# Parking Lot Sealcoat: An Unrecognized Source of Urban Polycyclic Aromatic Hydrocarbons

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Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous contaminant in urban environments. Although numerous sources of PAHs to urban runoff have been identified, their relative importance remains uncertain. We show that a previously unidentified source of urban PAHs, parking lot sealcoat, may dominate loading of PAHs to urban water bodies in the United States. Particles in runoff from parking lots with coal-tar emulsion sealcoat had mean concentrations of PAHs of 3500 mg/kg, 65 times higher than the mean concentration from unsealed asphalt and cement lots. Diagnostic ratios of individual PAHs indicating sources are similar for particles from coal-tar emulsion sealed lots and suspended sediment from four urban streams. Contaminant yields projected to the watershed scale for the four associated watersheds indicate that runoff from sealed parking lots could account for the majority of stream PAH loads.

## Introduction

Concentrations of polycyclic aromatic hydrocarbons (PAHs)— a group of widely recognized aquatic contaminants (*1*) comprising numerous carcinogens (*2*)—have been increasing in recent decades in many urban lakes, particularly in areas undergoing rapid urban growth (*3*). PAHs adversely affect mammals (including humans), birds, fish, amphibians, invertebrates, and plants; in the aquatic environment, the effects of PAHs on invertebrates include inhibited reproduction, delayed emergence, sediment avoidance, and mortality, and the effects on fish include fin erosion, liver abnormalities, cataracts, and immune system impairments (*4*). Numerous sources of PAHs to urban runoff have been identified, including automobile exhaust, lubricating oils, gasoline, tire particles, erosion of street material, and atmospheric deposition (*5−8*), but uncertainty remains as to their relative importance. Investigations of urban sources of PAHs have thus far overlooked a potentially major source: parking lot sealants, also called "sealcoat". Our objective in this study was to evaluate the contribution of PAHs from sealed parking lots to urban streams.

In the United States and Canada, sealcoat is applied to many parking lots and driveways in an effort to protect the underlying asphalt pavement and enhance appearance. The two primary sealcoat materials on the market are refined coal-tar-pitch-based emulsion and asphalt-based emulsion. Although similar in appearance (glossy black), coal tar and asphalt have different molecular structures stemming from their origins: coal tar is a byproduct of the production of coke from coal, whereas asphalt is derived from the refining of crude petroleum. Coal tar, a known human carcinogen, is 50% or more PAHs by weight (*2*); the predominant constituents of asphalt are bitumens, complex mixtures of hydrocarbons that include asphaltenes, saturates, aromatics, and resins (*9*). Coal-tar-emulsion- and asphalt-emulsion-based sealcoats typically contain 20−35% of the emulsion.

Parking lot sealants are used extensively in the United States and Canada. Although national use figures are not available, the *Blue Book of Building and Construction* (*10*), a directory for the construction industry, lists over 3300 pavement sealant companies in 28 U.S. states. One company advertises the application of 1.7 billion liters to date worldwide (*11*), and another reports having sealed over 33 million square meters (*12*). The City of Austin, population 650000 (2000 census), estimates that about 2.5 million liters of sealcoat is used annually in this city (*13*).

Sealcoat abrades from the parking lot surface relatively rapidly, and reapplication is recommended every two to three years (*14*). In 2003, the City of Austin identified abraded parking lot sealcoat as a possible source of high concentrations of PAHs in streambed sediment (*15*). Here we present evidence suggesting that parking lot sealcoat could indeed be the dominant source of PAHs to watersheds with residential and commercial development.

## Experimental Section

**Sample Collection.** We compared concentrations and yields of particulate PAHs in simulated runoff from parking lots sealed with coal-tar-based sealcoat, from lots sealed with asphalt-based sealcoat, and from unsealed asphalt and cement lots. Thirteen urban parking lots, representing a range of sealant types that are currently in use in Austin, TX, were sampled (Table 1). In addition, four test plots, each about 120 m² were sampled. Three of the test plots were sealed just prior to testing, and one was left unsealed (asphalt surface). The test plots are at the Robert Mueller Municipal Airport, Austin, TX, which has been closed since 1999. A full description of the sampling is given in ref *16*. In brief, 50 m² areas of each parking lot and the test plots were sprinkled with 2 mm of distilled water (100 L over a 50 m² area) to simulate a light rain, and concentrations of PAHs were analyzed in particles filtered from the runoff. The study focused on the particulate fraction, as PAHs in urban runoff, particularly those of higher molecular weight, are mostly associated with particulates (*7, 17*); for selected samples (test plots and seven parking lots), the dissolved phase also was analyzed. The testing followed a minimum of 5 days with no rainfall. The parking lots were sampled once, and the test plots were sampled three times over a 6 week period. Water was sprayed from a plastic hand-held sprayer at a rate of about 7 L/min from a height of about 0.75 to 1 m. Spill berms were used at the down-slope end of the delineated area to gather water, which was then pumped into high-density polyethylene (HDPE) containers (Figure S1, Supporting Information). Recovery of water and observations about losses of water to wetting and leakage under the berms were noted. The water was returned to the laboratory, poured into a 50 L churn to keep the sample well mixed, and filtered through 0.45 μm pore size PTFE filters. The filters were

