Comparative Study of PAHs in PM₁ and PM_{2.5} at a Background Site in the North China Plain

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are carcinogenic and mutagenic. They bounded in atmospheric fine (PM_{2.5}) and submicron (PM₁) particles severely affect human health. To characterize 18 PAHs at a background site (Mount Tai) in the heavily polluted North China Plain (NCP), PM₁ and PM_{2.5} samples were collected in the autumn of 2014. The sampling periods were classified into clean conditions and polluted conditions according to PM_{2.5} concentration. Biomass burning condition was selected from polluted conditions to clarify the impact of biomass burning to PAHs concentrations. The concentrations of $\Sigma 18$ PAHs were 14.5 and 24.5 ng m⁻³ and the contents were 515 and 607 $\mu\text{g g}^{-1}$ in PM₁ and PM_{2.5}, respectively. Three-ring PAHs were the primary contributors to the total PAHs. The major PAHs sources at Mount Tai were pyrogenic and traffic emission. Diesel combustion played more significant role to the emission of PM₁-bound PAHs, while wood burning source was more obvious for PM_{2.5}-bound PAHs. PAHs concentrations and cancer risks were the highest during biomass burning condition compared with those during polluted and clean conditions. The lifetime accumulated cancer risk of PM₁-bound PAHs was considered to be acceptable, whereas it elevated to “potential risk” (10⁻⁶) for adults (30–70 years old) exposed to PM_{2.5}-bound PAHs. The Concentration-weighted trajectory (CWT) model indicated long-distance transport from Northwest China was the major source of PM₁-bound PAHs under the clean conditions. Compare with clean conditions, PAHs were more strongly influenced by short-distance transported air masses from the South of Shandong Province under the polluted conditions.

Keywords: Polycyclic aromatic hydrocarbon; Biomass burning; Health risk assessment; Source identification; CWT model.

INTRODUCTION

Air pollution is a severe problem in China and has attracted widespread attention from the government, social organizations, and individuals. With the overall increases of population, vehicles and industrial activities, the emission of polycyclic aromatic hydrocarbons (PAHs) has also increased world widely (Yu *et al.*, 2016). PAHs exist in both gas and particulate phases. The carcinogenic and mutagenic potential risk of PAHs increases with an increase in the number of benzenoid rings (Wang *et al.*, 2017). PAHs with high molecular weight were dominate in particulate phase (Pratt *et al.*, 2018). Thus, many studies have focused on particles-bound PAHs for the adverse effects on human health (Fan *et al.*, 2017; Zhou *et al.*, 2017; Jin *et al.*, 2018).

PAHs are more commonly found in fine particles (PM_{2.5}, whose aerodynamic equivalent diameter is < 2.5 μm) or submicron particles (PM₁, whose aerodynamic equivalent diameter is < 1 μm) than in coarse particles. Mazquiaran and de Pinedo (2007) found that 60% of the PAHs were bounded to particles with a diameter of less than 0.61 μm in an urban area. Kong *et al.* (2010) reported that 90% of total PM₁₀-PAHs were in PM_{2.5}. Zhu *et al.* (2014) reported that particles-bound PAHs with high carcinogenicity were primarily in the < 1.8 μm size range. PM_{2.5} are inhalable and respirable, hence they can penetrate the human respiratory system and cause DNA damage (Mazquiaran and de Pinedo, 2007). Compared with PM_{2.5}, PM₁ possess larger specific area to absorb more toxic compounds and smaller sizes to be transported to deeper respiratory system, furtherly lead to more damage on human health (Agudelo-Castaneda *et al.*, 2015). Thus, understanding the concentrations and compositions of PAHs in PM₁ and PM_{2.5} is of significant importance.

PAHs are emitted from pyrogenic (e.g., produced by combustion) and petrogenic (produced by the incomplete combustion of petroleum) sources. Biomass burning (59%),

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domestic coal combustion (23%), and coke (fuel) production (15%) are the major PAH emission sources in China (Zhang *et al.*, 2007). PAHs, as persistent and semi-volatile organic pollutants, can transport over long distance to remote areas through the grasshopper effect and cold trapping process. Background site is defined as site far away from anthropogenic emission sources; therefore it is typically ideal to evaluate the impact of long-range transport of air pollutants and the pollution of surrounding areas (Zhu *et al.*, 2014; Liu *et al.*, 2017). Many studies have been conducted on PAHs in total suspended particulates (TSP) (Lee *et al.*, 2006; Mazquiaran and de Pinedo, 2007), PM_{10} (Mantis *et al.*, 2005), and $PM_{2.5}$ (Moon *et al.*, 2008) at background sites. However, limited research has focused on PM_1 -bound PAHs. This is because of the low sample masses typically observed at background sites (Verma *et al.*, 2014). North China Plain (NCP), with a population of approximately 350 million, is a densely populated area and chief contributor to PAH emissions in China (Shen *et al.*, 2013). Mount Tai is the highest mountain in the NCP and located far away from ground-level pollutants. Consequently, we chose Mount Tai as a background site to investigate PM_1 - and $PM_{2.5}$ -bound PAH concentrations, contents and composition profiles; analyze PAH concentrations under clean, polluted, and biomass burning conditions; assess cancer risk by using the BaP equivalent concentration (BaP_{eq}) and incremental lifetime cancer risk (ILCR) methods; identify PAH sources by diagnostic ratios; and determine potential source regions of PAHs using concentration-weighted trajectory (CWT) model.

