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Polycyclic Aromatic Hydrocarbons (PAHs) in Austin Sediments After a Ban on Pavement Sealers

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Polycyclic aromatic hydrocarbon (PAH) concentrations were measured in stream sediments collected before and after a municipal ban on the use of coal-tar-based pavement sealers in Austin, Texas. Samples were collected in October 2005, prior to the ban, and again in April, 2008, approximately 2 years after the ban. Differences in total PAH concentrations between samples collected before and after the ban show no net change in PAH levels in Austin stream sediments. Results of hydrocarbon fingerprinting reveal subtle differences in PAH profiles that appear to reflect the effects of weathering rather than a change in PAH sources.

Keywords: polycyclic aromatic hydrocarbons, principal components analysis, sediments, coal tar, pavement sealer

Most polycyclic aromatic hydrocarbons (PAHs) enter the environment via the atmosphere as byproducts of combustion. PAHs are formed by the incomplete combustion of any carbon-based fuel source such as coal, oil, gas, wood, and refuse and may be found in automobile exhaust, incinerator emissions, emissions from wood-burning stoves, and tobacco smoke (Oanh et al., 1999; Freeman and Cattell, 1990; Lim et al., 1999). In highly populated areas, vehicle emissions are believed to represent a major source of total PAH emissions (Dickhut et al., 2000; Christensen and Bzdusek, 2005; Yunker et al., 2002) and recent trends showing increasing PAH levels in lake sediments have been correlated to increases in automobile use (Van Metre et al., 2000; Van Metre and Mahler, 2005).

More recently, coatings applied to seal pavement have been identified as a potentially major source of PAH loadings to urban and suburban water bodies (Mahler et al., 2004; 2005). Common pavement sealers in use in the United States (US) contain either a refined distillate of coal tar (RT-12) or asphalt and they are used predominantly on parking lots and similar paved surfaces, as opposed to roads where the heavy, high-speed traffic wears off any coating too rapidly to warrant sealing. The US Geological Survey evaluated PAH concentrations washed off sealed and un-sealed parking lots in Austin, Texas under simulated rainfall conditions and suggested that parking lot sealer could account for the majority of PAH loadings to urban creeks and streams (Mahler et al., 2005). Consequently, the City of Austin (COA) enacted a ban on the use coal tar-based (CT) pavement sealer within its jurisdiction effective January 1, 2006.

This article presents results of analyses of PAH concentrations detected in Austin creek sediments collected prior to, and two-years following the COA ban on the use of CT pavement sealers. The multi-year lifetime of pavement sealer means that historically applied material remains and presents a source for continued transport of PAH to rivers and stream. However, the City of Austin cited an anticipated reapplication interval of 2–3 years and an annual usage rate of 2.5 million liters of sealcoat annually prior to the ban (Mahler et al., 2005). Given that a 2-year interval amounts to a substantial fraction of the anticipated service life and the potentially large volume of input material excluded by the complete ban, we wished to see if this reduction in PAH inputs had any effect on PAH concentrations and source profiles in Austin area creek sediments approximately 2 years following the ban.

The stream conditions found in a series of Austin creeks make it possible to evaluate changes in sediment over this relatively short period. Many of the sampled stream segments were characterized by bare, flat rock that is scoured during rain events and serves to translocate the prior depositional sediment load downstream. Flow regimes for the systems are intermittently very high velocity during and after storm events and minimal to dry for extended periods between storms. These characteristics, common to stream systems in the arid western US but atypical compared with common stream dynamics from the eastern US, provide the opportunity to examine comparative snapshots in time by analyzing sediments expected to be dominated by recent inputs between scouring events. We made use of this circumstance to assess changes in the creek sediments before and after the COA sealer ban. By concentrating on stream locations and streambed types that were scoured extensively and repeatedly after the ban was put in place, we could collect samples

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representing in particular material released from paved surfaces since the ban.

Analytical Methods

Sample Collection and Analysis

A total of 44 sediment samples were collected over two separate sampling events conducted in October and November 2005 and in April 2008. Sampling locations are described in Table 1. Samples were collected from 12 different creek systems, two drainage swales along Interstate Highway 35 (IH-35) and three stormwater retention ponds. Sampling locations are shown in Figure 1 and were selected to reflect a mix of land use categories and drainage patterns including locations dominated by roadway drainage, locations characterized by large parking lots and dense commercial operations, locations surrounded by residential areas, and locations receiving parking lot runoff from newly constructed (post-ban) shopping center parking lots.

Samples were collected by Horizon Environmental Services, Inc., of Austin, TX, using stainless steel equipment decontaminated with Alco-Nox detergent and isopropanol prior to and between uses. Samples were collected in laboratory supplied, pre-cleaned sample jars, stored on ice in the field and frozen upon return to the laboratory. Where sediments were covered

with water and the streambed was not flat rock, samples were collected using a 10-cm diameter stainless steel coring device. The corer was gently advanced approximately 15 cm or until refusal and the lower end was occluded with a stainless steel plate. The core was gently retrieved, excess water was drained from the bottom of the corer, and the wet sediment transferred to a wide-mouth 0.5-L glass jar. At stations with rock substrate, submerged sediments were generally located in depressions or between rocks and a stainless steel trowel or spoon was used to retrieve the sample. These areas were generally shallow and had little or no flow such that the sample remained largely intact during collection.

Where no water was present and the sediment was desiccated or only a thin layer of sediment was present on flat rock surfaces, samples were collected with a stainless steel trowel or spoon and transferred to a wide-mouth 0.5-L glass jar. Field duplicates were homogenized in a stainless steel bowl prior to transfer to two separate jars.

2005 sampling event

On October 27–28, 2005, 17 sediment samples were collected from 12 different creek and stream systems that flow from various directions and discharge to an impoundment of the Colorado River (Town Lake or Ladybird Johnson Lake) near downtown Austin. The distribution was intended to reflect the progression from lower population density areas toward the central downtown urban/commercial core of Austin. More than one location was sampled along three of the creeks (Williamson, Shoal and Waller) where land-use characteristics varied along the length of the creek. In addition, two composite samples were collected from the roadside drainage along IH-35. Composites composed of five subsamples were collected from ditches and culverts along an approximately 1-km segment along each side of the highway. Samples are designated by the location and year sampled (e.g., 1A-05).

