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Distribution, Seasonal Variations and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in Foliar Dust of Nanjing, China

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Abstract
Polycyclic aromatic hydrocarbons (PAHs) are of concern for both ecosystem and human health due to their potential teratogenic, carcinogenic, and mutagenic properties. The concentration of $\sum_{16}$PAHs in foliar dust ranged from 49.4 to 19,018.1 μg kg^{-1}, with a mean value of 7074.5 μg kg^{-1}. There were significant seasonal variations in the concentration of $\sum_{16}$PAHs, with the concentration in winter being almost twice as high as in summer. Similarly, the differences between PAH profiles in different seasons indicated that they had common sources, which were attributed to the combined effect of regional transport and local emissions. The diagnostic ratios of indicator compounds indicated that PAHs detected in foliar dust originated from a mixture of gasoline vehicle emissions, biomass, and coal combustion in Nanjing. According to the ecological risk classification of $\sum_{16}$PAHs, the ecological risk caused by PAHs was high since the value of $RQ_{\sum 16PAHs(MPCs)}$ was ≥ 1 and $RQ_{\sum 16PAHs(NCs)}$ were ≥ 800. The mean values for $RQ\sum_{16}PAHs_{(MPCs)}$ and $RQ\sum_{16}PAHs_{(NCs)}$ were 14.8 and 2368.9, which indicated a relatively high ecological risks of PAHs in foliar dust in Nanjing.

Keywords PAHs · Compositional profile · Foliar dust · Ecological risk assessment

Polycyclic aromatic hydrocarbons (PAHs) are composed of two or more benzenes and are widely distributed in the atmosphere, surface waters, sediment, street dust, and soil (Kaya et al. 2012; Li et al. 2017). As persistent organic pollutants, PAHs are derived from sources that are both natural (forest fires and volcanic activities) and anthropogenic (traffic, industrial processes, and fossil fuel combustion) (Wang et al. 2015; Aydin et al. 2014). Due to their toxicity, the European Community (EC) and the United States Environment Protection Agency (USEPA) have listed 16 PAHs as priority pollutants (Manoli et al. 2000). Among these 16 PAHs, 4–7 ring compounds are carcinogenic and mutagenic, while two or three ring PAHs are less mutagenic, but can be highly toxic (Fernandes et al. 1997).

Leaves are sensitive organs that are exposed to air pollution (Nicola et al. 2017), and determining emission have been used as a viable tool for estimating the levels of pollutants and inventorying emission sources (Dias et al. 2015; Callén et al. 2013). Dust, and especially atmospheric particles, acts as a source and sink of pollutants, and can be used to evaluate the concentration, source, and potential risk of PAHs (Xu et al. 2012). Foliar dust is of great concern because of the frequent hand-to-mouth activity of children, which increases their exposure to contaminants (Shi et al. 2011). Foliar dust is deposited on roadside shrubs that are of the same height as some children (0.5–1.5 m), and can easily be taken up by children through direct inhalation (Yin et al. 2014). Several studies have determined the elemental composition (Ram et al. 2014; Simon et al. 2014) and heavy metal concentrations of foliar dust (Yin et al. 2014). Despite the rapid economic development experienced in China, very little data are available regarding PAH concentrations in foliar dust resulting from various complex anthropogenic processes.

In this study, the main objectives were to (1) investigate the distribution, composition, and seasonal variations of

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PAHs in foliar dust; (2) identify possible sources of PAHs from the diagnostic ratios of indicator compounds; and (3) evaluate the potential ecological risks of PAHs in foliar dust to provide effective measures for atmospheric management.

Materials and Methods

Pittosporum tobira is a wide-spread shrub species in Nanjing. The foliar dust samples were collected from eight districts (31°52″–32°14″N118°34″–119°14″E). Sampling were collected following periods of heavy rain and strong wind during September and December, 2015, and March and July, 2016. Five shrubs were selected for sampling at each site (Fig. 1). All leaves sampled (100–150 g) were not suffering from obvious pest damage or disease. They were collected from the inner and outer canopies of east, south, west, and north facing aspects at a height of approximately 1–2 m above ground level.

The leaf samples were washed with Milli-Q water (250 mL, Millipore, Bedford, MA, USA) in an ultrasonic cleaner (HS-1010A, Shenzhen, China) for 10 min (Baranyai et al. 2015). The dust-containing suspension was filtered through a 150-μm sieve. The procedure was repeated with 50 mL Milli-Q water and this was filtered and added to the samples. This 300 mL of dust-containing suspension was dried in a vacuum freeze-drier (Labconco, Kansas City, MO, USA) for 3 days at − 83°C to a constant and then stored at − 20°C until further extraction.

