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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 ($\sum BaP_{TEF}$) and mutagenicity equivalent factors ($\sum BaPM_{EF}$). 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), indicateing 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

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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 molecuar 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. Anotherpurpose 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 km^2 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 ℃ 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 m^3 min^{-1}) with glass fiber filters (GFF) were used to collect particle phase PAHs in PM_{10} and $PM_{2.5}$, 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

Table 1. Characteristic of the sampling sites in Nanjing.

Functional area	Sampling site	Regional characteristics
Background area (BGA)	Nanjing Sport Institute 32°2'36.72"N; 118°52'1.04"E	Scenic tourist area; few vehicles; many trees
Residential area (RDA)	Ruijin Country of Nanjng 32°1'54.55"N; 118°48'44.34"E	Densely populated; many vehicles; city center
Business area (BNA)	Nanjing Institute of Airspace Management 32°1'11.72"N; 118°47'10.96"E	Commercial network intensive area; large flow of people
Traffic area (TFA)	Nanjing Normal University of Suiyuan Campus 32°3'12.55"N; 118°45'58.94"E	city center, many vehicles, convenient transportation
Industrial area (IDA)	Nanjing Yangzi Vocational Training Co. Ltd. 32°14'35.76"N; 118°45'46.83"E	Chemical plant gathering area

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:

$$K_{p,OM} = \frac{K_p}{f_{OM}} = \frac{F/M_{OM}}{A} \quad (1)$$

$$K_{p,OM} = \frac{RT}{10^6 \overline{MW}_{OM} \xi_{OM} P_L^0} \quad (2)$$

$$A = \frac{10^6 \overline{MW}_{OM} \xi_{OM} P_L^0 F}{RT} \times \frac{1}{M_{OM}} \quad (3)$$

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}). $\underline{M}_{OM}$ and $\overline{MW}_{OM}$ 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 Xie *et al.*, (2013), $\overline{MW}_{OM}$ 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 (m^3 atm K^{-1} mol) and T is the ambient temperature (K). ξ_{OM} and P^0_L 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_{jk})

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 CD_{jk} method for identifying the differences of PAH composition profiles was described in detail elsewhere (Wongphatarakul, 1998), which was defined as follows:

$$CD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{X_{ij} - X_{ik}}{X_{ij} + X_{ik}}\right)^2} \quad (4)$$

where x_{ij} represents the average concentration for a chemical component i at site j, j and k represent two sampling sites, and p is the number of chemical components. If the value of CD_{jk} approaches zero, the PAH composition in 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_{jk} 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 (BaP_{TEQ}) (Han *et al.*, 2011). To normalize the toxicity of different PAHs in $PM_{2.5}$ and PM_{10}, 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 ($BaPM_{EQ}$) was calculated as well.

And the BaP_{TEQ} and $BaPM_{EQ}$ of the air were calculated according to Eqs. (5) and (6):

$$\sum BaP_{TEQ} = \sum_{i=1}^{n} C_i \times TEF_i \quad (5)$$

$$\sum BaP_{MEQ} = \sum_{i=1}^{n} C_i \times MEF_i \quad (6)$$

where C_i = concentration of PAH congener i; TEF_i = the toxic equivalency factors (TEFs) of PAH congener i; 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 ($\sum BaP_{TEF}$) and mutagenicity ($\sum BaPM_{EF}$).

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):

$$E = \sum_{i=1}^{n} BaP_{TEQ_i} \times IR_i \times T_i \quad (7)$$

where T_i = daily exposure time span in the ith 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); BaP_{TEQi} = B(a)P equivalent concentration of 10 PAHs in the ith area (ng m^{-3}) (for all groups of urban area: n = 1, i = 1 refers to urban area); 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):

$$LADD = \frac{C_i \times EF}{AT} \times \left(\frac{IR_{child} \times ED_{child}}{BW_{child}} + \frac{IR_{adult} \times ED_{adult}}{BW_{adult}} \right) \quad (8)$$

$$ILCR = q \times LADD \quad (9)$$

where LADD = Lifetime Average Daily Doses; C_i =

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).