METHODS

Site Description and Sample Collection

The sampling site was located on the summit of Mount

Tai (36.25°N, 117.10°E and 1532.7 m a.s.l.) in Shandong Province in the NCP (Fig. 1) and less impacted by tourists, temples and restaurants. It is about 15 km north of Tai'an, 60 km south of Ji'nan, and 230 km from the Pacific Ocean. Experiments were conducted in the autumn of 2014 from October 3 to 11 for two 11.5-h periods every day (daytime: 8:00 am to 07:30 pm; nighttime: 08:00 pm to 7:30 am next day). Samplings were not conducted on October 4 because of rainy weather. PM_1 and $PM_{2.5}$ samples were collected simultaneously with quartz fiber filters (88 mm in diameter) using a mid-volume air sampler (TH-150A, Wuhan Tian Hong Corporation, China) at a flow rate of 100 L min^{-1} . Prior to sampling, each filter was combusted for 6 h at 600°C in a muffle furnace to eliminate any interference from organic contaminants. After sampling, the filter was placed in plastic box, wrapped with aluminum foil, and stored at -20°C until analysis. Before and after collection, the filters were stored under conditions of $50\% \pm 2\%$ relative humidity and $20^\circ\text{C} \pm 1^\circ\text{C}$ for 24 h and then weighed using a Sartorius analytical balance (Sartorius ME5-F Filter Microbalance, Germany, detection limit: $1\text{ }\mu\text{g}$) to obtain the concentrations of PM_1 and $PM_{2.5}$.

Sample Extraction and Analysis

The detailed procedures for sample extraction and analysis are described previously (Gao *et al.*, 2018). Briefly, a 47-mm patch was cut from the filter and Soxhlet extracted with 150 mL dichloromethane (DCM) for 8 h. The extract was concentrated to approximately 1 mL. The concentrated sample was purified through a silica gel and alumina column and sequentially eluted with 20 mL n-hexane (discharged) and 70 mL of a n-hexane and DCM mixture (1:1, v:v) (collected). The extract was concentrated to approximately 1 mL, and 10 mL n-hexane was added. The solution was

Fig. 1. The sampling site at Mount Tai.

evaporated to approximately 1–2 mL; subsequently, the extract was exactly concentrated to 1 mL under a nitrogen stream and transferred to Agilent bottles. The PAHs were doped with 100 ng of the internal standards: naphthalene-d₈, anthracene-d₁₀, pyrene-d₁₀, and perylene-d₁₂ (AccuStandard, USA). The final extracts were stored at –4°C before sample injection. Analysis was completed using an Agilent gas chromatograph equipped with a triple quadrupole mass spectrometer. Experimental data were statistically analyzed by Predictive Analytics Software (PASW Statistics 18).

Quality Control

Solvent and field blanks were analyzed to assess the interference of background values. The concentrations of the studied PAHs detected in the blanks were negligible, except for naphthalene (NAP). The pesticide-grade solvents used in our process (i.e., n-hexane and DCM) may contain NAP. Consequently, NAP was excluded from quantification. One duplicate sample was performed for every 10 samples, and the mean variation of all measured PAHs was 9.7%. The method recoveries were conducted by adding a mixture of the PAH standards to blank filters and analyzing with the same procedure as all samples. The average method recoveries were 69%–125%. The surrogate recoveries were obtained by spiking 100 ng of surrogate PAHs (acenaphthene-d₁₀ and chrysene-d₁₂) to one-third of the samples before extraction. The surrogate recoveries of acenaphthene-d₁₀ were 64%–110% and chrysene-d₁₂ were 68%–105%. Eighteen PAHs and their abbreviations quantified in this study are shown in Table 1.

Weather Condition Classification

Mount Tai is a scenic spot. According to the ambient air quality standards (GB 3095-2012) published by the Ministry of Environmental Protection of China, we classified the sampling day with PM_{2.5} mass concentration exceeding 35 µg m⁻³ (24-h average value for Grade I) as the polluted

condition. Otherwise, we classified the sampling day as the clean condition. To elucidate the impact of biomass burning, we utilized K⁺_{excess} as biomass burning indicator (Yao *et al.*, 2016; Gao *et al.*, 2018). Because K⁺_{excess} was the highest (0.75) during the night on October 11, we used this period as a representative time for biomass burning. Detailed calculations of K⁺_{excess} are described in Gao *et al.* (2018), and the concentrations of PM₁, PM_{2.5}, K⁺, Ca²⁺, and Na⁺ were acquired from Zhao *et al.* (2017).

