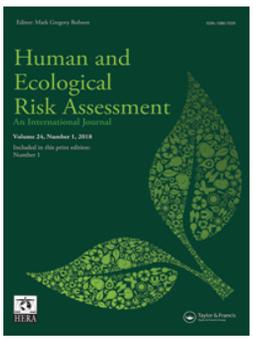

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Polycyclic aromatic hydrocarbons (PAHs) concentration levels, pattern, source identification, and human risk assessment in foliar dust from urban to rural areas in Nanjing, China

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ABSTRACT

Environmental health is an essential component of quality of life in modern societies. Foliar dust contains polycyclic aromatic hydrocarbons (PAHs) that may have harmful effects on human health. The PAHs concentration of foliar dust is useful to assess environmental air pollution. Our results indicate that: (1) the highest levels of PAHs were distributed in urban areas, with a mean of 3430.23 $ng{\cdot}g^{-1}$, lower mean concentrations were found in suburban (2282.12 $ng{\cdot}g^{-1}$), and rural areas (1671.06 $ng{\cdot}g^{-1}$). (2) Diagnostic ratios and principal component analysis were used to identify the sources of PAHs: Gasoline vehicle traffic emissions were the predominant source in urban areas, along with coal and coke combustion. In suburban areas, the main sources were petroleum combustion (especially liquid fossil fuels) and coal combustion. Coal and wood combustion were the primary source of PAHs in foliar dust in rural areas. (3) The incremental lifetime cancer risk (ILCR), estimated based on the results of this study indicate that urban residents were potentially exposed to high cancer risk via both dust ingestion and dermal contact. We conclude that urbanization has significant effects on the PAH concentrations of foliar dust, illustrating the importance of trees in improving air quality in urban areas.

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foliar dust; PAHs concentration; sources analysis; health risk assessment

Introduction

Dust is a sink and source of pollutants, especially atmospheric particles, and can provide useful information about the aggregation of specific particulate materials from local pollution sources over a long period of time (Xu *et al.* 2014; Xu *et al.* 2016; Adachi *et al.* 2005). Rapid urbanization has resulted in the emission of several pollutants in urban areas (Ahmed *et al.* 2006), which have placed a heavy burden on the local environment. One group of contaminants in dust are polycyclic aromatic hydrocarbons (PAHs), which have become a matter of major concern (Ravindra *et al.* 2008). They are released from both natural and anthropogenic

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sources (vehicle emissions, coal and fossil fuel combustion, chemical, oil spill coal tar, industrial processing, straw and firewood burning, etc.) (Kang *et al.* 2010; Pongpiachan *et al.* 2015). As a set of Persistent Organic Pollutants (POPs), PAHs are typical aggregate pollutants that are toxic and have long-term persistence in the environment (Song *et al.* 2015).

PAHs produced by human activities have been detected in various environmental media, such as atmosphere, soil, urban surface dust, sediment and precipitation (He *et al.* 2014), and house dust (inhalation and ingestion), which has received a great deal of attention, and people spend > 90% of their times in house environments, leading to investigations of these environments for PAHs (Mercier *et al.* 2011. Yang *et al.* 2015). It has been discussed in the literature that vegetation plays a key role in the cycling of PAHs in terrestrial ecosystems (Nicola *et al.* 2017; Li *et al.* 2014; Bakker *et al.* 2001; Howsam *et al.* 2010). Previous research has reported that vegetation may alleviate approximately 41% of the total PAHs emission in urban areas and 4% in rural areas (Wagrowski *et al.* 1996). Foliar represents an exchange surface between air and vegetation, and is always taken into account when modelling PAH cycling (Behrendt *et al.* 1993; Priemer *et al.* 2002). Gaseous PAHs easily pass into the stomatal pathway or diffuse into the cuticle and further inside the leaf (Bakker *et al.* 2001), whereas particle-bound PAHs are deposited on the leaf surface (Belis *et al.* 2011). Urban fugitive dust can accumulate on the leaf surface to form foliar dust. However, interactions of environment factors can result in the complicated dynamics of dust-retention by leaves. Hence, foliar dust deserves particular attention. Given that children engage in frequent hand-to-mouth activities, they are likely to be exposed to foliar dust (Shi *et al.* 2011). Therefore, a better understanding of the accumulation of PAHs accumulation in leaves could effectively help identify emissions sources and estimate the contamination levels of PAHs in the atmosphere (Marsili *et al.* 2001; Librando *et al.* 2002; Barber *et al.* 2003).

Several previous studies quantitatively analyzed the element (Ram *et al.* 2014; Simon *et al.* 2014; Simon *et al.* 2011) and heavy metal concentrations of foliar dust (Yin *et al.* 2011; Qiu *et al.* 2009; Bhattacharya *et al.* 2013). However, the existing literature provides limited results of the comprehensive assessment of the levels, source, and cancer risk of PAHs in foliar dust. Therefore, PAH emissions have the potential to affect human health, especially when aggregated in human environments located in areas of rapid industrialization and urbanization, such as Nanjing (Xu *et al.* 2016). This is attributed to the fact that urbanization substantially affects the PAH distribution (Wang *et al.* 2015). Thus, it is critical to select an appropriate technique that can cost-effectively provide quantitative measurements of the PAH pollution levels. In this study, the specific objectives were: (1) to measure the concentrations of PAHs of urban to rural foliar dust in Nanjing; (2) to identify of various sources of PAHs by diagnostic ratios and principal component analysis (PCA); (3) to evaluate the risk of human exposure to PAHs in Nanjing foliar dust.

Methods and materials

Study area

As an eastern city located in the Yangtze Delta Region (YDR), with rapid urbanization and industrialization as well as rapidly increases levels of traffic and population density, Nanjing is a core economic development zone in China, and has become a complex industrial city, and process electronics, automobiles, and chemicals (Xu *et al.* 2013; Su *et al.* 2012; Guo *et al.* 2003).

The current study was carried out in the city of Nanjing, which is characterized by high levels of human activities. The study site was an area of afforestation in the city Centre, as well as into urban, suburban, and rural areas. The sampling sites were specific classified into urban areas (31°52′∼32°14′N 118°34′∼119°14′E), which included eight districts (Xuanwu, Baixia, Gulou, Qinhuai, Jianye, Xiaguan, Yuhuatai, and Qixia), with high-density population and heavy traffic around suburban areas (31°37′∼32°36′N 118°21′∼119°06′E), which included three districts (Pukou, Liuhe, and Jiangning) with lower traffic and other anthropogenic activities, and rural areas (31°13′∼31°47′N 118°41′∼119°13′E), which were far from city Centre, where the low density of residents and traffic lead to low pressure in this area (Lishui and Gaochun) (Figure 1).

