



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 $\Sigma 14\text{PAHs}$ in Xi'an and Guangzhou are 57 ± 20 and $18 \pm 23 \text{ ng m}^{-3}$ 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 $\Sigma 7\text{OPAHs}$ during winter are 54 ± 15 and $23 \pm 32 \text{ ng m}^{-3}$ 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; Eiguen-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 km² 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 km² 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⁻¹. 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⁻¹ and then to 300 °C with 5 °C min⁻¹, 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 (BgHiP) 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⁻¹, while those of OPAHs are in the ranges of 0.007–0.37 and 0.024–1.23 ng µL⁻¹, 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⁻¹ 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⁻³ in Xi'an and Guangzhou, respectively, around 5–10 times higher than those (6.0 ± 2.9 ng m⁻³ Xi'an and 2.8 ± 0.81 ng m⁻³ 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⁻³) (Wei et al., 2015) but lower than those in 2005/2007 (137 ± 57 ng

Table 1Total suspended particle (TSP)-equivalent concentrations (ng m^{-3}) of PAHs and OPAHs in Xi'an and Guangzhou, China.

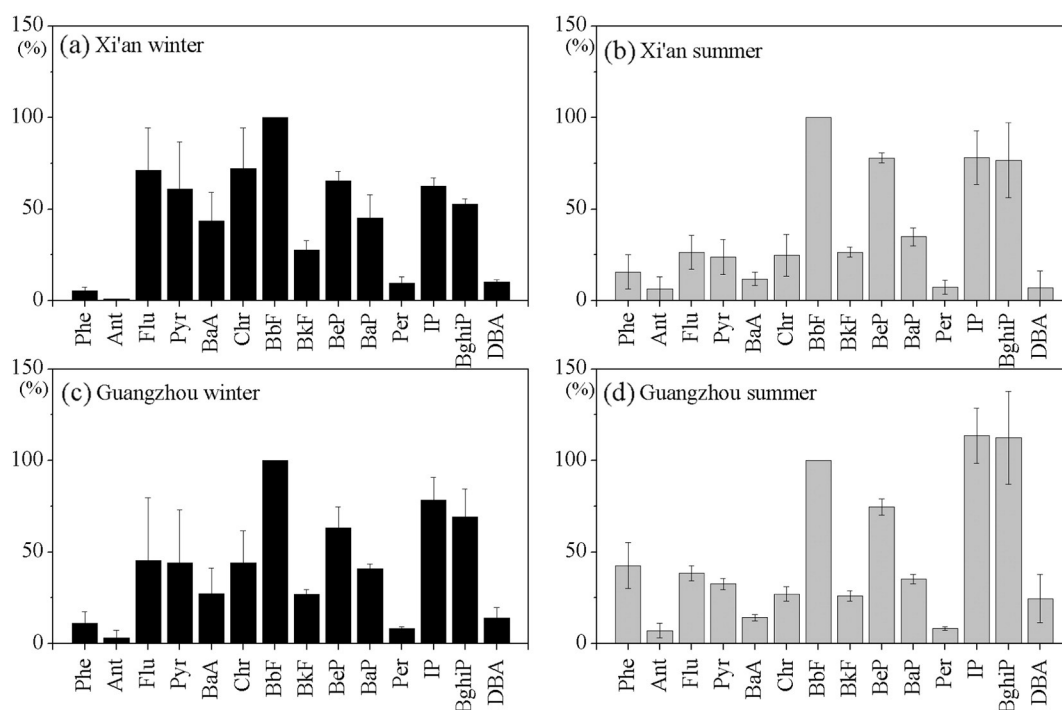
	Winter		Summer	
	Xi'an	Guangzhou	Xi'an	Guangzhou
I. PAHs				
Phe	0.49 ± 0.18 (0.2–0.71)	0.31 ± 0.41 (0.03–1.19)	0.15 ± 0.05 (0.1–0.21)	0.17 ± 0.04 (0.12–0.23)
Ant	0.07 ± 0.02 (0.05–0.11)	0.07 ± 0.08 (0.004–0.2)	0.05 ± 0.01 (0.04–0.07)	0.03 ± 0.01 (0.01–0.04)
Flu	6.3 ± 2.9 (2.6–10)	2.1 ± 3.9 (0.07–11)	0.27 ± 0.07 (0.15–0.35)	0.15 ± 0.04 (0.12–0.22)
Pyr	5.6 ± 2.8 (1.8–9.5)	1.9 ± 3.4 (0.09–9.5)	0.24 ± 0.06 (0.15–0.32)	0.14 ± 0.04 (0.1–0.2)
BaA	4.2 ± 1.9 (1.5–6)	1.2 ± 1.9 (0.07–5.6)	0.15 ± 0.09 (0.03–0.28)	0.06 ± 0.03 (0.04–0.1)
Chr	6.8 ± 3.1 (2.4–11)	1.5 ± 1.9 (0.08–5.4)	0.29 ± 0.17 (0.06–0.5)	0.13 ± 0.06 (0.06–0.21)
BbF	8.9 ± 2.6 (6.1–13)	2.9 ± 3.4 (0.38–9.8)	1.2 ± 0.59 (0.4–1.9)	0.45 ± 0.16 (0.29–0.68)
BkF	2.5 ± 1.0 (1.4–4.4)	0.73 ± 0.78 (0.1–2.2)	0.3 ± 0.14 (0.12–0.43)	0.12 ± 0.06 (0.07–0.2)
BeP	5.8 ± 1.7 (3.7–8)	1.6 ± 1.6 (0.28–4.2)	0.92 ± 0.44 (0.31–1.4)	0.33 ± 0.12 (0.21–0.5)
BaP	4.4 ± 1.8 (1.7–6.2)	1.2 ± 1.5 (0.16–4.2)	0.42 ± 0.24 (0.16–0.69)	0.16 ± 0.06 (0.1–0.23)
Per	0.96 ± 0.45 (0.34–1.5)	0.22 ± 0.25 (0.04–0.74)	0.08 ± 0.06 (0.02–0.15)	0.04 ± 0.01 (0.03–0.05)
IP	5.8 ± 1.9 (3.6–8.5)	2.0 ± 2.0 (0.34–5.7)	0.92 ± 0.5 (0.39–1.5)	0.49 ± 0.13 (0.33–0.66)
BghiP	4.8 ± 1.4 (3–6.7)	1.6 ± 1.5 (0.35–4.3)	0.9 ± 0.53 (0.4–1.5)	0.47 ± 0.09 (0.34–0.56)
DBA	0.95 ± 0.31 (0.58–1.4)	0.31 ± 0.33 (0.07–1.0)	0.1 ± 0.15 (0.002–0.36)	0.09 ± 0.03 (0.05–0.13)
Subtotal	57 ± 20 (29–82)	18 ± 23 (2.3–65)	6 ± 2.9 (2.4–9)	2.8 ± 0.81 (2–4)
II. OPAHs				
9-FO	6.4 ± 1.7 (4.7–8.9)	2.3 ± 3.1 (0.2–7.8)	ND ^a	ND
ATQ	11 ± 3.1 (7.5–16)	6.0 ± 7.8 (0.78–20)	29 ± 30 (5.4–79)	11 ± 10 (2.8–29)
BZA	6.6 ± 2.2 (3.7–9.5)	2.8 ± 4 (0.33–9.8)	ND	ND
7,12-BaAQ	1.8 ± 0.6 (1.1–2.8)	0.7 ± 0.9 (nd–2.3)	ND	ND
1,4-CQ	6.3 ± 4.3 (1.3–11)	1.3 ± 2.3 (nd–5.3)	ND	ND
5,12-NAQ	0.8 ± 0.3 (0.4–1.3)	0.5 ± 0.9 (nd–2)	ND	ND
BPYRone	21 ± 6.7 (12–29)	10 ± 13 (1.4–33)	ND	ND
Subtotal	54 ± 15 (35–70)	23 ± 32 (2.7–80)	29 ± 30 (5.4–79)	11 ± 10 (2.8–29)