Subsequent to a heavy rainfall in the evening of October 31, 2005, four of the creek sampling locations were re-sampled on November 2, 2005. Locations selected for re-sampling included each of the most upstream locations of Williamson, Waller, and Shoal Creeks and the location closest to the downtown urban core on Waller Creek. The IH-35 west side roadside ditch was also re-sampled at this time. Samples are designated by the location and year sampled followed by “R” (e.g., 1A-05R).

2008 sampling event

On April 21–23, 2008, 20 additional sediment samples were collected, 28 months after the COA sealer ban came into effect. The 2008 sampling event was conducted 4–6 days after a moderate rain event that followed a lengthy period of no rain. A total of 14 samples (including one duplicate) were collected from 13 locations previously sampled in 2005 and six samples were collected elsewhere including three additional locations along Waller Creek and three stormwater retention ponds receiving runoff from newly constructed (post-ban) parking lots

Table 1. Sediment sampling locations

Water Body	Station	Sampling Event	
		2005	2008
Williamson Creek	1A	xx	x
	1B	x	x
	1C*	x	
East Bouldin Creek	4A	x	x
Blunn Creek	5A	x	x
Shoal Creek	7A	xx	x
	7B	x	x
	7C	x	x
	7D*	—	x
Waller Creek	8A	xx	x
	8B	xx	—
	8C	—	x
	8D	—	x
	8E	—	x
Boggy Creek	9A	x	x
Tannehill Branch	10A	x	x
Little Walnut Creek	11A	x	x
Walnut Creek	12A	x	x
Onion Creek	14A	x	
Wells Branch	15A	x	x
Barton Creek	16A	x	—
Drainage easement at IH35	18C	xx	—
	19C	x	—
Adjacent to Slaughter Creek	20A	—	x
Adjacent to Shoal Creek	21A	—	x
Adjacent to Barton Creek	22A	—	X

X, sample collected; XX, sample collected pre- and post-rain event; *field duplicate (1A/1C and 7A/7D).

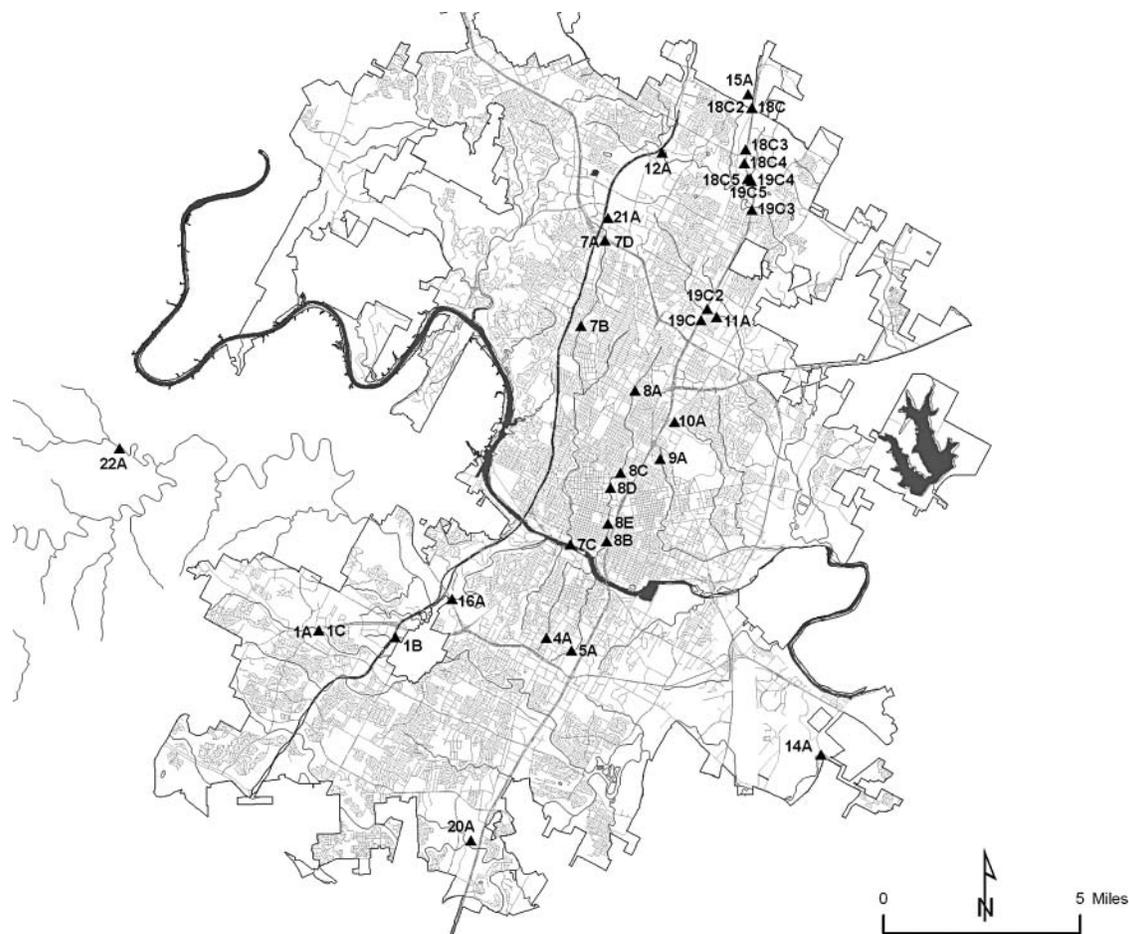


Figure 1. Map of the Austin area sediment sampling locations.

servicing three new shopping centers in the Austin area. Samples are designated by the location and year sampled (e.g., 1A-08).

Chemical analysis

All sediment samples were analyzed for the presence of PAHs (parent compounds and alkyl homologues) and benzothiophene compounds by TDI Brooks International, College Station, TX. PAHs were extracted from pre-dried sediment using a pressurized fluid extraction technique (modified EPA Method 3545). Samples (2–15 g) were extracted with methylene chloride in stainless steel extraction cells (100°C, 2000 psi) using an automated extraction apparatus (Dionex ASE200 Accelerated Solvent Extractor, Dionex Corporation, Sunnyvale, CA, USA). Extracts were cleaned up on a silica gel/alumina/copper/sodium sulfate column and volume was reduced to 1 mL by evaporation. Extracts were analyzed using gas chromatography/mass spectrometry (GC/MS) in selected ion monitoring (SIM) mode (modified EPA Method 8270) using an Agilent Technologies HP-5MS (60 m long by 0.25 mm ID and 0.25 μm film thickness) column.

