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Influence of Coal-Tar Sealcoat and Other Carbonaceous Materials on Polycyclic Aromatic Hydrocarbon Loading in an Urban Watershed

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Carbonaceous material (CM) particles are the principal vectors transporting polycyclic aromatic hydrocarbons (PAHs) into urban waters via runoff; however, characteristics of CM particles in urban watersheds and their relative contributions to PAH contamination remain unclear. Our objectives were to identify the sources and distribution of CM particles in an urban watershed and to determine the types of CMs that were the dominant sources of PAHs in the lake and stream sediments. Samples of soils, parking lot and street dust, and streambed and lake sediment were collected from the Lake Como watershed in Fort Worth, Texas. Characteristics of CM particles determined by organic petrography and a significant correlation between PAH concentrations and organic carbon in coal tar, asphalt, and soot indicate that these three CM particle types are the major sources and carriers of PAHs in the watershed. Estimates of the distribution of PAHs in CM particles indicate that coal-tar pitch, used in some pavement sealcoats, is a dominant source of PAHs in the watershed, and contributes as much as 99% of the PAHs in sealed parking lot dust, 92% in unsealed parking lot dust, 88% in commercial area soil, 71% in streambed sediment, and 84% in surficial lake sediment.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common contaminants in the environment. Many PAHs and their metabolites are toxic, mutagenic, and/or carcinogenic, and adversely affect human health and aquatic ecosystems. Over the past 30 years, total PAH concentrations ($\sum$PAH) in urban fresh-water sediments generally have increased (*1–3*) and increasing $\sum$PAH are correlated with increases in urban land use (*1, 3*). Numerous urban sources of PAHs have been identified, including coal-tar and asphalt-based sealcoats, combustion of fossil fuels, tire debris, asphalt pavement, roofing tar, and used motor oil (*2, 4−7*). In small urban watersheds, surface water runoff is the most important pathway for the introduction of PAHs into aquatic environments (*3, 8, 9*) and the majority of PAHs in runoff are associated with carbonaceous material (CM) particles (*10*). However, the role of CM particles as PAH sources and carriers in urban streams and lakes remains unclear.

There is a large body of literature on source identification and apportionment of PAHs in contaminated sediments (e.g., refs *11–14*), however most of this research has focused on PAH assemblages, and not on the types, amounts, and origins of PAH-associated CM particles in urban stream and lake sediments. CM particles in urban runoff originate from different land covers and are derived from a heterogeneous mix of source materials, including recent organic debris of plants and animals, partially humified materials, kerogen, coal, various types of char and soot, and coal and petroleum byproducts (*15, 16*). All these source materials can be altered in the environment by physical, chemical, and biological processes. In recent years, efforts have been made to measure PAHs in a variety of CM particles, including combustion-derived soot (*17, 18*) and charcoal (*18*), and coal- and petroleum-derived CMs such as coal (*18*), coke (*19*), coal tar (*20*), and asphalt (*7*).

Coal-tar-based parking lot sealcoat has recently been identified as a major urban PAH source in the U.S (*2, 21*). Mahler et al. (*2*) found that particles in simulated runoff from coal-tar-sealed parking lots had a mean $\sum$PAH (3500 mg/kg) 65 times higher than particles from unsealed asphalt and concrete parking lots. Van Metre et al. (*21*) found that PAH concentrations in dust swept from sealed parking lots in the central and eastern U.S., where coal-tar sealcoat is predominantly used, were about 1000 times higher than those in dust swept from sealed parking lots in the western U.S., where asphalt-based sealcoat is predominantly used (median concentrations of 2200 and 2.1 mg/kg, respectively). Although it is clear that coal-tar sealcoat contributes to PAHs in urban stream and lake sediments (*2, 21*), there remains uncertainty regarding the relative contribution of this CM to overall PAH loadings, and to the fate of PAHs associated with coal-tar sealcoats in the environment.

The objectives of this work are to identify the sources and distribution of CM particles in a small urban watershed, and to determine the types of CMs that are the dominant sources of PAHs in lake and stream sediments. CM particles and PAHs were characterized in the Lake Como watershed in Fort Worth, Texas. Samples of soils and dust from paved surfaces that likely are mobilized by runoff, and samples of sediment from the lake and its influent stream were collected and analyzed. CM particles were characterized using organic petrography and the estimated masses of the types of CMs identified were compared to PAH concentrations to identify the types of CMs that are most strongly associated with PAHs in urban soils, pavement dust, and aquatic sediments.

