal tar sealant PAHs has not been determined, but monitoring results, combined with the correlation of PAH hot spots to sealed parking lot areas, strongly implicate sealants as a primary/concentrated source of PAHs in Austin stream sediments. Documenting the connection between sealed parking lots and stream sediment PAHs was the first step in ongoing investigations to determine the potential for impacts to aquatic life from this previously unidentified pollutant source.

The City of Austin also conducted investigations of pavement sealants as concentrated source of PAHs. This paper presents data from 1) direct measurement of Polycyclic Aromatic Hydrocarbon (PAH) content of pavement sealant products, 2) PAH analyses of scrapings and particulates from parking lots, and 3) preliminary results from biological studies examining the toxicity to benthic organisms from clean sediments spiked with dried pavement sealants and several measures of community impacts. The data provide significant insight into the potential toxicity of these products, which are eroding daily into surface water sediments across the nation.

Since pavement sealants were first targeted as potential concentrated sources of localized high PAHs in stream sediments of Austin, Texas, chemical analysis of the two types of commercially available pavement sealants demonstrated that coal-tar based products contain significantly higher PAH concentrations than asphalt-based products. Particulate analysis of scrapings from parking lot surfaces and eroded materials on parking lots confirmed this previously unidentified, concentrated source of PAHs. The significance of parking lot sealants as a source of PAHs in urban stream sediment is indicated by an estimated application rate of more than 600,000 gallons/year of undiluted sealant in the Austin area, which may contain 50 percent or more coal tar. Moreover, industry recommends reapplication every few years due to wear.

Both state and federal agencies emphasized to City representatives that the concern from an environmental assessment standpoint would be focused on the demonstration of impacts on aquatic life in the Austin environment. Two primary questions need to be addressed with respect

to biological impacts: 1) whether PAHs from coal tar sealants may cause toxicity and 2) whether impacts are being seen in the Austin stream aquatic communities. The first question needed to be addressed because the toxicity of PAHs in this particulate form had not been previously examined; therefore, a dried formulation of a sample of each sealant type was prepared and provided to a laboratory for standard sediment toxicity testing with benthic organisms at three dilutions. Results indicate that toxicity occurred beginning at 17.1 ppm, in the same total PAH range as the Probable Effects Concentration (PEC); toxicity was increased with UV exposure. A mesocosm study and the examination of the aquatic communities associated with upstream and downstream stream sites described above, where PAHs were measured, both showed evidence of degradation associated with increased PAHs. Further research into this source of PAHs as a potential impact on aquatic life in urban streams, as well as potential regulatory action to address this source, are suggested by these studies.

1 Introduction

Creek sediment sampling in Austin, Texas, identified unexpectedly high levels of polycyclic aromatic hydrocarbons (PAHs). Although PAHs have numerous urban sources, follow-up investigations indicated that particulates found in these samples appeared to be abraded from parking lot surfaces and were a significant contributing source in the localized areas with the highest PAH levels. Chemical analyses were performed on the source materials, on abraded materials, on soils found on and adjacent to parking lots, and on creek sediments in waterways downstream of parking lot surfaces. Results from these analyses are combined with analyses obtained through collaborative studies on this issue with the United States Geological Survey (USGS) and Texas State University (TSU). This paper compiles several investigations that the City of Austin conducted in efforts to identify the source of elevated sediment PAHs in a specific geographical area, while simultaneously attempting to assess the extent and severity of the problem.

1.1 Background

The City of Austin has historically conducted water quality sampling to evaluate the condition of its water resources. In the late 1980s and early 1990s, some initial sediment sampling was done as part of the U.S. Environmental Protection Agency's *National Urban Runoff Program* and *Clean Lakes* initiatives, which identified PAHs (USEPA 1983, USEPA 1989). Since PAHs are hydrophobic, they had not previously been detected in water samples and efforts detailed in these two studies focused on sediment sampling. PAHs were detected in sediments of Town Lake, a segment of the Colorado River that flows through downtown Austin and receives input from urbanized creeks (COA 1992). Further investigations under two grant programs identified these pollutants in urban creek mouth sediments and in sediments captured in water quality control structures. These investigations revealed unexpectedly high levels of PAHs, prompting further study. Sediments in four urban creeks were sampled, and these samples identified "hot spots" of PAHs that were higher than most literature values found in creeks nationwide.

One of these "hot spots" is upstream of Barton Springs Pool, a natural spring-fed swimming pool, that is an important recreational resource in Austin and home to an endangered species, the Barton

Springs salamander (final rule FWS 1997). Intermittently elevated levels of PAHs are also seen in the pool itself, probably introduced as a result of overflow from the upstream dam caused by water and sediment from the creek above entering the pool during major storm events. Studies on health threats to swimmers concluded that "swimming and playing in Barton Springs Pool poses no apparent public health hazard" (ATSDR 2003). This ruling was based primarily on the low exposure received by swimmers and other recreationists. Assessment of potential effects on the aquatic life in the pool is ongoing by both the City of Austin and the Texas Commission on Environmental Quality (TCEQ) to evaluate the infrequently elevated PAHs found in the pool sediments (http://www.tceq.state.tx.us/comm_exec/tox/bsp/BartonMain.html, "Environmental Assessments of Barton Springs Pool and Barton Creek," TCEQ, accessed May 23, 2005). The studies also tracked the levels of PAHs in Barton Creek above the pool to elevated levels along a dry tributary. The tributary's level increased upstream, near the location of an apartment complex parking lot. As these studies have progressed, the data in this report confirm the dominance of PAH inputs in environmental sediments from coal-tar based sealants.

The USGS (USGS 1999, USGS 2001) has documented increasing PAHs in sediment cores from urban lakes. Studies by other agencies have demonstrated the relationship between PAH contamination and human activity (Sanger, et al. 2004). Typical sources cited include automotive exhaust, lubricating oils, gasoline, tire particles, and atmospheric deposition. A few have even included abrasion of road surface materials as a source (Pengchai et al. 2003). This report will provide evidence that PAH concentrations in areas associated with sealed parking lots are distinguished from other sources by significantly elevated levels. In addition, chemical analyses of the two prevalent types of pavement sealants indicate that coal-tar based sealants contain PAH concentrations one to three orders of magnitude higher than those found in asphalt-based sealants, which offer an alternative with lower potential for contributing PAHs to the environment.

1.2 Scope and Continuity of Investigations

Although the investigations worked in a logical progression upstream from the discovery of elevated PAHs in the environment, these investigations, of necessity, included studies by different agencies; investigations of dead ends, such as core investigations to rule out buried waste as a source; and overlapping studies with different objectives (site specific source location investigations vs. citywide studies). These investigations were carried out concurrently in some cases, and sequentially in others. For documentation of these investigations, this paper will present data from the source materials to the resultant chemistry and potential impacts to the environment in the following sections:

- Parking Lot Sealants
  - Wet Before Application
  - Dried Material for Analysis and Studies
  - Parking Lot Scrapings
- Particulate Material from Parking Lots
  - Material Accumulated on Parking Lots Currently in Use
  - Material Washed off Paved Surfaces with Simulated Rainfall
    - Test Lots With No Traffic
    - Test Lots With Traffic
- Transport and Local Impacts (Studies Immediately in and Adjacent to Small Tributaries from Sealed Parking Lots)
  - Sediments Along a Dry Tributary to Receiving Water Body (Primary Drainage from a Sealed Parking Lot)
  - Sediment Chemistry in Austin Creeks Upstream and Downstream of Large Sealed Parking Lots
- PAH Concentrations in Receiving Water Sediments
  - Sediments from Small Watersheds Correlated to Watershed Characteristics Including Percent of Sealed Pavement Area.
  - Sediments in Receiving Waters Citywide Compared to Biological Effects Levels

Finally, this report will include a discussion of biological studies in which the City is participating with cooperating agencies to evaluate the significance of the sediment PAH levels if a significant portion may be transported in particulate form from parking lot surfaces. The purpose of this report is to provide enough data for local, state, and federal environmental agencies to determine what actions to take in addressing PAH-contaminated sediment from coal tar parking lot sealants. While the investigations described herein are not exhaustive, they provide a solid basis for follow-up studies recommended for funding through state or federal grant programs.

2 Parking Lot Sealants

Pavement sealants are surface finishes for parking lots, driveways, and airport runways that provide a protective barrier against weather and chemicals. Because the sealants wear off, recommendations call for reapplication every two or three years. An estimated 660,000 gallons of sealants are applied annually in the Austin area (City of Austin estimates, unpub. data 2003). At the vendor specified application of 0.2 gal/yd^2, this would cover approximately 682 acres of parking lot. The sealants are primarily of two types. One type is an emulsion containing up to 35 percent coal tar and the other is an asphalt emulsion. Streets are also resurfaced on a regular basis, and typically use an asphaltic emulsion with an aggregate material.

When parking lot sealants were identified as a potential source for the high levels of PAHs found in creek sediments, several readily available products were tested. Analyses were conducted to:

1) determine the levels of contaminants available for movement into the environment,
2) determine whether the contaminants found in the products were consistent and at levels that could yield the in-situ concentrations observed in receiving waters, and
3) evaluate whether the contaminant levels in one type of sealant were significantly lower than the other type, for assessment of alternatives available to minimize environmental impacts.

Product classifications (asphalt or coal tar) were determined based on Material Safety Data Sheets (MSDS), contact with the manufacturer, or from product labels; these sources generally identified a generic coal tar or asphalt content rather than specific PAH formulations. Inconsistencies between information sources were identified, and some products contained both asphalt and coal tar.

2.1 Raw Product Sampling methods

Products were sampled in raw form, as prepared for application, dried on an inert material, and scraped from the surface of parking lots. Different forms of the product were evaluated to allow interpretation of the variation in data, such as differences in products and between “batches” of sealants, effects of different application methods, and contributions and abrasive wear from automobiles on parking lots that are in use.

Methods for sampling each product type are described in the following sections. Each sample was submitted to a contract laboratory for chemical analyses using EPA approved methods. USGS studies employed the National Water Quality Laboratory (NWQL) in Denver, Colorado. Quality assurance samples included split samples and standard laboratory quality control samples. The City of Austin will provide detailed results upon request.

2.1.1 Raw Products

Products for chemical analyses were selected from those readily available at local building and hardware stores for homeowner application to driveways and other paved areas. Raw products for testing were obtained from several sources:

1) retail purchase of sealant products for resurfacing or repair of driveways,
2) purchase from commercial distributors who provide products to applicators for resurfacing residential and commercial parking lots and driveways, and
3) samples of materials used for resurfacing city streets.

Retail products are generally an emulsion of either coal tar or asphalt (and sometimes both) and water, clay and/or sand, and sometimes a solvent. Commercial products generally require the addition of water (to thin the substance for spraying) and sand or clay before application. All results, however, are reported on a dry-weight basis. Commercial products were purchased or obtained directly from the distributor. Eleven of both the coal-tar and asphalt-based products were obtained. Duplicates of four of the products were analyzed.

Each product was obtained in its original bucket or provided in a bucket by the distributor. The contents of each bucket were manually mixed thoroughly with a new wooden paint stirrer. A composite sample was obtained by submerging a clean glass sample jar into the product until full, extracting and sealing it immediately with a Teflon-lined lid. The samples were stored on ice and delivered with standard City of Austin chain-of-custody to the selected laboratories.

2.1.2 Dried Material Preparation

Commercial products were dried to simulate the sealant materials after application to a parking lot surface with no vehicular traffic or other source of PAH contamination or dilution. An additional use for this dried material was to spike the matrices used for ambient toxicity testing and verify toxicity from PAHs in the form of a dried sealant product. The availability for biological PAH uptake in a solid, high-carbon content matrix was originally thought to be very different from other forms.

Two readily available commercial products, a coal-tar and an asphalt-based emulsion, were formulated for the dry preparation by painting onto glass, drying for 72 hours and scraping off. A standard preparation method was followed to obtain sufficient material for sample analyses (Appendix A). A sample of each dried sealant material was deposited into a clean glass sample jar with Teflon-lined lid and submitted for laboratory analyses.

2.1.3 Parking lot scrapings

Parking lot scrapings were obtained by a consultant to the City of Austin, Geomatrix (Geomatrix Consultants, Inc. 2003) and by the USGS (USGS 2003). The procedure was to manually scrape a small area of a sealed parking lot (less than .25 square meters) with a metal paint scraper. The particulates removed during this process were brushed onto a piece of new card stock and placed in a clean sample jar. The paint scraper was decontaminated between sites. Most of the samples were from lots with traffic use that would introduce particulates and hydrocarbons; air deposition could also introduce PAHs. The USGS study also included isolated lots where new sealant products had been applied by City staff to a currently unused airport parking lot in Austin. Although these lots had possibly been sealed with a coal-tar sealant in the past, the shallow scrapings taken included primarily the recently applied and dried material and did not include any materials from vehicular traffic.

2.2 Raw Product Results

All results from sealants were reported on a dry-weight basis for comparison. As expected, PAHs comprised a substantial portion of the coal-tar based sealants. Other toxins identified included metals and some volatiles, particularly in products with solvents in the formulation. Figure 2.1 displays the PAH profile of the sealant products in individual asphalt and coal tar based sealants. Although the scales are dramatically different (a maximum of 1,800 ppm total PAHs for asphalt-based and 50,000 ppm for coal-tar based sealants), the profiles are remarkably similar, with phenanthrene and fluoranthene dominating the composition. Substantial variation was observed within each group of products, again with a similar profile of specific PAHs, although ratios were less consistent within the asphalt group.

In general, the commercial products were higher in PAHs than the retail products (and similarly in coal tar percent, discussed further in Section 2.2.2), and street-paving products fell to the bottom of the range of asphalt-based products.

2.2.1 Comparison of Sealant Types

When comparing the groups of products, it was apparent that, despite the variation within the groups, the total PAH content of coal-tar based sealants is much higher than in the asphalt-based sealants (and roadway products). The total of the 16 parent PAHs (values less than method detection limits were set to zero) are shown below in Figure 2.2. The median of asphalt-based sealants is approximately 50 ppm, while that of the coal-tar based sealants is more than three orders of magnitude greater, or >50,000 ppm. The data verify that PAH content of coal-tar sealant products is significantly higher than that in asphalt-based products, and suggests that the asphalt-based products would have fewer environmental effects, based on the magnitude of that difference. Figure 2.2 also demonstrates, when examined more closely, that not all products labeled as having the lower coal tar content had the lowest levels of PAHs. The highest total PAH is for a product with 23 percent coal tar, while the 34 percent product had less than half the concentration. The relation between coal tar content and PAH proportion is examined in the next section.

