Comparative Study of PAHs in PM$_1$ 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 (PM$_1$) particles severely affect human health. To characterize 18 PAHs at a background site (Mount Tai) in the heavily polluted North China Plain (NCP), PM$_1$ 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 $\sum$18 PAHs were 14.5 and 24.5 ng m$^{-3}$ and the contents were 515 and 607 µg g$^{-1}$ in PM$_1$ 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 PM$_1$-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 PM$_1$-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 PM$_1$-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 (PM$_1$, 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 PM$_{10}$-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$_{2.5}$, PM$_1$ 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 PM$_1$ 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%),
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 (BaPeq) 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% ± 2% relative humidity and 20°C ± 1°C for 24 h and then weighed using a Sartorius analytical balance (Sartorius ME5-F Filter Microbalance, Germany, detection limit: 1 µg) 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.](image-url)
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.

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

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

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 PM2.5 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, PM2.5, K⁺, Ca²⁺, and Na⁺ were acquired from Zhao et al. (2017).

Cancer Risk Assessment
The BaP equivalent concentration (BaPeq) computed using Eq. (1) integrates the different carcinogenicities of individual compounds and reflects the probabilistic risk of PAHs.

$$\text{BaPeq} = \sum_{i=1}^{n} (\text{PAH}_i \times \text{TEF}_i)$$

where PAHᵢ is the iᵗʰ PAH concentration (ng m⁻³), and TEFᵢ is the corresponding toxic equivalent factor of iᵗʰ 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):

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

where CSF is the cancer slope factor for each age group; IR is the intake ratio; ED is the exposure duration; EF is the exposure frequency; BW is the body weight; and ALT is the average life time.
where \(CSF_{ inhalation}\) is the cancer slope factor (mg kg\(^{-1}\) day\(^{-1}\))\(^{-1}\), \(C\) is the total BaP\(_4\) 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 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 (Yunker et al., 2002; Yang et al., 2017). A FLA/(FLA + PYR) ratio ranging from 0.4 to 0.5 suggests the source of petroleum combustion, and an IcdP/(IcdP + BghiP) ratio lower than 0.2 indicates a petrogenic source. 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 values imply that air parcels passing through the \(i\)th cell are associated with high concentrations. In this study, the CWT value was calculated using Eq. (3):

\[
C_{ \text{WTI} } = \frac{1}{\sum_{j} w_{ij}} \sum_{j} C_{i} r_{ij}
\]

where \(C_i\) is the weighted average concentration for the \(i\)th cell, \(l\) is the index of trajectory, \(M\) is the total number of trajectories, \(C_i\) is the concentration observed on arrival of the trajectory \(l\), and \(r_{ij}\) is the time spent in the \(i\)th cell by the trajectory \(l\). To minimize uncertainty in cells with small \(n_{ij}\) values (the number of endpoints that fall in the \(i\)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:

\[
W_{ij} = \begin{cases} 
1 & 3n_{ave} \leq n_{ij} \\
0.70 & 1.5 n_{ave} < n_{ij} < 3n_{ave} \\
0.40 & n_{ave} < n_{ij} < 1.5n_{ave} \\
0.20 & 0 < n_{ij} < n_{ave}
\end{cases}
\]

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° × 0.5°.

**RESULTS AND DISCUSSION**

**Concentrations and Contents**

The combined PAH concentrations in PM\(_1\) 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 PM\(_1\) and PM\(_{2.5}\) were 515 and 607 µg g\(^{-1}\) with the range from 144 to 2005 µg g\(^{-1}\), respectively (Fig. 2(b)). The concentration and content of combined PM\(_1\)-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 µm. This was consistent with Wang et al. (2009) which found that \(\sum_{17}\) PAHs concentrations in PM\(_1\) accounted 73.5% to \(\sum_{17}\) PAHs in PM\(_{2.5}\) 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 µm.

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 (\(\sum_{15}\) 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 PM₂.₅.

