Characteristics of PM_{2.5}-bound PAHs at an Urban Site and a Suburban Site in Jinan in North China Plain

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ABSTRACT

The PM_{2.5} samples at an urban site (JN) and a suburban site (QXT) were simultaneously collected in a heavily polluted city in North China Plain (Jinan) from March to December in 2016, and eighteen polycyclic aromatic hydrocarbons (PAHs) were analyzed. The annual average Σ PAHs concentrations were 39.8 ± 36.6 and 23.6 ± 14.0 ng m⁻³ at JN and QXT, respectively, with the highest concentrations observed during winter. PHE and CHY were the two most abundant PAHs, accounting for 31.1% at JN and 34.2% at QXT. Source apportionment analyses from the results of Principal Component Analysis (PCA) revealed that coal/biomass combustion and vehicle emission were the major PAH sources in PM_{2.5}. The ratio of LMW + MMW (LMW: low molecular weight; MMW: middle molecular weight) PAHs to Σ PAHs at JN was significantly lower ($p < 0.001$) than that at QXT, indicating coal/biomass burning made more significant contribution to suburban area than that to urban area. Conversely, vehicle emission worked more effectively to urban area. The total benzo[a]pyrene (BaP) equivalent concentration (BaP_{eq}) of PAHs (gas + particle phases) was 9.66 times higher than the standard value (1.00 ng m⁻³) and mainly originated from PAHs in particles (93.1%) with the highest contributor of Benzo(a)pyrene (BaP, 60.8%) at the urban site of Jinan in winter. The total incremental lifetime cancer risk (ILCR) assessment suggested that all age groups may have potential health risk at JN in winter except for infant. The Concentration Weighted Trajectory (CWT) model indicated that local emission and short-distance transport were the main sources of PAHs during spring and winter, and long-range transport played a key role on PAH concentrations in summer and autumn.

Keywords: Seasonal variation; Diurnal variation; PCA; Health risk assessment; CWT.

INTRODUCTION

The biggest emitter of PAHs in the world is China in 2007 with 21.0% (106 Gg a⁻¹) burden of the global emissions (Zhang *et al.*, 2007; Shen *et al.*, 2013). North China Plain is one of the most developed regions in China and produces massive PAHs in both urban and suburban areas (Zhang *et al.*, 2007; Zhao *et al.*, 2011). PAHs are a group of semi-volatile and toxic organic compounds and exist both in the gaseous and particulate phases in atmosphere (Ravindra *et al.*, 2008; Dat *et al.*, 2018). PAHs with the lowest molecular weight and highest vapor pressure are tend to present in the gaseous phase and the highest molecular weight, lowest vapor pressure PAHs mainly be found in particulate phase

(Lai *et al.*, 2017; Liu *et al.*, 2017; Pratt *et al.*, 2018). Strongly toxic PAHs mainly occur in particles (Jin *et al.*, 2018) and the total BaP equivalent concentrations (BaP_{eq}) of PAHs in particulate phase account for 87.9% to 97.0% in previous studies (Table S1) (Wang *et al.*, 2011a; Tomaz *et al.*, 2016; Pratt *et al.*, 2018; Zhang *et al.*, 2018a; Gaga and Ari, 2019). Thus, studies on particulate-bound PAHs are with more significant importance. Furthermore, the highest risk for human health originates from fine particles (PM_{2.5}) (Cheruiyot *et al.*, 2015; Lelieveld *et al.*, 2015; Bowe *et al.*, 2018a, b; Zhang *et al.*, 2018c), due to their large surface area and high organic carbon content which can bind with abundant poisonous compounds (Yang *et al.*, 2017). Consequently, PM_{2.5}-bound PAHs have received more academic concern (Wang *et al.*, 2011b; Kim *et al.*, 2013; Wang *et al.*, 2016; Alves *et al.*, 2017; Simayi *et al.*, 2018).

Numerous studies on the composition, toxicity, seasonal variation, and source of PM_{2.5}-bound PAHs have been conducted in North China Plain (i.e., Beijing, Tianjin, and

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Jinan) (Zhu *et al.*, 2014; Chen *et al.*, 2017; Li *et al.*, 2017). PAH concentrations usually exhibit significant seasonal variation owing to the distinct emissions such as residential heating and straw burning (Longhin *et al.*, 2013; Xia *et al.*, 2013), and different meteorological conditions including pressure, temperature, and relative humidity (Chen *et al.*, 2016). Coal combustion and biomass burning are major sources of PAHs in North China Plain, especially in Shandong province (Lu *et al.*, 2016; Dat and Chang, 2017; Ma *et al.*, 2018; Yin and Xu, 2018; Zheng *et al.*, 2018; Shen *et al.*, 2019; Wang *et al.*, 2019). Most recent studies on atmospheric PAHs have been completed at only one sampling site (Zhuo *et al.*, 2017; Liu *et al.*, 2018; Yin and Xu, 2018; Wang *et al.*, 2019). However, the atmospheric behaviors of PAHs in a megacity cannot be fully understood using only one sampling site when considering the complex energy structures and meteorological conditions. Hence, long term studies simultaneously conducted in different areas of a megacity (such as urban and suburban sites) are necessary for further understanding the PAHs characteristics.