Figure 2.1 PAH Profile of Asphalt-Based Sealant Products

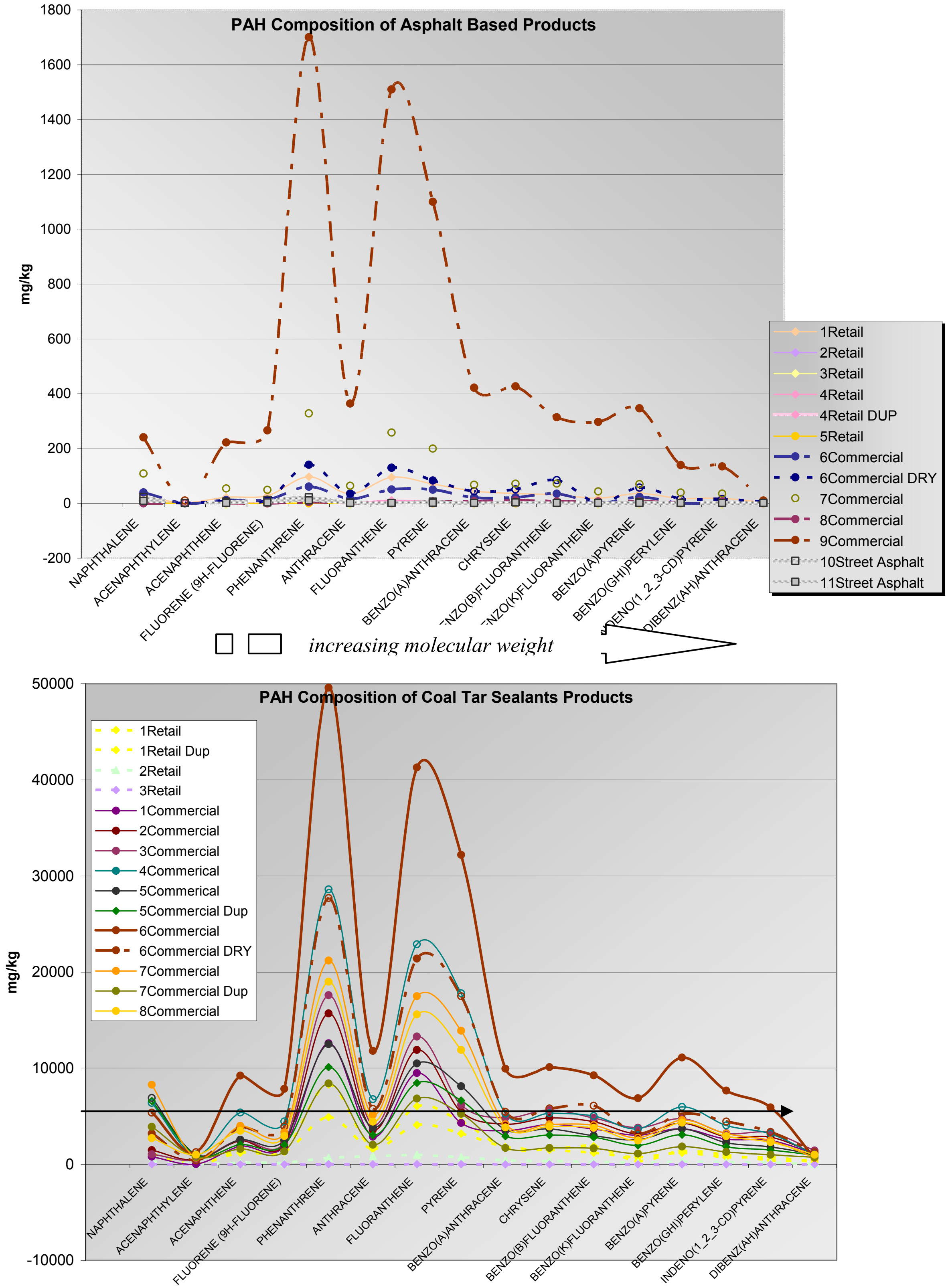
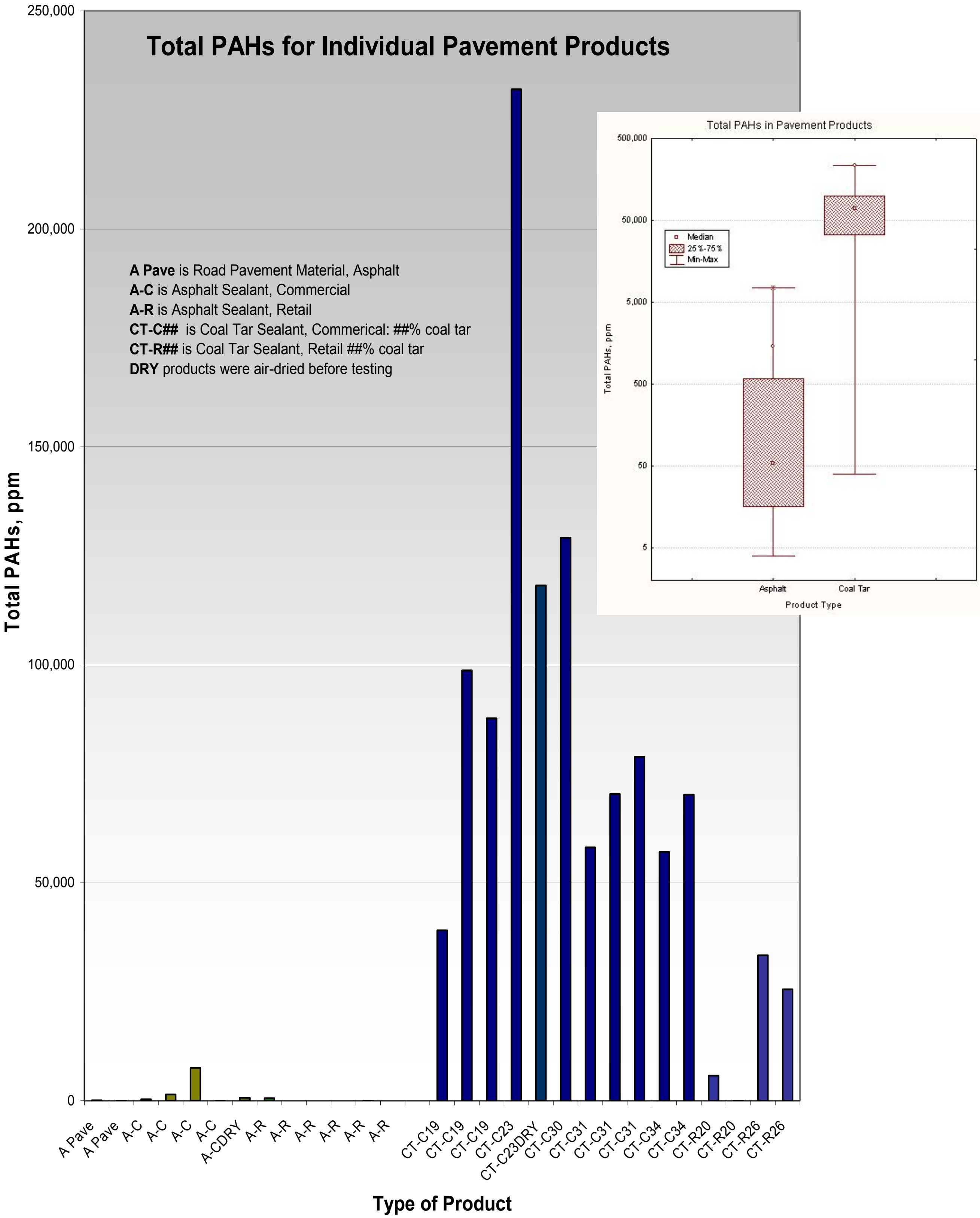


Figure 2.2 Product-Type Comparison of total PAH Content



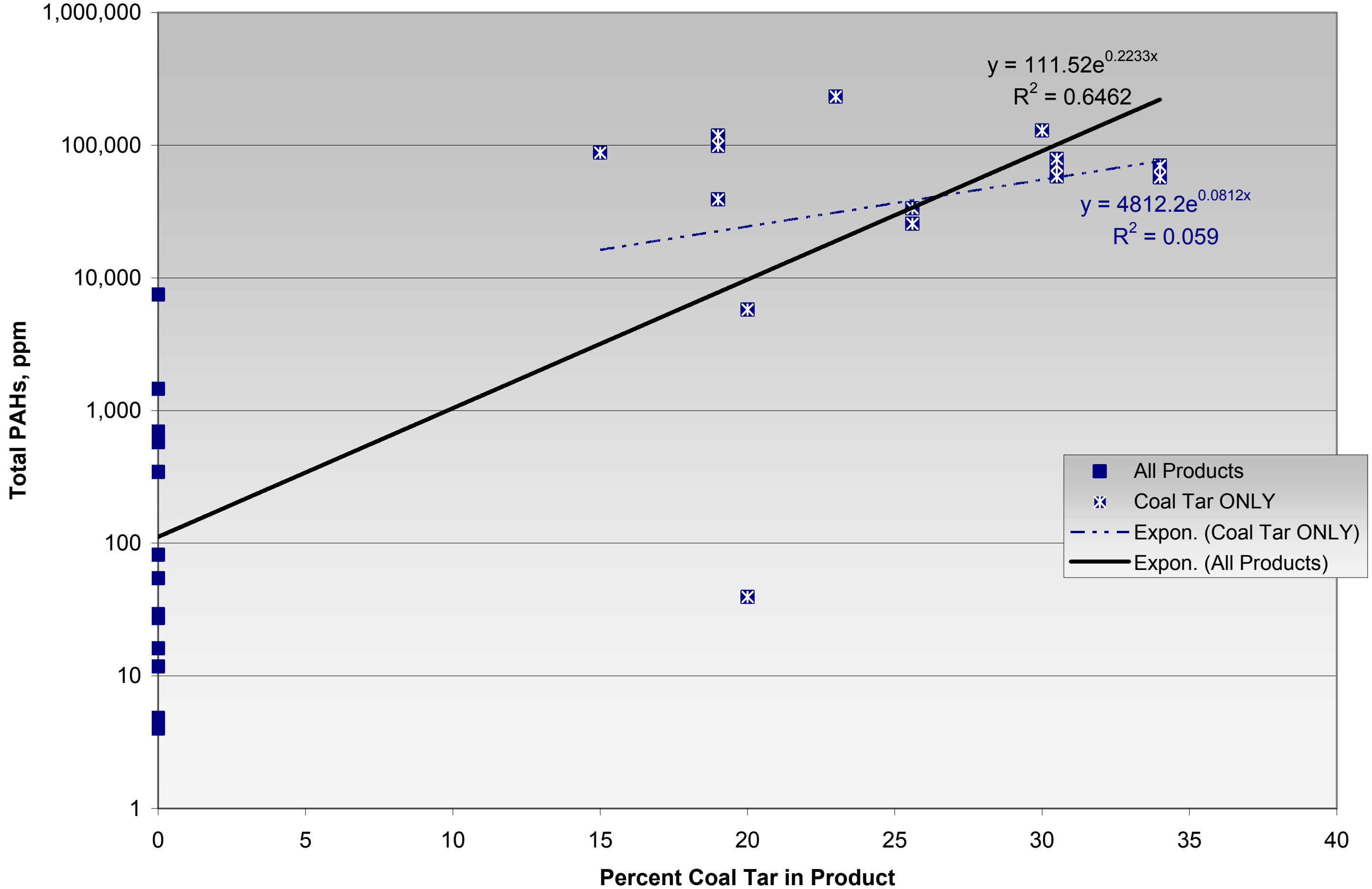
2.2.2 Coal Tar Content and PAH levels

When examining sealant products, the information that is readily available is limited to how the mixture was formulated; specifically, what percent of coal tar it contains (by weight or volume and sometimes it is not specified). The lack of direct correspondence between PAH concentration and coal tar content is contrary to the sealant source of the PAHs. However, industry representatives and limited coal tar analyses (ATSDR 2002) indicate that products sometimes vary significantly between batches and the coal tar manufacturing process does not produce a consistent product. Therefore, the labeled coal tar content may not be an accurate representation of the coal tar content of a particular batch of product. This complicates the examination and identification of this product as a source of PAHs in the environment.

To verify that the coal tar content was the primary contributor to PAHs in the products, and examine the consistency of this finding, the relation between percent coal tar content of the product and the total PAHs was examined. Some assumptions needed to be made, because the MSDS information is generalized for all batches of a product type. For many products, a range of content was provided on the MSDS or product label (for example, 25 percent to 30 percent); for these, the coal tar content was assumed to be the average. Based on discussion with manufacturers, it was assumed that the content for a value reported as "<35 percent", was assumed to approach that number and was set at the number (=35 percent). Products with insufficient content data or conflicting data on the MSDS and product labels were excluded from this analysis.

When all products were included, including asphalt-based products with a labeled zero percent coal tar, a strong exponential relationship between coal tar and total PAHs was observed, as shown in Figure 2.3. However, among the coal tar products alone, a regression explains little of the variation within the total PAHs, thus indicating, within the products studied, the importance of the presence of the coal tar rather than its percentage in the mixture. This information may be useful in indicating that recommendations about the preferred type of product (asphalt-based vs. coal-tar based) would be supported by the data rather than recommendations on an allowable level of coal tar content.

Figure 2.3 Relation Between Coal Tar Percent and Total PAHs



2.3 Applied Product Results

The properties of asphalt, asphalt-based sealant, and coal-tar based sealant products after application to parking lots were examined through chemical analyses of scrapings from unsealed and sealed asphalt lots. As described in Section 2.1, scrapings were taken from plots located in parking lots currently in use and in test plots, where traffic was not allowed. The majority of the data were collected by the USGS as part of a cooperative monitoring program. Many of the scraping samples were taken from parking lots in use and include any PAHs from oil drippings, gasoline, air deposition, etc. that had adhered to the surface. PAH variability is expected to be even greater in applied sealant product due to a number of factors, such as the wear rate, how long ago the sealant was applied, the breakdown of the PAH components, etc. Of greatest interest are the answers to two questions: 1) whether the same level of PAHs are available for wash-off after the product is applied and 2) whether parking lots in use have higher PAHs in the surface material than those with no traffic (labeled as test plots in the following sections).

In scrapings and dried products, the PAH profiles were similar and in a range substantially lower than the wet product shown in previous Figures 2.1 and 2.2. Although loss of volatiles was expected with drying, the decrease that was seen in most of the individual PAHs was unexpected. Because of these rapid changes in PAHs seen with application and drying, the appropriate data to assess for the contaminants available for release into the aquatic environment from the sealants themselves may be the dried or scraping chemical analysis results rather than raw wet product results.

Asphalt and coal-tar based products were examined separately, and scrapings PAH profiles of the different plots from used parking lots, test plots (with no traffic), and dried sealant are shown in Figures 2.4 and 2.5, along with scrapings PAH profiles from lots with unsealed asphalt. Findings from the scrapings are summarized as follows:

- The asphalt materials and scrapings from unsealed asphalt surfaces had lower PAHs than any of the sealants or scrapings. Total PAHs for these materials were significantly lower than scrapings from either asphalt-based or coal-tar based sealed lots.