PAH	PAH abbreviation	IARC class	TEFs	MEFs
Fluoranthene	Flu	3	0.001	/
Pyrene	Pyr	3	0.001	/
Benz[a]anthrancene	BaA	2B	0.1	0.082
Chrysene	Chr	2B	0.01	0.017
Benzo[b]fluoranthene	BbF	2B	0.1	0.25
Benzo[k]fluoranthene	BkF	2B	0.1	0.11
Benzo[a]pyrene	BaP	1	1	1
Dibenz[a,h]anthracene	Daha	2A	1	0.29
Benzo[ghi]perylene	BghiP	3	0.01	0.19
Indeno[1,2,3-cd]pyrene	IcdP	2B	0.1	0.31

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

Parameter	Children and adolescents	Male	Female	Units
T_i	1	1	1	
C_i	/	/	/	mg m^{-3}
IR	8.6	18	14.5	m^3 d^{-1}
EF	365	365	365	d a^{-1}
ED	1—18	19—71.95	19—77.06	a
AT	365•18	365•71.95	365•77.06	d
BW	16	65	56.8	kg
q	3.14	3.14	3.14	

$\sum BaP_{TEQ}$ (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 $PM_{2.5}$ and PM_{10}

Descriptive statistics for all valid observations of P-PAH concentration-ratios in $PM_{2.5}$ and PM_{10} from 5 sites in Nanjing are summarized in Fig. 1. The average 24-h total P-PAH concentrations of $PM_{2.5}$ and PM_{10} 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 $PM_{2.5}$ and 53.57% for PM_{10}, 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 $PM_{2.5}$ and 36.31 ± 5.35 ng m^{-3} for PM_{10}. The results suggest that C-PAHs may be related with the coal combustion and coal processing industries.