(a)

(b)

Total PM₁-bound PAHs concentration in our study was higher than that in Mount Tai (Σ₁₇, 2.60 ng m⁻³ in PM₁,1) during the summer of 2008 (Wang et al., 2009) but lower than that in Mount Tai (Σ₁₇, 5.50 ng m⁻³ in PM₁,1) during the winter of 2008 (Wang et al., 2009). Compared with other urban sites, the concentration was higher than those observed at Canoas (Σ₁₆, 1.52 ng m⁻³) and Sapucaia do Sul in Brazil (Σ₁₆, 1.99 ng m⁻³) from August 2011 to July 2013 (Agudelo-Castaneda and Teixeira, 2014), Brno (Σ₁₆, 5.01 ng m⁻³) and Slapanice (Σ₁₆, 5.41 ng m⁻³) in Czech Republic during summer of 2009 (Krumal et al., 2013), Warsaw in central Poland (Σ₁₆, 11.1 ng m⁻³) during spring of 2015 (Rogulka-Kozlowska et al., 2018) and Zagreb in Croatian (Σ₁₀, 5.07 ng m⁻³) during autumn of 2014 (Pehnec and Jakovljevic, 2018), but lower than those observed at Brno (Σ₁₆, 22.2 ng m⁻³) and Slapanice (Σ₁₆, 21.0 ng m⁻³) in Czech Republic during winter of 2009 (Krumal et al., 2013), and Gliwice in Southern Poland (Σ₁₆, 21.2 ng m⁻³) during spring of 2015 (Rogulka-Kozlowska 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 PM₂.₅ (Fig. 2(a)). The result
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 PM1 and 2.92:1.24:1.00 in PM2.5 (Fig. 2(a)). LMW, MMW, and HMW PAHs in PM1 accounted for 66.0%, 49.3%, and 51.8% to those in PM2.5. 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 PM1 and PM2.5, respectively. The COMPAHs in PM1 comprised 84.1% of that in PM2.5 indicating COMPAHs were generally found at the particle size less than 1 µm.

The composition profile of PAHs contents was similar to the PAHs concentrations (Fig. 2(b)). FLU and PHE dominated total PAHs in PM1 (45.4%) and PM2.5 (41.4%). The COMPAHs contents were 143 µg g⁻¹ and 211 µg g⁻¹, accounted 30.3% and 36.0% to total PAHs in PM1 and PM2.5, respectively. The ratios of LMW: MMW: HMW PAHs were 3.60:1.10:1.00 in PM1 and 3.21:1.34:1.00 in PM2.5. The COMPAHs, LMW PAHs, MMW PAHs and HMW PAHs in PM1 contributed 67.5%, 92.7%, 68.0% and 82.6% of corresponding PAHs in PM2.5.

**Comparison of PAH Concentrations by Weather Condition**

PAHs concentrations under clean, polluted, and biomass burning conditions are displayed in Fig. 3. For PM1-bound PAHs, no significant changes in the total PAHs concentrations or ring distributions were observed between clean and polluted conditions. Whereas, the total PM1-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 PM2.5-bound PAHs, the average concentration of combined PAHs was 27.9 ± 9.08 ng m⁻³ under the polluted conditions, which was higher than the observed concentration under the clean conditions (18.9 ± 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 PM2.5-bound PAHs, and biomass burning was a main contributor to PM2.5-bound PAHs. All individual PM2.5-bound PAH concentrations were enhanced to different degrees under the polluted condition, varied from CHA (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**

**BaPeq Concentrations of PAHs in PM1 and PM2.5**

The mean BaP eq concentration in PM1 was 0.764 ± 0.350 ng m⁻³, significantly lower (p < 0.05) than the WHO standard (1 ng m⁻³). In PM2.5, the BaP eq value was 1.58 ± 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.
(Table 2). The BaP\textsubscript{eq} value in PM\textsubscript{1} was lower than those observed at Gliwice and Warszawa in Poland (Rogula-Kozlowska et al., 2018) and an urban site in Croatian (Pehnec and Jakovljevic, 2018). The value of BaP\textsubscript{eq} in PM\textsubscript{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\textsubscript{eq} value in PM\textsubscript{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\textsubscript{eq} in PM\textsubscript{1} were 0.842 ± 0.479, 0.704 ± 0.234, and 1.09 ng m\textsuperscript{-3}. Correspondingly, BaP\textsubscript{eq} in PM\textsubscript{2.5} were 0.839 ± 0.414, 2.02 ± 0.909, and 3.03 ng m\textsuperscript{-3}, respectively (Fig. 4). The percentage of PM\textsubscript{1}-bound BaP\textsubscript{eq} in PM\textsubscript{2.5}-bound BaP\textsubscript{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\textsubscript{eq} in PM\textsubscript{1,2.5} increased under polluted and biomass burning conditions.