Figure 2.4 Asphalt-Based Parking Lot Scrapings, Sealed and Unsealed

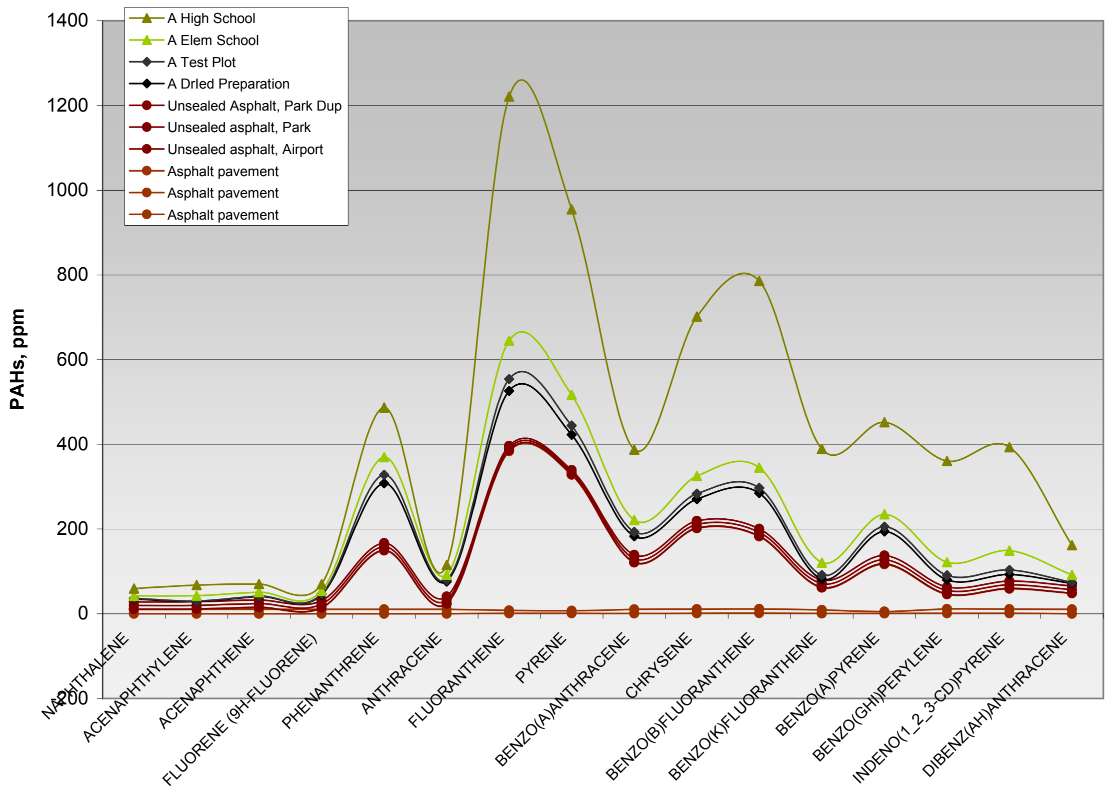
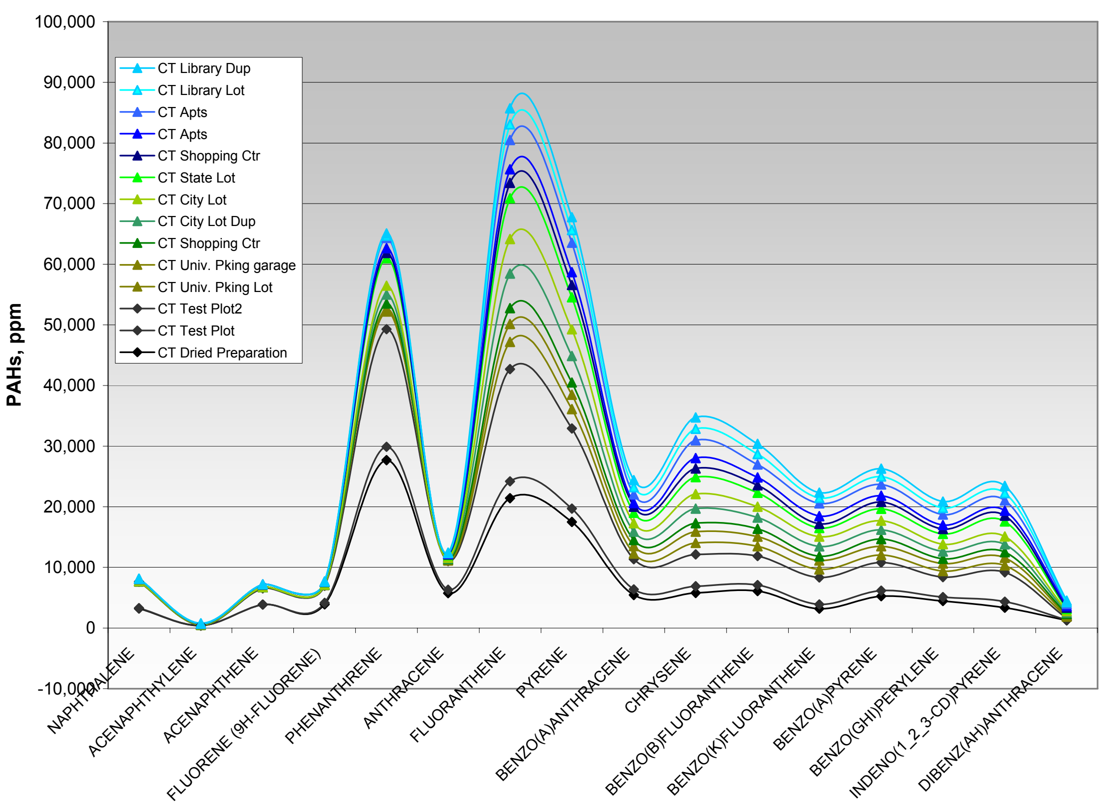


Figure 2.5 Scrapings from Lots with Coal-tar Based Sealants

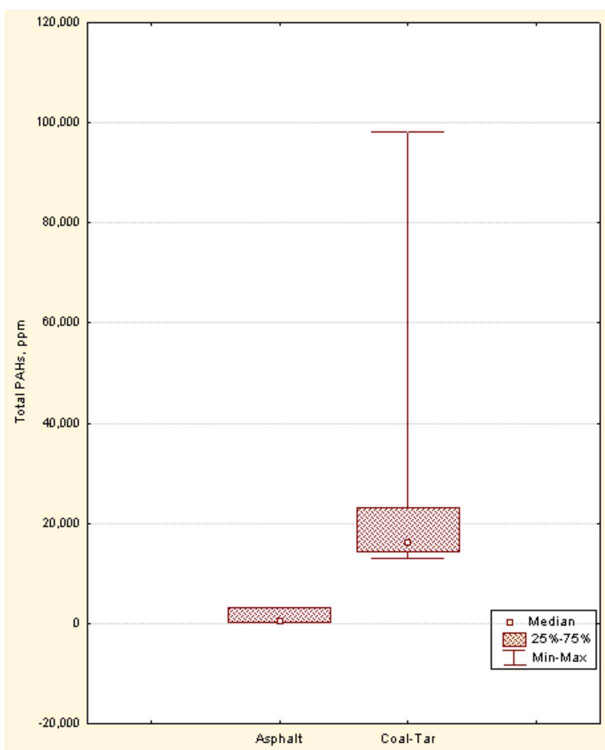


- The dried product and scrapings from the test plots were similar. (Only one pair each of dried product and test-plot scrapings was available for each product; therefore, statistical comparison by product is not possible.)

- The used lots had significantly higher levels of total PAHs in the scrapings than the test plots within each type (coal-tar and asphalt). This may indicate that traffic is providing an additional input of PAHs. This conclusion is strongest for the asphalt-based sealants; for asphalt-sealant analyses, the same product was used for all lots where scrapings were made. The individual products, however, could not be identified for all coal-tar lots, so the contribution of PAHs from the sealants compared to the traffic cannot yet be determined. Of interest is the similar profile of individual PAHs for both the used and test plots.

- The primary findings from scraping results continue to support the results found for raw products. The total PAHs seen in scrapings from coal-tar sealed lots is significantly higher than found in scrapings from asphalt-based sealant lots; see Figure 2.6.

Figure 2.6 Total PAHs in Scrapings Only



2.5 Product Investigation Conclusions

A summary of the primary conclusions from analyses of raw and applied products is provided below.

- The total PAH content of coal-tar based sealants is much greater than in the asphalt-based sealants (and roadway products). This is true in both raw product and applied product testing.
- When all products were included, a strong exponential relationship exists between coal tar percentage and total PAHs; however, within the coal tar products studied, the percentage of coal tar in the mixture was not a significant predictor of total PAHs.
- The commercial products were higher in PAHs and in coal tar percentage than the retail products; street paving products fell at the bottom of the range of asphalt-based products.
- The asphalt materials and scrapings from unsealed asphalt surfaces had lower PAHs than any of the sealants or scrapings. Total PAHs for these materials were significantly lower than scrapings from either asphalt-based or coal-tar based sealed lots.

3 Particulates

Parking lots accumulate dirt and dust, along with associated pollutants: gasoline and oil drips/spills, deposition of exhaust products, and particulates from wear of tire, brake and pavement materials. Urban landscaping practices can also produce vegetation cuttings, as well as fertilizer and pesticide washoff, all of which may contribute to contaminants found in parking areas. Other common sources of contaminants in urban areas include animal waste and sanitary sewer leaks and overflows. In addition, resuspension and deposition of pollutants/particles via the atmosphere can increase or decrease the contribution potential of a source area. All of this mixture of contaminants deposited in urban areas may accumulate on paved surfaces, adhere to particulates in dust and dirt on the pavement, and become part of the materials washed off during a storm event.

Particulates washing off the surfaces of parking lots were collected to examine the material and pollutants readily available for transport to the stream system. The majority of this work was performed through a cooperative program with the USGS (USGS 2004), and the USGS is continuing to examine the potential PAH load contribution portion from parking lot sealants (Mahler et al. draft 2004).

3.1 Particulate Sampling methods

Samples were collected by two methods for results seen in this section: 1) particulates were collected from used parking lot surfaces, and 2) particulates were washed off of parking lot surfaces where 2a) normal traffic occurred and 2b) sealants were applied to controlled test lots and no traffic was allowed.

Loose particulate samples were collected from dry particulates accumulated at the lowest points of several parking lots in the Austin area. For each of these lots, a scoop was used to collect sediment from the accumulated area and deposit it into a glass sample jar with Teflon lid. A minimum of three scoops were used to composite the material. This study primarily sampled coal-tar sealed lots currently in use. This was a preliminary study to identify the potential source of PAHs.

Washoff samples were collected by the USGS by simulating rainfall runoff on segregated parking areas, capturing the runoff and filtering the particulates from the runoff. The sampling methods are described in detail in USGS 2004-1208 (Mahler et al. draft 2004). Several types of parking lots were sampled for this study. Sediment was sampled from lots with both coal-tar and asphalt-based sealants, as well as from concrete and unsealed asphalt lots. In addition to locating lots currently in use, the City's Mueller airport (no longer active) was used. New sealant products were applied to Mueller's parking lots and rainfall runoff was simulated on surfaces that did not have on-going vehicular traffic. Table 3.1 below describes the sampling sites by agency and lot material. Particulates from sealed lots were first analyzed by the City chronologically before type of sealant (coal tar or asphalt based) was determined to be of importance. Historical records of sealant materials were unavailable for many of these lots. The data were not included in these analyses if the sealant application history was unknown based on the PAH differentiation by type of sealant from product testing.

Table 3.1. Sampling Sites for Particulate Analyses

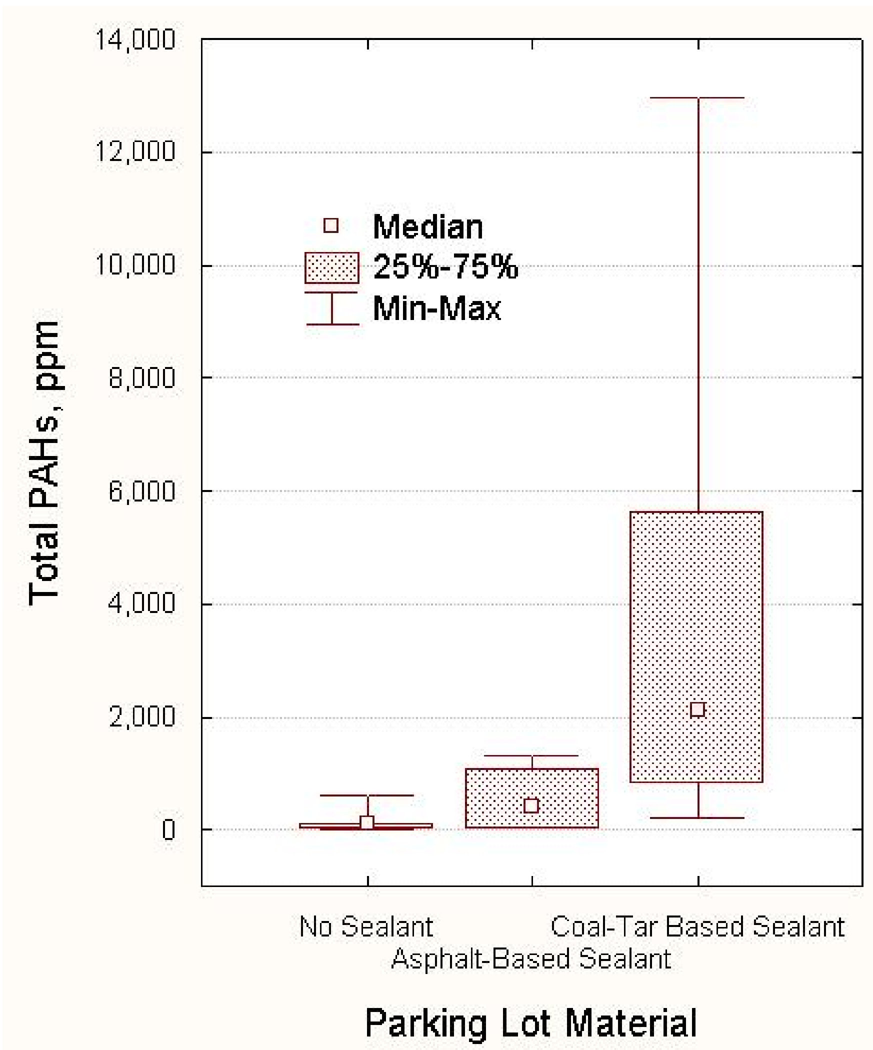
	Sealant Type: **Lot Type:**	**Coal Tar Sealant**	**Asphalt Sealant**	**Unsealed Asphalt**	**Concrete**
City of Austin	**"In-situ"** particulates collected dry from in-use lots.	2			
USGS Simulated rainfall to washoff, collected, and filter particulates.	**Test Lots** (No traffic)	2	1	1	
	In-Use	6	4	2	2

Analyses of all of these particulates included the primary PAHs, which will be examined in the following section. Each sample was submitted to a contract laboratory for chemical analyses using EPA-approved methods. USGS studies employed the USGS laboratory. Quality assurance samples included split samples and standard laboratory quality control samples. Detailed results will be provided by the City of Austin upon request.

