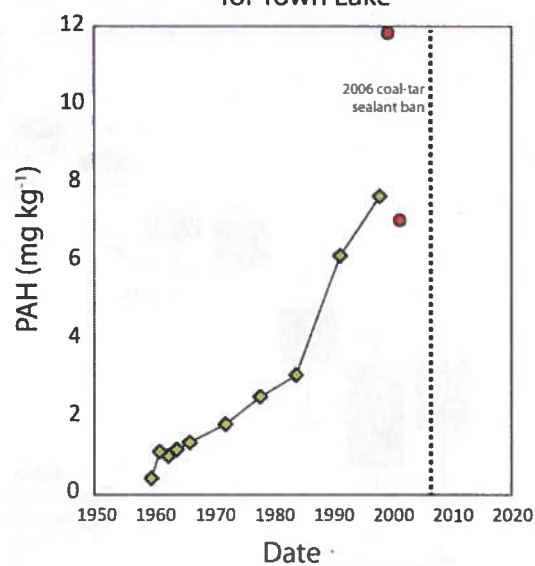


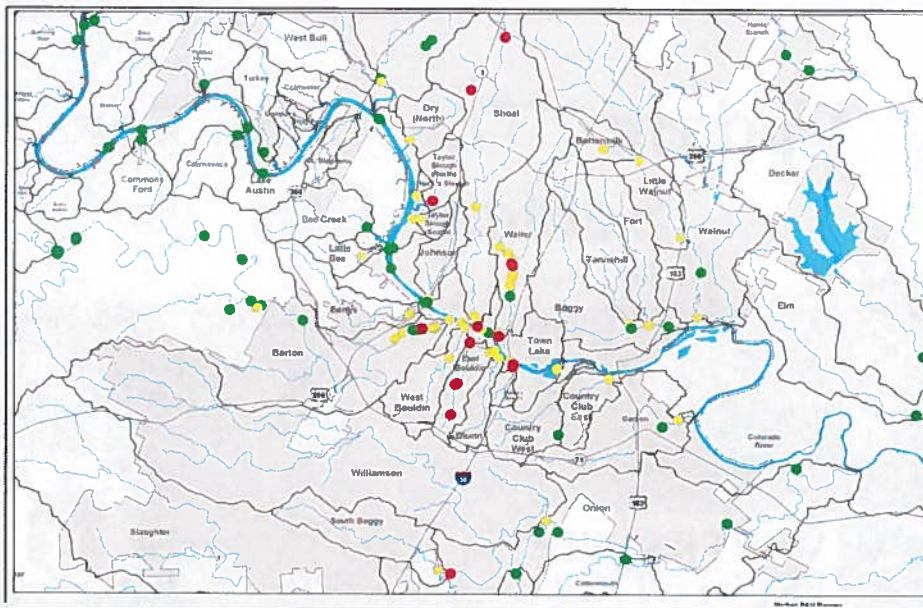
Update: The Coal Tar Sealant Ban



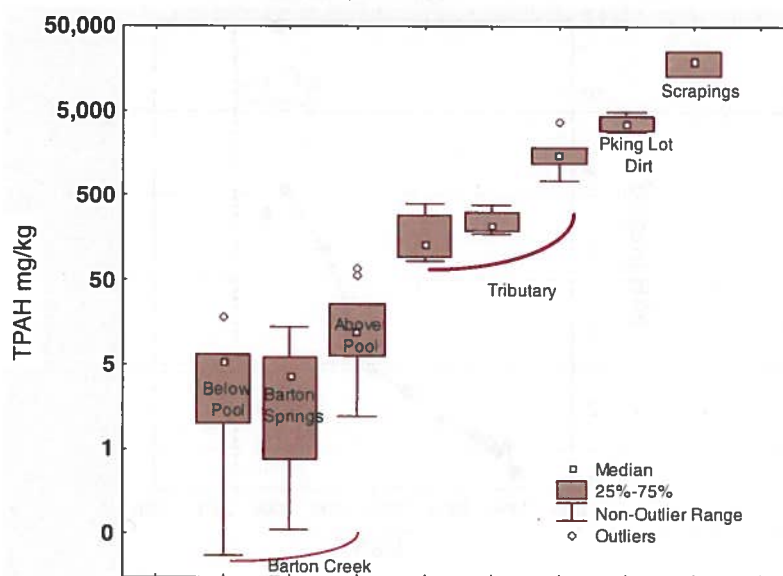
Pre-2006 USGS sediment data
for Town Lake



PAH hotspots in streams



Tracing the source



The Case

- ❑ > 600,000 gallons of CTS applied annually.
- ❑ PAH's increasing in LBL and over 13% of Austin streams have PAH hot spots (c. 2005).
- ❑ Coal tar sealants are concentrated source of PAHs.
- ❑ Ecological impacts demonstrated:
 - Chemical tracing, toxicity, field verification

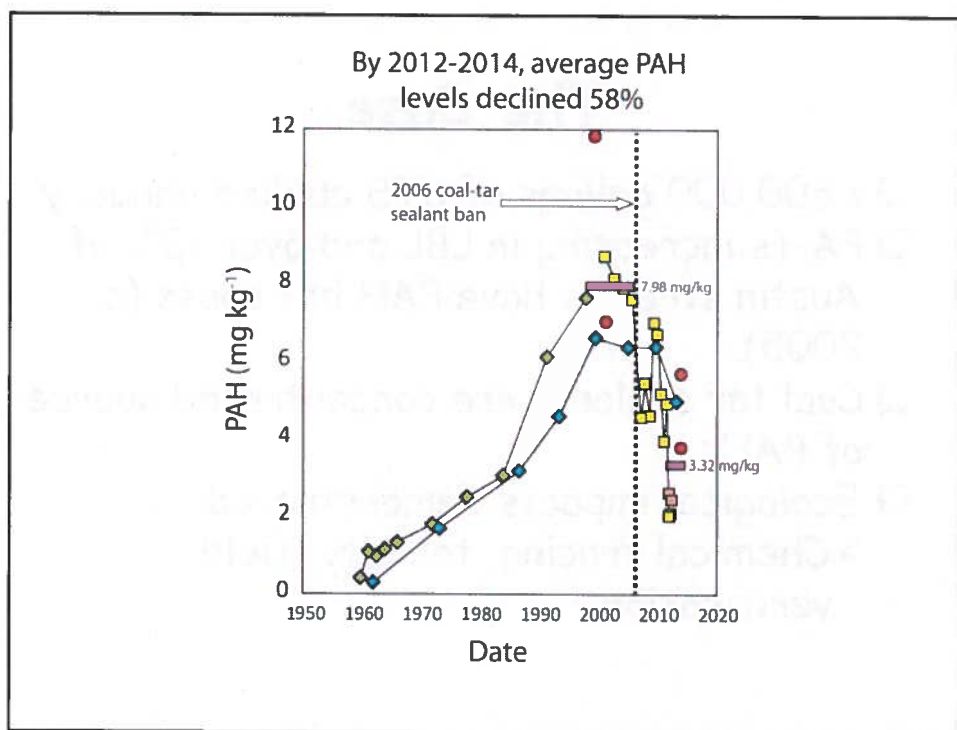
The Ban

- ❑ Use prohibited in the City jurisdiction
- ❑ Sale prohibited unless intended application outside jurisdiction
- ❑ Enforcement is complaint and staff driven

ATTENTION! **COAL TAR SEALANT**

USE IS BANNED IN AUSTIN
AND ITS PLANNING
JURISDICTION (ETJ). FINES
UP TO \$2,000 PER DAY
WILL BE ENFORCED.