Materials and Methods

Details of sampling and analytical methods and all PAH data are presented in Wilson et al. (*22*) and are summarized briefly here. Residential soil no. 1 (*22*) was used in our study.

Sample Collection. Samples of lake sediment, soil, and pavement dust were collected October 19−21, 2004 from the Lake Como watershed in Fort Worth (Supporting Information

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(SI) Figure S1). The watershed area is 2.75 km^2, of which 90% is urbanized. About one-half of the urbanized land is residential area (47.6%) and the other half is commercial, industrial, and transportation area (ref *23* and references therein). Three sediment cores were collected with a box corer from a single site in Lake Como, corresponding to the lower lake site in Van Metre et al. (*23*). Cores were collected several meters apart to avoid sampling of disturbed sediment. The cores were vertically extruded and sliced at 5 cm intervals. Subsamples from the same depths (0−5, 10−15, and 25−30 cm) were combined from the three cores to create three large-volume samples. Influent suspended-sediment samples were obtained by filtering 75 L of stormwater through a 0.45 μm polytetrafluoroethylene (PTFE) membrane; the stormwater was collected from the influent stream during a runoff event October 22, 2004, three days after the lake cores were collected (*24*). An influent streambed sediment sample was collected at the same location three days after the runoff event. Streambed sediment was collected from depositional areas of the channel by scooping the soft, relatively fine-grained top sediment with a stainless steel scoop. Numerous scoops were combined to obtain a composite sample. Two composite surface soil samples—one from a residential neighborhood and the other from a commercial area—were collected by random sampling at approximately 40 locations near roads, sidewalks, and driveways using stainless steel scoops. One composite residential street dust sample was collected from three asphalt-paved residential streets using nylon push brooms and stainless steel dust pans. Two composite parking lot dust samples were collected; one from three coal-tar-sealed commercial parking lots and the other from three unsealed asphalt or cement commercial parking lots. There is no standard method for sampling pavement dust; further work is necessary to determine if sweeping captures representative samples. Composite sampling was used to characterize mean chemical concentrations and CM characteristics of each medium sampled. For some media (e.g., coal-tar sealed pavement, unsealed pavement, and lake sediment), variability in PAH concentrations is reasonably well known and in general is smaller within each medium than between media (*21, 23*).

Each sample of streambed sediment, soil, and pavement dust was homogenized and split after passing through a 1 mm sieve. One part of the split sample was analyzed at the University of Illinois at Urbana−Champaign (UIUC) and the other part was sent to the U.S. Geological Survey (USGS) National Water Quality Laboratory in Denver, Colorado.

Sample Characterization. Total CM contents were estimated by measuring weight loss after heating samples at 550 °C for 4 h in a Thermolyne F62700 muffle furnace (Barnstead International) (*25*). Total organic carbon (TOC) contents were determined with a CE 440 CHN analyzer (Exeter Analytical, Inc.) following Schumacher (*26*).

Organic Petrography. Quantitative petrographic analysis was done on all samples except the suspended-sediment (because of insufficient sample mass) after the removal of carbonate and silicate minerals by treatment with HCl/HF. The CM-enriched sample first was embedded in an epoxy resin, which was subsequently hardened. Resin surfaces were polished and the embedded CMs were observed with a Leitz DMRX-MPVSP photometer microscope using reflected white light, polarized light in conjunction with a lambda plate (characterization of anthracite, coke, char, and soot), and UV+violet-light illumination (fluorescence mode especially for the characterization of asphalt- and bitumen-like substances and coal-tar pitch). CM particles were identified and classified according to maceral groups and their subgroups per Taylor et al. (*27*). Maceral volume fractions in each sample were determined by point counting of at least 500 macerals using a multipoint cross-hair ocular and a 50× oil-immersion objective. A water-immersion objective was used for bitumen-like substances and coal-tar pitch. The overall accuracy of the maceral volume fractions is reported to be approximately ±2% (*27*). In our own control study, excellent agreement was obtained between petrograpic results and the known composition of a premixed sample of soot, coal-tar pitch, asphalt, and humic acid (SI Table S1). Three types of CM particles were physically separated by picking with tweezers from samples for microscale PAH extraction and analysis: recent organic matter (OM) from residential soil, asphalt-, and bitumen-like substances (hereafter, asphalt) from un-sealed parking lot dust, and coal-tar pitch from sealed parking lot dust. The latter two particle types could not be picked from other sample types because of their small volume fractions. Other types of CMs were not physically separated due to their small volume in all samples (i.e., coal, coke, char), or small particle sizes that were not amenable to picking (i.e., soot).