^a ND: not detected.

m^{-3} in summer and $344 \pm 150 \text{ ng m}^{-3}$ in winter, respectively) (Okuda et al., 2010). The TSP-equivalent concentrations of PAHs in Guangzhou are similar to those in 2010 ($5.1 \pm 1.9 \text{ ng m}^{-3}$ in summer and $16 \pm 6.2 \text{ ng m}^{-3}$ in winter, respectively) (Zhang et al., 2012) but lower than those reported for PM_{10} in 2002/2003 ($9.3\text{--}27 \text{ ng m}^{-3}$ in summer and $8\text{--}106 \text{ ng m}^{-3}$ in winter) (Tan et al., 2006). Such decreases in PAH concentrations in both cities during 2013 suggest the effectiveness of air pollution control in China. Compared with those in Guangzhou, the local basin-like topography, less precipitation and more coal combustion in Xi'an are the major

factors causing higher levels of pollutants including PAHs (Bandowe et al., 2014b; Wang et al., 2006).

As shown in Fig. 1a and b, BbF is the most abundant PAH congener in Xi'an in both seasons, followed by Chr, Flu, BeP and IP during winter and BeP, IP and BghiP during summer. In contrast, in Guangzhou BbF is the most abundant species during winter while IP and BghiP are the highest congeners during summer (Fig. 1c and d). As illustrated in Fig. 2, high molecular weight (HMW) PAHs, i.e., the 5-ring and 6-ring congeners, are the dominant species especially in summer, accounting for 49–79%

**Fig. 1.** Abundances of PAHs relative to BbF in TSP during the winter and summer of 2013 in Xi'an and Guangzhou, China.

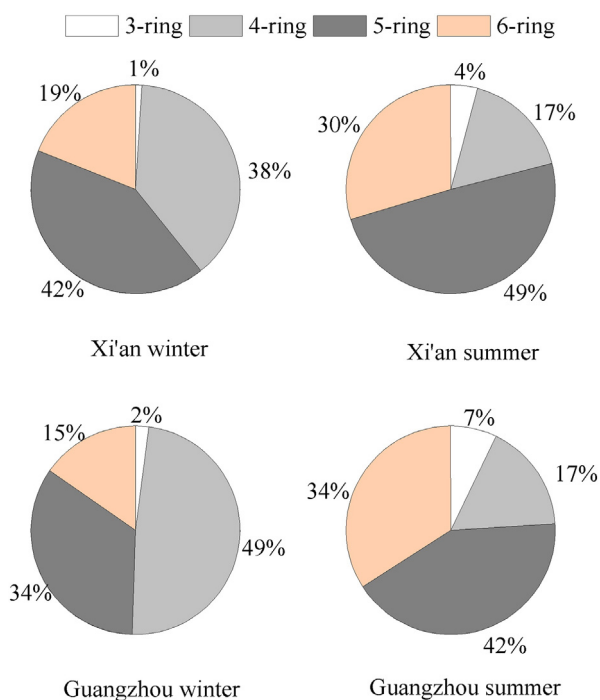


Fig. 2. Distribution of ring number of PAHs in TSP during the winter and summer of 2013 in Xi'an and Guangzhou, China.

of the total in the two cities during both seasons. Compared to those during winter the lower relative abundances of particulate low molecular weight (LMW) PAHs, i.e., 3- and 4-ring PAHs, during summer in Xi'an (21%) and Guangzhou (24%) are likely due to summertime higher temperatures that are favorable for the LMW PAHs partitioning into the gas phase because of their more volatile nature.