A composite standard solution of 16 PAHs was purchased from Sigma-Aldrich (Dr, Ehrenstorfer, Germany), A mixture of acetonitrile (ACN) and water was used as the mobile phase, with a solvent gradient method and a flow rate of 1.0 mL min^{-1} at 35°C. 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 by a vacuum rotary evaporator, then combined with 4 mL hexane and passed through a silica column chromatography [10 mm (ID) × 350 mm (L), 10 g of silica gel, and 20 mm length of anhydrous sodium sulfate], and then eluted with 25 mL hexane. After extraction, the liquid was filtered through a 0.22-μm fiberglass membrane and re-concentrated with a gentle stream of nitrogen to exactly 1 mL by a blowing process at 25°C. The concentrations of PAHs in solution were determined using high performance liquid

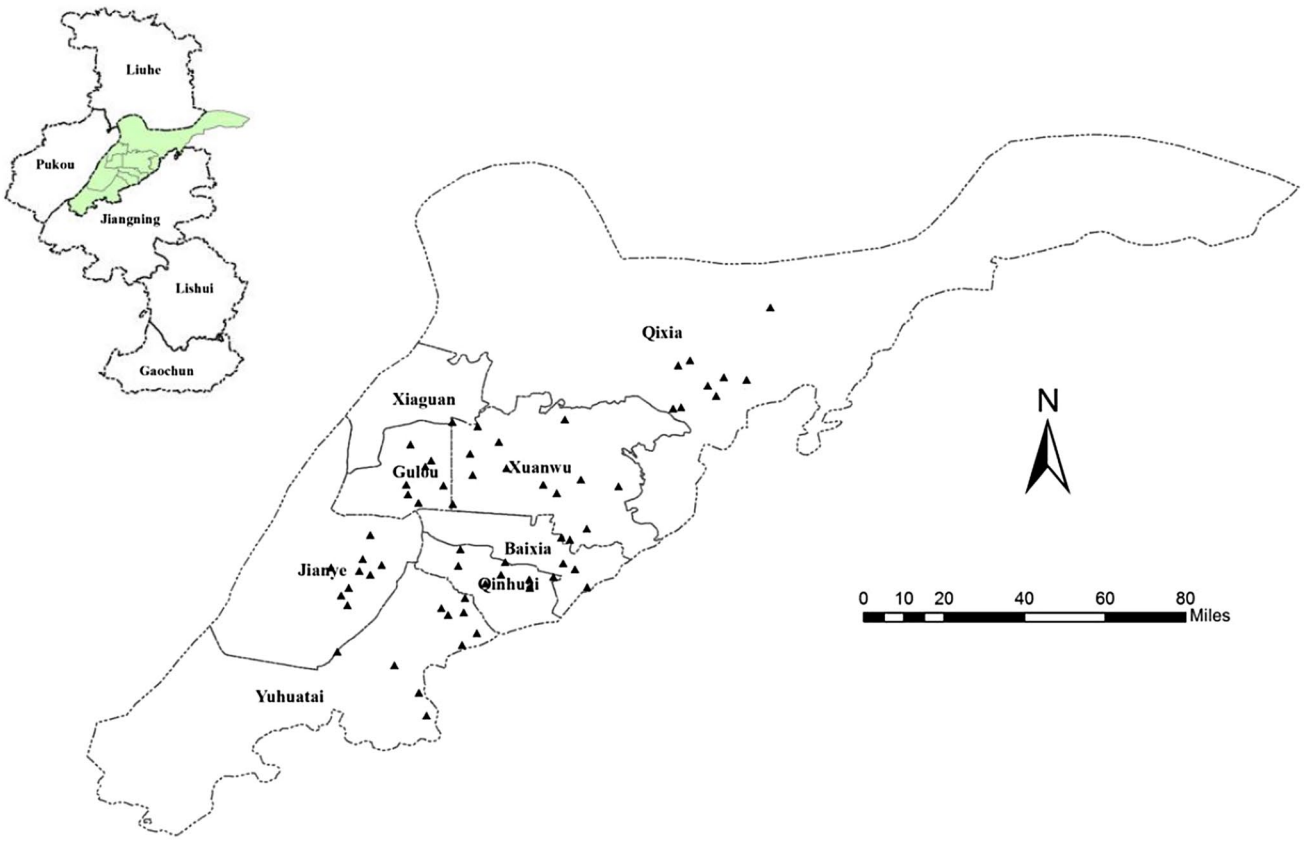

Fig. 1 Map of Nanjing showing location of foliar dust sampling areas

chromatography (HPLC), with a 4.6 mm (ID) × 250 mm (L) column and a 310 UV detector at 260 nm.

The calibration cure was performed by analysing, in triplicate, five standards solutions at concentrations 50, 100, 400, 500 and 1000 ng mL^{-1}. The correlation coefficients of the PAH standard curves were higher than 0.983 based on the internal calibration method. Accuracy of the method was estimated by means of recovery experiments performed in triplicate on samples spiked at two levels (100 and 400 ng g^{-1}). The average recoveries of 16 PAHs in spiked blanks ranged from 71.6% to 111.2% (RSD < 18.88%). The limit of detection (LOD) ranged from 0.20 ng g^{-1} (Phe) to 6.62 ng g^{-1} (Acy). Besides, the lowest validated levels, 0.67 ng g^{-1} (BaA) to 7.08 ng g^{-1} (Acy) were established as limit of quantification (LOQ) objectives.

