The following publication Chen, Q., Luo, X. S., Chen, Y., Zhao, Z., Hong, Y., Pang, Y., ... & Jin, L. (2019). Seasonally varied cytotoxicity of organic components in PM2. 5 from urban and industrial areas of a Chinese megacity. Chemosphere, 230, 424-431 is available at https://doi.org/10.1016/j.chemosphere.2019.04.226.

Seasonally varied cytotoxicity of organic components in $PM_{2.5}$ in industrial and urban areas of a China megacity

Qi Chen[1], Yan Chen[1], Xiao-San Luo[1,*], Youwei Hong[2], Zhenyu Hong[2], Zhen Zhao[1], Jinsheng Chen[2]

[1]*International Center for Ecology, Meteorology, and Environment, and Collaborative Innovation Center of Atmospheric Environment and Equipment Technology (AEET), School of Applied Meteorology, Nanjing University of Information Science & Technology, Nanjing 210044, China*

[2]*Center for Excellence in Regional Atmospheric Environment, Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, 361021,China*

(*Corresponding Author Email: xsluo@nuist.edu.cn; https://orcid.org/0000-0003-4314-7216)

Abstract

Organic pollutants are important harmful components in atmospheric fine particulate matters ($PM_{2.5}$), health risks of which varied with temporal and spatial distributions. To clarify the characteristics of atmospheric organic pollution, the concentrations, sources, and human health risks of typical organic compositions in $PM_{2.5}$ samples from both industrial and urban areas of Nanjing in eastern China were investigated monthly for a year. Results showed that, the concentrations of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (PAHs) and n-alkanes were higher in winter and spring than those in summer and autumn. The organic pollution was slightly higher in industrial than urban area, though the PAHs in autumn and the n-alkanes in warm season (summer and autumn) were higher in urban area. With regards to the pollutant sources, the atmospheric PAHs were dominated by motor vehicle exhaust in the urban area, and combined with coal combustion emission in the industrial area. Airborne n-alkanes were mainly from biological source accompanied by fossil fuel combustion in industrial area. The $PM_{2.5}$-bound PAHs indicated higher risks to adults in industrial area than in urban area with the seasonal patterns: winter > spring > autumn > summer. More attention should be paid to the health risks of exposure to organic pollutants accumulated in $PM_{2.5}$ during

cold season. Controlling vehicle emissions might be the key measure for alleviating atmospheric PAHs and n-alkanes pollution in megacities, while coal purification can be an effective control method in industrial areas.

Keywords: Aerosol pollution, PAHs, N-alkanes, Spatial-temporal distributions, Source apportionments, Human health risk assessments

1. Introduction

Due to significant impacts on air quality and human health (Curtis et al., 2006; Fontes et al., 2017), atmospheric particulate matter (PM) pollution has attracted worldwide attention (Chen et al., 2018; Luo et al., 2019). Epidemiological studies confirmed that exposure to PM was associated with increased risks of mortality, lung cancer, respiratory and cardiovascular disease incidences (Feng et al., 2018). There were approximately 223,000 deaths from lung cancer (15% of all lung cancer deaths) in 2010 worldwide attribute to PM exposure, of which 139,000 occurred in China (Lim et al., 2012; Feng et al., 2018). Fine particles ($PM_{2.5}$) with aerodynamic diameter of 2.5 μm or less were especially related to adverse health effects (Nagy and Szabó, 2017). Moreover, the chemical compositions of atmospheric PM can better identify pollution sources and explain related health effects (Chen et al., 2013). The diversified components of $PM_{2.5}$ include inorganic ions, metals (Luo et al., 2014) and organics (Billet et al., 2007; Gutiérrez-Castillo et al., 2006), among which, polycyclic aromatic hydrocarbons (PAHs) and n-alkanes are key organic compounds. As a group of persistent organic pollutants and environmental priority pollutants, PAHs have been proved to be toxic, carcinogenic and mutagenic (Samanta et al., 2002; Armstrong et al., 2004; Wang et al., 2016), and have become the main organic compounds threatening public health (Feng et al., 2018). The same series of n-alkanes can come from both natural and artificial sources and are highly resistant to biochemical degradation, that are particularly suitable for tracking the origin and fate of different samples (Pietrogrande et al., 2010). The distribution features and characteristic parameters of n-alkanes varied with different sources, which can provide important geochemical information, and have been used for the source

analysis of $PM_{2.5}$ (Li et al., 2010; Li et al., 2013).

However, previous studies mostly focus on the pollution levels of airborne PAHs or n-alkanes in single site of a city (Hong et al., 2017; Fan et al., 2018; Kang et al., 2018). This study combined the concentration levels and corresponding source identification methods to explore the distribution patterns of two organic pollutants in $PM_{2.5}$. The objectives were to investigate and compare the spatial and seasonal characteristics of $PM_{2.5}$, regarding concentrations and sources of PAHs and n-alkanes in industrial and urban areas, and the associated human health risk of a typical megacity in China.

2. Materials and methods

2.1. Study site

Located in the southwest of Jiangsu Province in eastern China, Nanjing (N31°14′-32°37′, E118°22′-119°14′) is an important megacity with a total area of 6587 km^2 in the Yangtze River Delta (YRD) region (Fig. S1). The population is 8.34 million with urbanization rate of 82.3%. Nanjing is a national transportation hub, with the density of road network ranking top of the China's central cities. Nanjing has a subtropical monsoon climate, mainly characterized by four distinct seasons and abundant rainfall (the average number of annual rainy days are 117 days, with a mean annual rainfall of 1106 mm). The winter in Nanjing is mainly dominated by the northwest wind, while the summer is dominated by the southeast wind. The 2015 Bulletin of Nanjing Environmental Status indicated that the major air pollutants were PM_{10}, NO_2, O_3 and $PM_{2.5}$ (the primary pollutant). In 2015, the number of days exceeding the secondary standard of ambient air quality was 130. The main sources of air pollution in Nanjing were motor vehicle exhaust, industrial emissions, coal combustion, construction dust and mixed pollution caused by pollutant transport from other regions (Luo et al., 2017).

2.2. Sampling and chemical characterization of $PM_{2.5}$

2.2.1. Sampling

$PM_{2.5}$ samples were collected synchronously from one site in industrial area and

the other site in urban area about 18.5 km apart (Fig. S1). Many chemical and metallurgical industries were near the industrial sampling site, while the urban site in downtown was surrounded by heavy traffic, schools, communities and business districts. High-volume (1000 L/min) air samplers were both set on the building roof (20-30m from the ground) for daily 23 h sampling (8:00-7:00), and the quartz fiber filters (QMA, 203mm×254 mm, Whatman, UK) were prebaked at 500 °C for 3 h before sampling. Before and after sampling, filters were equilibrated for more than 24 h in a constant temperature and humidity environment for weighing. From January to December of 2015, two samples were taken from a site each month, and a total of 48 samples were obtained from the two sites for current investigation. No rainfall on the sampling date and the previous day was recorded as non-precipitation day, and rainfall on the day of sampling was recorded as precipitation day.

2.2.2. Pretreatments and analyses of organic components in $PM_{2.5}$

The sample filters were placed in an accelerated solvent extraction (ASE) kettle with added substitutes, and then extracted for 30 min by ASE (Dionex 350) using mixture of dichloromethane (DCM)/methanol (2:1, V/V). The extracts were concentrated by rotary evaporator (RE-52CS) and nitrogen evaporator (HSC-12B), and then adjusted to constant volume with n-hexane for analysis.