BaP is labile to photochemical oxidation, while its isomer BeP is much more chemically stable. Therefore, BeP/BaP ratio is indicative of aerosol photochemical ageing (Okuda et al., 2002; Tang et al., 2006). In the current work, the ratios are 2.3 ± 0.4 and 2.9 ± 1.2 in Xi'an and Guangzhou during summer, respectively, which are statistically higher ($p < 0.05$) than those (1.4 ± 0.4 and 2.0 ± 0.2 in Xi'an and Guangzhou, respectively) during winter (Fig. 3), suggesting an enhanced photochemical oxidation in the hot season.

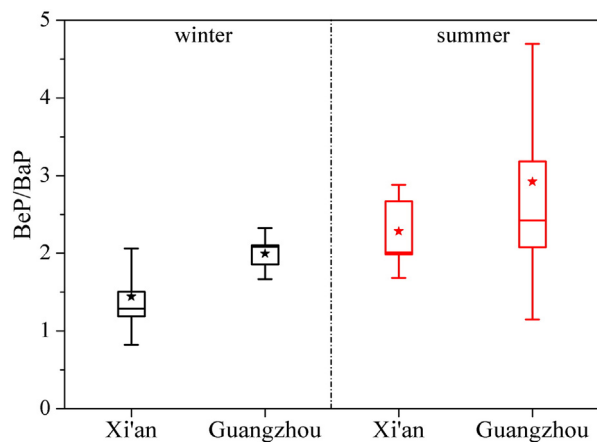


Fig. 3. TSP-equivalent concentration ratio of BeP/BaP during the winter and summer of 2013 in Xi'an and Guangzhou, China.

3.2. OPAHs

All the seven OPAHs were detected in the winter samples but only anthraquinone (ATQ) was detectable in the summer samples in both cities (Table 1). TSP-equivalent concentrations of the total OPAHs are 54 ± 15 and 23 ± 32 ng m⁻³ in Xi'an and Guangzhou during the winter and 29 ± 30 and 11 ± 10 ng m⁻³ in both cities during summer (Table 1). The values from Xi'an are higher than those in the spring of 2012 (25 ± 3.9 ng m⁻³) (Wei et al., 2015), which is mainly due to the difference in seasons, but comparable to those in the summer of 2012 (16 ± 6 ng m⁻³) (Wei et al., 2015).

BPYRone is the most abundant OPAH during winter in Xi'an and Guangzhou and accounts for nearly 40% of the total, followed by ATQ, 9-FO, BZA and 1,4-CQ (Fig. 4). The lowest OPAH in both cities is 5,12-NAQ, which is 0.8 ± 0.3 and 0.5 ± 0.9 ng m⁻³ in Xi'an and Guangzhou, respectively. OPAHs in the two Chinese megacities are higher than those in developed countries. For instance, the summertime concentrations (29 ± 30 ng m⁻³ in Xi'an and 11 ± 10 ng m⁻³ in Guangzhou, Table 1) of ATQ in this work are about two orders of magnitude higher than those (82.0 – 659.8 pg m⁻³) at an urban traffic site in Paris (Ringuelet et al., 2012), demonstrating the severe air pollution in China. 5-ring OPAHs are dominant during winter (Fig. 5), accounting for 38% and 45% of the total OPAHs in Xi'an and Guangzhou, respectively.

3.3. Size distribution

Chemical-based particle size information is indispensable for an accurate understanding on the environmental fate and transport of atmospheric particles, their deposition behavior in the human pulmonary system and climate effects. Here we investigate size distribution characteristics of PAHs and OPAHs in the two cities to discuss their atmospheric behavior (Table 2 and Figs. 6, 7 and 8). In Xi'an PAHs of PM_{1,1} in winter and summer account for $60 \pm 6.7\%$ and $61 \pm 33\%$ of the total airborne particulate PAHs, while those in Guangzhou account for $79 \pm 19\%$ and $78 \pm 5.2\%$ of the total (Table 2). As seen in Fig. 6a, 4- and 5-ring PAHs are the dominant species in each size range in Xi'an during winter, accounting for about 80% of the total. 4- and 5-ring PAHs are also the major species in each size range in Guangzhou during winter, but in comparison with those in Xi'an their abundances are relatively lower with the fraction varying from 70% of the total in the size range of < 1.1 μm to about 50% of the total in the size range of > 9.0 μm (Fig. 6b). During summer in both cities PAHs are dominated by 5- and 6-ring congeners in the size ranges of < 1.1 and 1.1 – 3.3 μm and by 3- and 4-ring congeners in the size ranges of 3.3 – 9.0 and > 9.0 μm, respectively (Fig. 6). During both seasons HMW PAHs such as the 6-ring congeners in the two cities mostly stay in the smaller size range (< 3.3 μm)

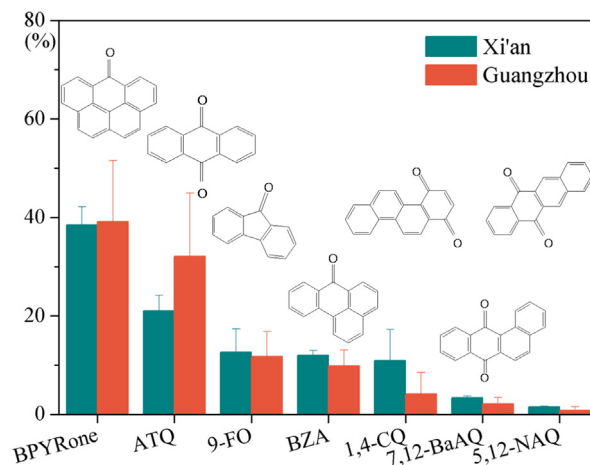


Fig. 4. Compositions of OPAHs in TSP during the winter of 2013 in Xi'an and Guangzhou, China.

