Analysis of PAHs Associated with PM₁₀ 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}, PM₁₀) 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 ($\Sigma\text{BaP}_{\text{TEF}}$) and mutagenicity equivalent factors ($\Sigma\text{BaPM}_{\text{EF}}$). 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), 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

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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 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 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 Nanjing 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}). $\overline{M}_{OM}$ 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 (m³ atm K^{−1} mol) and T is the ambient temperature (K). ξ_{OM} and P_L^0 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 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, $T_1 = 1$); BaP_{TEQ_i} = B(a)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); 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]anthracene	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	

$\Sigma\text{BaP}_{\text{TEQ}}$ (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 $3.14 (\text{mg kg}^{-1} \text{day}^{-1})^{-1}$ and a geometric standard deviation of 1.80] (Chen and Liao 2006).

RESULTS AND DISCUSSION

Pollution Level of Particle PAHs (P-PAHs) in $\text{PM}_{2.5}$ and PM_{10}

Descriptive statistics for all valid observations of P-PAH

concentration-ratios in $\text{PM}_{2.5}$ and PM_{10} from 5 sites in Nanjing are summarized in Fig. 1. The average 24-h total P-PAH concentrations of $\text{PM}_{2.5}$ and PM_{10} were in the ranges of $10.95\text{--}59.10 \text{ ng m}^{-3}$ and $35.38\text{--}97.33 \text{ ng m}^{-3}$, respectively. Among the 5 sites, the average mass of carcinogenic PAHs (C-PAHs) including BaA, BbF, BkF, BaP, IcdP and Dha, at the Business area reached the highest proportion (61.19% for $\text{PM}_{2.5}$ 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 $20.13 \pm 5.39 \text{ ng m}^{-3}$ for $\text{PM}_{2.5}$ and $36.31 \pm 5.35 \text{ ng m}^{-3}$ 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 $\text{PM}_{2.5}$ 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, Doha) (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 PM₁₀.

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 PM₁₀ 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 PM₁₀, 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 PM₁₀. 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 PM₁₀ - CD_{jk} values ranged from 0.27 to 0.37 suggesting a heterogeneous distribution of PM_{2.5} and PM₁₀ in the 5 sites, indicating significant differences in PAH composition.

For the comparison of P-PAHs between PM_{2.5} and PM₁₀, the diagrams characterized by scatter plots of P-PAHs component mass concentrations between PM_{2.5} and PM₁₀ 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 PM₁₀ 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 PM₁₀ 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 PM₁₀, 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 PM₁₀. 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 PM₁₀. It can be found that the main source is focusing on traffic emissions for PM₁₀. 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 PM₁₀ 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 $3.14 \pm 1.27 \text{ ng m}^{-3}$ for PM_{2.5} and $8.23 \pm 1.55 \text{ ng m}^{-3}$ for PM₁₀, 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 $\Sigma\text{BaP}_{\text{TEQ}}$ 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 $\Sigma\text{BaPM}_{\text{EQ}}$ were $3.14 \pm 1.85 \text{ ng m}^{-3}$ for PM_{2.5} and $11.23 \pm 2.70 \text{ ng m}^{-3}$ for PM₁₀, being higher than those at the Chinese background sites ($1.26 \pm 1.75 \text{ ng m}^{-3}$ for PM_{2.5} and $1.41 \pm 1.98 \text{ ng m}^{-3}$ for PM₁₀) (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 PM₁₀. 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 $\Sigma\text{BaP}_{\text{TEQ}}$ and $\Sigma\text{BaPM}_{\text{EQ}}$ 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 PM₁₀ (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	0.02	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	0.001	0.001	0.01	0.003	0.01
BbF	0.01	0.01	0.02	0.04	0.01	0.01	0.004	0.02	0.01	0.02
BkF	0.01	0.01	0.03	0.02	0.01	0.01	0.01	0.007	0.02	0.005
BaP	0.002	0.01	0.002	0.01	0.001	0.001	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	0.001	0.01	0.02	0.02	0.02
IND	0.01	0.03	0.01	0.09	0.008	0.008	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 Σ P-PAHs in PM_{2.5} and PM₁₀ 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 Σ BaP_{TEQ} for PM_{2.5} and PM₁₀ 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 Σ BaPM_{EQ} for PM_{2.5} and PM₁₀ were approximately 2 and 8 times higher than those in the backgrounds of China. In PM_{2.5}, the Σ BaPM_{EQ} concentration was similar to that in Venice-Mestre (Masiol *et al.*, 2012). The calculated ILCR average values for PM_{2.5} and PM₁₀ in Nanjing were also higher than those in Thessaloniki (Northeastern 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 PM₁₀, respectively. Thereby, the main source of pollution was the combustion of fossil fuels. Furthermore, the gas

