



Contribution of PAHs from coal–tar pavement sealcoat and other sources to 40 U.S. lakes

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ARTICLE INFO

Article history:

Received 19 February 2010

Received in revised form 28 July 2010

Accepted 6 August 2010

Keywords:

Sediment

PAH

Trends

Sources

Receptor modeling

Cores

Pavement

Urban

ABSTRACT

Contamination of urban lakes and streams by polycyclic aromatic hydrocarbons (PAHs) has increased in the United States during the past 40 years. We evaluated sources of PAHs in post-1990 sediments in cores from 40 lakes in urban areas across the United States using a contaminant mass-balance receptor model and including as a potential source coal-tar-based (CT) sealcoat, a recently recognized source of urban PAH. Other PAH sources considered included several coal- and vehicle-related sources, wood combustion, and fuel–oil combustion. The four best modeling scenarios all indicate CT sealcoat is the largest PAH source when averaged across all 40 lakes, contributing about one-half of PAH in sediment, followed by vehicle-related sources and coal combustion. PAH concentrations in the lakes were highly correlated with PAH loading from CT sealcoat (Spearman's $\rho = 0.98$), and the mean proportional PAH profile for the 40 lakes was highly correlated with the PAH profile for dust from CT-sealed pavement ($r = 0.95$). PAH concentrations and mass and fractional loading from CT sealcoat were significantly greater in the central and eastern United States than in the western United States, reflecting regional differences in use of different sealcoat product types. The model was used to calculate temporal trends in PAH source contributions during the last 40 to 100 years to eight of the 40 lakes. In seven of the lakes, CT sealcoat has been the largest source of PAHs since the 1960s, and in six of those lakes PAH trends are upward. Traffic is the largest source to the eighth lake, located in southern California where use of CT sealcoat is rare.

Published by Elsevier B.V.

1. Introduction

Contamination of urban lakes and streams by polycyclic aromatic hydrocarbons (PAHs) is widespread in the United States and has been increasing during the past 40 years (Lopes et al., 1997; Van Metre et al., 2000; Van Metre and Mahler, 2005). PAHs are of environmental concern because they are toxic to aquatic life and because many are probable or suspected carcinogens (U.S. EPA, 1993). PAHs are a large group of chemically related compounds comprising two or more fused benzene rings. Extensive research has been done to characterize the chemical assemblages of various suspected PAH sources, which include vehicle emissions, tire particles, motor oil, crude oil, and power plant and industrial emissions (Rogge et al., 1993b; Li et al., 2003; Boonyatumanond et al., 2007). These source characterizations have been used by researchers to quantify, or apportion, PAH source contributions to the atmosphere, soils, and aquatic sediments (e.g., Simcik et al., 1999; Motelay-Massei et al., 2007; Tian et al., 2009; Wang et al., 2009). Such efforts are termed source-receptor modeling because the goal is to quantify contributions of different sources to a receptor, for example lake-bottom sediment.

Source-receptor modeling has been used to quantify contributions of PAHs from different sources to aqueous sediment for more than a decade (Christensen et al., 1997; Rachdawong et al., 1998; Simcik et al., 1999; Li et al., 2001; Li et al., 2003; Bzdusek et al., 2004; Christensen and Bzdusek, 2005; Sofowote et al., 2008); such studies in North America predominantly have been in water bodies in the Great Lakes region affected by industrial land use. The two principal methods, multi-variate analysis (frequently factor analysis with non-negative constraints) and mass-balance modeling, approach the question from opposite directions. Multi-variate analysis applies factor analysis to the receptor assemblages to hypothesize PAH source profiles, assumed to be represented by the factors. Mass-balance modeling starts with the PAH profiles of known sources and determines the fractional contribution required from each source to reproduce the PAH profile measured in the receptor. A third approach, ratio analysis, also has been used to identify PAH sources (Yunker et al., 2002), but multi-variate analysis and mass-balance modeling have the advantage of considering a larger number of PAH simultaneously and providing quantitative as opposed to qualitative source contributions (Christensen et al., 1997; Li et al., 2003).

Source-receptor modeling relies on the assumption that there is no change in PAH profile from source to receptor. Some researchers have rationalized that the assumption is justified for PAHs in lake sediment because PAHs are relatively conservative, the transport pathway is short, burial is rapid, and(or) sediments are anoxic (Christensen et al., 1997;

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Rachdawong et al., 1998; Li et al., 2003; Bzdusek et al., 2004). More critical approaches include those of Simcik et al. (1999), who reported little change in measured PAH profiles between the atmosphere and surficial lake sediment, and Li et al. (2001), whose modeling results demonstrated that only phenanthrene underwent significant degradation in aerobic sediment and that no degradation occurred in deeper, anoxic sediment layers.

A second assumption is that all sources have been identified and have a “fingerprint”. For any source-receptor model, the apportionment is limited to those sources of which the researcher is aware and for which chemical profile information is available. No PAH receptor-modeling study to date has considered coal-tar-based (CT) pavement sealcoat as a potential source. Sealcoat is a black, shiny liquid frequently sprayed or painted on the asphalt pavement of parking lots and driveways in an attempt to enhance their appearance and improve the longevity of the underlying asphalt pavement. Most sealcoat products have either a refined coal-tar or asphalt (crude oil) base. The CT products typically are 15–35% coal tar pitch, a known carcinogen that is about 50% PAH (U.S. Department of Health and Human Services, 2002). The median concentration of the sum of 16 PAHs for CT sealcoat products is more than 50,000 mg/kg (dry weight basis), and the median for asphalt-based sealcoat products is about 50 mg/kg (City of Austin, Texas, 2005). Sealcoat use is widespread; an informal survey on the internet located sealcoat applicators in all 50 U.S. states and Canada (Van Metre et al., 2009). Of five watersheds mapped (four in Texas and one in Illinois), sealcoated parking lots constituted 1 to 4% of the total watershed area (Mahler et al., 2005; U.S. Geological Survey, unpublished data, 2009). It has been estimated that sealcoat wears off parking lots at an overall rate of about 2.4% per year (Scoggins et al., 2009).

CT pavement sealcoat was first identified as a potentially important PAH source in 2005 (Mahler et al., 2005). Subsequent research expanded the results to the national scale in the U.S. (Van Metre et al., 2009): PAH concentrations in dust from sealcoated pavement in six U.S. cities east of the Continental Divide, where the CT sealcoat product is predominant, were on the order of thousands of milligrams per kilogram (median 2200 mg/kg), about 1,000 times greater than in dust from sealcoated pavement in three western cities, where asphalt-based sealcoat is more commonly used. Diagnostic PAH ratios in sediment from urban lakes in six central and eastern U.S. cities were similar to ratios in dust from CT-sealcoated parking lots in the lake watersheds (Van Metre et al., 2009), supporting the hypothesis that, where widely used, CT sealcoat is a major, perhaps dominant PAH source to lakes.

Here we expand the source-receptor approach to a quantitative analysis of PAH sources to 40 urban lakes across the United States. We test the hypothesis that CT sealcoat is a major source of PAHs to urban lakes in the United States and that its use since the 1950s is contributing to increasing trends in PAHs in many U.S. lakes. The 40 lakes are among those sampled by the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program (Van Metre and Mahler, 2005; Mahler et al., 2006). The NAWQA program is using paleolimnology to identify trends in sediment quality, and by inference, water quality in the United States. PAH sources to sediment deposited since about 1990 were evaluated for 40 lakes using a mass-balance receptor model. Historical trends in fractional contributions from different PAH sources for the last 40 to 100 years for eight of the 40 lakes were analyzed using the same model. This is the first PAH source-receptor modeling study of such large scale in terms of the number of lakes and geographic extent, and the first to evaluate PAH contamination sources in numerous watersheds with non-industrial urban land uses.

