

# Particle-Associated Polycyclic Aromatic Hydrocarbons (PAHs) in the Atmosphere of Hefei, China: Levels, Characterizations and Health Risks

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**Abstract** Airborne PM<sub>2.5</sub> and PM<sub>10</sub> samples were collected in summertime (August 2015) and wintertime (December 2015–January 2016) in an industrial complex area in Hefei, China. The average concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> (90.5 and 114.5 μg/m<sup>3</sup>, respectively) were higher than the regulated levels of China National Ambient Air Quality Standard (grade I) and the WHO Ambient (outdoor) Air Quality and Health Guideline Value. Seasonal variations in PM<sub>2.5</sub>/PM<sub>10</sub> indicated that the secondary sources of particulate matters, formed by gas-to-particle conversion, were enhanced in summer due to longer time of solar radiation and higher temperature. The total concentrations of PM<sub>2.5</sub>- and PM<sub>10</sub>-associated PAHs were 5.89 and 17.70 ng/m<sup>3</sup> in summer as well as 63.41 and 78.26 ng/m<sup>3</sup> in winter, respectively. Both PM<sub>2.5</sub>- and PM<sub>10</sub>-associated PAHs were dominated by 4- to 6-ring PAHs, suggesting that the fossil fuel combustion and vehicle emissions were the primary sources of PAHs in atmospheric particulate matters in Hefei. The total concentration of PAHs had a slightly higher correlation coefficient with PM<sub>2.5</sub> ( $R = 0.499$ ,  $P < 0.05$ ) than PM<sub>10</sub> ( $R = 0.431$ ,  $P > 0.05$ ), indicating the higher association tendency of PAHs with PM<sub>2.5</sub>. The coefficient of divergence analysis showed that the compositions of PAH were quite

different between summer and winter. Total BaP equivalent concentration (BaP-TEQ) for particulate-bound PAHs in winter (58.87 ng/m<sup>3</sup>) was higher than that in summer (5.53 ng/m<sup>3</sup>). In addition, particulate-bound PAHs in winter had an inhalation cancer risk (ICR) value of  $2.8 \times 10^{-3}$ , which was higher than the safe range ( $10^{-4}$ – $10^{-6}$ ).

In recent years, rapid development of economy has resulted in dramatic increase in air pollutant emissions (Chan and Yao 2008), especially in developing countries. Particulate matters have become the primary air pollutants and drawn more attentions due to their critical roles in forming hazy weather (Zhou et al. 2016). PM<sub>2.5</sub> and PM<sub>10</sub> represent particulate matters whose aerodynamic diameters are less than 2.5 and 10 μm, respectively. They could be inhaled through the respiratory system and probably lead to certain serious health problems (Yang et al. 2012). In addition, PM<sub>2.5</sub>, which consists of a substantial part of PM<sub>10</sub>, is able to bypass the respiratory tract and penetrate deep into the lungs owing to their minute size (Mao et al. 2007; Marcuzzan et al. 2001). Particulate matters would arise from both anthropogenic and natural sources. The primary sources come from direct emissions, and the secondary sources derive mainly from the conversion from gas to particles (Tian et al. 2016; Zheng et al. 2005).

PAHs are hydrocarbon compounds consisting of at least two benzene rings (Wiriya et al. 2013). They are primarily produced from pyrolysis of fossil fuels and incomplete combustion. US Environmental Protection Agency (US EPA 1982) recommends 16 PAHs as priority pollutants (Bojes and Pope 2007; Yan et al. 2004). Benzo[a]pyrene has been classified as known carcinogen by International Agency for Research on Cancer (IARC 2010), while other PAHs are considered to be possible human carcinogens. Organic

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compounds like polycyclic aromatic hydrocarbons (PAHs) can be adsorbed by particulate matters, and they are highly carcinogenic and mutagenic (Kim et al. 2013; Wu et al. 2014).

Many studies investigated PAHs in particulate matter in recent years in China. For example, Zhang et al. (2016) reported the spatial and seasonal variation of PAHs in PM<sub>2.5</sub> and PM<sub>10</sub> in Beijing, Tianjin and Shijiazhuang. PAHs in particles of different sizes in Hong Kong were characterized by Guo et al. (2003). Similar studies have been reported for some industrial cities, such as the Guangzhou, Zhengzhou and Taiyuan (Wang et al. 2006; Wei et al. 2012; Xia et al. 2013). For other countries, large cities are still main research subjects. Wiriya et al. (2013) conducted the source identification and health risk assessment of PM<sub>10</sub>-bound PAHs in Chiang Mai, Thailand. The profile of PAHs in the inhalable particulate fraction from Delhi (the capital city of India) has been reported by Sarkar and Khillare (2013). Seasonal and spatial variation of polycyclic aromatic hydrocarbons in vapor and PM<sub>2.5</sub> phase has been studied in California (Eiguren-Fernandez et al. 2004). However, most of the previous studies were conducted in megacities or industrial cities. The study of PAHs in particulate matters of the developing midsize cities is still limited.

Hefei is the capital and largest city in Anhui Province, which is a developing city in eastern China. It has a population of 7,800,000 and covers an area of ~ 11,000 km<sup>2</sup> (Deng et al. 2016; Hu et al. 2017). To study the variation in PAH concentration and distribution patterns associated with PM<sub>2.5</sub> and PM<sub>10</sub> in Hefei City, PM<sub>2.5</sub> and PM<sub>10</sub> samples

were sampled in both summer (August 2015) and winter (December 2015–January 2016). The source tracing and their associated health risks have been assessed based on the index of toxic equivalent concentrations (TEQs). Moreover, investigation of the characteristics of atmospheric PAHs could provide useful information to solve atmospheric pollution problems and thus to improve air quality in similar cities.