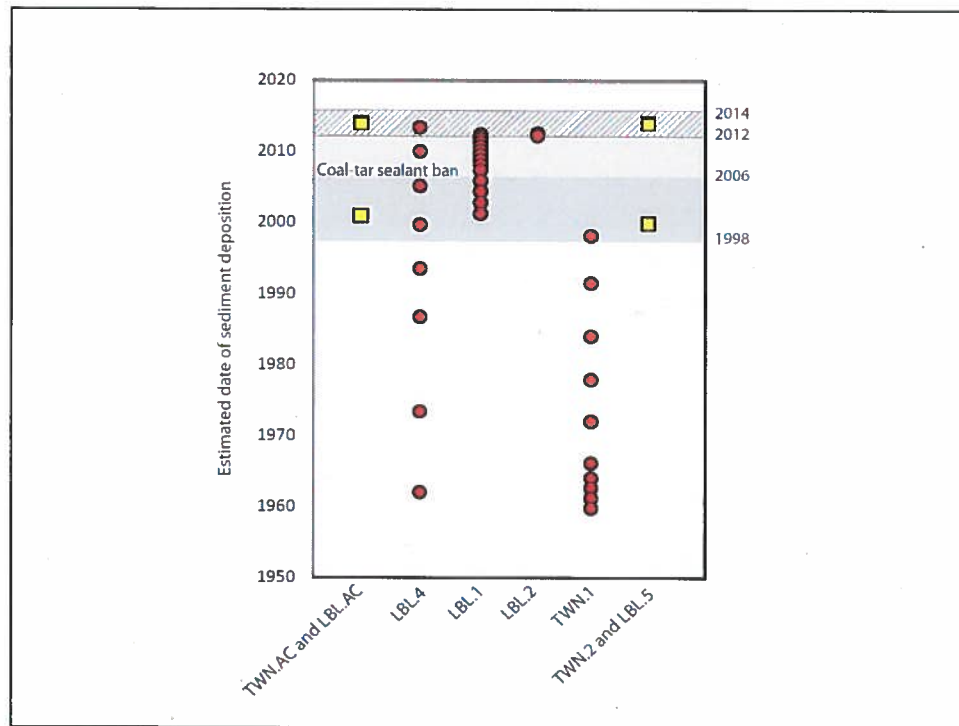
FOR MORE INFORMATION
CALL 512-974-2550



Questions?

- ☐ Central Texas?
- ☐ WPD monitoring?
- ☐ Human Health?
- ☐ Dogget's National Ban bill?





Coal-Tar-Based Pavement Sealcoat, Polycyclic Aromatic Hydrocarbons (PAHs), and Environmental Health

6d

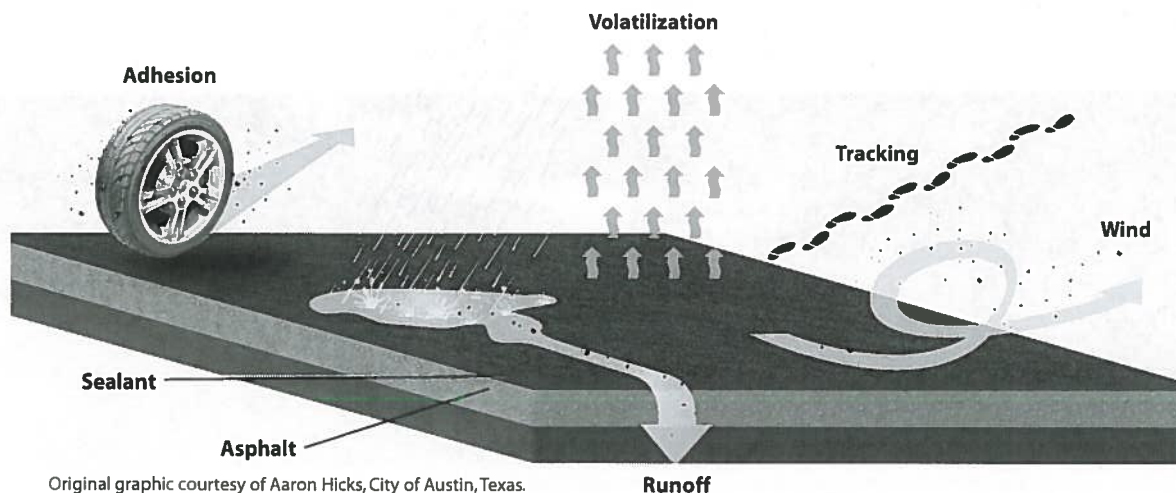
Studies by the U.S. Geological Survey (USGS) have identified coal-tar-based sealcoat—the black, viscous liquid sprayed or painted on asphalt pavement such as parking lots—as a major source of polycyclic aromatic hydrocarbon (PAH) contamination in urban areas for large parts of the Nation. Several PAHs are suspected human carcinogens and are toxic to aquatic life.



Sealcoat is the black, viscous liquid sprayed or painted on the asphalt pavement of many parking lots, driveways, and playgrounds.

Key Findings

- Dust from pavement with coal-tar-based sealcoat has greatly elevated PAH concentrations compared to dust from unsealed pavement.
- Coal-tar-based sealcoat is the largest source of PAH contamination to 40 urban lakes studied, accounting for one-half of all PAH inputs.
- Coal-tar-based sealcoat use is the primary cause of upward trends in PAHs, since the 1960s, in urban lake sediment.
- Residences adjacent to parking lots with coal-tar-based sealcoat have PAH concentrations in house dust that are 25 times higher than those in house dust in residences adjacent to parking lots without coal-tar-based sealcoat.
- PAHs move from a sealcoated surface into our environment by many mechanisms: storm runoff, adhesion to tires, wind, foot traffic, and volatilization.



Original graphic courtesy of Aaron Hicks, City of Austin, Texas.

What are Sealcoat, PAHs, and Coal Tar?

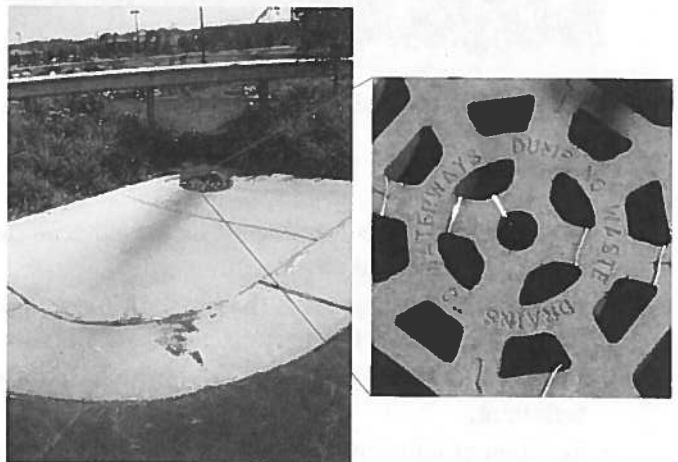
Pavement sealcoat (also called sealant) is a black liquid that is sprayed or painted on some asphalt pavement. It is marketed as protecting and beautifying the underlying pavement, and is used commercially and by homeowners across the Nation. It is applied to parking lots associated with commercial businesses, apartment and condominium complexes, churches, schools, and business parks, to residential driveways, and even to some playgrounds. Most sealcoat products have a coal-tar-pitch or asphalt (oil) base. Coal-tar-based sealcoat is commonly used in the central, southern, and eastern United States, and asphalt-based sealcoat is commonly used in the western United States.

PAHs are a group of chemical compounds that form whenever anything with a carbon base is burned, from wood and gasoline to cigarettes and meat. PAHs also are in objects and materials, such as automobile tires and coal tar, the production of which involves the heating of carbon-based materials. PAHs are of environmental concern because several are toxic, carcinogenic, mutagenic, and/or teratogenic (causing birth defects) to aquatic life, and seven are probable human carcinogens (U.S. Environmental Protection Agency, 2009).

Coal tar is a byproduct of the coking of coal for the steel industry and coal-tar pitch is the residue remaining after the distillation of coal tar. Coal-tar pitch is 50 percent or more PAHs by weight and is known to cause cancer in humans (International Agency for Research on Cancer, 1980). Coal-tar-based sealcoat products typically are 20 to 35 percent coal-tar pitch. Product analyses indicate that coal-tar-based sealcoat products contain about 1,000 times more PAHs than sealcoat products with an asphalt base (City of Austin, 2005).