The PAHs and n-alkanes in $PM_{2.5}$ organic extracts were determined by gas chromatography-mass spectrometry (GC-MS, Agilent 6890/5975B, USA). Splitless injection method was used, with the front inlet temperature of 300 ℃ and ion source temperature of 230 ℃. Column (HP-5 MS capillary column 30 m*0.25 mm*0.25 mm) flow rate of 1.0 ml/min was used and 10μl sample was injected in per measurement. 16 PAHs selected as priority control pollutants by the US EPA were analyzed, namely Naphthalene (Nap), Acenaphthylene (Acey), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluotanthene (Flua), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluorantene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Indeo[1,2,3-cd]pyrene (IcdP), Dibenzo[a, h]anthracene (DahA),

and Benzo[ghi]pyrene (BghiP). The C_{13}-C_{40} among the n-alkanes were selected. According to the characteristic ion and chromatographic retention time, the internal standard method and the calibration curve were used for quantitative determination. The recovery rates were all higher than 80%. All the above quality control results met the experimental requirements.

2.2.3. Source analysis of airborne PAHs

Both relative abundance method and characteristic ratio method were conducted. Relative abundances were calculated as the concentration ratio of the middle and high ring (4-6 ring) PAHs to the low ring (2-3 ring) PAHs. When the ratio was larger than 1, the PAHs were mainly derived from combustion, otherwise they were mainly from petroleum pollution (Soclo et al., 2000).

The sources of PAHs can also be identified based on their characteristic ratios (Table S1). The correlations between the contents of BghiP and the ∑PAHs can indicate main source from vehicle exhaust (Liu et al., 2017). Various characteristic ratios include: IcdP/BghiP, BaP/BghiP, Phe/Ant, BaA/Chr, BbF/BkF, IcdP/(IcdP+BghiP) (Simcik et al., 1999; Qi et al., 2002; Fang et al., 2004).

2.2.4. Source analysis airborne n-alkanes

Both correlation analysis and carbon preference index (CPI) were applied. The Pearson correlation coefficients were analyzed between the concentrations of $PM_{2.5}$-bound total alkanes and higher plant-derived alkanes ($C_n \geq C_{25}$), anthropogenic alkanes ($C_n \leq C_{24}$), skin-damaging alkanes ($Cn \geq C_{17}$) and stimulating alkanes (n-C_8~n-C_{16}), respectively. When the correlation coefficient $R^2 > 0.8$, it indicates significant correlation, and the values 0.3-0.8 imply weak correlation, while there is no correlation when $R^2 <$ 0.3.

To distinguish the relative contributions of biological sources and fossil fuel sources to n-alkanes, carbon preference index of the total n-alkanes (CPI), as well as those for their anthropogenic (CPI_1) and biological (CPI_2) sources were calculated respectively as follows (Chow et al., 1994; Hong et al., 2017):

Total n-alkanes: $CPI = \sum (C_{17}\text{-}C_{39}) / \sum (C_{16}\text{-}C_{40})$. (1)

Anthropogenic n-alkanes: $CPI_1 = \sum (C_{17}\text{-}C_{15}) / \sum (C_{16}\text{-}C_{24})$. (2)

Bio-source n-alkanes: $CPI_2=\sum (C_{27}-C_{39})/ \sum (C_{26}-C_{38})$. (3)

2.3. Human health risk assessments

2.3.1. Carcinogenic and mutagenic equivalent concentrations

US EPA studies have shown that Benzo[a]pyrene (BaP) among PAHs is highly carcinogenic and teratogenic. Based on PAHs concentration and its corresponding carcinogenic equivalent factor (TEF) with reference to BaP (Nisbet and Lagoy, 1992), the BaP toxic equivalent quantity (TEQ) and total equivalent toxicity (∑TEQ) of BaA, Chr, BbF, BkF, BaP, IcdP, BghiP and DahA monomers were calculated to evaluate the carcinogenic risk of PAHs. And the mutagenic equivalent quantity (MEQ) was also calculated with reference to BaP as follows (Jung et al., 2010; Qu et al., 2015):

$$TEQ = \sum C_i \times TEF_i. \quad (4)$$

$$MEQ = \sum C_i \times MEF_i. \quad (5)$$

C_i, the i-type PAHs concentration, ng·m^{-3}; TEFi and MEFi, the carcinogenic and mutagenic equivalent factors of the i-th PAHs.

2.3.2. Lifetime carcinogenic excess risk and loss of life expectancy

The US EPA incremental carcinogenic risk model was used to assess the risk of lifetime carcinogenic excess of $PM_{2.5}$-bound PAHs. Relevant parameters were derived from the US EPA Exposure Factor Manual, Superfund Health Risk Assessment Manual (US EPA, 1986; US EPA, 1989; US EPA, 1997) and actual situation in Nanjing (Table S2). Daily exposure dose of BaP for respiratory pathway was calculated by the following equations:

$$ADD=C\times IR\times ET\times EF\times ED/(BW\times AT). \quad (6)$$

$$R=q\times ADD. \quad (7)$$

Where ADD was the average daily exposure dose, mg/(kg·d); R was the population lifetime carcinogenic excess risk, dimensionless; Q was the carcinogenic strength coefficient of pollutants. According to the IRIS information database, the carcinogenic intensity of BaP coefficient (CSF) was 3.14 kg·d/mg. C was the concentration of BaP equivalent exposure, ng/m^3; IR was the respiration rate, m^3/h; ET was the frequency of

daily exposure, h/d; EF was the frequency of annual exposure, d/year; ED was the exposure duration, year; BW was the body weight, kg; AT was average contact time, d (Li et al., 2017).

Assuming that the loss of life caused by carcinogens was equivalent to the loss of life expectancy (LLE) caused by the risk of carcinogenicity 1×10^{-5} (Gamo et al., 1995), the LLE values were calculated by the equation (Yang et al., 2005):

$$LLE=62.16\times (R/10^{-5}). \quad (8)$$

2.4. Statistical analysis

Data analysis was plotted by Origin 2016, and performed by IBM SPSS statistics 24 for correlation, divergence, and principal component analysis (PCA). Correlation analysis was used to measure the closeness of the two variables. The discrepancy between areas (industrial vs urban) or seasons was statistically analyzed by t-test. The divergence was significant when the statistical test level was $P < 0.05$, and extremely significant when $P < 0.01$. PCA was based on the obtained chemical composition data and the correlation between different components. The principal component factors were summarized from multiple variables, and the load of each factor was calculated. Each common factor represents a different source, therefore, the source and contribution of the receptor pollutants can be identified. The PCA was conducted using maximum variance rotation factor according to the obtained factor load and distribution characteristics of each factor (Hopke et al., 1976), and the principle components can be extracted based on the feature root greater than 1.

3. Results and discussion

3.1. Seasonal variations of $PM_{2.5}$ concentrations in industrial and urban areas

The $PM_{2.5}$ levels in Nanjing (Fig. 1) were much higher than the WHO Air quality guidelines (AQG), and most were higher than the secondary China Air Quality Standard (AQS; GB3095-2012), especially in the industrial area and during the cold season (spring and winter). The $PM_{2.5}$ concentration characteristics of Nanjing showed spatial-temporal variation, which was 97.6±31.9 and 92.8±32.1 μg/m^3 in industrial and urban

area, respectively. From June to December in winter, it was higher in the industrial area than that in the urban area, but from January to March the urban area was higher. Based on the average value of each season, except for winter, the $PM_{2.5}$ concentrations were higher in industrial than urban area. According to the t-test, no significant $PM_{2.5}$ concentrations were recorded between industrial and urban areas ($p>0.05$), and the winter concentration in urban area were significantly different from other seasons.