Quantitation was performed using calibration standards prepared at five concentrations ranging from 0.02 to 1 $\mu\text{g}/\text{mL}$. For

each analyte of interest, a relative response factor (RRF) was determined for each calibration level and these were averaged to produce a mean relative response factor for each analyte. Each batch of extracts was analyzed along with sediment quality control samples. PAHs quantified in the analysis are identified in Table 2. Detection limits varied for individual compounds but were generally less than 0.5 $\mu\text{g}/\text{kg}$ for undiluted samples. All concentrations are reported on a dry-weight basis.

Principal components analysis (PCA)

Principal components analysis (PCA) was used to identify similarities and differences in PAH profiles in sediments collected before and after the ban on CT sealers. The PCA was completed using Systat Version 11 (Systat Software, Inc., Richmond, CA, USA). The PCA comparing Austin sediment samples collected before and after the ban includes all 51 constituents listed in Table 2. Individual constituent concentrations were first normalized to the sum of constituents detected in each sample to eliminate the influence of samples with higher concentrations. Additionally, the PCA was performed on the correlation matrix, which scales the data to zero mean and unit standard deviation.

Table 2. Selected polycyclic aromatic hydrocarbons (PAHs) included in sediment analyses

Analyte	Abbrevaiton	Analyte	Abbrevaiton
Naphthalene	N0*	Fluoranthene	FL*
C1-Naphthalenes	N1	Pyrene	PY*
C2-Naphthalenes	N2	C1-Fluoranthene/Pyrene	FP1
C3-Naphthalenes	N3	C2-Fluoranthene/Pyrene	FP2
C4-Naphthalenes	N4	C3-Fluoranthene/Pyrene	FP3
Biphenyl	Bph	Naphthobenzothiophene	NB0
Acenaphthylene	Ac1*	C1-Naphthobenzothiophenes	NB1
Acenaphthene	Ace*	C2-Naphthobenzothiophenes	NB2
Dibenzofuran	DbF	C3-Naphthobenzothiophenes	NB3
Fluorene	F0*	Benz(a)anthracene	BaA*
C1-Fluorenes	F1	Chrysene	C0*
C2-Fluorenes	F2	C1-Chrysenes	C1
C3-Fluorenes	F3	C2-Chrysenes	C2
Phenanthrene	P0*	C3-Chrysenes	C3
Anthracene	AN*	C4-Chrysenes	C4
C1-Phenanthrenes/ Anthracenes	P1	Benzo(b)fluoranthene	BbF*
C2-Phenanthrenes/ Anthracenes	P2	Benzo(k)fluoranthene	BkF*
C3-Phenanthrenes/ Anthracenes	P3	Benzo(e)pyrene	BeP
C4-Phenanthrenes/ Anthracenes	P4	Benzo(a)pyrene	BaP*
Carbazole	Cz	Perylene	Per
Benzo(b)thiophene	B0	Indeno(1,2,3-c,d)pyrene	ID*
C1-benzothiophenes	B1	Dibenzo(a,h)anthracene	DA*
C2-benzothiophenes	B2	Benzo(g,h,i)perylene	BgP*
C3-benzothiophenes	B3	—	—
Dibenzothiophene	D0	—	—
C1-Dibenzothiophenes	D1	—	—
C2-Dibenzothiophenes	D2	—	—
C3-Dibenzothiophenes	D3	—	—

*priority pollutant PAH

Results and Discussion

Several approaches for characterizing contributions of PAHs from different sources were used to analyze the Austin sediment samples. The goal was to determine whether differences in PAH characteristics could be identified and whether contributions from various sources could be quantified or proportionately ranked so that the any reduction in PAH source inputs from the ban on coal tar-derived pavement sealers could be evaluated. The approaches used included 1) comparing total PAH concentrations in sediments collected before and after the ban on CT sealers, 2) comparing PAH homolog distribution profiles indicative of pyrogenic versus petrogenic sources, 3) comparing relative PAH concentrations using principal components analysis (PCA), and 4) evaluating ratios between specific PAH compounds.

Σ Polycyclic Aromatic Hydrocarbons (PAH) Concentrations

To characterize overall PAH levels in the sediment samples, concentrations reported for the 16 priority pollutant PAHs were summed to yield a cumulative value termed Σ PAH. This commonly used approach facilitates comparisons with other studies (Brown and Peak, 2006; Marvin et al., 2000; Stout et al., 2004). For example, Stout et al. (2004) summarized PAH concentra-

Table 3. Summary statistics for the sum of 16 priority pollutant polycyclic aromatic hydrocarbons (Σ PAHs)(mg/kg)

Parameter	Combined Sampling Events	2005 Sampling Event	2008 Sampling Event
Number of samples	44	24	20
Minimum	0.022	0.022	0.26
Arithmetic mean	13.8	11.1	17.0
Median	8.2	6.0	9.6
Maximum	82.8	82.8	61.1
Variance	287	271	301

tions representative of urban background in samples collected from nine urban waterways and concluded that, as a “rule-of-thumb,” sediments containing 20 mg/kg or less of the 16 priority pollutant PAHs are likely dominated by general urban background; whereas, higher concentrations may reflect one or more point sources.

As shown in Table 3, Σ PAH concentrations in the 44 sediment samples collected from the Austin area, including field duplicates, ranged from 0.02–82.8 mg/kg. One set of field duplicates was collected during each sampling event. The relative percent difference in Σ PAH concentrations in field duplicate samples collected in 2005 and 2008 was 42% and 87%, respectively.