Cancer Risk Assessment

The BaP equivalent concentration (BaP_{eq}) computed using Eq. (1) integrates the different carcinogenicities of individual compounds and reflects the probabilistic risk of PAHs.

$$\sum \text{BaP}_{\text{eq}} = \sum_{i=1}^n (\text{PAH}_i \times \text{TEF}_i) \quad (1)$$

where PAH_{*i*} is the *i*th PAH concentration (ng m⁻³), and TEF_{*i*} is the corresponding toxic equivalent factor of *i*th PAH (i.e., 0.001 for ACY, ACE, FLU, PHE, FLA, PYR, and COR; 0.01 for ANT, CHR, BeP, and BghiP; 0.1 for BbF, BkF, BaA, and IcdP; and 1 for BaP and DahA) (Nisbet and LaGoy, 1992; Chen and Liao, 2006).

The incremental lifetime cancer risk (ILCR) method was used to quantitatively assess the exposure risk of PAHs through inhalation among six age groups: infants (0–1 year), toddlers (1–6 years), children (6–12 years), adolescents (12–18 years), adults (18–30 years), and older adults (30–70 years). This approach was established by the United States Environmental Protection Agency (Chen and Liao, 2006; Gao *et al.*, 2018). In this study, the ILCR was calculated using Eq. (2):

$$\text{ILCR}_{\text{inhalation}} = \text{CSF}_{\text{inhalation}} \times \frac{\text{C} \times \text{IR}_{\text{inhalation}} \times \text{ED} \times \text{EF}}{\text{BW} \times \text{ALT}} \quad (2)$$

Table 1. The abbreviations, molecular weight and rings for 18 PAH compounds.

PAH species	Abbreviation	Molecular Weight (g L ⁻¹)	Rings
Biphenyl	BYL	154	2
Acenaphthylene	ACY	152	3
Acenaphthene	ACE	154	3
Fluorene	FLU	166	3
Phenanthrene	PHE	178	3
Anthracene	ANT	178	3
Fluoranthene	FLA	202	4
Pyrene	PYR	202	4
Benzo(a)anthracene	BaA	228	4
Chrysen	CHR	228	4
Benzo(b)fluoranthene	BbF	252	5
Benzo(k)fluoranthene	BkF	252	5
Benzo(e)pyrene	BeP	252	5
Benzo(a)pyrene	BaP	252	5
Dibenzo(ah)anthracene	DahA	278	5
Indeno(123cd)pyrene	IcdP	276	6
Benzo(ghi)perylene	BghiP	276	6
Coronene	COR	300	7

where $CSF_{inhalation}$ is the cancer slope factor ($mg\ kg^{-1}\ day^{-1}$)⁻¹, C is the total BaP_{eq} concentration ($ng\ m^{-3}$), $IR_{inhalation}$ is the air inhalation rate ($m^3\ day^{-1}$), ED is the life exposure duration (years), EF is the exposure frequency ($day\ year^{-1}$), BW is the body weight (kg), and ALT is the average lifetime for the carcinogenic substance (years). More detailed information is provided in Lu *et al.* (2016).

Source Identification

Diagnostic ratios are a convenient and simple method to identify PAH sources and have been broadly applied in previous studies (Liu *et al.*, 2007; Kong *et al.*, 2010; Yu *et al.*, 2018; Zhang *et al.*, 2018b).

In this study, the ratio of BaP/(BaP + BeP) was used to identify whether the air mass was fresh (local emission) or age (long-distance transport) (Zhang *et al.*, 2018b), since BaP is more susceptible to photolytic process than its isomer BeP (Tobiszewski and Namiesnik, 2012). A BaP/(BaP + BeP) ratio be close to 0.5 implies the particles are fresh and a ratio lower than 0.5 implies the aging of particles (Oliveira *et al.*, 2011; Tobiszewski and Namiesnik, 2012). The ratio of BaP/BghiP was applied to differentiate traffic emission source (> 0.6) and non-traffic emission source (< 0.6) (Katsoyiannis *et al.*, 2007; Tobiszewski and Namiesnik, 2012). The ratios of FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) were used to identify pyrogenic source and petrogenic source because the isomer pairs of FLA and PYR, IcdP and BghiP have comparable degradation rates (Zhang *et al.*, 2018b). A FLA/(FLA + PYR) ratio below 0.4 suggests that the source is unburned petroleum. A FLA/(FLA + PYR) ratio ranging from 0.4 to 0.5 suggests the source of petroleum combustion, and a ratio higher than 0.5 suggests a pyrogenic source (Yunker *et al.*, 2002; Simayi *et al.*, 2018). An IcdP/(IcdP + BghiP) ratio lower than 0.2 indicates a petrogenic source. An IcdP/(IcdP + BghiP) ratio ranging from 0.2 to 0.5 suggests a petroleum combustion source, and an IcdP/(IcdP + BghiP) ratio higher than 0.5 indicates a pyrogenic source (Yunker *et al.*, 2002; Yang *et al.*, 2017). Car, diesel, and wood burning sources would produce IcdP/(IcdP + BghiP) ratios of 0.20, 0.37, and 0.62, respectively (Ravindra *et al.*, 2008).