In order to estimate the environmental risk posed by PAHs, the risk quotient (RQ) approach was used to assess the potential ecological risk of PAHs in foliar dust (Kalf et al. 1997). Individual PAH species RQ values were calculated as shown in Eq. (1). The negligible concentration of (NCs) and the maximum permissible concentrations (MPCs) were calculated according to (2) and (3), respectively (Kalf et al. 1997); where C_{PAHs} was detected concentration of certain PAH in foliar dust samples, respectively. C_{QV} was the corresponding quality values of certain PAHs in the medium, and $C_{QV(NCs)}$ and $C_{QV(MPCs)}$ were the quality values of the NCs and MPCs of PAHs in foliar dust. The RQ could only be used to assess the ecosystem risk of 10 individual PAHs. In order to evaluate the ecosystem risk of other six individual PAHs [acenaphthylene (Acy), acenaphthene (Ace), fluoranthene (Flu), pyrene(Pyr), benzo(b)fluoranthene (BbF) and dibenzo(a,h)anthracene (DBA), the toxic equivalency factors (TEFs)] (Nisbet and LaGoy 1992) were used to infer that the NCs and MPCs of Acy, Ace, Flu, and Pyr were equal to Phenanthrene (Phe) or Nap, BbF was equal to benzo(a)anthracene (BaA) and dibenzo(a,h)anthracene (DBA) was equal to benzo(a)pyrene (BaP). Risk quotient values for total sampled PAHs were calculated as shown in Eq. (4) with analogous variants for negligible concentrations (NCs) Eq. (5) and maximum permissible concentrations (MPCs) (Eq. 6) as shown below:

$$RQ_j = \frac{C_{PAHs}}{C_{QV}} \tag{1}$$

$$RQ_{NCs} = \frac{C_{PAHs}}{C_{QV(NCs)}} \tag{2}$$

$$RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV(MPCs)}} \tag{3}$$

$$RQ_{\sum PAHs} = \frac{C_{\sum PAHs}}{C_{QV(\sum PAHs)}} \tag{4}$$

$$RQ_{\sum PAHs(NCs)} = \frac{C_{\sum PAHs}}{\sum C_{QV(NCs)}} \tag{5}$$

$$RQ_{\sum PAHs(MPCs)} = \frac{C_{\sum PAHs}}{\sum C_{QV(MPCs)}} \tag{6}$$

Statistical analysis was performed using SPSS 18.0 (SPSS Inc., Chicago, IL, USA) and origin 9.0 (Northampton, MA, USA). Geographic information system (GIS) (ArcGis 9.3, Esri Corporation, Tokyo, Japan) software was used to generate raster-based pollution contour maps of the PAHs at the urban sites.

Results and Discussion

Table 1 shows that the concentration of the 16 PAHs ($\sum_{16}$PAHs) in foliar dust ranged from 49.4 to 19,018.1 μg kg^{-1}, with a mean value of 7074.5 μg kg^{-1}. Generally, carcinogenic PAHs (i.e., $\sum_{7C}$PAHs include BaA, Chr, BbF, BkF, BaP, IcdP and DBA), had concentrations in the range of 32.69–9950.4 μg kg, with a mean value of 4105.4 μg kg^{-1}. Comparing with urban street dust around the world, the average concentration of total PAHs was slightly higher than those in Iran (1074.6 μg kg^{-1} Soltani et al. 2015), Beijing (3700 μg kg^{-1} Li et al. 2017) and Guangzhou (4800 μg kg^{-1}, Wang et al. 2011), but lower than those in Guwahati (23,294.7 μg kg^{-1} Hussain et al. 2015) and Shanghai (13,840 μg kg^{-1} Zheng et al. 2016). Obviously, the comparison indicated that PAH pollution in foliar dust was still at a relatively high level. At both sites, the mean concentration of $\sum_{16}$PAHs and $\sum_{7C}$PAHs displayed significant seasonal variations in the order of winter > autumn > spring > summer. The highest mean concentration in winter was nearly twice as high as in summer. Our conclusion was consistent with that of He et al. (2014). These seasonal variations have been mainly attributed to the influence of emission sources (Tian et al. 2009). Other meteorological factors such as precipitation and mixing layer also played roles in the seasonal variation of atmospheric PAHs (Lee and Tasy 1994; Liu et al. 2008).

The most abundant PAHs in the different seasons were 5–6 ring compounds, followed by four, three, and two ring PAHs (Fig. 2). High molecular weight (HMW, 5- and 6-rings) PAHs predominated in foliar dust samples, accounting for 52.8%, 49.6%, 51.2%, and 53.4% of all PAHs in spring, summer, autumn, and winter, respectively. This might be attributable to HMW PAHs being resistant to degradation and being more easily absorbed in sediment (Yun et al. 2016), which indicates that foliar dust is an important source of HMW PAHs. These compounds are more toxic