PAH Analysis. Eighteen parent PAHs, nine alkyl-PAHs, and the homologous series of alkyl-PAHs in bulk samples were determined at the USGS laboratory (*28*). Briefly, samples were extracted overnight with dichloromethane in a Soxhlet apparatus. The extracts were injected into a polystyrene-divinylbenzene gel permeation column and eluted with dichloromethane to remove sulfur and partially isolate the target analytes. PAHs and alkyl-PAHs were analyzed by gas chromatography (GC) with mass spectrometry (MS). Separated CM particles (20−90 mg) were extracted with acetone and dichloromethane by accelerated solvent extraction (ASE) at UIUC (EPA method 3545). The extract was cleaned with silica gel (EPA method 3630c), and 16 EPA priority PAHs were analyzed with GC/MS following EPA method 8270c. Quality assurance was provided by analyzing duplicate samples, blanks, and spiked reagent samples, and monitoring recovery of surrogate compounds. The sum of 13 PAHs in bulk samples (Σ_{13}PAH) is used when comparing with the consensus-based sediment-quality-guideline (SQG) probable effect concentration (PEC) (*29*). For comparison to literature values of PAHs on specific CM particles, the sum of 11 PAHs (Σ_{11}PAH) is used.

Data Analysis. Mass percentages of individual CMs in each sample were calculated from measured volume fractions and densities determined from the literature or in the UIUC laboratory, and they were used to calculate the mass contribution of individual CMs to total CMs. Organic carbon (OC) contributions of different CMs in each sample were calculated from the calculated mass percentages, OC contents of CMs determined from the literature or in the UIUC laboratory, and the measured TOC of bulk samples. Potential PAH loading from identified CMs were calculated using PAH concentrations in CM particles determined from the literature or measured in the UIUC laboratory. Uncertainty of predicted parameters was estimated by Monte Carlo simulation with Crystal Ball 2000 (Oracle Corp.). The resulting distribution of simulated output was analyzed by least trimmed squares regression (Systat 12, Systat Software, Inc.). The estimated means are reported. The data sources, calculation methods, and other analysis details are included in SI (Tables S2−S7).

Results and Discussion

PAH Concentrations. The Σ_{13}PAH varied over a range of about 3 orders of magnitude, with the largest concentrations in coal-tar-sealed parking lot dust (Figure 1). The Σ_{13}PAH in that sample (980 mg/kg) greatly exceeds concentrations in all other urban dust and soil samples (30−2000 times greater). PAH concentrations in stream and lake sediments show a pattern similar to previous studies (*8*), with the suspended-sediment Σ_{13}PAH (43 mg/kg) higher than that in streambed sediment (11 mg/kg), and streambed sediment Σ_{13}PAH higher than that in lake sediments (5.7−10 mg/kg). This pattern of
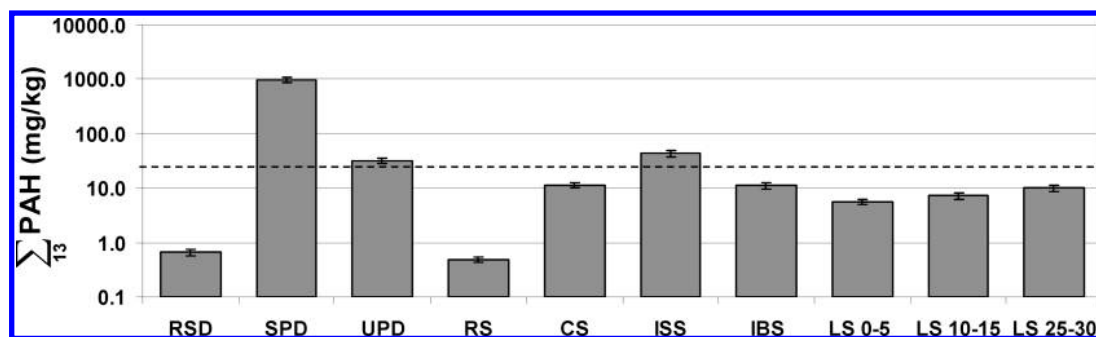
FIGURE 1. Total PAH concentrations in samples of residential street dust (RSD), sealed parking lot dust (SPD), unsealed parking lot dust (UPD), residential area soil (RS), commercial area soil (CS), influent suspended sediment (ISS), influent streambed sediment (IBS), lake sediment from 0−5 cm depth (LS 0−5), lake sediment from 10−15 cm depth (LS 15−20), and lake sediment from 25−30 cm depth (LS 25−30) ($\sum_{13}$PAH as used here is the sum of the detected and estimated concentrations of 13 PAHs as used in the consensus-based SQG: acenaphthene, acenaphthylene, anthracene, fluorene, 2-methylnaphthalene, naphthalene, phenanthrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene, benzo[*a*]pyrene, chrysene, fluoranthene, and pyrene; the dashed line indicates the PEC of 22.8 mg/kg (*29*)).