Fig. 5. $\Sigma\text{BaP}_{\text{TEQ}}$ and $\Sigma\text{BaP}_{\text{MEQ}}$ concentrations of PAHs in $\text{PM}_{2.5}$ and PM_{10} at the five sites.

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

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

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

Compounds	Mean concentrations in $\text{PM}_{2.5}$	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	$1.7 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$	Urban traffic site in Feb.–Mar. 2012	Manoli et al., 2016
ILCR	$1.1 \cdot 10^{-4}$	-	Xiamen in Winter	Zhang et al., 2018
ILCR	$4.0 \cdot 10^{-6}$	$1.0 \cdot 10^{-5}$	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

BaP_{MEQ} 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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REFERENCES

- Abdel-Shafy, H.I. and Mansour, M.S.M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* 25: 107–123.
- Andreou, G., Alexiou, S.D., Loupa, G. and Rapsomanikis, S. (2008). Identification, abundance and origin of aliphatic hydrocarbons in the fine atmospheric particulate matter of Athens, Greece. *Water Air Soil Pollut. Focus* 8: 99–106.
- Ballesta, P.P., Saeger, E.D. and Kotzias, D. (1999). State of the art of the PAHs' analysis in ambient air. *Fresenius Environ. Bull.* 8: 499–505.
- Beelen, R., Raaschou-Nielsen, O., Stafoggia, M., Andersen, Z.J., Weinmayr, G., Hoffmann, B. et al. (2014). Effects of long-term exposure to air pollution on natural-cause mortality: an analysis of 22 European cohorts within the multicentre ESCAPE project. *Lancet* 383: 785–795.
- Boström, C.E., Gerde, P., Hanberg, A., Jernström, B., Johansson, C., Kyrklund, T., Rannug, A., Törnqvist, M., Victorin, K. and Westerholm, R. (2002). Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air. *Environ. Health Perspect.* 110: 451–488.
- Brook, R.D., Rajagopalan, S., Pope III, C.A., Brook, J.R., Bhatnagar, A., Diez-Roux, A.V., Holguin, F., Hong, Y., Luepker, R.V. and Mittleman, M.A. (2010). Particulate matter air pollution and cardiovascular disease: An update to the scientific statement from the American Heart Association. *Circulation* 121: 2331–2378.
- Chen, S.C. and Liao, C.M. (2006). Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci. Total Environ.* 366: 112–123.
- Cheruiyot, N.K., Lee, W.J., Mwangi, J.K., Wang, L.C., Lin, N.H., Lin, Y.C., Cao, J., Zhang, R. and Chang-Chien, G.P. (2015). An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient air. *Aerosol Air Qual. Res.* 15: 2730–2762.
- Cohen, A.J., Ross Anderson, H., Ostro, B., Pandey, K.D., Krzyzanowski, M., Künzli, N., Gutschmidt, K., Pope, A., Romieu, I., Samet, J.M. and Smith, K. (2005). The global burden of disease due to outdoor air pollution. *J. Toxicol. Environ. Health A* 68: 1301–1307.
- Demarini, D.M., Brooks, L.R., Warren, S.H., Takahiro, K., Iain, G.M. and Pramila, S. (2004). Bioassay-directed fractionation and salmonella mutagenicity of automobile and forklift diesel exhaust particles. *Environ. Health Perspect.* 112: 814–819.
- Ding, X., Wang, X.M., Xie, Z.Q., Xiang, C.H., Mai, B.X., Sun, L.G., Zheng, M., Sheng, G.Y., Fu, J.M. and Pöschl, U. (2007). Atmospheric polycyclic aromatic hydrocarbons observed over the North Pacific Ocean and the Arctic area: Spatial distribution and source identification. *Atmos. Environ.* 41: 2061–2072.
- Du, W., Zhang, Y., Chen, Y., Xu, L., Chen, J., Deng, J., Hong, Y. and Xiao, H. (2017). Chemical characterization and source apportionment of PM_{2.5} during spring and winter in the Yangtze River Delta, China. *Aerosol Air Qual. Res.* 17: 2165–2180.
- Durant, J.L., Busby, W.F., Lafleur, A.L., Penman, B.W. and Crespi, C.L. (1996). Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat. Res.* 371: 123–157.
- Fang, G.C., Wu, Y.S., Chen, J.C., Fu, P.P.C., Chang, C.N., Ho, T.T. and Chen, M.H. (2005). Characteristic study of polycyclic aromatic hydrocarbons for fine and coarse particulates at Pastureland near Industrial Park sampling site of central Taiwan. *Chemosphere* 60: 427–433.
- Gao, B., Wang, X.M., Zhao, X.Y., Ding, X., Fu, X.X., Zhang, Y.L., He, Q.F., Zhang, Z., Liu, T.Y., Huang, Z.Z., Chen, L.G., Peng, Y. and Guo, H. (2015). Source apportionment of atmospheric PAHs and their toxicity using PMF: Impact of gas/particle partitioning. *Atmos. Environ.* 103: 114–120.
- Garban, B., Blanchoud, H., Motelay-Massei, A., Chevreuil, M. and Ollivon, D. (2002). Atmospheric bulk deposition of PAHs onto France: Trends from urban to remote sites. *Atmos. Environ.* 36: 5395–5403.
- Goldstein, L.S. (2001). To BaP or not to BaP? That is the question. *Environ. Health Perspect.* 109: A356–A357.
- Guo, H., Lee, S.C., Ho, K.F., Wang, X.M. and Zou, S.C. (2003). Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos. Environ.* 37: 5307–5317.
- Han, B., Ding, X., Bai, Z., Kong, S. and Guo, G. (2011). Source analysis of particulate matter associated polycyclic aromatic hydrocarbons (PAHs) in an industrial city in northeastern China. *J. Environ. Monit.* 13: 2597–2604.
- Harrison, R.M., Smith, D.J.T. and Luhana, L. (1996). Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. *Environ. Sci. Technol.* 30: 825–832.
- He, J., Fan, S., Meng, Q., Sun, Y., Zhang, J. and Zu, F. (2014). Polycyclic aromatic hydrocarbons (PAHs) associated with fine particulate matters in Nanjing, China: Distributions, sources and meteorological influences. *Atmos. Environ.* 89: 207–215.
- Hoek, G., Brunekreef, B., Goldbohm, S., Fischer, P. and van den Brandt, P.A. (2002). Association between mortality and indicators of traffic-related air pollution in the

