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# Modeling and evaluating spatial variation of polycyclic aromatic hydrocarbons in urban lake surface sediments in Shanghai☆

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ABSTRACT

To explore the influence of rapid urbanization development on the accumulation of 16 priority PAHs in urban environment, thirty-three surface sediments from city lakes in different urbanized areas of Shanghai were collected to evaluate the occurrence characteristic and source apportionment of PAHs. The concentrations of $\Sigma_{16}$PAHs in lake surface sediments ranged from 55.7 to 4928 ng $g^{-1}$ with a mean value of 1131 ng $g^{-1}$ (standard deviation, 1228 ng $g^{-1}$), of which 4-, 5- and 6-ring PAHs were the dominant components. Spatial distribution of PAHs in lake surface sediments showed a significantly declining trend along with a decreasing urbanization gradient (one-way ANOVA, $p < .05$). Two hotspots of sediment PAHs were mainly distributed at highly urbanized areas with intensive population density and heavy traffic activities and at burgeoning industrial towns in the suburb. Source apportionment of total PAHs identified by a constrained positive matrix factorization model revealed that vehicle emission and combustion of coal, biomass and natural gas were the absolutely predominant sources, respectively accounting for 55.0% and 40.45% of total PAHs burden in lake sediments. Land use regression (LUR) models were successfully developed to evaluate spatial variation of PAHs contamination in urban sediments based on their significant correlations with residential land, commercial land, traffic variables, industrial sources, and population density. All PAH compounds showed strong associations with one or two source indicators (the traffic congestion index and the number of industrial sources), with the fitting $R^2$ varying from 0.529 to 0.984. Our findings suggest that energy consumption related to land use activities obviously promoted PAH accumulations in urban sediment environment during rapid development of urbanization and industrialization in Shanghai.



## 1. Introduction

By 2050, two out of every three people in the world will live in cities (UN, 2012). As an important social, economic and cultural center, urban area has a profound impact on the environment, and the enormity and scale of human impacts and the flux of chemicals into the environment in urban regions are extremely large (Lyons and Harmon, 2012). In 1990, the term “urban geochemistry” was defined as “the interface of environmental geochemistry and urban pollution”, and recently it has become a scientific discipline “frontier” (Wong et al., 2006; Jartun and Ottesen, 2011). Within the scope of urban geochemistry, one of the most important urbanization characteristics is the impervious surface. Through the urbanization process, dramatic modification of land cover, especially the increase in impervious surfaces lead to hydrological, physicchemical, environmental and ecological perturbations in the urban system. Urban stormwater ponds/artificial lakes are developed to receive urban runoff and mitigate stormwater impacts. Therefore, in an urban area, stormwater runoff passes through the impervious surface areas, such as roofs, streets and parking lots, carries all kinds of pollutants, such as nutrients, trace metals, oil, salts, and persistent organic pollutants (POPs) into the city lakes (Wong et al., 2006; Tixier et al., 2011).

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Polycyclic aromatic hydrocarbons (PAHs), a family of chemical compounds having at least two condensed benzene rings, are well-known as a class of toxic, mutagenic, and carcinogenic organic contaminants with widespread concern in modern times. Intensive anthropogenic activities in urban areas have released massive gaseous and particulate PAHs into the atmosphere mainly by the pyrolytic processes such as fossil fuel combustion, biomass burning, waste incineration, coke production, etc (Zhang and Tao, 2009). Subsequently experiencing atmospheric diffusion and deposition, PAHs were ubiquitously concentrated in various urban media such as water, sediments, soils, dusts and organisms (Andersson et al., 2014; Jang et al., 2013; Liu et al., 2016; Wang et al., 2013; Yang et al., 2017; Zheng et al., 2016). The risk assessment of PAHs contamination based on numerous indexes revealed high incidence of biological toxicity and human health damage by ingestion, dermal contact and inhalation in highly urbanized areas (Cao et al., 2010; Liu et al., 2016; Wang et al., 2013). As a crucial sink of PAHs, sediment in urban park lakes can serve as a reliable medium to evaluate their pollution level and potential source (Andersson et al., 2014; Guo et al., 2010; Van Metre and Mahler, 2010).

So far, numerous studies focused on source apportionment based on positive matrix factorization (PMF) receptor model to identify and quantify source profiles and contributions of PAHs in various environmental media from the perspective of emission control (Bullock et al., 2008; Manousakas et al., 2017; Van Metre and Mahler, 2010; Xue et al., 2016; Yang et al., 2013). However, few attentions has been paid to factors influencing the emission and distribution of PAHs, including land use, population migration, industrial layout and energy structure (Machado et al., 2014; Huang et al., 2017; Zhang et al., 2017). Recently, some researchers have successfully utilized land use regression (LUR) model to evaluate the spatial distribution of PAHs in urban vegetations and airborne particulates by extracting high-resolution urbanization characteristics (e.g., land use, socioeconomic and traffic data) around sampling sites (Noth et al., 2011, 2013). Until now, no LUR study was conducted to model the spatial distribution of PAHs in urban lake sediments. More investigations should be carried out on the influence of urbanization characteristics on PAH accumulations in urban media, such as the changes of PAH inventories in lake sediment related to land use and energy consumption (Andersson et al., 2014; Yan et al., 2014).

