



## Composition and size distribution of airborne particulate PAHs and oxygenated PAHs in two Chinese megacities



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### ABSTRACT

Concentrations and compositions of PAHs and oxygenated PAHs (OPAHs) in four size ranges of ambient particles (<1.1, 1.1–3.3, 3.3–9.0 and >9.0 μm) collected in Xi'an and Guangzhou, two megacities of China, during the winter and summer of 2013 were measured and compared with those in 2003. The TSP-equivalent concentrations of Σ14PAHs in Xi'an and Guangzhou are 57 ± 20 and 18 ± 23 ng m<sup>-3</sup> in winter, 5–10 times higher than those in summer. PAHs in both cities are dominated by 5- and 6-ring congeners in summer. In contrast, they are dominated by 4- and 5-ring congeners in winter, probably due to enhanced gas-to-particle phase partitioning of the semi-volatile PAHs. TSP-equivalent Σ7OPAHs during winter are 54 ± 15 and 23 ± 32 ng m<sup>-3</sup> in Xi'an and Guangzhou and dominated by 5-ring OPAHs.

Size distribution results showed that the fine modes (<3.3 μm) of PAHs and OPAHs in both cities are dominated by 4- and 5-ring congeners in winter and 5- and 6-ring congeners in summer. Relative abundances of 3-ring PAHs and OPAHs increased along with an increase in particle sizes, accounting for from about 1% of the total PAHs or OPAHs in the smallest particles (<1.1 μm) to >90% of the total in the largest particles (>9.0 μm). The toxicity of PAH assessment indicated that atmospheric particles in Xi'an and Guangzhou during winter are much more toxic than those during summer and fine particles are more toxic than coarse particles. Compared to those in 2003, fine particulate PAHs and OPAHs in both cities during winter decreased by 50–90%, most likely due to the replacement of coal by natural gas in the country.

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are semi-volatile compounds consisting of two or more fused aromatic rings and are ubiquitous in the environment. Global emission of PAHs was estimated to be around 500 Gg in 2008 (Shen et al., 2013). PAHs have been intensively studied, because most of them are highly carcinogenic and/or mutagenic (Gao et al., 2016; Mittal and Van Grieken, 2001). It has been reported that as much as 1.6% of lung cancer cases in China can be attributed to inhalation of PAHs from polluted air (Zhang et al., 2009). PAHs are ubiquitously formed during the incomplete combustion process of carbon-containing matter, such as biomass, coal, petroleum, garbage,

tobacco and charbroiled meat (Chen et al., 2005; del Rosario Sienra et al., 2005; Kashiwakura and Sakamoto, 2010; Liu et al., 2009; Mittal and Van Grieken, 2001; Shen et al., 2010). Because of their semi-volatile nature atmospheric PAHs partition between gas and aerosol phases and both the vapor and particulate forms undergo chemical reactions.

Oxygenated PAHs (OPAHs) contain one or more carbonyl oxygen(s) attached to the aromatic ring structure and consist of ketones and quinones. OPAHs are typically of lower vapor pressures compared to their parent PAHs, and thus have a higher tendency to stay in particle phase. Some OPAHs are more toxic than their parent PAHs, because they are direct acting mutagens and also produce reactive oxygen species, both of which result in toxicity (Bandowe et al., 2010; Bolton et al., 2000; Chung et al., 2006; Pedersen et al., 2005). OPAHs can be produced directly from the incomplete combustion of organic matter (Jakober et al., 2007; Oda et al., 2001) and secondarily from photochemical reactions of PAHs with ozone and hydroxyl and nitro radicals (Albinet et al., 2008; Bandowe et al., 2014a; Eiguren-Fernandez et al., 2008; Wang et al., 2011).