3.2 Particulate PAH Analyses Results

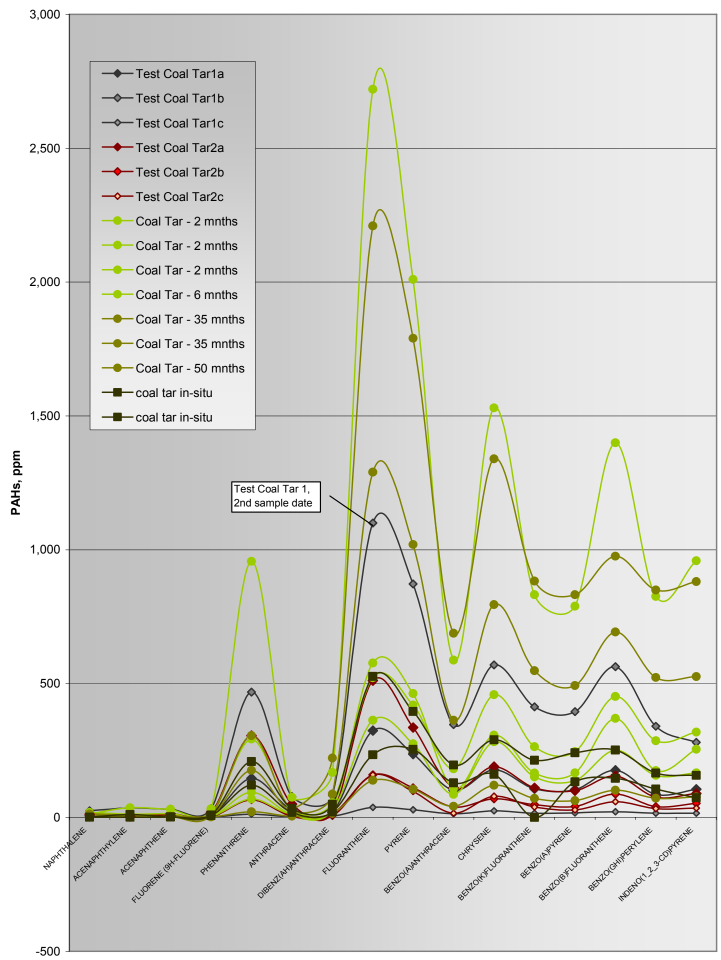
As with the products, the particulates from parking lots where coal-tar based sealants had been applied had significantly higher total PAHs ($p=0.05$) than parking lots with asphalt-based sealants or no sealants, shown in Figure 3.1. Parking lots with asphalt-based sealant also had significantly higher total PAHs than the unsealed lots. The unsealed lots include both asphalt and concrete lots. These results included data from parking lots that have been in use and test lots where sealants were recently applied. The primary conclusion to be drawn here is that the sealant PAHs available for export to stream sediment (in the form of particulates from sealed parking lots) are significantly higher than those from vehicular and air deposition alone (unsealed lots).

Figure 3.1 Particulates from Parking Lots



The individual PAHs in particulates from the coal-tar sealed lots are shown in Figure 3.2. The time of application was not known for the in-situ lots. The time indicated for test lots is the amount of time between application of the product and washoff simulation and testing. The PAHs from in-use lots were generally higher than the test lots, indicating that some additional PAHs are derived from vehicular traffic or abrasion. However, the general signature of these primary 16 PAHs did not change greatly, with fluoranthene and phenanthrene remaining the highest peaks for both the test and in-use lots. Therefore, the PAH signature derived from sealants either overwhelmed or was similar to the traffic source signature. No clear temporal trend is seen on either the test or in-use sites. One test site showed decreasing PAHs with each sample (approx. 2 ½ weeks between sample dates), but Test Site One had the highest values at the middle sampling date (Test Coal Tar 1b in Figure 3.2: also the highest of all the test site results).

Figure 3.2 Analyses of Particulates from Coal-tar Sealed Parking Lots



PAHs in particulates from the asphalt-based sealant lots, in addition to results from unsealed asphalt lots and concrete lots, are shown in Figure 3.3. The scale of Figure 3.3 for asphalt-based lots is an order of magnitude less than Figure 3.2 for the coal-tar sealed lots. Within the asphalt-based sealants, the in-use lots were generally higher than the test lots or the concrete and unsealed asphalt lots; however, Figure 3.4 shows the asphalt-based and unsealed lots on a log scale that emphasizes the overlap.

Figure 3.3 Analyses of Particulates from Concrete, Asphalt, and Asphalt-Based Sealant Parking Lots

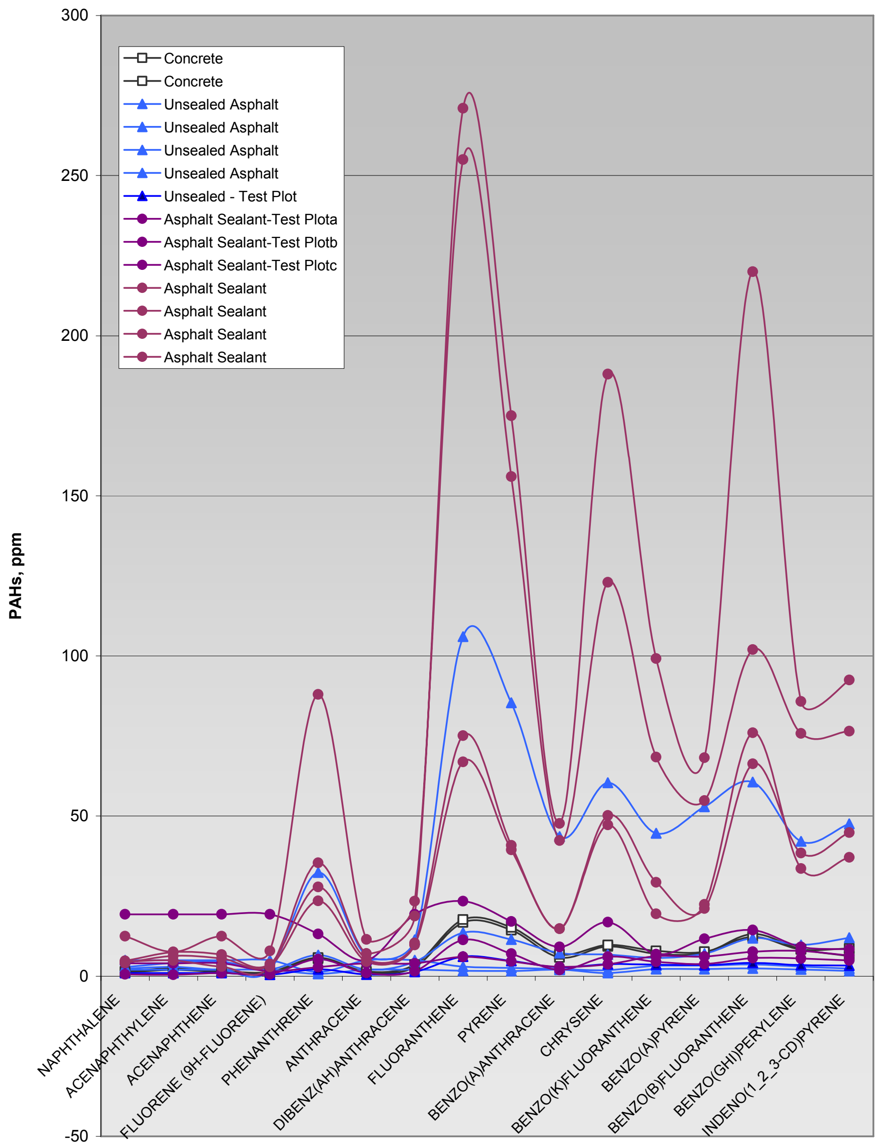
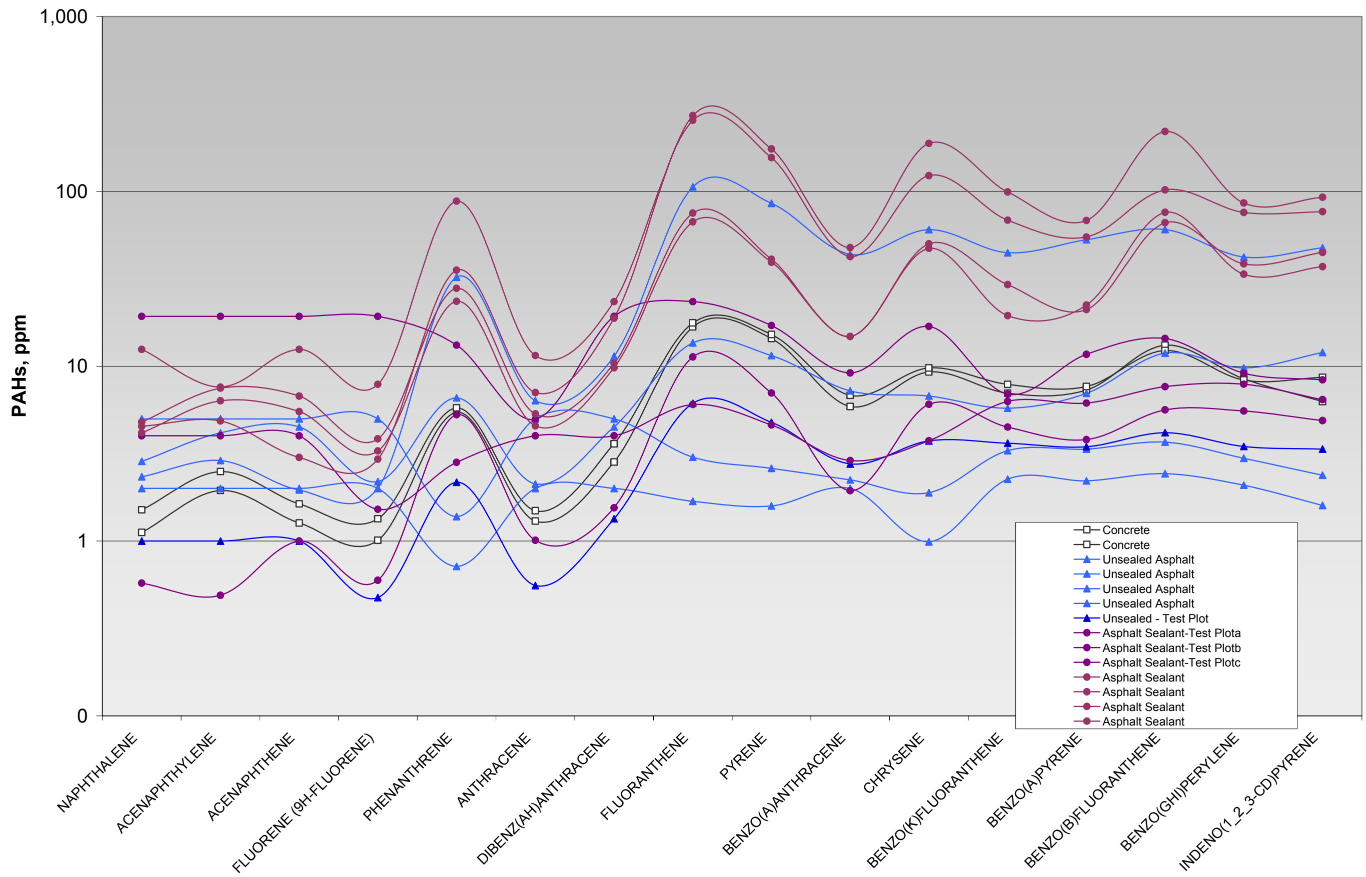


Figure 3.4 Unsealed Lots and Lots with Asphalt-based Sealants, Log-Scale



Two reports by the USGS (USGS 2003 and Mahler et al. 2004 draft) verify that significantly higher PAH levels are found in washoff particulates from coal-tar sealed lots than from asphalt-sealed or unsealed lots. The USGS studies are continuing to look at additional lots and evaluate the derivation of loads from parking lots. Preliminary loading estimates from the USGS indicate that parking lot particulates may account for a significant portion of PAHs transported in the sediment load of urban creeks (USGS in press).

3.3 Particulate Conclusions

The following conclusions can be summarized from both USGS and COA parking lot sealant particulate analyses:

- Sealant PAHs available for export to stream sediment (attached to particulates from sealed parking lots) are significantly higher than those from vehicular and air deposition alone (unsealed lots).
- Within the asphalt-based sealants, the in-use lots were generally higher than the test lots or the concrete and unsealed asphalt lots, indicating the additional vehicular-associated source of PAHs and the adherence of vehicular PAHs to sealants.
- The general signature of the primary 16 PAHs was very similar between the test and in-use lots, indicating that the sealant signature may be similar to or overwhelmed by any unique vehicular-source signature.

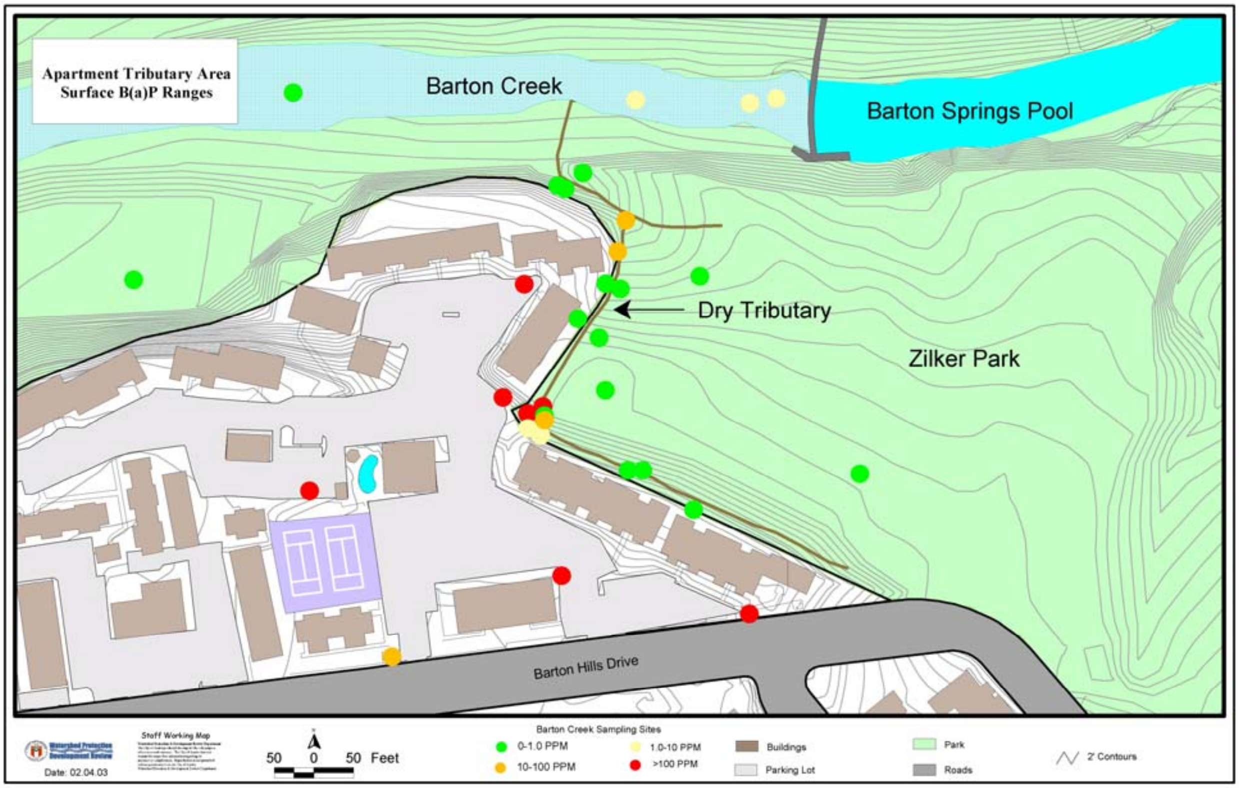
4 Transport and Local Impacts

Pavement sealant products, along with scrapings and particulates from the parking lots where they have been applied, were examined in the Sections 2 and 3. The following section will examine their destination in the aquatic environment. In tracing the source of the PAHs in the habitat of the endangered Barton Springs salamander, the City of Austin conducted extensive sampling in a localized area above Barton Springs Pool, including a dry tributary and its headwater drainage where an apartment complex with a sealed parking lot is located. In preliminary investigations, a screening analysis procedure using an immunoassay method was used to isolate sources (COA 1998). Conventional sediment sampling was conducted in several phases of the study to determine the source of PAHs, to assess the threat to the downstream Barton Springs Pool (habitat of the endangered salamander and high-use recreational facility), and to evaluate actions to address the PAHs in the soils and sediments. Because of the multiple-focus objectives of the studies, they were not conducted simultaneously. This section of the report consolidates the results of several studies to examine the distribution of PAHs from the parking lot surface to the creek bed sediments and examines the individual PAHs and their changes in the aquatic environment. In addition, a brief discussion of chemistry data for paired sites above and below runoff from sealed parking areas adjacent to Austin creeks will be presented.