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**TABLE 1. Sampling Site Characteristics**

| site name | surface type | date of sealant application | sampling date | study component |
|---|---|---|---|---|
| CT$_{TP}$1 | coal-tar emulsion sealant | Aug 5–6, 2003 | 8/21/2003 | test plot |
| CT$_{TP}$2 | coal-tar emulsion sealant | Aug 5–6, 2003 | 8/21/2003 | test plot |
| AS$_{TP}$ | asphalt emulsion sealant | Aug 5–6, 2003 | 8/21/2003 | test plot |
| UNSAS$_{TP}$ | unsealed asphalt pavement | Aug 5–6, 2003 | 8/21/2003 | test plot |
| CT$_{TP}$1 | coal-tar emulsion sealant | | 9/9/2003 | test plot |
| CT$_{TP}$2 | coal-tar emulsion sealant | | 9/9/2003 | test plot |
| AS$_{TP}$ | asphalt emulsion sealant | | 9/9/2003 | test plot |
| UNSAS$_{TP}$ | unsealed asphalt pavement | | 9/9/2003 | test plot |
| CT$_{TP}$1 | coal-tar emulsion sealant | | 9/26/2003 | test plot |
| CT$_{TP}$2 | coal-tar emulsion sealant | | 9/26/2003 | test plot |
| AS$_{TP}$ | asphalt emulsion sealant | | 9/26/2003 | test plot |
| UNSAS$_{TP}$ | unsealed asphalt pavement | | 9/26/2003 | test plot |
| AS$_{PL}$1 | asphalt emulsion sealant | June 2003 | 9/7/2003 | parking lot |
| AS$_{PL}$2 | asphalt emulsion sealant | June 2003 | 9/7/2003 | parking lot |
| AS$_{PL}$3 | asphalt emulsion sealant | July 2003 | 9/28/2003 | parking lot |
| CT$_{PL}$1 | coal-tar emulsion sealant | March 2003 | 9/7/2003 | parking lot |
| CT$_{PL}$2 | coal-tar emulsion sealant | July 2003 | 9/28/2003 | parking lot |
| CT$_{PL}$3 | coal-tar emulsion sealant | July 2003 | 9/28/2003 | parking lot |
| CT$_{PL}$4 | coal-tar emulsion sealant | July 2003 | 9/30/2003 | parking lot |
| CT$_{PL}$5 | coal-tar emulsion sealant | July 1999 | 9/30/2003 | parking lot |
| CT$_{PL}$6 | coal-tar emulsion sealant | Nov 2000 | 9/30/2003 | parking lot |
| UNSAS$_{PL}$1 | unsealed asphalt pavement | | 9/8/2003 | parking lot |
| UNSAS$_{PL}$2 | unsealed asphalt pavement | | 9/30/2003 | parking lot |
| UNSCON$_{PL}$1 | unsealed concrete pavement | | 9/8/2003 | parking lot |
| UNSCON$_{PL}$2 | unsealed concrete pavement | | 9/8/2003 | parking lot |

massaged inside locking bags to remove retained particles, as described in ref *18*, and the recovered particulates were submitted as chilled slurries in clean glass vials to the U.S. Geological Survey National Water Quality Laboratory (NWQL) for analysis. In some cases the filtrate also was shipped, in chilled and clean amber glass bottles, to the NWQL for analysis of dissolved PAH. One or more samples of unfiltered water were collected from the churn for measurement of suspended sediment concentration (SSC), used to determine the mass of sediment recovered during each test. Although the 2 mm of simulated rain was not enough to wash off all of the mobile sediment, the recovered water was visibly clearer toward the end of each application. In samples from the five sites in which SSC was measured in the first 50 L and final 50 L of water, SSC decreased by a mean of 65% (range of 39–84%). We therefore assumed that the tests recovered most of the sediment that would be mobilized from the parking lot surfaces by a rain event, regardless of magnitude. Large, intense storms, however, likely would generate a higher yield of sediment.

The test plot and parking lot scrapings were obtained by scraping a small area (less than 0.25 m²) with a metal paint scraper. The particulates removed were brushed onto a piece of new cardstock and then into a cleaned glass jar. The paint scraper was cleaned between sites, and a new brush was used at each site. Scrapings were examined by light and electron microscopy (Figure S2, Supporting Information), and submitted to the NWQL for PAH analysis.