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China is one of the largest PAH-emitting countries in the world due to its huge amount of coal combustion without efficient emission control (Xie et al., 2009; Liu et al., 2016). In addition, biomass burning activities including combustion of biofuel and field burning of crop residue are still very common in rural area of China, which is also an important source of PAHs in the country. Annual emission of PAHs from both urban and rural regions of China was around 106 Gg in 2007, accounting for 21% of the total global emission (Shen et al., 2013). Field observations on atmospheric PAHs from China have been intensively reported. However, only a limited number of field measurements about atmospheric OPAHs from the country have been documented but with no information about their size distribution (Bandowe et al., 2014b; Lin et al., 2015; Wang et al., 2011; Wei et al., 2015; Wei et al., 2012). Here we present our field observation results about airborne particulate PAHs and OPAHs from Xi'an in central China and Guangzhou in southern China. First we identified the differences in concentrations, and compositions of PAHs and OPAHs between the two megacities during the winter and summer of 2013. Then we investigated size distribution characteristics of the two classes of organics and toxicity of PAHs. Finally, we compared the abundance and compositions of PAHs and OPAHs with those in 2003, ten years ago, to discuss the potential causes resulting in the changes.

## 2. Methodology

### 2.1. Descriptions for sampling sites and sampling protocol

Xi'an (34.3°N and 108.9°E) is the capital city of the Shaanxi Province in central China with an area of 10,097 km<sup>2</sup> and a population of 8.5 million. This megacity is located on the Guanzhong Basin at the south edge of the Loess Plateau. Guangzhou (23.4°N and 113.3°E) is the capital city of the Guangdong Province in southern China with an area of 7434 km<sup>2</sup> and a population of 13 million. In Xi'an, aerosol samples were collected on the rooftop of a three-story building (about 10 m above the ground) on the campus of the Institute of Earth Environment of CAS, which is located in the downtown area of the city. In Guangzhou, aerosol samples were collected on the rooftop (50 m above the ground) of a building on the campus of the South China Institute of Environmental Science, which is located in the urban center of Guangzhou.

Size-segregated samples were collected by using an Anderson 9-stage air sampler (Thermo-electronic Company, USA) with the cutoff points of 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8 and 9.0 μm at an airflow rate of 28.3 L min<sup>-1</sup>. In both cities the size-resolved aerosol samples were collected for 3 days in each set and twice a month from 1st to 3rd and 15th to 17th of the month, respectively, during the summer (June, July and August of 2013) and winter (November and December of 2013 and January of 2014). Field blank filters were collected in each season at the beginning and the end of sampling campaign by mounting blank filters onto the sampler for about 10 min without sucking any air. A total of 32 sets of size-resolved filter samples including 8 sets of field blanks were collected. All the samples were collected on pre-baked (450 °C for 8 h) quartz fiber filters (Whatman 42). After sampling, the filter samples were sealed individually in an aluminum foil bag and stored in a freezer at -18 °C prior to analysis.

### 2.2. Sample analysis

In this work 288 filter samples (32 sets, each with 9 samples) were collected. In order to reduce the analysis time, we grouped the size-segregated samples into four size ranges: <1.1, 1.1–3.3, 3.3–9.0, and >9.0 μm for organic aerosol analysis. The details of sample extraction and derivatization were documented elsewhere (Wang et al., 2006; Wang et al., 2009). Briefly, filter aliquot was cut into pieces and extracted with a mixture of dichloromethane/methanol. Then the extracts were concentrated to dryness and derivatized with *N*, *O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA). Finally, the derivatized

samples were analyzed by using gas chromatography (GC) (HP 7890A, Agilent Co., USA) coupled with mass spectroscopy detector (HP 5975, Agilent Co., USA). The GC separation was carried out on a DB-5MS fused silica capillary column, and the GC oven temperature programmed from 50 °C (2 min) to 120 °C with 15 °C min<sup>-1</sup> and then to 300 °C with 5 °C min<sup>-1</sup>, with a final isothermal hold at 300 °C for 16 min. The sample was injected in a splitless mode at an injector temperature of 280 °C, and scanned from 50 to 650 Da using electron impact (EI) mode at 70 eV.

