



# Indoor/outdoor relationships and diurnal/nocturnal variations in water-soluble ion and PAH concentrations in the atmospheric PM<sub>2.5</sub> of a business office area in Jinan, a heavily polluted city in China



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## ABSTRACT

Indoor/outdoor and diurnal/nocturnal variations in PM<sub>2.5</sub> and associated water-soluble ions and polycyclic aromatic hydrocarbons (PAHs) were examined in a business office during the summer and autumn of 2010 in Jinan, China. Both indoor and outdoor PM<sub>2.5</sub> levels were higher than the value recommended by the WHO, and outdoor sources were found to be the major contributors to indoor PM<sub>2.5</sub>. SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were the dominant water-soluble ions in both indoor and outdoor particles. During daytime, NO<sub>3</sub><sup>-</sup> mainly came from indoor sources, which was related to the temperature difference between the indoor and outdoor air. During daytime, the 15 monitored PAHs were all largely from indoor sources, while during nighttime, the 3–4-ring PAHs were mainly generated indoors and the 5–6-ring PAHs predominantly came from the outdoor air. The diurnal/nocturnal variations of PAHs suggested that gas/particle partitioning driven by temperature makes a significant contribution to the variation in PAH concentrations. The diagnostic ratios revealed that biomass burning had an important contribution to outdoor PAH concentrations in autumn. The results of a risk assessment of PAH pollution suggested that indoor PAHs present more carcinogenic and mutagenic risks during daytime. Our results indicated that serious indoor air pollution in a business office presents a high health risk for workers.

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## 1. Introduction

Over the last twenty years, considerable efforts around the world have been made to clarify the influence of indoor air quality on human health (Gupta et al., 1996; Hayakawa et al., 1999; Lee and Chang, 2000; Jo and Seo, 2005; Kotzias et al., 2009; Yang et al., 2009; Pegas et al., 2011; Hasheminassab et al., 2014). The results of these studies showed that people are

exposed to a multitude of chemical and biological stressors, some of which cause health problems (allergy, asthma, sensory irritation, lung cancer, etc.) (Samet and Spengler, 2003; Bernstein et al., 2008; Rios et al., 2009; Jie et al., 2011; Zhou et al., 2013; Jovanović et al., 2014). However, previous studies of indoor air have mainly been conducted in residential and school buildings (e.g., Blondeau et al., 2005; Fromme et al., 2008; Polidori et al., 2009; Massey et al., 2012; Krugly et al., 2014; Rivas et al., 2014), while, in comparison, few studies have been performed in business offices (Saraga et al., 2010; Sangiorgi et al., 2011, 2013), despite the fact that they are the workplace for most urban office workers. In addition, few studies have

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focused on the diurnal/nocturnal differences in indoor and outdoor pollution levels (Reisen and Arey, 2005; Wang et al., 2007, 2010; Zimmermann et al., 2012; Souza et al., 2014), though the differences in anthropogenic emissions between daytime and nighttime could affect the contributions from various sources of pollution.

PM<sub>2.5</sub>, which can easily move from the outdoors into the indoors due to its effective penetration ability (Massey et al., 2012; Barraza et al., 2014; Hassanvand et al., 2014), is an important pollutant in indoor environments. Water-soluble ions are a major chemical component of PM<sub>2.5</sub> and account for one-third or more of the particulate mass in Chinese urban regions (Saliba et al., 2009; Chithra and Shiva Nagendra, 2013; Hassanvand et al., 2014). Moreover, the acidity of PM<sub>2.5</sub>, which depends on the balance between sulphate and nitrate as the acidic compounds and ammonium as a neutralizing species (Seinfeld and Pandis, 2006), has also been associated with negative effects on human health, mainly in terms of lung function. In addition, by acting as surface-active reagents, water-soluble ions can increase the solubility of toxic organic compounds, such as PAHs, and therefore increase their toxicity to humans (Pongpiachan et al., 2013; Krugly et al., 2014; Kamal et al., 2014). PAHs have received increased attention in recent years in indoor air pollution research due to their potential cytotoxicity, mutagenicity and carcinogenicity in humans (WHO, 1998) and their ability to directly or indirectly damage DNA (Baird et al., 2005; Novotna et al., 2007; Li et al., 2014). Therefore, the presence of water-soluble ions and PAHs within PM<sub>2.5</sub> strongly increases their potential for adverse health effects.

Shandong Province, which is located in northern China, is China's third-biggest economic power, and anthropogenic emissions there contributed approximately 10.00% of SO<sub>2</sub>, 8.46% of NO<sub>x</sub>, 9.02% of VOC, 9.11% of PM<sub>2.5</sub>, 7.33% of BC and 6.66% of OC to China's overall emissions in 2006 (National Bureau of Statistics of China, 2009; Zhang et al., 2009). Jinan, as the capital of Shandong Province, was listed in the group of large cities with the highest pollution concentrations, including SO<sub>2</sub>, NO<sub>x</sub>, PAHs and PM<sub>2.5</sub> (Baldasano et al., 2003; Gao et al., 2011). In such industrial cities, scientific evidence has shown that indoor air environments can become seriously polluted (Balasubramanian and Lee, 2007). Moreover, with economic development, the number of large office buildings equipped with air-conditioning is increasing. Advances in information technology have also increased the quantity of and transformed the nature of electronic equipment (such as computers, printers, copier machines and fax machines) used by office workers. These office tools have been found to be a source of ozone, particulate matter and volatile organic compounds and have a serious impact on indoor air quality (Wolkoff et al., 2006; Destailats et al., 2006). Hence, the indoor air quality in business offices could have a significant influence on human health. The objectives of this study were as follows: (1) to measure and understand the indoor and outdoor PM<sub>2.5</sub> mass concentrations and associated water-soluble ion and PAH concentrations in a business office and in Shandong University; (2) to examine the indoor to outdoor ratios (I/O) and the relationships (R<sup>2</sup>) between the indoor and outdoor concentrations of PM<sub>2.5</sub>, water-soluble ions and PAHs and analyse their source implications; (3) to illustrate the diurnal and nocturnal variations in PM<sub>2.5</sub>, water-soluble ions and PAHs and assess

their potential controlling factors; and (4) to assess the sources and health risks of PAHs in the air of indoor and outdoor environments in a business office.

