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Sources and spatial distribution of particulate polycyclic aromatic hydrocarbons in Shanghai, China

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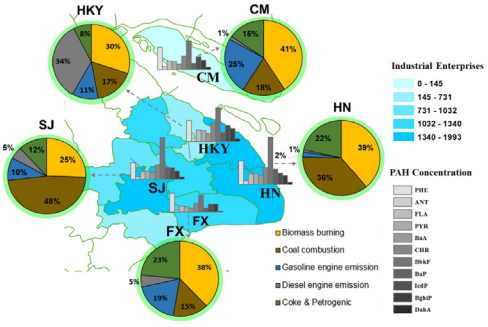
HIGHLIGHTS

- HMW PAHs were more homogeneously distributed compared to LMW PAHs.
- Suburban sites were subjected to higher BaPeq values in winter, suggesting higher health risks.
- Vehicle emission was a major source of PAHs (32–43%) in urban and urban buildup areas.
- Biomass and coal combustion were major sources in suburban areas in winter.

GRAPHICAL ABSTRACT



Chemical profiles and sources of PAHs in Shanghai in winter

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ABSTRACT

Atmospheric particulate polycyclic aromatic hydrocarbons (PAHs) have been drawing sustained attention due to their health risk and effects on air pollution. It is essential to determine the main sources and reduce atmospheric levels of PAHs to protect human health. PAHs in $PM_{2.5}$ have been detected at five sites located in five districts in Shanghai, a modern metropolitan city in China. Spatial and temporal variations of composition profiles and sources of PAHs at each site in each season were investigated. The results showed that atmospheric particulate PAHs level in Shanghai was the lowest in summer and the highest in winter, dominated by high molecular weight (HMW) PAHs. Analysis with a combination of coefficients of Pearson's correlation and coefficient of divergences indicated heterogeneous spatial and temporal distribution for LMW PAHs and homogenous distribution for HMW PAHs. Diagnostic ratios and positive matrix factorization (PMF) model both identified pyrogenic sources as the main contributor of PAHs in Shanghai, with vehicular source contribution of 32– 43% to the total PAHs annually and around 20% from biomass burning emissions in urban and urban buildup areas. While in winter, coal combustion and biomass burning could act as two major sources of PAHs in suburban areas, which could contribute to >70% of total PAHs measured in $PM_{2.5}$ in Shanghai.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), by-products of incomplete combustion or pyrolysis of organic materials and fossil fuels, are ubiquitous pollutants in the urban atmosphere. PAH is one of the main pollutants that can adversely affect human health, and has attracted much attention over the last several decades due to its potential carcinogenic and mutagenic properties (Chen et al., 2011; Wang et al., 2015b). The pathways for atmospheric PAHs to get into human body include various processes such as inhalation, ingestion and skin contact, which could result in potential risks on human health such as lung cancer and other severe diseases (Baek et al., 1991; Kawanaka et al., 2009; Menzie et al., 1992). Lan et al. (2004) found that high exposure to PAHs could lead to high morbidity of cancer. Recently, Wei et al. (2010) identified significant effect of exposure to individual PAHs on increasing oxidative DNA damage in human body. Ravindra et al. (2001) noted the presence of PAHs in placental tissue and the blood of newborn babies, indicating that atmospheric particles are posing health impacts worldwide.

PAHs in the atmosphere could be derived from a number of nature sources (e.g., volcanic eruption, forest and prairie fires) and anthropogenic sources (e.g., domestic and industrial coal combustion, vehicular and biomass burning emissions) (Harrison et al., 1996; Khalili et al., 1995; Larsen and Baker, 2003; Zhang et al., 2004). Since PAHs originate from a variety of sources, it is necessary to investigate the characteristics of PAHs pollution in urban atmosphere and apportion their sources to better ameliorate air quality. Several approaches have been applied for determining the origin of PAHs. For example, diagnostic ratios of individual PAHs and principal component analysis (PCA) have been widely adopted as useful tools for source identification of atmospheric PAHs (Guo et al., 2003a; Li et al., 2006; Manoli et al., 2004; Ravindra et al., 2006; Thurston and Spengler, 1985). To further quantify the contribution of each source to atmospheric particulate PAHs, principal component analysis followed by multiple linear regression (PCA-MLR) model (Li et al., 2006; Li et al., 2012; Shi et al., 2009), positive matrix factorization model (PMF) (Wang et al., 2013; Wang et al., 2015b), and chemical mass balance model (CMB) (Chen et al., 2009; Yang and Chen, 2004; Zhang, 2006), were frequently used. Recently, the development of carbon isotope analysis, especially the advances in molecular-level radiocarbon analysis, has allowed class-specific radiocarbon analysis of PAHs and realized the possibilities of providing effective information of the relative contribution of fossil fuel and biomass combustion to each PAH (Mandalakis et al., 2005; Sheesley et al., 2009; Xu et al., 2012). Besides, particulate PAHs resulted from natural burning processes could also be distinguished from those stemming from various anthropogenic combustion processes by utilizing fingerprinting and $\delta^{13}C$ analysis of individual compounds (Okuda et al., 2002; Schmidt et al., 2004).