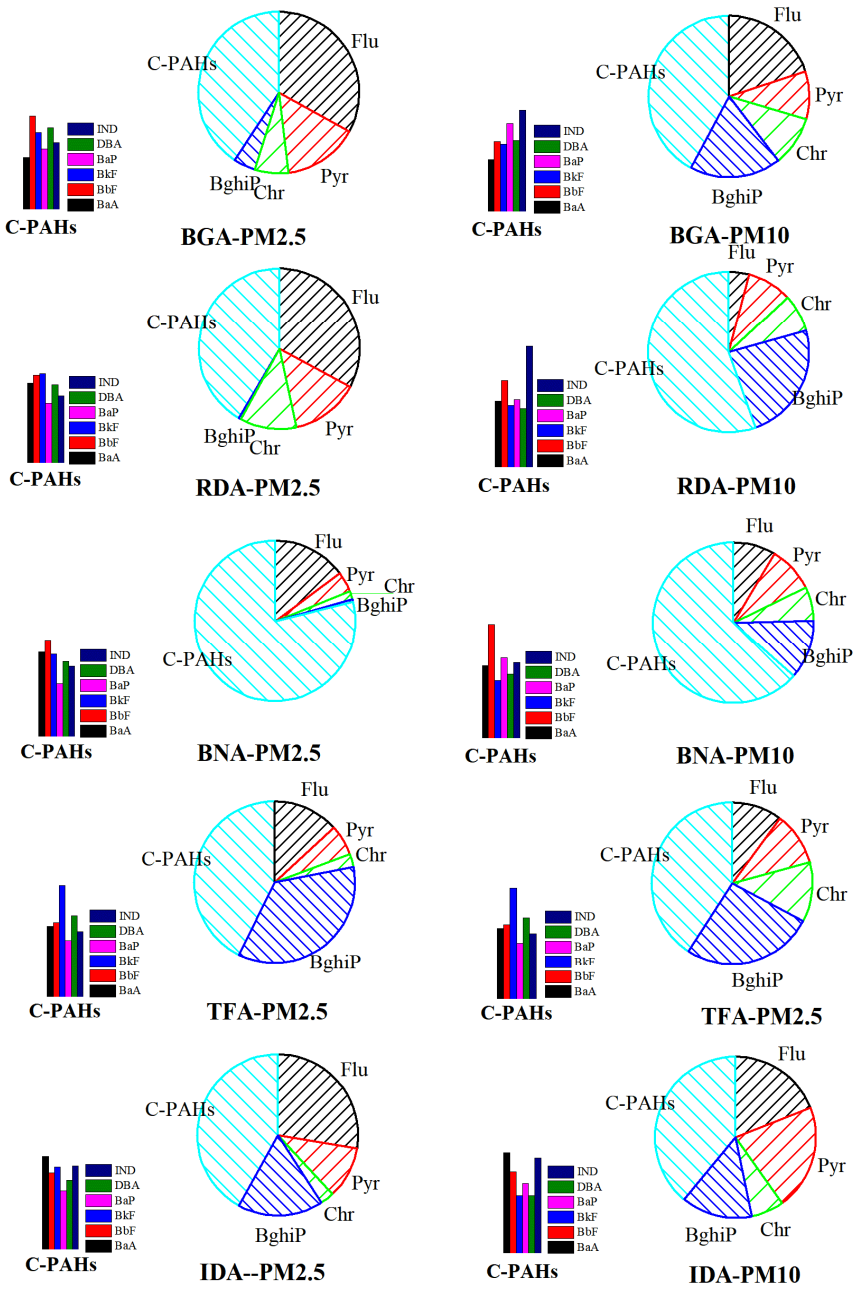

Fig. 1. The proportion of each P-PAH in different functional areas in $PM_{2.5}$ and PM_{10}.