## 2. Methodology

### 2.1. Site description

As shown in Fig. 1, a business office was selected as the indoor sampling site, and it is located in an area characterized by considerable human activity and intense traffic. There were no smoking areas at the indoor site. However, electronic equipment (computers, printers, copier machines, etc.) was operated during daytime for all of the sampling periods. The air supply systems were operated in summer, but natural ventilation was provided in autumn. The outdoor sampling site was located on the roof (approximately 20.36 m above the ground) of the Information Science and Engineering School, Central Campus, Shandong University. This building is surrounded by commercial and residential areas, and a busy road is located in front of the site.

### 2.2. Sampling strategy

Two sampling campaigns were conducted (Table 1): summer (17 July–26 July 2010) and autumn (11 October–27 October 2010). The sampling was performed simultaneously at both the indoor and outdoor sites. For daytime and nighttime PM<sub>2.5</sub> measurements, indoor and outdoor sampling works were conducted from 8:30 to 18:30 and from 19:30 to 8:00 the next day, respectively. To guarantee the quality of the PM<sub>2.5</sub> measurements and chemical analyses, field blank filters were collected during each campaign. PM<sub>2.5</sub> samples were not collected on July 20 or during the nighttime of October 18, October 20 and October 21 due to rainfall. Half of each filter was used to determine the ionic constituents, and the other half was used for the PAH analysis.

### 2.3. PM<sub>2.5</sub> collection

In this study, two TH-16A Intelligent PM<sub>2.5</sub> samplers (Wuhan Tianhong Corporation, China) were used to collect indoor and outdoor PM<sub>2.5</sub> samples simultaneously at a flow rate of 100 L min<sup>-1</sup>. Before and after sampling, the airflow rates of the two samplers were calibrated. All quartz fibre-filters were pre-treated by baking at 600 °C for 4 h to remove any organic contaminants. After baking, the filters were transferred to a room with a constant temperature and humidity (temperature of 20 ± 1 °C, relative humidity of 50 ± 2%) for 24 h, and then, they were weighed using a Sartorius analytical balance (detection limit 0.001 mg). Loaded filters were similarly conditioned for 24 h before weighing. The weighed filters were placed in plastic petri dishes and stored at a -4 °C in a refrigerator before further analysis of PAHs.

### 2.4. Analysis of ionic components

Particulates on the quartz filters were dissolved completely in an ultrasonic bath in ultra-pure water of 18.2 MU cm (purified by Millipore Water Purification System) for 60 min. The water extracts were filtered through a 13-mm filter with

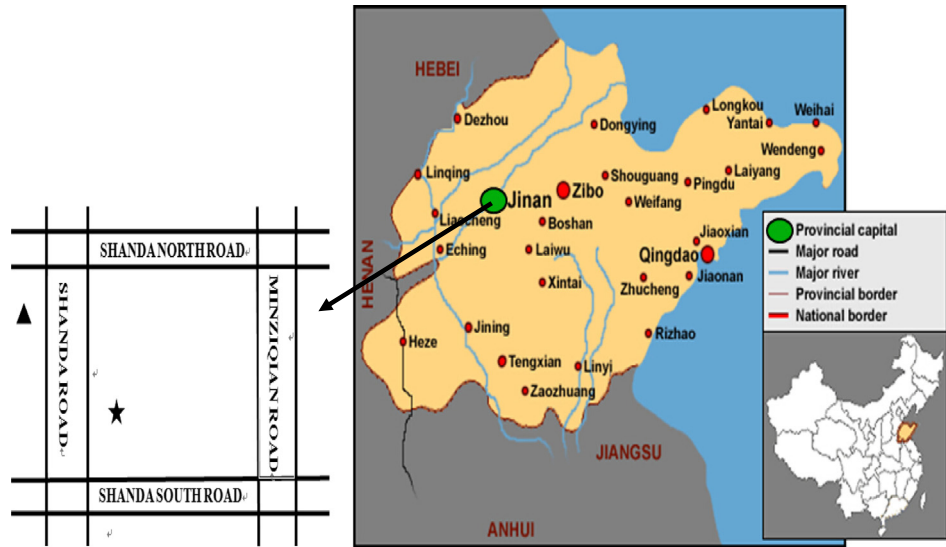


Fig. 1. Location of the sampling site (five-pointed star: Shandong University; triangle: business office) in Jinan, Shandong Province, China.

0.2  $\mu\text{m}$  pores (13JP020AN, ADVANTEC). An ion chromatography system (Dionex ICS-90, Dionex Corporation, USA) was deployed to analyse the water-soluble ions in  $\text{PM}_{2.5}$ . The anions, including  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , were analysed using an AS14A Column with an AMMS 300 Suppressor and were eluted with  $3.5 \text{ mmol L}^{-1} \text{Na}_2\text{CO}_3/1.0 \text{ mmol L}^{-1} \text{NaHCO}_3$ . The cations,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , were analysed using a CS12A Column with a CSRS Ultra II Suppressor and were eluted with  $20.0 \text{ mmol L}^{-1}$  methanesulfonic acid. The minimum detection limit (MDL) values for all of the ions ranged from 0.01 to  $0.08 \mu\text{g m}^{-3}$ .

2.5. Analysis of PAH components

The samples were extracted with a 4:1 (v/v) mixture of dichloromethane and n-hexane using an accelerated solvent extraction (ASE 300, Dionex) for 15 min. Then, the extracts were concentrated in a rotary evaporator under a purified nitrogen stream (99.99%, purified by an activated carbon column) to a volume of 1 mL. Internal standards, including naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D10 and perylene-D12, were added into the samples immediately prior to analysis.