How does Sealcoat get from Driveways and Parking Lots into Streams and Lakes, Homes, and the Air?

Friction from vehicle tires abrades pavement sealcoat into small particles. These particles are washed off pavement by rain and carried down storm drains and into streams. Other sealcoat particles adhere to vehicle tires and are transported to other surfaces, blown offsite by wind, or tracked indoors on the soles of shoes. Some of the PAHs in sealcoat volatilize (evaporate), which is why sealed parking lots and driveways frequently give off a "mothball" smell. Sealcoat wear is visible in high traffic areas within a few months after application, and sealcoat manufacturers recommend reapplication every 2 to 4 years.



Runoff from sealcoated pavement (black surface) enters storm drains that lead to local streams. Drain grate (inset) is marked "DUMP NO WASTE" and "DRAINS TO WATERWAYS."

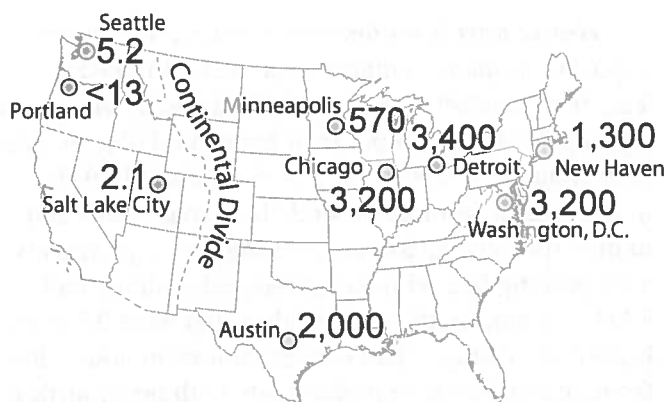


Gray asphalt pavement shows through where sealcoat has worn off the driveway of an apartment complex.

The East-West Divide

Regional Product Use Translates to Large Differences in PAH Concentrations

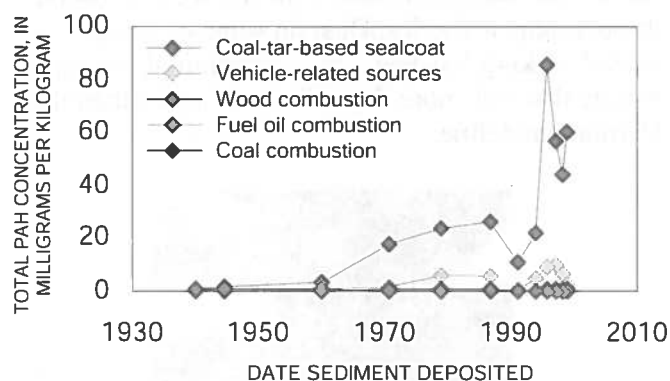
Does product type really matter? PAH concentrations in the coal-tar-based sealcoat product are about 1,000 times higher than in the asphalt-based product (more than 50,000 milligrams per kilogram [mg/kg] in coal-tar-based products and 50 mg/kg in asphalt-based products [City of Austin, 2005]). Anecdotal reports, such as Web sites, blogs, and comments by industry representatives, indicate that the coal-tar-based product is used predominantly east of the Continental Divide and the asphalt-based product is used predominantly west of the Continental Divide. During 2007–08, the USGS swept dust from sealcoated and unsealcoated parking lots in nine cities across the United States and analyzed the dust for PAHs. For six cities in the central and eastern United States, the median PAH concentration in dust from sealcoated parking lots was 2,200 mg/kg, about 1,000 times higher than in dust from sealcoated parking lots in the western United States, where the median concentration was 2.1 mg/kg. Although both product types are available nationally, these results confirm the regional difference in use patterns (Van Metre and others, 2009).



Concentrations of PAHs in dust swept from sealed parking lots in central and eastern U.S. cities, where coal-tar-based-sealcoat use dominates, were about 1,000 times higher than in western U.S. cities, where asphalt-based-sealcoat use dominates. Concentrations shown on the map are the sum of 12 PAHs, in milligrams per kilogram (Van Metre and others, 2009).



“Fingerprinting” Shows that Coal-Tar Sealant is the Largest Source of PAHs to Urban Lakes



Coal-tar-based sealcoat (orange symbol) is the largest contributor to increasing concentrations of PAHs in Lake Killarney, Orlando, Florida, as determined by chemical fingerprinting. Similar patterns were seen in lakes across the central and eastern United States (Van Metre and Mahler, 2010).

PAHs are increasing in urban lakes across the United States. To better understand why this might be happening, USGS scientists collected sediment cores from 40 lakes in cities from Anchorage, Alaska, to Orlando, Florida, analyzed the cores for PAHs, and determined the contribution of PAHs from many different sources by using a chemical mass-balance model. The model is based on differences in the chemical “fingerprint” of PAHs from each source. Coal-tar-based sealcoat accounted for one-half of all PAHs in the lakes, on average, while vehicle-related sources accounted for about one-fourth. Lakes with a large contribution of PAHs from sealcoat tended to have high PAH concentrations; in many cases, at levels that can be harmful to aquatic life. Analysis of historical trends in PAH sources to 8 of the 40 lakes indicates that sealcoat use is the primary cause of increases in PAH concentrations since the 1960s. Identifying where PAHs are coming from is essential for developing environmental management strategies (Van Metre and Mahler, 2010).

From Outside to Inside

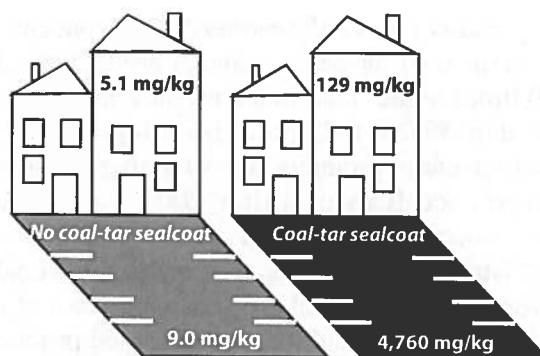
Coal-Tar Pavement Sealant Linked to PAHs in House Dust

House dust is an important source for human exposure to many contaminants, including PAHs. This is particularly true for small children, who spend time on the floor and put their hands and objects into their mouths. In 2008, the USGS measured PAHs in house dust from 23 ground-floor apartments and in dust from the apartment parking lots. Apartments with parking lots with coal-tar-based sealcoat had PAH concentrations in house dust that were 25 times higher, on average, than concentrations in house dust from apartments with parking lots with other surface types (concrete, unsealed asphalt, and asphalt-based sealcoat). PAH concentrations in the dust from the parking lots with coal-tar-based sealcoat were 530 times higher, on average, than concentrations on the parking lots with other surface types.



Photograph obtained from Jupiter Images.

What about other sources of PAHs? Although tobacco smoking, candle and incense burning, and barbecue and fireplace use have been suggested to affect PAH concentrations in house dust, this study found no relation between any of these, or the many other factors considered, and PAH concentrations in the house dust. The presence or absence of coal-tar-based sealcoat on the apartment complex parking lot was strongly correlated with PAH concentrations in house dust; the only other variable that was related to PAH concentrations in house dust was urban land-use intensity (the percentage of land near the apartment dedicated to multifamily residential, commercial, office, warehouse, or streets) (Mahler and others, 2010).



Apartments with coal-tar-based sealcoat on the parking lot had much higher concentrations of PAHs, both in indoor dust and in parking lot dust, than apartments with an unsealed asphalt or concrete parking lot or with a parking lot with asphalt-based sealcoat. Concentrations shown are for the sum of the 16 U.S. Environmental Protection Agency priority pollutant PAHs (Mahler and others, 2010), in milligrams per kilogram (mg/kg).