higher PAH concentrations in the suspended-sediment compared to the streambed sediment likely results from PAH losses to desorption and solubilization of OM during transport and early diagenesis, and from dilution of bottom sediment by coarser material, especially in the streambed (*8, 30, 31*). For comparison, the PEC for $\sum_{13}$PAH in fresh water aquatic sediments is 22.8 mg/kg (*29*).

The $\sum_{11}$PAH in recent OM particles separated from residential area soil is 68 mg/kg (SI Table S4), which, as expected, is lower than that measured by Ahn et al. (170 mg/kg) (*32*) or by Khalil et al. (990 mg/kg) (*20*), who analyzed PAHs associated with recent OM particles in soil from a coke oven site and sediment from a manufactured gas plant (MGP) site, respectively. The $\sum_{11}$PAH in asphalt and coal-tar pitch particles from this study are 2850 and 75 000 mg/kg, respectively. The $\sum_{11}$PAH in asphalt is larger than corresponding values reported in the literature (range ∼2−200 mg/kg (*13, 33−35*)), but similar to asphalt-based sealcoat (2760 mg/kg (*2*)). This may be because some literature values are for ground asphalt pavement containing aggregate, or because picked asphalt particles are associated with small amounts of coal-tar pitch in the unsealed parking lot dust sample. The $\sum_{11}$PAH in coal-tar pitch is similar to those values in fresh coal-tar-based sealcoats (87 000 mg/kg) (*2*) and coal-tar particles from a MGP site (53 000 mg/kg) (*20*), but higher than those in scrapings from six Austin parking lots with sealcoats of varying age (19 600 mg/kg) (*2*). One of the sealed parking lots sampled in this study was freshly coated with coal-tar-based sealcoat, which likely explains the higher value.

Proportional concentrations of 12 individual PAHs to their sum were evaluated (SI Figure S2); they indicate combustion sources dominate PAHs in all samples, typical of PAHs in urban settings across the U.S. (*1*).

Organic Petrography. Identified macerals in samples, which consist of multiple subgroups with different optical properties, origins, and volume fractions, are classified into two categories: (i) Recent OM and (ii) CMs resulting from anthropogenic contamination (SI Table S2). Recent OM is composed of huminite, vitrinite, liptinite, and inertinite. CMs resulting from anthropogenic contamination include hard coal, coke, char, soot, and coal- and petroleum-derived materials such as coal-tar pitch and asphalt. Some characteristics of maceral groups are presented in SI Table S3. Morphologies of various CM particles such as recent OM, coal, char, and coal-tar pitch in soil or sediment samples have been presented elsewhere (*36, 37*), thus, only photographs of representative anthropogenic CM particles in selected samples are presented here (SI Figure S3).

Recent OM, asphalt, and soot were found in all samples, whereas hard coal, char, and coke often were below the

detection limit (0.2 vol % for particles larger than 1−2 μm) and never exceeded 1.0% (SI Table S2). Estimation of mass percentages of CMs in each sample indicates that recent OM dominates all soil and sediment samples, ranging from 52.4 to 79.0% (Figure 2). The fractions of soot are higher in lake sediments and unsealed parking lot dust than in other samples, ranging from 17.3 to 20.9%. Asphalt dominates unsealed parking lot dust (50.9%), and is a major component of residential street dust (45.1%), along with recent OM (43.7%). The fraction of asphalt decreases progressively from unsealed parking lot and residential street dust, to streambed sediment (36.1%), to lake sediments (5.1−11.1%). This progressive decrease suggests that these particles are transported to the lake with runoff, diluted by other CM particles, and possibly removed/degraded over time in buried sediments.