The samples were analysed using a gas chromatograph (GC) system (Agilent 6890N) that was equipped with an Agilent 5973 Network Mass Selective Detector. A  $30 \text{ m} \times 0.25 \text{ mm} \times 0.50 \mu\text{m}$  DB5 capillary column was used for the separation of the PAHs. The injections were splitless, and the sample volume was

1  $\mu\text{L}$ . High-purity helium was used as the carrier gas at a constant flow rate of  $1 \text{ mL min}^{-1}$ . The chromatographic conditions were  $60^\circ\text{C}$  (maintained for 1 min), ramping from 60 to  $290^\circ\text{C}$  at  $18^\circ\text{C min}^{-1}$  and  $290^\circ\text{C}$  (maintained for 15 min). The MS detection was conducted by electron impact ionization of 70 eV, and the mass fragment scan was from 50 to 550 amu. The organic compounds in the samples were identified by comparing the sample mass spectra with those in the National Institute of Standards and Technology mass spectral reference library (NIST05a) and were further confirmed by comparison with standards for retention time and mass spectra. Compound quantification was based on the calibration curves of the corresponding standards. The values of the MDLs for the PAHs ranged from  $0.01 \text{ ng m}^{-3}$  (Ace) to  $0.14 \text{ ng m}^{-3}$  (BgHiP).

The PAHs monitored in this study are abbreviated as follows: acenaphthylene (Acy, m/z 152), acenaphthene (Ace, m/z 154), fluorene (Fl, m/z 166), phenanthrene (Phe, m/z 178), anthracene (Ant, m/z 178), fluoranthene (Flu, m/z 202), pyrene (Pyr, m/z 202), benz[a]anthracene (BaA, m/z 228), chrysene (Chr, m/z 228), benzo[b]fluoranthene (BbF, m/z 252), benzo[k]fluoranthene (BkF, m/z 252), benzo[a]pyrene (BaP, m/z 252), indeno[1,2,3-cd]pyrene (IcdP, m/z 276), dibenz[a, h]anthracene (DBA, m/z 278) and benzo[ghi]perylene (BgHiP, m/z 276).

2.6. Quality control

The analytical method was based on the USEPA method TO-13. Field blanks were performed to identify the level of

Table 1  
Characteristics of the indoor environment and sampling locations as well as sample numbers.

Site	Area/ $\text{m}^2$	Ventilation type	Sampling season	Sampling periods	PM <sub>2.5</sub> sample number		Ion sample number		PAH sample number	
					Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Business office	60	Mechanical	Summer	07/17/2010–07/26/2010	17	17	17	17	10	10
Business office	60	Natural	Autumn	10/11/2010–10/27/2010	28	28	28	28	10	10

background contamination from the sampling sites. Method blanks and spiked filter samples were also analysed to ensure the quality of the pre-treatment, ICs and GC–MS analysis steps. These blanks were extracted and analysed in the same manner as the samples. Neither water-soluble ions nor PAHs were detected in any of the blank samples. In this study, concentrations of  $F^-$  and  $NO_2^-$  below the detection limit were excluded from discussion. The mean recoveries for the 15 PAHs ranged from 70.45% to 125.32%, and the data reported in the study were corrected for their recoveries. Because the recovery of naphthalene-D8 was low, the naphthalene results were not included in this study. The PAHs found in the field blanks were generally below the instrumental detection limits (IDLs) (the amount of analyte that would generate a signal-to-noise ratio of 3:1). The MDLs were assigned to be 3 times the IDLs.

### 3. Results and discussion

#### 3.1. Occurrence of $PM_{2.5}$

##### 3.1.1. $PM_{2.5}$ mass concentrations

As shown in Table 2, the mean indoor  $PM_{2.5}$  concentration levels were  $51.52 \pm 28.22$  and  $93.52 \pm 41.07 \mu g m^{-3}$  in summer and autumn, respectively, which were 2.06 and 3.74 times the WHO-recommended daily  $PM_{2.5}$  standard value of  $25 \mu g m^{-3}$  (WHO, 2006). Thus, the daily concentration over-limit ratio was 86.72%–100.00%, indicating that the indoor air quality was very poor. In summer and autumn, the mean outdoor  $PM_{2.5}$  concentration levels were  $115.92 \pm 44.84$  and  $150.88 \pm 73.07 \mu g m^{-3}$ , which were 1.77 and 2.32 times the outdoor  $PM_{2.5}$  daily standard of  $65 \mu g m^{-3}$  recommended by

the National Ambient Air Quality Standard (NAAQS), suggesting that Jinan suffers from serious air pollution.

##### 3.1.2. Indoor–outdoor concentration relationships and diurnal and nocturnal variations in $PM_{2.5}$

The ratio of indoor-to-outdoor concentrations is commonly used to describe the I/O relationships of air pollutants (Wang et al., 2003, 2006; Duan et al., 2007). In general, if I/O is greater than 1.00, the source is mainly from the indoors; when I/O is less than or equal to 1.00, pollutants are mainly from the ambient air. The correlation coefficient ( $R^2$ ) between the indoor and outdoor concentrations was used to indicate whether the PM species measured indoors originated from the outdoors.

In this study, the I/O ratios in Table 2 (0.44 in summer and 0.62 in autumn were all smaller than 1.00) and  $R^2$  values in Fig. 2 (0.21 in summer and 0.65 in autumn, suggesting that indoor and outdoor  $PM_{2.5}$  concentrations have good correlation) indicated that the indoor concentrations of these respirable pollutants were dominated by outdoor sources. The lower I/O ratio and  $R^2$  value in the summer can be attributed to the extensive use of air conditioning at the office. It has been reported that the use of air conditioning in a room can reduce particle concentrations and the infiltration rates of outdoor particles (Vette et al., 2001; Guo et al., 2008; Lv and Zhu, 2013). However, in autumn, the office relied on natural ventilation, and doors and windows were left open.

As shown in Fig. 4, during daytime and nighttime, the I/O ratios for  $PM_{2.5}$  in summer were 0.51 and 0.43, respectively, while in autumn, these I/O ratios were 0.72 and 0.58, respectively. The daytime ratios were higher than those at nighttime, which could be due to the operation of electronic equipment during daytime.

**Table 2**

Average concentrations of  $PM_{2.5}$  ( $\mu g m^{-3}$ ), inorganic ions ( $\mu g m^{-3}$ ) and 15 PAHs ( $ng m^{-3}$ ) monitored in indoor and outdoor air samples in summer and autumn.