In 2005, two samples contained Σ PAH concentrations exceeding 20 mg/kg samples 4A-05 and 10A-05 with concentrations of 82.8 and 26.7 mg/kg, respectively. All other samples contained less than 20 mg/kg total PAHs. Sample 4A-05 was collected from East Bouldin Creek at a location north of Highway 290 at Lightsey Road. This creek receives runoff from Highway 290. Geismar (2000) recorded a total PAH concentration of 17.3 mg/kg in sediments collected from this area. Sample 10A-05 was collected from Tannehill Branch north of Lancaster. A mixed single family and multi-unit residential area along with a large shopping center is located on one side of the stream and extensive commercial facilities are present on the other side. IH-35 also affects the drainage in this location.

Σ PAH concentrations exceeded 20 mg/kg at four of the locations sampled in 2008 including 4A and 10A at 56.9 and 40.4 mg/kg, respectively (see location descriptions above), as well as 9A with 29.7 mg/kg and 8C with 61.2 mg/kg. Sample 9A-08 was collected from Boggy Creek in an area influenced by highway traffic as well as residential and commercial areas. When sampled in 2005, results for this location were 3.6 mg/kg Σ PAH. Sample 8C-08 was collected from Waller Creek in a residential area, a location not sampled in 2005.

Grouping all samples from each event, Σ PAH concentrations from the 2008 sampling event were slightly higher on average (mean = 17.0, n = 19) compared to 2005 pre-ban levels (mean = 11.1, n = 24). This difference is not significant (Student's t test, $p = 0.29$). When comparisons are based just on the thirteen locations sampled in both 2008 and 2005 events, the trend remains the same, with Σ PAH concentrations averaging 13.7 mg/kg in 2005 and 17.8 mg/kg in 2008 (Figure 2). Again, this difference is not significant (Student's t test, $p = 0.58$).

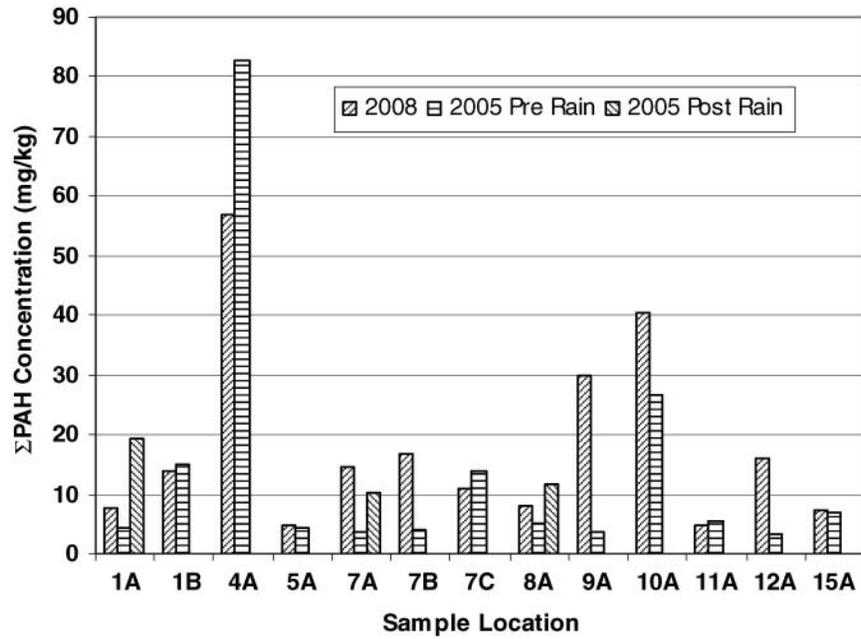


Figure 2. Graph of the comparison of the sum of 16 priority pollutant polycyclic aromatic hydrocarbon (Σ PAH) concentrations detected at locations sampled in both 2005 and 2008.

Comparing results from all five locations sampled before and after the 2005 rain event (Figure 3), Σ PAH concentrations were generally higher in samples collected after the rain event. The reasons for this are unclear but may be related to a number of factors including cumulative runoff volume, rainfall intensity and antecedent dry conditions (Neary et al., 2002).

The results presented here represent the first time series capturing sediment condition snapshots before and after the Austin ban on pavement sealers. The approximately 2-year timeframe captured in this analysis is informative due to the specific stream flow and sediment translocation characteristics that dominate the sampled locations. Scouring of the shallow (frequently less than 15 cm) depositional pockets followed by new inputs from the

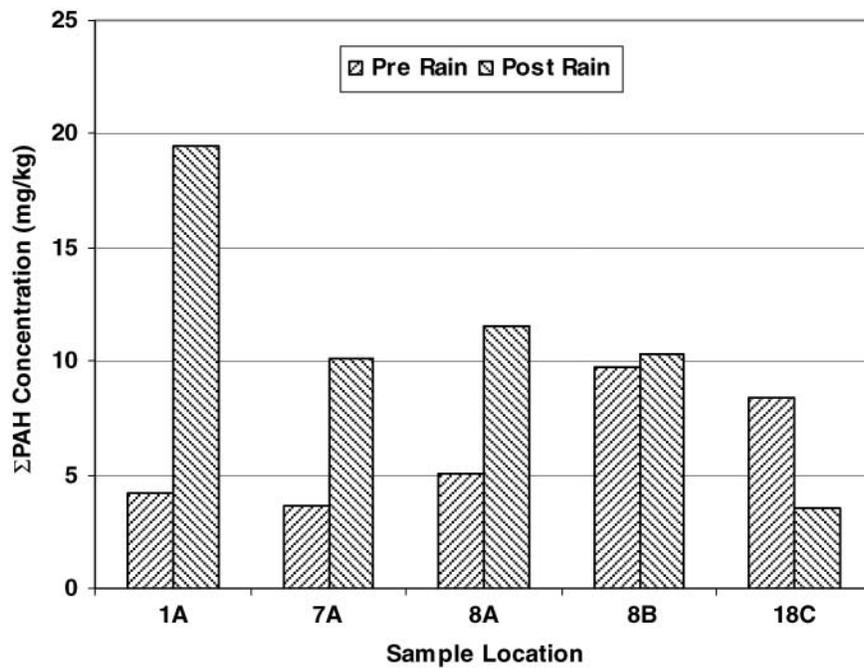


Figure 3. Graph of the comparison of the sum of 16 priority pollutant polycyclic aromatic hydrocarbon (Σ PAH) concentrations detected at locations sampled in 2005 before and after a significant rain event.