Coal-tar pitch was detected in six samples, and its percent contribution to sample mass varies widely. Coal-tar pitch dominates sealed parking lot dust (57.5%) but is a small part of unsealed parking lot dust, commercial area soil, surficial lake sediment, and streambed sediment (7.8, 3.6, 3.2, and 1.4%, respectively). Occurrence of coal-tar pitch in unsealed parking lot dust and commercial soil might result from offsite transport from sealed parking lots by vehicle tracking or wind (*21*). The likely source of coal-tar pitch found in streambed sediment and surficial lake sediment is parking lot runoff. Coal-tar pitch either was not detected or was detected as a very low part of total sample mass (within ±2% uncertainty) in deeper lake sediment (SI Table S2). This decrease in coal-tar pitch with increasing sediment depth suggests that (1) runoff of coal-tar particles in the Lake Como watershed has increased in recent years, (2) runoff of other particle types relative to coal tar has decreased in recent years, and/or (3) coal-tar particles are unstable in water or water-saturated sediment and are removed/degraded with time.

Distribution of OC. The TOC in each sample, and the OC contributed by different types of CMs, vary among samples (SI Table S8). The TOC in lake sediments are 3.92, 4.71, and 5.04 g OC/100 g bulk sample for depths of 0−5, 10−15, and 25−30 cm, respectively, and the trend of increasing TOC with depth suggests either greater OM accumulation in past years or a recent increase in erosion of low-OM sediment (e.g., bank material). These lake sediment TOC values are higher than those for bed sediment in the influent stream (2.22 g OC/100 g bulk sample), indicating that lake sediment acts as a sink for CMs. The mass distribution of OC among CMs in each sample also varies (SI Figure S4), and generally mirrors the mass distribution of CMs in each sample (Figure 2), with small relative differences in percent contributions.
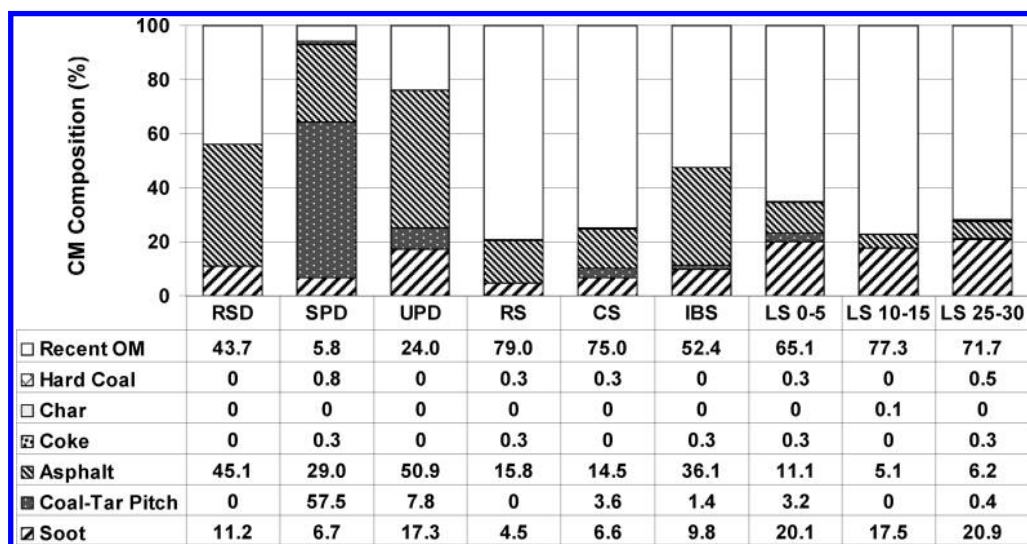
	RSD	SPD	UPD	RS	CS	IBS	LS 0-5	LS 10-15	LS 25-30
☐ Recent OM	43.7	5.8	24.0	79.0	75.0	52.4	65.1	77.3	71.7
☑ Hard Coal	0	0.8	0	0.3	0.3	0	0.3	0	0.5
☐ Char	0	0	0	0	0	0	0	0.1	0
⊞ Coke	0	0.3	0	0.3	0	0.3	0.3	0	0.3
◩ Asphalt	45.1	29.0	50.9	15.8	14.5	36.1	11.1	5.1	6.2
▨ Coal-Tar Pitch	0	57.5	7.8	0	3.6	1.4	3.2	0	0.4
▨ Soot	11.2	6.7	17.3	4.5	6.6	9.8	20.1	17.5	20.9

FIGURE 2. Mass percentages of carbonaceous materials (CMs) in samples (one standard deviation of every maceral in every sample is within 3%).

