Analysis of PAHs Associated with PM\(_{10}\) and PM\(_{2.5}\) from Different Districts in Nanjing

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ABSTRACT

Nanjing has areas with different degrees of pollution and is therefore predestined for the analysis of particle phase polycyclic aromatic hydrocarbons (P-PAHs) in different functional areas and their correlation with the latter. The functional sites include a background area (BGA), an industrial area (IDA), a traffic area (TFA), a business area (BNA) and a residential area (RDA), where parameters such as PAH composition, content, carcinogenic and mutagenic potencies were analyzed. The results revealed increasing P-PAH contents (PM\(_{2.5}\), PM\(_{10}\)) in the following order: BGA (14.02 ng m\(^{-3}\), 38.45 ng m\(^{-3}\)) < BNA (16.33 ng m\(^{-3}\), 44.13 ng m\(^{-3}\)) < TFA (17.13 ng m\(^{-3}\), 48.31 ng m\(^{-3}\)) < RDA (21.11 ng m\(^{-3}\), 61.03 ng m\(^{-3}\)) < IDA (50.00 ng m\(^{-3}\), 93.08 ng m\(^{-3}\)). Thereby, the P-PAH content in the industrial area was significantly higher than in the other functional zones (\(P < 0.01\)). Furthermore, the gas phase PAH concentrations were also estimated by the G/P partitioning model and the total PAH toxicity was assessed applying toxicity equivalent factors (\(\Sigma\)BaPTEF) and mutagenicity equivalent factors (\(\Sigma\)BaPMEF). Finally, the incremental lifetime cancer risk (ILCR) value of children and adolescents in Nanjing was higher than that of adults.

Keywords: Particle phase PAHs; Different functional areas; Toxicity assessment; Incremental lifetime cancer risk.

INTRODUCTION

It is well-known, that the primary particles are emitted directly as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven or traffic-related suspension of road, soil, and mineral dust, sea salt, and biological materials (Abdel-Shafy et al., 2016; Du et al., 2017). Ambient particulate matter (PM) is a growing concern worldwide due to its associations between elevated concentrations and increased incidences of cardiopulmonary disease (Ning et al., 2010), including chronic obstructive pulmonary disease (Zhang et al., 2017). According to the Global Burden of Disease study, fine particulate matter (PM\(_{2.5}\)) is the seventh largest important death risk factor in the world and the fourth largest important death risk factor in China (Cohen et al., 2005; Lim et al., 2012).

Many studies suggest that organic carbon constituents may play a significant role in PM-induced health effects (Li et al., 2003). Recently, polycyclic aromatic hydrocarbons (PAHs) have brought great environmental concerns as they are ubiquitous in the ambient air and the presence of PAH directly affects humans, especially to vulnerable groups such as the elderly and children (Brook et al., 2010; Beelen et al., 2014; Wang et al., 2017a; Wright et al., 2018). In addition, some PAH-compounds, such as benzo[a]pyrene and benz[a]anthracene, are well known carcinogens (Nisbet et al., 1992; Goldstein, 2001; Li et al., 2009). So it is important to investigate the PAHs in the atmosphere and reduce human exposure to these toxic chemicals.

EPA Carcinogenicity Risk Assessment Endeavor Work Group has verified the carcinogenicity classifications in 1994 (U.S. EPA, 1994), indicating that BaA, BbF, BkF, BaP, Chr, DahA and IcdP are considered to be probable human carcinogens. It has been found that the PAHs are carcinogenic and that BaP is the most serious (Garban et al., 2002) among the listed carcinogens. Moreover, some special PAHs are mutagenic (Durant et al., 1996) associated with...
some health effects, i.e., pulmonary diseases (DeMarini et al., 2004). Many studies have attempted to estimate the carcinogenic potency of PAHs using BaP equivalent concentration, but less attention was given to mutagenicity. Therefore, in the studies, mutagenicity should be given similar attention when attempting to estimate the carcinogenic potency of PAHs.

In recent decades, with the rapid increase in energy consumption, public health has been a matter of great concern to scientists and policy makers in China. The PAHs occur in the atmosphere as complex mixtures of congeners with different molecular weights: Lighter PAHs (2–3 aromatic rings) are almost exclusively present in the vapor phase, whereas PAHs with higher molecular weights (≥4 rings) are almost completely adsorbed to the particulate matter (Cheruiyot et al., 2015; Manoli et al., 2016). Meanwhile, the carcinogenic contributions of particle phase PAHs is much higher than those of gas phase PAHs. The current research focuses mainly on particulate matter. Nevertheless, in order to take the concentration of PAHs fully into account, this study estimated the concentration of PAHs in the gas phase by using the gas/particle partitioning model (Xie et al., 2013; Gao et al., 2015) and focused primarily on the higher molecular weight PAHs (4–6 rings). Due to the fact that the atmospheric pollution is a persistent problem in Nanjing (Wang et al., 2006), numerous studies were conducted in the Nanjing area, such as sources of PAHs in the atmosphere, analysis of concentration distribution of particulate matter, meteorological factors and the seasonal trends of indoor fine particulate matter (Wang et al., 2006; He et al., 2014; Shao et al., 2017; Wang et al., 2017b). However, very few studies have considered the different functional areas (Jiang et al., 2018; Simayi et al., 2018) and the distribution characteristics of PAHs in the atmospheric particulate matter for a comprehensive comparison and analysis, one example for PAHs is the study of Manoli et al. (2016), who compared the PAH levels between traffic and urban background. Another purpose of the study was to support future epidemiology and health impact research. Therefore, the carcinogenic and mutagenic potencies were assessed as well to estimate their potential impact on human health. In addition, a lifetime lung cancer risk assessment in relation to different groups was carried out.