4.1 Transport in an Isolated Tributary Area

Figure 4.1 displays the study area of the tributary entering Barton Creek immediately above Barton Springs Pool. The City of Austin has ongoing intensive monitoring in the Barton Springs Pool area and Barton Creek due to the presence of the endangered Barton Springs salamander, which resides in the pool. The pool itself is fed primarily from a large underground spring, which may transport materials through the aquifer from the extensive recharge zone covering both urban and non-urban areas southwest of Austin. During storm events, flow from Barton Creek, which normally flows through a bypass channel around Barton Springs Pool, may overtop the upstream dam and carry floodwaters and sediment into the pool. These events introduce more urban contaminants from the downstream portions of the Barton Creek watershed into the pool. The spring water from the pool and flow from Barton Creek both discharge just a short distance below the pool into Town Lake, the portion of the Colorado River passing through downtown Austin.

Figure 4.1 Dry Tributary to Barton Creek Above Barton Springs Pool



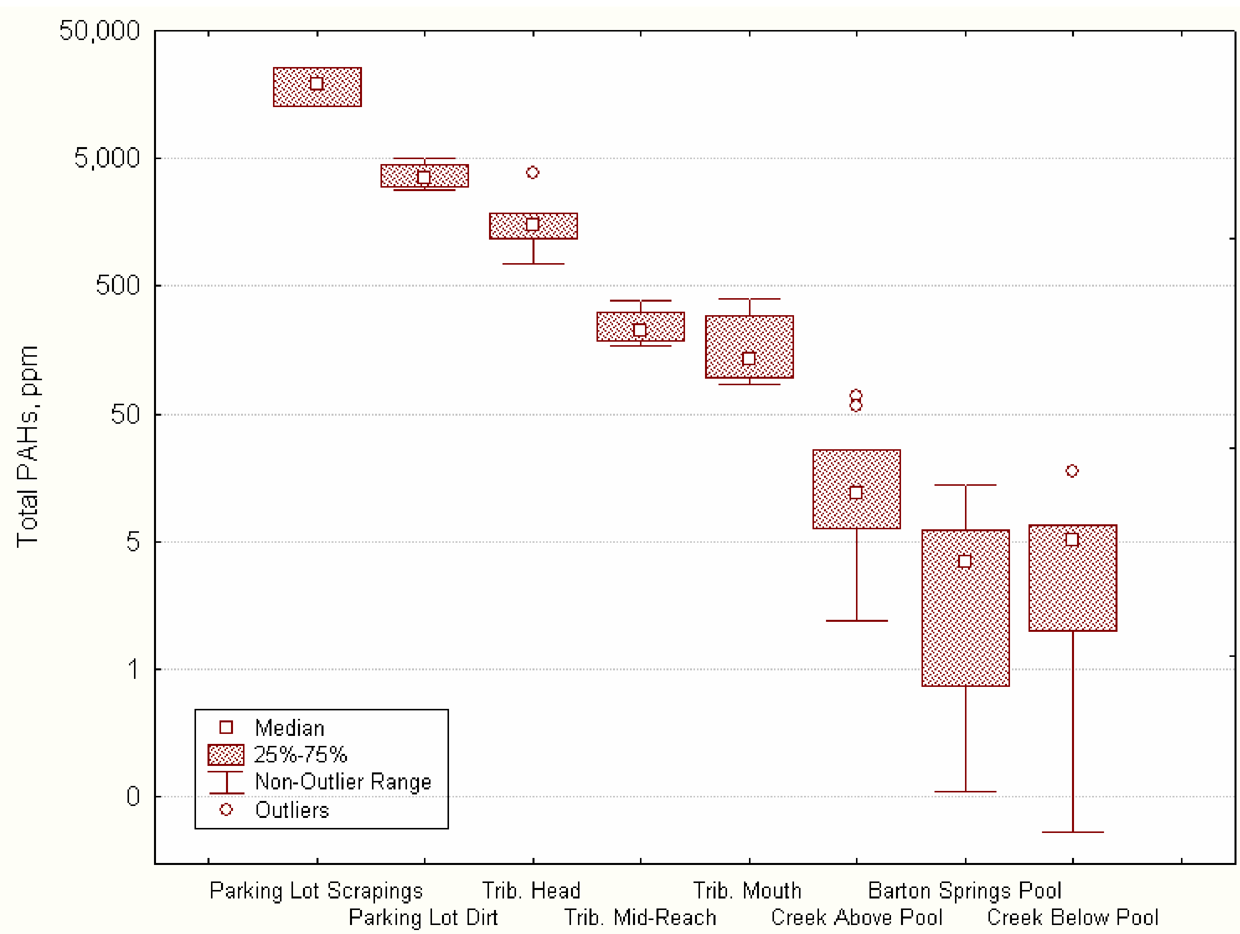
Above the pool, along Barton Creek, tributaries carry runoff from central Austin neighborhoods and the Mopac Expressway to the creek. Some of the development in these tributary watersheds occurred before the City's requirement for structural water quality controls were in place. The development in the dry tributary that enters directly above the pool was not required to construct these controls. Data for this tributary were evaluated in detail due to extremely high PAH levels in preliminary screening, the sensitive nature of the endangered species habitat, and the recreational resource value of Barton Springs Pool. The watershed for this tributary was determined to consist entirely of the apartment property, primarily the rooftop and the parking lot area at the head of the tributary. Records and communication with property management indicated that a coal-tar sealant had been applied to the parking lot.

Other source areas were excluded as the primary origin of the PAHs found through upstream and local sampling. Although determinations were made of elevated PAH levels in additional dry tributaries upstream along Barton Creek, each had reduced levels in the mainstem below the tributary confluence and above the immediate pool area. One-quarter mile immediately above the pool, PAHs were below detection limits. Sediments were also tested from parking lots in Zilker Park on the opposite bank, which drain into the immediate creek area, but these did not approach the PAH levels found in the tributary or above the pool.

4.1.1 PAHs in Tributary and Receiving Creek Sediments

When tracing the apparent path of PAHs from the parking lot to the creek, a decisive pattern is seen, as demonstrated in Figure 4.2. The total PAHs decrease exponentially along the drainage network path from the material scraped and collected in the parking lot, through the tributary, and into the receiving water body, Barton Creek.

Figure 4.2 PAHs from Parking Lot Downstream to Barton Springs Pool

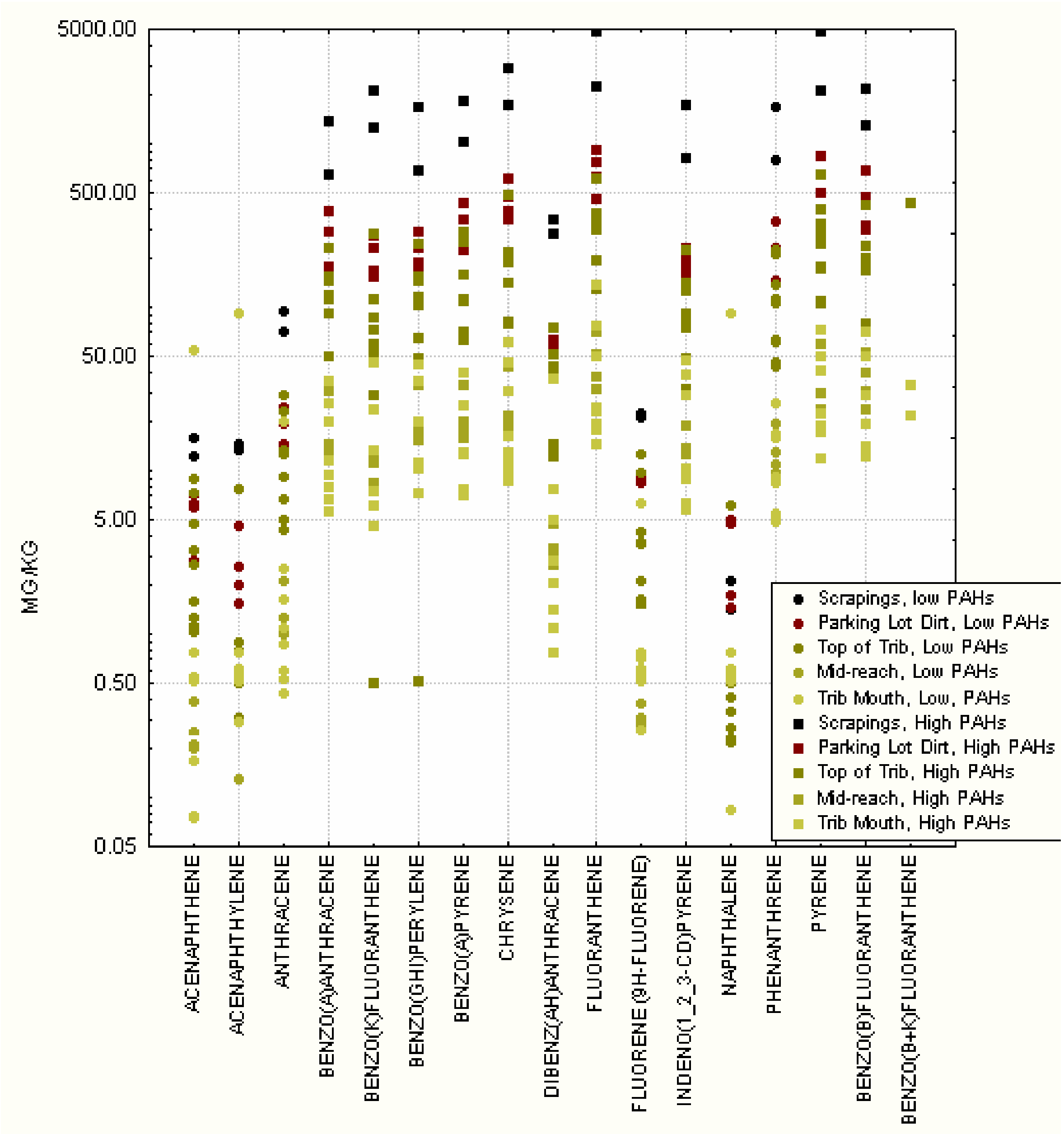


Below Barton Creek, in Town Lake itself, samples taken of sediments below the Lamar Street bridge in 2001 had a concentration of 3.4 ppm, continuing the pattern of concentrations decreasing downstream.

Overall, Town Lake shows concentrations in the same range as Barton Creek and Barton Springs Pool, with elevated levels where urban creeks such as Shoal and Waller enter the lake (COA 1992 and COA in press 2003). The median of detected values over the last 10 years in Town Lake downstream of Barton Creek inflow is 4.2 ppm.

Because of the elevated PAH levels in sediments at the site below the tributary confluence, and lower levels upstream of the confluence, the tributary is indicated as a source. The pattern of PAHs along the path from the parking lot to the creek shows a decrease that appears to be a result of at least two factors. The most apparent is the addition of erosive sediments and sediments from other sources to the bed sediments collected. Reduction in concentration, as dilution of the source particulate matter occurs, is part of the introduction of any concentrated pollutant to a natural system. Within this dry tributary, in fact, excessive bank erosion was visually confirmed, and testing of the bank sediments yielded no evidence of PAH contamination within those materials. The second factor in the sequential decrease of total PAHs down the drainage network is the degradation or transformation of individual PAHs. Two observations indicate that some degradation and transformation is occurring, although it is difficult to quantify. First, within the individual PAH data, various PAH ratios were examined and found to be changing along the tributary. This can be observed in Figure 4.3, which shows the individual PAHs along the tributary reach. The pattern between the colors (locations) remains similar, but some obvious changes are seen, such as the higher ratio of the lower molecular-weight PAHs (acenapthylene, acenapthene, and naphthalene) at some of lower tributary sites. At this particular site, additional sources of other PAHs appear that could be entering the tributary and altering the pattern from upstream.

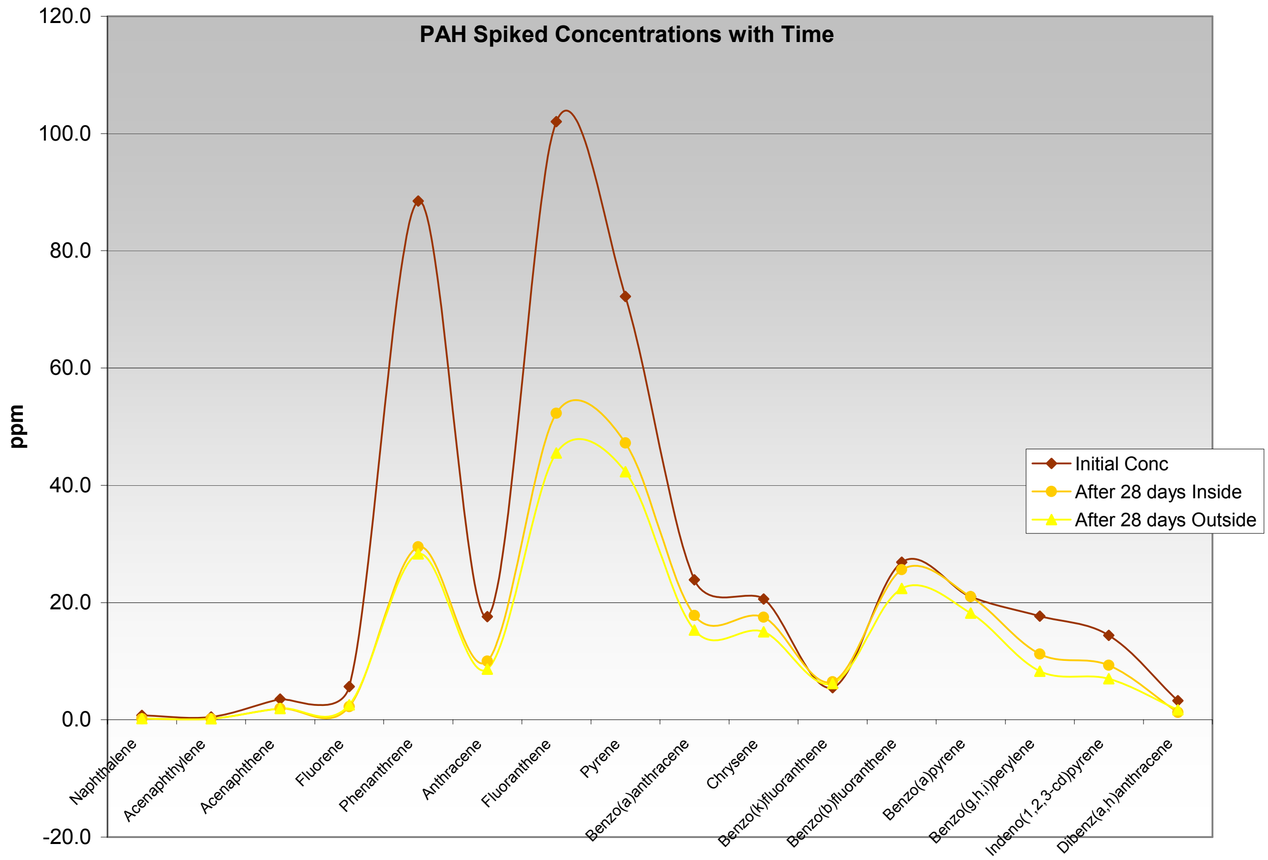
Figure 4.3 Individual PAHs From Parking Lot Through Tributary



4.1.2 Transport Data from Biological Studies

Other data that illustrate the transformations in PAHs from sealant source to stream sediment were obtained as part of a biological effects study. City staff worked with staff at Texas State University in San Marcos to prepare sediment spiked with dried coal-tar sealant material. The dried coal-tar sealant was added to a dried sediment and then established in two mesocosm systems with spring water added, one in an inside laboratory and one in an outside environment. The prepared materials were tested upon preparation and tested again after they were allowed to remain in these systems with no organisms introduced for a 28-day period. The results are shown in Figure 4.5. The reduction in the concentrations of 16 primary PAHs was considerable, thus indicating that some transformation or loss from the system occurs in an aquatic system where biological transformations are primarily microbial. Again, the change between individual PAHs was not consistent. PAHs with highest concentrations (phenanthrene and fluoranthene) decreased to less than half the original concentrations, while other PAHs were reduced by smaller percentages.