Correlations between PAHs and CMs. The logarithm of total PAHs (log (Σ_{13}PAH)) were plotted against OC of selected CMs (SI Figure S5), and the correlation coefficients are discussed below and summarized in SI Table S9. Extensive research has shown positive correlations between ΣPAH (or log(ΣPAH)) and TOC or soot carbon (SC) in soil and sediment (38, 39), but no such correlation was observed here. However, values of log (Σ_{13}PAH) were positively correlated to the sum of OC in coal-tar pitch and asphalt ($R^2 = 0.56$, $p = 0.021$) and also to the sum of OC in coal-tar pitch, asphalt, and soot ($R^2 = 0.66$, $p = 0.008$). These correlations were much improved ($R^2 = 0.96$ and $p < 0.001$ for both) when residential area soil and residential street dust were excluded (SI Figure S5 and Table S9). The improved correlation likely results because residential sources of OC have large contributions from recent OM and much lower PAH concentrations, suggesting different PAH–OC dynamics than for commercial source materials. These correlations indicate that coal-tar, asphalt, and soot particles are likely sources or carriers of PAHs in the Fort Worth watershed, and that PAH levels in the stream and lake are more affected by CMs from commercial land use areas than from residential areas. Additional data sets should be evaluated to confirm the results, particularly in other urban areas and watersheds.

PAH Loadings from Coal-Tar Pitch, Asphalt, and Soot. The amount and distribution of PAHs among CMs that comprise each sample were estimated using measured and/ or literature values of PAHs in CM particles, volume percentages of CMs from quantitative petrography, and measured or literature values of CM density (see SI for details). Measured (estimate no. 1) and literature (estimate no. 2) values for PAHs in asphalt and coal-tar pitch were available, so both were used. The Σ_{11}PAH for estimate no. 1 was not significantly different from the measured value for the sealed parking lot dust, but exceeded measured values for all remaining samples by 2–70 times (SI Table S10). The Σ_{11}PAH for estimate no. 2 was less than the measured value for the sealed parking lot dust, but was not significantly different from measured values for streambed sediment and deeper lake sediments, and exceeded measured values by 2–7 times for the remaining samples (SI Table S10). These results suggest that measured PAHs on picked coal-tar pitch particles were accurately determined, but that the sealed parking lot dust sample is either not representative of all parking lots in the Lake Como watershed, or that substantial losses of PAHs occurred during transport and weathering of coal-tar particles. Overestimation of measured PAHs using both methods

is not surprising, because all PAH concentrations are determined with particles taken from their points of origin, and particle transport and weathering reduce PAH concentrations over time (2).

The estimated relative contributions to total PAHs in samples by each type of CM were calculated and results are shown in Figure 3. Literature values of PAH loadings on coal-tar and asphalt particles were used in order to obtain conservative estimates of relative PAH loadings from these CMs. The majority of PAHs in residential street dust are associated with asphalt (47%), although the estimated amount of asphalt and recent OM are similar (Figure 2). Coal-tar pitch dominated the distribution of PAHs in sealed parking lot dust, unsealed parking lot dust, commercial area soil, streambed sediment, and surficial lake sediment (99, 92, 88, 71, and 84%, respectively). In lake sediment for the 10–15 cm depth, recent OM and soot contributed similar amounts of PAHs (49 and 45%, respectively). In lake sediment for the 25–30 cm depth, PAHs are primarily associated with coal-tar pitch, soot, and recent OM (37, 31, and 27%, respectively), despite the estimates that the amount of recent OM was 3 times that of soot and 180 times of that of coal-tar pitch (Figure 2). In residential area soil, where no coal-tar pitch was detected and soot content was low (Figure 2), the majority of PAHs are associated with recent OM (62%). The results suggest that coal-tar pitch, asphalt, and soot are important PAH sources in urban lake sediments, soils, and dust. These results are consistent with the correlations between log (Σ_{13}PAH) and OC in coal-tar pitch, asphalt, and soot.