**EXPERIMENTAL**

**Sampling Area and Site Description**

The sampling sites were located in Nanjing in eastern China in the heartland of the drainage area of the lower reaches of the Yangtze River, with longitudes and latitudes of 118°22′–119°14′ and 31°14′–32°36′, respectively. Its area is 4,736 km² with 140 km in length (west–east direction) and 80 km in width (north–south direction). The mean annual temperature and precipitation are 15.7 °C and 1106.5 mm, respectively (Xu et al., 2007). The four seasons are distinct, with damp conditions throughout the year, very hot and muggy summers, cold and damp winters, and in between, spring and autumn are of reasonable length. A detailed description of the sampling areas is listed in Table 1.

**Sampling Collection**

Sampling was carried out in Nanjing at five sites during 47 days. High volume air samplers (KC-1000, flow rate 1.05 m³ min⁻¹) with glass fiber filters (GFF) were used to collect particle phase PAHs in PM10 and PM2.5, respectively. All filters have been baked at 450°C for 4 h in a muffle furnace (MF-2.5-10A, Shanghai) and stabilized for 24 h under constant temperature (21°C) using a dryer. Samples were collected in triplicate every 24 h. All filters were weighed before and after sampling and finally stored at –1°C until analysis.

**Analytical Procedure**

For the PAH analysis, brown glass tubes were cleaned three times with tap water and ethyl alcohol prior to use. Impurities were removed with a clean brush used only for this study. Each filter was cut into small pieces and extracted by Soxhlet with 200 mL dichloromethane at 46°C for 16 h. Rotary evaporator (R-201, Shanghai, China) was adopted to purify the concentrated solution with water at 37°C. In order to reduce the loss, the extraction was concentrated altogether three times with dichloromethane in a flat bottom flask. The total extracts were subsequently transferred to alumina silica gel columns for purification, consisting of 3 cm alumina, 6 cm silica gel and 1 cm anhydrous sodium sulfate. Prior to purification, the alumina silica gel column has been washed for two times using a 20 mL 1:1 mixture of n-hexane and acetone. After the sample transfer, the bottom flasks have

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**Table 1.** Characteristic of the sampling sites in Nanjing.

<table>
<thead>
<tr>
<th>Functional area</th>
<th>Sampling site</th>
<th>Regional characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background area (BGA)</td>
<td>Nanjing Sport Institute</td>
<td>Scenic tourist area; few vehicles; many trees</td>
</tr>
<tr>
<td></td>
<td>32°21′26.72″N; 118°52′1.04″E</td>
<td></td>
</tr>
<tr>
<td>Residential area (RDA)</td>
<td>Ruijin Country of Nanjing</td>
<td>Densely populated; many vehicles; city center</td>
</tr>
<tr>
<td></td>
<td>32°1′54.55″N; 118°48′44.34″E</td>
<td></td>
</tr>
<tr>
<td>Business area (BNA)</td>
<td>Nanjing Institute of Airspace Management</td>
<td>Commercial network intensive area; large flow of people</td>
</tr>
<tr>
<td></td>
<td>32°1′11.72″N; 118°47′10.96″E</td>
<td></td>
</tr>
<tr>
<td>Traffic area (TFA)</td>
<td>Nanjing Normal University of Suiyuan Campus</td>
<td>city center, many vehicles, convenient transportation</td>
</tr>
<tr>
<td></td>
<td>32°3′12.55″N; 118°45′58.94″E</td>
<td></td>
</tr>
<tr>
<td>Industrial area (IDA)</td>
<td>Nanjing Yangzi Vocational Training Co. Ltd.</td>
<td>Chemical plant gathering area</td>
</tr>
<tr>
<td></td>
<td>32°14′35.76″N; 118°45′46.83″E</td>
<td></td>
</tr>
</tbody>
</table>
been cleaned three times with dichloromethane. The eluted mixture from the column was brought to approximately 1 mL by rotary evaporator at 37°C. Finally, they were diluted with n-hexane to exactly 1 mL, sealed in vials and stored at −18°C before PAH analysis.

**Determination of PAHs**

PAH levels were determined by GC/MS according to previous studies (Xia et al., 2013; Wu et al., 2014) using the Agilent 7890A/5975MSD (Agilent, USA) with a J&W Scientific column DB-5MS (30 m × 0.25 mm ID × 0.25 µm film, Agilent, USA). The GC was running under following conditions: 1 min at 40°C, heated from 40°C to 200°C at a rate of 10°C min⁻¹ and heated from 200°C to 310°C at 5°C min⁻¹, then held at 310°C for 5 min. The sample was injected on a splitless mode at the injector temperature of 280°C. The EI-MS conditions were as follows: ion-source temperature, 230°C; ionizing voltage, 70 eV; scan range, m/z 40–350 amu; cycle time, 0.5 s. 10 PAHs were determined listed by the IARC as class 1, class 2A, 2B and class 3 (fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-cd]pyrene and dibenz[a,h]anthracene), mainly associated to the particle-phase.