2. Experimental methods

2.1. Sampling and analytical

Sediment cores were collected from 40 lakes (29 reservoirs and 11 natural lakes) in the United States during 1996 through 2008, age

dated, and analyzed chemically (Fig. 1; additional details in Supplementary Information Table S1). Urban areas for this study were selected on the basis of NAWQA Program study units, metropolitan statistical areas (U.S. Department of Commerce, 1996), and ecoregions (Omernik, 1987) to represent a diversity of ecoregions where a majority of United States cities and urban populations are located. Trends in organic compounds were reported for 26 of these lakes previously (Van Metre and Mahler, 2005); 15 of these 26 lakes had upward trends in total PAH since 1970 and two had downward trends. Eight of the 40 lakes were selected for analysis of historical trends in PAH source contributions. Six of these lakes – one lake in the northern part and one in the southern part of each of the western, central, and eastern regions of the U.S. – were selected to represent the effects of rapid urbanization on PAH source loading regionally, and two lakes were selected to represent the effects of historical changes in PAH source loading in older urban areas in the north-central and north-eastern U.S. Population density for these lakes ranges from 223 (Railroad Canyon Lake [CYN]) to about 2900 (Newbridge Pond [NEW]) people/km².

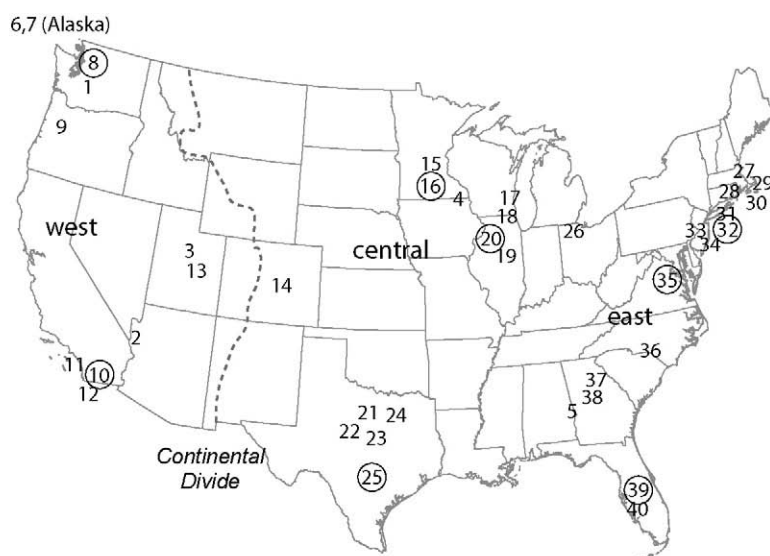
Thirty-five of the 40 lakes have relatively small drainage basins (most <100 km², computed as sediment-contributing area, i.e., excluding area upstream from major dams) with mixtures of commercial, residential, and undeveloped land uses; a few have some industrial land use. Five of the lakes have larger watersheds (~300–6000 km²) with a mix of urban and non-urban land uses including industry, agriculture, and undeveloped lands. These lakes are included to assess PAH sources to larger water bodies with large, mixed-land-use watersheds.

Most cores were collected from the deepest part of a natural lake or in the middle or lower part of a reservoir. Cores were sectioned into vertically discrete samples for analysis of major and trace elements, ¹³⁷Cs, ²¹⁰Pb, organochlorine pesticides, PCBs, and PAHs (Van Metre et al., 2004). Samples for analysis of organic compounds were transferred to baked glass jars and chilled pending shipment to the laboratory. All PAH data used for source modeling here are from analyses done soon after original core collection.

Activities of ¹³⁷Cs were measured by counting freeze-dried sediments in fixed geometry with a high-resolution, intrinsic germanium detector gamma spectrometer, using a method similar to that reported by Fuller et al. (1999). Activities of ²¹⁰Pb were measured on freeze-dried sediments by high-precision gamma-ray spectrometry similar to methodology described in Fuller et al. (1999).

Sampling and analytical methods and descriptions of age dating for the 29 cores collected through 2001 are presented in Van Metre et al. (2004). The same approaches were used for the 11 lakes sampled after 2001. The primary basis for age dating cores from the reservoirs was the ¹³⁷Cs profile and the pre-lacustrine sediment interface, and for cores from the natural lakes was the ²¹⁰Pb profile and the constant rate of supply model (Appleby and Oldfield, 1992). Age dating based on the ¹³⁷Cs profile is preferred in reservoirs because the large and variable fluvial inputs of sediment common to many reservoirs leads to violation of the basic assumptions of the ²¹⁰Pb dating models, and because the constant rate of supply model requires that the full excess ²¹⁰Pb inventory be sampled (100+ year time frame). Dates were assigned to individual samples between date-depth markers or using ²¹⁰Pb models on the basis of accumulation of dry mass per unit area in the core.

PAHs and alkyl-substituted PAHs were extracted, isolated, and analyzed in sediment from 39 of 40 lakes using the procedures of Olson et al. (2003). Briefly, samples were extracted with dichloromethane in a Soxhlet apparatus; extracts were cleaned using a polystyrene-divinylbenzene gel permeation column; and PAHs and alkyl-PAHs were quantified by capillary-column gas chromatography (GC) with detection either by full-scan mass spectrometry (MS) (most cores from 2003 to 2006) or by selected ion monitoring MS (all other cores). Nineteen parent PAHs, 10 specific alkyl-PAHs, and the homologous series of alkyl-PAHs for 2- to 7-ringed PAH were



map #	lake	abbrev.	map #	lake	abbrev.
1	Lake Washington	WAS	21	Lake Como	CMO
2	Las Vegas Bay, Lake Mead	LVB	22	Echo Lake	ECO
3	Farmington Bay, Great Salt Lake	FAR	23	Fosdic Lake	FOS
4	Lake Pepin	PEP	24	White Rock Lake	WRL
5	West Point Lake	WP	25	Lady Bird Lake (formerly Town Lake)	TWN
6	Westchester Lagoon	WES	26	South Commerce Lake	SCM
7	Hillstrand Pond	HIL	27	Maple Street Pond	MAP
8	Lake Ballinger	BAL	28	Upper Mystic Lake	MYS
9	Middle Tanasbrook Pond	TNB	29	Charles River	CHA
10	Railroad Canyon Lake	CYN	30	Harris Pond	HSP
11	West Street Basin	WST	31	Lake Whitney	WTY
12	Sweetwater Reservoir	SWT	32	Newbridge Pond	NEW
13	Decker Lake	DEK	33	Clyde Potts Reservoir	NJCP
14	Sloans Lake	SLN	34	Orange Reservoir	NJOR
15	Palmer Lake	PLM	35	Lake Anne	ANN
16	Lake Harriet	HAR	36	Wheeler Lake	WEE
17	Northridge Lake	NTR	37	Lake Berkeley	BRK
18	Lake Whittall	WTN	38	Lakewood Park Lake	LKW
19	Beck Lake	BEC	39	Lake Killarney	KIL
20	Lake in the Hills	LKH	40	Lake Orlando (formerly Wekiva Lake)	ORL

Fig. 1. Locations of 40 lakes presented in this study and associated abbreviations. The eight lakes used in the trend analysis are circled.

determined. In one lake (Lake Ann [ANN], sampled in 2008), PAH were analyzed using the procedures of Zaugg et al. (2006). Quality assurance was provided by analyzing duplicate samples (environmental samples split at the laboratory), laboratory blanks, and spiked reagent samples, and by monitoring recovery of surrogate compounds. Median relative percent difference for PAHs was 11.9% for 41 duplicate samples (Van Metre et al., 2004).