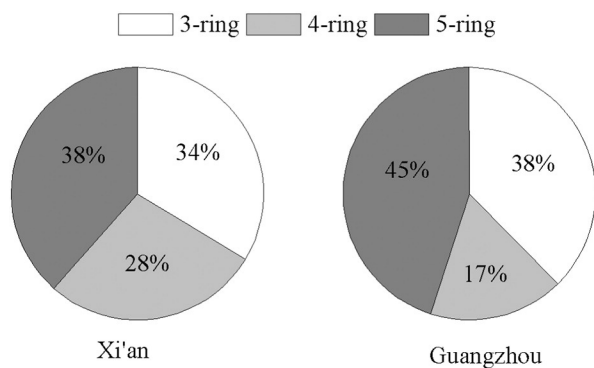


Fig. 5. Distribution of ring number of OPAHs in TSP during the winter of 2013 in Xi'an and Guangzhou, China.

(Fig. 6), which is consistent with work done in earlier studies. For example, Hays et al. (2003) measured the size distribution of PAHs emitted from wood burning and found that HMW PAHs spread over smaller diameter, while LMW PAHs tend to associate with large aerosols. Relative concentrations of 6-ring PAHs in each size range are higher in Guangzhou than in Xi'an and are generally higher in summer than in winter.

LMW PAHs are much more volatile than HMW ones. For example, vapor pressure (1×10^{-3} Pa at 298 K, Table S1) of 3-ring Ant is seven orders of magnitude higher than 5-ring DBA (3.7×10^{-10} Pa at 298 K, Table S1). After being emitted into the ambient air with fine particles, LMW PAHs can evaporate into the gas phase and re-condense and/or adsorb onto coarse particles (Wang et al., 2010). Such a shift toward larger particles is more significant in summer due to higher temperature. Therefore, Ant peaked in the fine mode ($<3.3 \mu\text{m}$) in winter and the coarse mode ($>3.3 \mu\text{m}$) in summer in both cities, respectively (Fig. 7a, b). In contrast, HMW PAHs only stay in fine particle due to their non-volatile nature (Wang et al., 2010). Thus, IP peaked in the fine mode during the two seasons in both cities (Fig. 7c, d).

Because only ATQ was detected in summer, here we solely focus on wintertime OPAHs and discuss their compositions in different size ranges. As seen in Tables 2, $58 \pm 9.5\%$ and $72 \pm 24\%$ OPAHs in Xi'an and Guangzhou stay in $\text{PM}_{1.1}$ during winter with 5-ring OPAHs being the dominant species (Fig. 8). In both cities small molecules such as 3-ring OPAHs account for $<30\%$ of the total in $\text{PM}_{1.1}$ but $>90\%$ of the total in coarse particles ($>3.3 \mu\text{m}$) (Fig. 8). As shown in Table S1, vapor pressure of 9-FO is 1.6×10^{-2} Pa at 298 K, which is three orders of magnitude higher than that (2×10^{-5} Pa at 298 K) of BZA. Thus, a large fraction of 9-FO stay in the coarse mode ($>3.3 \mu\text{m}$) (Fig. 7e, f), while BZA almost entirely stays in the fine mode ($<3.3 \mu\text{m}$) (Fig. 7g, h). Such differences in size distribution result in 4- and 5-ring OPAHs in Xi'an and

Table 2

Concentration (ng m^{-3}) and percentage of total PAHs in different size range of particles.

Size range	Xi'an				Guangzhou			
	Winter		Summer		Winter		Summer	
	Concentration	Percentage	Concentration	Percentage	Concentration	Percentage	Concentration	Percentage
I. PAHs								
$>9.0 (\mu\text{m})$	0.6 ± 0.3	$1.0 \pm 0.4\%$	1.3 ± 2.8	$14 \pm 30\%$	0.2 ± 0.4	$2.9 \pm 3.3\%$	0.1 ± 0.1	$2.9 \pm 3.3\%$
$3.3\text{--}9.0 (\mu\text{m})$	2.7 ± 1.9	$4.8 \pm 2.1\%$	0.2 ± 0.1	$3.3 \pm 1.9\%$	0.9 ± 1.7	$9.9 \pm 15\%$	0.3 ± 0.2	$9.4 \pm 4.4\%$
$1.1\text{--}3.3 (\mu\text{m})$	19 ± 8.4	$34 \pm 4.7\%$	1.2 ± 0.9	$22 \pm 16\%$	0.6 ± 0.6	$8.3 \pm 7.4\%$	0.2 ± 0.1	$8.3 \pm 2.3\%$
$<1.1 (\mu\text{m})$	33 ± 13	$60 \pm 6.7\%$	3.4 ± 1.9	$61 \pm 33\%$	4.4 ± 2.2	$79 \pm 19\%$	2.2 ± 0.5	$78 \pm 5.2\%$
II. OPAHs								
$>9.0 (\mu\text{m})$	0.9 ± 0.3	$1.9 \pm 0.5\%$	0.5 ± 0.5	$1.7 \pm 0.6\%$	1.5 ± 3.0	$6.3 \pm 10\%$	1.2 ± 1.5	$10 \pm 11\%$
$3.3\text{--}9.0 (\mu\text{m})$	4.7 ± 1.7	$9.3 \pm 2.2\%$	15 ± 32	$24 \pm 39\%$	3.1 ± 4.9	$16 \pm 15\%$	4.6 ± 7.3	$29 \pm 22\%$
$1.1\text{--}3.3 (\mu\text{m})$	16 ± 6.8	$31 \pm 8.4\%$	7.9 ± 13	$38 \pm 38\%$	0.9 ± 0.8	$6.5 \pm 6.1\%$	1.3 ± 0.9	$13 \pm 7.6\%$
$<1.1 (\mu\text{m})$	30 ± 10	$58 \pm 9.5\%$	5.1 ± 5.0	$36 \pm 37\%$	7.4 ± 3.1	$72 \pm 24\%$	3.5 ± 1.4	$48 \pm 27\%$