**Prediction of Gas-phase PAH Concentrations**

The semi-volatile organic compounds of PAHs encounter gas-particle phase distribution when transported in the atmosphere. In order to fully understand the concentration of PAHs in Nanjing, the concentration of PAHs in the gas phase was calculated by the gas/particle (G/P) partitioning theory (Pankow, 1994a, b). The theory was described in detail elsewhere (Xie et al., 2013; Gao et al., 2015; Xie et al., 2015), which was defined as follows:

\[ K_{p,OM} = \frac{K_p}{f_{OM}} = \frac{F/M_{OM}}{A} \]  \hspace{1cm} (1)

\[ K_{p,OM} = \frac{RT}{10^6MW_{OM}\xi_{OM}P_L^\phi} \]  \hspace{1cm} (2)

\[ A = \frac{10^6MW_{OM}\xi_{OM}P_L^\phi}{RT} \times \frac{1}{M_{OM}} \]  \hspace{1cm} (3)

where \( K_{p,OM} \) represents the absorptive G/P partitioning coefficient of each PAH, \( K_p \) is the G/P partitioning coefficient and \( f_{OM} \) is the weight fraction of the absorptive OM phase in the total PM phase. \( F \) and \( A \) are a concentration of each PAH in the particle phase (ng m⁻³) and a concentration of each PAH in the gas phase (ng m⁻³). \( M_{OM} \) and \( MW_{OM} \) are the concentrations of the particle-phase OM (µg m⁻³) and the average molecular weight (MW) of the absorbing OM phase (g mol⁻¹). Referring to Xia et al., (2013), \( MW_{OM} \) is 200 g mol⁻¹ and referring to Zhai et al., (2016), this work estimated that the \( M_{OM} \) concentration was equal to the 50% of the PM concentration. \( R \) is the ideal gas constant (m³ atm K⁻¹ mol⁻¹) and \( T \) is the ambient temperature (K). \( \xi_{OM} \) and \( P_L^\phi \) are the mole fraction scale activity coefficient of each compound in the absorbing OM phase and vapor pressure of each pure compound.

**Quality Control and Analysis**

All procedures were strictly quality-controlled, with quality control and blank control samples added into the sequence in order to assess the data repeatability, and no significant contamination was found. Quantification of PAHs was standardized by the retention times and peak areas of the calibration standards. It was performed by the internal standard method using 2-fluoro-1,10-biphenyl and p-terphenyl-d14 (2.0 mg mL⁻¹; J&K Chemical, Beijing, China). The instruments were calculated using at least five standard concentrations covering the concentration of interest for ambient air work and the analytical precision, measured as the relative standard deviation, was < 10% (Liu et al., 2017a).

Data analysis was performed using the Statistical Package of the Social Sciences 18.0 (SPSS 18.0) Software for Windows (SPCC Co., 2001). For the mathematical statistics analysis, the one-way analysis of variance (ANOVA) and correlation analysis with Bivariate Correlations Analysis were completed. The relationships between the concentrations of compounds were subsequently explored by linear correlation analysis.

**Data Processing**

**Coefficient of Divergence (CD)***

Recent research shows that the intraurban spatial distributions of PM concentrations in some study areas are heterogeneous. Therefore, a coefficient of variation (CV) or a coefficient of divergence (CD) is used for the heterogeneous distributions of particulates to describe relative intra urban concentration heterogeneity (Wilson, et al., 2005). The CDₖ, method for identifying the differences of PAH composition profiles was described in detail elsewhere (Wongphatarakul, 1998), which was defined as follows:

\[ CD_k = \sqrt{\frac{1}{p} \sum_{i=1}^{p} \left( \frac{X_{ji} - X_{kj}}{X_{ji} + X_{kj}} \right)^2} \]  \hspace{1cm} (4)

where \( X_{ji} \) represents the average concentration for a chemical component \( i \) at site \( j \) and \( k \) represent two sampling sites, and \( p \) is the number of chemical components. If the value of \( CD_k \) approaches zero, the PAH composition at \( j \) and \( k \) is similar, and if it approaches one, it is significantly different (Wongphatarakul, 1998). Kong et al. (2012) found that if the value of \( CD_k \) is lower than 0.2, the source of the two sites is the same.

**Diagnostic Ratios of PAH**

The binary ratio method for PAH source identification was described in detail elsewhere (Ravindra et al., 2008), which involves comparing ratios of pairs of frequently found PAH emissions. The diagnostic ratio method can also characterize the diversity in PAH sources and distinguishing
emissions (Venkataraman et al., 1994; Harrison et al., 1996; Ravindra et al., 2008).