Table 1 Mean PAHs concentrations (μg/kg) in foliar dust in Nanjing urban sites

seasons	PAHs	Nap	Acy	Ace	Phe	Ant	Fl	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	IcdP	DBA	BghiP	$\sum_{7C}$PAHs[a]	$\sum_{16}$PAHs[b]
spring	Min	ND	ND	ND	3.8	3.6	ND	4.2	5.6	2.7	1.1	2.8	4.1	6.0	3.8	ND	ND	44.6	76.2
	Max	153.5	24.6	29.6	1144.9	456.2	123.9	1857.3	1763.3	479.0	1133.8	600.5	404.3	593.8	3412.6	354.2	597.8	8744.3	12120.1
	Mean	41.4	7.3	15.1	289.7	159.8	34.0	732.1	704.0	196.8	492.6	294.6	206.5	281.6	1749.9	149.7	288.8	3415.5	5738.3
	SD	28.1	4.2	9.7	218.3	136.1	28.0	460.2	513.1	133.2	344.4	193.3	123.5	176.0	828.7	106.0	142.2	2241.4	3719.1
summer	Min	ND	ND	ND	ND	ND	1.21	1.9	2.6	1.9	0.9	0.9	3.6	ND	2.6	ND	ND	32.7	49.4
	Max	114.5	18.5	13.5	1565.3	500.9	520.5	1704.7	1603.2	419.5	850.3	705.1	483.9	655.8	5341.8	354.9	881.1	6978.2	14490.9
	Mean	27.5	6.6	7.1	617.8	123.6	71.5	715.3	680.6	142.2	360.0	232.8	154.3	220.9	1512.7	116.8	284.9	2739.7	5067.5
	SD	28.5	4.8	4.4	426.2	173.3	69.8	481.4	491.7	110.4	238.7	167.8	112.7	171.1	1236.3	87.7	222.8	1963.5	3391.9
autumn	Min	ND	ND	ND	4.7	5.5	3.6	2.1	4.5	4.5	3.6	6.2	6.8	10.0	4.6	ND	ND	58.4	84.9
	Max	146.0	20.6	22.2	1130.6	793.8	131.8	2286.3	1855.6	348.0	1513.1	684.9	409.9	548.8	5049.3	311.4	763.7	8797.5	15298.2
	Mean	53.3	9.8	23.4	515.5	144.4	56.5	1042.8	916.3	192.2	653.0	340.0	225.7	283.3	2435.0	161.5	391.0	4290.8	7613.8
	SD	42.9	5.3	15.8	312.8	88.5	38.7	578.6	466.2	96.0	475.0	174.5	105.3	144.8	1474.4	78.3	201.5	2447.8	4275.4
winter	Min	ND	ND	ND	5.6	5.5	4.3	5.2	6.5	6.4	4.1	6.7	7.0	7.0	5.2	2.4	6.9	74.3	104.4
	Max	171.4	57.9	45.4	982.1	6151.2	87.2	5763.2	5245.5	1444.2	3746.1	1217.5	669.5	1085.3	5866.0	375.3	793.3	9950.3	19018.1
	Mean	65.6	22.0	28.7	533.4	499.9	41.7	1242.0	1166.7	324.3	805.7	473.8	336.0	439.0	3433.0	207.7	458.2	6019.5	9707.3
	SD	41.7	11.8	19.6	277.7	264.8	23.5	798.8	861.8	238.0	612.7	307.0	155.0	248.4	1537.3	106.3	204.1	2166.5	5641.2

[a]The PAH concentration of seven carcinogenic PAHs

[b]The PAH concentration of 16 priority PAHs

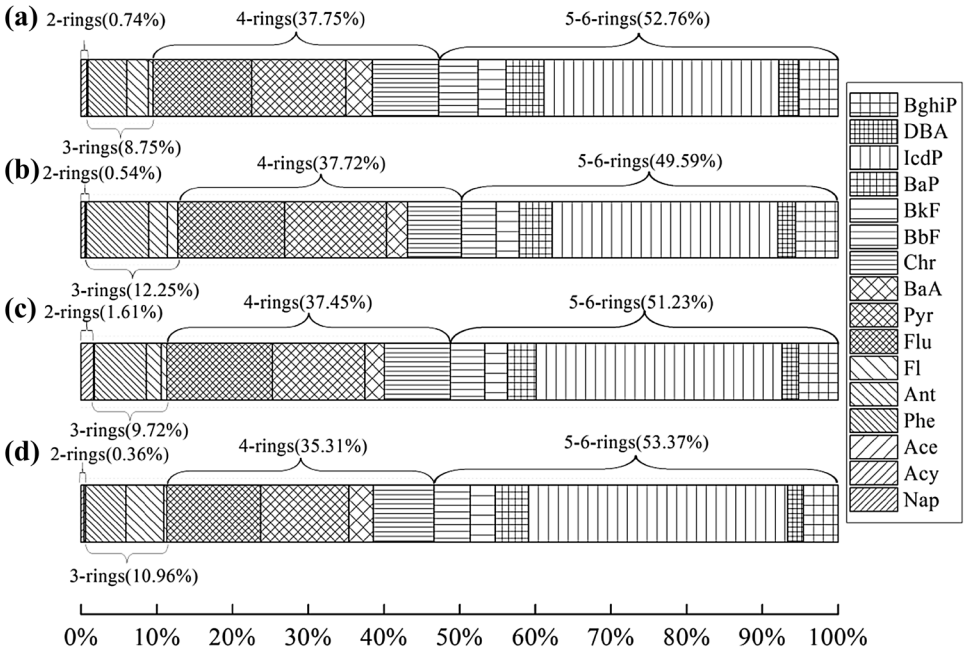

Fig. 2 Mean proportion of individual PAHs in foliar dust. **a** Spring. **b** Summer. **c** Autumn. **d** Winter

and persistent in the environment than low molecular weight (LMW) PAHs.

Figure 3 shows that IcdP was the PAH present at the highest concentration, followed by Flu, Pyr, BghiP, and BbF. The concentrations of Phe, Flu, Pyr, Chr, and IcdP varied more than the other PAHs among the different seasons. The higher seasonal variation of IcdP may reflect the changes of gas- and diesel-fueled vehicle emissions. In addition, as indicators of coal and wood combustion, Pyr, Chr and Fl also showed strong seasonal variation (Wu et al. 2014) due to the increased combustion in winter for heating. The concentrations of Acy, Ace, Fl, and DBA were relatively low in all seasons. A Kruskal–Wallis test showed that the differences among Nap, Acy, Phe, BaA, BkF, BaP, IcdP concentrations in each different season were significant ($p < 0.05$), which were attributed to emissions from local sources (Liu et al. 2017).