2.2. Chemical mass-balance model

The CMB model was used to evaluate PAH sources to the 40 lakes; CMB is supported by the U.S. Environmental Protection Agency (U.S. EPA, 2008). The model requires source profiles (proportional concentrations of PAHs) and receptor data (PAH concentrations for lake sediment). The CMB model quantifies source contributions by solving a system of linear equations that express each receptor chemical concentration (C_i) as a linear sum of products of source profile abundances and source contributions (Coulter, 2004). The model solves for source contributions to the receptor by minimizing chi square (X^2 ; the sum of squares of the differences between the measured and calculated values of C_i) weighted by the uncertainty of C_i of both the source and receptor profiles. Assumptions of the model are that (1) the composition of each source emission is consistent over the period represented by receptor data, (2) chemical species do not react with each other or with the environment, (3) all sources that

contribute significantly to the receptor have been identified and their chemical profile is known, (4) the composition of each source is linearly independent of other sources, and (5) measurement uncertainties are random, uncorrelated, and normally distributed (Li et al., 2003).

Twelve parent PAHs were used in the CMB modeling because all 12 were frequently detected in lake sediment samples ($\geq 96\%$) and are included in many source profiles available in the literature (Table 1). The 12 PAHs are phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Py), benz[a]anthracene (BaA), chrysene (Chy), benzo-[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), and benzo-[ghi]perylene (BgP). For this analysis, Σ PAH is the sum of these 12 PAHs. To provide a consistent dataset for the 40 lakes for CMB modeling, three samples dated as post-1990 were selected systematically from each lake core (top three samples, or every other sample if five or more available). Concentrations of the 12 PAH and Σ PAH for individual samples were entered into the model (model input data available in Supplementary Information Table S2); modeling results (i.e., source mass loadings and fractional contributions) were averaged for each lake.

A large number of source profiles representing a variety of source types were considered here (Table 1). Many of the source profiles used are from Li et al. (2003), who did a comprehensive compilation of coal- and traffic-related PAH profiles reported in the literature. Recognizing that PAHs in aquatic sediment are mostly those originally

Table 1
PAH source categories and source profiles considered. [CT, coal–tar-based].

Source category	PAH source	Reference
Coal combustion	Power plant emissions	Li et al., 2003
	Residential heating emissions	Li et al., 2003
	Coke oven emissions	Li et al., 2003
	Coal average (defined in Li et al., 2003)	Li et al., 2003
Vehicle related	Diesel vehicle particulate emissions	Li et al., 2003
	Gasoline vehicle particulate emissions	Li et al., 2003
	Traffic tunnel air	Li et al., 2003
	Traffic average (defined in Li et al., 2003)	Li et al., 2003
	Used motor oil 1	Wang et al., 2000
	Used motor oil 2	Boonyatumanond et al., 2007
	Tire particles	Boonyatumanond et al., 2007
	Asphalt	Boonyatumanond et al., 2007
	NIST diesel particles	NIST, 2000
	Fuel–oil combustion	Fuel–oil combustion particles
Wood burning	Pine–wood soot particles	Schauer et al., 2001
CT–sealcoat related	NIST coal tar	NIST, 1992
	CT–sealcoat products	Mahler et al., 2005
	CT–sealcoat scrapings, fresh	Mahler et al., 2005
	CT–sealcoat scrapings, Milwaukee	Van Metre et al., 2008
	CT–sealcoat scrapings, Austin	Mahler et al., 2004
	CT–sealcoated pavement dust, six cities (SC–dust)	Mahler et al., 2004; Van Metre et al., 2008
	CT–sealcoated pavement dust, Austin (SC–Austin)	Mahler et al., 2004; Van Metre et al., 2008

associated with particles (either in air, soils, or surface dusts), Li et al. (2003) used reported gas–particulate partition coefficients to convert literature source profiles containing both gaseous and particulate PAHs to particulate-only profiles. With the exception of fuel–oil combustion, the other profiles used in model runs were from PAHs measured in the particulate phase from wood burning (Schauer et al., 2001), tires and asphalt (Boonyatumanond et al., 2007), and CT sealcoat (Mahler et al., 2005; Van Metre et al., 2009).

The CT–sealcoat profile (SC–dust) used in most CMB modeling scenarios presented here is the mean of proportional PAH concentrations for dust from sealcoated pavement in six cities: Minneapolis, Minn., Chicago, Ill., Detroit, Mich., Washington, D.C., New Haven, Conn., and Austin, Tex. (Mahler et al., 2005; Van Metre et al., 2009). These profiles are for particulates from pavement assumed, on the basis of the very high PAH concentrations in associated dust (median of 2200 mg/kg total PAH), to be sealed with CT sealcoat. The pavement–dust profiles from Austin studies (SC–Austin) and the profiles of scraping samples (SC scrape; sealcoat scraped from parking lot surfaces) collected in Milwaukee, Wis., and Austin (Mahler et al., 2005; Van Metre et al., 2009) also were evaluated relative to other profiles and were used in several model runs.

Our evaluation of model results relied on model performance measures (X^2 , R^2 of the estimate, and percentage of measured total and individual PAH mass estimated by the model) and qualitative agreement with known regional and temporal patterns in sources. The qualitative agreement criteria were: (1) some contribution of PAHs from vehicle-related sources in most or all urban lakes; (2) a smaller contribution of PAHs from coal combustion to western lakes than to central and eastern lakes; and (3) little or no CT sealcoat contribution to samples deposited prior to the beginning of widespread use of CT sealcoat in the 1950s.

CMB modeling results are sensitive to uncertainty in input data, but uncertainty is not well defined for most sources or consistently defined among sources. The compilation of sources by Li et al. (2003) computes a mean and standard deviation (SD) for each source type

from data from various studies, thus SD is dependent on the number of studies evaluated (zero if only one study) and on variations in study design, sampling methods, etc., in addition to differences in specific sources tested within the source type. Lacking a consistent measure of uncertainty, we followed the approach of Li et al. (2003) and used an uncertainty of 40% for all source profiles. In contrast, the lake sediment data were collected by a single study and analyzed using consistent methods (Van Metre et al., 2004). Uncertainty for receptor profiles was estimated using the mean relative percent difference for each of the 12 PAHs and for Σ PAH from 41 duplicate samples (Van Metre, unpublished data; presentation of some median values in Van Metre et al., 2004). Lake sediment data used for modeling are in Supplementary Information Tables S2 and S3.

3. Results

3.1. Source profiles

PAH source profiles were compiled and correlated to one another and to the mean lake–sediment PAH profile for the 40 lakes and for subsets of lakes. This analysis provides insight into which sources are most likely to be important contributors of PAHs to the lake sediments (i.e., those that have the greatest statistical similarity to the lake profiles) and helped to guide the choices of sources to include in models. Chi-square (Table 2) and Pearson correlation (Supplementary Information, Table S4) were used to quantitatively evaluate similarity between source and lake–sediment profiles. Chi-square was calculated as the square of the difference in proportional PAH concentrations divided by the mean of the two values, summed for the 12 PAH; the lower the X^2 , the more similar the two profiles. The sources with PAH profiles that are most similar to the mean profile for the 40 lakes (Fig. 2; Table 2) are SC–Austin ($r=0.97$; $X^2=0.049$), SC–dust ($r=0.94$; $X^2=0.067$), and SC scrape Austin ($r=0.94$; $X^2=0.046$). Correlations to profiles of some vehicle-related sources also are strong (e.g., traffic tunnel air, $r=0.67$; $X^2=0.088$). Correlation coefficients are lowest and X^2 values highest between the mean lake–sediment profile and residential coal combustion, used motor oil, and diesel particles.

3.2. Model performance

The CMB model was run more than 200 times using various combinations of source profiles, fitting parameters (PAHs), estimates of uncertainty, and combinations of lake–sediment samples. At least one individual source representing each of five general source categories (Table 1) was included in most of the model runs. Models tested used 12, 11 (excluding Phe), or 10 (excluding Phe and An) PAHs as fitting parameters. Phe and An were omitted from some models because 3–ring PAH are more soluble and volatile than higher molecular weight PAH and might, therefore, be lost between source and receptor. This instability was confirmed for Phe (but not An) by the frequent overestimation of Phe by the model (Fig. 3); similar results were reported by Li et al. (2001).