**Toxic and Mutagenic Equivalent Factors**

The carcinogenic risk of a PAH mixture is often expressed by its BaP equivalent concentration (BaPTEQ) (Han et al., 2011). To normalize the toxicity of different PAHs in PM2.5 and PM10, it has been calculated by the equivalent mass concentration based on BaP and the value of toxic equivalency factors, TEFs (Table 2). Similarly, just with the replacement of TEF with MEF (Mutagenic Equivalency Factors), the mutagenicity related to BaP (BaPMEQ) was calculated as well.

And the BaPTEQ and BaPMEQ of the air were calculated according to Eqs. (5) and (6):

\[
\sum \text{BaP}_{\text{TEQ}} = \sum_{i} C_i \times \text{TEF}_i
\]

\[
\sum \text{BaP}_{\text{MEQ}} = \sum_{i} C_i \times \text{MEF}_i
\]

where \(C_i\) = concentration of PAH congener \(i\); \(\text{TEF}_i\) = the toxic equivalency factors (TEFs) of PAH congener \(i\); \(\text{MEF}_i\) = the mutagenic equivalency factors (MEFs) of PAH congener \(i\). The toxicity assessment of PAHs was determined by benzo(a)pyrene, an equivalent for carcinogenicity (\(\sum \text{BaP}_{\text{TEQ}}\)) and mutagenicity (\(\sum \text{BaP}_{\text{MEQ}}\)).

In urban areas, the citizens were divided into three population groups according to the age and gender: children and adolescents (1–18 years), male (19–71.95 years) and female (19–77.06 years). Daily inhalation exposure level (E) for each population group was calculated as follows in Eq. (7):

\[
E = \sum_{i=1}^{n} \text{BaP}_{\text{TEQ}_i} \times \text{IR}_i \times T_i
\]

where \(T_i\) = daily exposure time span in the \(i\)th area (for all groups of the urban area on one day: they spend the whole day in the urban area, thus \(n = 1, i = 1\) refers to urban area, \(T1 = 1\); \(\text{BaP}_{\text{TEQ}_i}\) = \(B(a)\text{P}\) equivalent concentration of 10 PAHs in the \(i\)th area (ng m\(^{-3}\)) (for all groups of urban area: \(n = 1, i = 1\) refers to urban area); \(\text{IR}\) = inhalation rate (m\(^3\) day\(^{-1}\); Table 3) (Xia et al., 2013; Lin, 2016; Zhang et al., 2019).

**Cancer Risk Estimates**

The incremental lifetime cancer risk (ILCR) of population groups in Nanjing caused by PAHs inhalation exposure was calculated based on Eqs. (8) and (9):

\[
LADD = \frac{C_i \times \text{EF} \times \text{AT} \times \left(\frac{\text{IR}_{\text{child}} \times \text{ED}_{\text{child}}}{\text{BW}_{\text{child}}} + \frac{\text{IR}_{\text{adult}} \times \text{ED}_{\text{adult}}}{\text{BW}_{\text{adult}}}\right)}{2\pi}
\]

\[
\text{ILCR} = q \times LADD
\]

where \(\text{LADD}\) = Lifetime Average Daily Doses; \(C_i\) =

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Table 2. Abbreviations used for PAHs in this paper and carcinogenic and mutagenic potencies of PAHs (Nisbet and LaGoy, 1992; Malcom and Dobson, 1994; Durant et al., 1996).

<table>
<thead>
<tr>
<th>PAH</th>
<th>PAH abbreviation</th>
<th>IARC class</th>
<th>TEFs</th>
<th>MEFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoranthene</td>
<td>Flu</td>
<td>3</td>
<td>0.001</td>
<td>/</td>
</tr>
<tr>
<td>Pyrene</td>
<td>Pyr</td>
<td>3</td>
<td>0.001</td>
<td>/</td>
</tr>
<tr>
<td>Benz[a]anthracene</td>
<td>BaA</td>
<td>2B</td>
<td>0.1</td>
<td>0.082</td>
</tr>
<tr>
<td>Chrysene</td>
<td>Chr</td>
<td>2B</td>
<td>0.01</td>
<td>0.017</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>BbF</td>
<td>2B</td>
<td>0.1</td>
<td>0.25</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>BkF</td>
<td>2B</td>
<td>0.1</td>
<td>0.11</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>BaP</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>Daha</td>
<td>2A</td>
<td>1</td>
<td>0.29</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>BghiP</td>
<td>3</td>
<td>0.01</td>
<td>0.19</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>IndP</td>
<td>2B</td>
<td>0.1</td>
<td>0.31</td>
</tr>
</tbody>
</table>

a Agents Classified by the IARC Monographs, Volumes 1e100 (IARC, 2012): 1, Carcinogenic to humans; 2A, Probably carcinogenic to humans; 2B, Possibly carcinogenic to humans; 3, Not classifiable as to its carcinogenicity to humans.