Jinan is a major city in North China Plain that suffers from severe haze during the winter (Zhang *et al.*, 2014; Lu *et al.*, 2016). Li *et al.* (2017) investigated the indoor/outdoor concentrations and sources of PAHs in urban and suburban in Jinan during winter and indicated that coal, biomass, diesel fuel and gasoline combustions were the main sources of PAHs. Zhang *et al.* (2018a) reported the gas-particulate partitioning of PAHs in Jinan and indicated the gas-particle partitioning might be non-equilibrium and be strongly influenced by absorption. The diurnal variation of PAHs in Jinan during summer revealed that the PAH concentrations were influenced by the change of boundary layer (Zhang *et al.*, 2018b). However, few studies have focused on the seasonal variation of PM_{2.5}-bound PAHs at urban and suburban sites in Jinan. The objectives of this study were: (1) to analyze the concentrations, seasonal variations and diurnal variations of PM_{2.5}-bound PAHs at urban and suburban sites in Jinan; (2) to identify the sources of PM_{2.5}-bound PAHs using PCA method; (3) to evaluate potential health risks of PAHs (including gas and particle phases) by combining methods of BaP_{eq} and ILCR and (4) to identify the potential source regions of PM_{2.5}-bound PAHs in Jinan by CWT model.

METHODS

Sampling Site and Sample Collection

PM_{2.5} samples were collected simultaneously at an urban site and a suburban site in Jinan. The urban sampling site was located on the rooftop of the teaching building (about 20 m above ground level) on the central campus of Shandong University (36°40'N 117°03'E), and abbreviated as JN (Fig. 1). The suburban site was selected at Qixing Tai hotel (36°29'N, 117°19'E, abbreviated as QXT) in Qixing Tai which is a scenic spot located in the suburbs of Jinan and about 50 km away from Jinan downtown area (Fig. 1). Samples were collected in 2016 during four seasons (spring: March 6 to 15, summer: June 3 to 15, autumn: September 20 to 29, and winter: December 2 to 11) on quartz

filters using medium-volume air samplers (TH-150A, Wuhan Tianhong Instrument, China) at a flow rate of 100 L min⁻¹. The collection period of all samples was 11.5 h in daytime (from 8:00 am to 7:30 pm) and night time (from 8:00 pm to 7:30 am next day). After sampling, the filter was wrapped in aluminum foil and stored at -20°C prior to analysis. All quartz filters and aluminum foils were prebaked at 600°C for 6 h. The meteorological data was acquired from a National basic meteorological station (Tables S2). At JN, meteorological data was only available for spring and summer.

Sample Extraction and Analysis

The detailed methods of extraction and analysis have been described previously in Li *et al.* (2017). Briefly, each of the sample was extracted by Soxhlet extraction with 150 mL of dichloromethane (DCM, J.T. Baker, USA) for 8 h. Next, the extract was concentrated to 1–2 mL using a rotary evaporator and purified through a silicone and alumina column. The column was eluted with 20 mL n-hexane (discharged) and 70 mL n-hexane/DCM (1:1, v/v, collected). The elution was concentrated to 1–2 mL, and then 10 mL n-hexane was added to the solvent. Finally, the elution was concentrated to 1–2 mL again and further concentrated to 1 mL under a nitrogen stream. Then 100 ng internal standards: naphthalene-d₈, anthracene-d₁₀, pyrene-d₁₀, and perylene-d₁₂ were spiked for quantification. A gas chromatograph (GC, Agilent 7890A) with a triple quadrupole mass spectrometer (MS/MS, Agilent 7001B), coupled with a 5% phenyl substituted methylpolysiloxane GC column (HP-5MS, length: 30 m, diameter: 0.25 mm, film thickness: 0.25 µm, Agilent, USA) was used to measure PAHs. The oven temperature program was: 60°C for 1 min, then increased to 150°C at the rate of 40°C min⁻¹, hold for 5 min, to 300°C at the rate of 4°C min⁻¹ and hold for 15 min.

Eighteen PAHs were quantified: biphenyl (BYL, 2 ring), acenaphthylene (ACY, 3 ring), acenaphthene (ACE, 3 ring), fluorene (FLU, 3 ring), phenanthrene (PHE, 3 ring), anthracene (ANT, 3 ring), fluoranthene (FLT, 4 ring), pyrene (PYR, 4 ring), benzo(a)anthracene (BaA, 4 ring), chrysene (CHY, 4 ring), benzo(b)fluoranthene (BbF, 5 ring), benzo(k)fluoranthene (BkF, 5 ring), benzo(e)pyrene (BeP, 5 ring), benzo(a)pyrene (BaP, 5 ring), indeno(123cd)pyrene (IcdP, 6 ring), dibenzo(ah)anthracene (DahA, 5 ring), benzo(ghi)perylene (BghiP, 6 ring), and coronene (COR, 7 ring). Those PAHs can be classified into LMW (2, 3-rings, low molecular weight), MMW (4 rings, middle molecular weight) and HMW (5, 6, 7-rings, high molecular weight) PAHs according to the number of rings. LMW and MMW PAHs mainly be generated from coal/biomass combustion and the major source of HMW PAHs was vehicle emission (Kong *et al.*, 2010; Chen *et al.*, 2017). Predictive Analytics Software (PASW Statistics 18) was performed for data statistical analysis.