- Netherlands: A cohort study. *Lancet* 360: 1203–1209.
- IARC (International Agency for Research on Cancer) (2012). Agents Classified by the IARC Monographs. List of Classifications by Alphabetical Order, vol. 1e105 <http://monographs.iarc.fr/ENG/Classification/ClassificationsAlphaOrder.pdf>, Last Access: January 2012.
- Jiang, N., Yin, S., Guo, Y., Li, J., Kang, P., Zhang, R. and Tang, X. (2018). Characteristics of mass concentration, chemical composition, source apportionment of PM_{2.5} and PM₁₀ and health risk assessment in the emerging megacity in China. *Atmos. Pollut. Res.* 9: 309–321.
- Kavouras, I.G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E.G., Von Baer, D. and Oyola, P. (2001). Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environ. Sci. Technol.* 35: 2288–2294.
- Kong, S., Lu, B., Ji, Y., Bai, Z., Xu, Y., Liu, Y. and Jiang, H. (2012). Distribution and sources of polycyclic aromatic hydrocarbons in size-differentiated re-suspended dust on building surfaces in an oilfield city, China. *Atmos. Environ.* 55: 7–16.
- Laden, F., Neas, L.M., Dockery, D.W. and Schwartz, J. (2000). Association of fine particulate matter from different sources with daily mortality in six US cities. *Environ. Health Perspect.* 108: 941–947.
- Li, G., Xia, X., Yang, Z., Wang, R. and Voulvoulis, N. (2006a). Distribution and sources of polycyclic aromatic hydrocarbons in the middle and lower reaches of the Yellow River, China. *Environ. Pollut.* 144: 985–993.
- Li, J., Zhang, G., Li, X.D., Qi, S.H., Liu, G.Q. and Peng, X.Z. (2006b). Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Sci. Total Environ.* 355: 145–155.
- Li, N., Sioutas, C., Cho, A., Schmitz, D., Misra, C., Sempf, J., Wang, M., Oberley, T., Froines, J. and Nel, A. (2003). Ultrafine particulate pollutants induce oxidative stress and mitochondrial damage. *Environ. Health Perspect.* 111: 455–460.
- Li, Z., Porter, E.N., Sjödin, A., Needham, L.L., Lee, S., Russell, A.G. and Mulholland, J.A. (2009). Characterization of PM_{2.5}-bound polycyclic aromatic hydrocarbons in Atlanta—Seasonal variations at urban, suburban, and rural ambient air monitoring sites. *Atmos. Environ.* 43: 4187–4193.
- Lim, S.S., Vos, T., Flaxman, A.D., Danaei, G., Shibuya, K., Adair-Rohani, H. et al. (2012). A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990–2010: a systematic analysis for the Global Burden of Disease study 2010. *Lancet* 380: 2224–2260.
- Lin, X. (2016). Chemical composition characteristics and source apportionment in PM_{2.5} in Autumn of Nanchang City. Huaqiao University (in Chinese).
- Liu, X., Shi, C., Xu, X., Li, X., Xu, Y., Huang, H., Zhao, Y., Zhou, Y., Shen, H., Chen, C. and Wang, G. (2017a). Spatial distributions of β -cyclocitral and β -ionone in the sediment and overlying water of the west shore of Taihu Lake. *Sci. Total Environ.* 579: 430–438.