Concentration-weighted Trajectory (CWT) Model

In the CWT model, each grid cell is assigned a weighted concentration by averaging the sample concentrations with associated trajectories that have crossed the grid cell (Hsu *et al.*, 2003). High CWT_{*ij*} values imply that air parcels passing through the *ij*th cell are associated with high concentrations. In this study, the CWT value was calculated using Eq. (3):

$$C_{ij} = \frac{1}{\sum_{l=1}^M \tau_{ijl}} \sum_{l=1}^M C_l \tau_{ijl} \quad (3)$$

where C_{ij} is the weighted average concentration for the *ij*th cell, l is the index of trajectory, M is the total number of trajectories, C_l is the concentration observed on arrival of the trajectory l , and τ_{ijl} is the time spent in the *ij*th cell by the

trajectory l . To minimize uncertainty in cells with small n_{ij} values (the number of endpoints that fall in the *ij*th cell), CWT values were multiplied by an arbitrary weight function (W_{ij}) to yield WCWT (Dimitriou *et al.*, 2015; Dimitriou and Kassomenos, 2017). The W_{ij} was defined as following:

$$W_{ij} = \begin{cases} 1 & 3n_{ave} \leq n_{ij} \\ 0.70 & 1.5n_{ave} < n_{ij} < 3n_{ave} \\ 0.40 & n_{ave} < n_{ij} < 1.5n_{ave} \\ 0.20 & 0 < n_{ij} < n_{ave} \end{cases} \quad (4)$$

WCWT values were obtained using TrajStat software. The Hybrid Single Particle Lagrangian Integrated Trajectory model from the National Oceanic and Atmospheric Administration was used to produce 3-day backward air mass trajectories starting at a height of 1534 m above the ground. Meteorological data were obtained from <ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1>. For each day, 24 trajectories at 00:00–23:00 UTC (Universal Time Coordinated) were calculated. The WCWT grids were in the range of 30°N–60°N and 90°E–130°E with a resolution of $0.5^\circ \times 0.5^\circ$.

RESULTS AND DISCUSSION

Concentrations and Contents

The combined PAH concentrations in PM₁ and PM_{2.5} varied from 5.99 to 28.8 $ng\ m^{-3}$ and from 8.33 to 36.6 $ng\ m^{-3}$, with the mean values of 14.5 and 24.5 $ng\ m^{-3}$, respectively (Fig. 2(a)). The combined PAH contents in PM₁ and PM_{2.5} were 515 and 607 $\mu g\ g^{-1}$ with the range from 144 to 2005 $\mu g\ g^{-1}$ and 183 to 2186 $\mu g\ g^{-1}$ (Fig. 2(b)). The concentration and content of combined PM₁-bound PAHs comprised 59.2% and 84.9% of PM_{2.5}-bound PAHs, revealing that PAHs were dominated by particles in the size range of $< 1\ \mu m$. This was consistent with Wang *et al.* (2009) which found that $\sum 17$ PAHs concentrations in PM_{1.1} accounted 73.5% to $\sum 17$ PAHs in PM_{2.1} during the winter of 2008 at Mount Tai. Shen *et al.* (2019) investigated 10 sampling sites over China from January 2013 to December 2014 and also pointed out that particulate PAHs were main in fine size range of $< 1.1\ \mu m$.

Compared the total concentrations of common PAHs species in our study with those collected at Mount Tai in previous studies, our result in PM_{2.5} was 3.31 times higher than that measured during the winter in 2008 (6.88 $ng\ m^{-3}$, excluding BYL and COR) (Li *et al.*, 2010) and 4.32 times higher than that measured during the summer in 2015 (5.39 $ng\ m^{-3}$, excluding BYL) (Zhang *et al.*, 2018a). The result of the former may be related to the increasing PAH pollution from 2008 to 2014, and the preferred reasons of the latter were the lower photo degradation, chemical oxidation, and temperature in autumn (Manoli *et al.*, 2016).

Compared with other mountains or background sites, our result ($\sum 18, 24.5\ ng\ m^{-3}$) in PM_{2.5} was much higher than those measured at Mount Lu in East China ($\sum 15, 6.98\ ng\ m^{-3}$ in PM_{2.5}) (Yang *et al.*, 2018), Mount Heng in Central China ($\sum 15, 6.03\ ng\ m^{-3}$ in TSP) (Li *et al.*, 2015), Gosan in Korea

Fig. 2. The (a) concentrations (ng m⁻³) and (b) contents (μg g⁻¹) of 18 PAHs in PM₁ and PM_{2.5}.