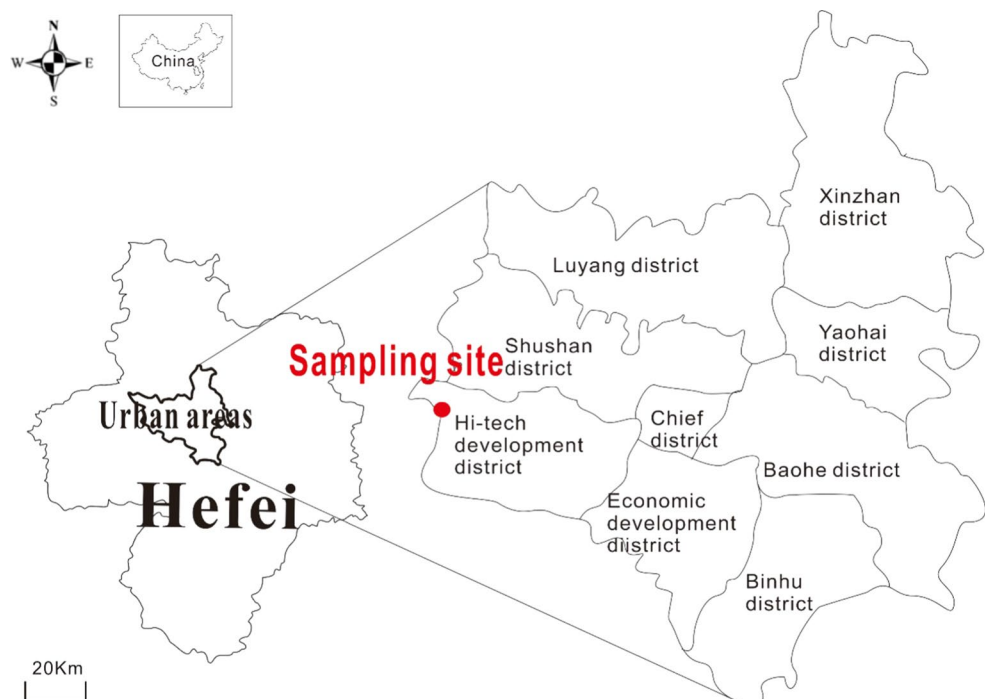
## Materials and Methods

### Sampling

Particulate matter samples were collected in Hefei, China (31°50'N, 117°16'E). The sampling site was located at the environmental monitoring station of Hefei Hi-tech industry development district (Fig. 1), which was close to a road with heavy traffic. The samplers were set up on the rooftop of the building at a height of 15 m above ground level and a distance of 20 m away from the nearest highway. Totally, fifty-seven samples of PMs (i.e., PM<sub>2.5</sub> and PM<sub>10</sub>) were collected in summer, and sixty-three samples were collected in winter seasons.

Middle-volume air samplers (LaoYing 2030, Laoshan Electronic Instrument, Qingdao, China) were used to collect the particulate matters on a glass fiber filter (Whatman EPM2000, UK, diameter = 90 mm) at a flow rate of 100–120 L/min for approximately 20 h. All filters were baked in a muffle furnace at 500 °C for 4 h to eliminate the

**Fig. 1** Location map of the sampling site in Hefei urban area



background organic matter. Filters were weighed in a microbalance (Sartorius MSA, Gottingen, DE,  $\pm 0.001$  mg) in a clean bench before and after sampling, in order to calculate the mass of collected particulate samples. After collection, the filters were stored in clean containers being kept at 4 °C.

### PAH Analysis

Each filter was cut into small pieces (1 cm  $\times$  1 cm) using stainless steel scissors and then extracted using dichloromethane (DCM) and acetone (chromatographically pure grade) in an accelerated solvent extraction apparatus (Dionex-ASE 350, Sunnyvale, CA, USA). Before extraction, a standard mixture consisting of phenanthrene-d10, chrysene-d12 and perylene-d12 was spiked onto the filters. The extracts were concentrated to  $\sim 1$  mL in a nitrogen blowing automatic parallel concentrate instrument at 40 °C (MultiVap-8, LabTech, Hopkinton, MA, USA) and then injected into a gas chromatograph (GC, Agilent Technologies 7890, Wilmington, DE, USA) coupled to mass spectrometer (MS, 5975 N). The GC equipped with a capillary column Rtx-1MS (length: 30 m; diameter: 0.25 mm; thickness: 0.25  $\mu$ m) was used. Temperature increasing program of the GC–MS (QP2010 Plus) was: Firstly, keep the initial temperature to 70 °C isotherm for 5 min, then ramping the temperature to 240 °C at a rate of 10 °C/min, at last ramping the temperature to 300 °C at a rate of 7 °C/min and keep for 8 min. High-purity (> 99.99%) helium was used as the carrier gas at a constant flow of 1.0 mL/min. The MS was operated in selective ion monitoring (SIM) mode at 70 eV, with an ion source temperature of 230 °C and an analyzer temperature of 150 °C. The scanning range was set among 50–550 amu.

Sixteen priority PAH compounds specified by Environmental Protection Agency, US EPA (US EPA 1982),

including NAP—naphthalene; ANY—acenaphthylene; ANA—acenaphthene; FL—fluorene; PHE—phenanthrene; An—anthracene; FLU—fluoranthene; PYR—pyrene; BaA—benz[a]anthracene; CHR—chrysene; BbF—benzo[b]fluoranthene; BkF—benzo[k]fluoranthene; BaP—benzo[a]pyrene; IcdP—indeno[1,2,3-cd]pyrene; DBA—dibenzo[a,h]anthracene; and Bghi—benzo[ghi]perylene, were analyzed.