Figure 4.4 Individual PAHs in A Spiked Sediment Equilibrated In An Aquatic Environment For One Month



4.2 Paired Sampling Above and Below Parking Lot Inflows

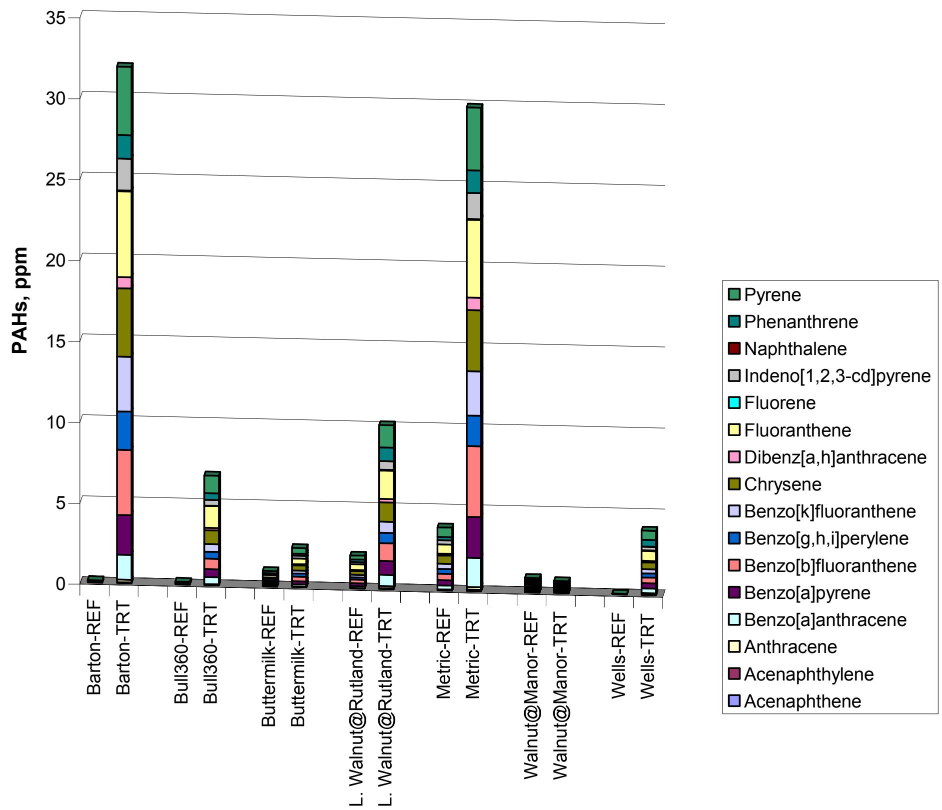
Because of the apparently localized elevated values seen in some creek areas from PAH inputs, City staff also conducted a study of biological effects in the streams. As a first evaluation, biological community impacts were assessed at sites that had been identified as having elevated PAH levels in local creek areas. To evaluate the relative impacts for each selected elevated PAH site, an upstream riffle site was identified and assessed for sediment chemistry and biological community metrics. The biological study results are briefly described in Section 6.0, and will be documented in two planned journal papers. The sediment chemistry results demonstrate the localized impacts of immediate runoff from parking lots on sediment PAHs.

Aerial photography was used to identify sealed parking lot surfaces that demonstrate the typical wear patterns associated with such lots along creeks in the Austin area. Where a large lot area was in close proximity to the creek and the upstream area had little adjacent parking area, a site visit was made. Each downstream site, therefore, represents a site receiving both upstream influences and runoff from a close, sealed parking lot. Although the industry has verified that a vast majority of lots in the area were sealed with coal-tar based sealants rather than asphalt-based sealants (Bruce Lowry, Wheeler Coatings, personal communication), the individual product for each site could not be verified. However, the elevated PAH results indicate that coal-tar based sealants were used.

Multiple paired upstream and downstream creek sites were visited and sediment samples collected. These were returned to the City of Austin laboratory and an immunoassay screening analysis for total PAHs was conducted. The results of the Ohmicron analyses were used to identify sites with a large differential between upstream and downstream sites. Laboratory analyses were conducted on seven paired sites, five of which showed a large differential between upstream and downstream as seen in Figure 4.5. Since the watershed areas of parking lots adjacent to each creek was a tiny potion of total watershed area, the large differential was quite unexpected. Two of the sites showed low PAHs and little differential, which could be caused by dilution from other contributing sediments in the watershed or movement of the parking lot materials to depositional areas farther downstream.

The smaller subset of five paired sites was selected for biological assessment. Following City of Austin standard protocols, biological collections were made (COA draft 2004), and sediment was collected using TCEQ SWQM protocols, as for all other sampling programs. The samples were submitted to an outside contract laboratory for analysis of PAHs using EPA-approved laboratory methodologies. The identification and analyses of the biological communities is incomplete, but the sediment chemistry is presented in the following section.

Figure 4.5 Total PAHs (Sum) Upstream and Downstream of Parking Lot Influence



Each of the sites selected for this study was located within a creek not expected to have extended dry periods. Such creeks will support a healthy biological community. Therefore, most of these sites had a substantial drainage area, and the parking lot area examined through aerial photography might represent a small portion of the total drainage area. The smallest drainage area for any of the sites was more than 1,000 acres. Moreover, when viewing the aerial photography, extensive residential and commercial roadway systems were frequently part of the immediate drainage area of the upstream and/or downstream sites, indicating an additional source of PAH contaminants. Nonetheless, the paired sites showed a significant differential between the upstream and downstream sites. These limited data further support that parking lot sources can have an immediate and local impact on the receiving water body's sediment chemistry.

4.3 Transport and Local Impact Study Conclusions

The following conclusions were derived from analyses of transport and local impact data:

- Paired sediment sampling upstream and downstream of parking lots adjacent to streams indicated a significant differential in total PAH concentrations, and verified that lots located in close proximity to creeks could have a detrimental local impact to sediment chemistry.
- Sediment chemistry associated with mesocosm studies of PAHs from sealants indicated that significant losses in total PAHs occur over a 28-day period from application, and the levels experienced in creek sediment habitat are likely to be far lower than the initial concentrations.
- In a tributary of lower Barton Creek, with headwaters originating from sealed parking lot drainage, the total PAHs decrease exponentially along the drainage network path from the material collected in the parking lot, through the tributary and into the receiving water body (Barton Creek), and ultimately into Town Lake. This decrease is explained by a combination of sediment dilution and chemical transformations of the PAHs.

5 Receiving Water Impacts

Previous studies documented in literature sources, combined with recent COA studies, make it clear that PAHs are available from multiple urban sources, including transport of particulate pavement sealer material to the receiving water. Therefore, the isolation of relative impacts to sediment chemistry from pavement sealer contributions to creek sediment PAHs was examined to determine if any special management of pavement sealers would be warranted. Methods of fingerprinting PAH patterns specific to sealants were investigated, comparisons of creek PAHs with geolocated parking lot and pavement areas were made, and values of PAHs in creeks over accepted biological effects criteria were examined with respect to sealed parking lot locations. The results indicate a concern for aquatic life in the receiving creeks based on sediment PAH levels observed to be associated with pavement sealer application. This concern was investigated further through biological testing discussed in Section 6.0.

Methods of PAH fingerprinting include simple molecular weight groupings, examination of various ratios of individual PAHs, prinicipal components analysis, and curve fitting the relative distributions of PAHs and their alkylated homologues. Although in-depth chemical analyses of PAH components have been made by USGS and some separation of the sources can be observed in virgin materials, a signature or ratio of PAH components specific to pavement sealants has not been identified (Mahler, 2004). Thus, fingerprint or signature analyses can not yet be used to separate sealant-source PAHs from various other urban sources yielding heavy PAHs, particularly when the materials may have been exposed in the environment for a length of time. Investigations into fingerprinting or identification of source markers continue, and several studies are currently under way that could be modified to help isolate sealant PAHs.

To determine the impact on receiving waters, the relationship between watershed characteristics and the PAH concentrations in the sediments for small watersheds was examined. Concentrations of PAHs in sediments have been shown to increase with common measures of urbanization (Paul, J.F. et al. 2001); however, no studies have used parking lot surface area or sealed parking lot area as an independent variable in correlation with sediment concentrations. The value of these concentrations found in the adjacent Austin creek sediments was then compared to literature indicators for biological impacts. The biological effects level selected for comparison was the freshwater consensus based sediment quality guidelines for expected impacts (Probably Effects Concentration [PEC] MacDonald et al. 2000).

5.1 Sampling and Analysis Methods

PAH concentrations in sediments from creeks and small tributaries were collected during several previous City studies. All sediment collections were made following standard field operating procedures and collection methods that comply with the TCEQ's Surface Water Quality Monitoring Manual (TCEQ 2004). Each sample is generally collected with a scoop, due to the shallow nature of these stream sediments. The scooped material is deposited directly into glass sample jars, which are then sealed with Teflon lids and transported on ice to the appropriate laboratory. Analyses were completed by approved USEPA methods at a contract laboratory and QAQC data can be provided by the City of Austin upon request.

Watershed data were compiled using a Geographic Information System (GIS) watershed delineation tool to determine flow direction based on topography (Robert Clayton pers. comm., November 2004) unless field documentation was made by staff conducting stormwater monitoring (Glick pers. comm., November 2004) or from site plans for a particular development. The source of data for each site is documented in the file associated with the GIS shape file. For each watershed, City of Austin planimetric data (COA 2003) for buildings, transportation features, and landmarks were used to develop impervious cover and parking area. Aerial photography from 2003 was then used to identify sealed parking lots using typical wear patterns field verified by City staff (Mateo Scoggins pers. comm., November 2004). Sealed lots exhibited a dark color with lighter areas in traffic and parking zones, while unsealed asphalt lots were generally lighter in color with darkened oil-stained areas in traffic and parking zones. The condition of the watersheds at the individual sampling dates and/or age and condition of sealed lots could not be confirmed in most cases, thus introducing substantial variation into the data.

5.2 PAHs and Watershed Metrics Results

Preceding sections have demonstrated that the concentrations of PAHs available for transport from unsealed surfaces and from asphalt-based sealants are much less substantial than from coal-tar based sealants and the surfaces to which they are applied. With this precept, it is expected that the result of the wear and transport of the coal-tar sealants will be reflected in higher PAH values near these sources than in other urban areas.

Watersheds with measurable runoff draining to a single point were examined to enable the comparison of watersheds with and without sealed parking lots, while excluding confounding factors such as transport and resuspension of sediments and heavy erosive inputs that would be factors in large watersheds. Table 5.1 describes the small watersheds included in this analysis.

Table 5.1 Watershed Characteristics

Sample Site	Drainage Area	% Impervious corrected*	Impervious Area	Parking Area	% Parking	% Sealed
	(acres)		acres	(acres)		
Service Station OIl Separator	0.2	98.4%	0.2	0.1	43.9%	0.0%
Commercial WQ Pond	1.8	100.0%	1.8	0.0	0.0%	0.0%
Commercial WQ Pond	3.0	91.2%	2.8	2.8	91.2%	52.6%
Apartment Trib.	4.2	73.8%	3.1	2.0	47.0%	37.9%
Park Tributary	5.8	16.2%	0.9	0.2	4.0%	0.0%
Downtown Inlet Filters	6.7	87.1%	5.8	0.2	3.3%	0.0%
Commercial WQ Pond	6.8	56.9%	3.9	3.5	51.2%	19.9%
Agricultural Pond	8.3	3.6%	0.3	0.0	0.0%	0.0%
Creek at Street Crossing	8.6	74.8%	6.4	2.7	31.2%	0.0%
Recreation Center Oil Separator	9.0	54.9%	4.9	2.7	30.5%	0.0%
Residential Trib	9.9	47.8%	4.7	2.1	20.8%	20.1%
Park INlet Filters	11.0	30.8%	3.4	2.8	25.8%	0.0%
Stormwater Station	13.7	87.2%	11.9	0.5	3.9%	0.6%
Convention Center Oil Separator	17.5	89.3%	15.6	1.3	7.4%	0.0%
Residential/Park Inlet Filters	47.7	53.3%	25.4	9.4	19.8%	0.8%
Stormwater Station	51.3	42.2%	21.7	1.0	1.9%	1.2%
Park Tributary	57.9	44.5%	25.8	4.3	7.5%	1.7%
Highway/Neighborhood Wet Pond	62.5	60.4%	37.8	8.8	14.1%	13.9%
Residential Wet Pond	120.1	29.0%	34.8	4.9	4.1%	0.6%
Residential/Apt. Trib.	120.5	29.5%	35.6	5.8	4.8%	3.4%
Highway Runoff	131.4	34.2%	45.0	10.7	8.2%	3.8%
Creek at Street Crossing	156.9	39.6%	62.2	2.7	1.7%	0.4%
Commerical Wet Pond	167.1	58.1%	97.1	35.8	21.4%	3.1%
Stormwater Station	202.9	70.5%	143.2	54.7	27.0%	7.4%
Residential/Commercial Trib	240.0	61.2%	146.9	55.1	22.9%	14.6%
Creek at Street Crossing	304.3	45.9%	139.7	28.6	9.4%	4.3%
Apartment Wet Pond	351.2	42.8%	150.2	12.8	3.7%	1.2%
Creek at Street Crossing	489.4	56.4%	276.0	74.5	15.2%	5.3%

*small constant assumed percentage added for sidewalks and driveways

Primarily, the sediments were collected in dry tributaries or water quality control structures. Figure 5.1 below demonstrates that the PAHs are significantly related to both the relative amount of parking area and the relative amount of sealed parking area in the watersheds. However, the percentage of sealed parking area is a much better predictor of the PAH concentrations in the sediment. These relationships are significant, whether evaluated parametrically or nonparametrically. In examining the individual PAHs, as well as their total, similar relationships can be seen with the watershed percent sealed parking lot, Figure 5.2.

