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Particle size distribution and characteristics of polycyclic aromatic hydrocarbons during a heavy haze episode in Nanjing, China

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ABSTRACT

A heavy haze episode caused by agricultural burning occurred in Nanjing from November 7 to November 8, 2009. PM_{10} samples were collected on normal and hazy days from November 1 to November 14, 2009 at both city and suburban sites of Nanjing. Sixteen PAHs were measured during the day and at night. The results show that the concentrations of the particles were as high as 579.55 and 573.43 μg/m^3 during the haze episode at the city and suburban sites, respectively, 3–4 times higher than those on a normal day. The proportions of fine particles during the haze episode were also higher than those on a normal day. The changes in the concentrations of PAHs were in accordance with the concentrations of the particles. High-molecular-weight PAHs composed approximately 80% of the total PAHs on normal days and during the haze episode. The concentration of PAHs in fine fractions significantly increased during the haze episode, and this increase was most obvious at night at the city site. The proportion of total carcinogenic PAHs in fine particles was relatively high during the haze episode at both sampling sites, particularly at night at the city site.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants that are ubiquitous in urban and suburban atmospheres. Atmospheric PAHs are partitioned between the gaseous phase and the particulate phase; the latter are called particle-bound polycyclic aromatic hydrocarbons (pPAHs). Although atmospheric PAHs are partitioned between two phases, PAHs are predominantly associated with particulate matter. pPAHs are a significant danger to human health through inhalation (Chetwittayachan, Shimazaki, & Yamamoto, 2002). Many PAHs have mutagenic and carcinogenic properties, and the hazard posed by these compounds increases as their molecular weight increases (Tsai et al., 2004). PAHs are primarily derived from the imperfect combustion processes of mobile sources (vehicular emissions) and of stationary sources (industries) (Ravindra, Sokhi, & van Grieken, 2008).

Haze is defined by relative humidity <80%, by visibility <10 km and by the concentration of particles when the relative humidity is between 80% and 95%. Haze is called as a heavy haze episode when the visibility is lower than 2 km (Wu et al., 2010). Haze is generally believed to be related to atmospheric particulate matter (Chan & Yao, 2008). Recent studies also showed that haze not only damages human health but also is important for the global energy balance (Huang, Yuan, Wang, & Wang, 2011; Menon, Hansen, Nazarenko, & Luo, 2002; Tao et al., 2009). There have been many studies concerning pPAHs in large cities in China, including Guangzhou (Tan et al., 2006, 2009a, 2009b), Shanghai (Cheng et al., 2007), Dalian (Kong et al., 2011; Tian et al., 2009), Hong Kong (Guo, Lee, Ho, Wang, & Zou, 2003), Fuzhou (Zhang et al., 2013), Xiamen (Hong, Yin, Wang, & Ye, 2007), Beijing (Liu, Gao, & An, 2008), and Nanjing (Wang, Huang, Zhao, Niu, & Dai, 2006). These authors found that the concentrations of PAHs were closely related to the sizes of atmospheric particles. Concentrated in the respirable size range of 0.1–1 μm, the burning of fossil fuels is the most important emission source of PAHs. Some studies also found that the main influencing factors of the concentration of pPAHs were emission sources

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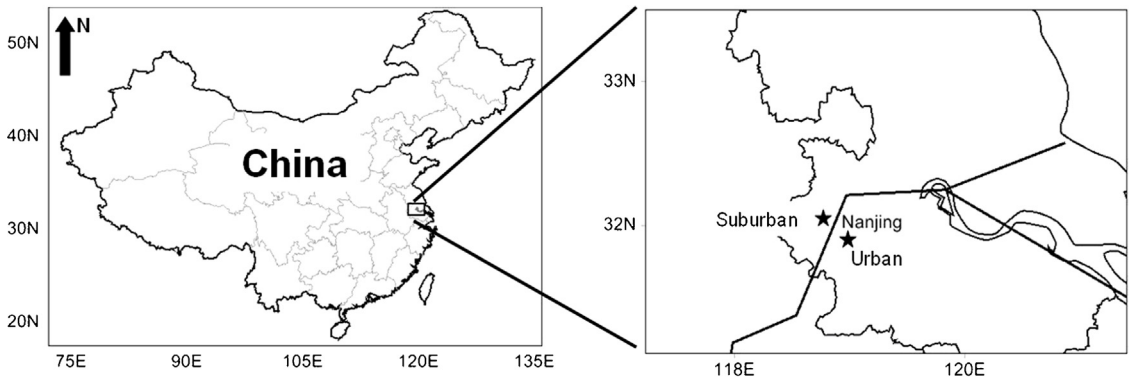

Fig. 1. Locations of sampling sites in Nanjing, China.