Quality Control

Solvent, filter, and field blanks were used to evaluate the background concentrations. Results showed that the PAHs concentrations in blank samples were negligible, except

Fig. 1. The locations of the urban (JN) and a suburban (QXT) sampling sites.

for naphthalene (NAP). NAP was detected in the pesticide grade solvents including n-hexane and DCM. Thus, NAP was excluded from the analysis. Surrogate recoveries were measured by randomly adding acenaphthene- d_{10} and chrysene- d_{12} as surrogate standards to one-third of the samples before sample extraction. The surrogate recoveries of acenaphthene- d_{10} and chrysene- d_{12} were: 64%–110% and 68%–105%, respectively. Method recoveries were obtained by spiking standards (100 ng each for the studied 18 PAHs) to clean filters, and the average method recoveries were 69%–125%. In this study, the PAHs concentrations were not corrected using blank results, surrogate recoveries, or method recoveries. For every ten samples, one repeated analysis was conducted. The mean relative standard deviation was 9.7%. The quantification limits of for PAHs in this work were 0.50–5.00 ng mL⁻³.

Health Risk Assessment of PAHs

To assess the health risk of PAHs more fully, we calculated the PAHs concentrations in total suspended particle (TSP) and gas. We converted the concentrations of PM_{2.5} obtained from Environmental Protection Agency of Jinan to TSP's concentrations using the ratio of PM_{2.5} and TSP (TSP/PM_{2.5} = 1.95) measured during the December of

2012 in Xi'an (Zhang *et al.*, 2015). The concentrations of TSP-bound PAHs (C_p) (only eleven toxic PHAs) (Table 4) were estimated according the result of Tan *et al.* (2011) in which the PAHs concentrations in PM_{2.5} and TSP were studied in Guangzhou. The partitioning coefficients (K_p , m³ μg⁻¹) of individual PAH between gas and particle in winter of Jinan were reported in Zhang *et al.* (2018a). We deduced the PAH concentrations in gas phase (C_g) from Eq. (1).

$$C_g = (C_p/TSP)/K_p \quad (1)$$

The toxicity of PAHs from gas and particle phases was assessed by total BaP_{eq} which was yield from Eq. (2):

$$\sum BaP_{eq} = \sum BaP_{eqi} = \sum (C_i \times TEF_i) \quad (2)$$

where C_i is the concentration of the i th PAH in gas and particle; TEF_i is the toxic equivalent factor (TEF) for the i th PAH. The TEF value of BaP is 1, and all other PAHs have been evaluated based on their carcinogenicity in comparison to BaP (Chen *et al.*, 2017). According to Nisbet and LaGoy (1992), the TEF for PHE, FLT and PYR are 0.001; for ANT, CHY and BghiP are 0.01; for BaA, BbF

and BkF are 0.1; for BaP and DahA are 1. The toxicities of BbF and BkF were combined as the toxicity of BbkF. Due to the limited applicability of K_p , we only calculated the PAH toxicity at the urban site of Jinan in winter.

The exposure risks of PAHs in gas and particle phases were calculated using the incremental lifetime cancer risk (ILCR) based on the standard model established by the United States Environmental Protection Agency (Chen and Liao, 2006; Gao et al., 2018). The ILCR is determined by Eq. (3):

$$ILCR_{inhalation} = CSF_{inhalation} \times \frac{c \times IR_{inhalation} \times ED \times EF}{BW \times ALT} \quad (3)$$

where the $CSF_{inhalation}$ is the cancer slope factor ($\text{mg kg}^{-1} \text{day}^{-1}$)⁻¹, c is ΣBaP_{eq} (ng m^{-3}), $IR_{inhalation}$ is the air inhalation rate ($\text{m}^3 \text{day}^{-1}$), ED is the lifetime exposure duration (years), EF is the exposure frequency (day year^{-1}), BW is the body weight (kg), and ALT is the averaging lifetime of the carcinogenic substance (years). A more detailed introduction can be found in previous studies (Lu et al., 2016; Gao et al., 2018).

CWT Model

The CWT model combines the background trajectories obtained from the Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) and air mass concentrations produced from experimental observation to identify the potential source areas. In a CWT model, each grid cell is assigned a weighted concentration by averaging the sample concentrations using Eq. (4):

$$C_{ij} = \frac{1}{\sum_{l=1}^M \tau_{ijl}} \sum_{l=1}^M C_l \tau_{ijl} \quad (4)$$

where C_{ij} is the average weighted concentration in the ij th cell, l is the index of the trajectory, M is the total number of trajectories, C_l is the concentration observed on arrival of trajectory l , and τ_{ijl} is the time spent in the ij th cell by trajectory l . Thus, more likely source cells exhibit higher CWT values. To reduce the uncertainty in cells with small n_{ij} (the number of endpoints that fall in the ij th cell) values, an additional weighting function (W_{ij}) was used to multiply the C_{ij} and output WCWT values. W_{ij} was defined as below (Dimitriou and Kassomenos, 2017):

$$W_{ij} = \begin{cases} 1.00 & 3n_{ave} \leq n_{ij} \\ 0.70 & 1.5n_{ave} < n_{ij} < 3n_{ave} \\ 0.40 & n_{ave} < n_{ij} < 1.5n_{ave} \\ 0.20 & 0 < n_{ij} < n_{ave} \end{cases} \quad (5)$$

In this study, n_{ave} is the average value of n_{ij} (contain non-zero values). 72h-h backward air trajectories were calculated using the NOAA HYSPLIT model at starting

times of 02, 06, 08, 14, 18, and 22 UTC respectively. The study site was located in the range of 30–60°N and 90–130°E with a resolution of $0.5 \times 0.5^\circ$.