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

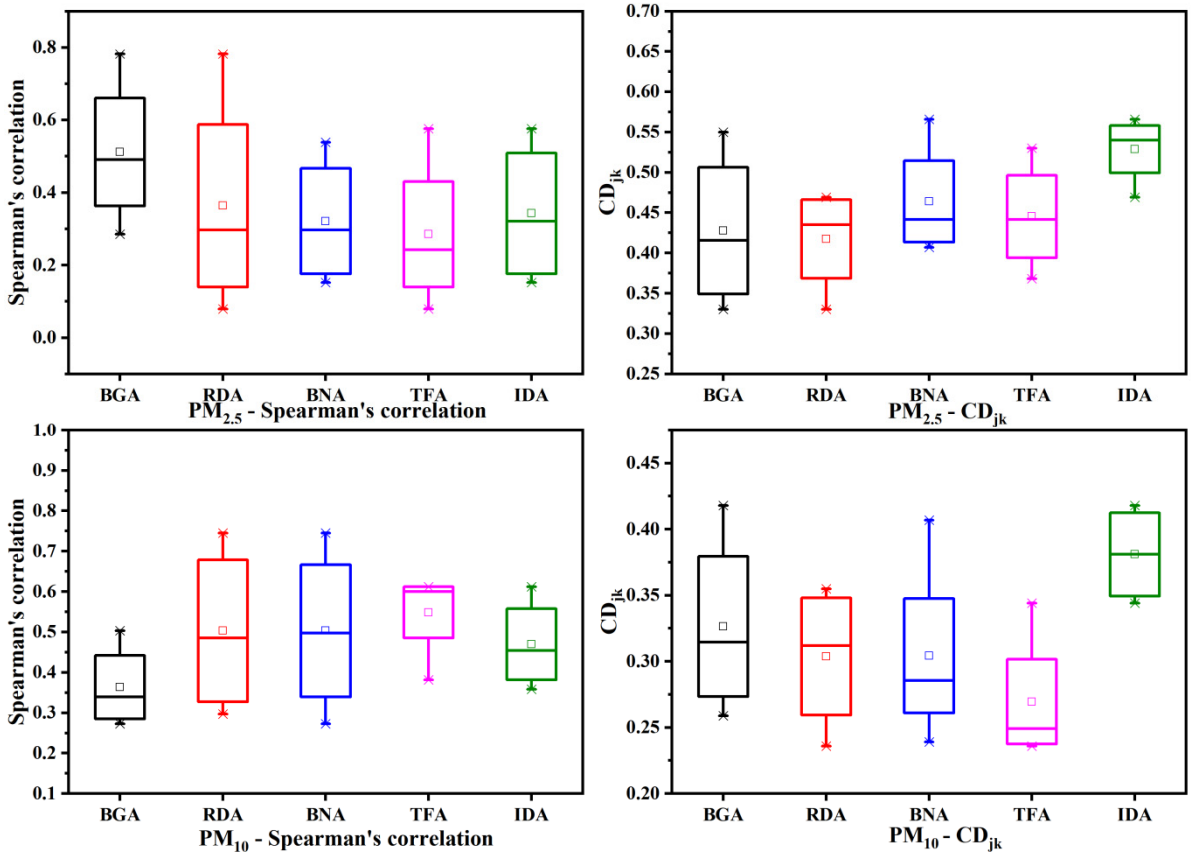

Fig. 2. Box plots of Spearman rank correlation coefficients (left) and coefficient of divergence (CD_{jk}, right) based on individual P-PAHs and the total P-PAHs concentrations between five different measurement sites. The box plots indicate the maximum, 75th percentile, the median, 25th percentile, and the minimum of all the data, respectively.