Sample collection

The tree species selected for this study included *Firmiana simplex, Osmanthus fragrans Lours, Photinia serrulata Lindl*, and *Symplocos sumuntia*, which have been widely used as

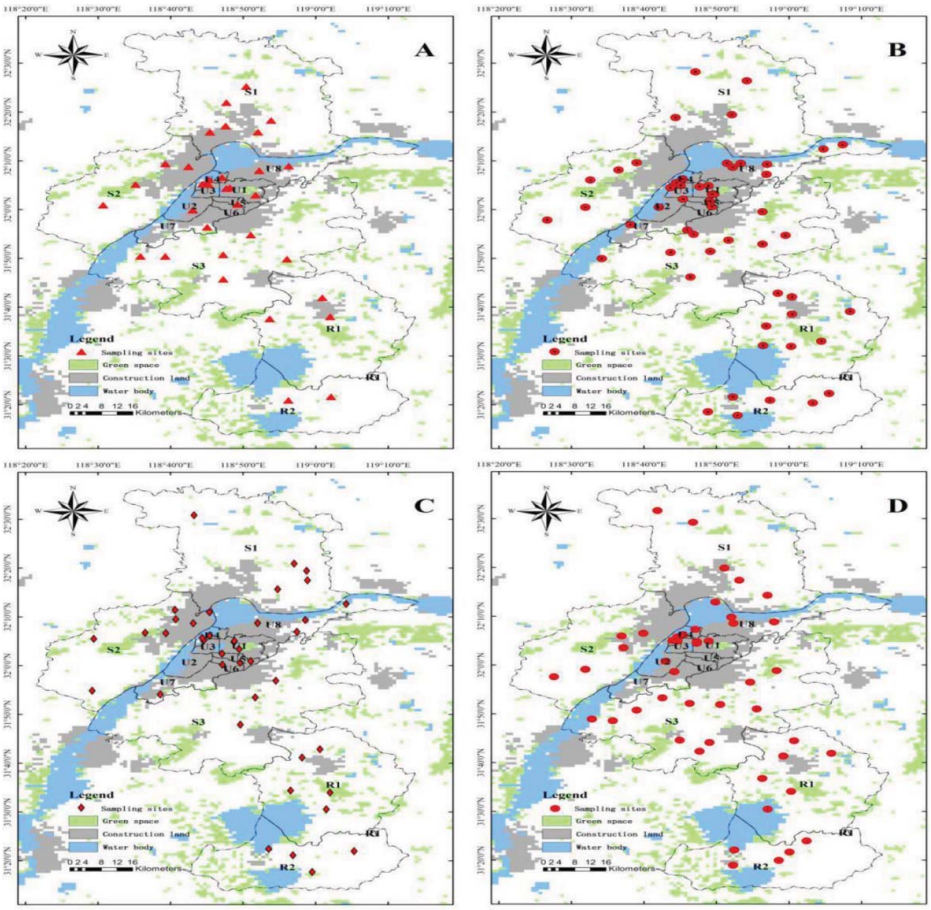

Figure 1. (A) Study areas and sampling sites of *Firmiana simplex* leaves. (B) Study areas and sampling sites of *Osmanthus fragrans Lours* leaves. (C) Study areas and sampling sites of *Photinia serrulata Lindl* leaves. (D) Study areas and sampling sites of *Symplocos sumuntia* leaves.

city-greening tree species in the south of China. Samples were collected in August 2015 after a period of heavy rain and strong winds. For each tree species in each area, five trees were selected for sampling. None of the tree leaf (100 pieces) samples was suffering from obvious pests or disease. They were collected from the inner and outer canopy of east, south, west, and north facing directions at a height of approximately 1.5∼4.0 m above ground level with a pruner. All sample leaves were carefully collected to minimize touching of the leaf surface and were kept in a cool box (−20°C) during transport and in the laboratory prior to analysis.

Sample preparation

The leaf samples were washed using Milli-Q water (250 mL, Milliporem Bedford, MA, USA) in an ultrasonic cleaner (HS-1010A, Shenzhen, China) for 10 min (Baranyai *et al.* 2015). The dust containing the suspension was filtered through a 150-μm sieve. The procedure was repeated with 50 mL of Milli-Q water, which was filtered and added to the samples. This 300 mL of dust containing suspension was dried with a vacuum freeze-drier (Labconco, Kansas City, MO, USA) for 5 d at −83°C to a constant weight and then stored at −20°C until further extraction.

Chemical and materials

A composite standard solution of 16 PAHs was purchased from Sigma-Aldrich (Dr, Germany), and included naphthalene (Nap), acenaphthylene (Acp), acenaphthene (Acp), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(*a*) anthracene (BaA), chrysene (Chr), benzo(*b*)fluoranthene (BbF), enzo(*k*)fluoranthene (BkF), benzo(*a*)pyrene (BaP), dibenzo(*a, h*)anthracene (DBA), benzo(*g, h, i*)perylene (BghiP), and indeno(*1,2,3-cd*)-pyrene (IcdP). In this study, the extracts were analyzed for PAHs using a high performance liquid chromatograph (HPLC, Shimadzu, LC-20A), with the 4.6 mm (ID) ×250 mm (L) column and 310 UV detector at 260 nm. A mixture of acetonitrile (ACN) and water was used as the mobile phase with solvent gradient method and a flow rate of 1.0 mL·min^{-1} at 35°C.

PAHs extraction

All PAHs were extracted from dust and leaves (0.5 g) with a 30-mL mixture of hexane and dichloromethane (v/v = 1:1) using an ultrasonic bath for 1.5 h. This step was repeated three times. The solvent fractions were concentrated using a vacuum rotary evaporator and solvent-exchanged to hexane. The concentrated extract was cleaned via a silica column chromatography (10 mm (ID) × 350 mm (L), 10 g of silica gel, and 20 mm length of anhydrous sodium sulfate). Then, the aliphatic fraction was abandoned by washing it with hexane (25 mL), whereas the PAHs fraction was washed with 40 mL of dichlomethane after extraction, followed by filtration through a 0.22-μm fiberglass membrane and reconcentrated with gentle stream of nitrogen to exactly 1 mL through a blowing process at 25°C. The concentrated extracts were then analyzed for PAHs with a high performance liquid chromatograph (LC-20AT; Shimadzu, Kyoto, Japan).

Quality assurance and quality control

All analytical procedures were monitored using strict quality assurance and control measures. During sample analyses, matrix-unpolluted blanks (PAHs-free) were analyzed every five samples. Duplicates were also run every 10 samples and the samples were reanalyzed if the difference exceeded ±15%. The 16 PAHs were quantified using external standard methods. Experiments to assess foliar dust recovery were conducted by spiking known concentration standards (200 $ng{\cdot}g^{-1}$). The foliar dust average recoveries based on matrix-polluted samples, ranged from 78.31% for Nap and 78.32%∼102.45% for the remaining 15 PAHs.