**Computation of Yields.** Losses of water to wetting and losses of water and sediment leaking under the berms were estimated. Recovery of water ranged from 19 to 85 L with a median of 58 L. The lowest recoveries were from flat, unsealed asphalt lots, and the highest recoveries were from sealed lots and cement lots with gentle slopes. On the basis of recoveries and field observations, it was concluded that about 18 L of water was retained on the surface of sealed lots and cement lots and that the remainder of the water loss was a result of leakage past the berms. It was assumed that no yield of

particles was associated with the water volume lost to surface wetting and that water leaking past the berms had the same SSC and contaminant levels as recovered water. For unsealed asphalt lots, the loss to wetting was estimated as 36 L for a maximum potential recovery of 64 L. Thus, to estimate the total yield of sediment from each lot, SSC was multiplied by the assumed maximum recovery (82 L for sealed and cement lots and 64 L for unsealed asphalt lots) to account for recovered water and leakage past the berms. Yields of PAH were estimated by multiplying the total yield of sediment times particle concentrations.

**Chemical Analysis.** Samples were prepared by extracting about 0.5 g dry weight of sample using pressurized solvent extraction at 120 and 200 °C with a mixture of water and isopropyl alcohol. The samples were extracted at each temperature at a pressure of 13800 kPa. Surrogate compounds were added to the sample prior to extraction to verify method recoveries. The extract was cleaned up using polystyrene divinylbenzene and Florisil solid-phase extraction cartridges. The extract was concentrated, solvent exchanged to ethyl acetate, and diluted to 10 mL. An internal standard mixture was added to an aliquot of the extract, and the extract was analyzed by full-scan gas chromatography/mass spectrometry (GC/MS). Difficult sample matrices were diluted before the full-scan analysis, and diluted surrogates were estimated in the samples.

Compound identifications were based on comparison of peak retention times and mass spectra to those of authentic standard compounds for the target compounds. Response factors were calculated for each compound from a set of calibration standards. Quantitation was carried out following the methods of Olson et al. (*19*). For PAHs in the particulate phase, the estimated method reporting limit (MRL) is 5 $\mu$g/kg for a 25 g sample. As less than 25 g was extracted, the MRL was raised accordingly, on a sample-by-sample basis. In some cases, MRLs were raised because of background interferences.

Dissolved-phase samples were analyzed following the method described by Fishman and Friedman (*20*), with the

difference that continuous liquid−liquid extraction was substituted for use of the separatory funnel. In brief, 1 L samples fortified with surrogate compounds were extracted by continuous liquid−liquid extraction for 6 h under acidic and then basic conditions. Internal standards were added and sample extracts concentrated to 1 mL. Samples were analyzed by GC/MS in electron impact mode. Sample identifications were made by matching retention times and mass spectra with those of standard compounds. Quantitation involved use of internal standards and calibration curves generated by standard compounds of known amounts.

Quality control (QC) consisted of environmental and internal laboratory samples. Two duplicate environmental samples for particulate analysis of PAH were collected. For one of the sets of duplicates, ΣPAH differed by 8%; for the second (which had ΣPAH > 4000 mg/kg), ΣPAH differed by 54%. In the equipment blank analyzed for dissolved PAH, three parent PAHs were detected at concentrations about half that of the environmental sample with the lowest concentrations, and less than 1% that of the environmental sample with the highest concentrations.

Laboratory QC samples for particulate PAH analyses consisted of analysis of spiked samples, blanks, and samples of certified reference material (CRM). The median recovery for the six spiked samples was 76%. For the six laboratory blanks, an analyte was detected in 85 of 336 possible cases. The detected concentrations ranged from 0.1% to 3.5% of that in the environmental sample with the lowest concentration for that analyte. For the two analyses of CRM, the recoveries were within the NWQL-established acceptable range for 83% of the cases.

Three commercially available asphalt-based emulsion sealcoat products and six coal-tar-based emulsion sealcoat products were analyzed at DHL Analytical, Round Rock, TX, using EPA method SW 8270 (21). In each case, the product sample was taken directly from the container. Concentrations of 16 parent PAHs were determined. The sealants analyzed were not necessarily the same as those applied to the test plots or on the parking lots in use, although there was some overlap (product $AS_PA$ was used on test plot $AS_{TP}$; product $CT_PF$ was used on test plot $CT_{TP}2$) (Table 2).