($\Sigma 17$, 2.22 ng m⁻³ in PM_{2.5}) (Moon *et al.*, 2008), Greater Athens Area in Greece ($\Sigma 13$, 0.656 ng m⁻³ in PM₁₀) (Mantis *et al.*, 2005), E'erdusi in Northwest China ($\Sigma 18$, 0.580 ng m⁻³ in PM_{2.5}) (Wu *et al.*, 2014), and Mt. Bachelor Observatory in the United States ($\Sigma 15$, maximum value: 0.516 ng m⁻³ in TSP) (Primbs *et al.*, 2008). The content of total PAHs in PM_{2.5} was higher than those in Mount Lu ($\Sigma 15$, 160 μg g⁻¹) (Yang *et al.*, 2018) and Mount Heng ($\Sigma 15$, 80.8 μg g⁻¹) (Yang *et al.*, 2015).

Total PM₁-bound PAHs concentration in our study was higher than that in Mount Tai ($\Sigma 17$, 5.50 ng m⁻³ in PM_{1.1}) during the summer of 2006 (Wang *et al.*, 2009) but lower than that in Mount Tai ($\Sigma 17$, 26.0 ng m⁻³ in PM_{1.1}) during the winter of 2008 (Wang *et al.*, 2009). Compared with other urban sites, the concentration was higher than those observed at Canoas ($\Sigma 16$, 1.52 ng m⁻³) and Sapucaia do Sul in Brazil ($\Sigma 16$, 1.99 ng m⁻³) from August 2011 to July 2013 (Agudelo-

Castaneda and Teixeira, 2014), Brno ($\Sigma 16$, 5.01 ng m⁻³) and Slapanice ($\Sigma 16$, 5.41 ng m⁻³) in Czech Republic during summer of 2009 (Krumal *et al.*, 2013), Warsaw in central Poland ($\Sigma 16$, 11.1 ng m⁻³) during spring of 2015 (Rogula-Kozłowska *et al.*, 2018) and Zagreb in Croatia ($\Sigma 10$, 5.07 ng m⁻³) during autumn of 2014 (Pehnec and Jakovljevic, 2018), but lower than those observed at Brno ($\Sigma 16$, 22.2 ng m⁻³) and Slapanice ($\Sigma 16$, 21.0 ng m⁻³) in Czech Republic during winter of 2009 (Krumal *et al.*, 2013), and Gliwice in Southern Poland ($\Sigma 16$, 21.2 ng m⁻³) during spring of 2015 (Rogula-Kozłowska *et al.*, 2018).

Composition Profile

In this study, PHE and FLU were the two most abundant compositions during the sampling period, accounting for 48% of the total PAHs concentrations in PM₁ and 42% of the total PAHs concentrations in PM_{2.5} (Fig. 2(a)). The result

in $PM_{2.5}$ is consistent with the value in Zhang *et al.* (2018a) (38.4% of $\Sigma 17$ PAHs at Mount Tai in the summer of 2015). Three-ring PAHs were the major contributors to total PAHs, followed by four-ring PAHs and five-ring PAHs. According to the number of aromatic rings, PAHs can be classified into lower molecular weight (LMW, two- and three-ring PAHs), middle molecular weight (MMW, four-ring PAHs), and higher molecular weight (HMW, five-, six-, and seven-ring PAHs). The ratios of LMW: MMW: HMW PAHs were 3.72:1.18:1.00 in PM_1 and 2.92:1.24:1.00 in $PM_{2.5}$ (Fig. 2(a)). LMW, MMW, and HMW PAHs in PM_1 accounted for 66.0%, 49.3%, and 51.8% to those in $PM_{2.5}$. Combustion-derived PAHs (COMPAHs), including FLA, PYR, CHR, BbF, BkF, BaA, BeP, BaP, IcdP, and BghiP (Bourotte *et al.*, 2005), accounted for 30.3% and 36.0% of the total PAHs in PM_1 and $PM_{2.5}$, respectively. The COMPAHs in PM_1 comprised 84.1% of that in $PM_{2.5}$ indicating COMPAHs were generally found at the particle size less than $1\ \mu m$.

The composition profile of PAHs contents was similar to the PAHs concentrations (Fig. 2(b)). FLU and PHE dominated total PAHs in PM_1 (45.4%) and $PM_{2.5}$ (41.4%). The COMPAHs contents were $143\ \mu g\ g^{-1}$ and $211\ \mu g\ g^{-1}$, accounted 30.3% and 36.0% to total PAHs in PM_1 and $PM_{2.5}$, respectively. The ratios of LMW: MMW: HMW PAHs were 3.60:1.10:1.00 in PM_1 and 3.21:1.34:1.00 in $PM_{2.5}$. The COMPAHs, LMW PAHs, MMW PAHs and HMW PAHs in PM_1 contributed 67.5%, 92.7%, 68.0% and 82.6% of corresponding PAHs in $PM_{2.5}$.