### Quality Control

Spiked blanks (internal standards added to filter) and procedural blanks (solvent) were analyzed to assure and control the analysis quality. In procedural blanks, none of the target compounds were detected. The limit of quantification (LOQ) for each compound was calculated for three times of the noise, which was taken as a standard deviation of the lowest level standard. Surrogate PAHs have recoveries between 77 and 95%. The calibration curves are linear, and these are fitted with correlation coefficients ( $R^2$ ) from 0.996 to 1 for all of the PAHs. All the results are not corrected for the surrogate standards.

## Results and Discussion

### PM2.5 and PM10 Concentrations

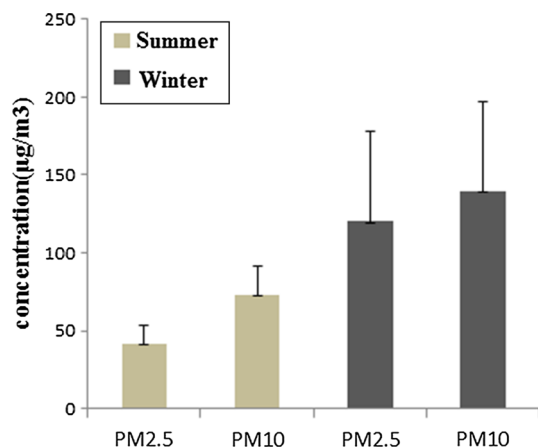
The daily PM2.5 and PM10 data were calculated based on the Hefei Air Pollution Index (HAPI) (published by Air quality online monitoring analysis platform of China (<http://www.aqistudy.cn/>)). The concentrations of particulate matters are shown in Table 1, and they are in the range of 17–243 and 36–255  $\mu$ g/m<sup>3</sup> for PM2.5 and PM10 during entire sampling period, respectively.

**Table 1** Maximum, minimum, median, mean concentration and standard deviation values for each fraction of the particulate matters and related PAHs collected during the sampling periods

Concentrations ( $\mu$ g/m <sup>3</sup> )	Summer		Winter	
	PM2.5	PM10	PM2.5	PM10
Minimum	17.0	36.0	39.0	47.0
Maximum	57.0	99.0	243.0	255.0
Median	42.0	73.0	103.5	128.5
Mean	41.8	73.4	120.2	139.6
Standard deviation	11.8	18.1	57.5	57.2
Concentrations (ng/m <sup>3</sup> )	PM2.5-PAHs	PM10-PAHs	PM2.5-PAHs	PM10-PAHs
Minimum	0.84	2.15	16.28	36.80
Maximum	19.36	50.20	208.68	191.58
Median	3.14	10.99	35.97	57.42
Mean	5.89	17.70	63.41	78.26
Standard deviation	6.55	16.61	66.12	53.70

Average concentration of PM<sub>10</sub> was 114.48  $\mu\text{g}/\text{m}^3$ , which was higher than the China National Ambient Air Quality Standard (GB 3095-2012 24 h standard) of 50  $\mu\text{g}/\text{m}^3$  and 2.3 times higher than the WHO standard of 50  $\mu\text{g}/\text{m}^3$ . Average concentration of PM<sub>2.5</sub> was 2.6 times higher than the National Ambient Air Quality Standard of China of 35  $\mu\text{g}/\text{m}^3$  and 3.6 times higher than the WHO standard of 25  $\mu\text{g}/\text{m}^3$ . Maximum, minimum, median, mean concentrations and standard deviation values for the particulate matters collected during the sampling periods are listed in Table 1.

Figure 2 shows the observed seasonal variations of PM<sub>2.5</sub> and PM<sub>10</sub>. During winter sampling period, the daily average concentrations of PM<sub>2.5</sub> reached 120.2  $\mu\text{g}/\text{m}^3$  and PM<sub>10</sub> reached 139.6  $\mu\text{g}/\text{m}^3$ , while in summer, the figures were 41.8 and 73.4  $\mu\text{g}/\text{m}^3$ . The higher concentrations in winter were likely caused by enhanced heating emissions, and also lower planetary boundary layer may lead to more stagnant weather conditions. In summer, due to the summer monsoon, higher precipitation resulted in lower PM concentrations values (Wang et al. 2015). Such seasonal variations of PM<sub>2.5</sub> and PM<sub>10</sub> were reported from Guo et al. (2003) in Hongkong and Pandey et al. (2013) in Lucknow, India. Tian et al. (2016) found high concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> (154.0 and 237.5  $\mu\text{g}/\text{m}^3$ ) in winter compared to summer (85.2 and 142.1  $\mu\text{g}/\text{m}^3$ ) in Chengdu, China. Liu et al. (2014) also reported that in winter, the PM<sub>2.5</sub> and PM<sub>10</sub> concentrations were 106.6 and 193.0  $\mu\text{g}/\text{m}^3$ , respectively, and in summer the concentrations were 155.9 and 73.8  $\mu\text{g}/\text{m}^3$ , respectively, in Beijing, China. Those data mentioned above indicate a similar pattern of seasonal variations of PM<sub>2.5</sub> and PM<sub>10</sub>.