	Summer				Autumn			
	Indoor	Outdoor	$R^2$	I/O	Indoor	Outdoor	$R^2$	I/O
$PM_{2.5}$	$51.52 \pm 28.22$	$115.92 \pm 44.84$	0.21	0.44	$93.52 \pm 41.07$	$150.88 \pm 73.07$	0.65	0.62
$Cl^-$	$0.60 \pm 0.03$	$0.50 \pm 0.37$	0.08	1.20	$3.25 \pm 0.87$	$2.56 \pm 3.22$	0.07	1.27
$NO_3^-$	$2.33 \pm 1.98$	$22.41 \pm 10.96$	0.65	0.13	$5.90 \pm 4.06$	$18.46 \pm 15.66$	0.54	0.31
$SO_4^{2-}$	$25.91 \pm 19.57$	$53.72 \pm 16.35$	0.75	0.50	$16.71 \pm 13.42$	$25.56 \pm 17.47$	0.87	0.66
$Na^+$	$0.10 \pm 0.09$	$0.21 \pm 0.10$	0.58	0.48	$0.62 \pm 0.40$	$0.67 \pm 0.24$	0.62	0.93
$NH_4^+$	$10.12 \pm 8.86$	$26.86 \pm 9.01$	0.60	0.39	$7.99 \pm 5.82$	$19.88 \pm 10.28$	0.77	0.40
$K^+$	$0.47 \pm 0.36$	$1.16 \pm 0.50$	0.52	0.42	$1.39 \pm 0.79$	$2.07 \pm 0.99$	0.74	0.68
$Mg^{2+}$	$0.07 \pm 0.02$	$0.06 \pm 0.04$	0.28	1.17	$0.21 \pm 0.09$	$0.19 \pm 0.11$	0.32	1.09
$Ca^{2+}$	$0.41 \pm 0.07$	$0.32 \pm 0.87$	0.30	1.28	$2.06 \pm 0.73$	$1.94 \pm 1.95$	0.29	1.06
Acy	$0.04 \pm 0.01$	$0.03 \pm 0.01$	0.46	1.33	$0.07 \pm 0.02$	$0.05 \pm 0.02$	0.48	1.40
Ace	$0.12 \pm 0.02$	$0.09 \pm 0.01$	0.21	1.33	$0.19 \pm 0.04$	$0.17 \pm 0.03$	0.32	1.12
Fl	$1.14 \pm 0.29$	$0.77 \pm 0.09$	0.12	1.48	$2.50 \pm 0.45$	$1.59 \pm 0.16$	0.06	1.57
Phe	$7.28 \pm 2.73$	$6.44 \pm 0.62$	0.23	1.13	$18.45 \pm 4.42$	$12.04 \pm 1.46$	0.19	1.53
Ant	$3.48 \pm 1.20$	$3.16 \pm 0.14$	0.35	1.10	$1.13 \pm 1.10$	$1.47 \pm 0.48$	0.21	0.77
Flu	$4.88 \pm 1.66$	$3.90 \pm 0.52$	0.05	1.25	$11.15 \pm 5.08$	$9.48 \pm 2.03$	0.04	1.18
Pyr	$3.40 \pm 0.96$	$2.59 \pm 0.36$	0.29	1.31	$8.15 \pm 4.00$	$7.72 \pm 1.70$	0.37	1.06
BaA	$1.09 \pm 0.34$	$0.89 \pm 0.23$	0.39	1.22	$4.20 \pm 2.14$	$7.65 \pm 3.07$	0.87	0.55
Chr	$2.89 \pm 0.79$	$2.32 \pm 0.39$	0.36	1.25	$11.84 \pm 7.45$	$21.10 \pm 7.89$	0.83	0.56
BbF	$3.41 \pm 0.47$	$5.01 \pm 0.92$	0.65	0.68	$14.82 \pm 9.32$	$20.75 \pm 7.82$	0.52	0.71
BkF	$0.41 \pm 0.47$	$2.01 \pm 0.92$	0.77	0.20	$14.82 \pm 9.32$	$20.75 \pm 7.82$	0.52	0.71
BaP	$0.40 \pm 0.14$	$0.99 \pm 0.44$	0.69	0.40	$5.60 \pm 3.80$	$10.66 \pm 5.02$	0.88	0.53
IcdP	$0.35 \pm 0.23$	$1.05 \pm 0.94$	0.83	0.17	$8.35 \pm 6.54$	$12.16 \pm 6.78$	0.79	0.69
DBA	$0.03 \pm 0.01$	$0.04 \pm 0.02$	0.75	0.25	$0.81 \pm 0.74$	$0.86 \pm 0.42$	0.65	0.94
BghiP	$0.28 \pm 0.12$	$1.47 \pm 0.86$	0.63	0.19	$8.89 \pm 6.59$	$13.98 \pm 8.01$	0.78	0.64
$\Sigma$ PAHs	$29.20 \pm 2.19$	$30.78 \pm 1.90$		0.94	$111.07 \pm 5.95$	$140.34 \pm 7.59$		0.79



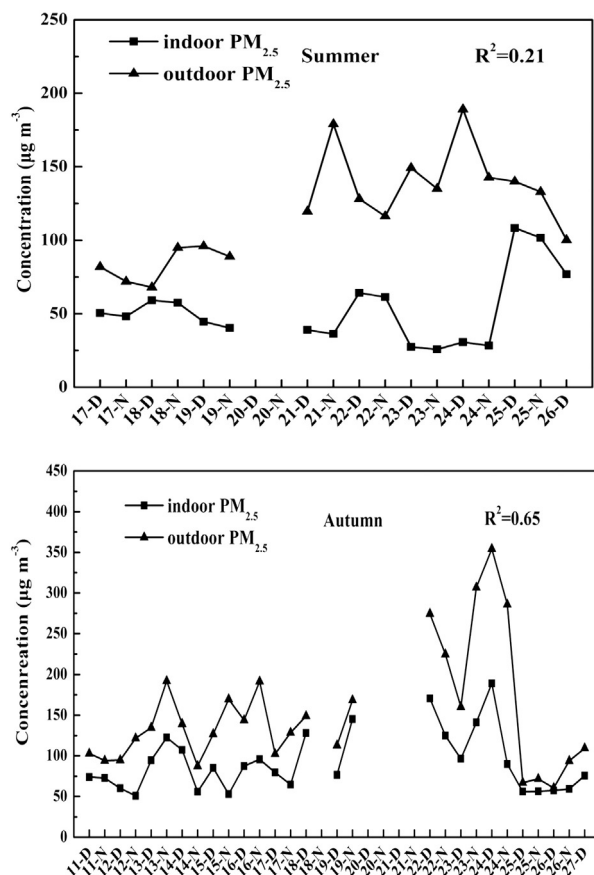


Fig. 2. Trends for the variations in the mass concentrations of indoor/outdoor  $PM_{2.5}$  in summer and autumn.