China has been reported as one of the major emitters of PAHs among the world (Shen et al., 2013). Some studies have been conducted on atmospheric PAHs pollution in urban areas in China. For example, Guo et al. (2003a) reported the concentration of PAHs in $PM_{2.5}$ and PM_{10}, and identified vehicular emission as the predominant source of airborne PAHs in Hong Kong. Okuda et al. (2006) analyzed the PAHs concentration in the aerosol of Beijing, and attributed the high concentrations of PAH in winter to residential heating. Atmospheric levels and sources of particulate PAHs in urban atmosphere have also been studied in other Chinese cities, such as Qingdao (Guo et al., 2003b), Tianjin (Shi et al., 2010), Ningbo (Liu et al., 2014), Nanjing (He et al., 2014; Wang et al., 2006) and Liaoning (Kong et al., 2010). Shanghai, one of the global financial centers as well as a large industrial city, has a population of >24 million by 2014. For several decades, it has experienced rapid urbanization, industrialization, and economic development. High consumption of natural resources such as fossil fuels and large emission of environmental pollutant have caused the deterioration of air quality in Shanghai.

By now, several studies have been conducted on the PAH pollution in sediments, soil, dust and atmosphere in Shanghai, with focuses on PAH levels, gas-particle partitioning and its sources (Chen et al., 2011; Cheng et al., 2007; Feng et al., 2009; Gu et al., 2010; Wang et al., 2014a, 2015b). For example, Wang et al. (2010) collected PAHs in gas phase at 6 sites, and identified mobile, wood combustion, and metal scrap burning as main sources of gaseous PAHs. Chen et al. (2011) analyzed the gas-particle partitioning and seasonal trends of PAH at 2 sites, and concluded that vehicle and coal combustion were the two important sources. However, there are still limited studies on atmospheric particle-bound PAHs, which are more easier to be transported over a long distance and into indoor atmosphere, and can be more harmful to human respiratory system, eliciting mutagenic and carcinogenic effects compared to gas-phase PAHs (Cheng et al., 2007; Kawanaka et al., 2009; Lv et al., 2015; Zhang et al., 2012). Especially, the 5, 6-ring PAHs including benzo(a)pyrene, which are predominantly particle-bound, have much higher carcinogenicity than gas-phase PAHs. Furthermore, the current studies were mainly based on 1 to at most 3 sites, only covering a small area of Shanghai, with little further discussion on spatial distribution of composition and sources of particulate PAHs. Therefore, the primary goal of this study was to better understand the chemical characteristics and potential sources of atmospheric particulate PAHs on a city scale and its seasonal variations, and to investigate the spatial distribution of the atmospheric particulate PAHs in different districts in Shanghai.

2. Materials and methods

2.1. Sampling

As shown in Fig. 1, fine particle (<2.5 μm in aerodynamic diameter, $PM_{2.5}$) samples were collected at five sites in Shanghai, which were located in five different districts, including Chong Ming (CM), Xu Hui (XH), Song Jiang (SJ), Hui Nan (HN) and Feng Xian (FX). The sampling sites covered a large area of the whole Shanghai city, and could be representative for the air quality of Shanghai. Detailed information of each sampling site was listed in Table 1. The HKY site in XH district was located on the rooftop of Shanghai Academy of Environmental Sciences, a representative urban site, which was surrounded by residential buildings and commercial premises with no major emission sources around except one viaduct and one main Road about 200– 300 m away. The other four sites were located on the rooftop of the environmental monitor station of each district. Among which, CM and FX sites were in urban buildup areas, while HN and SJ were in suburban areas, with relatively open environment.

Samples were collected during four sampling periods, including spring (March 2012–April 2012), summer (July 2012), autumn (October 2012–November 2012) and winter (January 2013), with ten samples collected in each sampling period. It should be noted that, due to the amount of available samplers, effective $PM_{2.5}$ samples were only simultaneously collected at three of the five sites (i.e., FX, CM and HKY sites) during all the four sampling periods. Additionally, simultaneous $PM_{2.5}$ samples were also collected at SJ site during the summer and winter periods and at HN site during the wintertime period. High volume samplers manufactured by Thermo Andersen were used at four sites (i.e., FX, CM, HKY and HN) and one high volume sampler by Tisch was adopted at SJ site. All samplers were operated at a flow rate of 1.13 m^3/min, with prebaked quartz filters (8 × 10 in., 2500 QAT-UP, Pall Corporation, NY, USA). Quartz filters were wrapped within aluminum foil and prebaked under 550 °C before sampling. After sampling, samples were also wrapped in prebaked aluminum foil in clean zip lock bags, and stored in freezer until analysis.

2.2. PAHs analysis

Sub-filters with an area of 1.45 cm^2 punched from each quartz filter were used to analyze organic carbon (OC) and elemental carbon (EC) by Sunset OC/EC analyzer (Sunset Laboratory Inc., USA) using the thermo-

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