Table 3. Exposure parameters for different age and gender groups of Nanjing city.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Parameter</th>
<th>Children and adolescents</th>
<th>Male</th>
<th>Female</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CI</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR</td>
<td>8.6</td>
<td>18</td>
<td>14.5</td>
<td></td>
<td>mg m(^{-3})</td>
</tr>
<tr>
<td>EF</td>
<td>365</td>
<td>365</td>
<td>365</td>
<td></td>
<td>m(^3) d(^{-1})</td>
</tr>
<tr>
<td>ED</td>
<td>1—18</td>
<td>19—71.95</td>
<td>19—77.06</td>
<td></td>
<td>d a(^{-1})</td>
</tr>
<tr>
<td>AT</td>
<td>365•18</td>
<td>365•71.95</td>
<td>365•77.06</td>
<td></td>
<td>d</td>
</tr>
<tr>
<td>BW</td>
<td>16</td>
<td>65</td>
<td>56.8</td>
<td></td>
<td>kg</td>
</tr>
<tr>
<td>q</td>
<td>3.14</td>
<td>3.14</td>
<td>3.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
∑BaPTEQ (mg m⁻³); EF = the exposure frequency (day year⁻¹); ED = exposure duration (year); BW = body weight (kg); AT = average lifespan for carcinogens (day).

ILCR = the incremental cancer risk of the inhalation exposure (dimensionless); q = the cancer slope factor for BaP inhalation exposure [a lognormal distribution with a geometric mean of 3.14 (mg kg⁻¹ day⁻¹)⁻¹ and a geometric standard deviation of 1.80] (Chen and Liao 2006).

RESULTS AND DISCUSSION

Pollution Level of Particle PAHs (P-PAHs) in PM₂.₅ and PM₁₀

Descriptive statistics for all valid observations of P-PAH concentration-ratios in PM₂.₅ and PM₁₀ from 5 sites in Nanjing are summarized in Fig. 1. The average 24-h total P-PAH concentrations of PM₂.₅ and PM₁₀ were in the ranges of 10.95–59.10 ng m⁻³ and 35.38–97.33 ng m⁻³, respectively. Among the 5 sites, the average mass of carcinogenic PAHs (C-PAHs) including BaA, Bbf, Bkf, Bap, Icdp and Daha, at the Business area reached the highest proportion (61.19% for PM₂.₅ and 53.57% for PM₁₀, respectively), apparently affected by many area emission sources distributed around the business district. However, the highest average 24-h C-PAH concentrations appeared in the industrial area, with 20.13 ± 5.39 ng m⁻³ for PM₂.₅ and 36.31 ± 5.35 ng m⁻³ for PM₁₀. The results suggest that C-PAHs may be related with the coal combustion and coal processing industries.

Fig. 1. The proportion of each P-PAH in different functional areas in PM₂.₅ and PM₁₀.
Among the 10 P-PAHs analyzed, the average concentrations of middle molecular weight PAHs (Flu, Pyr, BaA, Chr), and high molecular weight PAHs (BbF, BkF, BaP, Icdp, Bghip, Daha) (Yang et al., 1998) ranged from 4.72 to 24.91 ng m$^{-3}$ and 5.07 to 23.08 ng m$^{-3}$, respectively, for PM$_{2.5}$. The corresponding values were 14.63 to 54.77 ng m$^{-3}$, and 21.49 to 44.95 ng m$^{-3}$, respectively, for PM$_{10}$.

A one-way ANOVA was also used to test the significant differences using the BaP and total P-PAH data. This analysis suggests that the BaP levels were not statistically different for each site (ANOVA, p > 0.05) while clear regional trends were observed for the total P-PAH levels (p < 0.01). Meanwhile, there was a significant correlation between BaP and total P-PAHs in PM$_{2.5}$ (R = 0.713, p < 0.01) and the correlation of total P-PAH in PM$_{2.5}$ and PM$_{10}$ was also significant (R = 0.783, p < 0.01).

Spatial Variation

Fig. 2 shows the box plot of the Spearman rank correlation coefficients of each P-PAH and the total P-PAHs between five sites. In general, the medians of the correlation coefficients for all P-PAHs in PM$_{2.5}$ and PM$_{10}$, respectively, were approximately below 0.50 and 0.55. This means that the spatial correlations between all sites are not strong in Nanjing, especially for TFA in terms of PM$_{2.5}$ and BGA in terms of PM$_{10}$. In order to measure the spread of the data points for two datasets, mass concentrations characterized between different sites for j against k are also presented in Fig. 2. Low CD$_{jk}$ values (< 0.2) have been shown to indicate a high level of homogeneity between sites, while CD$_{jk}$ values larger than 0.2 indicate heterogeneous sites (Wilson et al., 2005). As can be seen, the median PM$_{2.5}$ - CD$_{jk}$ values ranged from 0.41 to 0.53 and PM$_{10}$ - CD$_{jk}$ values ranged from 0.27 to 0.37 suggesting a heterogeneous distribution of PM$_{2.5}$ and PM$_{10}$ in the 5 sites, indicating significant differences in PAH composition.

For the comparison of P-PAHs between PM$_{2.5}$ and PM$_{10}$, the diagrams characterized by scatter plots of P-PAHs component mass concentrations between PM$_{2.5}$ and PM$_{10}$ for j against k are also presented in Fig. 3. The CD$_{jk}$ values of BGA, RDA, BNA, TFA and IDA were 0.523, 0.566, 0.603, 0.584, and 0.426, being also higher than 0.2. It can be concluded that the P-PAHs compositions at the sites in PM$_{2.5}$ and PM$_{10}$ are different, indicating the influence of different sources.