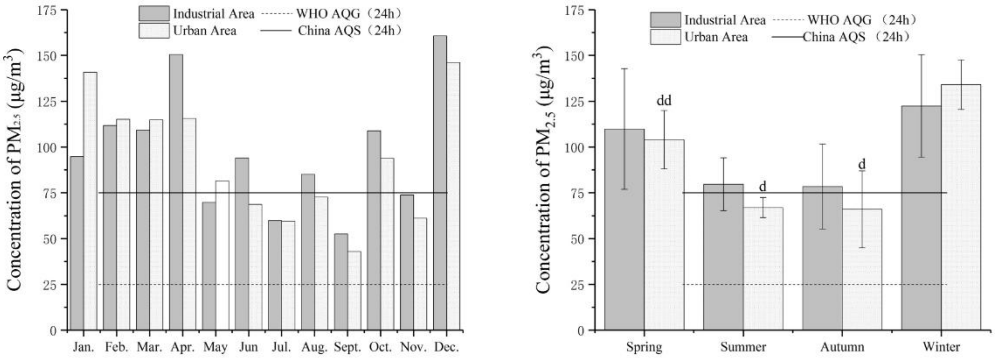

Fig. 1. Monthly and seasonal average concentrations of $PM_{2.5}$ in industrial and urban areas of Nanjing (^{d} $p < 0.05$ and ^{dd} $p<0.01$ implied the difference to winter season was significant).

3.2. Seasonal concentration characteristics of $PM_{2.5}$-bound PAHs between industrial and urban areas

Fig. 2 shows the concentrations of $PM_{2.5}$-bound PAHs in different areas. The annual average concentration of total PAHs in industrial area was 9.08 ± 4.57 ng/m^3, which was highest in February and lowest in May. In urban area, the PAHs pollution in December was most serious, and the lowest concentration was in July, with the annual average concentration of 7.97 ± 3.55 ng/m^3. For seasonal variations, it was highest in winter and lowest in summer. Except in autumn, the PAHs concentration in industrial area was higher than that in urban area. The average concentration of spring, summer, autumn and winter was 9.77 ± 4.41, 5.69 ± 0.12, 6.89 ± 1.67 and 14.0 ± 4.78 ng/m^3 in industrial area, respectively; and was 7.70 ± 2.82, 4.45 ± 0.38, 7.56 ± 4.01 and 12.2 ± 2.31 ng/m^3 in urban area, respectively. Although the difference between industrial and urban areas was mostly not significant, their difference in summer was significant, and there are some significant differences among the seasons, especially the difference to

winter.

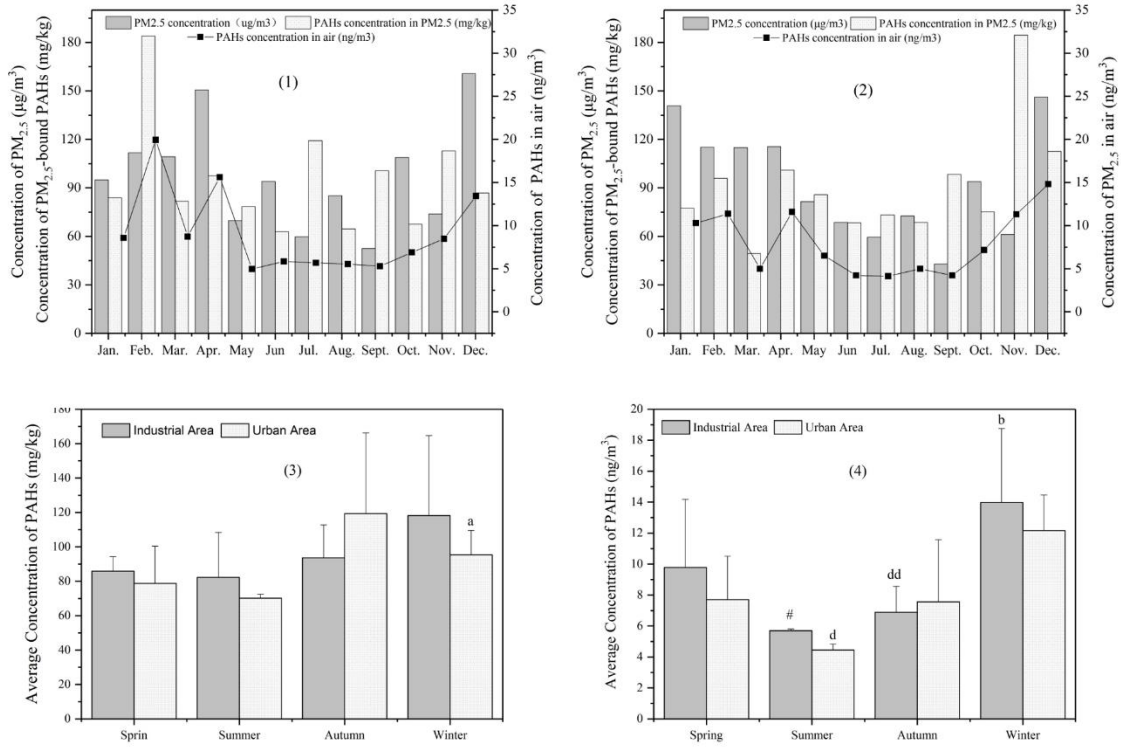

Fig. 2. Monthly (1: industrial area; 2: urban area) and seasonal (3, 4) average concentrations of $PM_{2.5}$-bound PAHs in industrial and urban areas of Nanjing (# $p < 0.05$, ## $p < 0.01$, implied the concentration difference between the industrial and urban areas was significant; ^{a} $p < 0.05$, ^{aa} $p < 0.01$ implied the difference to spring season was significant; and ^{d} $p < 0.05$, ^{dd} $p < 0.01$ implied the difference to winter was significant).

3.3. Seasonal concentration characteristics of $PM_{2.5}$-bound n-alkanes between industrial and urban areas

The concentration of $PM_{2.5}$-bound n-alkanes in Nanjing also showed significant spatiotemporal pattern (Fig. 3). The annual average concentration in industrial area was 68.4 ± 39.5 ng/m^3, which was highest in March and lowest in October. In urban area, it was 65.1 ± 24.1 ng/m^3, highest in December and lowest in March. In both areas, it was characterized by higher concentrations in winter and spring, and the lowest concentration in autumn. In winter and spring, the n-alkanes levels were much higher in industrial area than that in urban area, but in summer and autumn, they were much higher in urban area. The average concentration of spring, summer, autumn and winter was 98.5 ± 20.4, 42.0 ± 27.2, 28.9 ± 21.4 and 104 ± 14.0 ng/m^3 in industrial area, respectively; and was 62.0 ± 37.16, 52.1 ± 9.06, 54.5 ± 11.9 and 91.8 ± 11.3 ng/m^3 in urban area, respectively.

The difference between industrial and urban areas was different ($p<0.05$) in the warm seasons, and the n-alkanes level in summer and autumn was also significantly different from other seasons.