RESULTS AND DISCUSSION

PAH Concentrations

Average concentrations of the 18 $\text{PM}_{2.5}$ -bound PAHs obtained in this study are summarized in Table 1. The total PAHs concentrations (ΣPAHs) at JN varied from 8.18 to 246 ng m^{-3} , with average value of $39.8 \pm 36.6 \text{ ng m}^{-3}$, which was significantly higher ($p < 0.001$) than that at QXT (6.44–75.5 ng m^{-3} , average $23.6 \pm 14.0 \text{ ng m}^{-3}$). A comparison of the annual ΣPAHs concentrations in this study with previous reports is shown in Table 2. The ΣPAHs concentration measured at JN was similar to that in Guangzhou (Liu et al., 2015), lower than those in Beijing (Chen et al., 2017) and Nanjing (He et al., 2014), but higher than those in Huangshi (Hu et al., 2018), Zagreb (Jakovljević et al., 2018), Tehran (Taghvaei et al., 2018), Belluno (Khan et al., 2018) and Hsinchu (Yang et al., 2017). The ΣPAHs concentration at QXT presented higher concentration than those in Douai (Crenn et al., 2017), South Dekalb (Li et al., 2009) and Athens (Alves et al., 2017) but lower than that in Xi'an (Wang et al., 2017). The highest concentrations of the ΣPAHs were observed in winter, followed by spring at JN and QXT. The lowest concentration at JN was observed during summer which was accordant with previous works (Dat and Chang, 2017; Ma et al., 2018; Zheng et al., 2018). At QXT, the lowest ΣPAHs concentration occurred in autumn. Meteorological parameters were vital factors in influencing PAH concentrations. The correlation coefficients between the PAHs and meteorological parameters at JN and QXT are shown in Table S3. Air pressure was positively correlated with MMW and HMW PAHs at QXT and nearly all PAHs at JN. Increasing the air pressure suppresses PAHs condense into the particulate phase from the gas phase (Elorduy et al., 2016). Temperature was negatively correlated with PAH concentrations at both sites, except for LMW at QXT. High temperature enhances PAHs evaporate from particle to the gas (Kong et al., 2010; Pehnek et al., 2016). The air pressure/temperature in winter and spring were higher/lower than those in summer and autumn which partially explained the relatively higher PAH concentrations in winter and spring. Besides meteorological factors, increased residential heating, reduced rainfall and less photo-degradation also augmented higher PAH concentrations in winter (Pankow et al., 1993; Wang et al., 2012; Bandowe et al., 2014). The QXT, as a scenic spot, has increased rate of tourism during summer which lead to increased vehicle emission and energy consumption. Therefore, the total PAHs concentration in summer was slightly higher than that in autumn at QXT. The total PAHs concentration in winter was 5.08 times higher than that in summer at JN. Whereas at QXT, the winter/autumn ratio of 18 PAHs concentration was 2.40. The more prominent seasonal variation of PAH concentrations at JN may be attributed to more frequent impact of human activity in urban area.

Table 1. Average concentrations and standard deviations (mean $\pm$ SD) of PAHs at JN and QXT during the sampling period (ng m⁻³).