Four models (A through D) were chosen from the over 200 models tested on the basis of good quantitative and qualitative model performance (Table 3). These four models are in general agreement with the vast majority of the 200 models tested in terms of the relative importance of the five major source categories. All four have good model performance on the basis of X^2 , R^2 , and percentage of Σ PAH mass estimated, and all had no failures to converge on the 120 samples from the 40 lakes. With the exception of the overestimation of Phe, the models reasonably reproduced the PAH profile (Fig. 3). All four models use the traffic tunnel air profile to represent vehicle sources and the average coal profile (Li et al., 2003) to represent coal combustion. The distinctions between these models are in the profiles used to represent CT sealcoat and in the number of PAHs used for fitting. The mean dust profile from CT

Table 2
Chi-square difference between source and receptor (lake sediment) profiles. Source references are given in Table 1. Values less than 0.1 (indicating close match to source profiles) are in bold. [highest SC, having the highest contribution from coal–tar–based sealcoat; lowest SC, having the lowest contribution from coal–tar–based sealcoat; CT, coal–tar–based; SC–dust, CT–sealcoated pavement dust, six cities; SC scrape, sealcoat scraping; SC–Austin, CT–sealcoated pavement dust, Austin, TX].

Source category	Source	40 lakes, mean	Receptor (lake sediment)			
			31 central and eastern lakes, mean	9 western lakes, mean	10 highest SC lakes, mean	5 lowest SC lakes, mean
Coal combustion	Power plant emissions	0.33	0.35	0.31	0.33	0.43
	Residential heating emissions	0.78	0.79	0.77	0.77	0.81
	Coke oven emissions	0.16	0.17	0.15	0.21	0.16
	Coal average	0.19	0.20	0.18	0.21	0.23
Vehicle-related	Diesel vehicle emissions	0.61	0.62	0.60	0.58	0.70
	Gasoline vehicle emissions	0.20	0.21	0.18	0.19	0.24
	Traffic tunnel air	0.088	0.11	0.056	0.14	0.047
	Traffic average	0.19	0.21	0.16	0.20	0.22
	Used motor oil 1	0.85	0.89	0.77	0.94	0.69
	Used motor oil 2	0.75	0.78	0.69	0.78	0.70
	Tire particles	0.69	0.72	0.62	0.67	0.71
	Asphalt	0.28	0.32	0.20	0.34	0.20
	NIST diesel particles	0.90	0.92	0.87	0.88	0.97
Fuel–oil combustion	Fuel–oil combustion	0.59	0.60	0.57	0.62	0.53
Wood burning	Pine–wood soot particles	0.32	0.30	0.38	0.27	0.48
CTB sealcoat related	NIST coal tar	0.61	0.62	0.60	0.62	0.62
	CT sealcoat products	0.43	0.45	0.41	0.44	0.44
	SC scrape fresh	0.25	0.26	0.25	0.26	0.28
	SC scrape Milwaukee	0.27	0.28	0.29	0.26	0.37
	SC scrape Austin	0.046	0.043	0.078	0.029	0.14
	SC–dust	0.067	0.061	0.11	0.043	0.18
	SC–Austin	0.049	0.044	0.086	0.039	0.14

sealed lots in six central and eastern cities (SC–dust) was used in models A and B and the mean dust profile for samples from Austin (SC–Austin) was used in models C and D. Fitting for models A and C was based on all 12 PAHs and fitting for models B and D was based on 11 PAHs (Phe excluded). We use the averaged results of models A–D for interpretation and discussion of PAH sources to the 40 lakes and for analysis of trends in PAH sources to the eight lakes.

3.3. PAH sources to lakes

3.3.1. Recent sediment

Results of the CMB modeling indicate that CT sealcoat is the largest PAH source, on average, to these 40 U.S. lakes (Fig. 4), with a mean contribution of 50% of the total PAHs (Table 4; results for models A–D for 40 lakes are in Supplementary Information Table S5). The estimated mean fractional contribution and mean mass loading from CT sealcoat of about $50\% \pm 6\%$ and $10.9 \text{ mg/kg} \pm 0.5 \text{ mg/kg}$, respectively, are consistent among models. Mean fractional loading contributions from the vehicle and coal source categories are the second and third largest, contributing 23 and 17%, respectively (mean mass loadings of 2.4 and 2.7 mg/kg, respectively). Fuel–oil combustion and wood burning are minor PAH contributors.

There is a smaller difference between the mean fractional inputs from CT sealcoat and vehicle-related sources (50 and 23%, respectively) for the 40 lakes than between mean mass inputs (10.9 and 2.4 mg/kg, respectively). This is because fractional inputs are normally distributed whereas PAH concentrations and mass loading are log-normally distributed, and because source contributions are not evenly distributed over the range in PAH concentrations in the lakes. Lakes with low PAH concentrations tend to have high fractional vehicle inputs whereas lakes with high PAH concentrations tend to have high CT sealcoat inputs, resulting in a smaller difference between the mean fractional inputs from CT sealcoat and vehicle-related sources than between mean mass inputs.

Among individual lakes, there is wide variation in PAH concentrations and source contributions (Fig. 4). As a group, the 35 urban lakes have ΣPAH concentrations that are about 24 times higher than do the five lakes with large, mixed-land-use watersheds, and have a mean

fractional input from CT sealcoat of 53% compared to 24% for the large-watershed lakes. Vehicle-related sources contribute, on average, 20% of PAH to urban lakes and 47% of PAH to large-watershed lakes. There is a strong geographic gradient in mean mass contributions to urban lakes from CT sealcoat, increasing from 2.7 mg/kg in the western U.S. to 8.9 mg/kg in the central and 21 mg/kg in the eastern U.S. (Fig. 4). Total PAH concentrations and mass contributions from CT sealcoat are significantly higher in central and eastern urban lakes (tested separately and combined) than in urban western lakes but are not significantly different between central and eastern urban lakes or between western urban lakes and large-watershed lakes (Mann–Whitney U test; $\alpha > 0.95$).

3.3.2. Historical trends

Historical trends in PAH sources for the last 40 to 100 years were evaluated for eight lakes distributed across the U.S. (Figs. 1 and 5); the mean of results for the four models are presented here (results for individual models A–D for trend lakes are in Supplementary Information Table S6). The six new-urban lakes all have increases in PAH concentrations coincident with urbanization (Fig. 5), but there are large differences in ΣPAH concentrations among lakes, from a maximum of 0.19 mg/kg at CYN to a maximum of 95 mg/kg at Lake Killarney (KIL) (Supplementary Information, Table S3). In five of the six new-urban lakes, CT sealcoat is the principal contributor to the upward trends and is the largest source after about 1970. Vehicles, coal, fuel oil, and wood combustion sources generally are less important than CT sealcoat, except in the deeper parts of some cores that contain sediments deposited when urban land use was minimal and PAH concentrations were much lower. The largest PAH sources to the sixth new-urban lake, CYN near Los Angeles, are vehicles and coal combustion.

Trends in PAHs and PAH sources in the two lakes with older urban development, Lake Harriet (HAR) and Newbridge Pond (NEW), are somewhat different than in the new-urban lakes (Fig. 5). Large fractional contributions from coal are indicated to HAR and NEW in the middle of the 20th century (Supplementary Information, Table S3). Coal was replaced by contributions from CT sealcoat in the 1960s in both lakes.