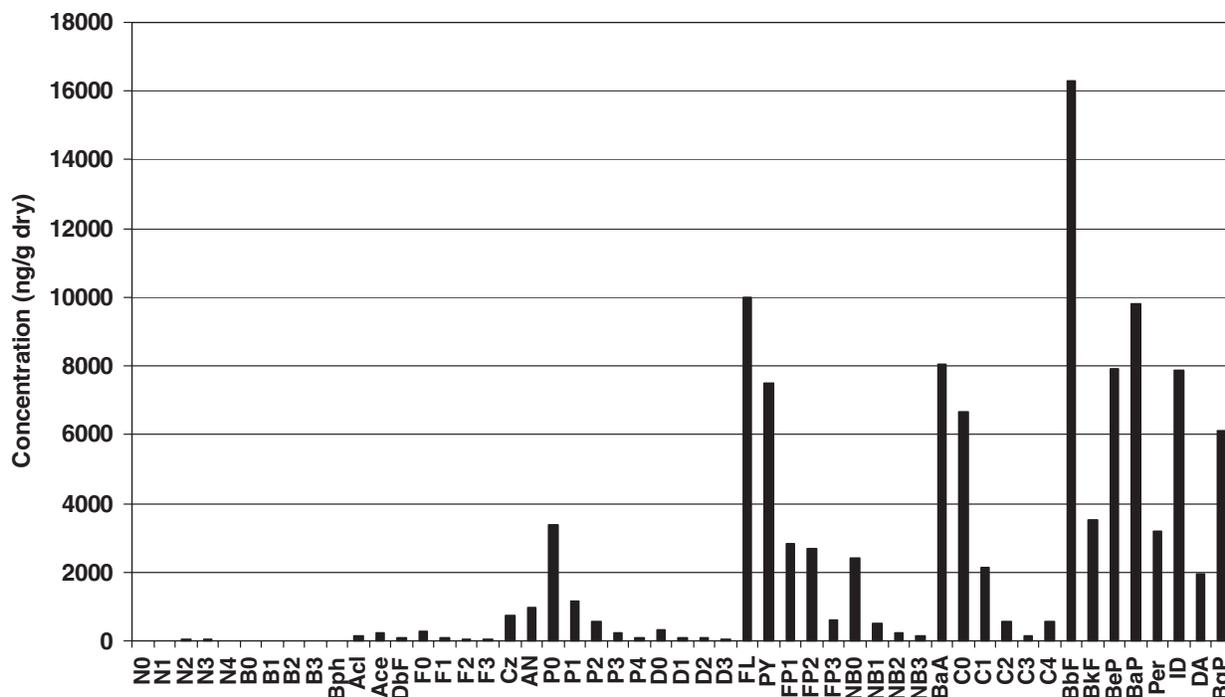


Figure 4. Graph of the typical polycyclic aromatic hydrocarbon (PAH) distribution profile reflecting a pyrogenic source.

corresponding drainage basins means sediment PAH measurements taken from such locations two years apart are useful as indicators of source inputs at each timepoint.

Comparisons across the two timepoints do not show decreases in sediment PAHs following a ban on pavement sealers in Austin. Although further time may be required to observe the full effects from the ban, the levels of PAH observed after two years did not change significantly as might be anticipated if pavement sealer inputs were the majority source of loadings to the stream (Mahler et al., 2004). Based on City of Austin estimates, a two-year ban represents a reduction in about 5 million liters of sealcoat use (Mahler et al., 2005), yet large-scale reductions in PAHs were not reflected in sediment samples. This suggests that two years may not be a sufficient time interval to observe effects for pavement sealer alone, among various sources, or that pavement sealer inputs likely represent much less than a majority source compared to the typical airborne and automotive sources (Christensen and Bzdusek, 2005; Yunker et al., 2002; Dickhut et al., 2000; Oanh et al., 1999; Freeman and Cattell, 1990) generally accepted to dominate PAH loadings.

Polycyclic Aromatic Hydrocarbons (PAH) Homolog Distribution Profiles

PAH homolog distribution profiles were examined to evaluate various PAH source inputs to sediment samples from Austin. All samples were characterized by an abundance of four-ring, five-ring and six-ring PAHs compared to the lower molecular weight two-ring and three-ring compounds. The predominance of higher molecular weight PAHs is consistent with a

distribution pattern representative of urban background (Stout et al., 2001). The PAH distribution profile for sample 4A-05, which contained the highest concentration of Σ PAH detected (Figure 4), is representative of the PAH profile pattern for the samples collected in this study.

An established method for distinguishing between pyrogenic and petrogenic PAH sources involves comparing the relative abundance of parent PAH compounds to their corresponding alkyl-substituted derivatives (Stout et al., 2001). When these concentrations are plotted, two differing profiles can emerge. If concentrations drop off consistently between the parent compound and the corresponding C1, C2 and C3 alkylated derivatives in sequence, the profile slopes downward in a "ski slope" shaped profile indicative of a pyrogenic source (Stout et al., 2002). If there is an increase between the parent and the lower-alkylated derivatives followed by a decrease again of higher alkylation derivatives, the profile appears to rise then fall in a bell-shaped profile indicative of a petrogenic source (Stout et al., 2002). The "ski slope" pattern observed for the phenanthrene, fluoranthene/pyrene and chrysene families of parent and alkylated PAHs in Sample 4A-05 indicate a pyrogenic source of PAHs for this sample. This pattern was apparent for most of the samples collected in this study. Only a few samples (e.g., 1B-05, 5A-05, 8A-05 and 14A-05 collected in 2005, and 8E-08, 9A-08 and 10A-08 in 2008) exhibited petrogenic characteristics.