Comparison of PAH Concentrations by Weather Condition

PAHs concentrations under clean, polluted, and biomass burning conditions are displayed in Fig. 3. For PM_1 -bound PAHs, no significant changes in the total PAHs concentrations or ring distributions were observed between clean and

polluted conditions. Whereas, the total PM_1 -bound PAHs concentration measured on the biomass burning condition ($25.1\ ng\ m^{-3}$) was significantly higher than those on clean conditions ($14.7\ ng\ m^{-3}$, $p < 0.05$) and the polluted conditions ($14.3\ ng\ m^{-3}$, $p < 0.01$).

For $PM_{2.5}$ -bound PAHs, the average concentration of combined PAHs was $27.9 \pm 9.08\ ng\ m^{-3}$ under the polluted conditions, which was higher than the observed concentration under the clean conditions ($18.9 \pm 9.54\ ng\ m^{-3}$, $p < 0.1$) but significantly lower than the concentration under the biomass burning condition ($36.6\ ng\ m^{-3}$, $p < 0.05$). This finding revealed that the polluted condition was favorable for the accumulation of $PM_{2.5}$ -bound PAHs, and biomass burning was a main contributor to $PM_{2.5}$ -bound PAHs. All individual $PM_{2.5}$ -bound PAH concentrations were enhanced to different degrees under the polluted condition, varied from CHR (1.09 times) to BaP (3.08 times), and the biomass burning condition, varied from ANT (1.30 times) to BbF (5.79 times), compared with those under the clean condition. HMW PAHs presented the most remarkable growth (2.23 times under the polluted condition and 3.40 times under the biomass burning condition) compared with the growth of HMW and LMW PAHs. HMW PAHs were mainly associated with vehicle emission (Chang *et al.*, 2006; Kong *et al.*, 2010). Thus, vehicle emission was an important PAHs source during the polluted and biomass burning conditions.

Cancer Risk Assessment

BaP_{eq} Concentrations of PAHs in PM_1 and $PM_{2.5}$

The mean BaP_{eq} concentration in PM_1 was $0.764 \pm 0.350\ ng\ m^{-3}$, significantly lower ($p < 0.05$) than the WHO standard ($1\ ng\ m^{-3}$). In $PM_{2.5}$, the BaP_{eq} value was $1.58 \pm 0.950\ ng\ m^{-3}$, significantly higher ($p < 0.05$) than the WHO standard. By using the same TEF, BaP_{eq} concentrations from this study were compared with those from previous studies

Fig. 3. Individual PM_1 - and $PM_{2.5}$ - bound PAH concentrations during sampling events (P: polluted conditions, C: clean conditions, BB: biomass burning day).

(Table 2). The BaP_{eq} value in PM_1 was lower than those observed at Gliwice and Warszawa in Poland (Rogula-Kozłowska *et al.*, 2018) and an urban site in Croatia (Pehnec and Jakovljevic, 2018). The value of BaP_{eq} in $PM_{2.5}$ was higher than those observed at Mount Lu (Yang *et al.*, 2018), Mount Heng (Li *et al.*, 2015), Qixing Tai (Zhang *et al.*, 2019) and some other background sites in outside of China including Gosan (Lee *et al.*, 2006) and Thracomacedones (Mantis *et al.*, 2005). Also, the BaP_{eq} value in $PM_{2.5}$ was higher than those measured at Mount Tai measured in 2008 (Li *et al.*, 2010) and 2015 (Liu *et al.*, 2017).

Under clean, polluted, and biomass burning conditions, the average values of BaP_{eq} in PM_1 were 0.842 ± 0.479 , 0.704 ± 0.234 , and 1.09 ng m^{-3} . Correspondingly, BaP_{eq} in $PM_{2.5}$ were 0.839 ± 0.414 , 2.02 ± 0.909 , and 3.03 ng m^{-3} , respectively (Fig. 4). The percentage of PM_1 -bound BaP_{eq} in $PM_{2.5}$ -bound BaP_{eq} was close to 100% under the clean condition, significantly higher than those under polluted (34.9%) and biomass burning conditions (36.0%), indicating that the contribution of BaP_{eq} in $PM_{1-2.5}$ increased under polluted and biomass burning conditions.