PAH	JN				QXT			
	Spring N = 18	Summer N = 20	Autumn N = 19	Winter N = 20	Spring N = 18	Summer N = 20	Autumn N = 19	Winter N = 20
BYL	0.712 $\pm$ 0.423	0.380 $\pm$ 0.218	0.643 $\pm$ 0.615	0.771 $\pm$ 0.601	0.435 $\pm$ 0.326	0.756 $\pm$ 0.476	0.449 $\pm$ 0.191	0.654 $\pm$ 0.531
ACY	0.306 $\pm$ 0.0611	0.211 $\pm$ 0.0540	0.201 $\pm$ 0.0354	0.356 $\pm$ 0.0925	0.245 $\pm$ 0.0672	0.234 $\pm$ 0.0650	0.223 $\pm$ 0.0625	0.289 $\pm$ 0.0734
ACE	0.388 $\pm$ 0.195	0.333 $\pm$ 0.217	0.353 $\pm$ 0.321	0.516 $\pm$ 0.357	0.511 $\pm$ 0.524	0.399 $\pm$ 0.231	0.315 $\pm$ 0.201	0.390 $\pm$ 0.303
FLU	2.42 $\pm$ 0.955	1.88 $\pm$ 1.10	2.47 $\pm$ 1.67	3.19 $\pm$ 2.03	3.39 $\pm$ 3.39	2.39 $\pm$ 1.06	1.64 $\pm$ 0.743	2.59 $\pm$ 1.71
PHE	4.82 $\pm$ 1.79	2.81 $\pm$ 1.32	4.68 $\pm$ 2.89	6.11 $\pm$ 3.24	6.43 $\pm$ 5.11	3.84 $\pm$ 1.59	2.71 $\pm$ 1.288	5.04 $\pm$ 2.84
ANT	0.304 $\pm$ 0.107	0.182 $\pm$ 0.0696	0.215 $\pm$ 0.118	0.456 $\pm$ 0.226	0.451 $\pm$ 0.370	0.207 $\pm$ 0.129	0.165 $\pm$ 0.0845	0.317 $\pm$ 0.170
FLT	5.10 $\pm$ 1.43	1.12 $\pm$ 0.237	1.43 $\pm$ 0.691	7.44 $\pm$ 4.52	2.989 $\pm$ 1.594	1.26 $\pm$ 0.372	1.20 $\pm$ 0.380	4.14 $\pm$ 1.83
PYR	3.09 $\pm$ 0.963	0.753 $\pm$ 0.146	1.04 $\pm$ 0.426	4.47 $\pm$ 2.66	1.67 $\pm$ 0.851	0.754 $\pm$ 0.188	0.735 $\pm$ 0.204	2.10 $\pm$ 0.766
BaA	3.96 $\pm$ 1.59	1.17 $\pm$ 0.219	1.27 $\pm$ 0.707	9.55 $\pm$ 10.1	1.65 $\pm$ 0.688	1.03 $\pm$ 0.192	1.06 $\pm$ 0.235	2.42 $\pm$ 0.855
CHY	6.49 $\pm$ 2.15	2.08 $\pm$ 0.380	2.32 $\pm$ 1.19	14.1 $\pm$ 12.1	2.85 $\pm$ 1.21	1.75 $\pm$ 0.250	1.78 $\pm$ 0.285	4.40 $\pm$ 1.63
BbF	2.96 $\pm$ 1.25	0.658 $\pm$ 0.287	1.43 $\pm$ 1.33	5.94 $\pm$ 5.79	1.21 $\pm$ 0.769	0.460 $\pm$ 0.187	0.507 $\pm$ 0.217	1.93 $\pm$ 0.776
BkF	1.73 $\pm$ 0.531	0.869 $\pm$ 0.221	1.26 $\pm$ 1.00	3.87 $\pm$ 2.72	1.09 $\pm$ 0.470	0.555 $\pm$ 0.151	0.583 $\pm$ 0.153	1.45 $\pm$ 0.469
BeP	2.19 $\pm$ 0.585	0.827 $\pm$ 0.235	1.31 $\pm$ 0.908	4.02 $\pm$ 2.96	1.20 $\pm$ 0.579	0.673 $\pm$ 0.216	0.715 $\pm$ 0.221	1.82 $\pm$ 0.661
BaP	1.85 $\pm$ 0.691	0.479 $\pm$ 0.220	0.833 $\pm$ 0.788	4.46 $\pm$ 4.25	0.980 $\pm$ 0.661	0.437 $\pm$ 0.256	0.478 $\pm$ 0.236	1.39 $\pm$ 0.599
IcdP	1.16 $\pm$ 0.510	0.224 $\pm$ 0.105	0.769 $\pm$ 0.705	3.21 $\pm$ 3.72	0.503 $\pm$ 0.305	0.151 $\pm$ 0.118	0.154 $\pm$ 0.113	0.926 $\pm$ 0.494
DahA	0.258 $\pm$ 0.104	0.0702 $\pm$ 0.0366	0.347 $\pm$ 0.437	0.679 $\pm$ 0.688	0.132 $\pm$ 0.0622	0.045 $\pm$ 0.028	0.0542 $\pm$ 0.0348	0.215 $\pm$ 0.0880
BghiP	1.23 $\pm$ 0.542	0.201 $\pm$ 0.135	0.730 $\pm$ 0.728	3.15 $\pm$ 3.43	0.494 $\pm$ 0.293	0.108 $\pm$ 0.121	0.127 $\pm$ 0.124	0.833 $\pm$ 0.399
COR	0.155 $\pm$ 0.0566	0.0470 $\pm$ 0.0211	0.644 $\pm$ 0.410	0.340 $\pm$ 0.330	0.097 $\pm$ 0.042	0.0347 $\pm$ 0.0191	0.0311 $\pm$ 0.0158	0.142 $\pm$ 0.0760
Σ PAHs	39.1 $\pm$ 11.0	14.3 $\pm$ 3.78	21.9 $\pm$ 11.3	72.6 $\pm$ 52.5	26.3 $\pm$ 15.8	15.1 $\pm$ 4.33	12.9 $\pm$ 3.67	31.0 $\pm$ 12.2

Table 2. A summary of PM_{2.5}-bound PAHs concentrations in various cities of the world.