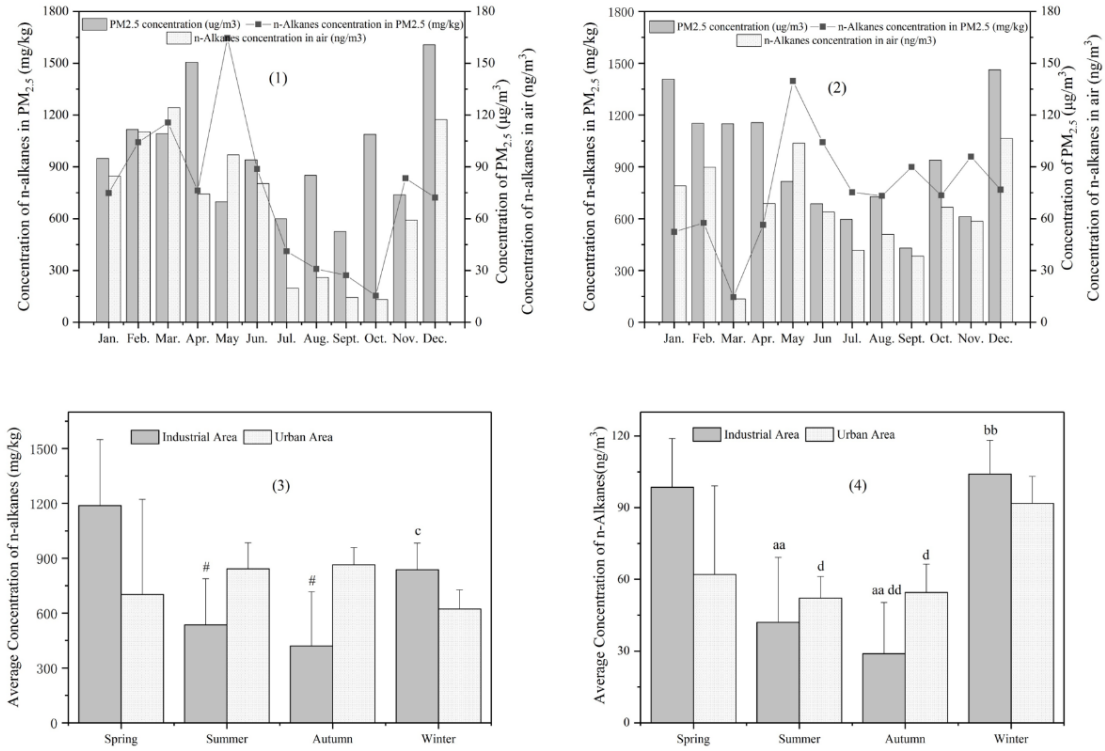

Fig. 3. Monthly (1: industrial area; 2: urban area) and seasonal (3, 4) average concentrations of $PM_{2.5}$-bound n-alkanes in industrial and urban areas of Nanjing (# $p < 0.05$, ## $p < 0.01$, implied the concentration difference between the industrial and urban areas was significant; ^{a} $p < 0.05$, ^{aa} $p < 0.01$ implied the difference to spring season was significant; ^{b} $p < 0.05$, ^{bb} $p < 0.01$ implied the difference to summer was significant; ^{c} $p < 0.05$, ^{cc} $p < 0.01$ implied the difference to autumn was significant; and ^{d} $p < 0.05$, ^{dd} $p < 0.01$ implied the difference to winter was significant).

3.4. Sources of $PM_{2.5}$-bound PAHs in industrial and urban areas

Fig. 4 shows the seasonal distribution of $PM_{2.5}$-bound 16 PAHs concentrations in industrial and urban areas, which did not exceed the China AQS limit of BaP in inhalable particles (2.5 ng/m^3). The relative abundance method confirmed that the source of airborne PAHs in Nanjing was combustion. The high correlation coefficients between single PAH component and total PAHs concentration indicated that, the sources of these compounds were similar. Especially implied by BaP (Fig. S2), the main source was motor vehicle exhaust. Atmospheric pollution in industrial areas was dominated by mixture of soot and motor vehicle exhaust. Indicated by the ratio judgment method,

PAHs in summer were mainly derived from diesel-type combustion; while in winter, they were mainly from the combustion of diesel and coal. Urban air pollution was dominated by motor vehicle exhaust, and the PAHs were mainly from diesel and gasoline-type combustion in warm season, and coal combustion in winter.

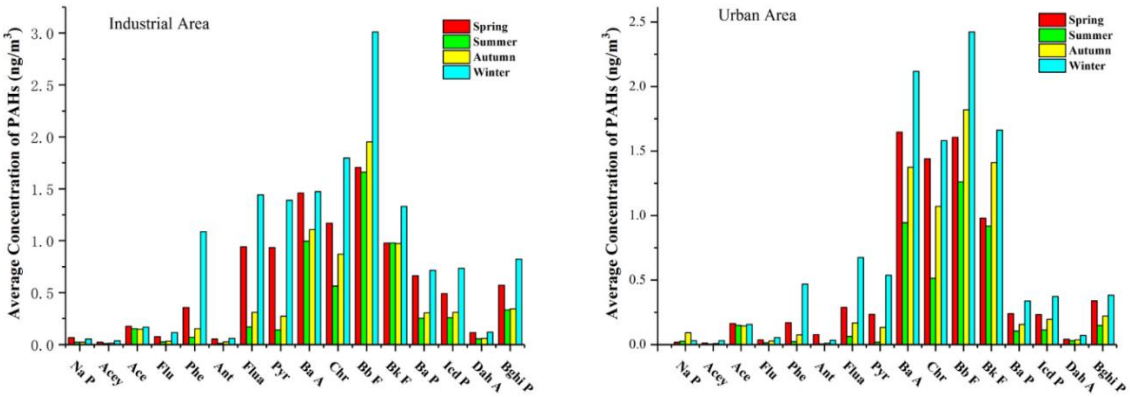

Fig. 4. Seasonal concentrations of $PM_{2.5}$-bound 16 PAH species in industrial and urban areas of Nanjing.

The PCA results are listed in Table 1. In industrial area, the cumulative contribution of three components was 94.62%. Factor 1 indicated the sources from natural gas, coal and motor vehicle exhaust emission, because the Flua, Pyr, Ba A, and Chr are the natural gas and coal combustion markers, while Bap, IcdP, Dah A and BghiP are the motor vehicle exhaust markers. Factor 2 represented the co-contribution of coke furnace and motor vehicle, because the Flu and Phe are the markers of coke oven volatilization, while Chr, BbF and BkF are typically from motor vehicle exhaust. The factor loading matrix of urban area, four components account for 92.2%. The Acey, Flu, Phe, Flua, Pyr in Factor 1 were from sources of coke oven and coal combustion; Nap, BaA, Chr, BbF, BkF in Factor 2 were from motor vehicle emission; Ace, Bap, IcdP, BghiP in Factor 3 indicated motor vehicle exhaust; and DahA with a high load Factor 4 was the source of cooking (Meng et al., 2015).

Table 1 PCA results of $PM_{2.5}$-bound 16 PAHs in industrial and urban areas of Nanjing.