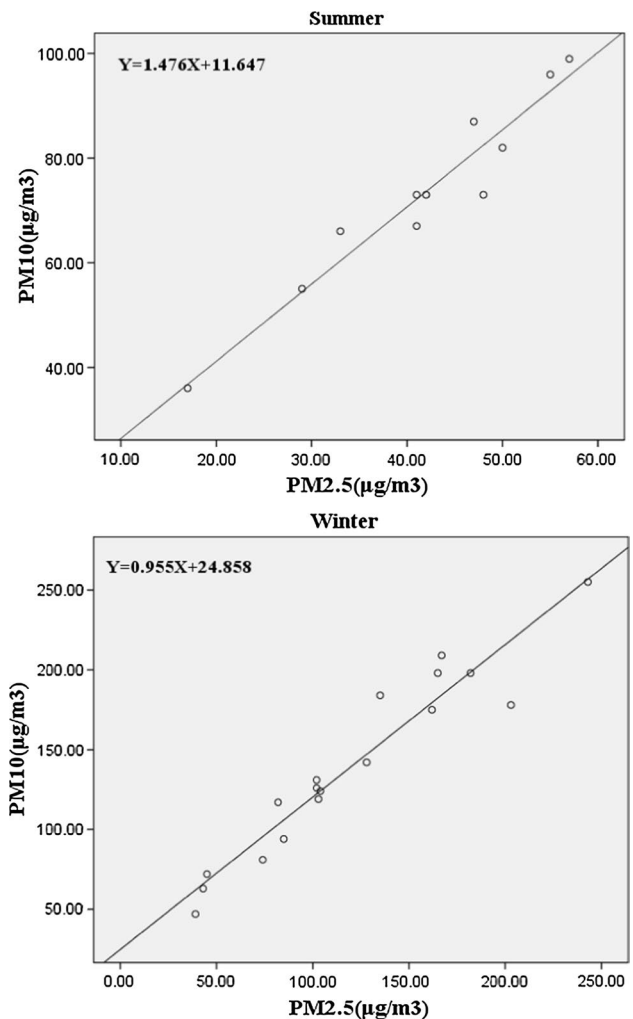


**Fig. 2** PM<sub>2.5</sub> and PM<sub>10</sub> concentrations (mean  $\pm$  SD) in winter and summer during the study periods

### Correlations Between PM<sub>2.5</sub> and PM<sub>10</sub>

The fine and coarse particles, which have different chemical compositions and physical properties, are generally derived from different activities and sources (Kong et al. 2010, 2013). As shown in Fig. 3, a strongly positive correlation ( $R = 0.966$ ,  $P < 0.01$  in summer and  $R = 0.978$ ,  $P < 0.01$  in winter) between PM<sub>2.5</sub> and PM<sub>10</sub> was observed, which indicated that they were influenced by the same sources and conditions (Akyuz and Cabuk 2009).

Since different sizes of atmospheric particles probably derive from different sources, these sources of PM<sub>2.5</sub> and PM<sub>10</sub> can be identified by the PM<sub>2.5</sub>/PM<sub>10</sub> ratios (Sun et al. 2004). Higher ratios (e.g.,  $> 0.6$ ) are ascribed to high contributions by secondary particulate formation from inorganics and some organics in general (Chan and Yao 2008; Sun et al. 2004). The lower ratios indicate that mineral dusts from suspended soil and road are the primary sources (Chan and Yao 2008; Perez et al. 2008).



**Fig. 3** Scatter plots of PM<sub>2.5</sub> and PM<sub>10</sub> in summer and winter

The ratio of PM<sub>2.5</sub>/PM<sub>10</sub> is 0.57 in summer and 0.83 in winter, suggesting that fine particles are dominant fraction in PM<sub>10</sub> (Zhou et al. 2016), which indicates that the crucial approach for controlling particulate matter pollution in Hefei is the reduction of PM<sub>2.5</sub>. The PM<sub>2.5</sub>/PM<sub>10</sub> ratios also exhibit seasonal variations with the lower values in summer and higher values in winter. Similar results have been found in other studies, and Akyuz and Cabuk (2009) reported an summer ratios of 0.47 and winter ratio of 0.70. Zhou et al. (2016) found that the average ratio of PM<sub>2.5</sub>/PM<sub>10</sub> was 0.67 in summer and 0.70 in winter in the southern part of China. Sun et al. (2004) found summer ratio of 0.45 and winter ratio of 0.73. Laakso et al. (2003) also reported similar seasonal patterns in the PM<sub>2.5</sub>/PM<sub>10</sub> ratio, in which the ratio was 0.52 in summer and 0.60 in winter. However, Parkhurst et al. (1999) reported different seasonal patterns that the ratio in summer was 0.68, higher than spring, autumn and winter, which was attributed to enhanced sunlight that induced the production and accumulation of secondary PM<sub>2.5</sub>. Chan and Kwok (2001) also reported a higher ratio in summer (0.84) than in winter (0.69).

### Concentrations of PAHs in PM<sub>2.5</sub> and PM<sub>10</sub>

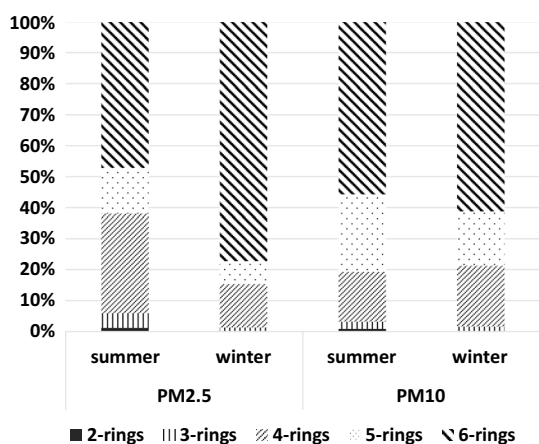
Table 2 shows the concentrations of individual PAH and specific PAHs in PM<sub>2.5</sub> and PM<sub>10</sub>. The number of aromatic rings is used to classify categories of PAHs: 2-rings including NAP; 3-rings including ANY, ANA, FL, PHE and An; 4-rings including FLU, PYR, BaA and CHR; 5-rings including BbF, BkF and BaP; 6-rings including IcdP, DBA and Bghi. The ring compositional patterns for total PAHs are illustrated in Fig. 4. They can be further classified into: lower molecular weight (LMW) which contains 2- and 3-ring PAHs; middle molecular weight (MMW) which contains 4-ring PAHs; higher molecular weight (HMW) which contains 5 and 6 rings (Kong et al. 2010).