There are no U.S. health-based guidelines for chronic exposure to PAHs in house dust. The only existing guideline is for a single PAH—benzo[a]pyrene—issued by the German Federal Environment Agency Indoor Air Hygiene Commission (Hansen and Volland, 1998). The guideline advises minimizing exposure to concentrations of benzo[a]pyrene greater than 10 mg/kg in dust to avoid adverse health effects. That guideline was exceeded for 4 of the 11 apartments with coal-tar-sealcoated parking lots and for 1 of the 12 apartments with a parking lot with a different surface type. Also of concern is exposure to the sealcoated pavement surfaces themselves through play activities. Dust on some of the sealcoated parking lots had a concentration of benzo[a]pyrene that was more than 50 times higher than the German guideline.



Photograph courtesy of CLEARCorps, Durham, North Carolina.

Our Environment and Us

What are the Concerns?

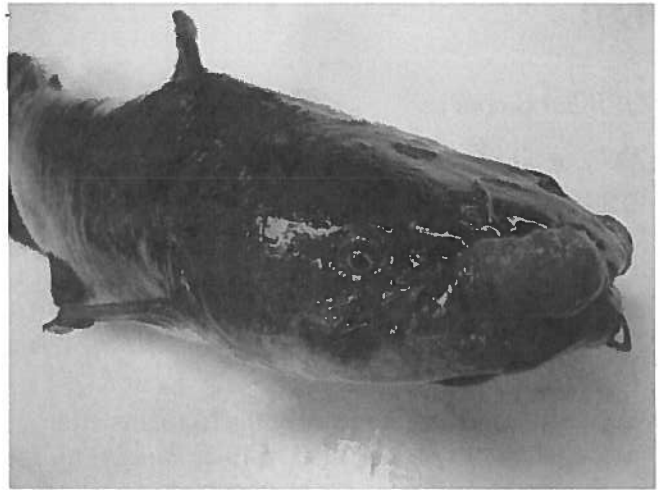
Some PAHs are toxic to mammals (including humans), birds, fish, amphibians (such as frogs and salamanders), and plants. The aquatic invertebrates—insects and other small creatures that live in streams and lakes—are particularly susceptible to PAH contamination, especially those that live in the mud where PAHs tend to accumulate. These invertebrates are an important part of the food chain and are often monitored as indicators of stream quality (analogous to the “canary in the coal mine” concept). Possible adverse effects of PAHs on aquatic invertebrates include inhibited reproduction, delayed emergence, sediment avoidance, and mortality. Possible adverse effects on fish include fin erosion, liver abnormalities, cataracts, and immune system impairments. The Probable Effect Concentration (PEC) of 22.8 mg/kg of total PAHs (MacDonald and others, 2000)—a widely used sediment quality guideline that is the concentration in bed sediment expected to have harmful effects on bottom-dwelling biota—is exceeded in one-third of the central and eastern U.S. urban lakes where PAH sources were studied.



When turned over, red spotted newts that had been exposed to sediment contaminated with coal-tar-based sealcoat had difficulty righting themselves (Bommarito and others, 2010b). Poor reflexes could result in decreased survival. Photograph by Megan Gibbons, Birmingham-Southern College.

Scientific studies have shown a relation between coal-tar-based pavement sealcoat and harmful effects on aquatic life.

- Aquatic communities downstream from storm-water runoff from sealcoated parking lots were impaired (Scoggins and others, 2007).
- Salamanders and newts exposed to sediment contaminated with coal-tar-based sealcoat had stunted growth, difficulty swimming or righting themselves, and liver problems (Bommarito and others, 2010a, b).
- Frogs exposed to sediment contaminated with coal-tar-based sealcoat died, had stunted growth, or developed more slowly than usual (Bryer and others, 2006).



Tumors in brown bullhead catfish from the Anacostia River, Washington, D.C., are believed to be related to elevated PAH concentrations (Pinkney and others, 2009). Photograph by A.E. Pinkney.

Human health risk from environmental contaminants usually is evaluated in terms of exposure pathways. For example, people could potentially be exposed to PAHs in sealcoat through ingestion of abraded particles from driveways, parking lots, or play grounds, or through skin contact with the abraded particles, either directly or by touching toys or other objects that have been in contact with the pavement. Inhalation of wind-blown particles and of fumes that volatilize from sealed parking lots are other possible pathways. PAHs in streams and lakes rarely pose a human health risk from contact recreation or drinking water because of their tendency to attach to sediment rather than to dissolve in water.



Skin contact is one way humans can be exposed to PAHs. Parking lots and driveways with coal-tar-based sealcoat have concentrations of PAHs hundreds to thousands of times higher than those with asphalt-based sealcoat or no sealcoat. Photograph obtained from Corbis Images, Inc.

FAQ

Q) *What is coal tar?*

A) Coal tar is a thick, black or brown liquid that is a byproduct of the carbonization of coal for the steel industry or the gasification of coal to make coal gas.

Q) *What is the difference between crude coal tar, coal-tar pitch, and “refined” coal tar?*

A) Coal-tar pitch is the residue that remains after various light oils are distilled from crude coal tar for commercial use. The coal-tar pitch is then separated (refined) into 12 different viscosities, RT-1 (the most fluid) through RT-12 (the most viscous). RT-12 is the viscosity used in coal-tar-based pavement sealcoat.

Q) *How can I tell if a product contains coal tar?*

A) To determine if the product has a coal-tar base, look for the Chemical Abstracts Service (CAS) number 65996-93-2 on the product Material Safety Data Sheet (MSDS). The words “coal tar,” “refined coal tar,” “refined tar,” “refined coal-tar pitch,” or other similar terms may be listed on the MSDS or on the product container.

Q) *Is sealcoat used on roads?*

A) Use on roads is extremely rare. Occasionally a private property, such as a housing development, will choose to have the roads sealcoated.

Q) *Is use of coal-tar-based sealant regulated?*

A) Several jurisdictions, including the City of Austin, Texas, the City of Washington, D.C., Dane County, Wisconsin, and several suburbs of Minneapolis, Minnesota, have banned use of coal-tar-based sealcoat. Similar bans are under consideration in other jurisdictions.

For more information on USGS research on PAHs and coal-tar-based sealcoat go to <http://tx.usgs.gov/coring/allthingssealcoat.html>.

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Lafayette Publishing Service Center

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Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

—B.J. Mahler and P.C. Van Metre

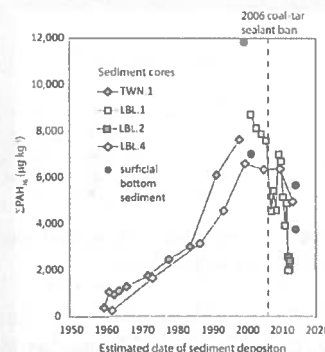
PAH Concentrations in Lake Sediment Decline Following Ban on Coal-Tar-Based Pavement Sealants in Austin, Texas

Peter C. Van Metre* and Barbara J. Mahler

U.S. Geological Survey, 1505 Ferguson Lane, Austin, Texas 78754, United States

Supporting Information

ABSTRACT: Recent studies have concluded that coal-tar-based pavement sealants are a major source of polycyclic aromatic hydrocarbons (PAHs) in urban settings in large parts of the United States. In 2006, Austin, TX, became the first jurisdiction in the U.S. to ban the use of coal-tar sealants. We evaluated the effect of Austin's ban by analyzing PAHs in sediment cores and bottom-sediment samples collected in 1998, 2000, 2001, 2012, and 2014 from Lady Bird Lake, the principal receiving water body for Austin urban runoff. The sum concentration of the 16 EPA Priority Pollutant PAHs (ΣPAH_{16}) in dated core intervals and surficial bottom-sediment samples collected from sites in the lower lake declined about 44% from 1998–2005 to 2006–2014 (means of 7980 and 4500 $\mu\text{g kg}^{-1}$, respectively), and by 2012–2014, the decline was about 58% (mean of 3320 $\mu\text{g kg}^{-1}$). Concentrations of ΣPAH_{16} in bottom sediment from two of three mid-lake sites decreased by about 71 and 35% from 2001 to 2014. Concentrations at a third site increased by about 14% from 2001 to 2014. The decreases since 2006 reverse a 40-year (1959–1998) upward trend. Despite declines in PAH concentrations, PAH profiles and source-receptor modeling results indicate that coal-tar sealants remain the largest PAH source to the lake, implying that PAH concentrations likely will continue to decline as stocks of previously applied sealant gradually become depleted.