### 3.2. Inorganic ions

#### 3.2.1. Inorganic ion concentrations

The mean concentrations of the sum of the 8 measured inorganic ions ( $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$ ) in the indoor and outdoor air were  $40.01 \pm 9.10$  and  $105.24 \pm 19.74 \mu g m^{-3}$  in summer, respectively, which were higher than those in autumn ( $38.13 \pm 5.52$  and  $71.33 \pm 10.48 \mu g m^{-3}$ ). In addition, in summer, the total concentrations of the 8 inorganic ions accounted for 77.53% and 90.29% of the indoor and outdoor  $PM_{2.5}$  mass concentrations, respectively, which were also higher than those in autumn (40.84% and 47.67%, respectively).  $SO_4^{2-}$ ,  $NO_3^-$  and  $NH_4^+$  were the three main inorganic ions, accounting for approximately 95.88% and 97.86% of the indoor and outdoor total ion concentrations in summer, respectively, and 80.76% and 89.58% of the indoor and outdoor total ion concentrations in autumn. Compared with other cities, the concentrations of  $SO_4^{2-}$ ,  $NH_4^+$  and  $NO_3^-$  were 3.36–10.66 times higher than those of foreign cities, such as Thessaloniki, Greece, in 1999 (Mouratidou and Samara, 2004) and Munich, Germany, in 2005 (Fromme et al., 2008), and 1.46–1.78 times higher than those of Chinese locations, such as Guizhou in 2008 (Wang et al., 2010).

Among the inorganic ions,  $SO_4^{2-}$  was the largest component, and the  $SO_4^{2-}$  concentrations exhibited a strong seasonal

variation, with a greater contribution observed during the summer.  $SO_4^{2-}$  is formed by the oxidation of  $SO_2$ , and in summer, the increase in photochemical reactions promotes the oxidation of the gaseous precursor  $SO_2$  by hydroxyl radicals (Mazzeza et al., 2001; Seguin et al., 2011). Significant reductions in the contributions of nitrate and ammonium were observed during summer when compared with autumn. The concentration of  $NO_3^-$  is mainly affected by the chemical equilibrium, which depends on temperature and relative humidity (Lin et al., 2010). Compared with summer, the low temperature in autumn is beneficial to the formation of nitrate. The contribution of the  $Cl^-$  ion to  $PM_{2.5}$  was higher in autumn, which may be related to a greater amount of coal combustion (Sun et al., 2006). Biomass burning around Shandong (<https://firms.modaps.eosdis.nasa.gov/firemap/>) was the main factor contributing to the higher contribution of  $K^+$  in autumn relative to that in summer.

#### 3.2.2. Indoor-outdoor concentration relationships and diurnal and nocturnal ion variations

As shown in Table 2, the average I/O ratios of  $NO_3^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $NH_4^+$  and  $K^+$  ions were less than 1.00 in summer and autumn, indicating that these ions were mainly from outdoor sources, whereas the I/O ratios of  $Cl^-$ ,  $Mg^{2+}$  and  $Ca^{2+}$  were greater than 1.00, indicating the presence of a significant indoor source. In the indoor environment, a  $NH_4NO_3$  aerosol is rapidly volatilized and adheres to room surfaces, which may be a reason for the lower indoor  $NO_3^-$  and  $NH_4^+$  concentrations (Fromme et al., 2008; Saliba et al., 2009). The large amount of chlorinated water used for cleaning and the associated evaporation of chlorine into the air during the cleaning process contributed to the indoor  $Cl^-$  concentrations. Several studies have found that cleaning products that contain bleach will release significant amounts of  $Cl^-$  (Loupa et al., 2007). The resuspension of particles in association with the movement of people across the office contributed to the indoor  $Ca^{2+}$  and  $Mg^{2+}$  concentrations.

The correlation coefficients ( $R^2$ ) between indoor and outdoor inorganic ion concentrations were evaluated to determine which ion species measured indoors are influenced by contributions from outdoors. The  $NO_3^-$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $NH_4^+$  and  $K^+$  ions had strong correlations ( $R^2$  values ranging from 0.52 to 0.87), which indicate that these ions predominantly originated from the transport of outdoor air. The indoor and outdoor  $Mg^{2+}$  and  $Ca^{2+}$  concentrations were moderately correlated ( $R^2 = 0.28$ – $0.32$ ), whereas the  $Cl^-$  correlation was very weak ( $R^2 = 0.07$ – $0.08$ ), indicating the significant contribution of  $Cl^-$  from indoor sources (cleaning activities).

As shown in Fig. 4, in summer, the I/O ratios for  $NO_3^-$  and  $Cl^-$  were higher during daytime than at nighttime, which may be related to the use of air conditioner systems in the office during daytime. Additionally, the indoor temperature was lower than the ambient temperature, which would reduce the reactions of  $NH_4NO_3$  and  $NH_4Cl$  that resulted to their decomposition into gaseous  $NH_3$ ,  $HNO_3$  and  $HCl$ . In autumn, the I/O ratios of  $NO_3^-$  and  $Cl^-$  measured during daytime exceeded the ratio observed during nighttime, which may be associated with the large temperature difference between day and night in autumn. Thus, when the outdoor temperature decreased, the decomposition of particulates  $NH_4NO_3$  and  $NH_4Cl$  was inhibited. Notably, during daytime, cleaning products were heavily used and there

was a great deal of human movement, which resulted in higher I/O ratios of  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , compared to nighttime. The I/O ratio of  $\text{K}^+$  in autumn was higher in daytime and may have been affected by biomass burning.