Figure 5.1 Total PAHs vs. Percent of Watershed Parking Area or, more specifically Sealed Parking Areas

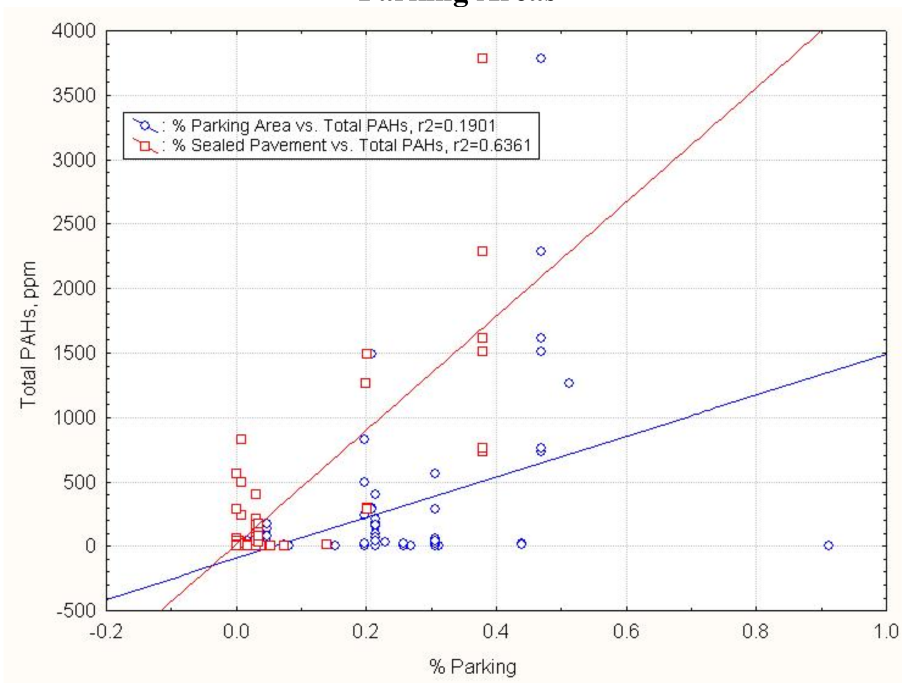
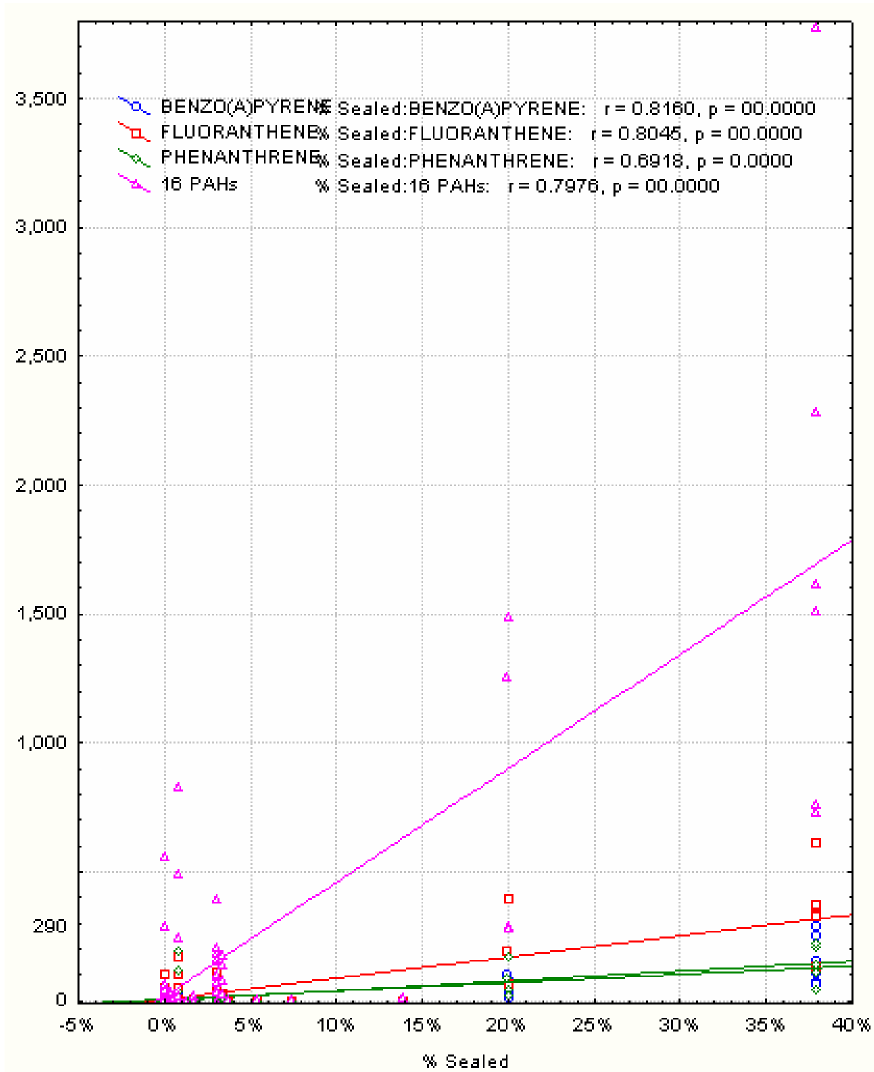


Figure 5.2 Individual PAH vs. Percent Sealed Surface in Watershed

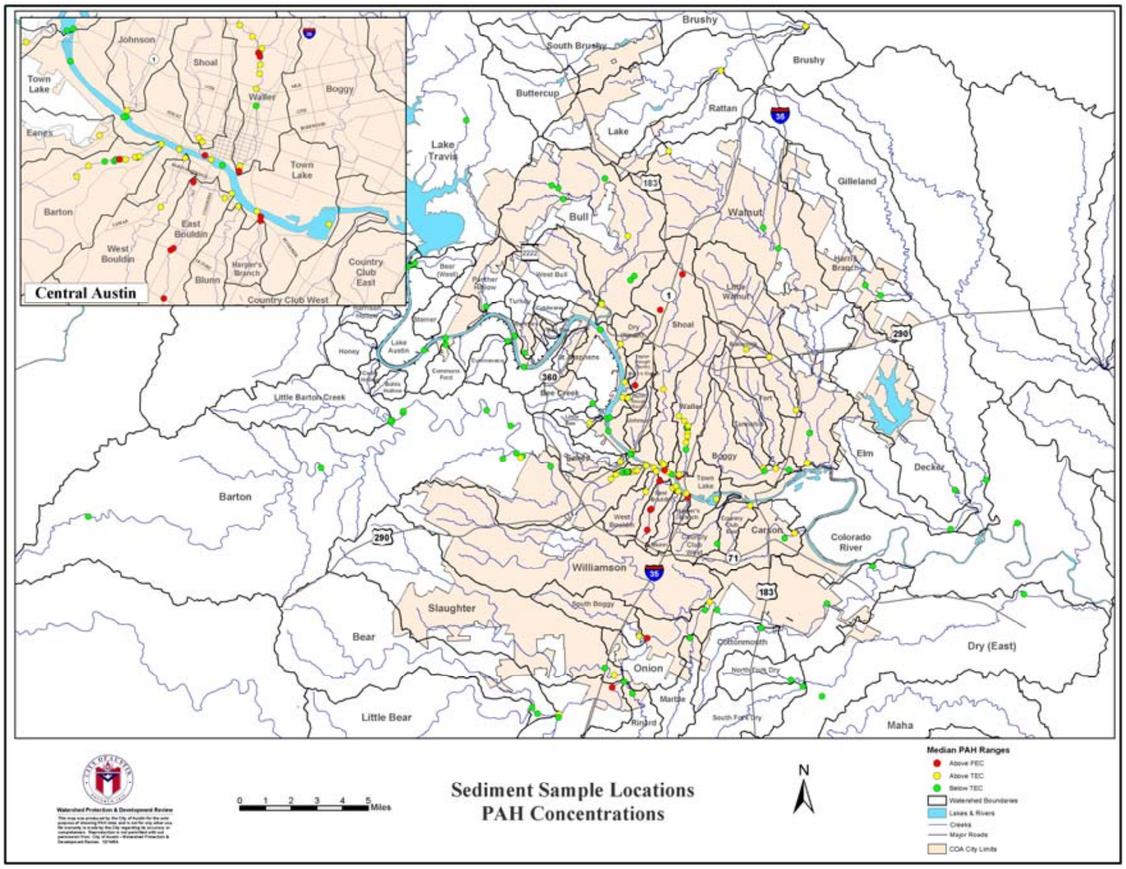


5.3 Creek PAH Concentrations and Biological Effects Levels Results

Many studies have examined the effects of PAH-contaminated sediments on aquatic organisms. In common use for freshwater systems are the Probable Effects Concentrations (PECs) and Threshold Effects Concentrations (TECs) established by a consensus-based method (MacDonald et al. 2000). In this section, the distribution and frequency of sediments exceeding these criteria in aquatic habitats will be examined. However, the actual toxicity of PAHs in this form was unknown prior to the testing that is described in Section 6.0. That is, at many of these Austin sites, the actual sediment sample collected contained black particulate matter. This material was perhaps abraded and carried intact (with PAHs in this solid form) from the surface of the adjacent parking lot. The form, movement, and toxicity of these PAHs have not been previously identified for coal-tar based sealants abraded from a parking lot surface and washed into a waterway. The PAHs may still be in an original coal-tar particulate forms, have solubilized and then adsorbed to sediment, or they may have partitioned to interstitial water. These processes have not been determined and quantified, which determine the uptake rate and processing by biological organisms in the receiving water habitats.

Every creek in Austin is assessed for its environmental integrity using a City-developed tool, the Environmental Integrity Index, or EII every third year (COA 1999). Most creeks have been assessed three times, with one-third of the creeks completing their third cycle in 2005. As part of the EII, a sediment sample is taken at the mouth of the creek and analyzed using EPA-approved methods for physical parameters, metals, pesticides, and PAHs. These data are supplemented by some special study data in creeks associated with a previously conducted EPA 319 grant program and in Barton Creek, where high PAHs were identified in the area of an important water resource, Barton Springs Pool. In general, single samples have been taken across several years at a few sites, but at most sites two to three samples have been taken. Numerous samples are taken at Barton Springs Pool.

Figure 5.3 Sediment Sample Locations and PAH Concentrations



To evaluate the data, the concentrations of total PAHs were compared with the TEC and PEC, and the three levels for median concentrations of creek sediments are illustrated in Figure 5.3. MacDonald et al. (2000) calculated this total for 13 of the primary PAHs, with nondetect individual PAHs summed at half the detection limit. The first level includes those where all values were nondetect and values where the total PAHs were below the TEC, or levels at which no effects are expected to be seen [incidence of toxicity = 18.5 percent, as reported from the compilation of studies reported by MacDonald et al. 2000]. The second level are concentrations above the Threshold Effects Concentration (TEC) but below the Probable Effects Concentration (PEC), where MacDonald et al (2000) report 65.1 percent incidence of toxicity, or where toxicity is beginning to be seen. The third level denotes an expected toxic level, above the Probable Effects Concentration (PEC) where 100 percent incidence of toxicity was seen in the independent data set used by MacDonald et al.

Figure 5.3 provides the median concentration of creek and lake sites (where benthic organisms might be expected to live) of total PAHs. The sampling in Austin has focused on creek mouths and four primary creeks in the urban areas (Shoal, Waller, East Bouldin, and Barton), and shows numerous sites in those areas over the TEC; lower levels are seen as sampling sites extend to nonurban areas. Even with the fairly restricted sampling areas, the number of "hot spots" of PAHs levels above the PEC has caused some concern. In addition, the USGS has documented increasing trends over time in the primary receiving water body, Town Lake, through core layer sampling (USGS 1998). If increasing trends in lake sediments are an indicator, then the more ubiquitous levels between the TEC and PEC may be indicators of future problems.

The frequency of sites and creeks showing median concentrations in each range is shown below in Table 5.1. The numbers are not additive, as creeks such as Barton Creek may have upstream sites with no PAHs detected and a downstream site with elevated concentrations. Maximum concentrations were also assessed for each site and only a small percentage (<10 percent) would have shown a change in the level at which they fell, with only a few having a concentration above the PEC that was not repeated at a later date. Some sites with elevated numbers, however, have not been adequately re-sampled. Town Lake sites had medians in all ranges of results (including historical data), with upstream sites having lower concentrations, downstream sites increasing, and sites near the mouths of urban creeks having the highest values. Lake Austin sites all had median values below the TEC.

Table 5.1 Summary of Site Median Results

Total PAHs	No. of Sites	No. of Creeks
ND or <TEC	73	29
>TEC (1.61)	54	19
>PEC (22.8)	16	7

Creek sampling and proximity and regression analyses indicate that "hot spots" and elevated values of PAHs in the creeks are related not only to paved surface area, but also to the amount of paved surface with sealant applied. Other sources of hot spots, such as oils spills, dumping of used oil in storm drains, burned materials, etc. may on occasion be an issue, but the ongoing transport of abraded materials from sealed pavement surfaces will continue to be a problem. The problems in the creeks themselves appear to be localized where untreated runoff from sealed lots is unabated by water quality controls, buffer zones, or dilution with erosive sediments, and perhaps particularly in areas where fine-grained sediments are trapped in-stream by dam-type features or natural pools. The threat to the primary receiving water body, however, may not be ameliorated by the scouring and periodic removal of these materials, as evidenced by the increasing trend of PAHs in Town Lake sediments.

5.3 Receiving Water Conclusions

The following conclusions were found from the study of PAHs in in-situ samples of sediment from creeks in the Austin area:

- PAHs are significantly related to both the relative amount of parking area and the relative amount of sealed parking area in the watersheds. However, the percentage of sealed parking area is a much better predictor of the PAH concentrations in the sediment.
- The number of "hot spots" of levels of PAHs above the PEC are concentrated in urban watersheds, but the number of PAH values above the TEC are spread throughout urban and some non-urban watersheds.
- The USGS has documented increasing trends over time in the primary receiving water body, Town Lake, indicating future problems in the areas of PAH levels between the TEC and PEC.

6 Ongoing Biological Studies

The City of Austin has several cooperative studies ongoing to assess the biological effects of PAHs, particularly with regard to parking lot runoff and coal-tar based parking lot sealants in the Austin area. An additional goal of ongoing and future studies is to assess whether the literature values such as the PEC and TEC are appropriate indicators for evaluating effects on environmental health in the Austin area from PAHs in the form of particulates worn from parking lot surfaces. As stated in previous sections of this report, the availability for uptake and processing of PAHs, either in the particulate form of pavement sealant containing coal tars or in some form of PAH released from the sealant and strongly sorbed to sediments, was previously unknown. In addition to ongoing studies, a limited amount of ambient toxicity testing has been completed by contract laboratories to the City of Austin (CERC 2001) and the Texas Commission for Environmental Quality (2002) with benthic organisms on sediment collected from Barton Creek and several of its tributaries. The results to date from all of these studies were compiled to develop conclusions about the impact of PAHs in the sediment environment, and to develop recommendations about product management policies.