The mass of PAHs associated with coal-tar pitch in different samples was estimated to more directly explore its potential contribution to total PAH loadings; both measured and literature values of Σ_{11}PAH in coal-tar particles were used to evaluate the potential range of PAH loadings (Figure 4). The estimated Σ_{11}PAH contributed by coal-tar particles to 1 kg of sealed parking lot dust is 1900 mg for estimate no. 1 and 527 mg for estimate no. 2; the former is not significantly different from the measured Σ_{11}PAH in this sample. Given that about 99% of the total PAHs in this sample are from coal tar (Figure 3), agreement between estimated and measured Σ_{11}PAH is expected. Extending the coal-tar loading results to other samples, the potential PAH loadings from coal-tar pitch range from 0.5 to 6 times greater than the measured Σ_{11}PAH in all samples where coal-tar particles were detected when literature values of PAH concentration on coal-tar particles were used (estimate no. 2), and 2–24 times greater when
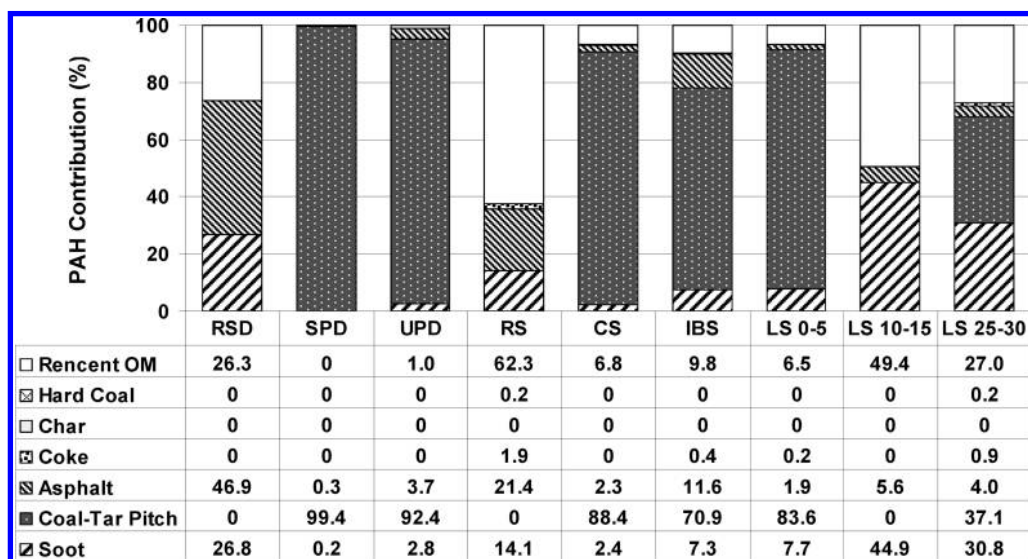
FIGURE 3. Estimated relative contributions to PAHs in samples by CMs using literature values of PAH loadings on CM particles (0 represents values below 0.05%; one standard deviation is within 7% for all relative contribution values, except for coal-tar pitch in LS 25–30 which is 14%).
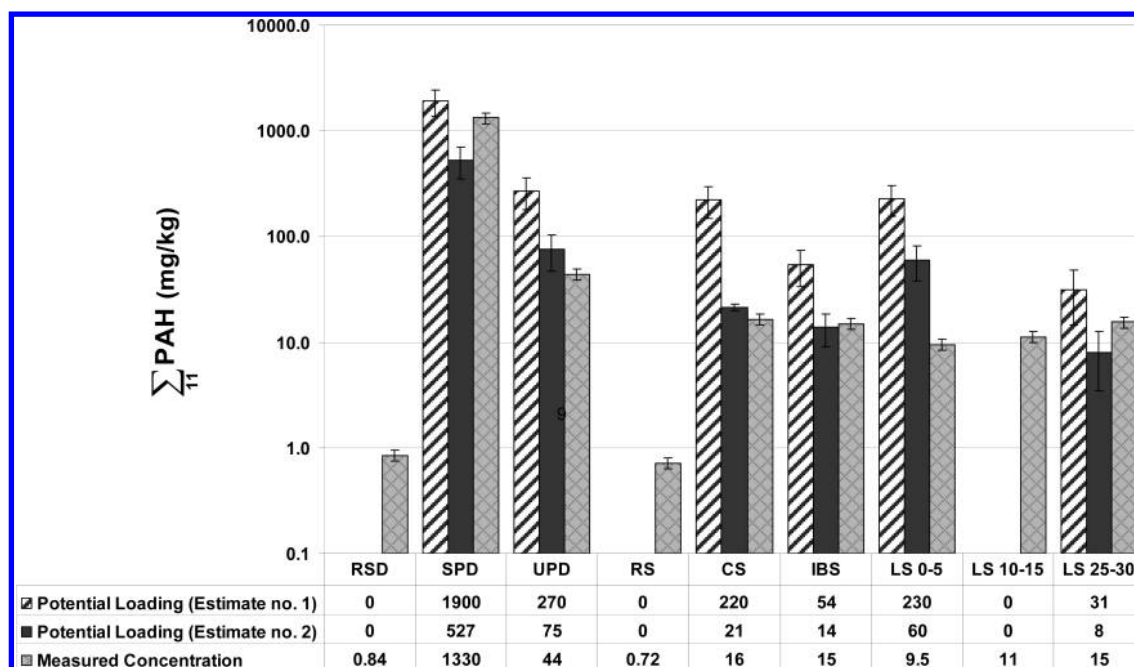
	RSD	SPD	UPD	RS	CS	IBS	LS 0-5	LS 10-15	LS 25-30
□ Rencent OM	26.3	0	1.0	62.3	6.8	9.8	6.5	49.4	27.0
⊠ Hard Coal	0	0	0	0.2	0	0	0	0	0.2
□ Char	0	0	0	0	0	0	0	0	0
⊡ Coke	0	0	0	1.9	0	0.4	0.2	0	0.9
⊠ Asphalt	46.9	0.3	3.7	21.4	2.3	11.6	1.9	5.6	4.0
■ Coal-Tar Pitch	0	99.4	92.4	0	88.4	70.9	83.6	0	37.1
▨ Soot	26.8	0.2	2.8	14.1	2.4	7.3	7.7	44.9	30.8