### 3.3. PAHs

#### 3.3.1. PAH concentrations

The mean concentrations of individual PAHs and the  $\Sigma$  PAHs in the indoor and outdoor environments are given in Table 2. The  $\Sigma$  PAH concentrations in the indoor and outdoor samples were  $111.07 \pm 5.95$  and  $140.34 \pm 7.59 \text{ ng m}^{-3}$ , respectively, in autumn, which were 3.83 and 4.56 times those in summer. Moreover, in autumn, the indoor PAH concentrations were more than 2.12 times higher than those at an urban sampling site with heating sources in China (Li et al., 2006) and Portuguesa, Venezuela (Castro et al., 2011). In addition, the outdoor PAH concentrations in autumn were much greater than those measured in residential areas located in North America, such as Houston (Fraser et al., 2002), Atlanta and Gulfport (Zheng et al., 2002), and more than 2.41 times greater than those at urban sites in Birmingham, Britain (Zheng et al., 2002) and Guangzhou, China (Li et al., 2006).

The higher  $\Sigma$  PAH concentrations in autumn may be associated with crop straw burning and the lower temperature during this sampling period. It was found that crop straw burning is common and represents a considerable source of PAHs (Zhang et al., 2007; Shen et al., 2013). Low temperatures can increase the transition of PAHs from the vapour phase to the particulate phase and decrease the photochemical decomposition of PAHs (Duan et al., 2007).

Fig. 3 shows the relative contributions of individual PAHs to the total PAH concentrations. In summer and autumn, the contribution profiles of all of the individual PAHs were very similar for both the indoor and outdoor samples. The 3–4-ring PAH compounds provided higher contributions in the indoor air, while the 5–6-ring PAHs were the predominant contributors in the outdoor air. Notably, a relatively low proportion of 5–6-ring PAHs was observed in the indoor air in summer. These lower concentrations may have been related to the use of air conditioner systems in the office. According to Lv and Zhu (2013), the concentrations and percentages of the indoor 5–6-ring PAHs decline when air conditioner systems are operated continuously compared with the use of natural ventilation.

#### 3.3.2. Indoor–outdoor concentration relationships and diurnal and nocturnal variations in PAHs

As shown in Table 2, in summer, the indoor concentrations of the 3–4-ring PAHs were considerably higher than those of the outdoors, resulting in I/O values greater than 1.00; however, for the less volatile 5–6-ring PAHs, the situation was reversed, and the mean I/O ratios were less than 1.00. In autumn, the I/O ratios of the 3-ring PAH concentrations were greater than 1.00, while the ratios for the 4–6-ring PAHs were less than 1.00. Moreover, in summer, the coefficients of determination,  $R^2$ , for the 3–4-ring PAHs were lower than 0.50 but were greater than 0.50 for the 5–6-ring PAHs. In autumn, the  $R^2$  values for the 3-ring PAHs were less than 0.50 but greater than 0.50 for the 4–6-ring PAHs. These results indicate that the low-ring PAHs mainly came from indoor sources, whereas the high-ring PAHs predominantly originated from the transport of outdoor air.

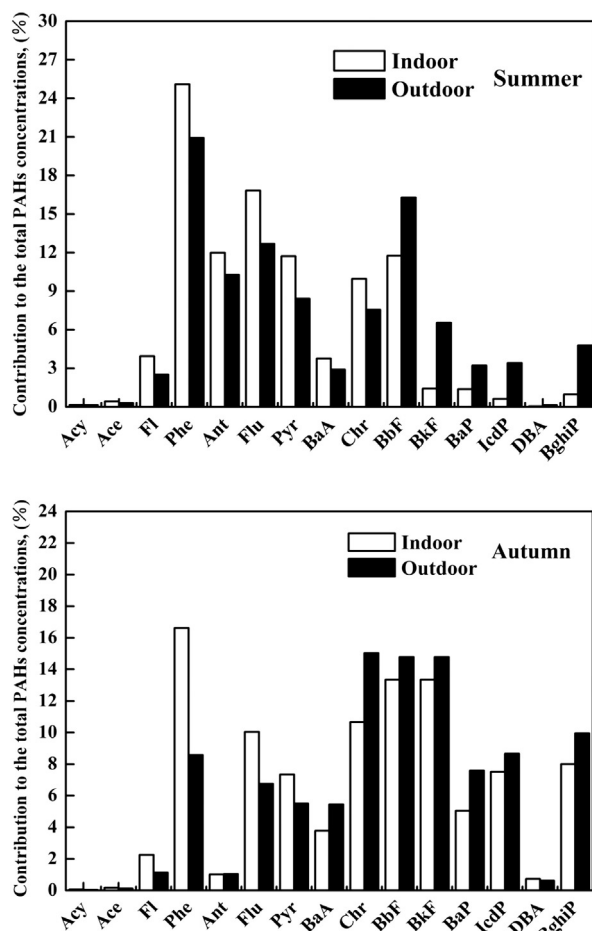


Fig. 3. Mean contributions of individual PAHs to total PAH concentrations. Indoor samples are shown in white, and outdoor samples are shown in black.

The diurnal and nocturnal I/O ratios for particulate PAHs are shown in Fig. 4. During the daytime in both summer and autumn, however, the I/O ratios of the 15 monitored PAHs were all greater than 1.00; thus, we believe that the PAHs were mainly from indoor sources. However, during nighttime, the I/O ratios for the 3–4-ring PAHs were greater than 1.00 in both summer and autumn, while those for the 5–6-ring PAHs were less than 1.00. These results indicate that the emission sources of 3–4-ring PAHs mainly derive from indoor air, while the 5–6-ring PAHs were predominantly from outdoor sources.

Some studies implied emission source as a predominant factor controlling the changes of PAHs with the evidence of positive correlation between PAH concentration and  $\text{PM}_{2.5}$  contents (Chen et al., 2009; Hu et al., 2012). Interestingly, in this study, the  $\text{PM}_{2.5}$  concentrations had no significant correlations with particulate PAH concentrations ( $r = 0.12$ ), which implied that not only emission sources but also gas-particle partitioning processes control the variations of the particulate PAH concentrations (Sitaras et al., 2004; Vasilakos et al., 2007). The results of diurnal and nocturnal I/O ratios for particulate PAHs were strong evidence for the contribution of gas-particle partitioning.