Based on the above extraction and derivatization technique, both polar and non-polar compounds in the samples were simultaneously measured (Wang et al., 2006; Wang et al., 2009). Here we only focused on PAHs and OPAHs, while other polar compounds such as sugars, biogenic secondary organic aerosols (BSOA), fatty acids and fatty alcohols were investigated by another paper (Ren et al., 2016). In this work 14 PAHs and 7 OPAH were analyzed. The 14 PAHs are phenanthrene (Phe), anthracene (Ant), fluranthene (Flu), pyrene (Pyr), benzo[*a*]-anthracene (BaA), chrysene (Chr), benzo[*b*] fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene (Per), indeno[1,2,3-*cd*] pyrene (IP), benzo[*g,h,i*] perylene (Bg<sub>hi</sub>P) and dibenz[*a,h*] anthracene (DBA)), while the 7 OPAHs are 9-fluorenone (9-FO), anthraquinone (ATQ), benzanthrone (BZA), benzo[*a*]anthracene-7,12-dione (7,12-BaAQ), 1,4-chrysenequinone (1,4-CQ), 5,12-naphthacenequinone (5,12-NAQ) and 6H-benzo[*cd*]pyrene-6-one (BPYRone).

### 2.3. Quality assurance and quality control (QA/QC)

All glassware used were rinsed with pure water and baked at 450 °C for 8 h and further rinsed with methanol, DCM and hexane immediately before using. Limits of detection (LOD) and quantification (LOQ) of the target compounds were calculated using signal-to-noise ratios of 3:1 and 10:1 following previous studies (Bandowe et al., 2014b; Li et al., 2016a), respectively. In this work LOD and LOQ of PAHs are in the ranges of 0.003–0.008 and 0.01–0.027 ng μL<sup>-1</sup>, while those of OPAHs are in the ranges of 0.007–0.37 and 0.024–1.23 ng μL<sup>-1</sup>, respectively (Table S1). Field blank sample analysis showed no serious contamination (<5% of real samples). The accuracy of the methodology was 98.2%, determined by the error obtained between the mean values of triplicates of a 2 ng μL<sup>-1</sup> standard solution. The precision of the methodology was 3.1%, calculated as the relative standard deviation (%RSD). The recovery experiment was done by spiking the standard solution, of which the amounts of target compounds including PAHs and OPAHs are similar to those in real samples, onto blank filters (*n* = 3) and analyzed using the above procedure. As shown in Table S1, the averaged recoveries are 102% for PAHs (range: 78% for Phe to 122% for BaA) and 110% for OPAHs (range: 80% for 9-FO to 137% for BPYRone), respectively. Data reported here were all corrected for the blanks but not corrected for the recoveries. Compounds used in a recovery experiment are pure agents, whereas those in real samples are a mixture with other organic and inorganic species. Thus, the recovery experiment could not entirely reflect the conditions of target compounds in the atmosphere.

## 3. Results and discussion

### 3.1. PAHs

In the current work concentrations of the 14 PAHs in the four grouped size ranges were summed as total suspended particle (TSP)-equivalent concentrations and summarized in Table 1. During winter TSP-equivalent concentrations of the total 14 PAHs are 57 ± 20 and 18 ± 23 ng m<sup>-3</sup> in Xi'an and Guangzhou, respectively, around 5–10 times higher than those (6.0 ± 2.9 ng m<sup>-3</sup> Xi'an and 2.8 ± 0.81 ng m<sup>-3</sup> in Guangzhou, respectively) in summer (Table 1) (Zhang et al., 2015). The Xi'an winter-time concentrations are comparable to those in 2012 (59 ± 21 ng m<sup>-3</sup>) (Wei et al., 2015) but lower than those in 2005/2007 (137 ± 57 ng

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