## Results

Concentrations and yields of total particulate PAH and total dissolved PAH in the runoff and total PAH in the scrapings were computed and compared between parking lot surface types (Table 2). The total particulate PAH (ΣPAH) concentration was computed for each sample as the sum of naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[a]pyrene, and dibenz[ah]anthracene, which are the same as those used for the consensus-based sediment quality guidelines of MacDonald et al. (22). For unsealed parking lots (asphalt pavement and concrete combined), the mean ΣPAH was 54 mg/kg (range of 7.2−75 mg/kg), more than twice the probable effect concentration sediment quality guideline of 22.8 mg/kg (22) (Table 2), and in the range of those found by others in urban and roadway runoff (e.g. refs 23−25). However, the mean ΣPAH concentration from the asphalt-sealed parking lots was more than 10 times higher (mean of 620 mg/kg, range of 250−830 mg/kg) than that from unsealed parking lots, and the mean ΣPAH concentration from the coal-tar-sealed parking lots was 65 times higher (mean of 3500 mg/kg, range of 520−9000 mg/kg) (Table 2; complete concentration data are given in ref 16). ΣPAH concentrations in runoff from coal-tar-sealed lots were significantly higher than in runoff from other surface types (Kruskal−Wallis test of comparisons, hypothesis of no difference between groups rejected for $p$ < 0.05). PAH concentrations from coal-tar-
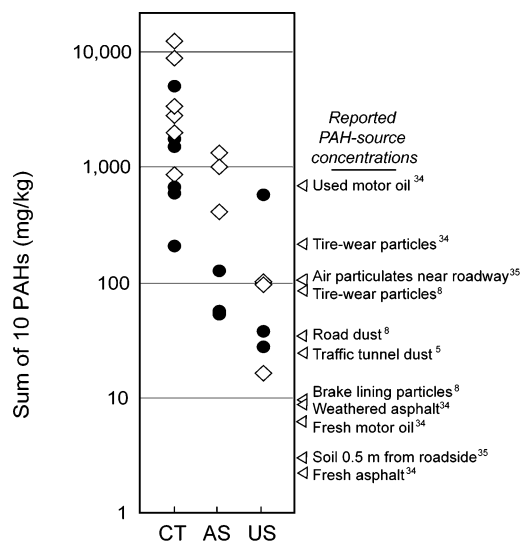


FIGURE 1. Sum of 10 PAHs (fluoranthene, pyrene, benz[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, indeno[1,2,3-cd]pyrene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, and benzo[ghi]perylene) in particles in runoff from simulated rainfall on coal-tar emulsion sealcoat (CT), asphalt emulsion sealcoat (AS), and unsealed cement and asphalt (US) parking lots (◇) and test plots (●). Parking lots were sampled once, and test plots were sampled three times. Concentrations for other PAH sources reported in the literature also are indicated. These 10 PAHs were summed for this graph to facilitate comparison between experimental and reported concentrations.

sealed lots also were much higher, in most cases by orders of magnitude, than PAH concentrations in other urban sources such as tire particles, motor oil, and weathered asphalt (Figure 1; note that this figure uses a different summation of PAH). ΣPAH concentrations in runoff from the sealed test plots were generally lower than those from the sealed parking lots, but the difference was not statistically significant, and concentrations from unsealed surfaces, with the exception of one outlier, were similar for test plots and parking lots.

Concentrations of ΣPAH in the scrapings ranged from 9500 to 83000 mg/kg for coal-tar-emulsion-sealed surfaces (including test plots) and from 110 to 2000 mg/kg for asphalt-emulsion-sealed surfaces (Table 2). Scrapings of two unsealed asphalt parking lots had ΣPAH concentrations of 7.1 and 20 mg/kg. Scrapings were observed under light and electron microscropy (Figure S2, Supporting Information).

Concentrations of total dissolved PAH (ΣPAH_diss, computed as the sum of the same PAHs as in ΣPAH excluding 2-methylnaphthalene; nondetections treated as zeros) for the test plots were about an order of magnitude greater in samples from the coal-tar-sealed test plots than concentrations in samples from the asphalt-sealed test plot, which in turn were about an order of magnitude greater than those from the unsealed test plot (Table 2). Nine of the 16 PAHs analyzed for were detected (complete data are in ref 16). Higher weight PAHs—benzo[b]fluoranthene, benzo[k]-fluoranthene, benzo[a]pyrene, indenopyrene, benzo[ghi]-perylene, benz[a]anthracene, and dibenz[ah]anthracene—were not detected at laboratory reporting levels ranging from 1.7 to 3.4 μg/L. Four PAHs (acenaphthylene, acenaphthene, chrysene, and fluorene) were detected only in runoff from the coal-tar-sealed test plots; anthracene was detected in runoff from all the sealed test plots but not from the unsealed site. A similar suite of PAHs were detected at those parking lots for which the filtrate was analyzed (Table 2; complete data are in ref 16).

Concentrations of ΣPAH in the commercially available sealant products and surface scrapings exceeded those of