These results could be explained by temperature fluctuations due to the use of air conditioning in summer and the

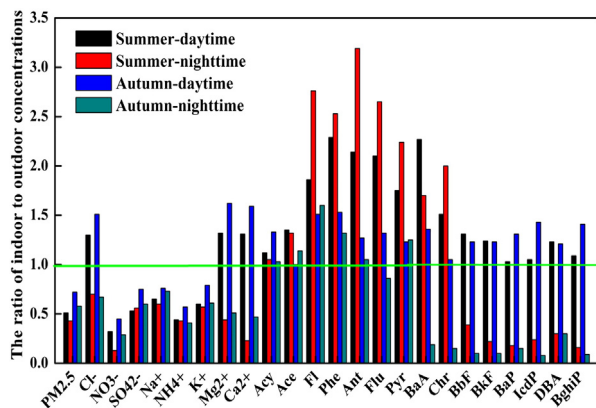


Fig. 4. The indoor-to-outdoor concentration ratios of PM<sub>2.5</sub>, water-soluble ions and PAHs during the daytime and nighttime in summer and autumn.

temperature difference between day and night in autumn in Jinan. In summer, air conditioning reduced the indoor temperature in the office, which decreased the transition of PAHs from the particulate phase to the vapour phase. Thus, during daytime, the concentration of particulate PAHs was high and the I/O ratios of the 15 monitored PAHs were all greater than 1.00. In autumn, the higher concentrations of 5–6-ring PAHs in the outdoor air at nighttime may have been associated with the temperature difference between day and night (Liu et al., 2013). Fig. 5 shows that the percentage contribution of 5–6-ring PAHs to the total PAH concentration was higher at nighttime than that during daytime. During nighttime, the low temperatures caused a decrease in the transition of 5–6-ring PAHs from the particulate phase to the vapour phase, which resulted in an increase in the 5–6-ring PAH concentrations. Moreover, significant correlations were observed between the percentage contribution of 5–6-ring PAHs and temperature in summer ( $r = -0.56$ ) and autumn ( $r = -0.49$ ). A number of studies have also reported that atmospheric temperature has an important influence on the variations in particulate PAH concentrations (Li et al., 2006; Tan et al., 2006; Vasilakos et al., 2007).

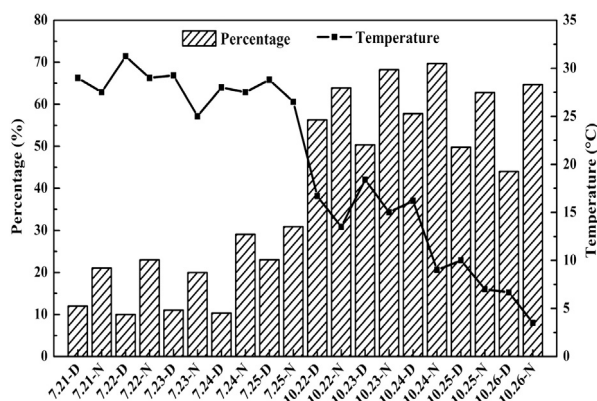


Fig. 5. Diurnal and nocturnal variations in the percentage contributions of 5–6-ring PAHs to total PAHs as well as the temperature fluctuation over the sampling period.

### 3.3.3. PAH source apportionment by diagnostic ratios

Considering the fact that outdoor particle sources have a strong impact on indoor environments, we used diagnostic ratios to analyse the sources of the outdoor particulate PAHs. Diagnostic ratios are useful indicators of PAH sources because isomer pairs are diluted to a similar extent when mixed with natural particulate matter. They are also distributed similarly among phases because they have comparable thermodynamic partitioning and mass transfer coefficients (Dickhut et al., 2000). Certain PAH isomer-pair ratios, including IcdP/(IcdP + BghiP), BaA/(BaA + Chr) and BaP/BghiP, have been widely used to distinguish among possible sources of PAHs due to their relatively stable features (Yunker et al., 2002). The results of these diagnostic ratios are listed in Table 3.

The ratio of IcdP/(IcdP + BghiP) was 0.46 in summer and 0.68 in autumn. The result indicated that PAHs mainly originated from fuel combustion outdoors in the summer, and in the autumn, outdoor PAHs primarily originated from coal/biomass combustion sources (Mandalakis et al., 2002; Hu et al., 2012). The value of the BaA/(BaA + Chr) ratio in summer was 0.41, indicating pyrolytic sources, whereas in autumn, the ratio was between 0.20 and 0.35, indicating a strong contribution from combustion (Soclo et al., 2000). The BaP/BghiP ratio in the outdoor air in summer was between 0.30 and 0.40, indicating a strong contribution from traffic (Park et al., 2002). In contrast, the ratio in autumn was greater than 0.41 but lower than 0.90, implying a mixture of contributions from coal/biomass combustion and traffic sources (Liu et al., 2007).

### 3.3.4. Risk assessment of PAH pollution in the indoor air of the office

The carcinogenic potency of each PAH was assessed in terms of its benzo[a]pyrene-equivalent concentration (BaPeq). The calculation of the BaPeq concentration for each individual PAH species requires the use of its toxic equivalent factor (TEF), which represents the relative cancer potency of a given species (Nisbet and LaGoy, 1992). The concentrations of carcinogenic PAHs were calculated as:

$$\text{BaPeq} = \text{PAH}_i * \text{TEF}_i \text{ and } \text{TEQ} = \sum (\text{PAH}_i * \text{TEF}_i)$$

where PAH<sub>i</sub> is the concentration of the PAH congener i; TEF<sub>i</sub> is the toxic equivalent factor for the PAH congener i; and TEQ is the toxic equivalent of the reference compound.

Table 3  
Diagnostic ratios of particulate PAHs in the outdoor air at the office.