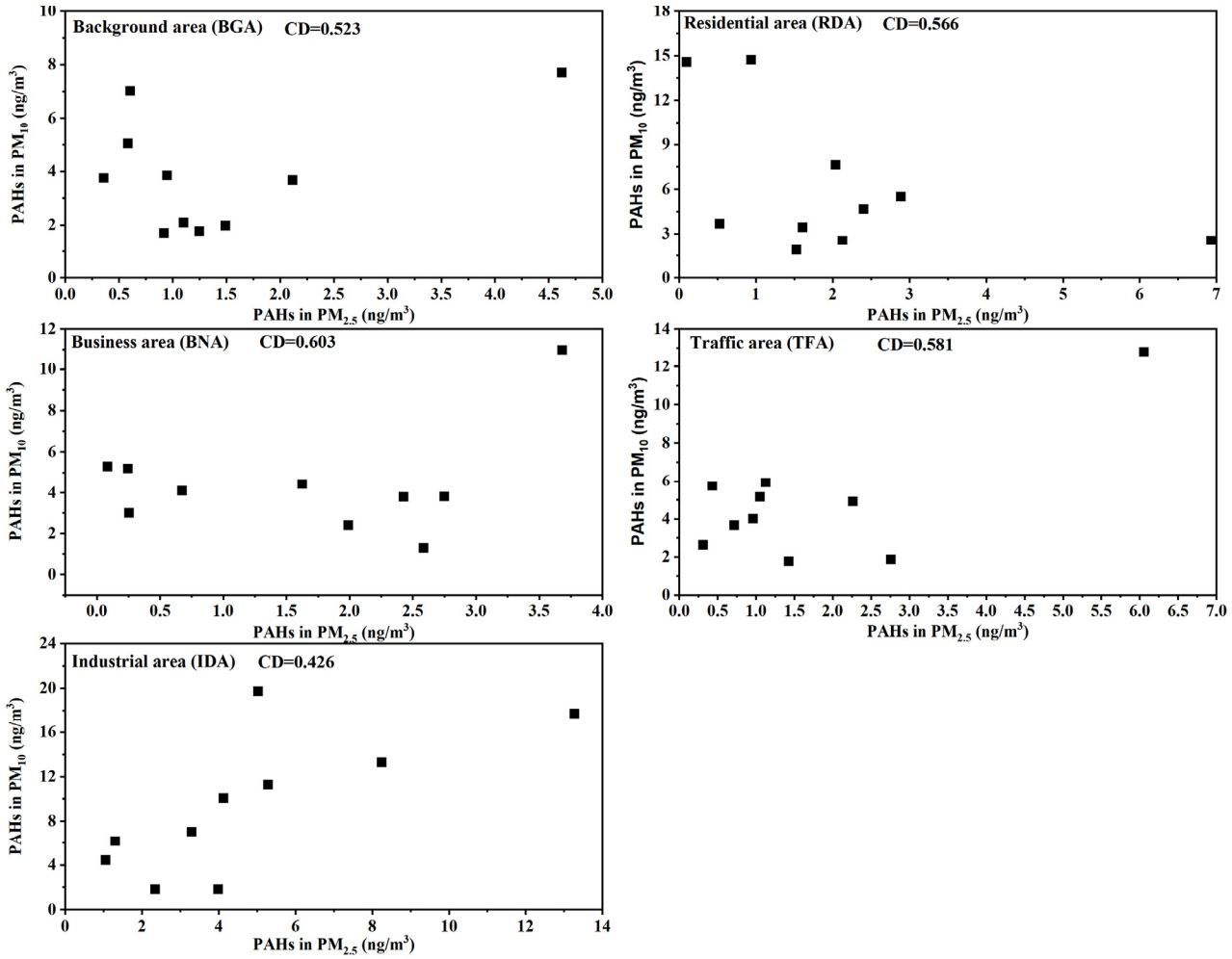

Fig. 3. Comparison of average concentrations of P-PAHs between $PM_{2.5}$ and PM_{10} for different sites in Nanjing.

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.