Contents of LMW-, MMW- and HMW-PAHs were in the ranges of 0.70–1.81, 1.90–9.68 and 3.28–51.92 ng/m<sup>3</sup> for PM<sub>2.5</sub>, respectively. The corresponding values were 0.94–2.45, 2.51–15.07 and 13.11–60.73 ng/m<sup>3</sup> for PM<sub>10</sub>, respectively. Figure 4 shows that the concentrations of HMW-PAHs in PM<sub>2.5</sub> were  $3.28 \pm 3.72$  ng/m<sup>3</sup> in summer and  $51.92 \pm 63.43$  ng/m<sup>3</sup> in winter, and the corresponding concentrations in PM<sub>10</sub> were  $15.63 \pm 16.34$  and  $75.80 \pm 52.86$  ng/m<sup>3</sup>, which were dominant in both PM<sub>2.5</sub> and PM<sub>10</sub>.

**Table 2** PAH concentrations in PM<sub>2.5</sub> and PM<sub>10</sub> (ng/m<sup>3</sup>, expressed as mean  $\pm$  1 SD) in summer and winter

	PM <sub>2.5</sub>		PM <sub>10</sub>	
	Summer	Winter	Summer	Winter
NAP	0.08 $\pm$ 0.09	0.1 $\pm$ 0.21	0.16 $\pm$ 0.13	0.1 $\pm$ 0.10
ANY	0.01 $\pm$ 0.01	0.05 $\pm$ 0.04	0.01 $\pm$ 0.01	0.06 $\pm$ 0.06
ANA	0.01 $\pm$ 0.07	0.02 $\pm$ 0.03	0.01 $\pm$ 0.01	0.09 $\pm$ 0.09
FL	0.02 $\pm$ 0.02	0.02 $\pm$ 0.02	0.04 $\pm$ 0.03	0.06 $\pm$ 0.04
PHE	0.29 $\pm$ 0.14	0.81 $\pm$ 1.17	0.36 $\pm$ 0.19	1.07 $\pm$ 0.53
An	0.29 $\pm$ 0.15	0.81 $\pm$ 1.17	0.36 $\pm$ 0.19	1.07 $\pm$ 0.53
FLU	0.19 $\pm$ 0.10	1.48 $\pm$ 2.4	0.26 $\pm$ 0.22	0.84 $\pm$ 1.20
PYR	0.19 $\pm$ 0.07	2.27 $\pm$ 3.40	0.30 $\pm$ 0.19	1.54 $\pm$ 1.53
BaA	0.12 $\pm$ 0.07	0.94 $\pm$ 1.18	0.20 $\pm$ 0.19	2.61 $\pm$ 5.30
CHR	1.40 $\pm$ 3.21	4.99 $\pm$ 6.29	1.75 $\pm$ 4.01	10.08 $\pm$ 11.77
BbF	0.42 $\pm$ 0.29	1.38 $\pm$ 1.25	1.93 $\pm$ 2.83	3.15 $\pm$ 4.74
BkF	0.42 $\pm$ 0.29	1.38 $\pm$ 1.25	1.91 $\pm$ 2.84	3.16 $\pm$ 4.73
BaP	0.17 $\pm$ 0.18	2.70 $\pm$ 6.24	0.6 $\pm$ 0.97	8.04 $\pm$ 10.07
IcdP	0.58 $\pm$ 0.47	13.35 $\pm$ 16.66	1.45 $\pm$ 1.43	8.86 $\pm$ 10.57
DBA	0.58 $\pm$ 0.47	13.01 $\pm$ 16.93	1.45 $\pm$ 1.43	9.47 $\pm$ 11.46
Bghi	2.05 $\pm$ 2.29	31.19 $\pm$ 42.26	7.02 $\pm$ 5.71	32.05 $\pm$ 33.59
$\Sigma$ PAHs	5.89 $\pm$ 6.55	63.41 $\pm$ 66.12	17.70 $\pm$ 16.61	78.26 $\pm$ 53.70
LMW-PAHs	0.70 $\pm$ 0.39	1.81 $\pm$ 2.29	0.93 $\pm$ 0.48	2.45 $\pm$ 1.15
MMW-PAHs	1.90 $\pm$ 3.30	9.68 $\pm$ 5.52	2.51 $\pm$ 4.10	15.07 $\pm$ 17.53
HMW-PAHs	3.28 $\pm$ 3.72	51.92 $\pm$ 63.43	13.11 $\pm$ 13.03	60.73 $\pm$ 57.12
COM-PAHs	4.82 $\pm$ 5.85	50.22 $\pm$ 49.48	14.36 $\pm$ 15.28	66.33 $\pm$ 42.44
C-PAHS	3.28 $\pm$ 4.32	34.46 $\pm$ 22.25	8.92 $\pm$ 10.48	45.37 $\pm$ 32.21

COM-PAHs combustion-derived PAHs, including FLU, PYR, CHR, BbF, BkF, BaA, BaP, IcdP and BghiP; C-PAHs carcinogenic PAHs including BaA, CHR, BbF, BkF, BaP, IcdP and DBA