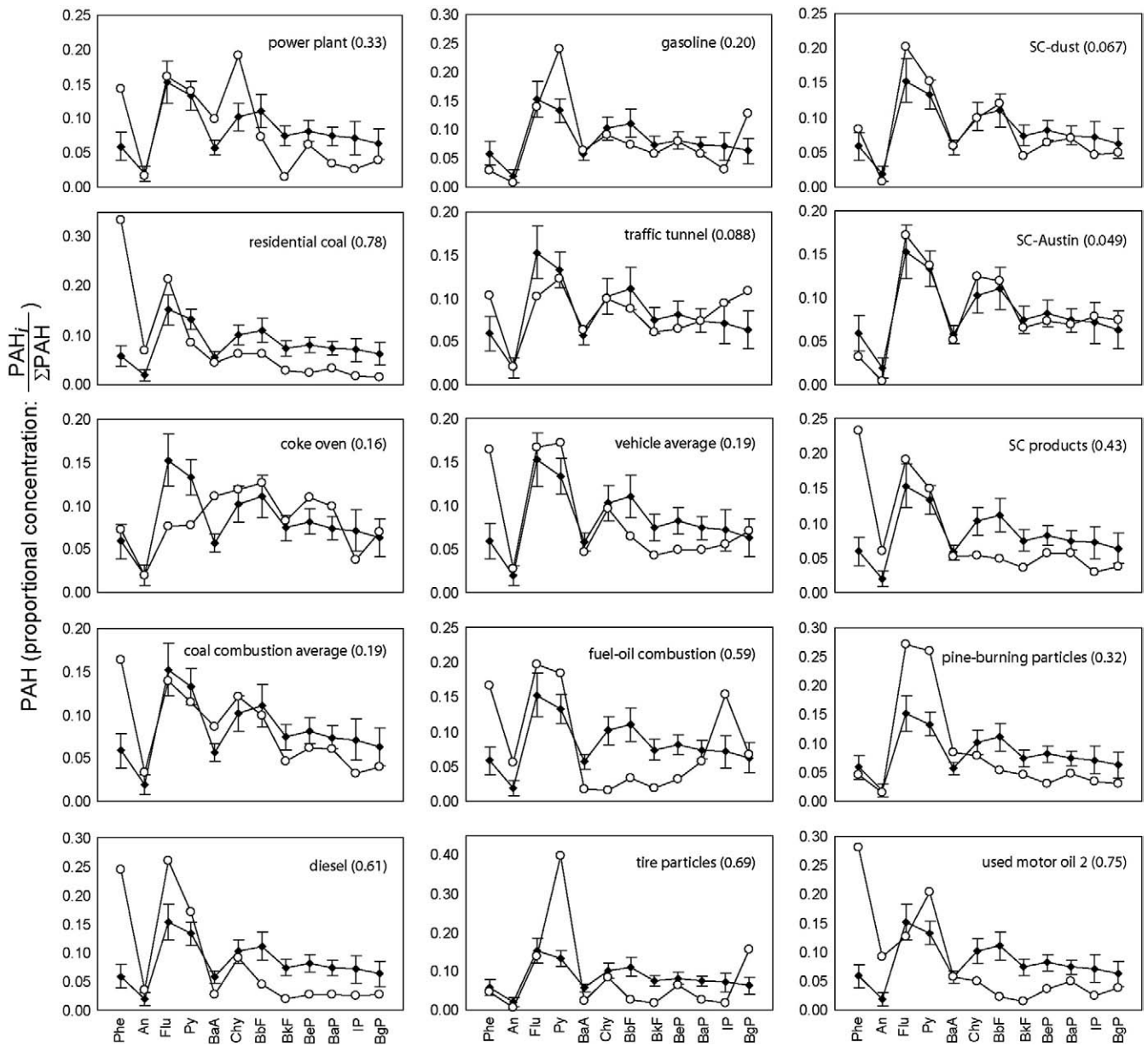


Fig. 2. Comparison of PAH profiles (from left to right along x-axis, low to high molecular weight) for various sources (○; Table 1) to the mean profile for 40 lakes (◆; uncertainty bars indicate the standard deviation). Chi-square statistic for each comparison shown in parentheses.

4. Discussion

4.1. Importance of coal-tar sealcoat as a PAH source

CMB receptor modeling of PAH sources indicates that CT pavement sealcoat is the largest source of PAHs to the majority of these 40 U.S. lakes, and on average accounts for about one-half of PAH loading. Lakes with higher PAH concentrations have significantly larger mass and fractional PAH loading from CT sealcoat than do lakes with lower PAH concentrations: the Spearman's rank correlation between Σ PAH concentration and mass loading from CT sealcoat is 0.98 (Fig. 6). The rank correlations between Σ PAH concentrations and fractional loading from CT sealcoat (0.58) and from vehicle sources (-0.51) are significant and inverse to each other, confirming that CT sealcoat is the more important source where PAH concentrations are higher and vehicles are the more important source where PAH concentrations are lower.

Large regional differences in PAH concentrations and PAH loading attributed to CT sealcoat are consistent with sealcoat product use patterns

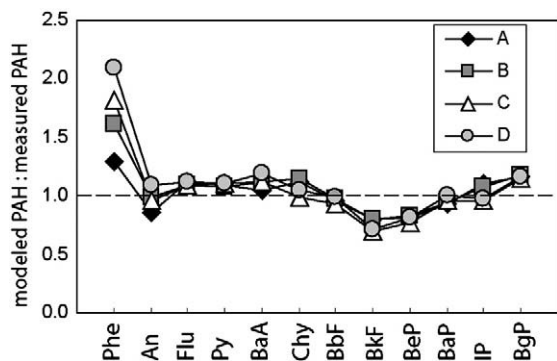


Fig. 3. The mean PAH profile for 40 lakes as determined by CMB models A to D. Dashed line indicates a 1:1 correspondence between modeled and measured mean value.

Table 3
CMB model performance and mass loading for individual PAH sources for four models. A blank field in mass loading indicates source was not entered in the model. [%Mass, percentage of ΣPAH mass estimated; SC-dust, coal-tar-based sealcoated pavement dust, six cities; SC-Austin, coal-tar-based sealcoated pavement dust, Austin, Tex.].

Model	No. of fitting PAH	Model performance			Mass loading by individual modeled source (mg/kg)					
					Coal-tar-based sealcoat		Vehicle	Coal	Oil	Wood
		R ²	X ²	%Mass	SC-dust	SC-Austin	Traffic tunnel air	Coal average	Fuel-oil burning	Pine-wood soot particles
A	12	0.93	0.94	0.99	10.4		4.41	0.94	0.24	1.10
B	11	0.95	0.62	1.04	11.1		3.75	2.51	0.36	0.16
C	12	0.95	0.65	1.00		11.6	0.54	3.11	0.75	1.19
D	11	0.96	0.54	1.02		10.6	1.01	4.28	0.61	0.87

(CT sealcoat in the central and eastern U.S., asphalt-based sealcoat in the western U.S.) and with measured PAH concentrations in dust from sealcoated pavement, which were about 1000 times higher in the central and eastern U.S. than in the western U.S. (Van Metre et al., 2009). Median ΣPAH concentrations in the 13 central U.S. urban lakes (9.31 mg/kg) and 14 eastern U.S. urban lakes (16.3 mg/kg) are about 6 and 10 times greater than the median concentration in the eight western urban lakes (1.58 mg/kg), and estimated mean sealcoat mass loading in the central and eastern lakes are 3.3 and 7.8 times greater than in the western lakes, respectively.

High PAH concentrations are not necessarily associated with density of urban land use or proximity to highways. The western urban lakes Tanasbrook Pond (TNB) in Portland, Ore., and Decker Lake (DEK) in Salt Lake City, Utah, have dense urban watersheds (population densities of 844 and 2,100/km², respectively, and a major highway in each) but low ΣPAH concentrations (1.34 and 0.76 mg/kg, respectively; means of the three samples used for modeling). In contrast, the watershed of Lake Anne (ANN) in

suburban Washington, D.C., has a population density of 2100/km², similar to that of DEK, but a ΣPAH concentration of 17.0 mg/kg, 22 times greater than that of DEK. The watershed of Palmer Lake (PLM) in suburban Minneapolis, Minn., has a population density of 939/km², similar to that of TNB, but a ΣPAH concentration of 34.1 mg/kg, about 25 times greater than that of TNB. Modeling results indicate that CT sealcoat contributes about 14 and 24 mg/kg of PAH to the sediment of ANN and PLM respectively, but contributes only 0.80 and 0.26 mg/kg to the sediment of TNB and DEK (Supporting Information Table S5). Thus loading from CT sealcoat appears to be a much stronger driver than urbanization or population density for elevated concentrations of PAHs in urban lake sediment.