Risk assessment of PAHs

The exposure risk from environmental PAHs was quantified using the incremental lifetime cancer risk (ILCR) based on the U.S. EPA standard models (US EPA 2014; Wang *et al.* 2011; Peng *et al.* 2011; Chen *et al.* 2006). The population of Nanjing area was divided into six groups according to age and gender: children (2∼10 years) male and female, adolescents (11∼17 years) male and female, and adults (18∼70 years), male and female. The ILCRs in terms of ingestion, dermal contact, and inhalation after exposure to foliar dust-borne PAHs in urbanization areas of Nanjing were calculated as follows:

$$ILCRs_{Ingestion} = CS \times (CSF_{Ingestion} \times (\sqrt[3]{BW\ /\ 70}) \times IR_{soil} \times EF \times ED)/(BW \times AT \times 10^6)$$

$$ILCRs_{Dermal} = CS \times (CSF_{Dermal} \times \left(\sqrt[3]{BW\ /\ 70}\right) \times SA \times AF \times ABS \times EF \times ED)/(BW \times AT \times PEF)$$

$$ILCRs_{Inhalation} = CS \times (CSF_{Inhalation} \times \left(\sqrt[3]{BW\ /\ 70}\right) \times IR_{air} \times EF \times ED)/(BW \times AT \times PEF)$$

$$ILCRs = ILCRS_{Ingastion} + ILCRs_{Dermal} + ILCRs_{Inhalation}$$

where CS is the sum of the converted PAH levels based on the toxic equivalents of BaP using the toxic equivalency factor (TEF). CSF is the carcinogenic slope factor ($mg{\cdot}kg^{-1}{\cdot}day^{-1}$). BW is body weight (kg), AT is average life span (years), EF is exposure frequency ($day{\cdot}year^{-1}$), ED is exposure duration (years), (for children: ED = 9; for adolescents: ED = 7; for adults: ED = 70) $IR_{Inhalation}$ is the inhalation rate ($m^3{\cdot}day^{-1}$), $IR_{Ingestion}$ is the soil intake rate ($mg{\cdot}day^{-1}$), SA is the dermal surface exposure (cm^2), AF is the dermal adherence factor ($mg{\cdot}cm^{-2}{\cdot}h^{-1}$), ABS is the dermal adsorption fraction, and PEF is the particle emission factor ($m^3{\cdot}kg^{-1}$). PEF is the particle emission factor ($m^3{\cdot}kg^{-1}$); and $CSF_{Ingestion}$, CSF_{Dermal}, and $CSF_{Inhalation}$ of BaP were addressed as 7.3, 25, and 3.85 ($mg{\cdot}kg^{-1}{\cdot}day^{-1}$), respectively, as determined by the cancer-causing ability of BaP.

Results and discussion

Levels and distribution of PAHs in foliar dust

The descriptive statistics of the total PAHs levels ($\sum_{16}$PAHs) and seven carcinogenic PAHs ($\sum_{7c}$PAHs) (BaA, Chr, BbF, BkF, BaP, IcdP, and DBA) in foliar dust from urban, suburban and rural areas from Nanjing are given in Table 1. In urban foliar dust, the sum of the 16 priority PAHs ($\sum_{16}$PAHs) varied from 139.82 to 13294.84 $ng{\cdot}g^{-1}$, with a mean of

Table 1. Concentrations of PAHs in foliar dust from different areas in Nanjing (ng·g^{-1}).

	Urban areas				Suburban areas				Rural areas			
Compounds	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
Nap	0.84	128.76	29.96	30.81	0.52	35.98	9.21	9.22	1.45	278.57	67.97	68.58
Acy	1.57	267.42	46.01	55.61	1.78	68.26	16.54	16.18	1.75	57.26	16.65	14.92
Ace	0.46	67.42	16.17	17.65	0.71	78.35	15.62	17.32	2.31	426.26	67.13	80.78
Phe	5.56	2167.74	430.34	484.60	4.26	874.51	218.83	245.74	3.05	285.51	71.69	74.07
Ant	0.17	156.65	26.15	31.15	2.55	110.63	27.34	28.02	1.03	95.35	16.83	17.61
Fl	0.53	88.09	19.11	20.48	0.49	202.67	23.59	38.24	0.26	138.53	20.91	26.56
Flu	5.34	1678.74	474.84	470.64	3.56	1643.24	416.90	399.14	2.56	1342.51	392.52	393.34
Pyr	2.34	3035.72	740.23	780.32	3.89	1322.52	402.36	388.22	1.94	983.51	272.34	257.47
BaA	1.56	287.98	63.44	63.33	0.52	543.14	84.00	109.54	2.45	328.52	97.72	95.95
Chr	5.41	1963.51	423.83	449.77	3.52	942.51	209.98	236.25	3.31	897.36	212.60	237.41
BbF	3.52	745.52	151.92	177.47	2.85	582.25	126.73	151.22	2.94	414.36	100.32	113.16
BkF	2.42	452.44	96.77	109.21	1.74	187.64	48.02	42.26	1.01	125.43	26.39	27.76
BaP	4.58	984.34	249.96	254.60	3.51	725.60	181.99	189.56	1.78	436.76	103.76	106.52
IcdP	3.75	3789.74	852.85	799.45	2.86	962.51	224.87	246.90	3.03	339.51	93.01	85.93
DBA	1.67	244.73	39.25	44.30	1.05	124.52	36.22	33.43	1.61	157.52	31.34	34.71
BghiP	2.89	1278.52	326.76	278.26	3.85	890.45	239.94	254.47	1.03	367.81	79.89	82.82
$\sum_{7c}$PAHs	70.44	4341.53	1261.94	1170.13	23.66	3503.77	911.81	885.67	18.83	2298.16	665.13	600.41
$\sum_{16}$PAHs	139.82	13294.84	3897.60	3430.23	101.91	8107.16	2282.12	2056.90	41.46	5479.95	1671.06	1473.00

Notes: SD denotes standard deviation; ND denotes not detected (below the detection limit).

3897.60 ng·g^{-1}. The mass concentrations of $\sum_{7c}$PAHs ranged from 70.44 to 4341.53 ng·g^{-1}, with a mean of 1261.94 ng·g^{-1}, which accounted for 12.09 to 73.86% of the $\sum_{16}$PAHs, with a mean of 34.01%. In suburban areas, the total concentrations of PAHs ranged from 101.91 to 8107.16 ng·g^{-1}, with a mean value of 2282.12 ng·g^{-1}. The mass concentrations of $\sum_{7c}$PAHs ranged from 23.66 to 3503.77 ng·g^{-1}, with a mean of 911.81 ng·g^{-1}, which accounted for 4.17% to 70.82% of $\sum_{16}$PAHs, with a mean of 38.54%. In rural foliar dust, the concentrations of $\sum_{16}$PAHs ranged from 18.83 to 5479.95 ng·g^{-1} in rural areas, with a mean value of 1671.06 ng·g^{-1}. The mass concentrations of $\sum_{7c}$PAHs ranged from 18.83 to 2298.16 ng·g^{-1}, with a mean of 665.13 ng·g^{-1}, which accounted for 9.59% to 54.76% of $\sum_{16}$PAHs.