The Arc Map 9.3 inverse distance weight (IDW) method was adopted to represent the spatial distribution of PAH concentrations in foliar dust in Nanjing city (Fig. 4). There was no area with a high concentration, which might be due to the heavy rainfall and heat island effect of the city in summer. The higher temperature in summer may increase the heat island effect, which can lead to lower levels of atmospheric

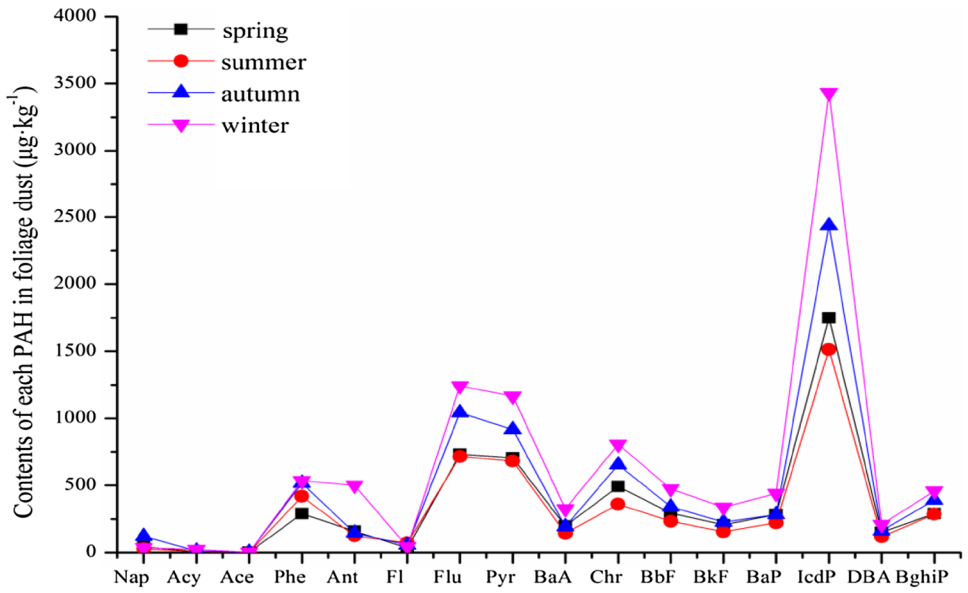

Fig. 3 Seasonal variations of contents of each PAH in urban sites

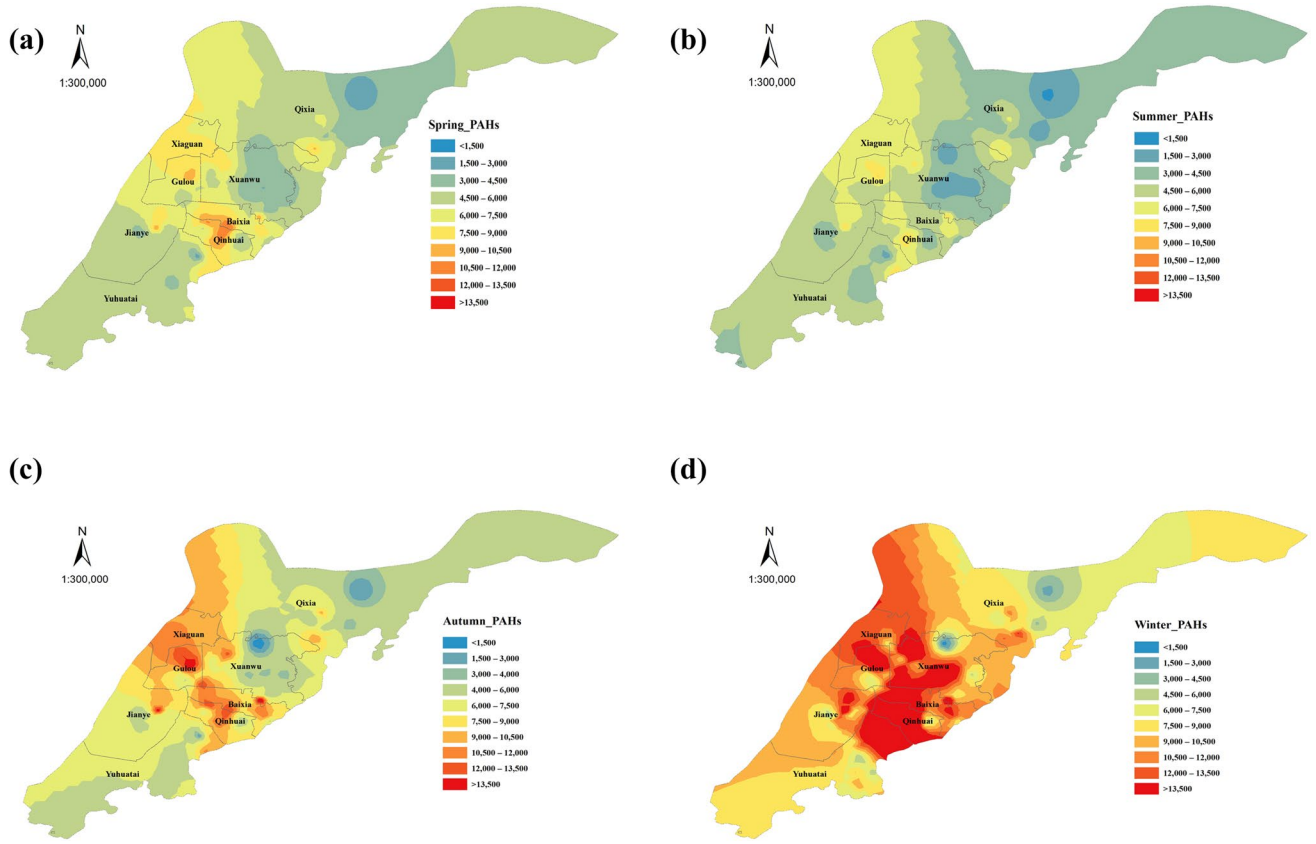

Fig. 4 Interpolated spatial variability of 16 PAHs in foliar dust. **a** Spring, **b** summer, **c** autumn, **d** winter