	Summer— outdoor	Autumn— outdoor	Reference source emissions
IcdP/(IcdP + BghiP)	0.46	0.68	<0.50 fuel combustion >0.50 coal/biomass combustion
BaA/(BaA + Chr)	0.41	0.26	<0.20 petrogenic 0.20–0.35 combustion >0.35 pyrolytic sources
BaP/BghiP	0.38	0.65	0.30–0.40 traffic 0.90–6.60 coal/biomass combustion

**Table 4**Toxic-equivalent concentrations ( $\text{ng m}^{-3}$ ) of particulate PAHs.

PAHs	TEF	Summer				Autumn			
		Indoor	Outdoor	Indoor–day	Indoor–night	Indoor	Outdoor	Indoor–day	Indoor–night
Acy	0.001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0002	0.0001
Ace	0.001	0.0001	0.0001	0.0001	0.0003	0.0002	0.0002	0.0004	0.0001
Fl	0.001	0.0011	0.0008	0.0007	0.0005	0.0025	0.0016	0.0014	0.0011
Phe	0.001	0.0103	0.0064	0.0053	0.0039	0.0185	0.0120	0.0104	0.0081
Ant	0.01	0.0348	0.0316	0.0156	0.0148	0.0113	0.0147	0.0084	0.0029
Flu	0.001	0.0049	0.0039	0.0027	0.0023	0.0112	0.0095	0.0082	0.0029
Pyr	0.001	0.0034	0.0026	0.0015	0.0014	0.0081	0.0077	0.0062	0.0019
BaA	0.1	0.1090	0.0890	0.0513	0.0419	0.4196	0.7646	0.3079	0.1117
Chr	0.01	0.0289	0.0232	0.0137	0.0110	0.1184	0.2110	0.0931	0.0253
BbF	0.1	0.3410	0.5010	0.0298	0.0091	1.4816	2.0753	1.3290	0.1526
BkF	0.1	0.0410	0.2010	0.0298	0.0091	1.4816	2.0753	1.3290	0.1526
BaP	1.0	0.4000	0.9900	0.2044	0.1490	5.6034	10.6638	4.3510	1.2524
IcdP	1.0	0.3500	1.0500	0.1252	0.0000	8.3469	12.1593	7.5980	0.7489
DBA	0.01	0.0001	0.0004	0.0001	0.0000	0.0086	0.0081	0.0074	0.0012
BghiP	0.1	0.0280	0.1470	0.0178	0.0063	0.8891	1.3980	0.7969	0.0923
TEQ		1.3528	3.0471	0.4980	0.2498	18.4011	29.4012	15.8476	2.5541

Table 4 shows that the TEQ values in summer were 1.3528 and 3.0471  $\text{ng m}^{-3}$  in the indoor and outdoor samples, respectively, which were lower than the national standard of 10  $\text{ng m}^{-3}$  but were significantly higher than the WHO standard (1  $\text{ng m}^{-3}$ , WHO, 1987). In autumn, the indoor and outdoor TEQ values were 18.4011 and 29.4012  $\text{ng m}^{-3}$ , respectively, which were much greater than the national standard and also approximately tenfold greater than those in the summer. Notably, although the indoor TEQ values were lower than the outdoor values in both summer and autumn, the contributions of carcinogenic PAHs, such as BaA, BkF, IcdP and DBA, to the inhalation exposure of TEQ in the indoor air were 36.97% in summer and 54.70% in autumn, suggesting a relatively higher human health risk in the indoor air in the office in Jinan compared to the values for the outdoor air in summer (43.99%) and in autumn (51.04%).

In addition, we also used the values of the  $\sum$  TEF-PAHs to assess the lifetime lung cancer risk attributed to the indoor and outdoor samples. The WHO proposed a unit of risk of  $8.70 \times 10^{-5}$  ( $\text{ng m}^{-3}$ )<sup>-1</sup> for a lifetime (70 years) of PAH exposure (WHO, 2000). The values of the lifetime lung cancer risks from the exposure to indoor particulate PAHs in the office in Jinan were  $1.18 \times 10^{-4}$  in summer and  $1.60 \times 10^{-3}$  in autumn, which exceed the health guideline ( $10^{-5}$ ) (Boström et al., 2002). Therefore, there was high health risk to individuals from exposure to PAHs in the indoor air in Jinan. Moreover, the values of the lifetime lung cancer risks from particulate PAHs in the outdoor air were  $2.65 \times 10^{-4}$  and  $2.56 \times 10^{-3}$  in summer and autumn, respectively, which were 2.57 and 1.60-fold greater than those of the indoor air, suggesting a relatively high human health risk in Jinan.

During daytime, the indoor TEQ value was 0.4980  $\text{ng m}^{-3}$  in summer and 15.8476  $\text{ng m}^{-3}$  in autumn, which was 1.99 and 6.20-fold greater than those at nighttime, respectively. Additionally, the values of the lifetime lung cancer risks during the daytime ( $4.33 \times 10^{-5}$  in summer and  $1.38 \times 10^{-3}$  in autumn) were also greater than those for the nighttime ( $2.17 \times 10^{-5}$  in summer and  $2.22 \times 10^{-4}$  in autumn). These results suggest that indoor PAHs have more carcinogenic and mutagenic effects during daytime.

#### 4. Summary

The mean indoor and outdoor PM<sub>2.5</sub> mass concentrations were  $51.52 \pm 28.22$  and  $115.92 \pm 44.84$   $\mu\text{g m}^{-3}$  in summer and  $93.52 \pm 41.07$  and  $150.88 \pm 73.07$   $\mu\text{g m}^{-3}$  in autumn. The average I/O ratios of the PM<sub>2.5</sub> indicated that the indoor PM<sub>2.5</sub> was mainly transported from outdoor sources. The  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  ions were the three main inorganic ions in the indoor and outdoor air. In summer and autumn,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$  and  $\text{K}^+$  ions mainly originated from outdoor sources, whereas  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  had significant indoor sources. During daytime, the I/O ratio for  $\text{NO}_3^-$  was higher than that at nighttime, which was related to the temperature difference between the indoor and outdoor air. The 3–4-ring PAH compounds provided a higher contribution to PAHs in the indoor air, while the 5–6-ring PAHs were the predominant contributor in the outdoor air. During daytime, the 15 monitored PAHs were all mainly from indoor sources. In contrast, during nighttime, the 3–4-ring PAHs were mainly generated indoors, but the 5–6-ring PAHs were predominantly transported indoors from the outdoor air. According to the correlations of PM<sub>2.5</sub> and particulate PAH concentrations, we can conclude that not only emission sources but also gas-particle partitioning processes control the variations in particulate PAH concentrations. Diagnostic ratios indicated that biomass burning had an important role in outdoor PAH concentrations in autumn. The results of the risk assessment of PAH pollution indicated that indoor PAHs have more carcinogenic and mutagenic effects during daytime.

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