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Atmospheric behaviors of particulate-bound polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in Beijing, China from 2004 to 2010

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HIGHLIGHTS

- Atmospheric PAHs and NPAHs were investigated in Beijing from 2004 to 2010.
- The PAH and NPAH levels decreased in heating season during our study periods.
- High wind speed can remove the PAHs and NPAHs in the heating season.
- High relative humidity can remove the PAHs and NPAHs in the non-heating season.
- Source control measures also helped to reduce air pollution in Beijing.

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ABSTRACT

Airborne particulates were collected at an urban site (site 1) from 2004 to 2010 and at a suburban site (site 2) in 2010 in Beijing. Nine polycyclic aromatic hydrocarbons (PAHs) and five nitropolycyclic aromatic hydrocarbons (NPAHs) in the airborne particulates were determined by HPLC with fluorescence and chemiluminescence detection, respectively. The concentrations of PAHs and NPAHs were higher in heating season than in non-heating season at the two sites. Both the concentrations of PAHs and NPAHs decreased in the non-heating season but only the concentrations of NPAHs decreased in heating season at site 1, from 2004 to 2010. These findings suggest that source control measures implemented by the city of Beijing helped to reduce air pollution in Beijing. The concentrations of PAHs increased at site 1 in 2010, possibly because of the transport of emissions from windward other areas, such as Shanxi province. Several diagnostic ratios of PAHs and NPAHs showed that the different sources contributed to Beijing's air pollution, although coal combustion was the main source in the heating season and vehicle emission was the main source in the non-heating season. An analysis of physical parameters at Beijing showed that high wind speed can remove atmospheric PAHs and NPAHs in the heating season and that high relative humidity can remove them in the non-heating season.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds consisting of two or more fused benzene rings, and nitropolycyclic aromatic hydrocarbons (NPAHs) are their nitrated derivatives. PAHs and NPAHs are ubiquitous environmental pollutants. Atmospheric PAHs and NPAHs mainly originate from imperfect combustion and pyrolysis of organic matters, although some NPAHs are formed in the atmosphere via reactions of their

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parent PAHs such as 2-nitropyrene and 2-nitrofluoranthene (Arey et al., 1986; Hayakawa et al., 1995; Rogge et al., 1993). PAHs and NPAHs exist in both the gas and particle phases in the atmosphere, and their gas/particulate partition depend on factors such as the vapor pressure, temperature and the concentration and properties of dust (Araki et al., 2009; Sitaras et al., 2004; Yamasaki et al., 1982). In urban areas, PAHs and NPAHs are mainly emitted from automobiles, power plants, domestic heating and industrial processes (Gachanja and Worsfold, 1993; Kavouras et al., 2001; Tang et al., 2005). Many PAHs and NPAHs have carcinogenic and/or mutagenic properties (Ames et al., 1975; Epstein et al., 1979). Benzo[*a*]pyrene (BaP) and 1-nitropyrene (1-NP) are categorized in groups 1 (*carcinogenic to humans*) and 2A (*probably carcinogenic to humans*), respectively (IARC, 2013). Several PAHs also exhibit estrogenic, antiestrogenic, antiandrogenic activities (Kizu et al., 2000) or reactive oxygen species producing activity (Motoyama et al., 2009). In addition, prenatal exposure to PAHs could impact cognitive development and learning ability (Perera et al., 2012).

In recent years the consumption of petroleum and coal has grown considerably in China, resulting in serious environmental problems. Our previous studies have reported the following results on atmospheric PAHs and NPAHs in three cities in the Northeast China: (1) The mean concentrations of PAHs and NPAHs in particulate matter were in the order Fushun > Tieling > Shenyang, even though greater amounts of petroleum and coal are consumed in Shenyang (Hattori et al., 2007). (2) Molecular diagnostic ratios of several PAHs and NPAHs showed that the major contributors of PAHs and NPAHs were coal combustion systems both in summer and winter in Fushun and Tieling and in winter in Shenyang (Hattori et al., 2007). (3) In Shenyang, the mean concentrations of PAHs in winter 2007 decreased significantly from the concentrations in winter 2002 and the mean concentrations of NPAHs in winter did not change markedly between 2001 and 2007. However, both PAH and NPAH concentrations in summer increased from 2001 to 2007. These results suggested that motor vehicles have become one of the major contributors of atmospheric PAHs and NPAHs in Shenyang in both seasons (Tang et al., 2011).