Source Identification and Source Contribution Assessment

Molecular diagnostic ratios, firstly used in organic geochemistry, have been a convenient approach to help identifying possible emission sources. Yunker et al. (1996) has used fluoranthene/pyrene and phenanthrene/anthracene...
Fig. 3. Comparison of average concentrations of P-PAHs between PM$_{2.5}$ and PM$_{10}$ for different sites in Nanjing.

to ascertain emission sources in sediment samples. Simoneit et al. (2004) and Andreou et al. (2008) have used this method to investigate the origin of organic species in the atmosphere.

Studies have revealed that the ratio of Flu/(Flu + Pyr) is lower than 0.40 for the petroleum source, and higher than 0.50 for biomass and coal combustion, and between 0.4 and 0.5 for fuel emissions caused by the exhaust (Li et al., 2006a; Ravindra and Grieken, 2008). Kavouras et al. (2001) has found the value of Icdp/(Icdp + BghiP) ratio is between 0.35 and 0.7 for diesel emissions. For both PM$_{2.5}$ and PM$_{10}$, the ratios of P-PAHs values for the background site and other sites are shown in Fig. 4.

As shown in Fig. 4, different ratios of compounds indicate different sources. However, the main source of pollution is the combustion of fossil fuels for PM$_{2.5}$ and PM$_{10}$. It is clear that the main sources are diesel emissions in BGA and pyrolytic sources in RDA, BNA, TFA and IDA. However, there is some difference between PM$_{2.5}$ and PM$_{10}$. It can be found that the main source is focusing on traffic emissions for PM$_{10}$. And several sources of ambient PM (Laden et al., 2000; Hoek et al., 2002) are under investigation, especially of interest are emissions from combustion sources with focus on traffic emissions (Mudway et al., 2004; Peters et al., 2004).

Meanwhile, the isomer ratio of a more reactive PAH to a stable PAH, such as BaA/Chr, can be employed to illustrate whether the air masses collected are fresh or aged (Ding et al., 2007). The values of the BaA/Chr were 1.32, 0.67, 10.74, 2.22 and 4.03 for BGA, RDA, BNA, TFA and IDA in PM$_{2.5}$, respectively. The high values were found in BNA, TFA and IDA, indicating relatively little photochemical reaction and a major impact from local sources. However, the low values were found in BGA and RDA, meaning more degradation happened in situ or during the process of air transport (He et al., 2014).

**Predicted Gas-phase PAH Concentrations**

The total PAH concentration data is the sum of the concentration of P-PAHs and gaseous PAHs (G-PAHs). The calculation of G-PAHs is presented in detail in Section 1.5. According to Zhai et al. (2016), the average gas-phase fraction of each PAH was calculated and listed in Table 4. By comparison, the total predicted PAH concentrations found in this study are consistent with those reported by Li et al. (2006b) and Gao et al. (2015), who found that the total PAH concentrations in PM$_{2.5}$ ranged from 10 to 40 ng m$^{-3}$ in December 2001 in Guangzhou, and 7.1 to 72.6 ng m$^{-3}$ in November–December 2009, respectively.
Health Risk of PAHs

Carcinogenic and Mutagenic Potencies

As shown in Fig. 5, the BaPTEQ and BaPMEQ values were computed applying the modified lists of TEFs and MEFs (Table 2) in all five investigated sites. There were higher carcinogenic risks of total PAHs in Nanjing, with average values of $3.14 \pm 1.27$ ng m$^{-3}$ for PM$_{2.5}$ and $8.23 \pm 1.55$ ng m$^{-3}$ for PM$_{10}$, respectively. European countries have been established the target annual mean values of BaP to range between 0.7 and 1.3 ng m$^{-3}$ (Ballesta, et al., 1999) and it has been suggested a concentration of 0.1 ng m$^{-3}$ of BaP as a health-based guideline in ambient air (Boström et al., 2002). The value of the $\sum$BaPTEQ in Nanjing has exceeded the standard value of 1 ng m$^{-3}$, indicating that many of the more toxic compounds are threatening human health in the urban city, nowadays. For mutagenic potencies, the average concentrations of $\sum$BaPMEQ were $3.14 \pm 1.85$ ng m$^{-3}$ for PM$_{2.5}$ and $11.23 \pm 2.70$ ng m$^{-3}$ for PM$_{10}$, being higher than those at the Chinese background sites ($1.26 \pm 1.75$ ng m$^{-3}$ for PM$_{2.5}$ and $1.41 \pm 1.98$ ng m$^{-3}$ for PM$_{10}$) (Wang et al., 2015).

As PAHs can be classified on different standard levels, this study has classified the total PAHs according to their number of aromatic rings to quantify the BaP TEQ and BaPMEQ. It can be found that the BaPTEQ of total PAHs with 4, 5 and 6 rings are dominant in both PM$_{2.5}$ and PM$_{10}$ Among all functional sites, 5-rings account for absolutely high ratios, up to nearly 80% or more. This may indicate that the high-numbered ring PAHs are the predominant compounds in PM$_{10}$.