Sampling site	Sampling type	PAHs concentrations (ng m ⁻³)	Sampling period	ΣPAHs	Reference
Jinan	Urban	39.8 (8.18–247)	2016/03–2016/12	Σ19	This study
Qixing Tai	Suburban	23.6 (6.44–75.5)	2016/03–2016/12	Σ19	This study
Beijing (China)	Urban	61.2 (5.10–788)	2015/03–2016/01	Σ16	(Chen <i>et al.</i> , 2017)
Nanjing (China)	Urban	56.0 (25.9–90.8)	2009/12–2010/7	Σ16	(He <i>et al.</i> , 2014)
Guangzhou (China)	Urban	33.9 (6.99–106)	2012/06–2013/05	Σ17	(Liu <i>et al.</i> , 2015)
Huangshi (China)	Urban	10.7 (1.51–44.5)	2013/01–2013/10	Σ16	(Hu <i>et al.</i> , 2018)
Zagreb (Croatia)	Urban	9.65	2013/01–2013/12	Σ10	(Jakovljević <i>et al.</i> , 2018)
Tehran (Iran)	Urban	12.2	2012/05–2013/05	Σ16	(Taghvaei <i>et al.</i> , 2018)
Belluno (Italy)	Urban	19.6 (0.400–66.2)	2012–2013	Σ8	(Khan <i>et al.</i> , 2018)
Rovigo (Italy)	Urban	7.00 (0.200–37.6)	2012–2013	Σ8	(Khan <i>et al.</i> , 2018)
Hsinchu (Taiwan, China)	Urban	1.76 (0.21–8.08)	2014/09–2015/08	Σ20	(Yang <i>et al.</i> , 2017)
Athens (Greece)	Suburban	0.658–3.44	2013/01–2014/02	Σ27	(Alves <i>et al.</i> , 2017)
Douai (France)	Suburban	2.17 (0.583–4.16)	2010/11–2011/08	Σ10	(Crenn <i>et al.</i> , 2017)
Xi'an (China)	Suburban	38.5 and 269	2013/06 and 2013/12	Σ18	(Wang <i>et al.</i> , 2017)

PAHs Composition Profiles

PHE and CHY were the two most abundant PAHs in total PAHs, accounting for 31.1% at JN and 34.2% at QXT (Table 1). BghiP exhibited the greatest seasonal variation with increased factors of 15.7 and 7.71 in winter compared with those in summer at JN and QXT, respectively (Table 1). The seasonal percentages of the different ring PAHs to total PAHs concentrations are shown in Fig. 2. At JN, LMW PAHs were dominate PAH components in summer (39.1%) and autumn (38.2%). While in spring and winter, LMW PAHs significantly decreased ($p < 0.001$) and MMW PAHs significantly increased ($p < 0.001$) to be the most abundant compounds (47.6% in spring and 33.5% in winter). At QXT, LMW PAHs also found to be major species of PAHs except for winter. MMW PAHs were the most abundant compositions ($p < 0.001$) in winter (42.2%). The ratio of LMW + MMW PAHs to ΣPAHs at JN was significantly lower ($p < 0.001$) than that at QXT, indicating coal/biomass burning made more significant contribution to suburban area than that to urban area. Conversely, significantly higher ratio of HMW PAHs to ΣPAHs at JN revealed that vehicle emission worked more effectively to urban area. At JN, the mean ratios of HMW PAHs to ΣPAHs were in the order: summer (24.0%) < spring (29.4%) < autumn (32.3%) < winter (33.5%) and the order at QXT were summer (16.5%) < autumn (20.5%) < spring (22.9%) < winter (28.2%) which indicated vehicle emissions were a more significant source in winter both at JN and QXT. Low atmosphere temperature and high cold starts effect were the main factors causing the increased HMW PAHs emission from vehicles in winter (Morville *et al.*, 2011).

Diurnal Variation of PAHs

The diurnal concentrations of the individual PAH during the sampling periods are presented in Fig. 3. Higher MMW and HMW PAHs concentrations were observed during the night sampling periods at JN in spring, autumn, and winter. Lower photochemical activity, evening rush hour peaks, heavy truck traffic and lower boundary layer height during the nighttime may have contributed to the higher MMW

and HMW PAHs concentrations (Miao and Liu, 2019). No significant diurnal variations of LMW, MMW, and HMW PAHs concentrations be observed at QXT.

Sources of PAHs

PCA is a method to reduce a set of variables to a few key factors which can be used to identify sources (Kong *et al.*, 2010; Li *et al.*, 2010). Three factors and two factors (Table 3) were identified for JN and QXT, accounting for 93.9% and 89.8% of the total variance, respectively.

In Jinan, Factor 1, which explained 56.8% of the variance, was associated with high loadings of FLT, PYR, BaA, CHY, BbF, BkF, BeP, BaP, IcdP, DahA, and BghiP. Among those compounds, BbF, BaP, IcdP, and BghiP are products of vehicle emissions (Miguel and Pereira, 1989). BaA and CHY are emitted from diesel and natural gas combustions (Rogge *et al.*, 1993; Kavouras *et al.*, 2001). The presence of FLT, PYR, BbF, and BkF indicates diesel-powered vehicle emissions (Ravindra *et al.*, 2006). FLT, PYR, CHY, (Harrison *et al.*, 1996; Mastral *et al.*, 1996; Simcik *et al.*, 1999; Limu *et al.*, 2013; Zhu *et al.*, 2014) and DahA (Fang *et al.*, 2004; He *et al.*, 2014) are related to coal combustion. Consequently, Factor 1 was identified as a mixture of coal combustion and diesel vehicle emissions at the urban site. Factor 2, which explained 28.3% of the total variance, exhibited high loadings of BYL, ACE, FLU, PHE, and ANT and a moderate loading of ACY. These LMW PAHs are largely produced at a relatively low combustion temperatures (such as in coal and biomass burning) (Chen *et al.*, 2017). FLU, ANT, ACY, and ACE are related to coal combustion. ACY, ACE, FLU, PHE, and ANT are mainly associated with the coal and tar/coal combustion (Sofowote *et al.*, 2008; He *et al.*, 2014) and have been used as a tracer of coal combustion (Guo *et al.*, 2003). ANT, PHE and FLU are markers for wood burning (Kong *et al.*, 2010). Thus, Factor 2 was identified as coal/wood combustion. Factor 3, which explained 8.68% of the total variance, had high loading of COR. COR mainly originates from gasoline vehicle emissions (Miguel *et al.*, 1998; Guo *et al.*, 2003). Therefore, Factor 3 was considered to be gasoline combustion source.