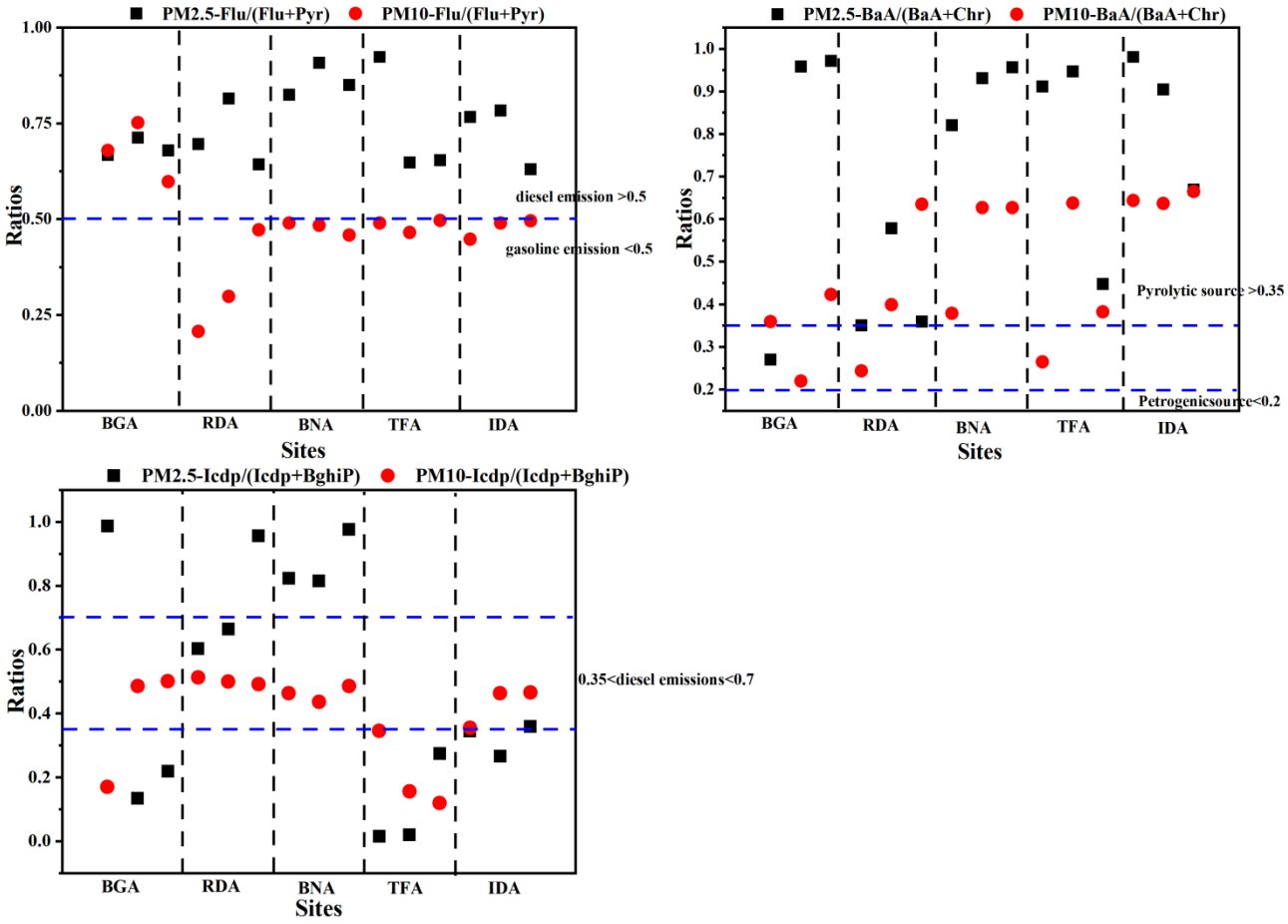

Fig. 4. Diagnostic ratios for Flu/(Flu + Pyr), BaA/(BaA + Chr) and Icdp/(Icdp + BghiP) of the five sites for $PM_{2.5}$ and PM_{10} in Nanjing.

Health Risk of PAHs

Carcinogenic and Mutagenic Potencies

As shown in Fig. 5, the BaP_{TEQ} and $BaPM_{EQ}$ 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 ± 1.27 ng m^{-3} for $PM_{2.5}$ and 8.23 ± 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 $\sum BaP_{TEQ}$ 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 $\sum BaPM_{EQ}$ were 3.14 ± 1.85 ng m^{-3} for $PM_{2.5}$ and 11.23 ± 2.70 ng m^{-3} for PM_{10}, being higher than those at the Chinese background sites (1.26 ± 1.75 ng m^{-3} for $PM_{2.5}$ and 1.41 ± 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 $BaPM_{EQ}$. It can be found that the BaP_{TEQ} 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.

Regarding the different functional areas, the values of $\sum BaP_{TEQ}$ and $\sum BaPM_{EQ}$ in the backgrond 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

Table 4. Average predicted g-PAH profile based on the P-PAH data sets of the five sampling sites in Nanjing (unit: ng m^{-3}).

PAHs	Background area (BGA)		Residential area (RDA)		Business area (BNA)		Traffic area (TFA)		Industrial area (IDA)	
	G-PAH-$PM_{2.5}$	G-PAH-PM_{10}	G-PAH-$PM_{2.5}$	G-PAH-PM_{10}	G-PAH-$PM_{2.5}$	G-PAH-PM_{10}	G-PAH-$PM_{2.5}$	G-PAH-PM_{10}	G-PAH-$PM_{2.5}$	G-PAH-PM_{10}
Flu	0.1	0.1	0.2	0.04	0.03	0.03	0.03	0.04	0.1	0.1
Pyr	0.1	0.1	0.1	0.2	0.02	0.07	0.02	0.08	0.1	0.3
BaA	0.01	0.01	0.01	0.02	0.01	0.01	0.004	0.01	0.02	0.03
Chr	0.005	0.01	0.01	0.02	0.001	0.01	0.001	0.01	0.003	0.01
BbF	0.01	0.01	0.02	0.04	0.01	0.03	0.004	0.02	0.01	0.02
BkF	0.01	0.01	0.03	0.02	0.01	0.005	0.01	0.007	0.02	0.005
BaP	0.002	0.01	0.002	0.01	0.001	0.008	0.001	0.004	0.002	0.005
DBA	0.02	0.03	0.03	0.03	0.02	0.02	0.01	0.01	0.02	0.01
BghiP	0.003	0.02	0.001	0.04	0.001	0.008	0.01	0.02	0.02	0.02
IND	0.01	0.03	0.01	0.09	0.008	0.01	0.003	0.01	0.02	0.03