Compounds	Industrial area			Urban area			
	PC1	PC2	PC3	PC1	PC2	PC3	PC4
Nap	0.383	0.195	**0.808**	0.360	**0.732**	-0.193	-0.093
Acey	0.464	**0.785**	0.400	**0.904**	0.266	0.265	-0.050

Ace	0.130	0.119	**0.896**	0.221	-0.172	**0.919**	-0.238
Flu	0.395	**0.772**	0.452	**0.924**	-0.097	-0.054	-0.028
Phe	0.515	**0.797**	0.114	**0.911**	0.144	0.284	-0.005
Ant	**0.840**	0.333	0.309	0.390	-0.220	-0.002	-0.720
Flua	**0.770**[a]	0.556	0.297	**0.870**	0.192	0.394	0.135
Pyr	**0.814**	0.508	0.203	**0.820**	0.084	0.502	0.232
BaA	**0.905**	0.265	0.302	0.369	**0.848**	0.322	-0.022
Chr	**0.744**	**0.620**	0.206	-0.061	**0.837**	0.495	0.102
BbF	0.199	**0.949**	0.052	0.111	**0.871**	0.142	0.431
BkF	0.286	**0.934**	0.109	-0.173	**0.891**	-0.184	0.310
BaP	**0.933**	0.246	0.236	0.426	0.197	**0.801**	0.368
IcdP	**0.819**	0.515	0.148	0.383	0.185	**0.681**	0.574
DahA	**0.962**	0.164	0.166	0.404	0.127	0.278	**0.777**
BghiP	**0.837**	0.481	0.112	0.198	0.208	**0.873**	0.336
Variance (%)	46.4	33.7	14.5	31.1	24.1	23.7	13.3

a Bold>0.6

According to the above combined methods, the PAHs in $PM_{2.5}$ of Nanjing were mainly derived from combustion. The air pollution in industrial area was dominated by soot, coke oven and motor vehicle exhaust; urban air pollution was dominated by motor vehicle exhaust. The coal combustion contributes more pollutants in cold season than in warm season, that was consistent with the need of house heating.

3.5. Sources of $PM_{2.5}$-bound n-alkanes in industrial and urban areas

Airborne N-alkanes have a variety of sources. Natural biological sources include higher plant waxes, few resin and pollen suspended in the air, microorganisms and insects (Gröllert and Puxbaum, 2000). Typical anthropogenic sources include incomplete combustion of fossil fuels and biomass. The n-alkanes produced by fossil fuel combustion do not have the odd-carbon predominance (Peng et al., 1999), while modern biological sources of n-alkanes such as higher plants have obvious odd-carbon number advantages (Rogge et al., 1993). Both the industrial and urban areas had obvious odd-carbon predominance (Fig. 5) indicated that the atmospheric n-alkanes in Nanjing were greatly affected by biological sources. It was also supported by the correlations between concentrations of total alkanes in $PM_{2.5}$ and higher plant-derived alkanes (Fig. S3). In industrial area, the correlation coefficient between total n-alkanes and fossil fuel-derived alkanes was high. Skin damage alkanes were significantly better correlated with total alkanes than stimulating alkanes (both in industrial and urban) and showed the highest correlation.

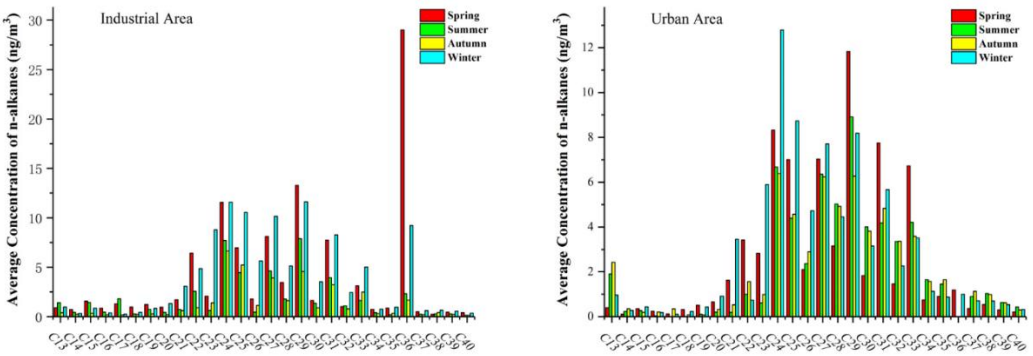

Fig. 5. Seasonal concentration variations of $PM_{2.5}$-bound n-alkanes components in industrial and urban areas of Nanjing.

In spring and summer, the airborne n-alkanes CPI values (Table S3) of the industrial area were much higher than urban area, that was opposite in autumn and winter. Compared with urban area, n-alkanes of the industrial area was more affected by plant sources in spring and summer but was more affected by fuel in autumn and winter. The values $CPI_2 > CPI_1$ indicated that the plant source was much stronger than the fossil fuel source. The relatively low winter CPI_2 value meant that winter was least affected by the plant source, which is consistent with the less growth of plants in winter.

Table 2 lists the factor loading matrices for $PM_{2.5}$-bound n-alkanes. The cumulative contribution rate of 5 factors for industrial area was 100%. Factor 1 indicated the microbial source, because it associated with higher molecular weight n-alkanes C_{13}-C_{19}, especially the C_{15} (Hong et al., 2017). Factor 2 indicated the sources of motor vehicles and coal due to its associated with C_{23} and C_{21}, and the source of paraffin due to its also associated with C_{30} and C_{32} (Schauer et al., 2002). Factors 3, 4 and 5 were described as contribution of plants due to its strong correlation with long-chain n-alkanes (> C_{25}). For the urban area, four factors contributed 98.2%. Factor 1 interpreted the motor vehicles emissions, and factor 2 was higher plants, factor 3 was microorganisms, and the main source of factor 4 was paraffin.

Table 2 PCA results of $PM_{2.5}$-bound n-alkanes (C_{13}-C_{40}) in industrial and urban areas of Nanjing.

n-alkanes	Industrial area					Urban area			
	PC1	PC2	PC3	PC4	PC5	PC1	PC2	PC3	PC4
C_{13}	**0.764**[a]	0.565	0.157	-0.247	0.106	-0.437	-0.278	0.431	-0.736
C_{14}	**0.975**	0.140	0.092	0.057	0.132	-0.417	-0.162	**0.828**	-0.164
C_{15}	**0.987**	-0.015	0.105	-0.114	-0.029	0.422	**0.784**	0.443	0.013
C_{16}	**0.958**	0.118	0.168	0.174	-0.102	0.589	0.382	**0.693**	-0.043
C_{17}	**0.698**	-0.347	-0.059	-0.614	-0.109	-0.216	0.071	**0.954**	-0.128
C_{18}	**0.975**	0.146	0.068	0.136	0.065	**0.985**	-0.037	0.151	-0.006
C_{19}	**0.834**	0.477	0.276	0.012	-0.012	**0.785**	0.526	-0.156	0.242
C_{20}	0.404	**0.892**	0.195	0.016	-0.049	**0.869**	0.361	0.011	0.334
C_{21}	-0.020	**0.960**	0.243	-0.017	-0.134	**0.996**	-0.042	-0.078	-0.003
C_{22}	0.437	**0.610**	**0.619**	0.221	-0.066	**0.869**	0.413	0.057	0.154
C_{23}	-0.079	**0.980**	0.179	-0.027	0.006	**0.977**	-0.194	0.009	0.081
C_{24}	0.195	-0.278	0.558	-0.079	0.753	**0.930**	-0.098	-0.014	0.211
C_{25}	0.187	**0.885**	-0.048	0.409	-0.113	**0.822**	0.440	0.054	0.357
C_{26}	0.303	**0.899**	-0.016	0.314	0.028	0.418	-0.682	0.348	0.480
C_{27}	0.133	0.387	**0.822**	0.386	0.086	0.223	**0.865**	0.044	0.446
C_{28}	0.462	0.580	**0.608**	0.269	0.091	-0.734	-0.228	-0.075	**0.629**
C_{29}	0.039	-0.172	**0.890**	-0.258	0.331	-0.094	**0.948**	-0.028	0.265
C_{30}	0.659	**0.718**	0.069	0.160	0.139	-0.935	-0.289	0.001	0.207
C_{31}	0.125	0.164	**0.968**	0.141	0.024	0.332	**0.892**	0.093	-0.131
C_{32}	0.558	**0.823**	-0.012	-0.002	-0.109	-0.912	-0.406	0.027	-0.043
C_{33}	0.037	0.092	0.186	0.266	**0.941**	-0.165	**0.977**	0.029	-0.129
C_{34}	**0.950**	0.092	0.069	0.077	0.281	-0.989	0.044	0.056	-0.040
C_{35}	**0.741**	0.540	0.285	0.242	-0.138	-0.843	0.438	0.258	0.090
C_{36}	0.279	0.365	0.344	0.597	-0.560	-0.019	**0.986**	0.126	-0.094
C_{37}	0.177	0.063	0.196	**0.950**	0.157	-0.807	-0.100	0.528	-0.246
C_{38}	-0.050	**0.708**	-0.368	0.592	0.100	-0.771	-0.582	0.005	-0.258
C_{39}	**0.617**	**0.651**	0.051	0.294	-0.325	-0.586	-0.757	-0.081	-0.204
C_{40}	**0.840**	0.376	0.011	0.175	-0.349	-0.329	-0.337	-0.845	-0.219
Variance (%)	34.8	31.0	14.9	10.8	8.50	48.3	28.8	13.4	7.75