- Liu, Y., Yan, C., Ding, X., Wang, X., Fu, Q., Zhao, Q., Zhang, Y., Duan, Y., Qiu, X. and Zheng, M. (2017b). Sources and spatial distribution of particulate polycyclic aromatic hydrocarbons in Shanghai, China. *Sci. Total Environ.* 584: 307–317.
- Malcolm, H.M. and Dobson, S. (1994). The calculation of an Environmental Assessment Level (EAL) for atmospheric PAHs using relative potencies. Department of the Environment, London.
- Manoli, E., Kouras, A., Karagkiozidou, O., Argyropoulos, G., Voutsas, D. and Samara, C. (2016). Polycyclic aromatic hydrocarbons (PAHs) at traffic and urban background sites of northern Greece: Source apportionment of ambient PAH levels and PAH-induced lung cancer risk. *Environ. Sci. Pollut. Res.* 23: 3556–3568.
- Martícid, R., Llobet, J.M., Castell, V. and Domingo, J.L. (2008). Evolution of the dietary exposure to polycyclic aromatic hydrocarbons in Catalonia, Spain. *Food Chem. Toxicol.* 46: 3163–3171.
- Masiol, M., Hofer, A., Squizzato, S., Piazza, R., Rampazzo, G. and Pavoni, B. (2012). Carcinogenic and mutagenic risk associated to airborne particle-phase polycyclic aromatic hydrocarbons: A source apportionment. *Atmos. Environ.* 60: 375–382.
- Mo, Z., Wang, Z., Mao, G., Pan, X., Wu, L., Xu, P., Chen, S., Wang, A., Zhang, Y., Luo, J., Ye, X., Wang, X., Chen, Z. and Lou, X. (2019). Characterization and health risk assessment of PM_{2.5}-bound polycyclic aromatic hydrocarbons in 5 urban cities of Zhejiang Province, China. *Sci. Rep.* 9: 7296.
- Mudway, I.S., Stenfors, N., Duggan, S.T., Roxborough, H., Zielinski, H., Marklund, S.L., Blomberg, A., Frew, A.J., Sandström, T. and Kelly, F.J. (2004). An in vitro and in vivo investigation of the effects of diesel exhaust on human airway lining fluid antioxidants. *Arch. Biochem. Biophys.* 423: 200–212.
- Ning, Z. and Sioutas, C. (2010). Atmospheric processes influencing aerosols generated by combustion and the inference of their impact on public exposure: A review. *Aerosol Air Qual. Res.* 10: 43–58.
- Nisbet, I.C. and Lagoy, P.K. (1992). Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharm.* 16: 290–300.
- Pankow, J.F. (1994a). An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.* 28: 185–188.
- Pankow, J.F. (1994b). An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.* 28: 189–193.
- Peters, A., von Klot, S., Heier, M., Trentinaglia, I., Hörmann, A., Wichmann, H.E. and Löwel, H. (2004). Exposure to traffic and the onset of myocardial infarction. *N. Engl. J. Med.* 351: 1721–1730.
- Ravindra, K., Bencs, L., Wauters, E., de Hoog, J., Deutsch, F., Roekens, E., Bleux, N., Berghmans, P. and Van Grieken, R. (2006). Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. *Atmos. Environ.* 40: 771–785.