Model results indicate that, in the absence of input from CT sealcoat, concentrations of ΣPAHs are very low: For the five lakes with 0–20% CT-sealcoat contribution, ΣPAH concentrations range from 0.093 to 1.40 mg/kg (median of 0.35 mg/kg) and the mean source profile for these lakes is most similar to that of the traffic tunnel air source (X²=0.047; Table 2). For the 10 lakes with the highest

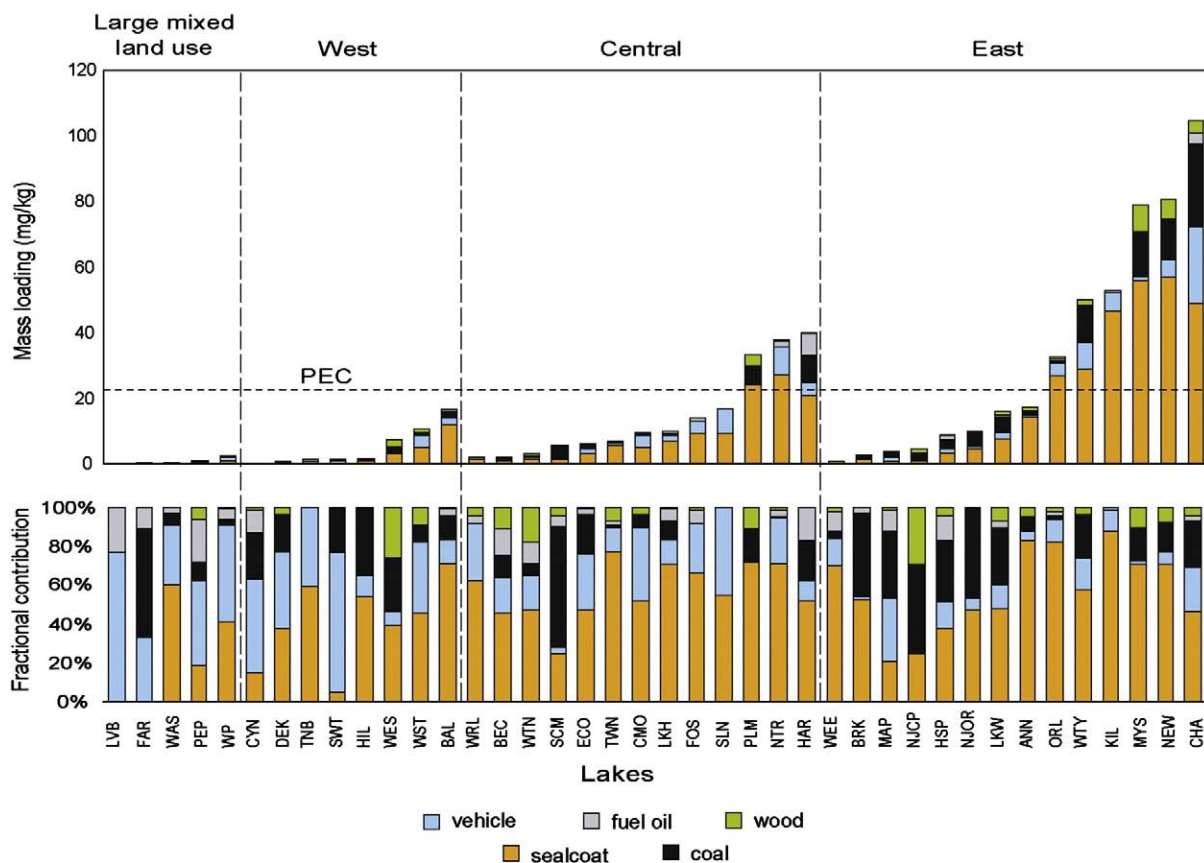


Fig. 4. PAH mass loading and fractional contribution from five source categories to ΣPAH (mean of four best CMB model runs). Lakes are grouped by region in order of increasing ΣPAH concentration. Horizontal dashed line indicates the probable effect concentration (PEC), the concentration of total PAH above which adverse effects to benthic biota are expected to occur (MacDonald et al., 2000).

Table 4

Summary of PAH mass loadings and fractional contributions to 40 lakes by source category estimated using the CMB model for four models (mean values for 40 lakes) and the mean for models A–D nationally and regionally.

Model	Mean mass loading by source category (mg/kg)					Mean fractional loading by source category				
	Sealcoat	Vehicle	Coal	Oil	Wood	Sealcoat	Vehicle	Coal	Oil	Wood
A	10.4	4.4	0.9	0.2	1.1	0.46	0.36	0.09	0.03	0.06
B	11.1	3.8	2.5	0.4	0.2	0.45	0.31	0.17	0.04	0.02
C	11.6	0.5	3.1	0.7	1.2	0.59	0.10	0.18	0.07	0.06
D	10.6	1.0	4.3	0.6	0.9	0.49	0.15	0.25	0.06	0.04
<i>National and regional summaries using mean of models A–D</i>										
Mean, 40 lakes	10.9	2.4	2.7	0.5	0.8	0.50	0.23	0.18	0.05	0.05
Std.dev., 40 lakes	0.5	1.9	1.4	0.2	0.5	0.06	0.12	0.07	0.02	0.02
5 large-watershed lakes	0.3	0.4	0.1	0.1	0.0	0.24	0.47	0.15	0.13	0.01
35 urban lakes	12.4	2.7	3.1	0.5	0.9	0.53	0.20	0.18	0.04	0.05
Western U.S. lakes	2.7	1.1	0.8	0.1	0.4	0.41	0.33	0.19	0.02	0.05
Central U.S. lakes	8.9	2.5	1.6	0.9	0.5	0.57	0.20	0.12	0.06	0.05
Eastern U.S. lakes	21.3	3.8	5.8	0.5	1.7	0.57	0.11	0.23	0.03	0.05