a Bold>0.6

Generally, the source of atmospheric n-alkanes pollution in Nanjing was mainly affected by plants and the exhaust of motor vehicles. Compared with urban area, the industrial area also has fossil fuels and coal-fired sources. Spring and summer are more affected by plant sources than winter, which was consistent with plant growth.

3.6. Influences of meteorological parameters on $PM_{2.5}$ and associated organic pollutants in industrial and urban areas

3.6.1. *Relationships between precipitation and concentrations of $PM_{2.5}$ and associated PAHs and n-alkanes*

The concentration of $PM_{2.5}$ during precipitation and non-precipitation days in industrial and urban areas of Nanjing are shown in Fig. S4, and Fig.6 shows the average levels of PAHs and n-alkanes. The $PM_{2.5}$ levels during precipitation day were lower than that of the non-precipitation day. In industrial area, the concentrations of PAHs and n-alkanes on rainy days were lower than those on non-precipitation days, implying that the precipitation effectively alleviated the particulate organic pollution.

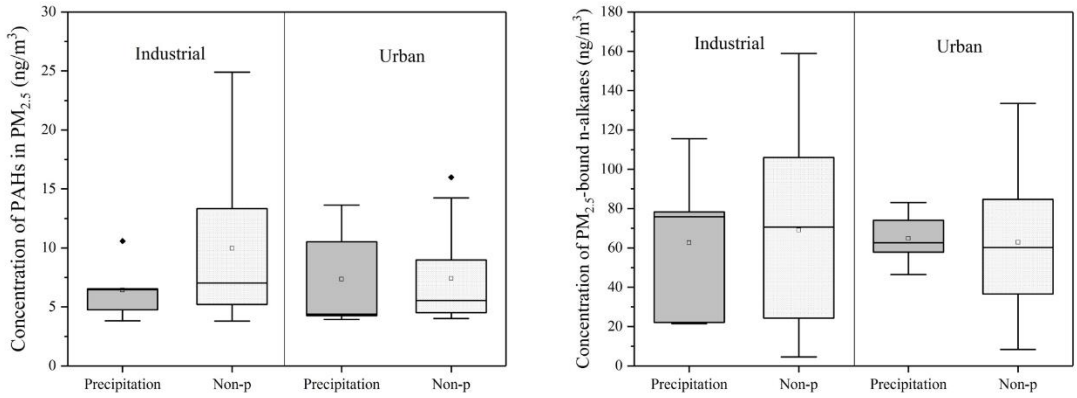

Fig.6. Concentrations of airborne PAHs and n-alkanes in industrial and urban areas of Nanjing during precipitation and non-precipitation days.

3.6.2. *Relationships between temperature and concentrations of $PM_{2.5}$ and associated PAHs and n-alkanes*

The concentration of organic pollutants in $PM_{2.5}$ was generally low with the increased temperature. As showed by Fig. 7, the temperature was slightly negatively correlated with each PM pollutant. Temperature was an important parameter affecting atmospheric nucleation. Overheating can cause new particles forming in summer, while in winter, the pollutants have weak diffusion ability and the atmospheric boundary layer was low that made it forming new particles easier (Hussein et al., 2006).

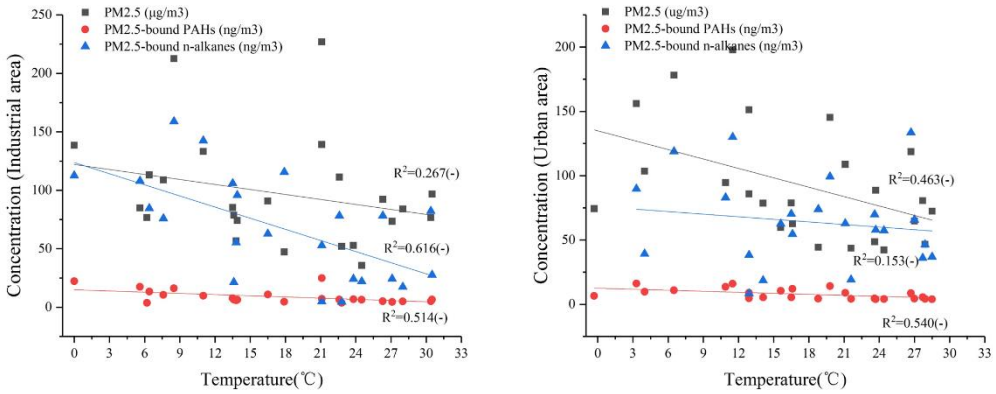

Fig. 7. Correlations between temperature and each airborne pollutant concentration in industrial and urban areas of Nanjing.

3.7. Health risks of $PM_{2.5}$-bound PAHs in industrial and urban areas

Because the Bap concentration significantly correlated with the concentration of ∑PAHs (Fig.S2), risks of $PM_{2.5}$-bound PAHs could be representatively reflected by Bap. The daily average exposure dose was obtained by equation (6), and the incremental lifetime cancer risk was calculated by equation (7). The life expectancy losses of adults and children in different areas and seasons were further estimated by equation (8). Tables 3 and 4 listed the related parameters of PAHs exposure, which in cold season were greater than the warm season and were highest in winter.

The lifetime cancer risk caused by $PM_{2.5}$-bound PAHs in industrial area was $0.311\sim0.581\times10^{-6}$ to adults and $0.195\sim0.367\times10^{-6}$ to children, respectively. While in urban area, it was the $0.286\sim0.414\times10^{-6}$ and $0.112\sim0.264\times10^{-6}$, respectively. The cancer risks were higher to adults and higher in industrial area, and highest in winter and lowest in summer. According to the acceptable risk values recommended by US EPA and the International Radiation Protection Association ($10^{-4}\sim10^{-6}$, 5.0×10^{-5}, respectively), the incremental lifetime cancer risk to adults and children through respiration of PAHs in Nanjing were low and acceptable.