A wide range of $\sum_{7c}$PAHs and $\sum_{16}$PAHs concentrations were observed in Nanjing foliar dust, and decreased in the following order: urban > suburban > rural areas. The mean level of $\sum_{16}$PAHs in this study was relatively higher than the mean levels in the United Kingdom (0.002 mg·kg^{-1}), Norway (0.0069 mg·kg^{-1}), Canada (0.0011 mg·kg^{-1}), and Australia (0.0033 mg·kg^{-1}) (Hassanien and Adbel-Latif. 2008). However, the results were lower than the urban street dust levels in Guangzhou (4800 ng·g^{-1}, Wang *et al.* 2011); Taiwan (65.8 mg·kg^{-1} in traffic site); Birmingham, UK (12.56−93.70 mg·kg^{-1}); and Ulsan, Korea (11.8−245 mg·kg^{-1}, Fang *et al.* 2004; Dong and Lee 2009). By contrast, the PAHs concentration of street dust, and the high contamination level of PAHs in foliar dust may be attributed to size-fractionated particles. Ram et al (2014) found that foliar dust from tree leaves consists of fine particles smaller than 30 μm, but street dust was composed of particles of different sizes, mainly particles larger than 30 μm. The intense urban traffic activities had a great impact on the environment, and fine and ultra-fine particles are mainly derived from vehicular emissions. As there are large numbers of cars in the traffic areas in Nanjing, fine and ultrafine particles that are produced adhere to the surface of leaves, and contribute to the high content of PAHs in foliar dust at urban sites, which suggests that adjacent

anthropogenic actives had a stronger effect on the pollution characteristics than land use types, our result agree with the conclusions of (Li *et al.* 2017).

Composition profiles in foliar dust

The 16 PAH compounds were divided into five groups: 2-ring, 3-ring, 4-ring, 5-ring, and 6-ring PAHs. In urban area, foliar dust PAHs with 4 rings and 5 rings were the primary components (Figure 2), and accounted for 43.68% and 34.68% of the total PAHs, on average, followed by the 3-, 6-, and 2-ring PAHs at 13.80%, 7.08%, and 0.77%, respectively. The high-molecular-weight (HMW) PAHs (4∼6 rings), ranged from 54.93% to 95.69 %, with a mean of 84.28%, and were the dominant PAH compounds in all of the foliar dust samples. IcdP was observed to have the highest concentration (852.85 $ng{\cdot}g^{-1}$), followed by the concentrations of Pyr, Flu, Phe, and Chr, with the concentrations of 740.23, 474.84, 430.34, and 423.83 $ng{\cdot}g^{-1}$, respectively. The concentrations of Nap, Ace, and Acy in foliar dust were lowest due to their solubility, vapor pressure, and input. In terms of the relative compositions of the foliar dust in suburban areas, 4-ring and 5-ring PAHs predominated at 58.36% and 19.36%, respectively, followed by 3-, 6-, and 2-ring PAHs at 13.23%, 12.10%, and 0.40%, respectively The HMW PAHs, ranged from 28.99 to 98.63%, with a mean of 82.68%, and were the dominant PAH compounds in all of the foliar dust samples. Flu was observed to have the highest concentration (416.90 $ng{\cdot}g^{-1}$), followed by Pyr, BghiP, IcdP, Chr with concentrations of 402.36, 239.94, 224.87, and 209.98 $ng{\cdot}g^{-1}$, respectively. In the rural area, the relative composition of the ring PAHs ranked from high to low prevalence as follows: 4-, 5-, 3-, 6-, and 2-ring PAHs, at 58.36%, 17.36%, 11.56%, 6.66%, and 4.07%, respectively. The HMW PAHs, ranged from 13.42 % to 92.69%, with a mean of 79.32%, and were the dominant PAH compounds in all of the foliar dust samples. Flu was observed to have the highest

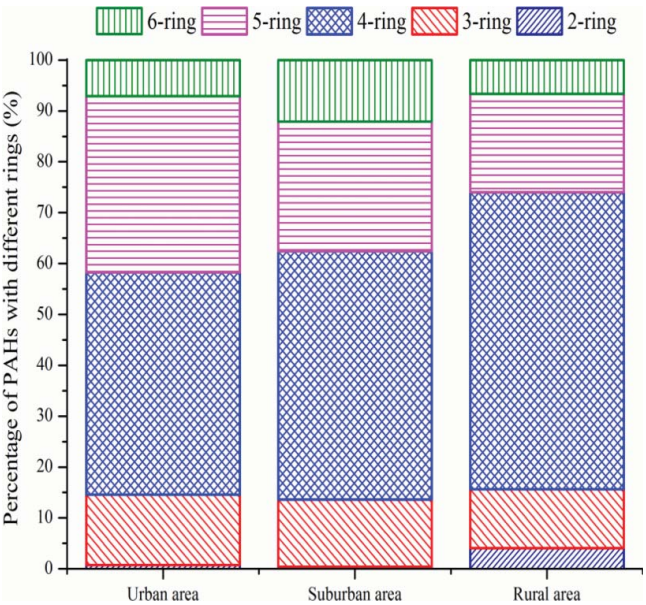

Figure 2. The percentage of PAHs with different rings of Nanjing area.

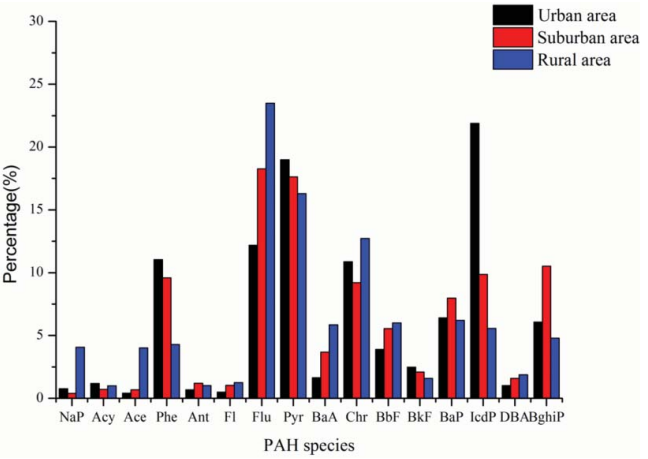

Figure 3. Mean of individual PAHs in foliar dust from different functional areas in Nanjing.

concentration (392.52 ng·g^{-1}), followed by Pyr, Chr, BaP, and BbF with concentrations of 272.34, 212.60, 103.76, and 100.32 ng·g^{-1}, respectively.