pollutants. The turbulent exchange can also enhance pollutant dispersion (He et al. 2014). Under inversion layer circumstances, the heat island will lift the inversion layer and reduce concentrations of atmospheric pollutants at the surface. Rainfall removed a large number of particles from the atmosphere and deposited contaminants on the ground, reducing the PAH concentration in the atmosphere. In autumn, the PAH concentration in foliar dust increased, which may have been the result of the remaining urban heat island and rain island effects.

In winter seasons, however, sampled PAHs showed a strong spatial variability, with a zone of elevated concentrations in the city centre and the northwest. There are several significant PAH sources in winter, including fossil fuel for commercial and residential space heating, which elevates the PAH concentrations in the atmosphere. Meteorological effects also contribute to higher PAH levels in winter, with a lower mixing height leading to a stable atmosphere and reducing the diffusion of these pollutants into the atmosphere (Zhou et al. 2012). A decrease in temperature may actually cause an increase in the concentration of primary pollutants (Fallman et al. 2016).

Diagnostic ratios were used to identify the possible sources of PAHs (Li et al. 2016; Tobiszewski and Namieśnik 2012). A ratio of Ant/(Ant + Phe) < 0.1, indicates a petroleum source, whereas Ant/(Ant + Phe) > 0.1 indicates mainly combustion sources (Dickhut et al. 2000). Our results are shown in Fig. 5. The ratios of Ant/(Ant + Phe) ranged from 0.01 to 0.97, with a mean of 0.23, which indicated a petroleum source (Fig. 5a). A ratio of Flu/(Flu + Pyr) > 0.5 is characteristic of biomass and coal combustion (Yunker et al. 2002). The ratios of Flu/(Flu + Pyr) ranged from 0.14 to 0.58, with a mean of 0.51 (Fig. 5A), which implied a major contribution from biomass and coal combustion. The ratios of Ant/(Ant + Phe) were generally higher than 0.1 while the ratios of Flu/(Flu + Pyr) were generally above 0.5, which suggested a mixture of combustion sources and traffic emissions (Yunker et al. 2002; Wang et al. 2011). The mean value of IcdP/(IcdP + BghiP) and BaA/(BaA + Chr) were 0.84, 0.30, respectively (Fig. 5b). According to Yunker et al. (2002), a ratio of BaA/(BaA + Chr) < 0.35 indicated that vehicular traffic emissions were the main source of PAHs (Yunker et al. 2002). A value of IcdP/(IcdP + BghiP) between 0.2 and 0.5 is usually due to petroleum combustion, whereas a ratio of IcdP/(IcdP + BghiP) > 0.5 indicates the contribution of biomass and coal (Ravindra et al. 2008; Tobiszewski and Namieśnik 2012). Thus, the diagnostic