Fig. 2. The percentages of low molecular weight (LMW), middle molecular weight (MMW), and high molecular weight (HMW) PAHs to total PAHs in four seasons at an urban site (JN) and a suburban site (QXT).

Fig. 3. Diurnal characteristics of PAHs in (a) spring, (b) summer, (c) autumn, and (d) winter.

Similar results were observed at QXT. Factor 1 reflected a mixture sources of vehicle emissions (including the combustions of diesel and gasoline) and coal combustion. Factor 2 represented coal/wood combustion source. Thus, coal/wood burning and vehicle emissions were important PAHs sources for both the urban site and suburban site. Similar findings were reported by previous studies (Li et

al., 2017; Zhang et al., 2018b).

Toxicity Risk Assessment of PAHs

The $\sum \text{BaP}_{\text{eq}}$ (Table 4) and the ILCR (Table 5) were used to assess the toxicity risk of PAHs in winter of JN. The $\sum \text{BaP}_{\text{eq}}$ was 9.66 ng m^{-3} , exceeding the recommended World Health Organization (WHO) limit of 1.00 ng m^{-3}

Table 3. Factor loadings of PCA analysis at JN and QXT.

PAHs	JN			QXT	
	PC1	PC2	PC3	PC1	PC2
BYL	0.04	0.93	0.03	0.03	0.79
ACY	0.54	0.69	−0.29	0.33	0.79
ACE	−0.01	0.96	0.07	0.02	0.97
FLU	0.04	0.97	0.11	0.18	0.96
PHE	0.20	0.95	0.14	0.34	0.90
ANT	0.57	0.76	−0.10	0.37	0.80
FLT	0.88	0.37	−0.15	0.87	0.43
PYR	0.87	0.39	−0.15	0.87	0.45
BaA	0.97	0.09	0.06	0.88	0.33
CHY	0.98	0.15	0.07	0.91	0.33
BbF	0.95	0.11	0.17	0.96	0.20
BkF	0.95	0.14	0.12	0.96	0.20
BeP	0.96	0.15	0.14	0.95	0.25
BaP	0.98	0.06	0.14	0.92	0.27
IcdP	0.93	0.02	0.30	0.96	0.16
DahA	0.78	0.17	0.55	0.96	0.09
BghiP	0.95	0.04	0.26	0.98	0.12
COR	0.27	0.10	0.91	0.91	−0.01
Variance (%)	56.8	28.3	8.68	59.6	30.1
Source	Diesel/coal	Coal	Gasoline	Vehicle/coal	Coal

Principal components with factor loading higher than 0.7 are shown in bold.

Extraction method: principal component analysis.

Rotation method: varimax with Kaiser normalization.

KOM in Jinan is 0.807 and in Qixing Tai is 0.882.

Table 4. The concentrations and BaP_{eq} of PAHs in gas and particle phases in winter at JN (ng m^{−3}).

PAH	TEF	Gas		TSP	
		Cg	BaP _{eqi}	Cp	BaP _{eqi}
PHE	0.001	168	0.168	8.03	0.00803
ANT	0.01	21.1	0.211	0.583	0.00583
FLT	0.001	19.8	0.0198	10.3	0.0103
PYR	0.001	12.3	0.0123	6.35	0.00635
BaA	0.1	0.698	0.0698	12.9	1.29
CHY	0.01	1.04	0.0104	18.8	0.188
BbkF	0.1	0.373	0.0373	11.8	1.18
BaP	1	0.113	0.113	5.47	5.47
DahA	1	0.0208	0.0208	0.801	0.801
BghiP	0.01	0.0703	0.000703	3.78	0.0378
Total BaP _{eq}			−0.663		9.00

Table 5. The ILCR and the total ILCR ($\times 10^{-6}$) of PAHs in gas and particle phases to age-specific group in winter at JN.