In terms of the composition profiles, HMW PAHs were the predominant PAHs in foliar dust from urban, suburban, and rural areas, which was similar to previously reported findings. HMW PAHs contributed 62%–94% of the $\sum_{16}$PAHs mass in the surface dust samples in Guangzhou (Wang *et al.* 2011). Lee et al (2009) reported that 4-rings PAHs accounted for the highest percentage in Ulsan, South Korea. As for the individual PAH compositions, the PAH profile was similar to the results found in street dust in Guangzhou (Wang *et al.* 2011), and Shanghai (Zheng *et al.* 2016), and was similar to those of PAHs associated with fine particulate matters in Nanjing (He *et al.* 2014). Indeed, LMW PAHs were dominant in the gas phase as reported previously, and HMW PAHs were exclusively present in the particulate phase (Possanzini *et al.* 2004; Alfani *et al.* 2005), demonstrating how foliar dust is an important source of HMW PAHs, which is reported to be more toxic and persistent in the environment.

Source identification of foliar dust PAHs

Diagnostic ratios analysis

Anthropogenic PAHs are mainly derived from incomplete combustion of fossil fuel or biomass, and leakage of oil or petroleum products (Boonyatumanond *et al.* 2007). Diagnostic ratios are the concentration ratios of specific pairs of PAHs, are generally used as tool to identify the origins of PAHs, such as Ant/(Ant + Phe), Flu/(Flu + Pyr), BaA/(BaA + Chr), and IcdP/(IcdP+BghiP) which were chosen for investigation in this study (Mannino and Orecchio. 2008; Yunker *et al.* 2002). The ratio of Ant/(Ant + Phe) was < 0.1 indicating a petroleum source, whereas values > 0.1, indicating a pyrogenic (Boonyatumanond *et al.* 2007). Meanwhile, Flu/(Flu+Pyr) < 0.4 indicates a petrogenic/unburned petroleum, between 0.4 and 0.5 implies fossil fuel combustion, and a ratio of > 0.5 is the characteristic of biomass orcoal combustion (Boonyatumanond *et al.* 2007; De *et al.* 2009). Ratios of BaA/(BaA+Chr) < 0.2 indicate petrogenic source, between 0.2 and 0.35 indicate petroleum combustion, and > 0.35 indicates biomass or coal combustion (Boonyatumanond *et al.* 2007;

Simcik *et al.* 1999). IcdP/(IcdP +BghiP) < 0.2, indicates petrogenic and petroleum sources, and IcdP/(IcdP+BghiP) between 0.2 and 0.5 indicates petroleum combustion, IcdP / (IcdP+BghiP) > 0.5 indicates contribution of biomass or coal combustion (Ravindra *et al.* 2008; Tobiszewski *et al.* 2012; Yunkerr *et al.* 1999).

As shown in Figure 4A, in urban foliar dust the ratios of Ant/(Ant+Phe) were generally lower than 0.1, whereas the ratios of Flu / (Flu+Pyr) were lower than 0.5, suggesting a mixed source of petroleum and liquid fossil fuel combustion. The ratios of BaA/(BaA+Chr), IcdP/(IcdP+BghiP) with averages of 0.19 and 0.22, which indicated the PAHs come from petroleum combustion (liquid fossil fuel, vehicle, and crude oil combustion). Furthermore, the result indicative of vehicular traffic emissions as the main sources of PAHs (Yunkerr *et al.* 1999). In suburban areas (Figure 4B), Ant/(Ant + Phe) and Flu/(Flu+Pyr),

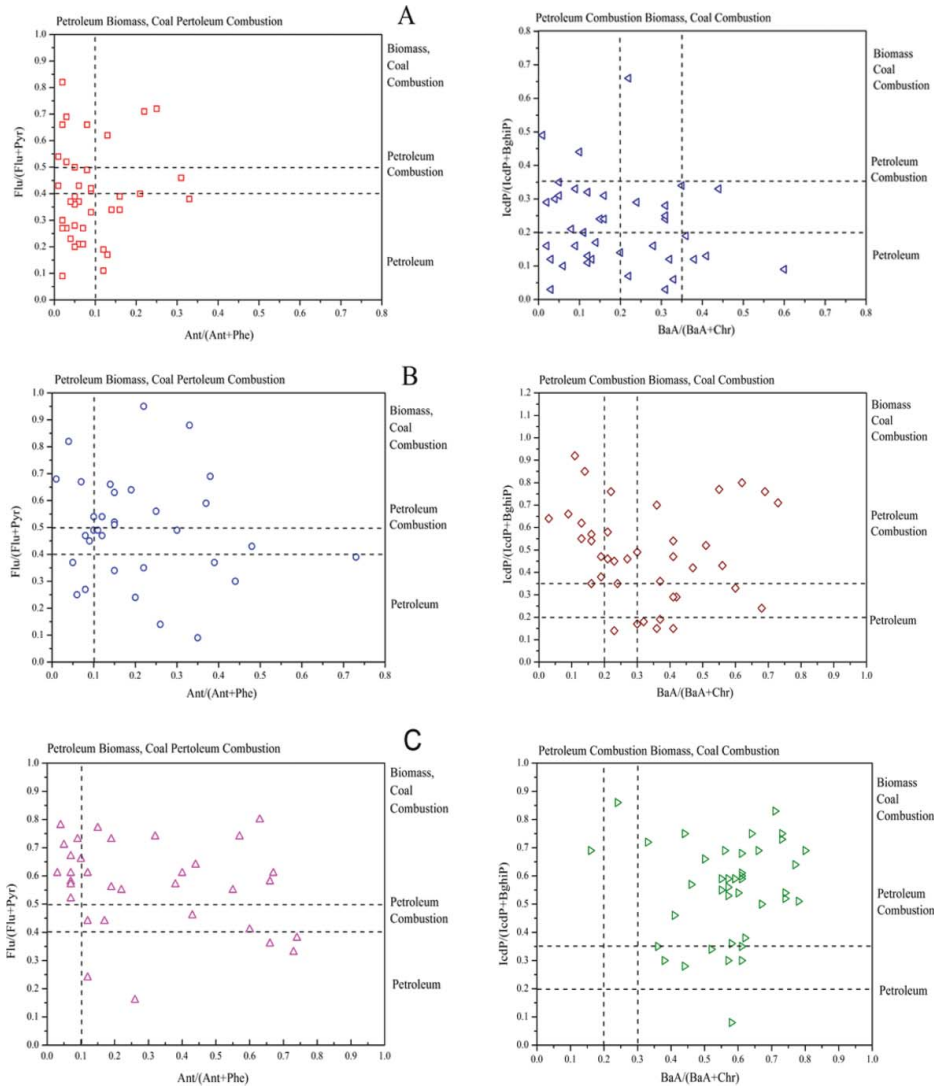

Figure 4. Cross plot for the isomeric ratios of Ant/(Ant+Phe) vs. Flu/(Flu+Pyr), and BaA/(BaA+Chr) vs. IcdP/(IcdP+BghiP) in foliar dust. (A) Urban area, (B) suburban area, and (C) rural area.

the averages were 0.18 and 0.50, respectively This result indicated that pyrogenic and liquid fossil fuel combustion were the main sources of PAHs. The value of BaA/(BaA+Chr), IcdP/(IcdP+BghiP) with means of 0.34 and 0.47, strongly indicates the contribution of petroleum combustion. In rural areas (Figure 4C), the ratios of Ant/(Ant + Phe) and Flu/(Flu+Pyr) were 0.28 and 0.57, respectively. This result suggests a mixed source of pyrogenic, biomass and coal combustion. The value of BaA/(BaA+Chr) > 0.35 (0.40) and IcdP/(IcdP+BghiP) > 0.5 (0.55), it strongly indicate the contribution of biomass, coal combustion.