- Ravindra, K. and Grieken, S.R.V. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmos. Environ.* 42: 2895–2921.
- Ravindra, K., Wauters, E. and Van Grieken, R. (2008). Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses. *Sci. Total Environ.* 396: 100–110.
- Shao, Z., Bi, J., Ma, Z. and Wang, J. (2017). Seasonal trends of indoor fine particulate matter and its determinants in urban residences in Nanjing, China. *Build. Environ.* 125: 319–325.
- Simayi, M., Yahefu, P. and Han, M. (2018). Spatiotemporal variation, source analysis, and health risk assessment of particle-bound PAHs in Urumqi, China. *Aerosol Air Qual. Res.* 18: 2728–2740.
- Simoneit, B.R.T., Kobayashi, M., Mochida, M., Kawamura, K., Lee, M., Lim, H.J., Turpin, B.J. and Komazaki, Y. (2004). Composition and major sources of organic compounds of aerosol particulate matter sampled during the ACE-Asia campaign. *J. Geophys. Res.* 109: D19S10.
- SPCC Co. (2001). SPSS for Windows in medical science. Ma, B.R. (Ed.), Science Press, Beijing (207 pp).
- Sun, S., Xia, Z., Wang, T., Wu, M., Zhang, Q., Yin, J., Zhou, Y., Yang, H., Wang, W., Yu, Y., Xu, J. and Chen, C. (2016). Pollution level, sources, and lung cancer risk of PM₁₀-bound polycyclic aromatic hydrocarbons (PAHs) in summer in Nanjing, China. *J. Chem.* 2016: 4546290.
- U.S. EPA (1989). Risk assessment guidance for Superfund, Volume I, Human health evaluation manual (Part A). U.S. Environmental Protection Agency.
- U.S. EPA (1994). Peer review and peer involvement at the U.S. Environmental Protection Agency. Science Policy Council, Office of the Science Advisor, United States Environmental Protection Agency, ID 2872, <http://epa.gov/osa/spc/htm/perevmem.htm>.
- Venkataraman, C., Lyons, J.M. and Friedlander, S.K. (1994). Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. sampling, measurement methods, and source characterization. *Environ. Sci. Technol.* 28: 555–562.
- Wang, C., Dao, X., Zhang, L.L., Lv, Y.B. and Teng, E.J. (2015). Characteristics and toxicity assessment of airborne particulate polycyclic aromatic hydrocarbons of four background sites in China. *China Environ. Sci.* 35: 3543–3549 (in Chinese).
- Wang, G., Huang, L., Zhao, X., Niu, H. and Dai, Z. (2006). Aliphatic and polycyclic aromatic hydrocarbons of atmospheric aerosols in five locations of Nanjing urban area, China. *Atmos. Res.* 81: 54–66.
- Wang, J., Guinot, B., Dong, Z., Li, X., Xu, H., Xiao, S., Ho, S.S.H., Liu, S. and Cao, J. (2017a). PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs), oxygenated-PAHs and phthalate esters (PAEs) inside and outside middle school classrooms in Xi'an, China: Concentration, Characteristics and health risk assessment. *Aerosol Air Qual. Res.* 17: 1811–1824.
- Wang, T., Xia, Z., Wu, M., Zhang, Q., Sun, S., Yin, J., Zhou, Y. and Yang, H. (2017b). Pollution characteristics, sources and lung cancer risk of atmospheric polycyclic aromatic hydrocarbons in a new urban district of Nanjing, China. *J. Environ. Sci.* 55: 118–128.
- Wilson, J.G., Kingham, S., Pearce, J. and Sturman, A.P. (2005). A review of intraurban variations in particulate air pollution: Implications for epidemiological research. *Atmos. Environ.* 39: 6444–6462.
