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Characterization and source identification of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (PAHs) in different seasons from Shanghai, China

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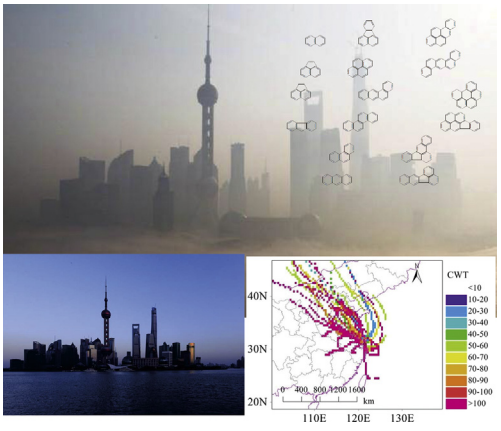
HIGHLIGHTS

- $PM_{2.5}$ concentrations were obviously higher than US air quality standards.
- PMF identified traffic emissions as the major source of $PM_{2.5}$-bound PAHs.
- The relationship between $PM_{2.5}$ and PAHs was positive.
- ILCRs indicated high cancer risks in autumn and winter.
- HYSPLIT showed monsoon greatly influenced the $PM_{2.5}$ concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

$PM_{2.5}$ samples in four representative periods were collected from a highly industrialized district in Shanghai, China. The concentrations of $PM_{2.5}$ and $PM_{2.5}$-bound PAHs were analyzed. Positive matrix factorization (PMF) model was used to identify the potential sources. Relationship between PAHs distribution and meteorological parameters was assessed meanwhile. The incremental lifetime cancer risks (ILCRs) model was applied to quantitatively evaluate the exposure risk of PAHs. Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLT) model was used to track the potential pollution area of $PM_{2.5}$ along with a Potential Source Contribution Function (PSCF) and Concentration Weighted Trajectory (CWT) methods. The results showed concentrations of $PM_{2.5}$ and PAHs ranged from 14.83 to 185.58 μg/m^3, 2.58 to 123.62 ng/m^3, respectively. The source apportionment model indicated that traffic emissions were the most important sources in each sampling season, which accounted for 38.44%, 34.48%, 39.04% and 45.03%, respectively. Spearman correlation coefficient showed that PAHs had negative correlation with ambient temperature and relative humidity in some periods, while had no significant correlation with atmospheric pressure and visibility. The average estimated lifetime cancer risk for total PAHs reached 4.7×10^{-5}, 4.5×10^{-5} and 4.1×10^{-5}, 4.0×10^{-5} to exposed children and adults in winter and autumn, respectively, meaning that $PM_{2.5}$-bound PAHs had high potential risk. HYSPLIT model suggested that monsoon greatly influenced the air quality in both winter and autumn.

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1. Introduction

PAHs are a class of hundreds of individual compounds defined to be composed of two or more fused aromatic rings. PAHs are released into the ambient air through the incomplete combustion of organic materials, including fossil fuel burning, motor vehicle emissions, waste incineration, oil refining, the coke and steel industry and coal combustion (Hedberg et al., 2005; Callén et al., 2014). Due to their toxic, mutagenic and carcinogenic properties, sixteen PAHs have been identified as priority pollutants by United States Environmental Protection Agency (US EPA) and seven of them are considered as the strongest known carcinogenic compounds (Cancer, 1995). PAHs are very hydrophobic and tend to bind on particles (Cai et al., 2007). Due to their resistance to degradation processes, especially when bound on particles, they are subjected to the long-range transport and could be detected even in remote areas.

PAHs associated with $PM_{2.5}$ (particulate matter in the air that is <2.5 μm in aerodynamic diameter) are of special concern because, when inhaled, $PM_{2.5}$ can effectively penetrate into the respiratory system and deposit deep in the bronchioles and alveoli of the lungs (Li et al., 2010), causing lung diseases, heart diseases and premature death. Thus, it is imperative to analyze the concentration, potential sources and assess the health risk of $PM_{2.5}$-PAHs in order to efficiently control air pollution caused by fine particulate matter.

The research of source apportionment is the essential to better understand pollution processes, several methods have been conducted to identify the source, such as chemical mass balance model (Li et al., 2003; Xue et al., 2010), molecular diagnostic ratio (MDR) (Katsoyiannis and Breivik, 2014), UNMIX model (Jain et al., 2018) and factor analysis with nonnegative constraints (Chen et al., 2012). As a receptor model, PMF was broadly used in the absence of chemical profiles of potentially contributing source (Wang et al., 2016a,b). MDR and PMF model revealed that coal combustion and vehicle sources were dominant PAHs sources in Shanghai urban soil (Wu et al., 2017). Wang et al. (2016a,b) evaluated quantitative source apportionment of $PM_{2.5}$-associated PAHs from Shanghai city and revealed coal combustion, and traffic emission with contributions of 34.9%, 27.5%, respectively.