**TABLE 2. Concentrations of PAH in Washoff Samples, Scrapings, and Unapplied Sealcoat Product[a]**

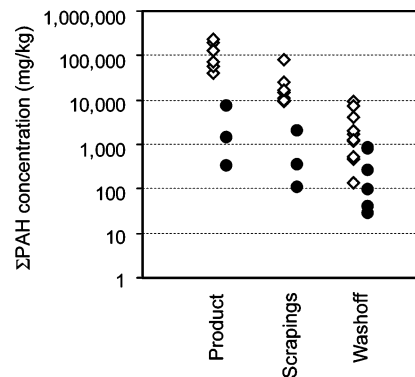| | washoff samples | | scrapings | product | |
|---|---|---|---|---|---|
| | $\Sigma$PAH, mg/kg | $\Sigma$PAH$_{diss}$, µg/L | $\Sigma$PAH, mg/kg | | $\Sigma$PAH(dry), mg/kg |
| **Test Plots** | | | | | |
| CT$_{TP}$1, 8/12/03 | | 21 | 83000 | CT$_P$A | 34000 |
| CT$_{TP}$1, 8/21/03 | 1700 | 14 | | CT$_P$B | 113000 |
| CT$_{TP}$1, 9/9/03 | 530 | | | CT$_P$C | 202000 |
| CT$_{TP}$1, 9/26/03 | 460 | 6.9 | | CT$_P$D | 86000 |
| | | | | CT$_P$E | 49000 |
| CT$_{TP}$2, 8/12/03 | | 11 | 11000 | CT$_P$F | 61000 |
| CT$_{TP}$2, 8/21/03 | 1200 | 7.3 | | | |
| CT$_{TP}$2, 9/9/03 | 4000 | | | AS$_P$A | 6600 |
| CT$_{TP}$2, 9/26/03 | 140 | 3.8 | | AS$_P$B | 1300 |
| | | | | AS$_P$C | 300 |
| AS$_{TP}$, 8/12/03 | | 1.3 | 110 | | |
| AS$_{TP}$, 8/21/03 | 96 | 1.2 | | | |
| AS$_{TP}$, 9/9/03 | 40 | | | | |
| AS$_{TP}$, 9/26/03 | 28 | 0.64 | | | |
| UNSAS$_{TP}$, 8/12/03 | | 0.16 | | | |
| UNSAS$_{TP}$, 8/21/03 | 410 | 0.34 | | | |
| UNSAS$_{TP}$, 9/9/03 | 25 | | | | |
| UNSAS$_{TP}$, 9/26/03 | 14 | 0.17 | | | |
| **Parking Lots** | | | | | |
| CT$_{PL}$1 | 2000 | NA | 25000 | | |
| CT$_{PL}$2 | 9000 | 5.4 | 15000 | | |
| CT$_{PL}$3 | 2000 | 7.1 | 11000 | | |
| CT$_{PL}$4 | 1300 | 12 | 9500 | | |
| CT$_{PL}$5 | 520 | 2.3 | 9900 | | |
| CT$_{PL}$6 | 5900 | 16 | 17000 | | |
| AS$_{PL}$1 | 250 | NA | 340 | | |
| AS$_{PL}$2 | 830 | NA | 2000 | | |
| AS$_{PL}$3 | 770 | 5.1 | 420 | | |
| UNSCON$_{PL}$1 | 75 | NA | NA | | |
| UNSCON$_{PL}$2 | 69 | NA | NA | | |
| UNSAS$_{PL}$1 | 64 | NA | 7.1 | | |
| UNSAS$_{PL}$2 | 7.2 | 0.24 | 20 | | |

[a] Sums are as defined in the text. NA = not analyzed, CT = coal-tar-based emulsion, AS = asphalt-based emulsion, UNSAS = unsealed asphalt pavement, and UNSCON = unsealed concrete pavement.



**FIGURE 2. Comparison of $\Sigma$PAH concentrations in commercially available sealcoat products, scrapings from parking lots, and particles in washoff from parking lots for coal tar ($\diamond$) and asphalt ($\bullet$) based sealants.**

concentrations for the different surface types suggest that abraded sealant products are a potentially important (and heretofore unrecognized) contributor to PAH contamination in urban and suburban water bodies.

**Comparison of Medium, Aging, and Vehicle Use on Concentrations and Yields.** For both coal-tar- and asphalt-emulsion-based sealants, the $\Sigma$PAH concentration decreased from the unapplied sealant products to the scrapings to the washoff samples, as did the difference in concentration between the coal-tar-based and asphalt-based sealant samples (Figure 2). The difference in the median $\Sigma$PAH concentration between the coal-tar-based and asphalt-based sealants was 70-fold for the products analyzed and decreased to 40-fold for the scrapings and to a factor of about 8 for the washoff samples. Although the chemical changes between the product pre- and postapplication were not the focus of this study, the decrease in $\Sigma$PAH concentrations from the scrapings to the washoff particulates and the magnitude of the difference between the coal-tar-sealed lots and the asphalt-sealed lots can be attributed to dilution of abraded particles with less contaminated street dust and the greater abrasion of the asphalt-sealed compared to the coal-tar-sealed surfaces. A simple mass balance, assuming dilution of the coal tar scrapings (median $\Sigma$PAH concentration of 13000 mg/kg) by street dust (median $\Sigma$PAH concentration of 50 mg/kg) at a proportion of 1 part abraded particles to 7 parts street dust, results in the concentration found in the washoff. If the proportion of abraded particles is increased for the asphalt lots on the basis of the increased yields measured for asphalt-sealed lots (assuming that the greater median particle yield of 320 mg/m$^2$ from asphalt-sealed lots versus 200 mg/m$^2$ from coal-tar-sealed lots results from increased abrasion), the concentration found in the washoff from asphalt-sealed lots is well approximated.