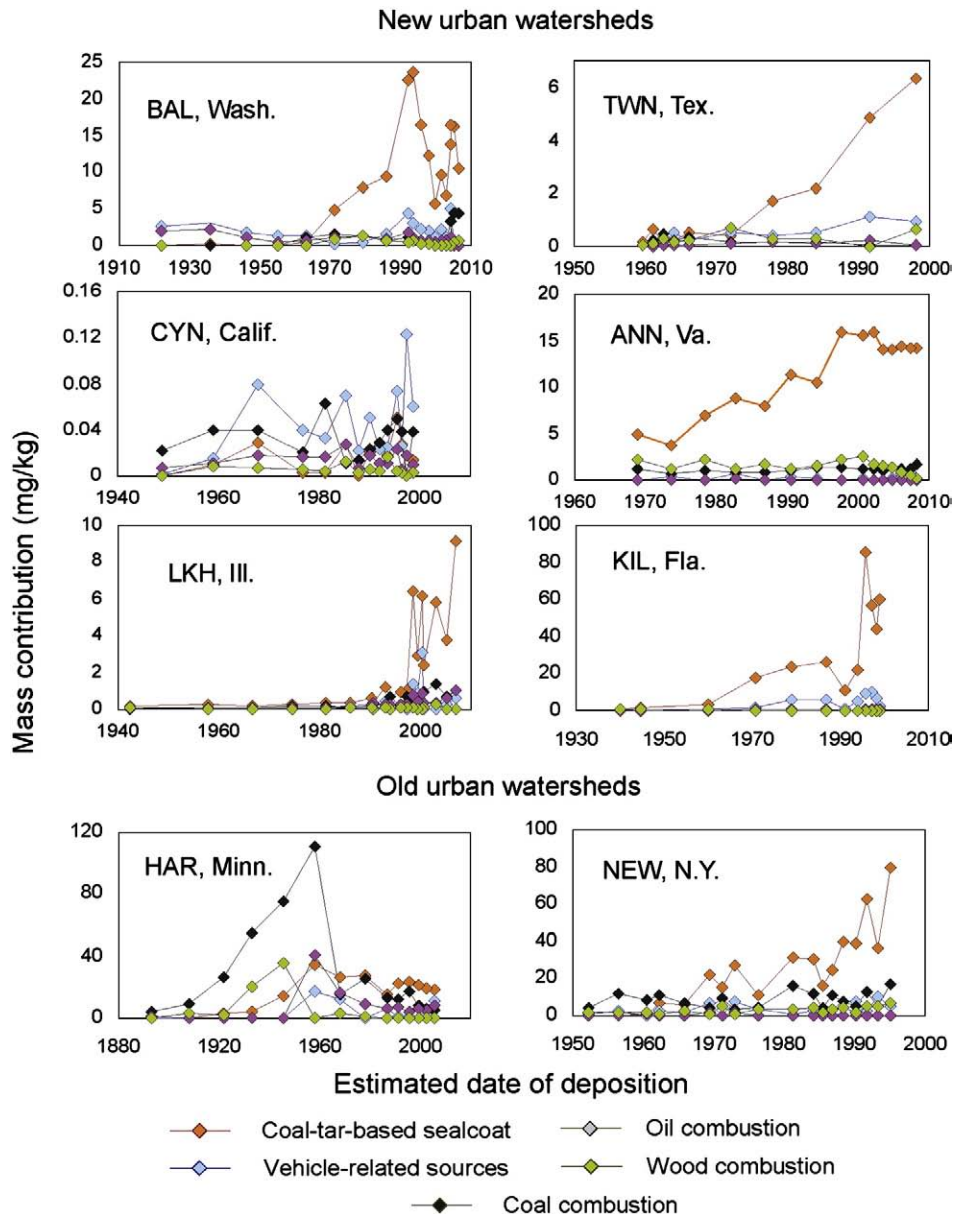


Fig. 5. Historical trends in mass contributions of Σ PAH from different sources to eight lakes; results are means from CMB models A–D.

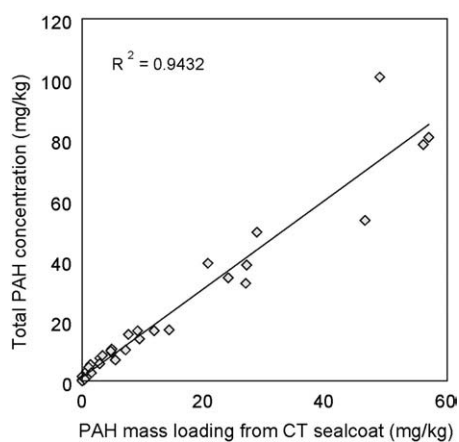


Fig. 6. Linear relation between mass loading of PAH from coal-tar-based sealcoat and total PAH concentration in 40 lakes.

fractional input from CT sealcoat (>70%), PAH concentrations are 6.9 to 81 mg/kg (median of 33 mg/kg) and the mean source profile for these 10 lakes is most similar to that of CT scrapings from Austin ($X^2 = 0.029$; Table 2). In the western U.S., despite limited use of CT sealcoat, fractional contributions from this source are in some cases relatively large even though the mass loading is small. This is because, where PAH concentrations are very low, even a small mass contribution from a source can translate to a large fractional contribution. Lake Washington (WAS), for example, has the fourth lowest Σ PAH concentration (0.40 mg/kg) and sixth lowest estimated CT sealcoat contribution of only 0.24 mg/kg, but this input comprises 60% of the Σ PAH.

PAH concentrations that exceeded a sediment-quality guideline for aquatic health were associated exclusively with lakes with high contributions from SC sealcoat. Mean Σ PAH concentrations in nine of the 40 lakes exceed the probable effect concentration (PEC; 22.8 mg/kg) indicating expected adverse effects on benthic biota (MacDonald et al., 2000) (Fig. 4). Of the 40 lakes, those same nine had the highest mass loading from CT-sealcoat (Fig. 4). Among the 120 individual samples from the 40 lakes used for modeling, 27 had Σ PAH concentrations that exceeded the PEC. For these 27 samples, the mean Σ PAH concentration, PAH mass loading from CT sealcoat, and fractional loading from CT sealcoat were 56 mg/kg, 37 mg/kg, and 67%, respectively. For the other 93 samples, these three values were 5.8 mg/kg, 3.2 mg/kg, and 45%, respectively.

The shift in the 1960s and 70s to CT sealcoat as the dominant source of PAHs in seven of the eight lakes analyzed for trends (Fig. 5) is in agreement with industry internet sites that report that CT sealcoat use began in the 1950s (Glacier Asphalt, 2010; JDK Pavement Maint, 2010). Large contributions from coal to the two older urban lakes (HAR and NEW) in the middle of the 20th century were replaced by contributions from CT sealcoat in the 1960s (Fig. 5); this is consistent with a report that, in 1940, 55% of American homes were heated with coal and another 23% used wood, but both uses “had virtually disappeared” by 1970 (U.S. Department of Commerce, 1997). Small contributions from CT sealcoat to some samples that predate the 1950s (KIL and HAR, Fig. 5) might be incorrect – PAH concentrations in these samples are low, and in most of them the uncertainty in the estimate of CT-sealcoat contribution exceeds the contribution. Very low Σ PAH concentrations (0.027–0.19 mg/kg, Supplementary Information Table S6), which result in an increase in analytical uncertainty, might also affect model results in some samples from CYN for which the model indicates coal as the largest PAH source (Fig. 5).

Various combinations of sources, other than those used in models A–D, were tested in other models. Replacing the traffic-tunnel air profile with profiles representing particulate emissions from gasoline-

and diesel-powered vehicles resulted in vehicle contributions in the same range as those estimated in models A–D. Replacing the average coal-combustion profile with profiles representing power-plant emissions and residential coal combustion produced similar coal contributions to those estimated by model A but lower than those estimated by models B–D. These other models resulted in similar or greater contribution of PAHs from CT sealcoat relative to those estimated by models A–D. Several other sources – tire particles, used motor oil, coke-oven emissions, and asphalt – were included in model runs. Tire particles, used motor oil, and asphalt resulted in no source contribution to any lake (tire particles) or negligible source contribution to only a few lakes (used motor oil and asphalt), and most models using these sources had multiple failures to converge. Modeled inputs to lakes from coke ovens were highly variable and not correlated to locations of active coking plants (only five of the 40 lakes are within ~200 km of active coking plants; U.S. EPA, 2009). Emissions from power boats were not included in any of the models but are unlikely to be an important source of PAHs to lake sediments: emissions from power boats were shown to be a PAH source to the water column but not the bottom sediment in one of the lakes studied here (Las Vegas Bay of Lake Mead [LVB]) (Rosen and Van Metre, 2010), and power boats are not allowed on many of the small urban lakes included in this study. The very low concentrations of PAHs in undeveloped reference lakes relative to those in most urban lakes (Van Metre and Mahler, 2005) indicates that natural sources are not important PAH contributors to urban lakes.

4.2. Effects of weathering on PAH profiles

One assumption of source-receptor modeling is that the chemical species in question do not react with each other or undergo transformation between source and receptor. PAH profiles often are measured at the source (e.g., tail-pipe emissions from vehicles [Rogge et al., 1993a]) and data generally are not available to evaluate weathering alteration of the profile in the environment. By weathering we mean changes in the proportional PAH profile resulting from volatilization, photolysis, desorption, and chemical degradation. For CT sealcoat, however, weathering can be evaluated by comparing PAH profiles through a progression from the NIST coal-tar standard (NIST, 1992), CT-sealcoat products (Mahler et al., 2005), scrapings of fresh and weathered CT-sealcoat from pavement, and dust from pavement with CT-sealcoat (Mahler et al., 2004; Van Metre et al., 2008).