- Wongphatarakul, V., Friedlander, S.K. and Pinto, J.P. (1998). A comparative study of PM_{2.5} ambient aerosol chemical databases. *Environ. Sci. Technol.* 32: 3926–3934.
- Wright, L.P., Zhang, L., Cheng, I., Aherne, J. and Wentworth, G.R. (2018). Impacts and effects indicators of atmospheric deposition of major pollutants to various ecosystems-A review. *Aerosol Air Qual. Res.* 18: 1953–1992.
- Wu, D., Wang, Z., Chen, J., Kong, S., Fu, X., Deng, H., Shao, G. and Wu, G. (2014). Polycyclic aromatic hydrocarbons (PAHs) in atmospheric PM_{2.5} and PM₁₀ at a coal-based industrial city: Implication for PAH control at industrial agglomeration regions, China. *Atmos. Res.* 149: 217–229.
- Xia, Z., Duan, X., Tao, S., Qiu, W., Liu, D., Wang, Y., Wei, S., Wang, B., Jiang, Q., Lu, B., Song, Y. and Hu, X. (2013). Pollution level, inhalation exposure and lung cancer risk of ambient atmospheric polycyclic aromatic hydrocarbons (PAHs) in Taiyuan, China. *Environ. Pollut.* 173: 150–156.
- Xie, M., Barsanti, K.C., Hannigan, M.P., Dutton, S.J. and Vedal, S. (2013). Positive matrix factorization of PM_{2.5} - eliminating the effects of gas/particle partitioning of semivolatile organic compounds. *Atmos. Chem. Phys.* 13: 7381–7393.
- Xie, M., Hannigan, M.P. and Barsanti, K.C. (2014). Impact of gas/particle partitioning of semivolatile organic compounds on source apportionment with positive matrix factorization. *Environ. Sci. Technol.* 48: 9053–9060.
- Xu, C., Liu, M., Zhang, C., An, S., Yu, W. and Chen, J.M. (2007). The spatiotemporal dynamics of rapid urban growth in the Nanjing metropolitan region of China. *Landscape Ecol.* 22: 925–937.
- Yang, H.H., Lee, W.J., Chen, S.J. and Lai, S.O. (1998). PAH emission from various industrial stacks. *J. Hazard. Mater.* 60: 159–174.
- Yang, Y., Guo, P., Zhang, Q., Li, D., Zhao, L. and Mu, D. (2010). Seasonal variation, sources and gas/particle partitioning of polycyclic aromatic hydrocarbons in Guangzhou, China. *Sci. Total Environ.* 408: 2492–2500.
- Yunker, M.B., Snowdon, L.R., Macdonald, R.W., Smith, J.N., Fowler, M.G., Skibo, D.N., McLaughlin, F.A., Danyushevskaya, A.I., Petrova, V.I. and Ivanov, G.I. (1996). Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. *Environ. Sci. Technol.* 30: 1310–1320.
- Zhai, Y., Li, P., Zhu, Y., Xu, B., Peng, C., Wang, T., Li, C. and Zeng, G. (2016). Source apportionment coupled with gas/particle partitioning theory and risk assessment of polycyclic aromatic hydrocarbons associated with size-segregated airborne particulate matter. *Water Air Soil Pollut.* 227: 44.
- Zhang, J., Li, S., Li, S., Chen, Y., Lei, Z. and Zhang, Z.

- (2017). Therapeutic effects of stemonine on particulate matter 2.5-induced chronic obstructive pulmonary disease in mice. *Exp. Ther. Med.* 14: 4453.
- Zhang, N., Cao, J., Li, L., Ho, S. S. H., Wang, Q., Zhu, C. and Wang, L. (2018). Characteristics and source identification of polycyclic aromatic hydrocarbons and n-alkanes in PM_{2.5} in Xiamen. *Aerosol Air Qual. Res.* 18: 1673–1683.
- Zhang, Y., Yang, L., Zhang, X., Li, J., Zhao, T., Gao, Y., Jiang, P., Li, Y., Chen, X. and Wang, W. (2019). Characteristics of PM_{2.5}-bound PAHs at an urban site and a suburban site in Jinan in North China Plain. *Aerosol Air Qual. Res.* 19: 871–884.

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