and meteorological factors, such as temperature, radiation, rainfall, wind speed and direction, boundary layer characteristics and so on (Hien, Thanh, Kameda, Takenaka, & Bandow, 2007; Ravindra et al., 2006; Tham, Takeda, & Sakugawa, 2008). To understand the distribution characteristics of PAHs under specific weather conditions, Fan et al. (2009) and Gu et al. (2011) analyzed the influence of foggy weather conditions. These authors found that fog could aggravate the pollution of $PM_{2.5}$ and PM_{10} near the ground layer and that size distributions of PM_{10} and the total PAHs in PM_{10} were greatly affected by the daytime fog and also by the duration of each fog event. Duan, Bi, Tan, Sheng, and Fu (2006) and Tan et al. (2009a, 2009b, 2011) performed research on pPAHs during haze periods in Guangzhou. These authors discovered differences between seasons, with low-ring PAHs displaying greater changes than high-ring PAHs.

Agricultural burning is a serious environmental problem in China, particularly in the middle and lower Yangtze River and in the southern part of China during autumn. Some scholars have found that the atmospheric particles of Nanjing were seriously affected by agricultural burning from the Jiangsu, Anhui, Hubei, and Hunan provinces, and agricultural burning was an important source of pPAHs (Keshtkar & Ashbaugh, 2007). Although there are several studies concerning the influence of haze episodes on atmospheric PAHs concentrations, less is known concerning PAHs size distributions, particularly under the influence of agricultural burning. The purpose of this study is to examine pPAHs concentrations and size distributions in an autumn haze episode in city and suburban sites around Nanjing, including periods with a strong influence from agricultural burning.

Experimental

Filter sampling

Filter samples were collected at two sites, as shown in Fig. 1. One site was in the suburban campus of the Nanjing University of Information Science and Technology (NUIST), approximately 17 km away from the downtown area. The sampler was set up on the roof at approximately 4–6 m above ground. There is a residential area between the campus and downtown, with a busy road and an industrial district east of the sampling site. The industrial district has many factories, such as petrochemical plants, iron-works, chemical plants, thermal power plants, and so on. The second sampling site was at the old campus of Nanjing University (NJU), which is in the downtown area of Nanjing. The sampler was set up on the roof of the building at approximately 8–9 m above the ground. The old campus was surrounded by roads with heavy traffic, residential areas and commercial centers.

A sampling campaign was conducted between November 1 and November 14, 2009. Each sampling period was usually 12 h, with daytime sampling from 08:00 to 20:00 (LST = GMT + 08:00), and nighttime sampling from 20:00 to 08:00 (LST). Because it was raining from the 9th to the 12th, 20 series samples could be used at each site.

The aerosol was collected on 80-mm-diameter glass microfiber filters (Shanghai Xingya, Shanghai, China) by a cascade impactor (Liaoning Kangjie) at a flow rate of 28.3 L/min. Particles were partitioned into nine fractions based on their aerodynamic diameters, with the size ranges of 10–9.0, 9.0–5.8, 5.8–4.7, 4.7–3.3, 3.3–2.1, 2.1–1.1, 1.1–0.68, and 0.68–0.43 μm, and another filter was used to collect particles smaller than 0.43 μm. Before collection, the filters were baked at 550 °C for 4–5 h to remove any absorbed organic materials. Then, after being weighed, the filters were sealed in aluminum foil pouches and transported to the sampling sites. After sampling, the filters were folded in half so that no particles would be lost. All of the filter samples were stored at −4 °C in the freezer before chemical analysis. Additionally, one group of blank samples was taken at each site for analysis every day.

Extraction and concentration

Samples on the filters were extracted following a modified procedure based on the EPA method TO-13 (US EPA, 1999). Briefly, the filters were extracted by a Soxhlet extractor for 18 h with 90 mL of dichloromethane at a constant temperature of 55 °C. The extract was reduced to 5 mL using a Kuderno–Danish (K–D) concentrator and further reduced to 1 mL under purified N_2 gas. The extract was then stored at −20 °C before analysis.

Sample analysis

An HP 6890 Plus gas chromatograph–mass spectrometer (GC–MS) (Agilent Technologies), with an HP-5MS column 30 m × 0.25 mm × 0.25 μm (Agilent, CA, USA), was used for the separation and quantification of the target PAHs. A master standard solution of 16 PAHs (2000 μg/mL in CH_2Cl_2:benzene (1:1), SUPELCO) and benzo(e)pyrene (100 μg/mL in cyclohexane, Dr. Ehrenstorfer) was used in GC calibration processes. A 1-μL sample was injected into the splitless injector at 300 °C and carried by high purity helium with a flow rate of 1 mL/min in splitless mode. The original oven temperature was 70 °C; after injection, the temperature was quickly increased to 230 °C at a rate of 10 °C/min; from 230 to 240 °C at a rate of 0.5 °C/min; from 240 to 270 °C at a rate of 10 °C/min; from 270 to 290 °C at a rate of 3 °C/min; and held at 290 °C for 5 min. Sixteen priority PAHs (ATSDR, 1995) were analyzed, including