Age group	Phase	Infant	Toddler	Children	Adolescent	Adult (18–30)	Adult (30–70)
ILCR	Gas	0.0220	0.0856	0.0658	0.0707	0.0814	0.271
	TSP	0.299	1.16	0.893	0.959	1.10	3.68
Years		1 years	6 years	12 years	18 years	30 years	70 years
Total ILCR	Gas	0.0220	0.108	0.173	0.244	0.326	0.597
	TSP	0.299	1.46	2.35	3.31	4.42	8.10

(Ventafridda *et al.*, 1987). The total BaP_{eq} mainly originated from particles (93.1%). This result was in accordance with previous studies (shown in Table S1) (Wang *et al.*, 2011a; Tomaz *et al.*, 2016; Pratt *et al.*, 2018; Zhang *et al.*, 2018a; Gaga and Ari, 2019). The major contributors of the total BaP_{eq}

in particle phase PAHs were BaP (60.8%), BaA (14.3%), BbkF (13.1%) and DahA (8.90%); in gas phase PAHs were ANT (31.8%), PHE (25.3%), BaP (17.0%) and BaA (10.5%); in Σ PAHs (gas + particle phases) were BaP (57.8%), BaA (14.1%), BbkF (12.6%) and DahA (8.51%) (Fig. 4).

Fig. 4. The percentages of eleven carcinogenic PAHs to total BaP_{eq} in gaseous PAHs, particulate PAHs and total PAHs (TPAHs: gas + particle phases PAHs) phase at JN in winter.

The ILCRs for adults (30–70 years) were highest (2.71×10^{-7} in gas phase and 3.68×10^{-6} in particle phase), followed by toddlers, adults (18–30 years), adolescents, children, and infants. According to Chen and Liao (2006), the annual ILCR value should be below 10^{-6} . Accordingly, the adults (30–70 years), toddlers, adults (18–30 years) and adolescent (Table 5) at the urban site of Jinan may experience a potential health risk. The total ILCR assessment revealed that except for infant, PAHs in atmosphere pose cancer risk for all other age groups at the urban site of Jinan during winter.

Potential Source Region

In order to study the seasonal variation of potential source regions in Jinan, we average the total PAHs concentrations of JN and QXT as the concentrations of Jinan to input into CWT model and the results are shown in Fig. 5. In spring and winter, local emission and short-distance transport from Shandong Province played significant roles in the PAH concentrations. The stable meteorological conditions which counted against PAH diffusion likely be responsible for the source regions. In summer, heavily polluted air masses originated from the southeast direction and passed through the Yellow Sea, Jiangsu Province, and the southeast of Shandong Province. According to Pongpiachan *et al.* (2015), shipping emissions from diesel engines significantly increase PM₁₀-bound PAHs. The Yellow Sea is notable for its extensive shipping, mariculture, and fishing (Liu *et al.*, 2008) in China. Prevailing wind direction from southeast China in summer also was a major factor to make Yellow Sea as an important source region of PAHs in summer. In autumn, polluted air masses from the northeast and southeast direction were dominant. In the northeast direction, major source regions were the east of Inner Mongolia, west of Liaoning Province, Bohai, and north of Shandong Province, and in the southeast direction, Yellow Sea, Jiangsu province, and south Shandong Province were major source areas.

CONCLUSIONS

In this study, 18 PM_{2.5}-bound PAHs were investigated at an urban site (JN) and a suburban site (QXT) in Jinan in North China Plain from March to December in 2016. The annual average Σ PAHs concentration was 39.8 ± 36.6 at JN, significantly higher ($p < 0.001$) than that at QXT (23.6 ± 14.0 ng m⁻³). The highest Σ PAHs concentrations were observed in winter. PHE and CHY were the most abundant compounds, accounting for 31.1% and 34.2% of the combined PAHs concentrations at JN and QXT, respectively. Source apportionment from PCA indicated coal/wood combustion and vehicle emission were the main PAH sources. The ratio of LMW + MMW PAHs to Σ PAHs at JN was significantly lower ($p < 0.001$) than that at QXT, indicating coal/wood burning made more significant contribution to suburban site compared with suburban site. Conversely, the ratio of HMW PAHs to Σ PAHs at JN significantly higher than that at QXT, revealing vehicle emission worked more effectively to urban area. Significantly higher ratio of HMW PAHs to Σ PAHs in winter indicated vehicle emissions were a more significant source in winter.

The toxicity risk assessment indicated the total BaP_{eq} of PAHs (gas + particle phases) exceeded the standard value (1.00 ng m⁻³) and mainly originated from particles (93.1%). BaP, BaA, BbkF and DahA were the main contributors to the total BaP_{eq} value in particulate PAHs and total PAHs, while ANT, PHE, BaP and BaA were the major contributors to the total BaP_{eq} in gaseous phase PAHs. The total incremental lifetime cancer risk assessment revealed that PAHs in atmosphere pose cancer risk for all age groups except for infant at the urban site of Jinan during winter.

According to the CWT analysis, the most likely source regions of PM_{2.5}-bound PAHs in spring and winter in Jinan was surrounding areas of Shandong province. In summer, heavily polluted air masses moved through the Yellow Sea, Jiangsu Province, and southeast Shandong Province.

Fig. 5. WCWT maps for $\Sigma 18$ $PM_{2.5}$ -bound PAHs in Jinan in spring, summer, autumn, and winter.

In autumn, the potential source regions were found in the north direction (east of Inner Mongolia, west of Liaoning Province, Bohia, and north Shandong Province) and southeast direction (Yellow Sea, Jiangsu Province, and south Shandong Province).

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DISCLAIMER

We declare that we have no conflict of interest.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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