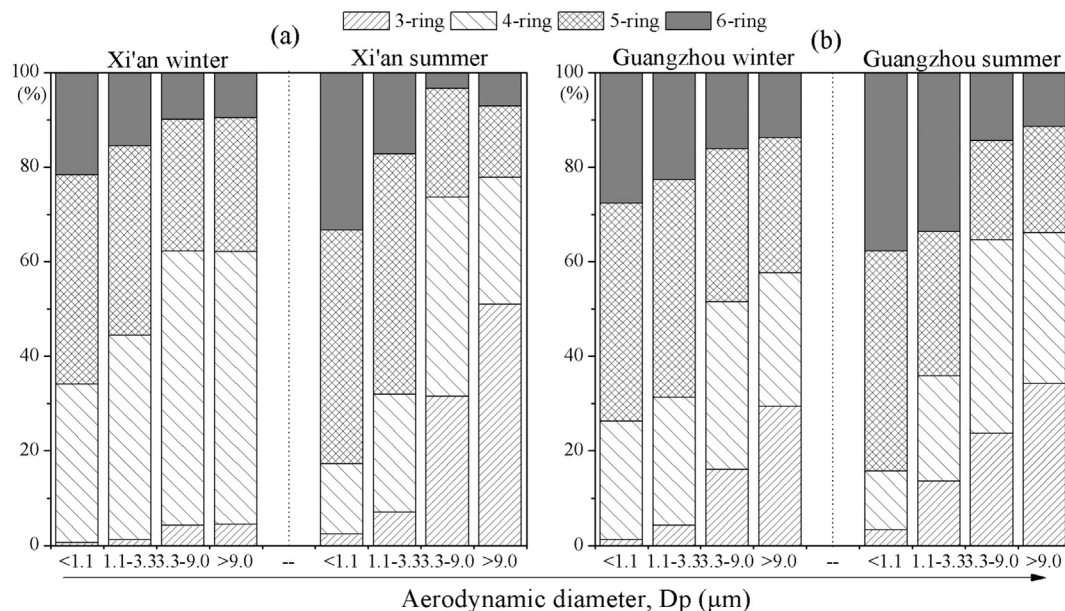


Fig. 6. Size-resolved compositions of PAHs in Xi'an and Guangzhou during the winter and summer of 2013.

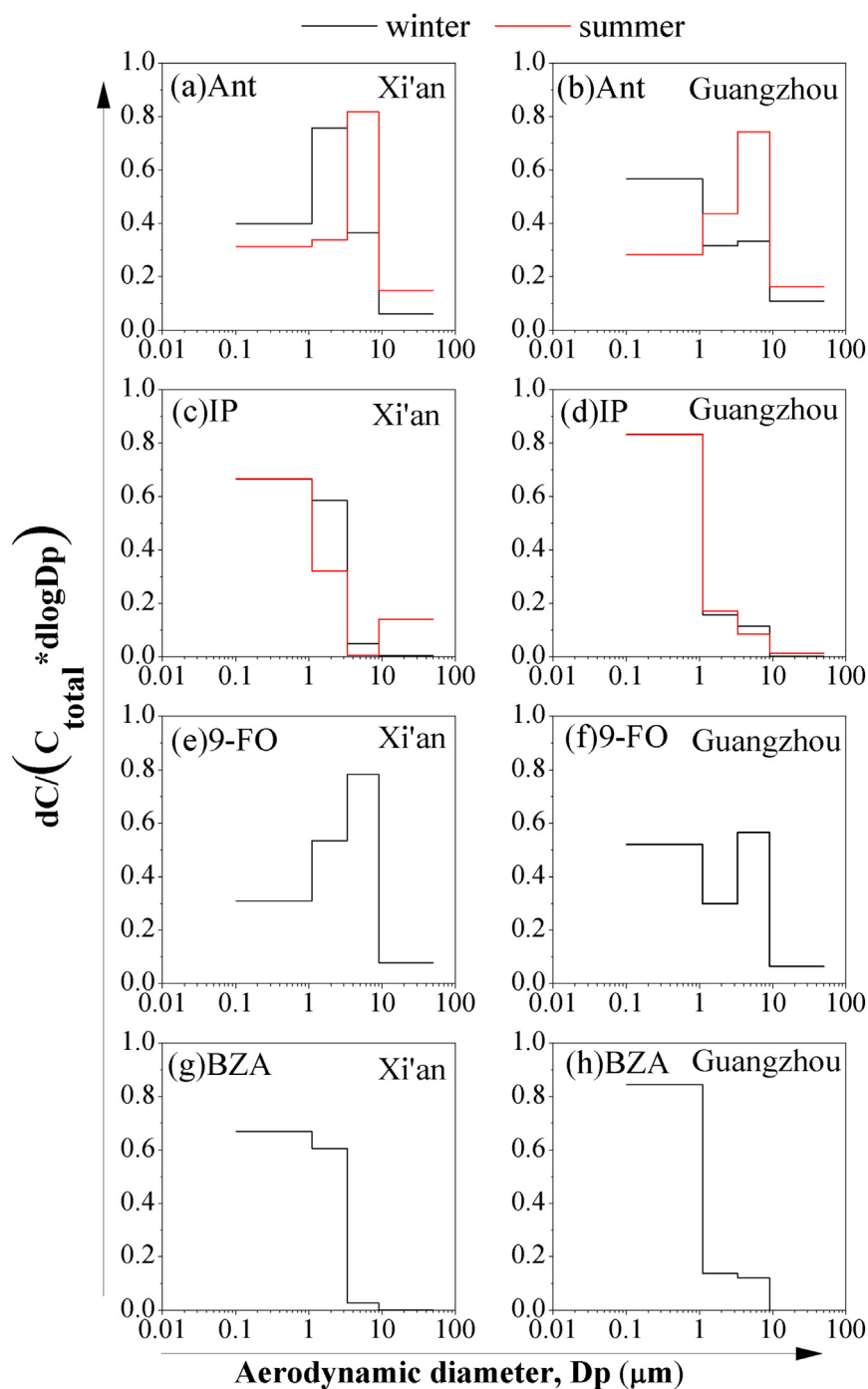


Fig. 7. Size distributions of selected PAHs (a-d) and OPAHs (e-h) in Xi'an and Guangzhou during the winter and summer of 2013.