INTRODUCTION

Coal-tar-based pavement sealants were first identified in 2005 as a potentially large source of polycyclic aromatic hydrocarbons (PAHs) in urban runoff.^{1,2} The initial studies were done in Austin, Texas, and, in response to the findings, the City of Austin banned coal-tar-sealant use beginning in January 2006, becoming the first jurisdiction in the U.S. to do so. Subsequent research has demonstrated that coal-tar sealants contribute PAHs to various environmental compartments where the chemicals pose potential risks to ecological communities^{3–7} and human health,^{8,9} and numerous cities, counties, and states have instituted bans.¹⁰ A key question, therefore, arises: Did banning coal-tar sealants affect environmental occurrence of PAHs in Austin?

Sealcoat is a black, shiny liquid sprayed or painted on the asphalt pavement of parking lots and driveways in the United States and Canada. Pavement sealants are marketed as protecting and beautifying the underlying asphalt pavement. Sealcoat use is widespread in North America;¹¹ an estimated 320 million liters of coal-tar sealant is used annually in the U.S.¹²

Most sealcoat products are made with either a crude coal tar (or coal-tar pitch) base or an asphalt base derived from crude oil. The coal-tar products, dominantly used east of the Continental Divide, typically are 15–35% coal tar or coal-tar pitch, both of which are known human carcinogens.¹³ The major chemicals in coal tar and coal-tar pitch that can cause harmful health effects are polycyclic aromatic hydrocarbons (PAHs), phenol, and cresols.¹⁴ The concentration of the sum of

the 16 U.S. Environmental Protection Agency Priority Pollutant PAHs (ΣPAH_{16})¹⁵ in coal-tar-sealant products is 66 000 mg kg^{-1} (mean; dry weight basis), about 1000 times greater than the mean concentration in asphalt-based sealcoat products (50 mg kg^{-1}).⁸

Lady Bird Lake in Austin, TX (formerly Town Lake, renamed in 2007), is uniquely situated to test the hypothesis that restricting use of coal-tar sealant will result in a measurable decrease in PAH concentrations in receiving water bodies. The lake is a receiving water body for urban runoff from much of Austin (Figure 1). At the time of sediment collection for this study, 6–8 years had passed since use of coal-tar sealant had been banned, potentially long enough that a downward trend might be evident in the concentrations of PAHs in lake sediments. Although the Colorado River has a large, mostly rural watershed (100 000 km^2 upstream from Austin), several large reservoirs upstream from the lake trap sediment, including Lake Austin, which is impounded by Tom Miller Dam immediately upstream from Lady Bird Lake. As a result, sediment deposited in the lake is dominantly from urban runoff from Austin and its Extra Territorial Jurisdiction (ETJ) (Supporting Information (SI) Figure S-1). Of the 410- km^2 local drainage area to the lake, 53% lies within Austin and its ETJ, where coal-tar-sealant use was banned, and in 2010, 92%

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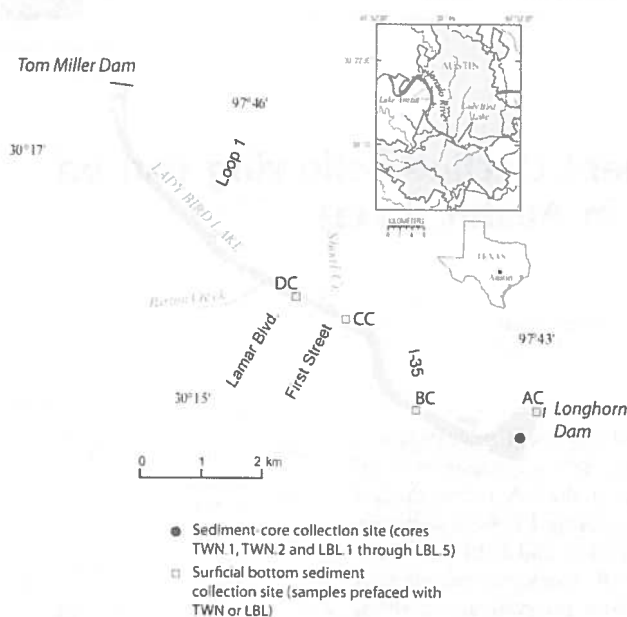


Figure 1. Lady Bird Lake on the Colorado River in Austin, Texas, and locations of sampling sites.

of the population within the lake's drainage area resided in Austin and its ETJ (Christopher Herrington, written commun., City of Austin, 2013).

Analyses of sediment cores have revealed important information about contaminant sources, fate, and transport, and can be a means to evaluate the effects of environmental regulations.¹⁶ Sediment cores have documented downward trends in DDT, PCBs, and lead, for example, following restrictions on use or emission of these chemicals.^{17–19} Sediment cores also have documented upward trends in some unregulated compounds, for example, PBDEs²⁰ and PAHs.²¹ A sediment core collected from Lady Bird Lake in 1998 (TWN.1, preface “TWN” is used in the sample id when Town Lake was the name of the lake at the time of sampling), 8 years prior to the ban on coal-tar-sealant use, indicated that PAH concentrations in the lake had increased about 20-fold from 1959 ($384 \mu\text{g kg}^{-1}$), when the dam that impounds the lake was built, to 1998 ($7640 \mu\text{g kg}^{-1}$).²¹ An analysis of PAH assemblages in the 1998 core estimated that 77% of PAHs deposited in the 1990s were from coal-tar sealants and that the sealants were the dominant cause of upward trends since the 1960s.²² A 9-cm box core (TWN.2; only the 0–3 cm sample is used herein) was collected in 2000 at the same location as TWN.1 and surficial bottom-sediment samples were collected at four locations in the lake in 2001 (TWN.AC, TWN.BC, TWN.CC, and TWN.DC, Figure 1). These historical PAH concentration data provide a preban baseline to which concentrations in recent, postban samples can be compared. Here we report on PAH concentrations in sediment cores and surficial bottom-sediment samples collected from the lake in August 2012 (6.5 years after the ban) and in February 2014 (8 years after the ban).

MATERIALS AND METHODS

Sampling, Analytical, and Quality Control. Two sediment cores (LBL.1 and LBL.2, preface “LBL” is used in the sample id when Lady Bird Lake was the name of the lake at the time of sampling) were collected within ~50 m of one

another on August 7, 2012, with a 14×14 -cm square, 50-cm tall box corer and one core (LBL.3) was collected with a 6.3-cm diameter free-fall gravity corer. The three cores recovered 19, 25, and 39 cm of sediment, respectively. The site sampled was within ~100 m of where cores TWN.1²³ and TWN.2 were collected in 1998 and 2000. Only core LBL.2 penetrated prereservoir soil, at a sediment depth of 37 cm. Following methods described previously,²⁴ cores LBL.1 and LBL.2 were sectioned on a 1-cm interval and core LBL.3 was sectioned on a 2-cm interval for chemical analyses. On February 14, 2014, a gravity core (LBL.4) and a box core (LBL.5) were collected at the coring locations sampled previously, and surficial bottom-sediment samples were collected using a box corer at four locations where samples had been collected and analyzed for PAHs in 2001 (Figure 1; LBL.AC, LBL.BC, LBL.CC, and LBL.DC). Gravity core LBL.4 recovered 65 cm of sediment and was sectioned on a 3-cm interval for chemical analysis. The top 1 cm of sediment from the box cores was used for chemical analysis to represent surficial bottom sediment deposited in 2014. Samples for analysis of PAHs were transferred to precleaned glass jars and chilled pending shipment to the laboratory. Samples for analysis of organic carbon and radionuclides were freeze-dried and ground to a powder prior to analysis.