**Fig. 4** Percentage of ring number distributions of PAHs in PM2.5 and PM10

For PM2.5, the sum of 4- to 6-ring PAHs occupied 94.0 and 98.7% of the total PAHs in summer and winter, respectively. For PM10, the sum of 4- to 6-ring PAHs accounted for 96.7 and 98.3% of the total PAHs in summer and winter, respectively. In addition, the concentrations of 4- to 6-ring PAHs were higher in winter than those in summer. Previous studies have indicated that the majority of MMW-PAHs (i.e., FLU, PYR, BaA and CHR) come from coal combustion, while gasoline vehicles were the major sources for 5- and 6-ring PAHs (BaP, BbF, Bghi and IcdP) (Kong et al. 2010; Wu et al. 2014). Therefore, the higher proportion of 4-ring PAHs was mainly attributed to the increased coal consumption and domestic heating activities in winter. Moreover, the higher 5- and 6-ring PAHs in winter at the high-traffic area may also be more influenced by the vehicle emission due to the vehicle's cold start effect (Dörr et al. 1996; Kong et al. 2010; Zhou et al. 2005). Other potential sources, such as diesel exhaust emission, wood combustion and some industrial processes, might mostly contributed to the ambient LMW-PAHs (Duan et al. 2005; Kong et al. 2010; Wu et al. 2014). However, the sum of 2- and 3- ring PAHs accounts for only 0.1% of the total PAHs. It can be concluded that the atmospheric PAHs in Hefei City were mainly influenced by coal combustion and vehicle emission.

### Relationship Between Particulate Matters and Associated PAHs

The total concentrations of PAHs were 5.89 ng/m<sup>3</sup> in PM2.5 and 17.70 ng/m<sup>3</sup> in PM10 in summer, whereas in winter times it reached 63.41 and 78.26 ng/m<sup>3</sup>, respectively. The observation indicates that lower PAH concentrations usually occur in summer (August, 2015), while higher PAH concentrations occur in winter (December 2015–January 2016) for both PM2.5 and PM10. Maximum, minimum, median, mean

concentration and standard deviation values for total PAHs are also shown in Table 1.

The data from 18 to 25 in August 2015 and 21 December 2015 to 2 January 2016 were chosen to conduct Pearson's correlation analysis, daily variations in particulate matters and associated PAHs, and the relationship between them is shown in Fig. 5. A significant correlation between PM2.5 and related PAHs ( $R = 0.499$ ,  $P < 0.05$ ) was found (Fig. 6), indicating that the increasing of PM2.5 concentrations could lead to the observably increase in PAH concentrations. Because of sources such as fossil fuels, combustion would create primarily PM2.5, carrying a large amount of PAHs. Their properties of small size, relatively large specific surface area and high concentration made them remarkable absorbents for various kinds of compounds including organics and inorganics (Sheu et al. 1997; Yang et al. 2012). No correlation was found between PM10- and PM10-associated PAHs ( $R = 0.431$ ,  $P > 0.05$ ) due to the different sources of them (Akyuz and Cabuk 2009).

### Coefficient of Divergence Analysis

A self-normalizing parameter is used in measuring the spread of the data points for two datasets and identifying the differences in PAH composition profiles in PM2.5 and PM10. The self-normalizing parameter is as follows:

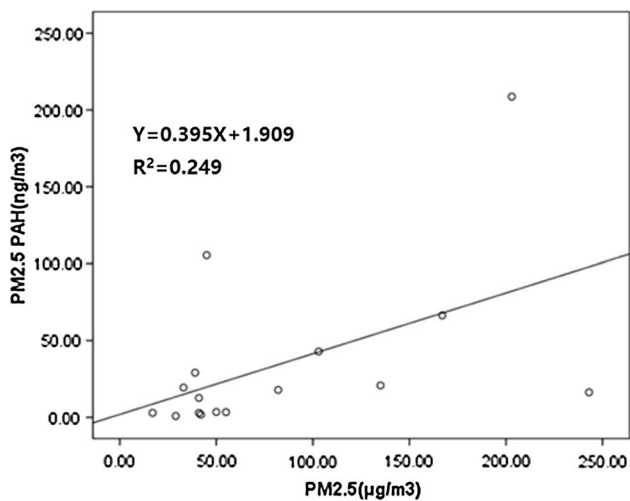
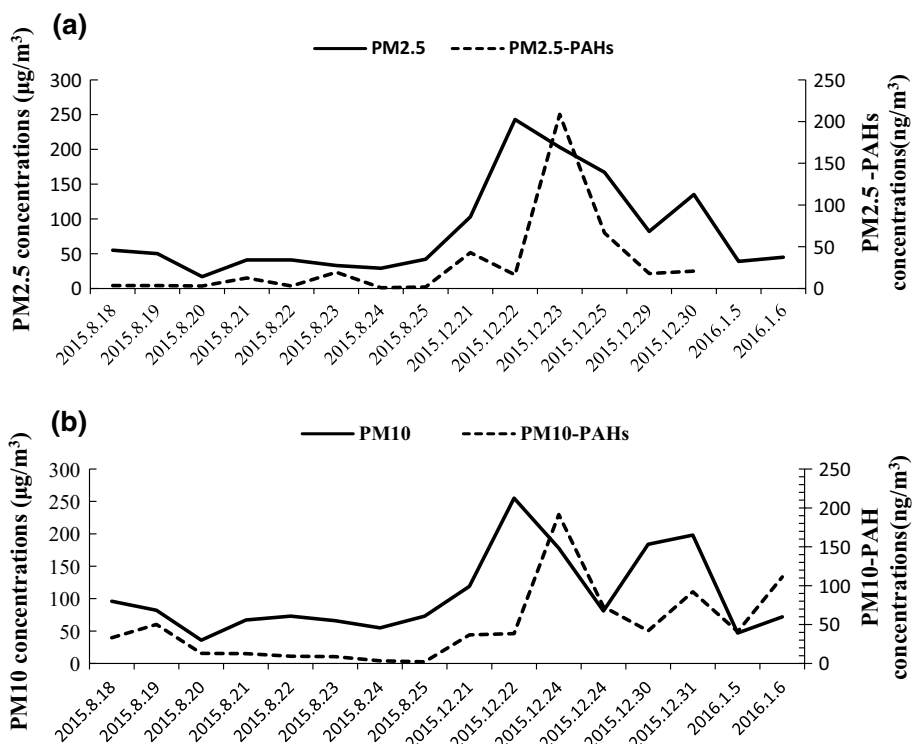
$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left( \frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2}$$