Guangzhou during winter dominant in small particles ($<1.1 \mu\text{m}$) and 3-ring OPAHs dominant in the coarse mode (Fig. 8), which is in agreement with those observed in Boston, USA (Allen et al., 1997) and Paris, France (Ringuet et al., 2012).

3.4. Toxicity of PAHs in Xi'an and Guangzhou

BaP-TEQ (toxic equivalents) and BaP-MEQ (mutagenic equivalents) have been utilized to indicate the potential health risk of PAHs to ecosystems and human beings (Durant et al., 1996; Jung et al., 2010), which are calculated by multiplying the concentrations of each PAH compound with its TEF (the carcinogenic equivalency factor) for cancer potency relative to BaP (Nisbet and LaGoy, 1992) and MEF (the

mutagenic equivalency factor) relative to BaP (Durant et al., 1996; Durant et al., 1999). Table 3 shows the BaP-TEQ and BaP-MEQ values for the sum of non-volatile PAH ($\text{MW} \geq 228$). The total BaP-TEQ during winter and summer are $11 \pm 3.8 \text{ ng m}^{-3}$ and $1.2 \pm 0.99 \text{ ng m}^{-3}$ in Xi'an and $3.4 \pm 3.9 \text{ ng m}^{-3}$ and $0.76 \pm 0.19 \text{ ng m}^{-3}$ in Guangzhou, while the mean BaP-MEQ during winter and summer are $10 \pm 3.5 \text{ ng m}^{-3}$ and $1.3 \pm 0.69 \text{ ng m}^{-3}$ in Xi'an and $3.1 \pm 3.6 \text{ ng m}^{-3}$ and $0.56 \pm 0.17 \text{ ng m}^{-3}$ in Guangzhou, respectively. The mean BaP-TEQ and BaP-MEQ concentrations are 4–9 times higher in winter than in summer and more than two times higher in Xi'an than in Guangzhou, indicating air pollution in Xi'an is more toxic especially in winter (see Table 3).

Fig. 9 shows the size distributions of BaP-TEQ and BaP-MEQ in the two cities. The values exhibit a decreasing pattern along with an

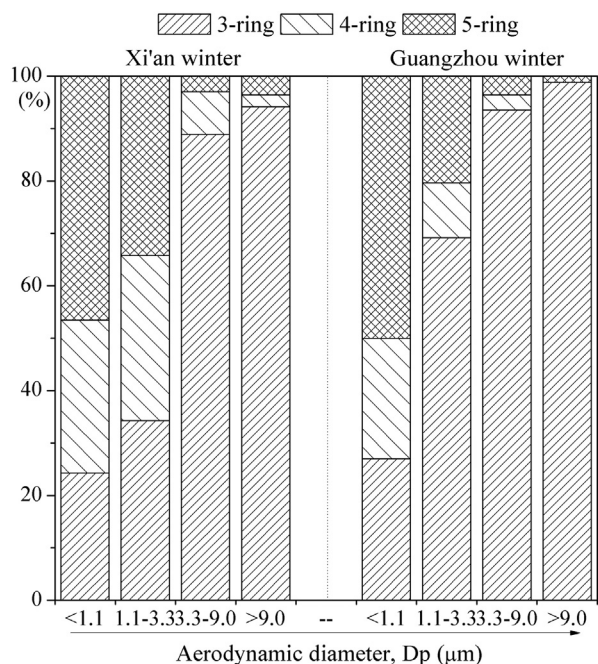


Fig. 8. Size-resolved compositions of OPAHs in Xi'an and Guangzhou during the winter of 2013.

increase in particle sizes, i.e., $PM_{1.1} > PM_{1.1-3.3} > PM_{3.3-9.0} > PM_{>9.0}$, except in Xi'an during summer, suggesting that small particles are more toxic.

3.5. PAHs and OPAHs between 2013 and 2003 in Xi'an and Guangzhou

A comparison of concentrations and mass ratios of PAHs and OPAHs between 2003 and 2013 is shown in Table 4. It should be noted that all the concentrations in 2003 are for $PM_{2.5}$ aerosols, while those in 2013 are for $PM_{3.3}$ aerosols (the sum of the concentrations on the stages of $<1.1 \mu m$ plus $1.1-3.3 \mu m$). In 2013 concentrations of $\Sigma 14PAHs$ in $PM_{3.3}$ are 54 ± 19 and $17 \pm 23 \text{ ng m}^{-3}$ during winter in Xi'an and Guangzhou, respectively, and $<10\%$ of those in the winter of 2003 (Wang et al., 2006). Compared to those in the summer of 2003, PAHs in 2013 decreased by about 50% and 70% in Xi'an and Guangzhou, respectively. The lower particle-bound PAH concentrations in 2013 is possibly attributed to a decrease in domestic coal consumption by replacing with natural gas or petroleum in both cities, because domestic coal burning has been demonstrated as the major source of PAHs in China (Li et al., 2016b; Zhang et al., 2009; Wang et al., 2006, 2007). For instance, total natural gas consumption in Xi'an increased from $3.2 \times 10^8 \text{ m}^3$ in 2003 to $1.5 \times 10^9 \text{ m}^3$ in 2013 (<http://www.xatj.gov.cn/ptl/def/def/2014/tjnj/index.htm>). Concentrations of OPAHs also significantly decreased because of the decreased parent PAHs. Except for that in the summer in Guangzhou the ratio of BeP/BaP is higher in 2013 than that in 2003 in both cities during summer and winter (Table 4), probably indicating

Table 3

The BaP-equivalent (BaP-TEQ and BaP-MEQ)^c concentrations calculated for individual PAHs component (MW ≥ 228) (ng m^{-3}).