Total and organic carbon were determined by combustion using a carbon/nitrogen analyzer.²⁵ Twenty sediment intervals from LBL.3 and 13 intervals from LBL.4 were analyzed by the U.S. Geological Survey laboratory in Menlo Park, CA (SI Table S-1) for radionuclides used for age dating the sediment cores. Activities of ^{137}Cs , ^{226}Ra , and ^{210}Pb were measured by counting freeze-dried sediments in fixed geometry with a high-resolution, intrinsic germanium detector gamma spectrometer; the method of analysis was similar to that reported by Fuller et al.²⁶ Fourteen intervals from LBL.4, 17 intervals from LBL.2, 8 intervals from LBL.4, and the 5 surficial bottom-sediment samples were analyzed for PAHs at the U.S. Geological Survey laboratory in Denver, CO. Extraction was by accelerated solvent extraction and analysis was by gas chromatograph/mass spectrometer (GC/MS).²⁷ The MS operated in both the electron impact, full-scan mode and in the selected ion monitoring mode. Concentrations of 18 parent PAHs, 10 specific alkyl-PAHs, and 10 other semivolatile organic compounds were determined (SI Table S-2). Full PAH data for the 1998, 2000, and 2001 sediment samples from Lady Bird Lake are presented in SI Table S-3.

Quality assurance for PAHs was provided by analyzing 7 of 44 environmental samples in duplicate (samples split in the field), laboratory blanks, and spiked reagent samples, and by monitoring recovery of surrogate compounds. Detections of PAHs in laboratory blank samples were for naphthalene at low concentrations (5 of 6 set blanks; $3.9 \mu\text{g kg}^{-1}$ or less) and for four other PAHs in a single blank sample ($2.0 \mu\text{g kg}^{-1}$ or less). All spike and surrogate recoveries were within established limits, with the exception of surrogate recovery for nitrobenzene-d5 in 14 samples, which was below the established range (data and established recovery limits are provided in SI Table S-2). No corrections were applied to the environmental data. The mean relative percent difference (RPD) for the 140 pairs of duplicates in which PAHs or alkyl-PAHs were detected was 13.7% (median of 11.5%), consistent with repeatability of PAH analyses in our previous studies.²⁴ Nondetections of PAHs were estimated for inclusion in ΣPAH_{16} concentration

(SI Table S-4) using ratios of strongly correlated PAHs, as described in SI.

Statistical Analyses of PAH Sources. Similarity between PAH profiles of proportional concentrations for urban PAH sources (SI Table S-5) and the lake sediment was evaluated statistically by computing the Chi-square (X^2) test statistic²⁸ between the proportional PAH profiles of each (SI Table S-6); the lower the X^2 , the more closely the profiles match. As computed here and in Van Metre and Mahler (2010),²² X^2 is the summation of the squared difference divided by the mean for each of 12 proportional PAH concentrations in the two profiles.

The mass and fractional contributions of PAHs from PAH sources to Lady Bird Lake sediments were evaluated using the Contaminant Mass Balance (CMB) model, a source-receptor model.^{29–31} In a previous analysis, we used the CMB model to evaluate PAH sources to 40 U.S. lakes, including Lady Bird Lake.²² Using the same modeling approach and PAH source profiles as previously,²² we applied the model to proportional PAH profiles for samples from the LBL.1 and LBL.4 cores and to recent (2014) and historical (2000, 2001) surficial bottom-sediment samples to evaluate potential PAH source contributions.

Sediment Age Dating. Core LBL.3 was age dated using the peak activity of ^{137}Cs (dated as 1964.0), the prelacustrine sediment interface (dated as 1959.0), and the top of the core (assigned the core-collection date of 2012.6). Constant mass accumulation rate (MAR) of sediment was assumed between these markers. Core LBL.4 was age dated using the peak activity of ^{137}Cs and the top of the core (2014.2); the dates assigned were consistent with dates based on the constant sedimentation rate, constant rate of supply ^{210}Pb model.³²

Deposition dates were assigned to the sediment intervals in box cores LBL.1 and LBL.2 by estimating the sedimentation rate on the basis of the dates assigned to core LBL.3 and assumed core shortening in the gravity core (LBL.3), as described in SI (Age Dating of 2012 Cores). The resulting estimates indicated that the deepest sample analyzed for PAHs in LBL.1 (17–18 cm) was deposited in about 2001 and in LBL.2 was deposited in about 1996 (23–24 cm). However, as described in SI (Effects of the 2007 Flood), sediment deposition in these cores appears to have been affected by a large flood on the Colorado River in Austin in July 2007 (SI Figure S-2), larger than any in the previous 20 years, as recorded at USGS stream gage 08158000 Colorado River at Austin, TX³³ (2.2 km downstream from Longhorn Dam (Figure 1)). In core LBL.1, flood-related sediment appears to occupy about a 4-cm interval, from 7 to 11 cm depth, in the core. In LBL.2, sediment from about 6 cm depth to the bottom of the core (25 cm depth) appears to have been disturbed by flooding. Core LBL.2 is considered less reliable than other cores, and use of data from this core therefore was limited to the top two intervals, which were deposited in 2012.

RESULTS

PAH Trends. Concentrations of PAHs in Lady Bird Lake increased by a factor of about 20 from 1959 until about 2000, flattened during the 2001–2010 decade, and decreased substantially since about 2010 (Figure 2 and SI Figure S-3). Sediment deposited during 1998–2005 in the lower part of the lake near the dam ($n = 9$; Figure 3) had a mean ΣPAH_{16} concentration of 7980 (standard deviation (\pm) 1630 $\mu\text{g kg}^{-1}$; SI Table S-4). Sediment from the same locations deposited

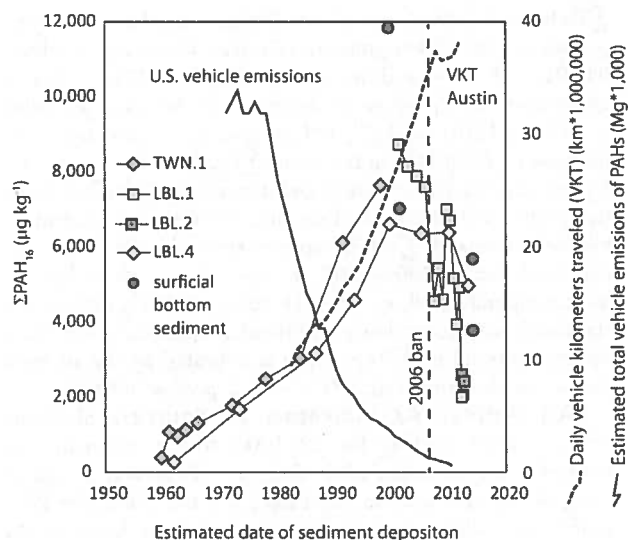


Figure 2. Trends in the sum of the concentrations of the 16 U.S. Environmental Protection Agency Priority Pollutant PAHs (ΣPAH_{16}) in four cores (TWN.1, LBL.1, LBL.2 (top 2 samples only), and LBL.4) and four bottom-sediment samples from the lower part of Lady Bird Lake, Austin, TX (TWN.2, TWN.AC, LBL.5, and LBL.AC). Also shown are estimated U.S. vehicle emissions,⁴⁷ and vehicle kilometers traveled for the city of Austin.⁴⁵