Principal Components Analysis (PCA)

PCA is a useful technique for simplifying data that contain a large number of correlated variables and the technique has been

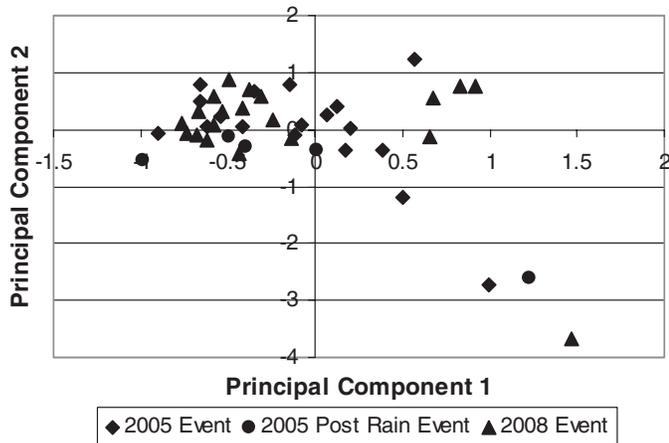


Figure 5. Principal components analysis (PCA) scores plot of the first two principal components—Austin sediment samples.

used to characterize the distribution and sources of PAHs in sediments (e.g., Hartmann et al., 2004; Stout et al., 2001; Walker et al., 2005; Yunker et al., 1996). The principal components are linear combinations of the original variables (in this case PAH and thiophene concentrations) that explain most of the variability in the dataset. The first principal component (PC) accounts for the greatest variability or most prominent trend in the dataset while successive PCs account for lesser trends in decreasing order of importance (Stout et al., 2001).

The benefit of performing a PCA is that relationships between multivariate samples can be visualized in a simple two- or three-dimensional PCA scores plot (Johnson and Ehrlich, 2002). Samples that plot near one another in a PCA scores plot have similar characteristics and samples that plot away from one another exhibit characteristic differences in the features being analyzed. The corresponding factor loadings plot illustrates the weights of each feature (i.e. PAH) in each principal compo-

nent. PAHs with low loadings (near zero) have little influence on where a sample falls on the PCA scores plot and PAHs with large positive or negative loadings essentially determine the PCA score for that PC.

Principal components analysis (PCA) of Austin Sediment Samples

PCA was performed on the 44 sediment samples collected in 2005 and in 2008, including the five samples collected in 2005 following a rain event. The first three PCs account for 35.4%, 17.8%, and 12.0% of the variability in the dataset. The PCA scores plot of the first two PCs (Figure 5) shows no overall distinction between sediments samples collected in 2005 (before the ban) and sediment samples collected in 2008 (after the ban). This plot suggests that the majority of the sediment samples collected in 2005 and 2008 contain PAHs derived from similar sources.

The PCA factor loadings cross-plot of the first two PCs (Figure 6) indicates that samples plotting along the negative PC1 axis are dominated by 4- to 6-ring PAH and samples plotting along the positive PC1 axis are enriched in 2- and 3-ring PAH, many of which are alkylated species. Because the lower molecular weight, 2- and 3-ring PAH are generally more susceptible to weathering processes (e.g., volatilization, solubilization, photolysis) the first PC may be interpreted as reflecting the extent of weathering in the sample with less weathered samples plotting to the right and more weathered samples plotting to the left. Note that the three samples with the highest low molecular weight to high molecular weight (LMW/HMW) ratios appear in the upper right quadrant of the scores plot in Figure 5. Soclo et al. (2000) suggests that the LMW/HMW ratio can be used to distinguish between pyrogenic and petrogenic PAHs in sediments where, $LMW = (AN + P0 + FL + PY)$ and $HMW = (BaA + C0 + BbF + BkF + BaP + BeP + Per + ID + DA +$

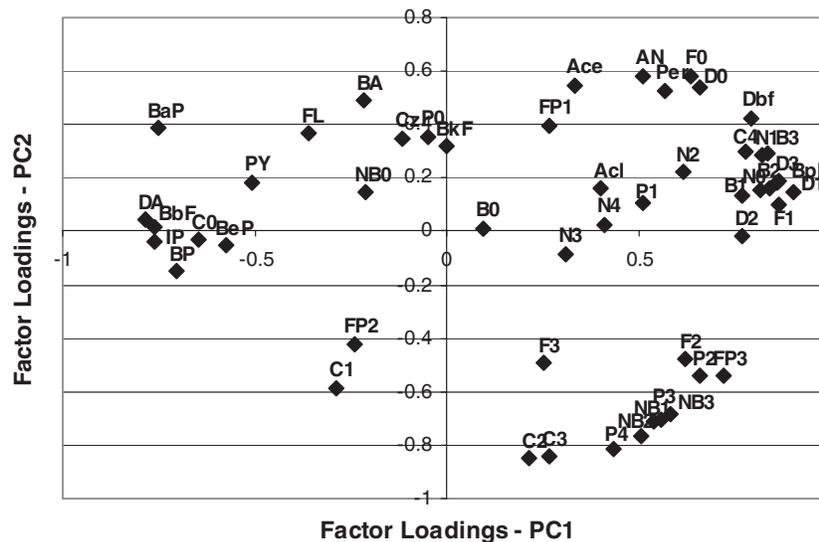


Figure 6. Principal components analysis (PCA) factor loadings plot of first two principal components—Austin sediment samples.

BgP). Alternatively, because it is the lower molecular weight PAH that are more soluble and more easily biodegraded, the LMW/HMW ratio may also reflect the degree of weathering. In this case, the three samples with the highest LMW/HMW ratios each exhibit the characteristic bell-shaped pattern of parent and alkylated PAHs, consistent with a petrogenic source.

Three other samples (1B-05, 18C-05R, and 22A-08) are located in the lower right quadrant of the figure, away from the main cluster of samples. These three samples, along with two other samples (8A-05 and 18C-05) are each characterized by a relatively high (>10%) thiophene content dominated by the naphthobenzothiophene compounds. All other samples contained less than 10% thiophene compounds. As indicated in Figure 6, the lower right quadrant of the PCA loadings plot is represented by the alkylated naphthobenzothiophenes (NB1, NB2 and NB3) as well as alkylated 2-ring to 4-ring PAHs, including alkylated fluorenes (F2, F3), alkylated phenanthrenes (P2, P3, P4) and alkylated chrysenes (C2, C3). Thiophene compounds are naturally present in fossil fuels and have been detected in automobile exhaust (Takada et al., 1990). Due to their relative enrichment in exhaust emissions, elevated thiophene content has been used as an indication of PAH contributions from vehicle-related sources (Takada et al., 1990).