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 ∑ 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 $\sum BaP_{TEQ}$ 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 backgrounds of China (Wang *et al.*, 2015) and much higher than those of Nanjing in summer (Sun *et al.*, 2016). The average concentrations of $\sum BaPM_{EQ}$ for $PM_{2.5}$ and PM_{10} were approximately 2 and 8 times higher than those in the backgrounds of China. In $PM_{2.5}$, the $\sum BaPM_{EQ}$ 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 (Northehern 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

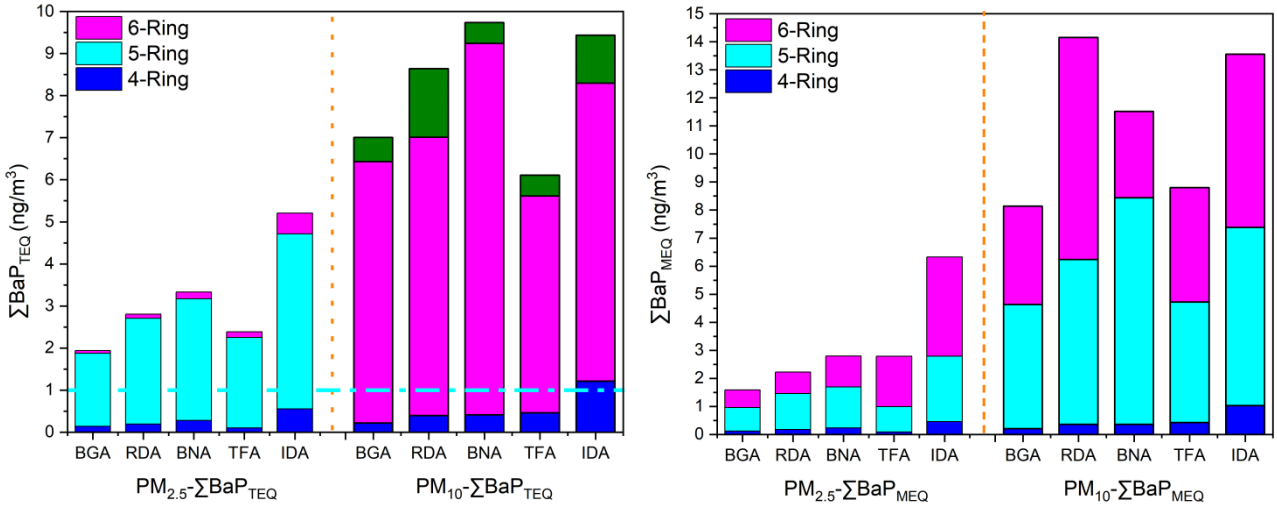

Fig. 5. $\sum BaP_{TEQ}$ and $\sum BaP_{MEF}$ concentrations of PAHs in $PM_{2.5}$ and PM_{10} at the five sites.

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

Groups	Children and adolescents		Males		Females	
PM	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}	$PM_{2.5}$	PM_{10}
E (ng)	26.93	70.39	56.38	147.34	45.42	118.69
LADD/mg (kg d)$^{-1}$	$1.68\cdot10^{-6}$	$4.39\cdot10^{-6}$	$1.07\cdot10^{-6}$	$2.80\cdot10^{-6}$	$1.01\cdot10^{-6}$	$2.63\cdot10^{-6}$
ILCR	$5.29\cdot10^{-6}$	$1.38\cdot10^{-5}$	$3.36\cdot10^{-6}$	$8.79\cdot10^{-6}$	$3.16\cdot10^{-6}$	$8.25\cdot10^{-6}$