Regarding the different functional areas, the values of $\sum$BaPTEQ and $\sum$BaPMEQ in the background area (BGA) were the lowest. Meanwhile, the high molecular weight compounds (6-ring compounds) have not been detected as frequently in the background site, TEF values of low-numbered ring compounds are lower than the high-numbered rings, and MEFs only belong to special PAHs. Certainly, this is also related to inconspicuous anthropogenic sources and more plants in the background site. For IDA and BNA, it should be noticed that 5-ring and 4-ring PAHs exhibit the highest mass percentages when compared with other sites. Ravindra et al. (2006) indicated that the major sources for BaP, BbF, BghiP and Icdp are gasoline vehicles.

Lung Cancer Risk of Assessment

With the average equivalent BaP concentration of total PAHs in PM$_{2.5}$ and PM$_{10}$ (Fig. 5) and the variables of exposure parameters (Table 3), the value of the lifetime carcinogenic risk for children and adolescents, males and females in Nanjing has been calculated (Table 5). As shown in Table 5, the LADD of children and adolescents
were approximately 1.6 times and 1.7 times higher than that of males and females. This may be due to the fact that children’s and adolescents’ breathing rate is greater than that of adults, while their bodyweight is lower. Furthermore, the ranking of ILCR in decreasing order basically was children and adolescents, males and females, indicating children and adolescents being a population group sensitive to health risks by pollutants (Martí-Cid et al., 2008). So, there are security risks for humans, especially children and adolescents, although the values are within an acceptable range (10^{-4}–10^{-6} made by U.S. EPA (1989)).

Comparison with Other Studies

According to previous study (Wang et al., 2006), there has been a decrease in P-PAH concentration in Nanjin since 2001, based on the average between the five study sites (Table 6). The P-PAHs concentrations in PM_{2.5} were similar to those analyzed by Ningbo (Mo et al., 2018) in winter and in spring in Shanghai (Liu et al., 2017b). In comparison, the total P-PAH concentrations found in this study are lower than those reported by Simayi et al. (2018), who also analyzed the P-PAHs in different functional areas. However, the average concentrations of \( \Sigma P \)-PAHs in PM_{2.5} and PM_{10} were approximately 7 and 14 times higher than those in the background of China (Wang et al., 2015) and in Hong Kong (Guo et al., 2003). When comparing the P+G PAHs, values are significantly lower in Nanjing than in Guangzhou (Yang et al., 2010), indicating that the G-PAHs are also noteworthy. Therefore, in the future, gas-phase samples should be collected for the analysis. It is worth noting that the values were higher as compared to those of the urban centre at the same sampling period in Taiwan (Fang et al., 2005) and much higher than those of Nanjing in summer (Sun et al., 2016).

Similarly, compared to the study by Wang et al., (2006), the average concentrations of \( \Sigma BaP \) for PM_{2.5} and PM_{10} decreased, similar to Jinhua (Mo et al., 2018) and Shanghai (Liu et al., 2017b). However, they were approximately 4 and 9 times higher than those in the backgounds of China (Wang et al., 2015) and much higher than those of Nanjing in summer (Sun et al., 2016). The average concentrations of \( \Sigma BaPM_{\text{Hg}} \) for PM_{2.5} and PM_{10} were approximately 2 and 8 times higher than those in the backgounds of China. In PM_{2.5}, the \( \Sigma BaPM_{\text{Hg}} \) concentration was similar to that in Venice-Mestre (Masiol et al., 2012). The calculated ILCR average values for PM_{2.5} and PM_{10} in Nanjing were also higher than those in Thessaloniki (Northern Greece) (Manoli et al., 2016) but lower than those in Xiamen (Zhang et al., 2018).

SUMMARY AND CONCLUSIONS

In this manuscript, daily ambient samples of particle PAHs were collected in Nanjing to examine chemical characteristics, regional variation, emission sources and the related carcinogenicity, mutagenicity and risks for human health. Total P-PAH concentrations ranged from 14.02 to 50.00 ng m^{-3} and from 38.45 to 93.08 ng m^{-3} in PM_{2.5} and PM_{10}, respectively. Thereby, the main source of pollution was the combustion of fossil fuels. Furthermore, the gas
Fig. 5. $\Sigma$BaPTEQ and $\Sigma$BaPMEF concentrations of PAHs in PM$_{2.5}$ and PM$_{10}$ at the five sites.

### Table 5. LADD and ILCR for different groups of Nanjing city.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Children and adolescents</th>
<th>Males</th>
<th>Females</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM (ng)</td>
<td>PM$_{2.5}$</td>
<td>PM$_{10}$</td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>E (ng/mg (kg d)$^{-1}$</td>
<td>1.68·10$^{-6}$</td>
<td>4.39·10$^{-6}$</td>
<td>1.07·10$^{-6}$</td>
</tr>
<tr>
<td>ILCR</td>
<td>5.29·10$^{-6}$</td>
<td>1.38·10$^{-5}$</td>
<td>3.36·10$^{-6}$</td>
</tr>
</tbody>
</table>