When PAH profiles of the NIST coal-tar standard, CT-sealcoat products, and CT-sealcoat scrapings are compared graphically and statistically, a logical progression is evident (Fig. 7a). Weathering, likely dominated by volatilization from the pavement, effectively rotates the profile counter-clockwise, with proportional decreases on the left (low molecular-weight compounds) and increases on the right (high molecular-weight compounds) pivoting around three 4-ring PAHs in the center: Flu, Py, and BaA. Statistical comparison to the profile of the NIST coal-tar standard indicates progressive weathering from the SC product ($r = 0.99$, $X^2 = 0.035$), to SC scrape fresh (1 week after sealing) ($r = 0.94$, $X^2 = 0.10$), SC scrape Milwaukee ($r = 0.91$, $X^2 = 0.16$), and SC scrape Austin ($r = 0.50$, $X^2 = 0.50$). These changes indicate that aging of the sealcoat and exposure to a hotter climate can cause proportional shifts in the PAH profile favoring high molecular-weight PAH. Additional weathering is indicated from the scrapings to the dust. SC-dust and SC-Austin have weathered to the point that their profiles no longer are significantly related to that of the NIST coal-tar standard ($r = 0.53$, $X^2 = 0.48$ and $r = 0.13$, $X^2 = 0.81$, respectively), demonstrating that the NIST coal-tar standard would not be an appropriate choice to represent a CT-sealcoat source in source-apportionment modeling.

Profiles for SC-dust and SC-Austin, the two CT-sealcoat dust profiles used in the models presented here, are similar to that for SC-Austin scrapings, the most weathered profile among those shown on

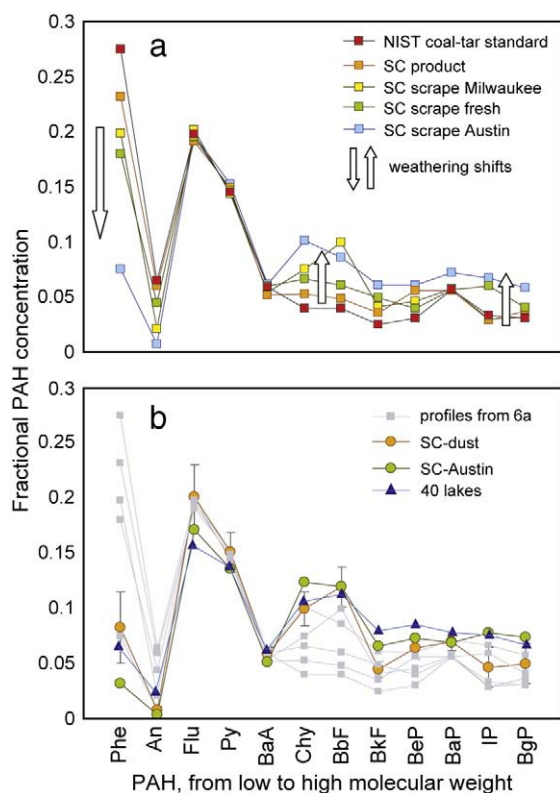


Fig. 7. PAH profiles indicating progressive weathering from (a) NIST standard for coal tar, coal-tar-sealcoat products, and coal-tar-sealcoat scrapings, to (b) dust from coal-tar-sealcoated pavement and mean profile for all 40 lakes. Weathering is indicated by a downward shift of low molecular-weight PAHs and an upward shift of high molecular-weight PAHs. [see Table 1 for PAH source definition].

Fig. 7a, and also are similar to the mean profile for the 40 lakes (Fig. 7b). Further, the two dust profiles closely match the mean profile of the 10 lakes with the highest contribution from CT-sealcoat (X^2 of 0.043 and 0.039, respectively; Table 2). The strong correlation between the SC-Austin and SC-dust profiles and profiles of these 10 lakes indicates that relatively little weathering of PAHs occurs during transport and deposition and burial of lake sediment.

4.3. Comparison to other PAH source assessments

Numerous investigators have used source-receptor modeling to identify the principal sources contributing PAHs to lake sediments and to quantify their contributions (e.g., Christensen et al., 1997; Rachdawong et al., 1998; Simcik et al., 1999; Li et al., 2001; Li et al., 2003; Bzdusek et al., 2004; Christensen and Bzdusek, 2005; Sofowote et al., 2008). The sources most frequently identified were coke-oven emissions and vehicle-related sources. In all of the examples cited here, a model was applied to only one or a few nearby sites; all of the sites were located in the Great Lakes region of the U.S., where there was historical use of coke ovens; and most of the sites were affected by industrial point sources. In our analysis of 40 urban U.S. lakes, however, coke-oven emissions were not identified as an important source of PAHs; although a coke-oven profile (Li et al., 2003) was included in some of the model runs, it was not retained in any of the four best models. Of the 40 lakes presented here, only five are within about 200 km of at least one of the 25 U.S. coking plants active in 1999 (U.S. EPA, 2009). Of these five lakes, Lake in the Hills (LKH; northwest of Chicago) is the most likely to be affected by coke-oven emissions, as it is within about 75–115 km of the five active coking plants in the

Chicago area. However, historical PAH concentrations in LKH (Fig. 5) indicate negligible PAH loading prior to the onset of urbanization of the watershed in about 1990, despite the long history of coking and coal gasification in Chicago (U.S. EPA, 2007). Inclusion of coke-oven emissions in the CMB model for LKH resulted in only an 8% contribution, less than uncertainty, indicating that atmospheric transport and deposition of PAH from coking to LKH are insignificant. It seems unlikely, therefore, that coke-oven emissions are a dominant source of PAHs to lakes unless a lake is in close proximity to coking facilities or downstream from point-source discharges.

The other major source identified by most previous source-apportionment modeling studies – vehicles – is in agreement with the results presented here. The contribution from vehicle-related sources to the 40 lakes, which included, in various runs, traffic-tunnel air, diesel-vehicle emissions, gasoline-vehicle emissions, tire-wear particles, and used motor oil, ranges from 0 to about 75%, and is the second most important source after CT sealcoat.

Results from the CMB approach for one of the lakes presented here can be compared to those obtained using a very different approach to source apportionment – petrographic analysis. Yang et al. (2010) used organic petrography to identify various carbonaceous materials (e.g., soot particles, coal, coal-tar-pitch, asphalt and bitumen) in pavement dust, soils, and aquatic sediment in the Lake Como (CMO) watershed; CMO is one of the 40 lakes to which we applied the CMB model. Yang et al. estimated that 99% of the PAHs in dust from CT-sealcoated parking lots were from coal-tar pitch. In dust from nearby unsealed parking lots and commercial soils, 92 and 88% of PAH, respectively, were from coal-tar pitch (Yang et al., 2010), indicating off-site transport by vehicle tracking and wind. Coal-tar pitch was estimated to account for 71% of PAH in stream-bottom sediment upstream from Lake Como and 84% of PAH in recent sediment (0–5 cm interval) from a sediment core from Lake Como (Yang et al., 2010). The CMB model (applied to samples from a different sediment core than that analyzed by Yang et al., 2010) indicates that, for recently deposited CMO sediment, 52% of PAH is from CT sealcoat and 38% from vehicles. The results from the two approaches are in reasonable agreement, especially given the independence of the approaches and the uncertainties involved.

4.4. Implications

Inclusion of CT sealcoat among potential PAH sources in receptor modeling demonstrates that this previously unconsidered source is a major contributor of PAHs to urban lakes across the United States. This result is supported by correlations between potential sources and PAH profiles in lake sediment and by regional and temporal patterns in PAH loading. Many lakes with large fractional contributions of PAHs from CT sealcoat are in watersheds that have undergone urban sprawl, are characterized by residential and commercial development, and have rapid increases in PAH concentrations. These rapid increases and the predominance of CT sealcoat as a source to the 40 lakes lead us to conclude that CT sealcoat likely is the primary cause of upward trends in PAHs in response to urban sprawl in much of the United States.

Supplementary materials related to this article can be found online at doi:10.1016/j.scitotenv.2010.08.014.

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