Sources of PAHs with PCA

To improve the accuracy of the emissions source identification, the PCA method was applied. The results are presented in Figure 5. Where two principal components, probably representing two source categories, were identified. In urban areas (Figure 5a), the first factor (62.43% of variance) had high loading values of Pyr, BaP, Flu, and especially BghiP, which occurred as a result of gasoline vehicle emissions (Hong *et al.* 2007; Ravindra *et al.* 2008) and the burning

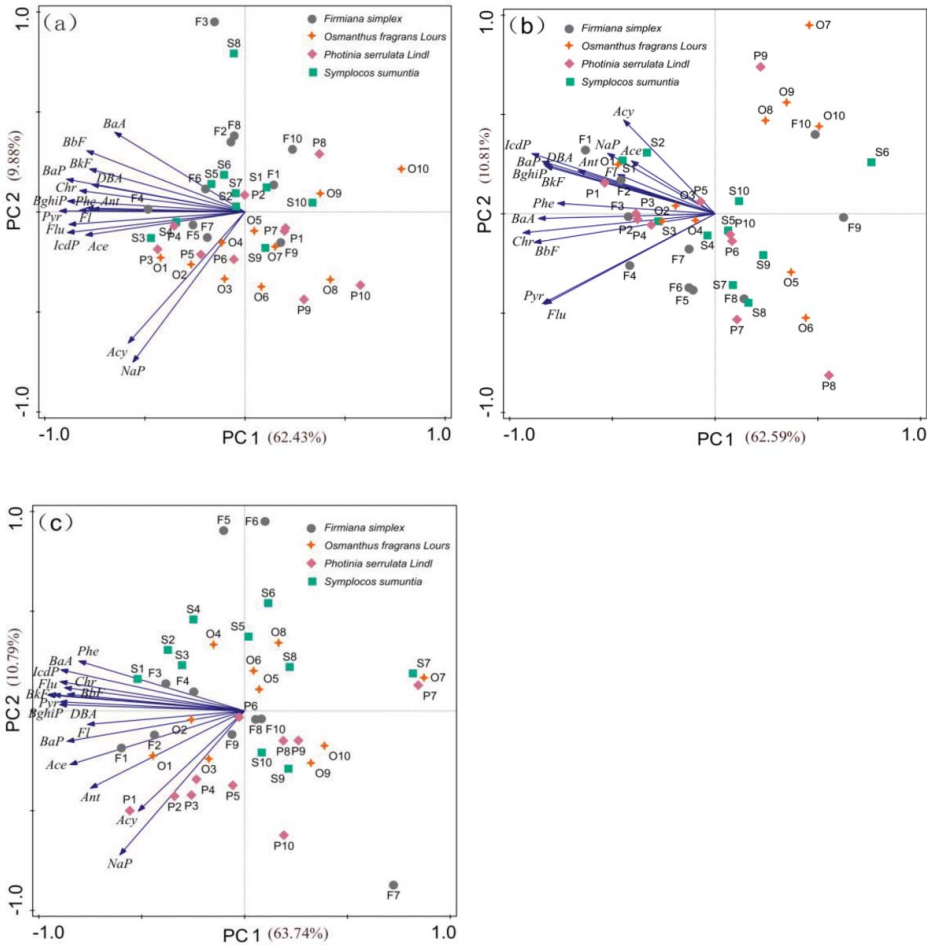

Figure 5. Principle component analysis of PAHs for urban area (A), suburban area (B), and rural area (C).

of coke combustion (Duval e al. 1981). The second factor, comprising 9.88% of the total variance, was high loading of Nap, Acy, Ace, Chr, and BbF, which were identified as markers of traffic tunnels (Nielsen *et al.* 1996). Hence, it could be suggested that vehicle emission and traffic tunnel suggested to be the main sources of PAHs in foliar dust in urban areas.

In suburban areas, Factor 1 explained 62.59% of the total PAH variance and was dominated by Phe, Ant, Flu, Pyr, Chr, BbF, BaP, IcdP, DBA, and BghiP (Figure 5b), which representative of vehicle emissions (Kong *et al.* 2010), whereas Ant and BbF are indicators of coal combustion (Kong *et al.* 2010). Factor 2 explained 10.81% of the total PAHs variances and was mainly dominated by Acy, Fl, and BaA. Acy is an indicator of industrial production (Wu *et al.* 2014), whereas Fl and BaA are coal combustion markers (Harrison *et al.* 1996; Li *et al.* 2003). Hence, the results from PCA revealed that vehicle emissions and coal combustion were probably the main sources of PAHs in foliar dust of Nanjing's suburban areas.

In rural areas, Factor 1 explained approximately 63.74% of the variance, with high loadings of Flu, Pyr, BaA, Chr, BbF, IcdP, and DBA (Figure 5c). Among these, DBA, Chr, and Flu, are indicators of vehicle emissions (Hong *et al.* 2007; Kong *et al.* 2010), whereas Pyr, Chr, and Flu, are indicators of coal and wood combustion (Wu *et al.* 2014). Furthermore, Flu is also an indicator of fossil fuel combustion and industrial processes, such as coke production (Lai *et al.* 2013). Factor 2 explained 10.79% of the total PAH variance and was dominated by Nap, Ace, Ant, and BaP. Among these, Ace, and BaP are indicators of vehicle emissions, whereas Nap indicates wood combustion (Kong *et al.* 2010). Furthermore, BaP is regarded to be a specific marker of coal combustion (Khalili *et al.* 1995). Hence, it suggested that automobile exhaust, coal, and wood combustion of PAHs were probably the main sources of PAHs in foliar dust in rural area.