As an industrial and economic center in China, Shanghai has experienced rapid urban sprawl and industrial town buildup in the last 30 years, accompanying large-scale land use change with vast agricultural land replaced by industrial, residential and commercial land (Zhao et al., 2006). According to the statistics in 2015 (Shanghai Statistics Bureau, 2015), the average population density in Shanghai was 3809 individuals·km$^{-2}$ with the urbanization rate up to 90.3%, and the average GDP per capita was 103795 RMB with an increasing rate of 11.7% since the early 1990s. However, rapid economic growth in Shanghai was at the cost of massive energy consumption with an increasing rate of 5.02% from 3.19 million tons of standard coal in 1990 to 11.39 million tons in 2015 (Shanghai Statistics Bureau, 2015). Previous studies inferred that the enrichments of PAHs in urban air, soils, dusts and river sediments were closely related with land use pattern, population expansion, economic growth, and energy consumption in Shanghai (Liu et al., 2016; Wang et al., 2013, 2016b; Zheng et al., 2016). The present study aims to examine the spatial distribution and identify the major sources of PAHs in urban lake sediments, as well as to evaluate the influence of urbanization on PAHs contamination by using a LUR model.

## 2. Materials and methods

### 2.1. Samples collection and pretreatment

Thirty-three sediment sampling sites were selected from numerous park lakes in Shanghai considering the discrepancy of urbanization gradient and less disturbance of anthropogenic activities (e.g., dredging). As shown in Fig. 1, these sampling sites were located at four different urbanized areas divided by population density based on the sixth population census in 2010, five sites of which came from the central urban core area (CUC, 28600 individuals·km$^{-2}$) inside the inner-ring highway, six from the developed urban area (DDU, 18400 individuals·km$^{-2}$) between the inner- and middle-ring highway, five from the developing urban area (DIU, 12000 individuals·km$^{-2}$) between the middle- and outer-ring highway, and seventeen from the suburban area (SU, 1939 individuals·km$^{-2}$) outside the outer-ring highway.

In July 2012, a representative surface sediment (0–5 cm in depth) sample was collected by mixing samples from eight to ten random sites in each lake, using a grab sampler (XDB0201, New Landmark). All samples were immediately taken to our laboratory, freeze-dried, ground and sieved into 200-mesh particles and finally stored at −20 °C for further analysis.

### 2.2. Analytical methods

The 200-mesh sediment samples (3–4 g) were extracted with mixed solvents of dichloromethane and acetone (1:1, V/V) by an accelerated solvent extractor (ASE350, Thermo Fisher) at a temperature of 100 °C and a pressure of 1500 psi. Before extraction, approximately 2 g diatomaceous earth and 0.5 g copper powders were added for dispersing samples and removing element sulfur, respectively. The extract was spiked with 200 ng of surrogate standard (terphenyl-$d_{14}$) as a recovery indicator. The further clean-up procedure was performed by a rotary evaporator and a silica-alumina column, and detailedly listed in our previous study (Liu et al., 2016). Before instrument analysis, 200 ng mixture of internal standards (naphthalene-$d_8$, acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, chrysene-$d_{12}$, and perylene-$d_{12}$) were added to the final sample extracts for quantitative analysis.

The 16 priority PAHs set by the US environmental Protection Agency (EPA) were measured by using a gas chromatograph-mass spectrometer (GC 7890B-MS 5977A, Agilent) equipped with a HP-5ms quartz capillary column (30 m × 0.25 mm × 0.25 μm): naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[*1, 2, 3-cd*]pyrene (InP), dibenz[*a, h*]anthracene (DahA), benzo[*ghi*]perylene (BghiP). The oven temperature program was set as follows: initial temperature of 55 °C was held for 2 min, increased to 280 °C at a rate of 20 °C/min, and then increased to 300 °C at a rate of 3 °C/min holding for 4 min. The injection volume was 1 μL in splitless mode. Under the selective ion monitoring mode, the ion source and quadrupole temperature of MS detector were 320 °C and 150 °C, respectively.

The basic physical-chemical parameters of surface sediments, including total organic carbon (TOC), organic materials (loss on ignition, LOI), pH value and particle size distribution, were also analyzed (Table S1, "S" means the Supporting Information here and thereafter). In brief, TOC was measured by using a total organic analyzer (TOC-LCPN, Shimadzu). LOI represented the weight loss of the dried sample after combustion for 6 h at 500 °C in a muffle