The major sources of atmospheric PAHs in Beijing have been identified as coal combustion systems in winter, long-range transport in spring and motor vehicles in the other seasons (Feng et al., 2005; Hayakawa et al., 2007; He et al., 2006; Hou et al., 2006; Huang et al., 2006; Jiang et al., 2009; Liu et al., 2007; Wang et al., 2008; Zhang et al., 2009; Zhou et al., 2005). However, only a few studies have examined atmospheric NPAHs, whose mutagenicity is much stronger, in Beijing (Li et al., 2015; Lin et al., 2015; Wang et al., 2011). To the best of our knowledge, there have been no reports on the characteristics of mid-to-long term changes in atmospheric PAHs and NPAHs in Beijing. Therefore, in this study, our objectives were to clarify the changes of concentrations, compositions and major contributors of atmospheric PAHs and NPAHs in Beijing from 2004 to 2010, and to identify the causes of these changes.

2. Experimental

2.1. Samplings and characteristics of test sites

Beijing (39°55′N; 116°26′E) is a large city in Asia and is located in the North Temperate Zone. The variations of population, gross domestic product (GDP), energy consumptions and numbers of registered cars during our sampling periods are shown in Table 1 (Beijing Statistical Information Net: http://www.bjstats.gov.cn/esite/and Beijing Municipal Environmental Monitoring Center: *http://www.bjmemc.com.cn*). Total suspended particles (TSP) were collected at two sites (Fig. 1), using a high-volume air sampler (HV) at a flow rate of 1 000 l/min (HV-700F, Shibata Sci. Tech., Tokyo, Japan) or an Andersen high-volume air sampler (AHV) at a flow rate of 566 L/min (HV-1000R, Shibata Sci. Tech.). Site 1 is located in urban area (No. 18 Shuangqing road, Haidian district) and site 2 is located in suburban area (Shenshan village, Huairou district). Samplings were carried out at site 1 on Dec. 18–31, 2004, Jan. 21 - Feb. 2, 2008 and Nov. 25 - Dec. 21, 2009 (heating season), and on May 9–24, 2005, Aug. 21 - Sep. 2, 2007 and Aug. 11 - Sep. 1, 2010 (non-heating season); and at site 2 on Jan. 20–31 (heating season) and Aug. 2–16, 2010 (non-heating season). A summary of meteorological conditions during the sampling periods is provided in Table 2 (The data of average temperature, dew point, wind speed and visibility in Beijing during the sampling periods were obtained from National Climatic Data Center, NOAA and average humidity were calculated by using the data of average temperature and dew point). AHV was used only to collect TSP in five fractions according to their aerodynamic size at site 1 in 2009 and 2010. TSP were collected on quartz fiber filters (2500QAT-UP, Pallflex Products,

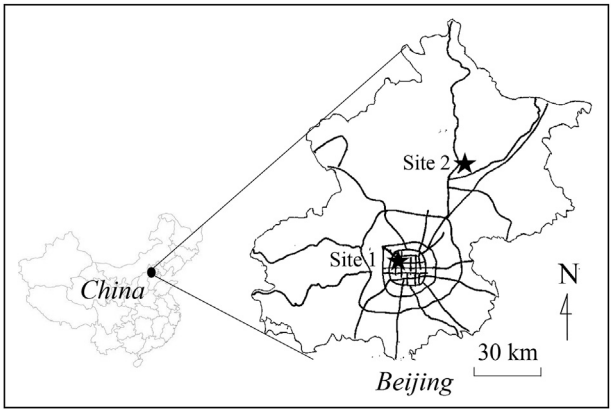

Fig. 1. Map of Beijing (39°55′N; 116°26′E) with air sampling sites. Site 1: an urban site located at No. 18 Shuangqing Road, Hiadian District. Site 2: a suburban site located at Shenshan Village, Huairou District.

Table 1
Population, gross domestic product (GDP), energy consumptions and numbers of registered cars,[a] and PM_{10}, SO_2 and NO_2 levels[b] in Beijing from 2004 to 2010.

Year	Population	GDP	Energy consumptions	No. of cars	PM_{10}	SO_2	NO_2
	(X 10^4)	(billion yuan)	(million tonnes coal equivalent)	(X 10^4)	($\mu g/m^3$)		
2004	1 493	428.3	51.4	187	0.149	0.055	0.071
2005	1 538	697.0	55.0	215	0.142	0.050	0.066
2006	1 581	811.8	59.1	244	0.161	0.053	0.066
2007	1 633	984.7	62.9	278	0.148	0.047	0.066
2008	1 695	1 112	63.4	318	0.122	0.036	0.049
2009	1755	1 215	65.8	402	0.121	0.034	0.053
2010	1961	1 378	69.5	481	0.121	0.032	0.057

[a] Beijing Statistical Information Net (http://www.bjstats.gov.cn/esite/).
[b] Beijing Municipal Environmental Monitoring Center (http://www.bjmemc.com.cn).