Health risk assessment of PAHs in foliar dust

The toxic equivalency factors of BaP (BaP_{eq}) were provided by Nisbet and LaGoy (1992). BaP is the only carcinogenic PAH homologue with sufficient toxicity data available. Therefore, this compound was used to evaluate the level of PAH contamination in foliar dust along an urban-rural gradient in Nanjing. A toxicity equivalent factor (TEF) was used to determine the carcinogenicity of the PAHs from foliar dust (Table 2). In this study, the $\sum_{16}$TEQs concentration was in the range of 9.17∼1344.29 ng·g^{-1}, with a mean of 358.89 ng·g^{-1} in urban areas. The mean concentration of $\sum_{7c}$TEQs was 348.34 ng·g^{-1}, which was close to that of $\sum_{16}$TEQs; these factors were the major contributors (97.06%) to the total BaP_{eq} in dust samples. The contribution of PAHs to total BaP_{eq} decreased in the following order: BaP > DBA > IcdP > BbF > BkF > BaA > Chr. In suburban area, the BaP_{eq} concentration of $\sum_{16}$PAHs in the foliar dust samples ranged from 7.24∼1021.50 ng·g^{-1}, with a mean value of 272.45 ng·g^{-1}. The mean concentration of $\sum_{7c}$TEQs was 268.67 ng·g^{-1}, which contribution 98.61% to the total BaP_{eq}. The contribution of PAHs to total BaP_{eq} decreased as follows: BaP > DBA > IcdP > BbF > BaA > BkF > Chr. In rural areas, the BaPeq concentration of $\sum_{16}$PAHs ranged from 5.46∼604.64 ng·g^{-1}, with a mean value of 170.84 ng·g^{-1}. According to Canadian soil quality soil quality guidelines for the protection of environmental and human health (CCME 2010), the safe value of BaP in soil was 700 ng·g^{-1} (Liu *et al.* 2010). In urban areas, 87.5% of the dust samples showed concentrations below the safe value of 700 ng·g^{-1}, indicating a generally low risk from PAHs in urban foliar dust in Nanjing. However, five foliar dust samples showed concentrations above this

Table 2. Toxic equivalent concentration (BaP_{eq}) ($ng \cdot g^{-1}$) of PAHs in foliar dust in Nanjing.

		Urban TEQ			Suburban TEQ			Rural TEQ		
Compounds	TEFs	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Nap	0.001	0.00	0.13	0.03	0.00	0.04	0.01	0.00	0.28	0.07
Acy	0.001	0.00	0.27	0.05	0.00	0.07	0.02	0.00	0.06	0.02
Ace	0.001	0.00	0.07	0.02	0.00	0.08	0.02	0.00	0.43	0.07
Phe	0.001	0.01	2.17	0.43	0.00	0.87	0.22	0.00	0.29	0.07
Ant	0.010	0.00	1.57	0.26	0.03	1.11	0.27	0.01	0.95	0.17
Fl	0.001	0.00	0.09	0.02	0.00	0.20	0.02	0.00	0.14	0.02
Flu	0.001	0.01	1.68	0.47	0.00	1.64	0.42	0.00	1.34	0.39
Pyr	0.001	0.00	3.04	0.74	0.00	1.32	0.40	0.00	0.98	0.27
BaA	0.100	0.16	28.80	6.34	0.05	54.31	8.40	0.25	32.85	9.77
Chr	0.010	0.05	19.64	4.24	0.04	9.43	2.10	0.03	8.97	2.13
BbF	0.100	0.35	74.55	15.19	0.29	58.23	12.67	0.29	41.44	10.03
BkF	0.100	0.24	45.24	9.68	0.17	18.76	4.80	0.10	12.54	2.64
BaP	1.000	4.58	984.34	249.96	3.51	725.60	181.99	1.78	436.76	103.76
IcdP	0.100	0.29	127.85	23.68	0.29	96.25	22.49	0.30	33.95	9.30
DBA	1.000	1.67	244.73	39.25	1.05	124.52	36.22	1.61	157.52	31.34
BghiP	0.010	0.04	37.90	8.53	0.04	8.90	2.40	0.01	3.68	0.80
$\sum_{7c}$TEQs	—	9.08	1312.72	348.34	6.40	1007.93	268.67	5.42	598.39	168.97
$\sum_{16}$TEQs	—	9.17	1344.29	358.89	7.24	1021.50	272.45	5.46	604.64	170.84

safe value. These sites were mainly contaminated as a result of industrial and vehicle emissions, with the highest concentration recorded at 1344.29 $ng \cdot g^{-1}$. In suburban areas, only three samples exhibited concentrations above the safe value of 700 $ng \cdot g^{-1}$. This site, one of Nanjing's leading industries, was the coal-based petrochemical industry, and was a primary source of PAHs pollution in Nanjing suburban areas. In rural areas, all of the dust samples were below the safe value.

Depending on TEF and the Carcinogenic slope factor (CSF), we estimated the risks incurred from inhalation, ingestion, and dermal contact. The results suggested that the cancer risk via ingestion and dermal contact ranged from 10^{-7} to 10^{-6} in all dust samples, which were 10^4 to 10^5 times higher than the levels via inhalation (10^{-11}) (Table 3). Therefore, oral ingestion and dermal contact were considered to be the main exposure routes of PAHs in foliar dust, inhalation of suspended particles through the mouth and nose was negligible compared with the other two routes. This finding was similar to that of ILCRs found for PAHs exposures in other studies, such as the urban street dust of Guangzhou (Wang *et al.* 2011), the Isfahan metropolis of Iran (Soltani *et al.* 2015), and the urban soil of Beijing, China (Peng *et al.* 2011).

As shown in Table 3, the value of ILCRs was the highest in urban areas, indicating a high potential carcinogenic risk for urban residents. The risk value of direct ingestion for children was slightly higher than the adolescences and adults. Children were the subpopulation that was most sensitive to foliar dust, because of their hand-to-mouth activity, whereby contaminated dust can be easily ingested (Meza-Figueroa *et al.* 2007). Furthermore, given the lower body weight of children, their PAH intake (mg/kg-body weight/day) was also believed to be greater than that of adults (Wang *et al.* 2011). Thus, the health risk for a child exposed to urban foliar dust PAHs was thought to be greater than that of an adult. Compared to children, dermal contact appeared to be the predominant exposure route for adults, and the value was slightly higher than for children and adolescents.

An ILCR between 10^{-6} and 10^{-4} indicated a potential risk, where virtual safety was denoted with an ILCR of 10^{-6} or less and a potentially high risk was estimated by an ILCR

Table 3. Risk of cancer due to human exposure to PAHs via foliar dust from Nanjing urban, suburban, and rural area.