	BaP-TEQ Levels			BaP-MEQ Levels		
	TEF ^a	Winter	Summer	MEF ^b	Winter	Summer
I. Xi'an						
BaA	0.1	$0.42 \pm 0.19(0.15-0.6)$	$0.02 \pm 0.009(0.003-0.03)$	0.082	$0.34 \pm 0.16(0.12-0.49)$	$0.01 \pm 0.008(0.002-0.02)$
Chr	0.01	$0.07 \pm 0.03(0.02-0.11)$	$0.003 \pm 0.002(0.001-0.005)$	0.017	$0.12 \pm 0.05(0.04-0.18)$	$0.005 \pm 0.003(0.001-0.008)$
BbF	0.1	$0.89 \pm 0.26(0.61-1.3)$	$0.12 \pm 0.06(0.04-0.19)$	0.25	$2.2 \pm 0.64(1.5-3.2)$	$0.29 \pm 0.15(0.1-0.47)$
BkF	0.1	$0.25 \pm 0.1(0.14-0.44)$	$0.03 \pm 0.01(0.01-0.04)$	0.11	$0.27 \pm 0.11(0.16-0.48)$	$0.03 \pm 0.02(0.01-0.05)$
BaP	1	$4.4 \pm 1.8(1.7-6.2)$	$0.42 \pm 0.24(0.16-0.69)$	1	$4.4 \pm 1.8(1.7-6.2)$	$0.42 \pm 0.24(0.16-0.69)$
IP	0.1	$0.58 \pm 0.19(0.36-0.85)$	$0.09 \pm 0.05(0.04-0.15)$	0.31	$1.8 \pm 0.58(1.1-2.6)$	$0.28 \pm 0.16(0.12-0.47)$
BghiP	0.01	$0.05 \pm 0.01(0.03-0.07)$	$0.009 \pm 0.005(0.004-0.02)$	0.19	$0.92 \pm 0.27(0.58-1.3)$	$0.17 \pm 0.1(0.08-0.28)$
DBA	5	$4.7 \pm 1.5(2.9-7.1)$	$0.51 \pm 0.76(0.008-1.8)$	0.29	$0.28 \pm 0.09(0.17-0.41)$	$0.03 \pm 0.04(0.0004-0.11)$
Total		$11 \pm 3.8(5.9-16)$	$1.2 \pm 0.99(0.27-2.8)$		$10 \pm 3.5(5.4-14)$	$1.3 \pm 0.69(0.48-1.9)$
II. Guangzhou						
BaA	0.1	$0.12 \pm 0.19(0.007-0.56)$	$0.006 \pm 0.003(0.004-0.01)$	0.082	$0.1 \pm 0.16(0.006-0.46)$	$0.005 \pm 0.002(0.003-0.008)$
Chr	0.01	$0.02 \pm 0.02(0.001-0.05)$	$0.001 \pm 0.001(0.001-0.002)$	0.017	$0.03 \pm 0.03(0.001-0.09)$	$0.002 \pm 0.001(0.001-0.004)$
BbF	0.1	$0.29 \pm 0.34(0.04-0.98)$	$0.05 \pm 0.02(0.03-0.07)$	0.25	$0.72 \pm 0.84(0.09-2.4)$	$0.11 \pm 0.04(0.07-0.17)$
BkF	0.1	$0.07 \pm 0.08(0.01-0.22)$	$0.01 \pm 0.006(0.007-0.02)$	0.11	$0.08 \pm 0.09(0.01-0.24)$	$0.01 \pm 0.006(0.008-0.02)$
BaP	1	$1.2 \pm 1.5(0.16-4.2)$	$0.16 \pm 0.06(0.1-0.23)$	1	$1.2 \pm 1.5(0.16-4.2)$	$0.16 \pm 0.06(0.1-0.23)$
IP	0.1	$0.19 \pm 0.2(0.03-0.57)$	$0.05 \pm 0.01(0.03-0.07)$	0.31	$0.61 \pm 0.62(0.11-1.8)$	$0.15 \pm 0.04(0.1-0.2)$
BghiP	0.01	$0.02 \pm 0.02(0.004-0.04)$	$0.005 \pm 0.001(0.003-0.006)$	0.19	$0.31 \pm 0.29(0.07-0.82)$	$0.09 \pm 0.02(0.07-0.11)$
DBA	5	$1.5 \pm 1.6(0.37-5.1)$	$0.48 \pm 0.15(0.23-0.64)$	0.29	$0.09 \pm 0.09(0.02-0.29)$	$0.03 \pm 0.009(0.013-0.037)$
Total		$3.4 \pm 3.9(0.69-12)$	$0.76 \pm 0.19(0.43-0.94)$		$3.1 \pm 3.6(0.47-10)$	$0.56 \pm 0.17(0.39-0.78)$

^a TEF: toxic equivalency factors for cancer potency relative to BaP (Nisbet and LaGoy, 1992).

^b MEF: mutagenic potency factor relative to BaP (Durant et al., 1996 and Durant et al., 1999).

^c BaP-TEQ and BaP-MEQ: Carcinogenic equivalents calculated from TEF and mutagenic equivalents calculated from MEF multiplied by the concentration of PAH in a sample, respectively.

Table 4

Concentrations and compositions of fine particulate PAHs and OPAHs in 2003 and 2013.