Diagnostic Polycyclic Aromatic Hydrocarbons (PAH) Ratios

Analyses of the ratios of certain PAHs in samples have been used widely to determine sources of PAHs in sediments, soils and atmospheric particulates. Yunker et al. (2002) provides a recent review for application in sediments and Lima et al. (2005) review PAH ratios for combustion-derived sources. PAH ratios suitable for distinguishing sources in sediments should be stable in the environment and provide a unique signature for the sources evaluated. A number of ratios have been evaluated in the literature with varying levels of success. The ratios cited most often include pairs of PAHs with the same molecular weight (structural isomers) but having differing thermodynamic stabilities.

Linear PAHs such as anthracene and benzo(a)anthracene and those containing five-membered rings such as fluoranthene are known to be less thermodynamically stable than their nonlinear isomers (Lima et al., 2005). However, during the combustion process, more of the less stable isomer may be formed depending upon the fuel, combustion temperature and duration of the process. Thus, certain ratios of PAH isomers may be useful for distinguishing between pyrogenic and petrogenic sources, as well as among pyrogenic sources of PAHs. Yunker et al. (2002) evaluated the relative thermodynamic stabilities of PAH isomers based on calculated heats of formation and concluded that the PAH isomers with molecular weights of 276 (e.g., BgP and ID), 252 (e.g., BaP, BeP, BbF and BkF) and 202 (e.g., FL and PY) offer the best opportunity for distinguishing between pyrogenic and petrogenic sources of PAHs from a thermodynamic standpoint. However, these diagnostic ratios must remain stable in the environment and insensitive to a variety of weathering

processes (e.g., volatilization, solubilization, photodegradation and biodegradation) in order to be useful for identifying sources (Costa and Sauer, 2005).

Uhler and Emsbo-Mattingly (2006) evaluated the environmental stability of 30 PAH ratios in relatively unweathered tar samples subjected to laboratory evaporation and aerobic biodegradation conditions. Many four-ring and all five- and six-ring PAH ratios remained relatively stable after 168 hours of evaporation; however, most PAH ratios composed of two- and three-ring compounds were unstable. The authors observed similar results after the tar samples were allowed to undergo aerobic biodegradation for seven weeks. In this report we examine five PAH ratios (BbF:BkF, FL:PY, BaA:C0, ID:BgP and BaP:BeP) for their potential to discriminate among possible sources. Of the five ratios examined, BbF:BkF offers promise for evaluating potential impacts from coal tar based sources. We suspect that both BaA:C0 and FL:PY ratios may be susceptible to photodegradation, and find ID:BgP and BaP:BeP not particularly useful for evaluating sources in this study. Calculated ratios are summarized in Table 4.

Benzo(b)fluoranthene:Benzo(k)fluoranthene (BbF:BbK).

BbF:BkF ratios measured in sediments collected during this study (both events) ranged from 2.04 to 6.77 with a median value of 2.57. Median ratios were similar for the 2005 and 2008 sampling events at 2.64 and 2.50, respectively. In contrast, the BbF:BkF ratios measured in samples of CT sealer produced at three different manufacturing plants varied only slightly, ranging from 1.49 to 1.51 (personal communication, Pavement Coatings Technology Council). The ratio reported in the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1597 for coal tar is 1.53 (NIST, 1992). In comparison, the NIST SRM 1650a for diesel particulate matter has a BbF:BkF ratio of 3.34 (NIST, 2000) which is very similar to the NIST SRM 1649a for urban dust with a ratio of 3.37 (NIST, 2001). These data suggest that BbF:BbK ratios may be useful for evaluating potential impacts from coal tar based sources. For this study, we note that BbF:BkF ratios in Austin sediments are more closely associated with ratios determined for vehicle emissions and urban dusts than a CT-based source.

Benzo(a)anthracene:Chrysene (BaA:C0).

BaA:C0 ratios in Austin sediments ranged from 0.36–1.43 with a median value of 0.6. There were distinct differences in ratios observed during the 2005 and 2008 sampling events. BaA:C0 ratios were consistently lower in samples collected in 2008 compared with 2005 (pre-rain) with values ranging from 0.38 to 0.88 with a median value of 0.55 in 2008 compared to a range of 0.49–1.43 with a median value of 0.87 in 2005. These differences might be interpreted to reflect potential effects from the ban; however, ratios were also lower in samples collected in 2005 after a heavy rain event, when no ban was in effect (median ratio = 0.43 with a range of 0.36 to 0.61). As described in following text, the lower BaA:C0 ratios observed in the 2008 and 2005 post-rain samples compared to the 2005 (pre-rain)

samples could be explained by longer antecedent dry periods for these two events allowing for a longer photodegradation period.

Plata et al. (2008) measured photodegradation loss rates for selected PAHs in oil-coated rocks in Buzzards Bay, Massachusetts. Benzo(a)anthracene was lost at a faster rate compared to chrysene resulting in decreasing BaA/C0 ratios over time. The authors reported half-lives on the order of 25 to 40 days for BaA and 35 to 80 days for C0 and note that loss rates were not attributed to evaporation or water washing (Arey et al., 2007). The rate of PAH photolysis on atmospheric soot particles is much greater with reported half-lives on the order of hours to days depending upon humidity and light conditions (Kamens et al., 1988). Loss rates for BaA were about a factor of two faster than for C0. This suggests that lower BaA/Co ratios should be observed in particulates associated with longer antecedent dry periods, consistent with the findings above.

BaA:C0 ratios observed in the NIST SRM for diesel particulates (0.44) and in the NIST SRM for urban dust (0.72) were similar to the median values reported for Austin stream sediments. In contrast, the BaA:C0 ratio observed in SRM Coal Tar is 1.37 and in CT-based sealer is 1.05 (median of three values).

Fluoranthene:Pyrene (FL:PY)

FL:PY ratios in Austin sediments collected in this study ranged from 0.93 to 2.02 with a median value of 1.23. There were distinct differences between ratios observed in 2005 (pre-rain) with values ranging from 0.93 to 1.33 with a median value of 1.12 and ratios observed in 2008 with values ranging from 1.10 to 2.02 with a median value of 1.34. Relative photolysis rates for fluoranthene and pyrene, which vary by about a factor two, suggest that higher FL/PY ratios should be observed in particulates associated with a longer photodegradation period (Chen et al., 2001; Matsuzawa et al., 2001).