			Urban areas			Suburban areas			Rural areas		
			Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Cs[a] ($ng \cdot g^{-1}$)			4.14E-01	7.48E-03	1.80E+00	2.72E-01	5.47E-03	1.10E+00	1.71E-01	4.40E-03	7.32E-01
Child	male	Ingestion	1.99E-06	3.59E-08	8.64E-06	1.31E-06	2.63E-08	5.29E-06	8.21E-07	2.11E-08	3.52E-06
		Dermal contact	2.48E-06	4.48E-08	1.08E-05	1.63E-06	3.28E-08	6.60E-06	1.02E-06	2.64E-08	4.39E-06
		Inhalation	4.21E-11	7.59E-13	1.83E-10	2.77E-11	5.56E-13	1.12E-10	1.73E-11	4.47E-13	7.44E-11
		Cancer risk	4.47E-06	8.07E-08	1.94E-05	2.94E-06	5.91E-08	1.19E-05	1.84E-06	4.75E-08	7.90E-06
	female	Ingestion	2.06E-06	3.71E-08	8.93E-06	1.35E-06	2.72E-08	5.47E-06	8.49E-07	2.19E-08	3.64E-06
		Dermal contact	2.57E-06	4.63E-08	1.11E-05	1.69E-06	3.39E-08	6.82E-06	1.06E-06	2.73E-08	4.53E-06
		Inhalation	4.35E-11	7.85E-13	1.89E-10	2.86E-11	5.75E-13	1.16E-10	1.79E-11	4.62E-13	7.69E-11
		Cancer risk	4.62E-06	8.35E-08	2.01E-05	3.04E-06	6.11E-08	1.23E-05	1.91E-06	4.91E-08	8.17E-06
Adolescence	male	Ingestion	1.03E-06	1.87E-08	4.49E-06	6.80E-07	1.37E-08	2.75E-06	4.27E-07	1.10E-08	1.83E-06
		Dermal contact	2.58E-06	4.65E-08	1.12E-05	1.70E-06	3.41E-08	6.86E-06	1.06E-06	2.74E-08	4.56E-06
		Inhalation	3.04E-11	5.49E-13	1.32E-10	2.00E-11	4.02E-13	8.09E-11	1.25E-11	3.23E-13	5.38E-11
		Cancer risk	3.61E-06	6.52E-08	1.57E-05	2.38E-06	4.77E-08	9.61E-06	1.49E-06	3.84E-08	6.39E-06
	female	Ingestion	1.08E-06	1.94E-08	4.67E-06	7.07E-07	1.42E-08	2.86E-06	4.43E-07	1.14E-08	1.90E-06
		Dermal contact	2.68E-06	4.84E-08	1.16E-05	1.76E-06	3.54E-08	7.13E-06	1.11E-06	2.85E-08	4.74E-06
		Inhalation	3.16E-11	5.71E-13	1.37E-10	2.08E-11	4.18E-13	8.41E-11	1.30E-11	3.36E-13	5.59E-11
		Cancer risk	3.76E-06	6.78E-08	1.63E-05	2.47E-06	4.96E-08	9.98E-06	1.55E-06	3.99E-08	6.64E-06
Adult	male	Ingestion	1.86E-06	3.35E-08	8.05E-06	1.22E-06	2.45E-08	4.93E-06	7.65E-07	1.97E-08	3.28E-06
		Dermal contact	3.30E-06	5.95E-08	1.43E-05	2.17E-06	4.35E-08	8.76E-06	1.36E-06	3.50E-08	5.83E-06
		Inhalation	2.52E-11	4.55E-13	1.09E-10	1.66E-11	3.33E-13	6.70E-11	1.04E-11	2.68E-13	4.45E-11
		Cancer risk	5.15E-06	9.30E-08	2.24E-05	3.39E-06	6.80E-08	1.37E-05	2.12E-06	5.47E-08	9.11E-06
	female	Ingestion	2.03E-06	3.67E-08	8.83E-06	1.34E-06	2.69E-08	5.41E-06	8.39E-07	2.16E-08	3.60E-06
		Dermal contact	3.61E-06	6.52E-08	1.57E-05	2.38E-06	4.77E-08	9.61E-06	1.49E-06	3.84E-08	6.39E-06
		Inhalation	2.76E-11	4.98E-13	1.20E-10	1.82E-11	3.65E-13	7.34E-11	1.14E-11	2.93E-13	4.88E-11
		Cancer risk	5.65E-06	1.02E-07	2.45E-05	3.71E-06	7.46E-08	1.50E-05	2.33E-06	6.00E-08	9.98E-06

[a]The sum of converted values of PAHs based on toxic equivalents of BaP using the Toxic Equivalency Factors (TEF) (Nisbet and LaGoy, 1992).

of greater than 10^{-4} (Chen *et al.* 2006). The results indicate that the risk due to foliar dust PAHs exposure was pervasive for urban residents in Nanjing. The highest ILCR was found in the Confucius Temple, followed by the Central Business District-Xinjiekou. Because these areas have large populations with heavy traffic, large amounts of PAHs are generated. This result was similar to the influence of local PAHs releases (regional transport and local emissions) from fine particulate matter in Nanjing (He *et al.* 2014). The highest concentrations of ILCRs occurred in some industrial zones in the suburban area, such as from the Jingling Petrochemical Company, whereas the lowest occurred in rural areas, however, some sensitive land uses, such as residential areas near the traffic zone, should not be overlooked. Children often play in these places.

Some studies showed that ultrafine particles ($< 2.5\ \mu$m) in dense urban areas cause harmful effects to human health (Power and Willis. 2004; Pope *et al.* 2002), which may be attributed to higher ILCRs in urban areas. Our results are consistent with this conclusion. Several studies have further quantified the small size fractions ($< 10\ \mu$m), which could easily adhere to foliage (Manes *et al.* 2016; Nowak *et al.* 2006; Ottelé *et al.* 2010; Sternberg *et al.* 2010). This suggests that the fine PM in foliar dust requires more attention to minimize the overall risk posed by PAHs, and select effective trees to capture fine PM associated with PAHs.

Conclusions

This is the first investigation of foliar dust contamination by PAHs from urban to rural foliar dust in Nanjing were analysis. In this study areas, urban, suburban, and rural areas were contaminated by PAHs with concentrations of 3430.23, 2282.12, and 1671.06 $ng{\cdot}g^{-1}$, respectively. The most abundant rings were 4-ring PAHs both found in urban, suburban, and rural areas. Two source identification methods showed the same outcomes: Gasoline vehicle traffic emission were the predominant source of PAHs in urban areas, along with coal and coke combustion. In suburban areas, the main source of PAHs was petroleum combustion (especially liquid fossil fuels) and coal combustion. Coal and wood combustion, burnt biomass were the primary sources of PAHs in foliar dust in rural areas. The ILCR results indicated that foliar dust contaminated with PAHs pose a higher risk in urban areas than in suburban and rural areas, and adults were likely to be exposed to higher levels of PAHs than that of children. This study reveals that the process of urbanization has a significant effect on the production of PAHs. In addition, it is necessary to pay more attention to the accumulation of PAHs associated with urbanization of Nanjing.

Conflicts of interest

The authors declare no conflict of interest.

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