ILCR Values of PAHs in PM_1 and $PM_{2.5}$

To further understand the health risks for different age groups, we analyzed ILCR and total accumulated risks (Fig. 5). ILCR and total risks in $PM_{2.5}$ were approximately two times higher than those in PM_1 . Among all age groups, PAHs exhibited the highest ILCR for adults (30–70 years) and the lowest ILCR for infants (0–1 years) due to the longest exposure duration (40 years) and the shortest exposure duration (1 years), respectively. However, PAHs presented higher ILCR for toddlers (1–6 years) with shorter exposure duration (5 years) compared with the ILCR for adults (18–30 years, exposure duration: 12 years), adolescents (12–18 years, exposure duration: 6 years) and children (6–12 years, exposure duration: 6 years). This was mainly attributed to the relatively lower body weight of toddlers. ILCRs and total risks were the highest under the biomass burning condition compared with those under clean and polluted conditions. The total accumulated risk reached 9.82×10^{-7} and 2.73×10^{-6} for adult (30–70 years) in PM_1 and $PM_{2.5}$, respectively. According to Chen and Liao (2006), the total accumulated risk of adults (30–70 years) increased to potential cancer risk

Table 2. Calculated BaP_{eq} (ng m^{-3}) concentrations in selected studies using the same TEFs.

Study area	Type	Sampling period	Size	BaP_{eq}	Reference
Mount Tai, North China Plain	Background	2014/10	$PM_{2.5}$	1.58	This study
Mount Tai, North China Plain	Background	2014/10	PM_1	0.764	This study
Gliwice, Poland	Urban	2015/04–2015/06	PM_1	4.29	Rogula-Kozłowska <i>et al.</i> , 2018
Warswa, Poland	Urban	2015/04–2015/06	PM_1	2.27	Rogula-Kozłowska <i>et al.</i> , 2018
Zagreb, Croatian	Urban	2014/09–2014/11	PM_1	0.917	Pehnec and Jakovljevic, 2018
Mount Heng, Southern China	Background	2009/04–2009/05	TSP	0.623	Li <i>et al.</i> , 2015
Mount Lu, Southern China	Background	2012/03–2012/05	$PM_{2.5}$	0.985	Yang <i>et al.</i> , 2018
Mount Tai, North China Plain	Background	2008/10–2008/12	$PM_{2.5}$	0.851	Li <i>et al.</i> , 2010
Qixing Tai, North China Plain	Suburban	2016/09	$PM_{2.5}$	0.796	Zhang <i>et al.</i> , 2019
Gosan, Korea	Background	2001/11–2003/08	$PM_{2.5}$	0.153	Lee <i>et al.</i> , 2006
Mount Tai, North China Plain	Background	2015/06–2015/08	$PM_{2.5}$	0.0949	Liu <i>et al.</i> , 2017
Thracomacedones, Greece	Background	2001/05–2011/11	PM_{10}	0.0776	Mantis <i>et al.</i> , 2005

Fig. 4. BaP_{eq} concentrations in PM_1 and $PM_{2.5}$ (1.0 ng m^{-3} represents WHO standard).

Fig. 5. Incremental lifetime cancer risk (ILCR) and total risk for age specific groups (1.0×10^{-6} is the “acceptable risk” level).

(10^{-6}) when they were exposed to $PM_{2.5}$ -bound PAHs. However, both the ILCR and total risk values were under the potential risk limit for PM_1 -bound PAHs.

Source Identification

The BaP/BghiP ratios plotted against BaP/(BaP + BeP) ratios and the IcdP/(IcdP + BghiP) ratios plotted against the FLA/(FLA + PYR) ratios for PM_1 - and $PM_{2.5}$ -bound PAHs are shown in Fig. 6. The average BaP/(BaP + BeP) ratios in PM_1 (Fig. 6(a)) were 0.329 ± 0.0706 , 0.339 ± 0.131 and 0.323 under clean, polluted, and biomass burning conditions, respectively. Thus, the PM_1 at Mount Tai was aged due to long-distance atmospheric transport. The average BaP/(BaP + BeP) ratio in $PM_{2.5}$ (Fig. 6(b)) was 0.310 ± 0.114 under clean conditions, significantly lower ($p < 0.05$) than those under polluted (0.495 ± 0.132) and biomass burning conditions (0.506). This suggested that the $PM_{2.5}$ -bound PAHs under clean conditions were aged. However, under polluted and biomass burning conditions, $PM_{2.5}$ -bound PAHs were fresh and mainly impacted by local emission. The BaP/BghiP ratios were all higher than 0.6 in PM_1 and $PM_{2.5}$ under clean, polluted and biomass burning conditions (Figs. 6(a) and 6(b)). Consequently, traffic emission was an important factor to PM_1 and $PM_{2.5}$ -bound PAHs.

Under the clean, polluted and biomass burning conditions, the FLA/(FLA + PYR) values in PM_1 (Fig. 6(c)) were 0.605 ± 0.0245 , 0.609 ± 0.0310 , and 0.631 and in $PM_{2.5}$ (Fig. 6(d)) were 0.528 ± 0.101 , 0.552 ± 0.0265 , and 0.520 ,

respectively. Except for the ratio measured during the daytime of 10 October in $PM_{2.5}$, all FLA/(FLA + PYR) values were higher than 0.5, suggesting PAHs were mainly originated from pyrogenic sources, such as coal, wood, and biomass combustion. Comparable results were found in previous studies in the North China Plain (Fig. 6(d)) (Liu et al., 2007; Li et al., 2010; Zhu et al., 2010; Li et al., 2017; Niu et al., 2017).