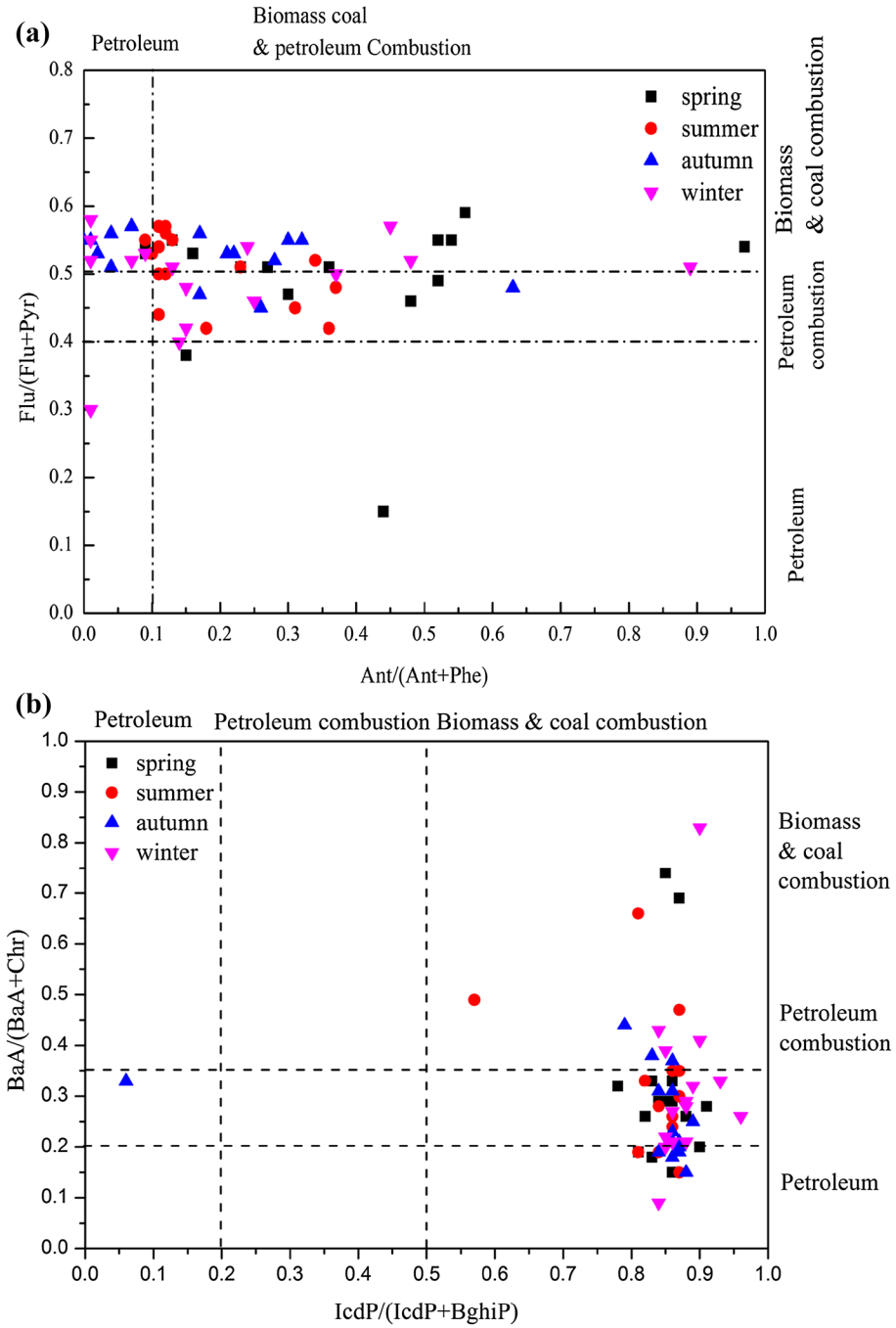

Fig. 5 Factor loading plots from factor analysis on various PAHs in foliar dust from Nanjing

ratios implied that PAHs were derived from mixtures of gasoline vehicle emissions, biomass, and coal combustion in Nanjing. However, Yunker et al. indicated that sources are difficult to distinguish even when several ratios are examined together (Yunker et al. 2002). Intrasource variability and intersource similarity suggest that PAH ratios are not specific to generic source types (Galarneau 2008). Despite these limitations, the diagnostic ratio analysis for the Nanjing data indicated locally relevant source types.

The mean values of $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ for PAHs in different seasons are listed in Table 2. The mean $RQ_{(NCs)}$ values of individual PAHs were all > 1, which indicated that the ecological risks in these sites caused by these individual PAHs were high. The mean $RQ_{(MPCs)}$ values of Ant, Pyr, and BbF were all > 1, indicating a high level of risk to the ecosystem, with severe toxicity (Table 3). The mean $RQ_{(MPCs)}$ values of other individual PAHs, such as Nap, Acy, Ace, Phe, Fl, Flu, BaA, Chr, BkF, BaP, IcdP, DBA, and BghiP in foliar dust were < 1 and $RQ_{(NCs)} > 1$, indicating a moderate

Table 2 Mean risk quotients of PAHs in foliar dust from Nanjing

PAHs		Spring (μg kg^{-1})		Summer (μg kg^{-1})		Autumn (μg kg^{-1})		Winter (μg kg^{-1})	
	TEFs[a]	RQ_{NCs}[b]	RQ_{MPCs}[c]	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}
Nap	0.001	29.6	0.3	19.6	0.2	85.9	0.9	25.4	0.3
Acy	0.001	6.1	0.1	5.5	0.1	8.2	0.1	18.3	0.2
Ace	0.001	1.7	0	1.2	0	1.2	0	1.4	0
Phe	0.001	56.8	0.6	81.9	0.8	101.1	1	104.6	1
Ant	0.01	133.1	1.3	103	1	120.3	1.2	416.6	4.2
Fl	0.001	28.3	0.3	59.5	0.6	47.1	0.5	34.7	0.3
Flu	0.001	28.2	0.3	27.5	0.3	40.1	0.4	47.8	0.5
Pyr	0.001	586.7	5.9	567.2	5.7	763.6	7.6	972.2	9.7
BaA	0.1	78.7	0.8	56.9	0.6	76.9	0.8	129.7	1.3
Chr	0.01	4.6	0	3.4	0	6.1	0.1	7.5	0.1
BbF	0.1	117.8	1.2	93.1	0.9	136	1.4	189.5	1.9
BkF	0.1	8.6	0.1	6.4	0.1	9.4	0.1	14	0.1
BaP	1	108.3	0.1	85	0.1	109	0.1	168.9	0.2
IcdP	0.1	673	0.7	581.8	0.6	936.6	0.9	1320.4	1.3
DBA	1	2.5	0	2	0	2.7	0	3.5	0
BghiP	0.01	3.9	0	3.8	0	5.2	0.1	6.1	0.1
$RQ\sum_{16}PAHs$[d]	/	1867.9	11.7	1697.8	11.0	2449.4	15.2	3460.6	21.2