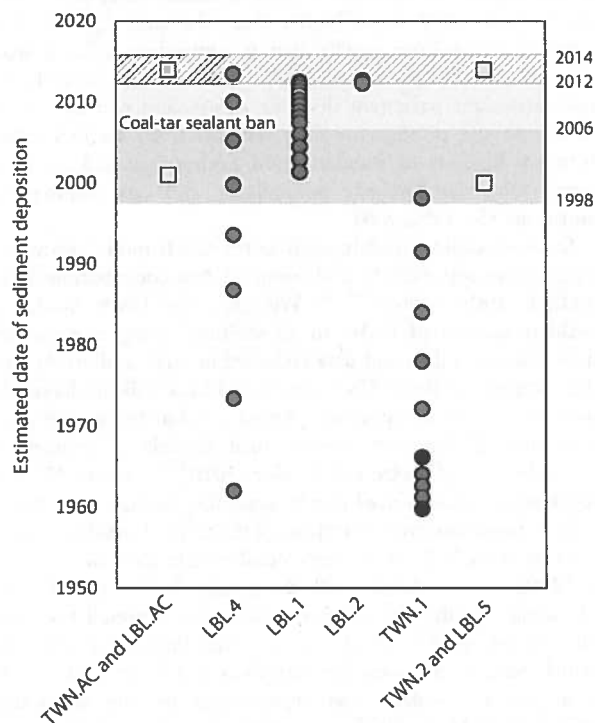


Figure 3. Estimated date of deposition for sediment samples collected from the lower part of Lady Bird Lake near Longhorn Dam. Data are for four cores (red circles; LBL.1, LBL.2 (top 2 samples only), LBL.4, and TWN.1) and for surficial bottom-sediment samples (yellow squares; TWN.2, TWN.AC, LBL.5, and LBL.AC). Gray shaded areas indicate date ranges of samples used in statistical comparisons of concentrations.

after January 2006 ($n = 16$; Figure 3) had a mean ΣPAH_{16} concentration of 4500 (± 1630) $\mu\text{g kg}^{-1}$. The decrease in mean

ΣPAH_{16} concentration of about 44% between these two 8-year periods is statistically significant (Kruskal-Wallis test, p -value = 0.0001). If only sediment deposited in 2012–2014 is considered ($n = 7$; Figure 3), the mean ΣPAH_{16} concentration is $3320 (\pm 1510) \mu\text{g kg}^{-1}$, reflecting a statistically significant decrease of about 58% in the mean ΣPAH_{16} concentration 6–8 years after the ban on use of coal-tar sealants (Kruskal-Wallis test, p -value = 0.0004). The Pearson's correlation coefficient (r) between time and ΣPAH_{16} concentration for the 7 samples deposited during 2009–2012 in core LBL.1, which has the most temporal detail, is -0.93 (p -value = 0.002), indicating a statistically significant downward trend. A statistically significant downward trend in ΣPAH_{16} also is indicated by the six most recent samples from LBL.2 ($r = -0.92$, p -value = 0.009).

PAH Profiles As Indicators of sources. Similarity between PAH profiles for 22 PAH source materials and sediment samples collected in 2012 and 2014 was compared using the X^2 test statistic (SI Tables S-5 and S-6). The PAH profile for coal-tar-sealant pavement dust from Austin is the closest match to Lady Bird Lake sediments on average (mean $X^2 = 0.070 \pm 0.05$). The next closest match is the slightly less-weathered coal-tar-dust profile that is the mean of dust samples from six U.S. cities (mean $X^2 = 0.092 \pm 0.03$). The closest match for a noncoal-tar-sealant-related source is gasoline-vehicle particulate emissions (mean $X^2 = 0.224 \pm 0.05$). Sample LBL.CC, which had an anomalously high ΣPAH_{16} concentration relative to the other bottom sediment samples (SI 600 $\mu\text{g kg}^{-1}$, about 9 times higher than the next highest 2014 sample), has a PAH profile that is somewhat different from those of all the other samples. The profile is less similar to the coal-tar-sealant pavement dust for Austin and relatively more similar to the profiles for dust samples from six U.S. cities, National Institute of Standards and Technology coal tar, pine-wood soot, diesel-vehicle particulates, and coal combustion emissions (SI Table S-6).

Source-receptor models, such as the CMB model, provide a quantitative approach to evaluating relative contributions from multiple PAH sources.^{29–31} We used the CMB model to evaluate sources of PAHs to all sediment samples presented here (historical data and data collected in 2012 and 2014) with the exception of the TWN1 core, for which CMB-model results have already been reported.²² Seven combinations of sources and input PAHs were tested: final models A through D presented in Van Metre and Mahler (2010);²² a model (E) that represents vehicle-related inputs using the gasoline- and diesel-vehicle emissions profiles instead of the traffic-tunnel-air profile used for models A–D, a source combination also used by Li et al. (2003);³⁰ a model (F) with the sources used in model E but excluding a profile for coal-tar sealant; and a model (G) with the sources used in model E but excluding the profiles for vehicle-related emissions. For models A and B, the contribution from coal-tar sealant was represented by the previously published PAH profile for pavement dust from 6 U.S. cities and for models C, D, E, and G, that contribution was represented by the previously published profile for pavement dust from Austin²² (SI Table S-5). Models F and G were included to test whether equally good model solutions could be achieved without considering coal-tar sealant or vehicles as sources. Summary statistics for model fitting parameters and results for total PAH (the sum of the 12 PAHs in the profile) are presented in SI Table S-7. Performance for models A–E and G was good, with overall mean r^2 between measured and calculated PAH concentrations of 0.92 to 0.96 and X^2 of 0.35 to

0.68. Model F, the model without a coal-tar-sealant source term, had weaker measures of model performance ($r^2 = 0$, $X^2 = 1.13$). The variations in model performance for models A–G indicate that a better model fit can be achieved if a coal-tar-sealant source term is included and that excluding a vehicle source term has little effect on model performance.

All of the models that included coal-tar-sealant and vehicle source terms (A–E) indicated that coal-tar sealant is the dominant source of PAHs to the lake, with the mean contribution across all samples of 78%. Models A–D apportioned slightly more of the PAH loading to coal-tar sealant (74–84%) than did model E (73%), and the overall results are consistent with the proportion of PAHs attributed to coal-tar sealant using the same models (A–D) applied to the 1998 TWN core (77%).²² On the basis of the mean results of models A–E, PAH mass loading from coal-tar sealant decreased from a mean of $6550 \mu\text{g kg}^{-1}$ 1998–2005 (samples from sites AC and TWN.2 and sediment intervals deposited between 1998 and 2006 from the TWN.1 and LBL cores, $n = 9$) to a mean of $3040 \mu\text{g kg}^{-1}$ in 2012–14 ($n = 7$), but proportional loading remained about the same (83 and 85% for the two time intervals, respectively) (SI Table S-7). The PAH mass loading from vehicles decreased from $540 \mu\text{g kg}^{-1}$ in 1998–2005 to $150 \mu\text{g kg}^{-1}$ in 2012–2014, and the proportional contribution decreased from 7 to 4%. Small contributions from coal, oil, and wood combustion were comparable to or less than the contribution from vehicles. Results for site CC were anomalous, with a large contribution from coal-tar sealant in the 2001 sample (88%) but a small contribution in the 2014 sample (23%) and larger contributions from coal (39%) and wood (37%) combustion (percentages are means of models A–E).

DISCUSSION

PAH Trends since the Coal-Tar-Sealant Ban. PAH concentrations in bed sediment in the lower part of Lady Bird Lake have declined substantially since the ban on coal-tar sealant was imposed in 2006. Prior to the 2006 ban on use, an estimated 2.5 million L of coal-tar-based sealant was used annually in Austin,³ and violations following the ban reportedly are rare (Mateo Scoggins, City of Austin, written commun., 2012). The downward trend in PAH concentrations in the lake following the ban can be compared with trends in concentrations of DDT and PCBs in lakes in response to actions taken to reduce the release of these contaminants into the environment. Multidecadal downward trends in DDT and PCBs indicate that typical half-times (the time taken for concentrations to decrease by one-half) are 10–15 years following cessation of use.^{34,35} The initial PAH decrease in the lake cores is more rapid, with concentrations decreasing by about one-half in 6–8 years, but within the range of rates reported for DDT and PCBs.