The effect of aging of sealants on concentration over the short term (7 weeks) was evident at the test plots (Figure 3a). Overall, the concentration of $\Sigma$PAH and $\Sigma$PAH$_{diss}$ in the washoff from each test plot decreased over the 7 week period following application. In one instance (CT$_{TP}$2, second sampling of washoff) $\Sigma$PAH exceeded that previously sampled, but in all cases the concentration at the end of the period was less than that at the beginning. The PAH assemblage changed over the same period as well, as represented by a comparison of higher molecular weight (MW) to lower MW PAHs. In the particulate samples the ratio of higher MW PAHs (represented by benzo[a]pyrene + chrysene) to the lower MW PAHs (represented by fluorene + phenanthrene; these two PAHs were chosen as they were detected in most of the samples) increased at all of the sealed test sites. As the lower MW PAHs are more volatile and soluble than the higher MW PAHs, volatilization and leaching of the lower MW PAHs

the particulates in the washoff. Concentrations of $\Sigma$PAH in commercially available coal-tar-based sealcoat products ranged from 3.4 to 20 wt %, compared to 0.03 to 0.66 wt % for asphalt-based sealcoat products analyzed (Table 2; complete data in Table S1, Supporting Information).

Yields of $\Sigma$PAH (mass of $\Sigma$PAH per unit area of parking lot) computed for the simulated rainfall followed patterns similar to those of concentrations. Complete data for yields can be found in Table S2 in the Supporting Information. As with the concentrations, there was a wide range in the yields for a given surface type, in most cases more than an order of magnitude. The mean yield from coal-tar-sealed lots exceeded that from asphalt-sealed lots by more than a factor of 2, although this difference was not statistically significant (Kruskal–Wallis test of comparison, $p < 0.05$). However, the mean yield from sealed lots (asphalt and coal tar combined) exceeded that from unsealed lots by a factor of 50, and the difference was statistically significant.

## Discussion

Runoff from parking lots typically is contaminated with PAHs from leaking motor oil, tire particles, vehicle exhaust, and atmospheric fallout, and it is not surprising that the mean concentration of $\Sigma$PAH in particles washed off each of the different surface types exceeded the probable effect sediment quality guideline. However, the large differences between
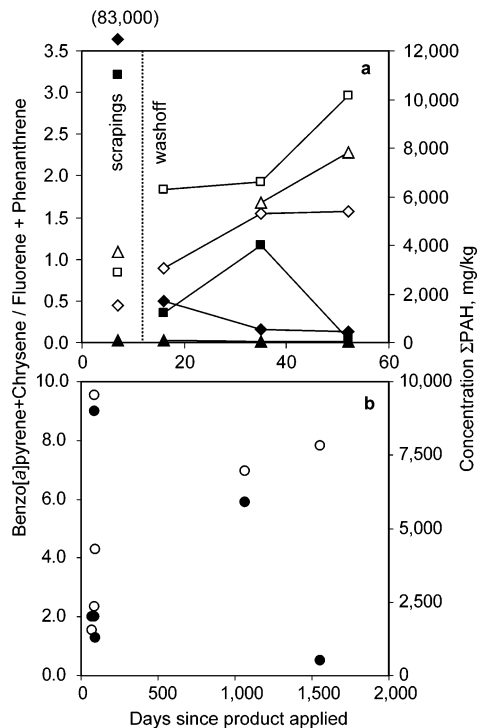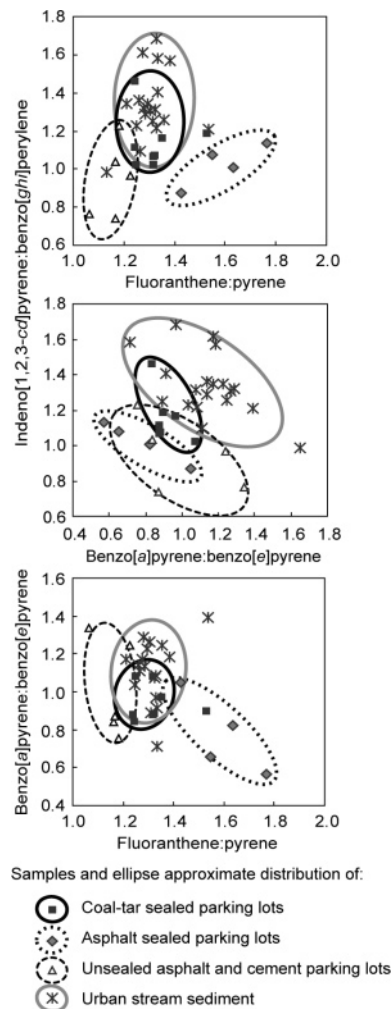
FIGURE 3. ΣPAH concentrations (closed symbols) and PAH ratios of higher and lower molecular weight PAHs (open symbols) (a) in scrapings and particles washed off coal-tar-sealed test plots (□, ◇) and an asphalt-sealed plot (△) and (b) as they relate to the age of coal-tar sealant in samples from parking lots in use.

from the newly applied sealant might be responsible for some of the decrease in concentration. For the parking lots, only coal-tar-sealed lots represented a range of ages, and for these lots there was no relationship between concentration or higher MW to lower MW PAH ratio and age of the sealant (Figure 3b). This might be because the parking lots were each sampled only once; the very wide range in PAH content between products, even those of a similar kind, may mask the effect of aging when time-series data are not available. Although the data are limited, they suggest that lots with older sealant tend to have a higher ratio of higher MW to lower MW PAHs, and that that ratio may reach a plateau after a period of time.