### ILCR Values of PAHs in PM\textsubscript{1} and PM\textsubscript{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\textsubscript{2.5} were approximately two times higher than those in PM\textsubscript{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 year), 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\textsuperscript{-7} and 2.73 × 10\textsuperscript{-6} for adult (30–70 years) in PM\textsubscript{1} and PM\textsubscript{2.5}, respectively. According to Chen and Liao (2006), the total accumulated risk of adults (30–70 years) increased to potential cancer risk

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**Table 2. Calculated BaP\textsubscript{eq} (ng m\textsuperscript{-3}) concentrations in selected studies using the same TEFs.**

<table>
<thead>
<tr>
<th>Study area</th>
<th>Type</th>
<th>Sampling period</th>
<th>Size</th>
<th>BaP\textsubscript{eq}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mount Tai, North China Plain</td>
<td>Background</td>
<td>2014/10</td>
<td>PM\textsubscript{2.5}</td>
<td>1.58</td>
<td>This study</td>
</tr>
<tr>
<td>Mount Tai, North China Plain</td>
<td>Background</td>
<td>2014/10</td>
<td>PM\textsubscript{1}</td>
<td>0.764</td>
<td>This study</td>
</tr>
<tr>
<td>Gliwice, Poland</td>
<td>Urban</td>
<td>2015/04–2015/06</td>
<td>PM\textsubscript{1}</td>
<td>4.29</td>
<td>Rogula-Kozlowska et al., 2018</td>
</tr>
<tr>
<td>Warszwa, Poland</td>
<td>Urban</td>
<td>2015/04–2015/06</td>
<td>PM\textsubscript{1}</td>
<td>2.27</td>
<td>Rogula-Kozlowska et al., 2018</td>
</tr>
<tr>
<td>Zagreb, Croatian</td>
<td>Urban</td>
<td>2014/09–2014/11</td>
<td>PM\textsubscript{1}</td>
<td>0.917</td>
<td>Peyne and Jakovljevic, 2018</td>
</tr>
<tr>
<td>Mount Heng, Southern China</td>
<td>Background</td>
<td>2009/04–2009/05</td>
<td>TSP</td>
<td>0.623</td>
<td>Li et al., 2015</td>
</tr>
<tr>
<td>Mount Lu, Southern China</td>
<td>Background</td>
<td>2012/03–2012/05</td>
<td>PM\textsubscript{2.5}</td>
<td>0.985</td>
<td>Yang et al., 2018</td>
</tr>
<tr>
<td>Mount Tai, North China Plain</td>
<td>Background</td>
<td>2008/10–2008/12</td>
<td>PM\textsubscript{2.5}</td>
<td>0.851</td>
<td>Li et al., 2010</td>
</tr>
<tr>
<td>Qixing Tai, North China Plain</td>
<td>Background</td>
<td>2016/09</td>
<td>PM\textsubscript{2.5}</td>
<td>0.796</td>
<td>Zhang et al., 2019</td>
</tr>
<tr>
<td>Gosan, Korea</td>
<td>Background</td>
<td>2001/11–2003/08</td>
<td>PM\textsubscript{2.5}</td>
<td>0.153</td>
<td>Lee et al., 2006</td>
</tr>
<tr>
<td>Mount Tai, North China Plain</td>
<td>Background</td>
<td>2015/06–2015/08</td>
<td>PM\textsubscript{2.5}</td>
<td>0.0949</td>
<td>Liu et al., 2017</td>
</tr>
<tr>
<td>Thracomacedones, Greece</td>
<td>Background</td>
<td>2001/05–2011/11</td>
<td>PM\textsubscript{10}</td>
<td>0.0776</td>
<td>Mantis et al., 2005</td>
</tr>
</tbody>
</table>

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![Fig. 4. BaP\textsubscript{eq} concentrations in PM\textsubscript{1} and PM\textsubscript{2.5} (1.0 ng m\textsuperscript{-3} represents WHO standard).](image-url)
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 PM2.5-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 PM2.5-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 PM2.5 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 PM2.5 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 PM2.5-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 PM2.5 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 PM2.5 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 BaPeq 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 PM2.5-bound PAHs.
Fig. 7. Spatial distributions of WCWT values of total PAHs in PM$_1$ 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$_1$, 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$_1$ under the polluted condition and in PM$_{2.5}$ under all conditions. For PM$_1$-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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