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PAHs in Chinese atmosphere Part I: Concentration, source and temperature dependence

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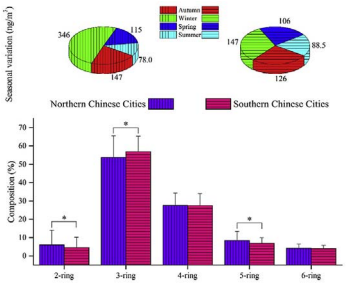
GRAPHICAL ABSTRACT



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ABSTRACT

The study on atmospheric polycyclic aromatic hydrocarbons (PAHs) in China has regional and global significance to understand the large scale atmospheric transport of PAHs. In this study, 16 US EPA priority PAHs were analyzed in more than 500 pairs of gas and particle phases samples, which were collected on the same schedule on a weekly basis from August 2008 to July 2009 at 11 urban sites (6 northern cities and 5 southern cities) across China. The average concentration was 239 ± 329 ng/m^3 and 165 ± 164 ng/m^3 for the northern cities and the southern cities, respectively. Different seasonal variations of atmospheric PAHs were observed between northern cities and southern cities, which were mainly caused by the different temperature effects in winter. Identified by principal component analysis, coal combustion and vehicle exhaust were the major sources of atmospheric PAHs in northern and southern cities of China, respectively. The temperature dependences of atmospheric PAHs were also different, which were caused by the different influences of temperature on identified sources. To our knowledge, this is the first comprehensive study to report the difference with concentrations, seasonal variations, sources and temperature dependences of atmospheric PAHs between northern cities and southern cities in China.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in atmosphere (Galarneau, 2008; Meijer et al., 2008; Park et al., 2002). Due to their toxicity, and capability for long range atmospheric transport (LRAT), PAHs are regarded as priority pollutants by both the United States Environmental Protection Agency (U.S. EPA) and the European Community (Dimashki et al., 2001). Therefore,

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atmospheric PAHs have been attracted frequent attentions worldwide in the past decades (Albuquerque et al., 2016; Liu et al., 2017; Zhang et al., 2016a, 2017). In China, PAHs are also listed as the most toxic organic pollutants of concern. Furthermore, China is one of the highest PAHs emission countries in the world (Zhang and Tao, 2009). In addition to local and national influence in China, the outflow of PAHs emitted from China can reach the neighbor countries and regions in northeast Asia and even western US through LRAT (Inomata et al., 2012; Lang et al., 2008; Primbs et al., 2008). Therefore, the national scale study on PAHs in China are necessary for both China and the world.

In order to study the regional and/or global scale atmospheric transport of PAHs, PAHs in atmosphere have been received more attentions in the past decades in China (Chang et al., 2006; He et al., 2017; Liu et al., 2007a, 2007b; Zhang et al., 2009). According to these studies, the highest PAHs emissions and pollution levels were often observed in densely populated urban area in China (Bi et al., 2003; Li et al., 2006; Liu et al., 2001). These studies provided an incentive for us to better understand urban contaminant dynamics (Melymuk et al., 2012). Generally, it was found that atmospheric PAHs in China are mainly originated from the incomplete combustion of fossil fuels and biomass, vehicle exhaust, and volatilization of un-combusted petroleum (Li et al., 2006; Tian et al., 2009). Beside the influence of emission sources, ambient temperature was another important factor for the concentration and fate of atmospheric PAHs. Usually, when temperature rises, air concentrations of semi-volatile organic compounds (SVOCs) increase as a result of stronger volatilization from surfaces, such as soil, water, and vegetation (Sofuoglu et al., 2001). In China, the differences with ambient temperature for different regions were significant. In north and northeast China, the average temperature in January can be as low as −20 °C, while, in the same month, the average temperature is about 10 °C in south China (Li et al., 2006; Zhang and Tao, 2008). Similarly, the economic development and urbanization are also different in different regions of China. However, limited effort has been conducted to study the difference of concentration, source and temperature dependence with atmospheric PAHs on national scale. Therefore, it is necessary to study atmospheric PAHs on national scale in China, which would also provide a scientific basis for the development of relevant policies on controlling PAHs pollution (Liu et al., 2016).

In order to deeply study the pollution status of persistent organic pollutants (POPs) in China on national scale, the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS) has carried out the Chinese POPs Soil and Air Monitoring Program (China-SAMP) since 2005 (Ren et al., 2007; Yang et al., 2013; Zhang et al., 2008). The details for this program can be found in Section S1 in Supporting Information. In this study, based on one year monitoring data from China-SAMP at 11 urban sites across China, atmospheric PAHs were comprehensively studied. The objectives of this study were: (1) to study concentration, spatial distribution and seasonal variation of atmospheric PAHs; (2) to identify the potential sources of atmospheric PAHs; and (3) to study the relationships between atmospheric PAHs, identified sources and ambient temperature. Therefore, the results of this study can draw a whole picture of atmospheric PAHs across China.