Comparison of the yields from the parking lots to those from the test plots, which receive no vehicle traffic, demonstrates the importance of abrasion of sealcoat by vehicles on ΣPAH yield: the mean ΣPAH yield was 20 and 160 times greater for the coal-tar-sealed and asphalt-sealed parking lots, respectively, than for the analogous test plots. This does not appear to be attributable to use patterns, although traffic counts were not made: the coal-tar-sealed lots are a mix of lots in constant use throughout the day (e.g., shopping center) and those with all-day parking (e.g., office), which are assumed to receive less use than those in constant use; all of the asphalt-sealed lots are all-day parking.

**Environmental Implications.** Given the extremely elevated concentrations of PAHs in particles washed from sealed parking lots, how important is this contribution to the total mass of PAHs in urban streams? To answer this question, we compared the PAH assemblages and estimated PAH loads associated with particulates in parking lot runoff to those associated with suspended sediment collected during storm flow in four streams: Williamson Creek (Austin, TX) (18) and influent streams to Echo Lake, Fosdic Lake, and Lake Como (Fort Worth, TX) (26). These four streams are in highly urbanized watersheds (land use for the Austin watershed is about 65% urban, and for the three Fort Worth



Samples and ellipse approximate distribution of:

- ⬤ Coal-tar sealed parking lots
- ◇ Asphalt sealed parking lots
- △ Unsealed asphalt and cement parking lots
- ✳ Urban stream sediment

FIGURE 4. Comparison of indicator ratios of PAHs in particles washed from parking lots with coal-tar emulsion sealcoat, asphalt emulsion sealcoat, and unsealed asphalt pavement and concrete pavement, and in suspended sediment collected from four urban streams after storms.

watersheds is more than 90% urban; full land use is given in Table S3, Supporting Information); the streams are ephemeral, and urban runoff is assumed to comprise a large component of storm flow.

PAHs comprise a large group of compounds, and PAH assemblage is often used to infer PAH sources (27). Differences in PAH assemblages can be investigated by computing the ratios of selected PAHs (28, 29). The best indicator ratios of coal tar as a PAH source have been identified as fluoranthene:pyrene, indeno[1,2,3-cd]pyrene:benzo[ghi]perylene, and benzo[a]pyrene:benzo[e]pyrene (30, 31). In graphs that combine these ratios, similarities and differences between parking lot and stream samples are apparent (Figure 4): ratios in the urban stream sediment group match those in runoff from coal-tar-sealed lots more closely than they do those from asphalt-sealed lots and from unsealed lots (asphalt and cement). We found these ratios were far more effective at distinguishing between the different parking lot samples and stream samples than ratios indicative of combustion versus noncombustion sources, or other approaches such as comparison of parent compound distribution (32). Although alkylated PAH homologues were analyzed (including C1−C5 homologues of the MW 128, 178, 202, 228, and 252 PAHs), their interpretation did not assist in discriminating between PAHs from the different parking lot surfaces.
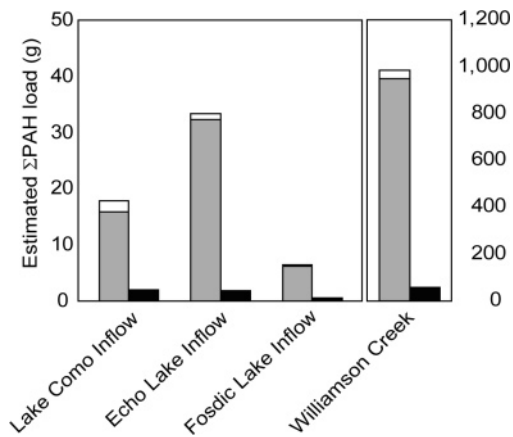
The relative amount of similarity between groups of samples, as defined by the ratios, was quantified through
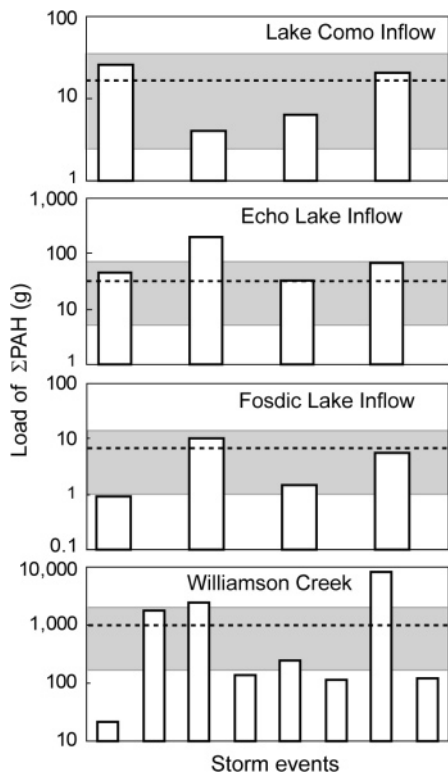
**FIGURE 5. Comparison of estimated event loads of ΣPAH from sealed parking lots and measured instream storm-event loads for four urban watersheds. The interquartile range of estimated loads is shown in gray shading, on the basis of 25th and 75th percentile yields computed for sealed parking lots; the mean estimated load is indicated by a dashed line. Measured instream loads for four to eight individual events are shown as bars.**



