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Seasonal variation, sources and gas/particle partitioning of polycyclic aromatic hydrocarbons in Guangzhou, China

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ABSTRACT

Air samples were collected weekly at an urban site and a suburban site in Guangzhou City, China, from April 2005 to March 2006, to measure the concentrations of polycyclic aromatic hydrocarbons (PAHs) in the ambient air and study their seasonal variations, gas/particle partitioning, origins and sources. The concentrations of $\sum$16-PAHs (particle + gas) were 129.9 ± 73.1 ng m^{-3} at the urban site and 120.4 ± 48.5 ng m^{-3} at the suburban site, respectively. It was found that there was no significant difference in PAH concentrations between the urban and suburban sites. Seasonal variations of PAH concentrations at the two sampling sites were similar, with higher levels in the winter that gradually decreased to the lowest levels in the summer. The average concentrations of $\sum$16-PAHs in the winter samples were approximately three times higher than those of the summer samples because in the summer local emissions dominated, and in the winter the contribution from outside sources or transported PAHs is increased. The plot of $\log K_p$ versus $\log P_L^0$ for the data sets of summer and winter season samples had significantly different slopes at both sampling sites. The slopes for the winter samples were steeper than those for the summer samples. It was also observed that gas/particle partitioning of PAHs showed different characteristics depending on air parcel trajectories. Steeper slopes were obtained for an air parcel that traveled across the continent to the sampling site from the northern or northeastern sector, whereas shallower slopes were obtained for air masses that traveled across the sea from the southern or eastern sector. Diagnostic ratio analytical results imply that the origins of PAHs were mainly from petroleum combustion and coal/biomass burning. The anthracene/phenanthrene and benzo[*a*]anthracene/chrysene ratios in the winter were significantly lower than those in the summer, which indicate that there might be long-range transported PAH input to Guangzhou in the winter.

1. Introduction

PAHs are a large group of organic compounds that are composed of two to eight fused aromatic rings and are derived mainly from incomplete combustion of organic materials and volatilization of uncombusted petroleum. They are identified as one of the major toxic air pollutants in the environment and have received increased attention in recent decades as the subject of air pollution studies due to their carcinogenicity and mutagenicity. PAHs are semivolatile organic compounds, they can exist both in the gas and particle phase (Vardar et al., 2008). Partitioning of PAHs between the gas and particle phases plays an important role in their environmental fate and transport in the atmosphere (Bidleman et al., 1986; Tasdemir and Esen, 2007; Esen et al., 2008; Vardar et al., 2008).

Atmospheric concentrations of PAHs in developing countries, including China, has been increasing and it was estimated that 116,000 tons of 16 US EPA priority PAHs were emitted by China in 2003 (Zhang et al., 2008). Health risks of the exposure to PAHs were also revealed in several regions in China (Wornat et al., 2001; Tao et al., 2006). Atmospheric PAH contamination in China has become a major concern for environmental scientists and policy makers (Liu et al., 2007). Guangzhou, longitude from 112°57′ to 114°3′ east and latitude from 22°26′ to 23º 56′ north, is the capital of the Guangdong province and covers an area of 7434.4 km^2. Guangzhou is located on the south coast of China and belongs to the Pearl River Delta (PRD), which is not only one of the most densely populated areas but is also one of the most rapidly developing regions in China over the last three decades. PRD is a typical subtropical climate region under strong influence of the Asian monsoon system, with a hot and wet climate in the summer, and a cool and dry climate in the winter. Investigations on PAHs in various environmental media of the PRD region, such as air, water and soil, have been conducted recently (Guo et al., 2003; Li et al., 2006; Duan et al., 2007; Li et al., 2009; Qiu et al., 2009; Yan et al., 2009).

The aim of this study was to investigate the air concentrations of atmospheric PAHs in Guangzhou for a period of one year and to study their seasonal trends, gas/particulate partitioning, primary origins and sources.

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2. Experimental

2.1. Sample collection

To observe PAHs in the ambient air in Guangzhou, two active atmospheric sampling sites were set up, including an urban site, Guangzhou Branch, Chinese Academy of Sciences (GCAS), and a suburban site, South China Botanical Garden (SCBG). The GCAS sampling site is located about 150 m from the Xianlie Middle Road where traffic is busy. There are shopping centers, residential areas and schools near GCAS. SCBG is the biggest southern subtropical botanical garden in China, covering an area of 300 hectares and located in the east–north suburban area of Guangzhou City. The SCBG sampling site was set up in the center of SCBG with many kinds of vegetation, e.g., magnolias, palms, gingers and orchids nearby. The distance between the two sampling sites is about 15 km.

Sampling was carried out every Tuesday at GCAS and every Friday at SCBG for a consecutive 24-hour period from April 2005 to March 2006 (except for during the Spring Festival, a traditional Chinese holiday, from January 25 to February 8, 2006), and a total of 49 samples at GCAS and 50 samples at SCBG were collected. Samples were collected with an Anderson high-volume sampler model PS-1 (Thermo, USA) at a flow rate of 0.17 m^3 min^{-1}, by which about 250 m^3 air was drawn through a 10.2 cm diameter quartz fiber filter (QFF, Whatman, USA) followed by a 8.0 cm diameter × 7.5 cm thick polyurethane foam (PUF, Supleco, USA) plug. The particle phases were mainly collected by QFFs and the gas phases were mainly collected by PUF plugs. Prior to sampling, QFFs were baked at 450 °C for 8 h to remove any organic contaminants and PUF plugs were pre-cleaned by an accelerated-solvent extraction (ASE) instrument model One PSE (Applied Separations, USA), were then dried overnight in a vacuum desiccator and were finally stored in solvent-rinsed glass jars with Teflon lined lids before use. After sampling, loaded QFFs were wrapped in aluminum foil and sealed in double layers of polyethylene bags, and PUF plugs were placed in solvent-rinsed glass jars with Teflon lined lids and were then transported to the laboratory and stored in a freezer until extraction.