The ratio of fluoranthene to pyrene is reported to be influenced by the temperature at which these PAHs are formed, with higher temperature processes resulting in higher FL:PY ratios (McCarthy et al., 2000). The FL:PY ratios measured in samples of CT sealer produced at three different manufacturing plants varied from 1.33 to 1.40 and the ratio found in the NIST SRM for coal tar is 1.37. In contrast, the median ratio observed in particulates collected from rooftops in Austin, Texas was 1.21 (Van Metre and Mahler, 2003) and the FL:PY ratio reported for NIST SRM for urban dust is 1.22. The FL:PY ratio in the NIST SRM for diesel particulate matter is somewhat lower at 1.05. Interestingly, the pre-ban 2005 sediment samples more closely reflect an urban dust/diesel particulate source; whereas, FL:PY ratios in samples collected more than two years following the ban more closely resemble a CT-based source. This difference could also reflect effects from differential photodegradation.

Indeno(1,2,3-cd)pyrene;Benzo(ghi)perylene (ID:BgP)

ID:BgP ratios observed in Austin sediments ranged from 1.02 to 1.36 with a median value of 1.15. These values are in the range of ratios observed for SRM coal tar (1.12) and fresh

Table 4. Polycyclic aromatic hydrocarbon (PAH) ratios measured in sediments and other media

Sediment ID	PAH Ratio				
	FL:PY	BaA:C0	BbF:BkF	ID:BgP	BaP:BeP
Austin Stream Sediments					
Median 2005 Sediment	1.12	0.87	2.64	1.14	1.14
Median 2005 rain	1.28	0.43	4.14	1.33	1.10
Median 2008 sediment	1.34	0.55	2.50	1.16	1.18
National Institute of Standards and Technology (NIST) Standard Reference Materials					
SRM urban dust	1.22	0.72	3.37	0.79	0.81
SRM diesel particulate	1.05	0.44	3.34	0.86	0.18
SRM coal tar	1.37	1.37	1.53	1.12	1.68
Coal Tar Sealer Product (Koppers Brand)					
CT sealer ^(b)	1.38	1.05	1.49	1.01	1.48
Austin Area Roof Tops					
Roof tops ^(b)	1.21	0.38	NA ^(c)	NA	NA

A) Sample 14A-05, which contained only 0.022 mg/kg PAHs appears as an outlier compared with all other sediment samples and is not considered in Table 4 summary statistics; B) median value cited; C) ratio could not be calculated because individual PAH concentrations were not reported.

coal tar sealer (median = 1.01). NIST SRM samples of diesel particulates and urban dust have lower ID:BgP ratios of 0.86 and 0.79. These data show that Austin sediments and CT-based products have similar ID:BgP ratios.

Benzo(a)pyrene:Benzo(e)pyrene (BaP:BeP)

The ratio of benzo(a)pyrene to benzo(e)pyrene (BaP:BeP) would appear to be a promising ratio for discriminating coal tar sources from mobile emission sources based on ratios reported in the NIST SRMs for coal tar (1.68) and diesel particulates (0.18). The BaP:BeP ratio in the NIST SRM for urban dust is 0.81. As indicated in Table 4, the coal tar SRM and pure coal tar sealer had similar BaP:BeP ratios at 1.68 and 1.48. BaP:BeP ratios in Austin sediments ranged from 0.83 to 1.51 with a median value of 1.14. There was no significant difference in ratios observed in 2005 and 2008 with values ranging from 0.88 to 1.51 with a median value of 1.14 in 2005 and values ranging from 0.88 to 1.48 with a median value of 1.17 in 2008. Thus BaP:BeP ratios in Austin stream sediments appear to fall midway between the ratios for urban dust and coal tar SRMs.

Conclusions

Total PAH concentrations in Austin stream sediments did not change significantly after two years of a municipal ban on CT pavement sealers. At an estimated annual usage of 2.5 million liters prior to the ban, some decrease in PAH concentrations might be expected if pavement sealers represented greater than half of PAH inputs, as previously suggested (Mahler et al., 2004). Although older sealcoat applications remain and further time may be required to see the full effects from the ban, this initial outcome is consistent with pavement sealer products representing a relatively small fraction of overall inputs. The stream systems studied in Austin are particularly suited for

being able to evaluate snapshots of sediment conditions 2 years apart because the flatrock streambeds, frequent shallow pockets and extensive scouring during rain events are not conducive to the establishment of stable depositional areas and available sediment deposits tend to reflect recent inputs.

PAH profiling made use of PCA and comparisons among PAH ratios. We found no unique clustering of samples in the PCA scores plot of sediment samples collected before and after the ban suggesting no major difference in source types for these samples. The observed variability among all samples appears to be consistent with effects due to surficial weathering, i.e., photodegradation and similar processes occurring on the order of weeks to months while substrates are exposed and desiccated—not long-term weathering of PAHs in saturated sediment columns.

Comparison of selected PAH ratios in sediment samples collected before and after the ban with PAH ratios measured in NIST SRMs yielded equivocal results. BbF:BkF, BaA:CO, and BaP:BeP ratios in Austin sediments more closely matched the urban dust SRM than the coal tar SRM; however, ID:BgP ratios in sediments more closely match the coal tar SRM. Interestingly, FL:PY ratios in the 2008 sediments (collected after the ban) more closely matched the coal tar SRM whereas the pre-ban 2005 sediments more closely matched the urban dust SRM. We also observed small but distinct differences between BaA:CO and FL:PY ratios in 2005 and 2008 sediments, which we suggest might be due to differences in photodegradation times between rain events rather than potential effects from the ban.

In summary, PAH concentrations in Austin streambed sediments did not decrease two years after a municipal ban on pavement sealers. While this one potential source was controlled, sources dominating new sediment inputs apparently remained similar. PAH profiling did not identify any marked changes indicating a shift away from coal tar based sources after the ban, but did suggest that PAH variability may be influenced by surficial weathering. Because two years may be an insufficient amount of time to realize the full effects from the ban, further monitoring of sediment PAHs over time will be useful for determining whether PAH control strategies directed at specific types of pavement sealers effectively reduce input concentrations in transient sediment accumulations and in the ultimate depositional receiving water body.

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