**FIGURE 6. Comparison of event loads of ΣPAH for four urban watersheds estimated for parking lots in their current (2004) state (sealed by gray bars and unsealed by white bars) and projected loads if all existing parking lots were unsealed (black bars). Loads were estimated on the basis of the yields from the runoff experiments and the area of parking lots in each watershed.**

discriminant function analysis. In discriminant function analysis, each significant independent variable adds to discrimination between multiple groups. The three ratios (fluoranthene:pyrene, indeno[1,2,3-*cd*]pyrene:benzo[*ghi*]-perylene, and benzo[*a*]pyrene:benzo[*e*]pyrene) were entered into the analysis as the independent variables, with the different types of samples (coal-tar-emulsion-sealed lots, asphalt-emulsion-sealed lots, unsealed lots, and urban stormflow stream sediments) defining four groups of dependent variables. All three variables were shown to contribute significantly to discrimination between the groups ($p$ < 0.001). The distances between the centroids of the groups were determined by computing the squared Mahalanobis distance, which is a measure of the distance between two points in the space defined by two or more correlated variables. The centroid of the group defined by the suspended sediment from urban streams is closest to the centroid of the coal-tar-based sealant group, next closest to that of the unsealed lot group, and farthest from that of the asphalt-based sealant group (squared Mahalanobis distances of 5.7, 13.0, and 25.0, respectively). Thus, on the basis of the three ratios diagnostic of coal-tar sources, the PAH assemblage of the suspended sediment from the urban streams most closely resembles that of the coal-tar-based sealant group, supporting the hypothesis that coal-tar-based sealants are an important source of PAHs in urban streams.

Moving to a mass-balance approach at the watershed scale for each of the four urban watersheds, we compared measured storm-event stream loads of ΣPAH to those estimated to be contributed by sealed parking lots. Digital land-use maps that included parking lots were provided by the Cities of Austin and Fort Worth and were updated using recent aerial photography and site inspections. Sealed and unsealed lots were identified by site inspection. We computed the hypothetical storm-event load generated by sealed parking lots in each watershed by multiplying the mean yield for sealed parking lots (coal-tar and asphalt emulsion sealcoat combined) determined from the runoff experiments by the sealed parking lot area of each watershed. We assumed that the 2 mm of water applied for the field tests mobilized all available particles, and that all runoff from parking lots entered storm sewers and was delivered to the stream. Although there is substantial variation in event loads for each stream (*18*, *26*), for all four watersheds the estimated ΣPAH loads contributed by sealed parking lots are similar in magnitude to measured stream loads, even though sealed parking lots cover only 1−2% of each watershed (Figure 5). These results might explain why an investigation carried out in Marquette, MI, found that runoff from commercial parking lots contributed 64% of the PAH load to the urban watershed studied (*33*).

What would be the effect on PAH loading to these watersheds if parking lots were not sealed? For each of the four watersheds, we compared the ΣPAH load contributed by parking lots (computed on the basis of the aerial extent of unsealed and sealed parking lots) to that obtained by applying the average yield for unsealed lots to all parking lots (Figure 6). We estimate that the ΣPAH load from parking lots in these watersheds would be reduced to 5−11% of the current loading if all lots were unsealed.

With the exception of the sealcoat itself, unsealed parking lots receive PAHs from the same urban sources as do sealed parking lots—e.g., tire particles, leaking motor oil, vehicle exhaust, atmospheric fallout—yet the average yield of PAHs from sealed parking lots is 50 times greater than that from unsealed lots. PAH assemblages and estimated loads further suggest that sealed parking lots could be dominating PAH loading in watersheds with commercial and residential land use. The implications of these results extend beyond Texas to the rest of the United States and Canada, where parking lot sealcoat is used extensively, and to other countries where sealcoat is being introduced. Previously identified urban sources of PAHs, such as automobile exhaust and atmospheric deposition, have been difficult to control or even quantify because of their nonpoint nature. In contrast, sealed parking lots are point sources, and use of the sealant is voluntary and controllable.

## Supporting Information Available

Two figures and three tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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