6.1 Field Assessment

Although the City of Austin has been conducting benthic biological assessments and sediment analyses in local creeks for a number of years, the assessments have not been coordinated to look at the possible effects of sediment toxins. Biological community metrics and sediment chemistry are measurements that integrate effects over time; separation of factors such as hydrology has not been incorporated into study designs for PAH effects. Sites were not selected to be coordinated for these purposes and benthic collections are generally in riffles, while sediment collections are in pools. Therefore, the City has pursued some limited coordinated studies to evaluate the impacts of elevated receiving water sediment PAHs on biological communities. The primary field study was briefly described in Section 5, with selection of upstream and downstream sites based on aerial photography and chemical analyses of the sediments. Both the chemistry data shown in Section 5 and a review of the biological data provide preliminary support that the elevated PAHs are impacting the biological communities at the pool sites below the parking lot areas ("treatment sites"). Assessments by TSU and City staff indicate that significant degradation of biological community in the pools at the treatment sites had occurred, as measured by eight indicators of community health, including the number of intolerant taxa, taxa richness, percent dominance, and the state's aquatic life use score. In riffles, three measures showed loss of community health, including the number of organisms and number of dipteran taxa.

6.2 MicroMicrocosm Experiment

Because of the significant influence of hydrology and upstream catchment effects on the benthic communities in short-term studies in the Austin climate, the City undertook micromicrocosm studies in coordination with Texas State University (Pam Bryer and Emily Willingham, TSU). MicroMicrocosms, using a native benthic community, were established with sediments that had been spiked with dried coal-tar sealants to achieve three treatments (PAH concentrations) plus a control. This study allowed the assessment of direct and indirect effects from a controlled toxicant (coal tar sealants) on biological community health while excluding effects other uncontrolled variables associated with field experiments. Preliminary results from the micromicrocosm study show that the treatment with the highest level of PAHs was severely degraded and that the three coal tar treatments show a dose response that was negative and proportional. The response of treatments with PAH levels below the PEC could be interpreted based on available carbon versus the toxicity and a complete analysis of these results will be provided with study publication in cooperation with participating TSU researchers.

6.3 Laboratory Toxicity Testing

Laboratory toxicity testing is the standard method for assessing the toxicity of compounds to aquatic organisms. In the case of sealant source PAHs in sediments, testing is complicated by several factors:

- the form of PAHs that may affect its uptake or availability to organisms
- if environmental sediments or samples are used, the source, or combination of sources and forms of PAHs are not known, and
- if a coal tar sealant is used for testing, it may contain other contaminants that are a source of toxicity and have not been subject to the same environmental exposure that a sealant applied to parking lot may have been.

Because all of these factors can be addressed with a single study, several designs have been initiated. Results of concluded studies and scope of additional studies under way are described below.

6.3.1 Ambient toxicity testing of Barton Creek sediments

Both the City of Austin and the TCEQ collected sediments from Barton Creek. The City also collected sediment from several dry tributaries with elevated PAHs; the TCEQ collected extensive samples from Barton Springs Pool. These sediments were submitted to contract laboratories for standard toxicity testing, using benthic organisms. The City samples showed toxicity with UV-exposure following the standard tests for the highest levels (above the PEC); the lower mainstem levels did not show toxicity (below the PEC). However, because of the wide variation in levels, confirmation of existing biological effects levels or establishment of new levels was not achieved. The TCEQ studies did not use UV-exposure, obtained sediment with much lower PAH levels, showed some growth effects, but have not demonstrated significant lethality. Sub-lethal effects were seen in some samples, but were not correlated to PAH values. However, because it has been documented that simultaneous exposure to UV radiation (as in direct sunlight) may greatly increase the toxicity of some PAHs, toxicity to benthic organisms is still likely.

TCEQ has recommended future monitoring and the City has recommended that UV exposure be a component of testing when evaluating biological impairments from PAHs in shallow creeks in the Austin area. These laboratory studies examine direct toxicity of in-situ sediments from local aquatic environments, but do not identify the source of toxicity, if found. Additional toxicity identification procedures involving sequential laboratory manipulation of sediment to isolate toxicity sources may provide this information.
The toxicity reports from the TCEQ can be found at:
http://www.tceq.state.tx.us/comm_exec/tox/bsp/BartonMain.html#protect.

6.3.2 Toxicity Testing of Parking Lot Particulates

To examine the toxicity of parking lot runoff, the City is continuing the cooperative parking lot study with the USGS to incorporate toxicity testing of parking lot particulates. Particulates were collected from water washed off of four types of parking lots: 1) concrete, 2) unsealed asphalt, 3) lots with asphalt-based sealant, and 4) lots with coal-tar based sealant. The particulates will be introduced as suspended sediments in an ambient water toxicity test with two benthic organisms, with the addition of UV exposure at the end of the test period. This study will allow the comparison of the relative toxicity of runoff from different parking surfaces. It will not allow segregation of toxicity from different PAH sources, as the particulates will be collected from parking lots currently in use and would be expected to have PAHs associated with oil, grease, and combusted gasoline. However, if no toxicity is shown to particulates from the concrete and unsealed lots, then the relative levels of PAHs can be assumed to be the problematic factor.

6.3.3 Spiked Sediment Toxicity Tests

Perhaps simplest to interpret, yet farthest from field conditions, is ambient toxicity testing of sediments spiked with coal-tar based sealants. The Great Lakes Environmental Center was contracted to conduct standard toxicity testing of sediment spiked with pavement sealant products. Sediments were spiked with coal-tar sealants to target three total PAH levels, the PEC being the lowest, the mid-range at approximately twice that, and the highest level at about 10 times that level; controls were provided. In addition to the coal-tar based sealant, an asphalt-based sealant was also studied. The dilutions used for each coal-tar sealant sediment mixture (dry-weight percent of sealant to clean sediment) were duplicated for the asphalt-based sealant sediment mixtures. All PAH levels examined have all been documented in Austin creek sediments, although the highest levels have been seen only at a few hot spots. For each spiked sediment level, a standard ambient sediment toxicity test was run with subsequent UV exposure. Although the materials tested were laboratory-made sediments, the results provide a clear evaluation of whether pavement sealants are toxic, with PAHs at biological effects levels as documented in scientific literature.

Toxicity, which could be attributed only to the chemical constituents in the pavement sealants, was demonstrated, both with and without UV exposure for the coal-tar based sealants as seen below in Tables 6.1 and 6.2 for two benthic organisms. UV exposure exacerbated toxicity in exposures where the PAH level did not show a significant change from the control without the UV exposure. The toxicity of the asphalt-based sealants with UVexposure, in particular, demonstrates the photo-induced toxicity of PAHs at these much smaller concentrations of PAHs.

Table 6.1 Whole Sediment Toxicity Test, *Hyalella Azteca*

Total PAH Concentration, mg/kg ***Geometric Mean Over Test Period***	***Survival after 28 days (%)***	***Survival After UV Exposure ($365\ \mu W/cm^2$ 12 hours/day: 96 hours)***
Control (0 mg/kg)	*100%*	*100%*
	Coal-tar based Sealant	
17.08	*81%**	*10%**
36.22	*29%**	*could not test***
199.7	*13%**	*could not test***
	Asphalt-based Sealant	
0.175	*98%*	*84%**
0.265	*95%*	*70%**
2.081	*94%*	*16%**

Table 6.2 Whole Sediment Toxicity Test, *Chironomus tentans*

Total PAH Concentration, mg/kg ***Geometric Mean Over Test Period***	***Survival after 20 days (%)***	***Survival After UV Exposure ($365\ \mu W/cm^2$ 12 hours/day: 96 hours)***
Control (0 mg/kg)	*97%*	*100%*
	Coal-tar based Sealant	
17.08	*43%**	*58%**
199.7	*0%**	*could not test***

* Significantly different from sediment control ($p \leq 0.05$)
** Paucity of survivors precluded additional testing with UV exposure.

6.3 Biological Studies Conclusions

The following preliminary conclusions were derived from the ongoing biological studies discussed above:

- Both the receiving water sediment chemistry data and biological data provide support that the elevated PAHs are impacting the biological communities at the pool sites below the parking lot areas.
- Significant degradation of the biological community in the pools below parking lot areas occurred as indicated by eight metrics. Benthic biological communities in riffles below parking lots showed loss of community health in three metrics, including the number of organisms and number of dipteran taxa.
- Preliminary results from the micromicrocosm study show that the highest level of PAHs resulted in the most severely degraded benthic biological community and that the three coal tar treatments show a dose response that was negative and proportional. The response of treatments with PAH levels below the PEC in the micromicrocosm study could be interpreted based on available carbon versus the toxicity.
- Although toxicity testing of in-situ sediment did not show consistent lethality, it has been documented that simultaneous exposure to UV radiation (as in direct sunlight) greatly increases the toxicity of some PAHs; therefore, exposure to shallow-dwelling organisms at harmful levels of PAHs is still likely.
- Toxicity, which could be attributed only to the chemical constituents in the pavement sealants, was demonstrated, both with and without UV exposure, for the coal-tar based sealants for two benthic organisms. UV exposure exacerbated toxicity in exposures where the PAH level did not show a significant change from the control without the UV exposure. The toxicity of the asphalt-based sealants with UV-exposure, in particular, demonstrates the photo-induced toxicity of PAHs at these much smaller concentrations of PAHs.

7 Conclusions and Recommendations

Studies to date have adequately identified coal-tar based sealants as a concentrated source of PAHs in the sediment "hot-spots" in Austin. Although follow-up by researchers and policy makers at state and national levels may be appropriate as a result of these compiled studies, a local response is also indicated.

Chemical analyses of the polycyclic aromatic hydrocarbons (PAHs) contained sealant products and environmental receptors that provide several lines of evidence demonstrating the movement of PAHs from sealed parking lots into the aquatic environment in Austin, Texas. The other significant finding, when addressing the issue of how to reduce or remove the PAHs from this source, was that the PAHs in coal-tar based sealants are significantly higher than those in asphalt-based sealants, and that sealed parking areas have significantly higher PAHs in washoff particulates than from unsealed parking areas. Distilling these findings in order from the creeks back to the source leads to the following conclusions:

- "Hot spots" of PAHs are seen in Austin creek sediments, above the Probable Effect Concentrations, which may cause impairment to aquatic life.
- High concentrations of PAHs in sediments are significantly, and best, correlated with the percentage of sealed parking lots in the drainage area.
- Particulates from sealed parking lots have significantly higher PAH concentrations than parking lots with no sealants (asphalt or concrete).
- PAHs are significantly higher in coal-tar based sealants than in asphalt-based sealants, and also significantly higher in particulate washoff and scrapings from parking lots where those were applied.

Ambient toxicity testing has demonstrated that PAHs in this form, from locally collected sediments and sediments spiked with a dried coal-tar based sealant, are toxic to benthic aquatic species when exposed to UV light. Therefore, the weight of evidence provided above supports a recommendation to limit the input of PAHs from coal-tar based sealants to the environment.

In addition to the chemical monitoring and analysis detailed above , the City of Austin has also recently conducted three biological investigations to evaluate the potential toxicity of coal tar sealants and the effects they may be having on stream communities. First, standard laboratory toxicity testing found that coal tar sealants, and to a lesser degree, asphalt sealants in a dried particulate form, are toxic to aquatic organisms at levels observed in Austin area streams. Secondly, in a controlled community experiment (microcosm), coal tar sealants, as a dried particulate, are toxic to Austin native stream communities at levels observed in area streams. Finally, in a multi-watershed, upstream vs. downstream field study, coal tar sealed parking lots were found to cause hot spots in stream sediments, and these hot spots degraded stream communities at study streams including sites where PAH concentrations were well below the Probable Effect Concentration of 22.8 mg/kg TPAH. The combination of chemical tracing, laboratory toxicity, and field verified degradation provides a weight of evidence approach that effectively identifies a significant source of PAH in Austin streams and its negative effect on stream ecosystems. Detailed results from these studies can be found in draft form at: http://www.ci.austin.tx.us/watershed/bs_coaltar.htm.

References

ATSDR., Agency for Toxic Substances and Disease Registry. 2003. Health Consultation, Barton Springs Pool, Austin, Texas. Facility ID: April 2003. U.S. Department of Health and Human Services, Public Health Service, ATSDR, Division of Health Assessment and Consultation. Atlanta, Georgia 30333.

ATSDR, Agency for Toxic Substances and Disease Registry. 2002. Toxicological Profile for Wood Creosote, Coal Tar Creosote, Coal Tar, Coal Tar Pitch, and Coal Tar Pitch Volatiles. U.S. Department of Health and Human Services, Public Health Service. September 2002.

A. Björseth, T. Ramdahl, in *Handbook of Polycyclic Aromatic Hydrocarbons* A. Björseth, T. Ramdahl, Eds. (Marcel Dekker, New York, 1985), vol. 2, pp. 1-20.

City of Austin, 1992, Diagnostic Study of Water Quality Conditions in Town Lake, Austin, Texas, Volume I. Water Quality Report Series COA-ERM/WRE 1992-01.

Geomatrix Consultants, Inc. 2003. Barton Springs Area Site Investigation, Austin, Texas. Prepared for City of Austin. Prepared by Geomatric Consultants, Austin, Texas. February 2003. Project No. 8683.

Jiries, A., *The Environmentalist* **23**, 205-210 (2003).

MacDonald, et al. 2000. Development and Evaluation of Consensus-based Sediment Quality Guidelines for Freshwater Ecosystems.

Paul, J.F., R.L. Comeleo, and J. Copeland. 2001. Landscape Metrics and Estuarine Sediment Contamination in the Mid-Atlantic and jSouthern New England Regions. J. of Environmental Quality 31:836-845 (2002).

Pengchai, P., Nakajima, F. and Furumai, H. 2003. "Estimation of Origins of Polycylic Aromatic Hydrocarbons in Size-Fractionated Road Dust in Tokyo with Multivariate Analysis. Diffuse Pollution Conference Dublin 2003.

U.S. Environmental Protection Agency, "The incidence and severity of sediment contamination in surface water of the United States" *EPA 823-R-97-006* (1997).

United States Geological Survey (USGS). 2004. Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) and Major and Trace Elements in Simulated Rainfall Runoff From Parking Lots, Austin, Texas, 2003. USGS Open-File Report 2004-1208- online only. By Mahler, B.J., P.C. Van Metre and J.T. Wilson.

U.S. Environmental Protection Agency. 1983. "Results of the Nationwide Urban Runoff Program, Volume I - Final Report." Washington, D.C.: U.S. Government Printing Office. National Technical Information Service Publication No. 83-185552.

U.S. Environmental Protection Agency. 1989. "Clean Lakes Program."

USFWS 1997. Final rule to list the Barton Springs salamander as endangered. Federal Register Volume 62, No. 83, pages 23377-23392.

Van Metre, P.C., B. J. Mahler, E. T. Furlong, *Environ Sci. Technol.* **34**, 4064-4070 (2000).