Table 3 Concentrations, TEF, MEF, Bap-TEQ, and Bap-MEQ of $PM_{2.5}$-bound PAHs in industrial and urban areas of Nanjing.

	Average concentration (ng/m^3)								TEF	MEF
	Industrial area				Urban area					
	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter		
BaA	1.460	0.995	1.106	1.473	1.646	0.943	1.374	2.116	0.1	0.082
Chr	1.169	0.564	0.870	1.797	1.439	0.514	1.071	1.580	0.01	0.017
BbF	1.706	1.660	1.952	3.010	1.606	1.260	1.819	2.422	0.1	0.250
BkF	0.977	0.978	0.973	1.330	0.980	0.917	1.411	1.662	0.1	0.110
BaP	0.664	0.252	0.304	0.716	0.239	0.104	0.155	0.338	1	1
IcdP	0.490	0.258	0.310	0.735	0.233	0.112	0.196	0.372	0.1	0.310
DahA	0.115	0.054	0.058	0.119	0.041	0.031	0.037	0.071	1	0.290
BghiP	0.571	0.334	0.344	0.822	0.339	0.148	0.220	0.383	0.01	0.190
TEQ	1.260	0.704	0.808	1.516	0.744	0.465	0.685	1.086		
MEQ	1.631	1.025	1.183	2.185	1.056	0.678	1.009	1.535		

Table 4 Daily average exposure doses and life expectancy losses of PAHs exposure in different seasons of industrial and urban areas in Nanjing for adults and children.

Population	Season	Industrial area		Urban area	
		Daily average exposure dose [$\times 10^{-6}$mg/(kg·d)]	Life expectancy loss (min）	Daily average exposure dose [$\times 10^{-6}$mg/(kg·d)]	Life expectancy loss (min)
Adult	Spring	0.154	2.999	0.091	1.772
	Summer	0.086	1.676	0.057	1.106
	Autumn	0.099	1.924	0.084	1.630
	Winter	0.185	3.609	0.132	2.585
Children	Spring	0.097	1.897	0.057	1.121
	Summer	0.054	1.060	0.036	0.700
	Autumn	0.062	1.217	0.053	1.031
	Winter	0.117	2.283	0.084	1.635

4. Conclusions

The $PM_{2.5}$ levels in this typical eastern China megacity were much higher than the WHO AQG, and most were higher than the secondary China AQS, especially in the industrial area and during the cold season. The concentrations of $PM_{2.5}$-bound PAHs and n-alkanes were higher in cold season than warm season, and were slightly higher in the industrial area than urban area. The PAHs were mainly derived from motor vehicle exhausts (diesel and gasoline), mixed with soot and coke oven emissions in industrial area. Coal combustion contribute more PAHs in cold season than in warm season. The main sources of n-alkanes were biological (plants, microorganisms and paraffin) and motor vehicle exhausts. The anthropogenic sources (fossil fuels and coal-fired

sources) of n-alkanes in industrial area was stronger than that in urban. Spring and summer are more affected by plant sources of n-alkanes than winter. The carcinogenic mutagenic equivalent concentration, incremental lifetime cancer risk and life expectancy loss of $PM_{2.5}$-bound PAHs in industrial area were higher than that in urban area, and the seasonal pattern was: winter > spring > autumn > summer. The incremental lifetime cancer risk to adults and children caused by inhaled airborne PAHs was at an acceptable level, and the incremental lifetime cancer risk and life loss for adults was higher than that of children. $PM_{2.5}$ and associated organic pollutants in megacity were affected by temperature and precipitation. Precipitation effectively alleviated the $PM_{2.5}$ pollution, and temperature was slightly negatively correlated with each particulate contaminant.

In winter and spring, the health risks of exposure to organic pollutants in $PM_{2.5}$ cannot be ignored. It was recommended that the motor vehicle emissions can be the key environmental management target for atmospheric PAHs and n-alkanes, while for the ambient air in industrial area, coal purification can be an effective control method. Moreover, artificial rainfall may also be an effective management choice to reduce $PM_{2.5}$ pollution.

Acknowledgements

This study was supported by the Natural Science Foundation of China (NSFC 41471418 and 91543205), and the Startup Foundation for Introducing Talent of NUIST (2017r001).

Supplementary materials

The supplementary materials related to this article are found in Tables S1-S3 and Figures S1-S4.

References

Armstrong, B., Hutchinson, E., Unwin, J., Fletcher, T., 2004. Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: a review and meta-analysis. Environ Health Perspect. 112, 970-978.

Billet, S., Garcon, G., Dagher, Z., Verdin, A., Ledoux, F., Cazier, F., Courcot, D., Aboukais, A.,

Shirali, P., 2007. Ambient particulate matter ($PM_{2.5}$): physicochemical characterization and metabolic activation of the organic fraction in human lung epithelial cells (A549). Environ. Res. 105, 212-223.

Chen, F., Hu, W., Zhong, Q., 2013. Emissions of particle-phase polycyclic aromatic hydrocarbons (PAHs) in the Fu Gui-shan Tunnel of Nanjing, China. Atmos. Res. 124, 53-60.

Chen, Y., Luo, X.S., Zhao, Z., Chen, Q., Wu, D., Sun, X., Wu, L., Jin, L., 2018. Summer-winter differences of $PM_{2.5}$ toxicity to human alveolar epithelial cells (A549) and the roles of transition metals. Ecotoxicol. Environ. Saf. 165, 505-509.

Chow, J.C., Watson, J.G., Fujita, E.M., Lu, Z., Lawson, D.R., Ashbaugh, L.L., 1994. Temporal and spatial variations of $PM_{2.5}$ and PM_{10} aerosol in the Southern California air quality study. Atmos. Environ. 28, 2061-2080.

Curtis, L., Rea, W., Smith-Willis, P., Fenyves, E., Pan, Y., 2006. Adverse health effects of outdoor air pollutants. Environ. Int. 32, 815-830.

Fan, X., Chen, Z., Liang, L., Qiu, G., 2018. Atmospheric $PM_{2.5}$-Bound polycyclic aromatic hydrocarbons (PAHs) in Guiyang city, southwest China: concentration, seasonal variation, sources and health risk assessment. Arch. Environ. Con. Tox. 1-12.

Fang, G.C., Chang, C.N., Wu, Y.S., Fu, P.C., Yang, I.L., Chen, M.H., 2004. Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung. Sci. Total Environ. 327, 135-146.

Feng, B., Li, L., Xu, H., Wang, T., Wu, R., Chen, J., Zhang, Y., Liu, S., Ho, S.S.H., Cao, J., 2018. $PM_{2.5}$-bound polycyclic aromatic hydrocarbons (PAHs) in Beijing: Seasonal variations, sources, and risk assessment. J. Environ. Sci-China. 77, 11-19.

Fontes, T., Li, P., Barros, N., Zhao, P., 2017. Trends of $PM_{2.5}$ concentrations in China: A long term approach. J. Environ. Manage. 196, 719-732.

Gamo, M., Oka, T., Nakanishi, J., 1995. A method evaluating population risks from chemical exposure: a case study concerning prohibition of chlordane use in Japan. Regul. Toxicol. Pharmacol. Rtp. 21, 151-157.