	2003 ($PM_{2.5}$) ^a				2003 ($PM_{3.3}$)			
	Winter		Summer		Winter		Summer	
	Xi'an	Guangzhou	Xi'an	Guangzhou	Xi'an	Guangzhou	Xi'an	Guangzhou
$\Sigma 14PAHs$ (ng m^{-3})	605	282	96	7.4	54 ± 19	17 ± 23	5 ± 2.4	2.4 ± 0.6
$\Sigma 70PAHs$ (ng m^{-3})	406	306	42	ND ^b	49 ± 14	33 ± 32	13 ± 12	4.7 ± 2.2
BeP/BaP	0.88	0.72	2.0	3.5	1.4 ± 0.42	1.5 ± 0.28	2.3 ± 0.38	2.0 ± 0.17

^a PAH concentrations are cited from Wang et al. (2006), while OPAHs in the 2003 $PM_{2.5}$ samples are quantified based on the mass spectrum data reserved in the lab GC/MS instrument.

^b ND: not detected.

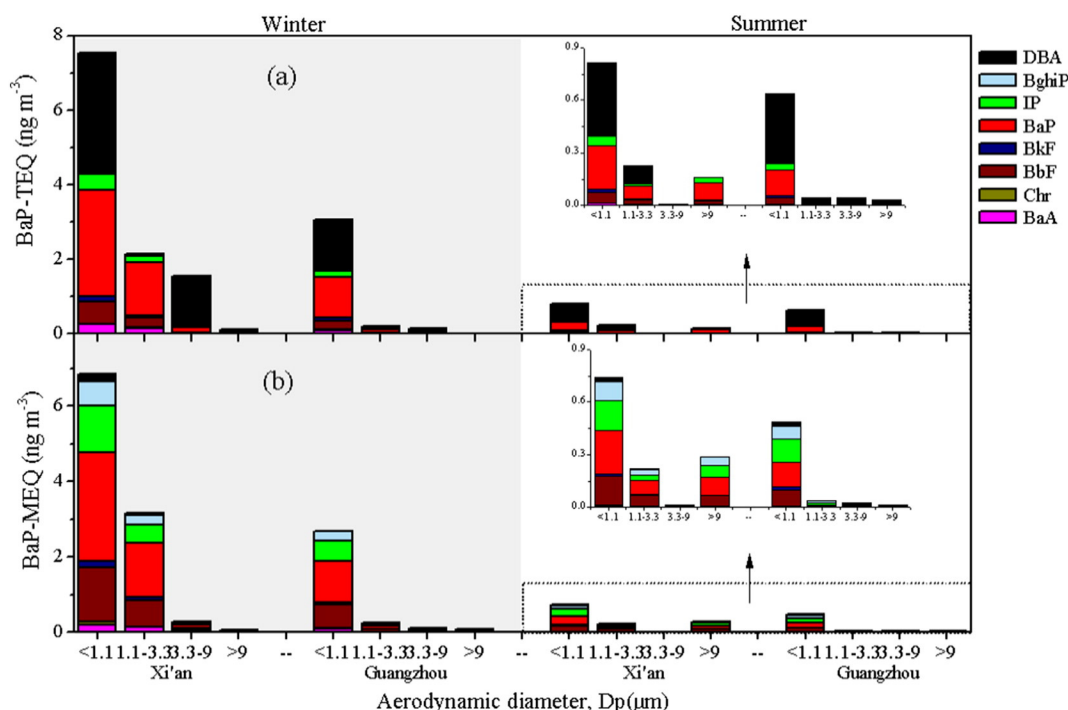


Fig. 9. Size-resolved BaP-TEQ (a) and BaP-MEQ (b) values in Xi'an and Guangzhou during the winter and summer of 2013.

that the current atmospheric environment in Chinese urban regions is more oxidative.

4. Summary and conclusions

PAHs and OPAHs in size-resolved particles from Xi'an and Guangzhou during the winter and summer of 2013 were determined. The wintertime TSP-equivalent concentrations of $\Sigma 14\text{PAHs}$ in Xi'an and Guangzhou are 57 ± 20 and $18 \pm 23 \text{ ng m}^{-3}$, about 5–10 times higher than those in summer. Summertime PAHs in both cities are dominated by 5- and 6-ring congeners, while those in wintertime are dominated by 4- and 5-ring congeners. Seven OPAHs were detected for the winter samples, but only ATQ was detected for the summer samples. The wintertime OPAHs are dominated by 5-ring oxygenated PAHs, of which BPyRone is the most abundant species and accounts for 40% of the total.

Size distribution results showed that PAHs of $\text{PM}_{1.1}$ during winter and summer account for $60 \pm 6.7\%$ and $61 \pm 33\%$ of the total ambient particulate PAHs in Xi'an, respectively, while those in Guangzhou account for $79 \pm 19\%$ and $78 \pm 5.2\%$ of the total. The fine modes ($<3.3 \mu\text{m}$) of PAHs in both cities are dominated by 4- and 5-ring congeners in winter and 5- and 6-ring congeners in summer. Relative abundance of 3-ring PAHs increases along with an increase in particle size, accounting for from $<1\%$ of the total PAHs in $\text{PM}_{1.1}$ to about 50% of the total in the largest size range ($>9.0 \mu\text{m}$). In winter 4- and 5-ring OPAHs are the dominant species in $\text{PM}_{1.1}$ in Xi'an and Guangzhou, accounting for $>70\%$ of the total, while 3-ring OPAHs dominated in coarse particles ($>3.3 \mu\text{m}$), accounting for $>90\%$ of the total.

The mean BaP-TEQ and BaP-MEQ concentrations are 4–9 times higher in winter than in summer in the two cities with those 2 times higher in Xi'an than in Guangzhou, indicating that atmospheric aerosols in Xi'an are more toxic especially in winter. Size distribution of BaP-TEQ and BaP-MEQ concentrations further showed that fine particles are more toxic than coarse particles.

A comparison of PAHs and OPAHs in fine particles between 2003 and 2013 indicated concentrations of PAHs and OPAHs significantly decreased during the last decade especially in winter, mainly because of the decrease in domestic coal consumption by replacing with natural gas or petroleum in China.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.atmosres.2016.09.015>.

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