The change in PAH concentrations at the three midlake locations where surficial bottom sediment was sampled in 2001 and 2014 (BC, CC, and DC; Figure 1) are variable, with concentrations at BC and DC decreasing about 71 and 35%, respectively, and concentrations at site CC increasing about 14%. The more fluvial nature of the sites compared with the lower-lake sites near the dam might lead to more variability in bulk sediment characteristics such as grain size and organic carbon content, affecting PAH concentrations. Organic carbon data are not available for the historical PAH data (1998–2001 samples), so the potential effect of variations in carbon content cannot be evaluated for samples TWN.BC, TWN.CC, and

TWN.DC. Trends in organic-carbon-normalized ΣPAH_{16} concentrations in cores LBL.1 and LBL.4, however, are similar to trends in ΣPAH_{16} concentrations but with a slightly greater relative decrease since pre-2006 (SI Figure S-3).

The decreases in ΣPAH_{16} concentrations at sites BC and DC are consistent with the response in PAH concentrations to the cessation of use of coal-tar-based sealants indicated by the cores and surficial bottom-sediment samples from the lower lake. Site CC, however, is an outlier in terms of PAH concentrations, trends, and assemblage. Although it is unclear whether other sources are contributing to the higher PAH concentrations and upward trend at site CC, the different PAH assemblages, modeled source contributions, and downward trends measured in sediments from the lower lake and at the two other bottom-sediment-sampling sites, relative to the results at site CC, indicates that the source of PAHs to site CC is localized.

An earlier study that tested for trends in PAH concentrations following the coal-tar-sealant ban in Austin proved inconclusive.³⁶ That study reported no statistical difference between PAH concentrations in 17 streambed sediment samples collected in October 2005 (preban) and 20 samples collected in April 2008 (postban); of those sites, 13 were sampled both pre- and postban. The authors concluded that the lack of a significant change in concentrations was “consistent with pavement sealer products representing a relatively small fraction of overall [PAH] inputs”. That study had several limitations that might have contributed to an inability to detect a trend in response to the ban, one of which being the relatively short amount of time (27 months) that had passed since the ban was imposed. As demonstrated in this study, about 6 years passed before a definitive trend in PAHs in Lady Bird Lake sediment was indicated (Figure 2). Additional factors that might have limited the ability of the earlier study to detect a trend include large spatial and temporal variability in the physical and chemical characteristics of streambed sediment, high analytical uncertainty in the PAH analyses (RPD of 42 and 87% in duplicate samples), and inclusion of sites in areas where coal-tar sealant was not used (e.g., drainage swales along an interstate highway and parking lots in new, postban developments).

PAH Sources. CMB modeling results and comparisons of PAH profiles indicate that, although PAH concentrations are declining, coal-tar sealants continue to be the largest PAH source proportionally to Lady Bird Lake sediment. This indicates that PAHs from coal-tar sealants continue to be transported to the lake as existing stocks of coal-tar sealant gradually are depleted.^{12,37} These stocks are on pavement but also likely have accumulated in other environmental compartments such as soils, stormwater ponds, and streambed sediments. Because coal-tar sealant is such a potent source of PAHs, a small mass contribution can account for a large proportion of the total PAH concentration. We reported a similar situation for some western U.S. lakes—in these settings PAH loading is small, but a small mass contribution of PAHs from coal-tar sealants (relative to eastern U.S. lakes) accounted for a substantial part of that loading.²² Yang et al. (2010)³⁸ found that a mass fraction of coal-tar pitch of only 3.2% of carbonaceous material accounted for 84% of the PAHs in lake sediment.

Could environmental factors other than the coal-tar-sealant ban have caused the large decline in PAH concentrations in Lady Bird Lake sediment in recent years? The decline is not

related to wastewater treatment: Austin’s two regional wastewater-treatment plants discharge downstream from the lake. Industrial point sources also are unlikely to be the cause: Austin has a relatively modest industrial sector dominated by high tech and construction (e.g., cement) and the larger industrial facilities are located east and south of the city, not in the watershed of Lady Bird Lake. Many studies have found that elevated levels of PAHs are associated with urbanization,^{39–42} however, population growth in Austin continues at a rapid pace, increasing 20% during the 2000–2010 decade.⁴³ Some of these studies and others^{30,44} have concluded that vehicle emissions are a major source of PAHs to urban water bodies. Before coal-tar sealants were recognized as an urban source of PAHs, we also hypothesized that the upward PAH trends in the TWN.1 core might be related to vehicle traffic.²¹ Although trends in vehicle kilometers traveled (original reference in vehicle miles traveled)⁴⁵ in Austin and PAH trends in the lake sediment from the 1960s to 2000 matched closely, since about 2000 vehicle kilometers traveled have continued to increase while PAH concentrations have dropped precipitously (Figure 2). Nationally, although vehicle kilometers traveled continue to increase in the United States, estimated vehicle emissions of PAHs have declined greatly since the introduction of catalytic converters in the 1970s,⁴⁶ from 32 000 Mg in 1971 to 3500 Mg in 2000 to 510 Mg in 2012⁴⁷ (Figure 2). Those large declines in vehicle emissions of PAHs are in contrast with upward trends in PAHs in U.S. urban lakes from the 1960s to the 2000s³⁵ and cannot explain the reversal from an upward to a downward trend in PAHs in Lady Bird Lake in recent years.

Elimination of coal-tar-sealant use coincides with a statistically significant decrease in PAH concentrations in Lady Bird Lake sediments, supporting the conclusion that coal-tar sealants were the largest source of PAHs and the primary cause of the upward trends in PAHs in Lady Bird Lake from the 1960s to about 2000.²² Modeling results indicate that, although PAH concentrations are declining, existing stocks of coal-tar sealants continue to contribute the largest proportion of PAHs to the lake sediments, implying that PAH concentrations should continue to decrease as those stocks are depleted. In an initial study of PAHs in runoff from coal-tar-sealed pavement in Austin, it was estimated that loading of PAHs from sealed parking lots would be reduced by 89–95% if the lots were not sealed.¹ Similarly, Pavlowsky⁴⁸ concluded that elimination of use of coal-tar sealants in Springfield, MO, would lead to a 80–90% reduction in PAH concentrations in streams and ponds, but noted that it might take years to decades for that reduction to be realized. The decline in PAH concentrations in sediment from Lady Bird Lake in Austin provides the first direct evidence that these estimates are not overstated.

■ ASSOCIATED CONTENT

● Supporting Information

Figure S-1, City of Austin, TX, and its Extra Territorial Jurisdiction (ETJ). Figure S-2, Trends in ΣPAH_{16} concentrations in sediment cores LBL.1 and LBL.2 collected in 2012 from Lady Bird Lake and monthly streamflow in the Colorado River at Austin. Figure S-3, Concentrations of ΣPAH_{16} normalized to organic carbon in sediment samples collected from the lower lake sites in 2012 and 2014. Additional details on estimation of PAH nondetections, age dating of cores collected in 2012, and effects of the 2007 flood on 2012 cores. Tables, provided separately in Microsoft Excel format: Table S-1, Radionuclide activities for samples from Lady Bird Lake

cores. Table S-2, Concentrations of PAHs, selected other organic compounds, and organic carbon in Lady Bird Lake cores and surficial bottom sediment sampled in 2012 and 2014. Table S-3, Concentrations of PAHs and selected other organic compounds in lake samples collected in 1998 to 2001. Table S-4, Concentrations of the 16 EPA Priority Pollutant PAHs with nondetected values replaced by estimated values. Table S-5, Proportional concentrations of 12 PAHs in 22 potential PAH sources. Table S-6, Chi square (χ^2) test statistic between PAH profiles for 22 urban PAH sources and PAH profiles in sediment samples from Lady Bird Lake. Table S-7, Summary of results of Contaminant Mass Balance modeling of PAH sources to the Lady Bird Lake sediments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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