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

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A R T I C L E I N F O

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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.

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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/km^2.

Thirty-five of the 40 lakes have relatively small drainage basins (most <100 km^2, 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 km^2) 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, ^{137}Cs, ^{210}Pb, 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 ^{137}Cs 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 ^{210}Pb 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 ^{137}Cs profile and the pre-lacustrine sediment interface, and for cores from the natural lakes was the ^{210}Pb profile and the constant rate of supply model (Appleby and Oldfield, 1992). Age dating based on the ^{137}Cs 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 ^{210}Pb dating models, and because the constant rate of supply model requires that the full excess ^{210}Pb inventory be sampled (100+ year time frame). Dates were assigned to individual samples between date-depth markers or using ^{210}Pb 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