Meteorological data, including temperature, air pressure, relative humidity and precipitation were recorded at each sampling site. Air mass origins were determined using the HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory. The 72-hour back-trajectory calculated air mass origins for each sampling event are given in Table 1. The four typical air mass origins arriving in Guangzhou during our sampling times (Fig. 1) came from the south (type a), east (type b), northeast (type c) or north (type d). Air masses coming from the south or east traveled over the sea from the southern or eastern Pacific Ocean. When coming from the northeast, they traveled across both the sea and the continent from northeastern China. While coming from the north, they traveled all over the land from northern China to Guangzhou.

2.2. Analytical procedure

Loaded QFFs and PUF plugs were extracted individually by an ASE instrument model One PSE (Applied Separations, USA), each for 15 min × 4 times with a mixture solvent of hexane/dichloromethane/ethyl ether (7:1:2, v/v) at the temperature of 100 °C and pressure of 150 bar. The extracts from each step were combined.

Extracts were concentrated by rotary evaporation at a temperature below 50 °C, were blown down with a gentle stream of nitrogen and exchanged into hexane, and then were cleaned up on a neutral silica solid phase extraction (SPE) column. The SPE column was eluted with 5 mL dichloromethane/hexane (1:1, v/v) to yield the PAHs fraction. The eluate was concentrated to a final volume of 0.5 mL under a gentle stream of nitrogen.

The samples were analyzed with a GC–MS system (Shimadzu QP-2010, Japan) equipped with a DB-1MS capillary column (J&W, 30 m × 0.25 mm i.d., 0.25 µm film thickness, USA), operating under the selected ion monitoring mode. The initial oven temperature was held at 60 °C for 3 min and was increased to 300 °C at the rate of 10 °C min^{-1}, and then was held constant for 5 min. Splitless injection of a 1 µL sample was performed with a 3 min solvent delay time. 16 US EPA priority PAHs were detected: naphthalene (Naph), acenaphthylene (Acpy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Flan), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (INP), dibenzo[*a*,*h*]anthracene (DBA) and benzo[*g*,*h*,*i*]perylene (BghiP).

2.3. Quality control

Quality assessment procedures were performed routinely. Laboratory and field blanks consisting of PUF and QFF were run during the first week of every month. A total of 12 laboratory blanks and 24 field blanks (12 at GCAS and 12 at SCBG) were extracted and analyzed in the same way as samples. There was no statistically recognizable difference between the field and laboratory blanks. PUF blanks were less than 3% of the sample amount and QFF blanks were around 8% less.

All samples were spiked with PAH surrogate standards prior to extraction. Recoveries of PAH surrogate standards were 50.6 ± 12.9% for naphthalene-d_8, 58.4 ± 10.8% for acenaphthylene-d_{10}, 78.7 ± 8.8% for phenanthrene-d_{10}, 91.8 ± 7.1% for chrysene-d_{12} and 95.9 ± 7.9% for perylene-d_{12}. The recoveries of the five following surrogate standards were used to correct the amounts of specific PAHs found in the samples: (1) naphthalene-d_8 for Naph, (2) acenaphthylene-d_{10} for Acpy, Ace and Flu, (3) phenanthrene-d_{10} for Phen, Ant, Flan and Pyr, (4) chrysene-d_{12} for BaA and Chr and (5) perylene-d_{12} for BbF, BkF, BaP, INP, DBA and BghiP.

Three clean PUF plugs and three clean QFFs were each spiked with a mixture containing 500 ng target PAHs. The PUF plugs and QFFs were then extracted, cleaned up and analyzed in the same way as the samples. The average recoveries of target PAHs were from 47.3% (Naph) to 97.2% (DBA) in PUF plugs and between 51.9% (Naph) and 103.6% (BghiP) in QFFs.

3. Results and discussion

3.1. Ambient concentrations and seasonal trends

Table 1 shows the $\sum$16-PAHs concentrations for each sampling event at GCAS and SCBG. Total $\sum$16-PAHs concentrations (particle + gas) of the GCAS samples ranged from 27.9 to 329.4 ng m^{-3} with an average of 129.9 ng m^{-3}. For the SCBG samples, total $\sum$16-PAHs concentrations (particle + gas) were between 34.1 and 215.5 ng m^{-3} with an average of 120.4 ng m^{-3}. The concentrations of $\sum$16-PAHs in the particle phase ranged from 2.2 to 90.5 ng m^{-3} for GCAS samples and from 2.3 to 63.1 ng m^{-3} for SCBG samples. The gas phase $\sum$16-PAHs concentrations were between 25.7 and 239.5 ng m^{-3} at GCAS and between 31.8 and 173.3 ng m^{-3} at SCBG. The average concentrations of PAHs in this study were higher than those of many other urban areas reported around the world (Baek et al., 1991; Halsall et al., 1994; Smith and Harrison, 1996; Mandalakis et al., 2002; Seung et al., 2002), but were lower than that have been reported in Bursa (Turkey) during the heating season (Esen et al., 2008; Vardar et al., 2008) and in Guangzhou by a previous study (Li et al., 2006). When all data for GCAS and SCBG samples were compared using the *t*-Test, the concentrations at the two sampling sites were not significantly different ($P > 0.05$). This suggests that the atmosphere was contaminated not only in urban areas, but also in suburban regions, of Guangzhou City.

A summary of the individual and total particle and gas PAH concentrations in this study and the previous study in Guangzhou by Li et al. (2006) are provided in Table 2. The previous study reported that the total $\sum$16-PAHs in the particle and gas phases in Guangzhou from April