Frequent exposure to $PM_{2.5}$-bound PAHs may lead to potential long-term adverse cancer risk. Numerous researches on the toxicity and cancer risk of PAHs for human have been conducted in western countries (Ravindra et al., 2011); however, studies on ILCRs about $PM_{2.5}$-bound PAHs for population groups are relatively scarce in urban China. Wu et al. (2017) reported the exposure health risk of PAHs pollution in Shanghai urban soil and indicated the potential health risk by ILCRs modeling. Jia et al. (2018) investigated the ILCRs values of six vegetables from Shanghai for different groups were ranged from 4.47×10^{-7} to 6.39×10^{-5} and most of values were higher than the acceptable risk level. The health risk assessment of PAHs in soils and crops in industrial areas of the Yangtze River Delta region indicated higher risks than Beijing, Lisbon, Taiyuan, and Korea (Wang et al., 2017). Zheng et al. (2016) reported the toxic equivalent concentrations PAHs in Shanghai road dusts with a mean of 2.44 μg/g. To our best of knowledge, the risk assessment of $PM_{2.5}$-bound PAHs in Shanghai is rare and the result is unclear.

Shanghai as one of the largest commercial and industrial city in China has serious atmospheric environmental problems because of the rapid urbanization and industrialization process. Much attention has been paid to this trouble. Although there were lots of studies on particulate PAHs in Shanghai, most of those studies focused on concentration, characteristics and potential sources with less attention given to the influence of meteorological conditions in Shanghai and cancer risks of $PM_{2.5}$-bound PAHs exposure are not expressly comprehended. Thus, the major objectives of this study were to (1) analyze the concentration of $PM_{2.5}$ and PAHs compounds in detail and identify potential PAHs sources using PMF model in four seasons; (2) clarify the relationship between $PM_{2.5}$-bound PAHs concentrations and meteorological conditions based on correlation studies; (3) evaluate the human health risks for PAHs exposure via inhalation, ingestion and dermal contact; (4) adopt HYSPLIT model to simulate the backward trajectories of $PM_{2.5}$ to analyze the potential pollution source areas (PPSA).

2. Experimental materials and analysis

2.1. Sampling site

The sampling site (SS) is located on the rooftop of Zihuan science building (five-storey, about 16 m above ground) at the East China Normal University in Minhang district of Shanghai, around which there were no barrier and outlet. As shown in Fig. 1, this sampling site is about 28 km far from the center of urban district, People square. The nearest main road is about 290 m away from the sampling site on the east with moderate traffic load. Another road under repair is 450 m away from the north of the site. In addition, the nearest highway on the west is 1.8 km away from the site and used by both heavy track and light vehicles. The sampling site is surrounded by residential communities in its northwest and southwest, by educational area in the east, by high-tech companies at south. In the North, there are industrial areas such as Wujin chemical factory (WF) and Wujin heat and power plant (WH). The campus weather station (WS) was 80 m at the southeast side of the sampling site. There is a gas station (GS) for gasoline car and diesel vehicle nearby.

2.2. Sampling

$PM_{2.5}$ samples were collected with an automatic sampler (2050 intelligent TSP, Qingdao Laoying Institute of Technology) from12:00 to next 12:00 at noon at a flow rate of 100 l/h on glass fiber filters (GM-A, baked at 450 °C in muffle for 4 h before use).The representative samplings were conducted from December 6 in 2014 to January 4 in 2015 (30 samples in winter), March 10 to April 9 in 2015 (31 samples in spring), July 15 to August 12 in 2015 (29 samples in summer), October 26 to November 26 in 2015 (32 samples in autumn). During the sampling time, meteorological parameters were kept recorded from campus weather station (WS). After sampling, the filters were folded and sealed in aluminum foil envelopes until weighting and then stored in refrigerator at −20 °C till analysis, the filters were weighed under constant temperature (20 °C) and relative humidity (45%) by a microbalance (XPE204) with a balance sensitivity of ±0.01 mg before and after sampling.

2.3. PAHs analysis

$PM_{2.5}$ samples were extracted with 120 ml acetone/dichloromethane (1:1, v/v) in a Soxhlet extraction apparatus for 20 h to obtain PAHs data. After the completion of extraction, an internal standard (consisting of Nap-d_8, Ace-d_{10}, Phe-d_{10}, Chry-d_{12} and Py-d_{12}) was injected into the organic reagent to calibrate the concentration of each PAHs compound. Then, the filter was cut into pieces; copper powder and anhydrous sodium sulfate were added to the filter pieces to get rid of impurity in the process. The extract was condensed with rotary evaporator. Then, the aliphatic hydrocarbons and PAHs were separated by the column with amorphous sodium sulfate, silica gel and alumina. The elute solvent was 15 ml hexane and 70 ml hexane-dichloromethane (3:7, v/v). Solvent was exchanged to hexane under vacuum afterwards. They were concentrated to 1 ml under a gentle and slow nitrogen stream in 40 °C water bath. The extracts are transferred into GC bottle with lids and the bottles were further sealed with parafilm, then, stored in a refrigerator at −20 °C until analysis.

Samples were analyzed by GC–MS (Agilent, 5975C, USA). A varian select PAHs capillary column (30 m × 0.25 mm × 0.25 μm) was used to quantify PAHs and 1 μl of the sample was injected in splitless mode. The selected ion monitoring mode was used to collect the data. Helium was used as the carrier gas at a flow rate of 1.0 ml/min. The GC oven of temperature program was 80 °C and held for 1 min at first stage, then to