$p$  is the number of investigated components,  $i$  stands for one type of chemical component, and  $j$  and  $k$  stand for two profiles for sampling sites or fractions. Therefore,  $x_{ij}$  and  $x_{ik}$  represent the average concentrations of chemical component  $i$  in  $j$  and  $k$ , respectively (Wu et al. 2014).

In addition, the scatter plots of PAH component mass concentrations for  $j$  against  $k$  are shown in Fig. 7, which characterize the concentration diagrams. If  $CD_{jk}$  approaches 1, then  $j$  and  $k$  are significantly different, and if  $CD_{jk}$  approaches 0, then  $j$  and  $k$  are similar. Previous studies have indicated that PAH compositions are similar when their  $CD_{jk}$  values approach to 0.3, whereas they are different when their  $CD_{jk}$  values are larger than 0.5 (Wongphatarakul et al. 1998; Wu et al. 2014).

Figure 7 shows that the  $CD_{jk}$  values for PM10- and PM2.5-bound PAHs were 0.37 in summer and 0.33 in winter, respectively, indicating that their compositions were similar in the same season. However, the  $CD_{jk}$  values for summer and winter were 0.66 for PM2.5 and 0.61 for PM10, respectively, indicating that the compositions of both PM10- and PM2.5-bound PAHs are dissimilar in the different seasons. The dissimilarity of PAH compositions indicates that

**Fig. 5** Daily variations of **a** PM2.5 and related PAHs, **b** PM10 and related PAH concentrations



**Fig. 6** Linear regression analysis between PM2.5 and related PAHs

the sources were different in different seasons, and it further supports the conclusion that the atmospheric PAHs in Hefei were mainly influenced by coal combustion and vehicle emission.

**Health Risk Assessment of PAHs**

The carcinogenic PAHs (C-PAHs) including the eight carcinogenic PAHs were classified by US EPA (BaA, CHR, BbF, BkF, BaP, IcdP, DBA and Bghi) (US EPA 2002). Their

total concentrations range in 3.28–34.46 and 8.92–45.37 ng/m<sup>3</sup> in PM2.5 and PM10, respectively. To estimate the risk of exposure C-PAHs, the toxicity equivalent quality (TEQ) equation was used as follows:

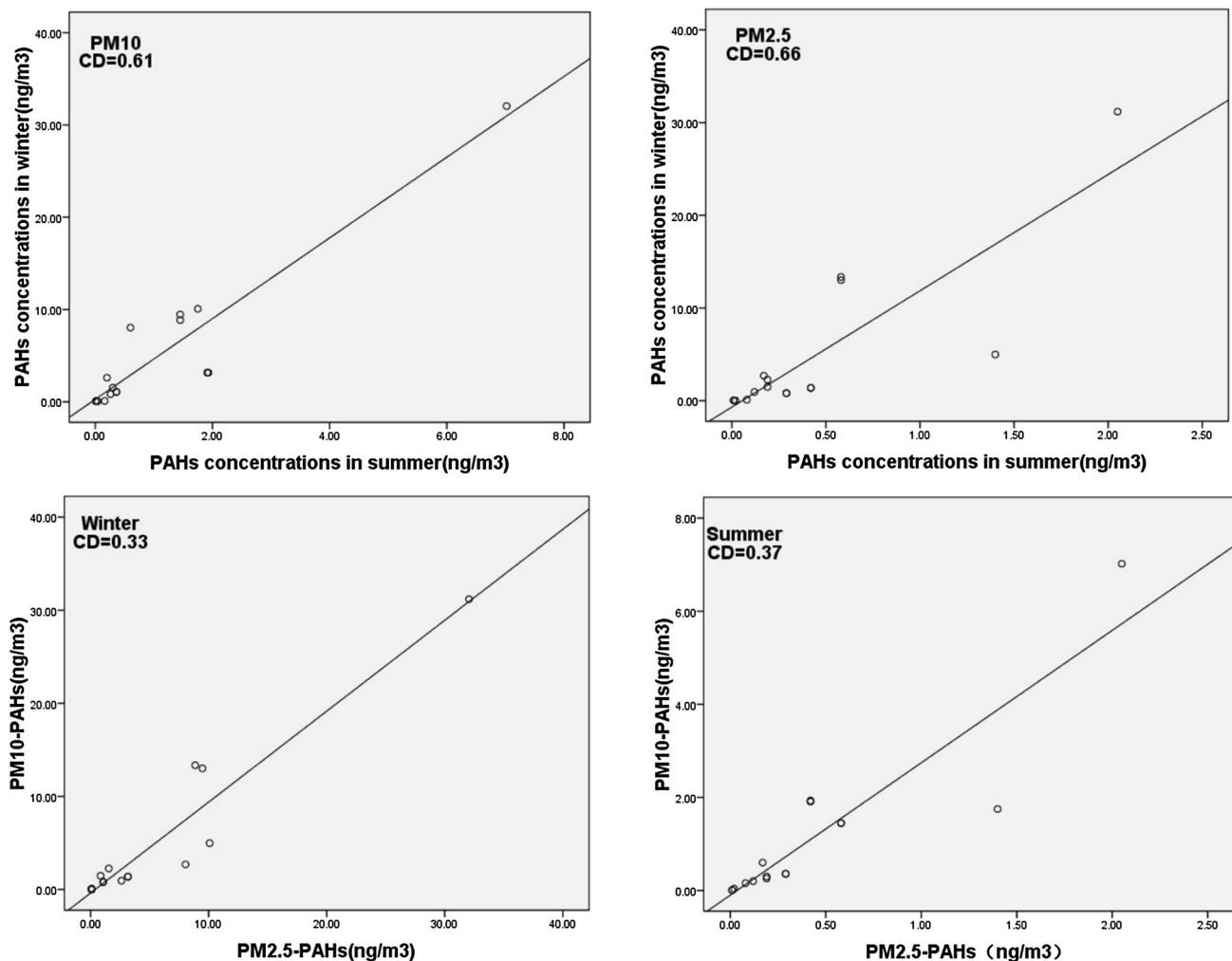
$$TEQ = \sum_i [c_i \times TEF_i]$$

TEF<sub>i</sub> is the toxic equivalent factor which represents the relative carcinogenic potency of the corresponding PAHs. C<sub>i</sub> is the concentration of an individual PAH. Benzo(a)pyrene (BaP) is used as a reference compound. Based on its BaP equivalent concentration (BaP-TEQ), we can assess the health risk levels of PAHs. The C-PAHs would be assigned to different TEF values suggested by BaP. Multiplying the concentrations of each PAH with its associated toxic equivalent factor (TEF) for cancer potency relative to BaP suggested by Nisbet and Lagoy has been widely used in calculating the BaP-TEQ (Jung et al. 2010; Nisbet and Lagoy 1992). BaP-TEQ levels for the sum of nonvolatile PAH (8 PAHs) were calculated as follows:

$$BaP - TEQ = [BaA] \times 0.1 + [CHR] \times 0.01 + [BbF] \times 0.1 + [BkF] \times 0.1 + [BaP] \times 0.1 + [IcdP] \times 0.1 + [DBA] \times 5 + [Bghi] \times 0.01$$

(The chemicals denote their mean concentrations in this formula).

The BaP-TEQ concentrations for PM2.5 were found to be 3.11 ng/m<sup>3</sup> in summer and 67.39 ng/m<sup>3</sup> in winter, while the



**Fig. 7** Similarity comparison of PAH profiles between  $PM_{2.5}$  and  $PM_{10}$  in summer and winter

values for  $PM_{10}$  were 7.95 and 50.35  $ng/m^3$  in summer and winter, respectively. It shows that the BaP-TEQ concentration for both  $PM_{2.5}$  and  $PM_{10}$  in winter is multifold higher than those in summer. It indicates that the PAH pollution in winter raises risks to human health. The TEQ concentrations for winter in this study were higher than those in Beijing (34.50  $ng/m^3$ , 2007) and Liaoning Province (40.05  $ng/m^3$ , 2010) (Kong et al. 2010; Liu et al. 2007). And the mean value of TEQ was 35.26  $ng/m^3$  for PAHs in  $PM_{2.5}$ , which was higher than 29.15  $ng/m^3$  in  $PM_{10}$ ; thus, PAHs in  $PM_{2.5}$  could exhibit higher risks to human health than in  $PM_{10}$ . Therefore, the PAH pollution in fine particles in Hefei should be paid attention to. In this study, DBA was the major contributor to the total BaP-TEQ (93.38 and 96.53% in  $PM_{2.5}$ , 84.51 and 88.94% in  $PM_{10}$ , during summer and winter, respectively) due to both its high TEF value and higher ambient levels.

When calculating inhalation cancer risks of exposed inhabitant, a quantitative value can be concluded about the health risks associated with airborne PAHs. The value of cancer risks when under PAH exposure can be estimated by ICR. The equation proposed by USEPA is as follows:

$$ICR = TEQ \times IUR_{BaP}$$

The World Health Organization (2000) recommended the  $IUR_{BaP}$  value to be  $8.7 \times 10^{-2} m^3/\mu g$  (in micrograms per cubic meter).  $IUR_{BaP}$  is the inhalation unit risk, which is the risk of cancer from inhalation of unit mass of PAHs during lifetime (70 years). ICR of  $10^{-6}$  generally represents a lower-bound zero risk value, whereas ICR higher than  $10^{-4}$  indicates high potential health risk (Liao and Chiang 2006; Sarkar and Khillare 2013). In this study, the ICR was  $4.18 \times 10^{-4}$  in summer and  $5.12 \times 10^{-3}$  in winter. PAHs in winter exhibited risks about 12 times higher than



that in summer, and the ICR was higher than safe range of  $10^{-4}$ – $10^{-6}$  (Wirriya et al. 2013; Xia et al. 2013).

## Conclusions

The characteristics of atmospheric PAHs associated with PM<sub>10</sub> and PM<sub>2.5</sub> have been studied in Hefei City, China. A seasonal variation trend was observed for the particulate matter-associated PAH concentrations (higher level in winter and lower in summer). HMW-PAHs were dominant in both PM<sub>2.5</sub> and PM<sub>10</sub>, and the COM-PAHs represent the majority of total PAHs, indicating that the dominant sources of atmospheric PAHs in Hefei are fuel combustion and vehicles emission. The BaP-TEQ values in winter were higher than those in summer, indicating that the PAH pollution in winter raises more risks to human health. The ICR is calculated as  $2.8 \times 10^{-3}$ , which exceeds the safety range. Thus, it is suggested that effective control measures to reduce particulate matter pollution in Hefei should be taken in a way to reduce the exposure risk of PAHs to humans.

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