2. Material and methods

2.1. Sampling

Sampling sites were selected to be representative urban areas without major industrial sources and other point sources around. 11 urban sampling sites (cities) were selected across China, including Beijing (BJ), Chengdu (CD), Dalian (DL), Guangzhou (GZ), Harbin (HRB), Kunming (KM), Lanzhou (LZ), Lhasa (LS), Nanchang (NC), Shihezi (SHZ) and Xi'an (XA). The 11 cities are uniformly distributed in the mainland of China (Fig. S3). The detailed introduction for the 11 cities can be found in S2. Briefly, the 11 cities can be divided into two groups according to their climates: northern Chinese cities (BJ, DL, HRB, LZ, SHZ and XA) and southern Chinese cities (CD, GZ, KM, LS and NC). For the northern Chinese cities, residential heating is needed for four to six months a year.

Details of air sampling procedure can be found in our previous study (Ma et al., 2010). Briefly, air samples in gas and particle phases were simultaneously collected using high volume air sampler (KB-1000, Kingstar Electronic Technology Co., China), and the sampling duration for one sample was 24 h on a weekly basis with the flow rate of 0.8 m^3/min. Therefore, sampling volume for one sample was approximately 1151 m^3. Particle phase was retained on glass fiber filters (GFF, 20 cm × 25 cm), and gas phase was absorbed on two polyurethane foam plugs (PUFs, 9.5 cm diameter and 5.0 cm length each). Air samples were collected on the same day for all the 11 cities. Totally, 289 and 249 pairs of gas and particle phases air samples were collected for northern Chinese cities and southern Chinese cities, respectively. After sampling, loaded GFFs and PUFs were sealed and transported to the IJRC-PTS laboratories, where they were stored frozen at −20 °C. The concentration of total suspended particle (TSP) was determined by weighing the GFFs before and after sampling with equilibration at least 24 h in desiccator.

2.2. Chemicals and standards

The pesticide analysis grade organic solvents, including acetone, hexane, dichloromethane and isooctane were purchased from J. T. Baker Co., USA. ACS grade silica gel (100–200 mesh) was purchased from Merck Co., Germany. The stock standard solution including 16 U.S. EPA priority PAHs (Nap, naphthalene; Ace, acenaphthene; Flu, fluorene; Phe, phenanthrene; Ant, anthracene; Fluo, fluoranthene; Pyr, pyrene; BaA, benz[a]anthracene; Chr, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benzo[a]pyrene; DahA, dibenz[a,h]anthracene; IcdP, indeno[l,2,3-cd]pyrene; BghiP, benzo[g;h;i]perylene) was purchased from Supelco Co., USA. The working standard solutions were prepared in isooctane from the stock solution to make calibration curves. Deuterated surrogates including naphthalene-D8, fluorene-D10, pyrene-D10 and perylene-D12 were purchased from Supelco Co., USA.

2.3. Analytical procedure

All the air samples were treated in the laboratories of IJRC-PTS for minimizing uncertainty. Details of extraction and clean-up procedure can be found in our previous study (Ma et al., 2010). Briefly, all the samples were spiked with four surrogates in order to check analytical recovery. GFF and PUF samples were Soxhlet extracted with dichloromethane, mixture of acetone: hexane (1:1, v/v) for 24 h, respectively. The extracts were solvent exchanged into hexane and concentrated to 5 mL by a rotary evaporator and further purified by a silica column, containing 7 g active silica gel and 2 g baked anhydrous sodium sulfate. The fraction of PAHs was eluted with mixture of hexane: dichloromethane (1:1, v/v). The final volume was reduced to 1 mL under a gentler nitrogen gas flow. Finally, the extract was transferred to GC vials for analysis.

PAHs were analyzed by an Agilent 6890N GC coupled with Agilent 5973 mass spectrometer detector and a HP-5MS capillary column (60 m × 0.25 mm × 0.25 μm, Agilent Co., USA). The mass spectrometer was operated under selected ion monitoring mode and 70-eV electron impact mode. Two most abundant ions were monitored as the quantification ion and the confirmation ion for each PAH, which was also confirmed by the retention time of standards. 2.0 μL of extract was injected in the splitless mode with high-purity helium as the carrier gas. The oven temperature programs were as follows: held at 90 °C for 1 min, then raised from 90 °C to 180 °C with 10 °C min^{-1}, held for 1 min, from 180 °C to 280 °C at 3 °C min^{-1}, held for 20 min. The typical