The IcdP/(IcdP + BghiP) ratio in PM_1 (0.585) was comparable to that in $PM_{2.5}$ (0.557) under biomass burning condition (Figs. 6(c) and (d)). However, under clean and polluted conditions, the ratios in PM_1 (0.296 ± 0.113 and 0.417 ± 0.0998) were significantly different ($p < 0.05$) from those in $PM_{2.5}$ (0.557 ± 0.0755 and 0.572 ± 0.0742), demonstrating that PAHs in PM_1 and $PM_{2.5}$ had discrete sources. The mean IcdP/(IcdP + BghiP) ratios in PM_1 ranged between 0.2 to 0.5 and were close to 0.37, indicating petroleum combustion source and diesel combustion played more significant roles. The mean IcdP/(IcdP + BghiP) ratios in $PM_{2.5}$ were mainly higher than 0.50 and close to 0.62, implying pyrogenic source and wood burning source were more prominent.

Potential Source Regions

The WCWT results for PM_1 - and $PM_{2.5}$ -bound PAHs under clean and polluted (including biomass burning) conditions are shown in Fig. 7. The potential source of PM_1 -bound PAHs under the clean condition was long-distance transport,

Fig. 6. Plot of BaP/BghiP against BaP/(BaP + BeP) and IcdP/(IcdP + BghiP) against FLA/(FLA + PYR) for PM₁-bound and PM_{2.5}-bound PAH under clean, polluted and biomass burning conditions. The data for cities or region (located in North China) from other researches are included as black star. Beijing (Niu *et al.*, 2017), Tianjin (Niu *et al.*, 2017), Shijiazhuang (Niu *et al.*, 2017), Hengshui (Niu *et al.*, 2010), Mount Tai (Li *et al.*, 2010), Yellow River Delta National Nature Reserve (YRDNNR) (Zhu *et al.*, 2014) and Jinan (Li *et al.*, 2017) are included.

and the transported air masses passed through Mongolia, Inner Mongolia, Shanxi Province, and Hebei Province (Fig. 7(a)). For PM₁-bound PAHs under the polluted condition and PM_{2.5}-bound PAHs under the clean conditions, the source regions were the South of Shandong Province and the Yellow Sea (Figs. 7(b) and 7(c)). In addition to a similar PAH source region near the Yellow Sea, for PAHs in PM_{2.5} under the polluted condition, the source regions extended from Shandong Province to Henan Province and Jiangsu Province (Fig. 7(d)).

Compared with the clean condition, PAHs in PM₁ and PM_{2.5} were more strongly influenced by short-distance transport from the South of Shandong Province under the polluted condition. This may be related to the presence of many mineral mining companies in the South of Shandong Province, such as the Yankuang group, Jining mining industry group, and Zaozhuang mining group. Coal mining and processing are major contributors to atmospheric PAHs.

CONCLUSIONS

PM₁- and PM_{2.5}-bound PAHs concentrations were measured at Mount Tai in the North China Plain during the autumn of 2014. The total PAHs concentrations in PM₁ and PM_{2.5} ranged from 5.99 to 28.8 ng m⁻³ and from 8.83 to 36.6 ng m⁻³, with mean values of 14.5 and 24.5 ng m⁻³, respectively. The combined PAH contents in PM₁ and PM_{2.5} were 515 and 607 µg g⁻¹ with the range from 144 to 2005 µg g⁻¹ and 183 to 2186 µg g⁻¹. Three-ring PAHs were the main contributors to the total PAHs. The concentration and content of total PAHs were dominated by PM₁. Compared with clean and polluted conditions, the total PAHs and BaP_{eq} concentrations under the biomass burning condition were the highest. The total accumulated risks were considered to be acceptable when people were exposed to PM₁-bound PAHs, whereas the risks were elevated to potential cancer risks when adults (30–70 years) were exposed to PM_{2.5}-bound PAHs.

Fig. 7. Spatial distributions of WCWT values of total PAHs in $PM_{1.0}$ and $PM_{2.5}$ during the sampling period.

According to diagnostic ratios, pyrogenic sources (coal, wood, and biomass burning) and traffic emission were the major PAH sources. Diesel combustion played a more significant role to the emission of PAHs in $PM_{1.0}$, while wood burning sources were more prominent for PAHs in $PM_{2.5}$. The CWT model indicated that Shandong Province and the Yellow Sea were the potential source regions of PAHs in $PM_{1.0}$ under the polluted condition and in $PM_{2.5}$ under all conditions. For $PM_{1.0}$ -bound PAHs under the clean condition, long-range transport from Northwest China was a major potential source. Compared with the clean condition, PAHs were more strongly influenced by short-distance transport from the South of Shandong Province under the polluted condition.

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DISCLAIMER

We declare that we have no conflict of interest.

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