[a]The toxic equivalency factors

[b]The negligible concentration

[c]The maximum permissible concentrations

[d]The risk quotients value of 16 PAHs

Table 3 Risk classification of individual PAHs and ∑PAHs

Individual PAHs	$RQ_{(NCs)}$	$RQ_{(MPCs)}$	∑PAHs	$RQ_{\sum PAHs(NCs)}$	$RQ_{\sum PAHs(MPCs)}$
Risk-free	< 1	< 1	Risk-free	< 1	< 1
Moderate-risk	≥ 1	< 1	Low-risk	≥ 1; < 800	< 1
High-risk	≥ 1	≥ 1	Moderate-risk1	≥ 800	< 1
			Moderate-risk2	≤ 800	≥ 1
			High-risk	≥ 800	≥ 1.0

risk. As shown in Fig. 6, the average risk of ∑PAHs, with the average values of $RQ_{(NCs)}$ in the different seasons followed the order of winter > autumn > spring > summer. The risk order was consistent with the order of the mean concentration of $\sum_{16}PAHs$, and the mean ecological risk in winter was nearly twice that in summer.

Furthermore, it can be seen that the proportion of HMW PAHs in foliar dust samples was highest in winter, and the $RQ_{(NCs)}$ value of HMW PAHs was also highest in winter. 5–6-ring PAHs accounted for most of the $RQ_{(NCs)}$ of PAHs in foliar dust. The contribution of individual PAHs to the overall ecological risk in different seasons is shown in Fig. 6. The contributions of individual PAHs to the $RQ_{(NCs)}$ were similar to their contributions to the $RQ_{(MPCs)}$. The dominant individual PAH was IcdP in all four seasons. In general, 5–6 ring and 4-ring PAHs accounted for most of the ecological risk, with mean values of 48.08% and 36.45%, respectively. $RQ_{(MPCs)}$ of ∑PAHs, namely $RQ\sum_{16}PAHs_{(MPCs)}$, were > 1 in all seasons, $RQ_{(NCs)}$ of ∑PAHs, namely $RQ\sum_{16}PAHs_{(NCs)}$, were > 800 in the different seasons (Table 2). These results indicated that the ecosystem was at high risk in Nanjing.

In conclusion, the PAH compositions were similar in the different seasons. The major compounds detected in foliar dust were IcdP, Flu, Pyr, BghiP, and BbF. The results of the diagnostic ratios indicated that PAHs in Nanjing originated from gasoline vehicle emissions, grass, wood, and coal combustion. The results of ecological risk assessments indicated a high risk of IcdP and Pyr in foliar dust. HMW PAHs accounted for much greater ecological risk than LMW PAHs. Generally, the HMW PAHs accounted for a higher proportion of RQ_{NQs} of PAHs in foliar dust, while $RQ_{(NCs)}$ and $RQ_{(MPCs)}$ values indicated a relatively moderate ecological risk from PAHs in foliar dust. The mean ecological risk in winter was twice that in summer. Therefore, several control measures and strict rules should be implemented by government to decrease the contamination.

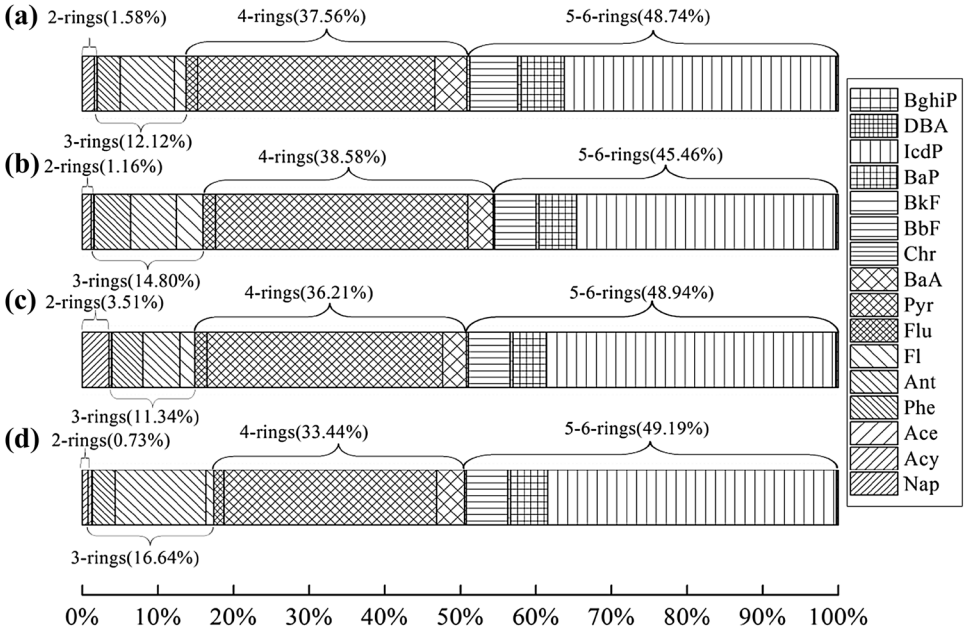

Fig. 6 $RQ_{(NCs)}$ of individual PAHs in foliar dust from Nanjing. **a** Spring; **b** summer; **c** autumn; **d** winter

We acknowledge that there are several limitations to our study. First, our foliar dust samples only captured particle phase PAHs, and HMW species are captured more effectively than LMW species because 2-, 3-, and 4-ring species more readily volatilize under higher seasonal temperatures. In addition, the diagnostic ratio we used in source analysis on PAHs has its limitation to partition vapor and particle phase. We also note that the TEF scheme we used in our study gives more weights to some species, such as DBA, and thus results in higher ecological risk value. Further studies should consider these aspects.

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