	RSD	SPD	UPD	RS	CS	IBS	LS 0-5	LS 10-15	LS 25-30
▨ Potential Loading (Estimate no. 1)	0	1900	270	0	220	54	230	0	31
■ Potential Loading (Estimate no. 2)	0	527	75	0	21	14	60	0	8
▨ Measured Concentration	0.84	1330	44	0.72	16	15	9.5	11	15

FIGURE 4. Comparison between potential PAH loadings from coal-tar pitch and measured total PAHs in samples ($\sum_{11}$PAH as used here is the sum of 11 PAHs: phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]perylene, and benzo[ghi]perylene. Estimate no. 1 used measured values and estimate no. 2 used literature values. Error bars represent the precision of estimation or measurement. For estimated potential PAH loadings from coal-tar pitch, it is ±1 standard deviation. For measured total PAHs in samples, it is absolute variation).

measured values of PAH concentration on coal-tar particles were used (estimate no. 1). These differences between potential and measured PAH loadings are expected because PAH concentrations associated with coal-tar particles will decrease during runoff from land surfaces, during fluvial and sediment transport processes culminating in the deposition of coal-tar particles to surface water bodies, and during the chemical transformation of coal-tar particles in lake bed sediments by processes including volatilization, solubilization, degradation, and mass transfer to other CMs (40). Nevertheless, the results suggest that coal-tar particles are an important source of PAHs in urban lake sediments.

The conclusion that coal-tar pitch is a primary source and carrier of PAHs in this watershed is supported by

comparison of PAH profiles in sources and receptors. Correlations between PAH assemblages in the Lake Como watershed samples and commonly reported PAH sources were evaluated using Pearson correlation (r) and chi squared (χ^2) values for proportional concentrations of 12 parent PAHs used in receptor modeling (14). Correlation coefficients are the highest for PAHs in Austin sealed parking lot scraping samples and the Lake Como watershed samples, ranging from 0.995 for the sealed parking lot dust to 0.805 for the surficial lake sediment (SI Table S11). Significant (p-value 0.05), but lower correlations (generally 0.65–0.80) occur for various vehicle emission, wood combustion, and coal combustion profiles, all of which are dominated by soot. The χ^2 values support the same conclusion, with the lowest values for coal-tar source

materials and samples with high potential coal-tar PAHs (indicating only a small difference) and the next lowest values for tunnel particulates (SI Table S12).

This study indicates that coal-tar-based sealcoat is an important source of PAHs to the Lake Como watershed. Several decades of research on urban sources of PAHs mainly focused on automobile exhaust, lubricating oils, gasoline, tire particles, asphalt and bitumen, and atmospheric deposition (7, 41−43), but only recently has coal-tar sealcoat been identified as an important urban PAH source (2). The conclusions drawn here regarding the importance of coal-tar based sealcoat as a PAH source and the role played by various CMs in source and fate of PAHs are based on relatively few samples from one urban watershed. Data for other cities and regions of the U.S. might shed additional light on the role of CMs in PAH source, transport, and fate.

Supporting Information Available

Additional details on data source, data analysis, 5 figures, and 12 tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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