Gröllert, C., Puxbaum, H., 2000. Lipid organic aerosol and snow composition at a high alpine site in the fall and the spring season and scavenging ratios for single compounds. Water Air Soil Poll. 117, 157-173.

Gutierrez-Castillo, M.E., Roubicek, D.A., Cebrian-Garcia, M.E., De Vizcaya-Ruiz, A., Sordo-Cedeno, M., Ostrosky-Wegman, P., 2006. Effect of chemical composition on the induction of DNA damage by urban airborne particulate matter. Environ. Mol. Mutagen. 47, 199-211.

Hong, Z., Hong, Y., Zhang, H., Chen, J., Xu, L., Deng, J., Du, W., Zhang, Y., Xiao, H., 2017. Pollution xharacteristics and source apportionment of $PM_{2.5}$-bound n-Alkanes in the Yangtze River Delta, China. Aerosol Air Qual. Res. 17, 1985–1998.

Hopke, P.K., Gladney, E.S., Gordon, G.E., Zoller, W.H., Jones, A.G., 1976. The use of multivariate analysis to identify sources of selected elements in the Boston urban aerosol. Atmos. Environ. 10, 1015-1025.

Hussein, T., Karppinen, A., Kukkonen, J., Härkönen, J., Aalto, P.P., Hämeri, K., Kerminen, V.-M., Kulmala, M., 2006. Meteorological dependence of size-fractionated number concentrations of urban aerosol particles. Atmos. Environ. 40, 1427-1440.

Jung, K.H., Yan, B., Chillrud, S.N., Perera, F.P., Whyatt, R., Camann, D., Kinney, P.L., Miller, R.L., 2010. Assessment of benzo(a)pyrene-equivalent carcinogenicity and mutagenicity of residential

indoor versus outdoor polycyclic aromatic hydrocarbons exposing young children in New York City. Inter. J. Env. Res. Pub. Heal. 7, 1889-1900.

Kang, M., Ren, L., Ren, H., Zhao, Y., Kawamura, K., Zhang, H., Wei, L., Sun, Y., Wang, Z., Fu, P., 2018. Primary biogenic and anthropogenic sources of organic aerosols in Beijing, China: Insights from saccharides and n-alkanes. Environ. Pollut. 243, 1579-1587.

Li, L., Ho, S.S.H., Chow, J.C., Watson, J.G., Lee, F.S.C., Cui, L., Gao, Y., Dai, W., Ho, K.F., Huang, Y., Cao, J., 2017. Characterization and health risk assessment of $PM_{2.5}$-bound organics inside and outside of Chinese smoking lounges. Chemosphere. 186, 438-445.

Li, W., Peng, Y., Bai, Z., 2010. Distributions and sources of -alkanes in $PM_{2.5}$ at urban, industrial and coastal sites in Tianjin, China. J. Environ. Sci-China. 22, 1551-1557.

Li, Y., Cao, J., Li, J., Zhou, J., Xu, H., Zhang, R., Ouyang, Z., 2013. Molecular distribution and seasonal variation of hydrocarbons in $PM_{2.5}$ from Beijing during 2006. China Part. 11, 78-85.

Lim, S.S., Vos, T., Flaxman, A.D., Danaei, G., Shibuya, K., Adair-Rohani, H., AlMazroa, M.A., Amann, M., Anderson, H.R., 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. The Lancet. 380, 2224-2260.

Liu, D., Lin, T., Syed, J.H., Cheng, Z., Xu, Y., Li, K., Zhang, G., Li, J., 2017. Concentration, source identification, and exposure risk assessment of $PM_{2.5}$-bound parent PAHs and nitro-PAHs in atmosphere from typical Chinese cities. Sci. Rep. 7, 10398.

Luo, X., Zhao, Z., Xie, J., Luo, J., Chen, Y., Li, H., Jin, L., 2019. Pulmonary bioaccessibility of trace metals in $PM_{2.5}$ from different megacities simulated by lung fluid extraction and DGT method. Chemosphere. 218, 915-921.

Luo, X.S., Ip, C.C.M., Li, W., Tao, S., Li, X.D., 2014. Spatial–temporal variations, sources, and transport of airborne inhalable metals (PM_{10}) in urban and rural areas of northern China. Atmos. Chem. Phys. 14, 13133-13165.

Luo, X.S., Zhao, Z., Chen, Y., Ge, X., Huang, Y., Suo, C., Sun, X., Zhang, D., 2017. Effects of emission control and meteorological parameters on urban air quality showed by the 2014 Youth Olympic Games in China. Fresen. Environ. Bull. 26, 4798-4807.

Meng, Q., Fan, S., Jiabao, H.E., Sun, Y., Zhang, J., Zhang, Y., 2015. Source apportionment of polycyclic aromatic hydrocarbons in fine and coarse particulate matter during winter in northern suburbs of Nanjing. Environ. Chem. . 33, 2172-2179.

Nagy, A.S., Szabó, J., 2017. Characterization of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in the ambient air of Győr, Hungary. Polycyclic Aromatic Compounds. 1-14.

Nisbet, I.C.T., Lagoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. Rtp. 16, 290-300.

Peng, L., Tian, J.M., Chen, M.L., Duan, Y., 1999. Distribution features of alkanes in TSP of Taiyuan city and its environmental significance. Acta Sedimentol. Sin. 17, 836-839.

Pietrogrande, M.C., Mercuriali, M., Perrone, M.G., Ferrero, L., Sangiorgi, G., Bolzacchini, E., 2010. Distribution of n-alkanes in the Northern Italy aerosols: data handling of GC-MS signals for homologous series characterization. Environ. Sci. Technol. 44, 4232-4240.

Qi, S.H., Sheng, G.Y., Fu, J.M., Wang, Z.S., Min, Y.S., 2002. Source apportionment experiment of polycyclic aromatic hydrocarbons (PAHs) in aerosols from Macao. Environ. Sci-China. 22, 118-122.

Qu, C., Li, B., Wu, H., Wang, S., Giesy, J.P., 2015. Multi-pathway assessment of human health risk

posed by polycyclic aromatic hydrocarbons. Environ. Geochem. Health. 37, 587-601.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. Environ. Sci. Technol. 27, 1892-1904.

Samanta, S.K., Singh, O.V., Jain, R.K., 2002. Polycyclic aromatic hydrocarbons: environmental pollution and bioremediation. Trends Biotechnol. 20, 243-248.

Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R., 2002. Measurement of emissions from air pollution sources. 5. C_1-C_{32} organic compounds from gasoline-powered motor vehicles. Environ. Scie. Technol. 35, 1716-1728.

Simcik, M.F., Eisenreich, S.J., Lioy, P.J., 1999. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmos. Environ. 33, 5071-5079.

Soclo, H.H., Garrigues, P., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar. Pollut. Bull. 40, 387-396.

US EPA, 1986. Superfund public health evaluation manual. EPA/540/186/060, 1-52.

US EPA, 1989. Risk assessment guidance for superfund volume1: Human health evaluation manual (Part A). EPA/540/1-89/002, 35-52.

US EPA, 1997. Exposure factors handbook. EPA/600/P-95/002, 104-126.

Wang, Q., Liu, M., Yu, Y., Li, Y., 2016. Characterization and source apportionment of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons from Shanghai city, China. Environ. Pollut. 218, 118-128.

Yang, Y., Hu, J., Tao, S., 2005. Loss of life expectancy analysis for cancer risk in Tianjin Area. Environ. Sci. 26, 168-172.