### Table 6. Comparison of the four factors analysed in the present study and with values reported in the literature.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mean concentrations in PM$_{2.5}$</th>
<th>Mean concentrations in PM$_{10}$</th>
<th>Area and Time</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-PAHs</td>
<td>62.6 ng m$^{-3}$</td>
<td>86.0 ng m$^{-3}$</td>
<td>Nanjing in 2001–2002</td>
<td>Wang et al., 2006</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>29.5 ng m$^{-3}$</td>
<td>-</td>
<td>Shanghai in Spring 2012</td>
<td>Liu et al., 2017b</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>25.34 ng m$^{-3}$</td>
<td>34.2 ng m$^{-3}$</td>
<td>Hong Kong in 2000–2001</td>
<td>Guo et al., 2003</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>4.30 ng m$^{-3}$</td>
<td>4.73 ng m$^{-3}$</td>
<td>Four background sites of China in 2013</td>
<td>Wang et al., 2015</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>16.35 ng m$^{-3}$</td>
<td>37.47 ng m$^{-3}$</td>
<td>Tunghai University in Mar.–Apr. 2002</td>
<td>Fang et al., 2005</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>128.10 ng m$^{-3}$</td>
<td>173.08 ng m$^{-3}$</td>
<td>Urumqi in Nov. 2015–Mar. 2016</td>
<td>Simayi et al., 2018</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>25.56 ng m$^{-3}$</td>
<td>-</td>
<td>Ningbo in winter 2015</td>
<td>Mo et al., 2018</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>23.31 ng m$^{-3}$</td>
<td>57.01 ng m$^{-3}$</td>
<td>Nanjing in Mar.–Apr. 2017</td>
<td>Sun et al., 2016</td>
</tr>
<tr>
<td>P-PAHs</td>
<td>129.34 ng m$^{-3}$</td>
<td>57.34 ng m$^{-3}$</td>
<td>Nanjing in Mar.–Apr. 2017</td>
<td>This study</td>
</tr>
<tr>
<td>P+$G$-PAHs</td>
<td>129 ng m$^{-3}$</td>
<td>7.49 ng m$^{-3}$</td>
<td>Nanjing in Summer 2015</td>
<td>Yang et al., 2010</td>
</tr>
<tr>
<td>P+$G$-PAHs</td>
<td>23.34 ng m$^{-3}$</td>
<td>57.34 ng m$^{-3}$</td>
<td>Nanjing in Mar.–Apr. 2017</td>
<td>This study</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>7.10 ng m$^{-3}$</td>
<td>9.3 ng m$^{-3}$</td>
<td>Nanjing in 2001–2002</td>
<td>Wang et al., 2006</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>1.5 ng m$^{-3}$</td>
<td>1.5 ng m$^{-3}$</td>
<td>Urban traffic site in Feb.–Mar. 2012</td>
<td>Manoli et al., 2016</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>3.6 ng m$^{-3}$</td>
<td>/</td>
<td>Shanghai in Spring 2012</td>
<td>Liu et al., 2017b</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>0.82 ng m$^{-3}$</td>
<td>0.91 ng m$^{-3}$</td>
<td>Four background sites of China in Spring 2013</td>
<td>Wang et al., 2015</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>3.1 ng m$^{-3}$</td>
<td>-</td>
<td>Jinhua in winter 2015</td>
<td>Mo et al., 2018</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>3.14 ng m$^{-3}$</td>
<td>8.23 ng m$^{-3}$</td>
<td>Nanjing in Mar.–Apr. 2017</td>
<td>This study</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>3.10 ng m$^{-3}$</td>
<td>/</td>
<td>Venice-Mestre in Mar. 2009</td>
<td>Masiol et al., 2012</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>1.26 ng m$^{-3}$</td>
<td>1.41 ng m$^{-3}$</td>
<td>Four background sites of China in Spring 2013</td>
<td>Wang et al., 2015</td>
</tr>
<tr>
<td>BaPTEQ</td>
<td>3.13 ng m$^{-3}$</td>
<td>11.20 ng m$^{-3}$</td>
<td>Nanjing in Mar.–Apr. 2017</td>
<td>This study</td>
</tr>
<tr>
<td>ILCR</td>
<td>1.7·10$^{-4}$</td>
<td>1.6·10$^{-6}$</td>
<td>Urban traffic site in Feb.–Mar. 2012</td>
<td>Manoli et al., 2016</td>
</tr>
<tr>
<td>ILCR</td>
<td>1.1·10$^{-4}$</td>
<td>-</td>
<td>Xiamen in Winter</td>
<td>Zhang et al., 2018</td>
</tr>
<tr>
<td>ILCR</td>
<td>4.0·10$^{-4}$</td>
<td>1.0·10$^{-5}$</td>
<td>Nanjing in Mar.–Apr. 2017</td>
<td>This study</td>
</tr>
</tbody>
</table>

PAHs were also estimated by the G/P partitioning model. The annual average concentrations of BaPTEQ was larger than both the Chinese national standard and the WHO guideline. Similarly, the annual average concentrations of BaPM$_{10}$ have exceeded the background sites of China many times. ILCR values caused by particle phase PAHs for humans were all greater than the significant level (10$^{-6}$), indicating a high potential lung cancer risk. Moreover, it is
necessary to pay more attention to children and adolescents, whose ILCR values were higher than those of adults.

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