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

Compounds	Mean concentrations in $PM_{2.5}$	Mean concentrations in PM_{10}	Area and Time	Source
P-PAHs	62.6 ng m^{-3}	86.0 ng m^{-3}	Nanjing in 2001–2002	Wang *et al.*, 2006
P-PAHs	29.5 ng m^{-3}	-	Shanghai in Spring 2012	Liu *et al.*, 2017b
P-PAHs	25.34 ng m^{-3}	34.2 ng m^{-3}	Hong Kong in 2000–2001	Guo *et al.*, 2003
P-PAHs	4.30 ng m^{-3}	4.73 ng m^{-3}	Four background sites of China in 2013	Wang *et al.*, 2015
P-PAHs	16.35 ng m^{-3}	37.47 ng m^{-3}	Tunghai University in Mar.–Apr. 2002	Fang *et al.*, 2005
P-PAHs	128.10 ng m^{-3}	173.08 ng m^{-3}	Urumqi in Nov. 2015–Mar. 2016	Simayi *et al.*, 2018
P-PAHs	25.56 ng m^{-3}	-	Ningbo in winter 2015	Mo *et al.*, 2018
P-PAHs	-	7.49 ng m^{-3}	Nanjing in Summer, 2015	Sun *et al.*, 2016
P-PAHs	23.31 ng m^{-3}	57.01 ng m^{-3}	Nanjing in Mar.–Apr. 2017	**This study**
P+G-PAHs		129 ng m^{-3}	Guangzhou in Apr. 2005–Mar. 2006	Yang *et al.*, 2010
P+G-PAHs	23.34 ng m^{-3}	57.34 ng m^{-3}	Nanjing in Mar.–Apr. 2017	**This study**
BaP_{TEQ}	7.10 ng m^{-3}	9.3 ng m^{-3}	Nanjing in 2001–2002	Wang *et al.*, 2006
BaP_{TEQ}	1.5 ng m^{-3}	1.5 ng m^{-3}	Urban traffic site in Feb.–Mar. 2012	Manoli *et al.*, 2016
BaP_{TEQ}	3.6 ng m^{-3}	/	Shanghai in Spring 2012	Liu *et al.*, 2017b
BaP_{TEQ}	0.82 ng m^{-3}	0.91 ng m^{-3}	Four background sites of China in Spring 2013	Wang *et al.*, 2015
BaP_{TEQ}	3.1 ng m^{-3}	-	Jinhua in winter 2015	Mo *et al.*, 2018
BaP_{TEQ}	3.14 ng m^{-3}	8.23 ng m^{-3}	Nanjing in Mar.–Apr. 2017	**This study**
BaP_{MEQ}	3.10 ng m^{-3}	/	Venice-Mestre in Mar. 2009	Masiol *et al.*, 2012
BaP_{MEQ}	1.26 ng m^{-3}	1.41 ng m^{-3}	Four background sites of China in Spring 2013	Wang *et al.*, 2015
BaP_{MEQ}	3.13 ng m^{-3}	11.20 ng m^{-3}	Nanjing in Mar.–Apr. 2017	**This study**
ILCR	$1.7\cdot10^{-6}$	$1.6\cdot10^{-6}$	Urban traffic site in Feb.–Mar. 2012	Manoli *et al.*, 2016
ILCR	$1.1\cdot10^{-4}$	-	Xiamen in Winter	Zhang *et al.*, 2018
ILCR	$4.0\cdot10^{-6}$	$1.0\cdot10^{-5}$	Nanjing in Mar.–Apr. 2017	**This study**

PAHs were also estimated by the G/P partitioning model. The annual average concentrations of BaP_{TEQ} was larger than both the Chinese national standard and the WHO guideline. Similarly, the annual average concentrations of $BaPM_{EQ}$ 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 ($l0^{-6}$), 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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