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Seasonal and Spatial Variations of Air Concentrations of Polycyclic Aromatic Hydrocarbons in Northeastern Chinese Urban Region

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Abstract Polyurethane foam disk passive air samplers were deployed along an urban–rural-background transect in a northeastern Chinese region (Harbin) to investigate the spatial and seasonal variations of polycyclic aromatic hydrocarbons (PAHs). The $\sum_{16}$PAHs concentrations [ng/(sample·day)] were high at urban sites (315 ± 206), followed by rural sites (222 ± 160), suburban site (142 ± 114) and background site (128 ± 107). The urban fractionation effect was observed along the transect with increasing proportions for low molecular weight PAHs and decreasing proportions for high molecular weight PAHs. PAHs were found to be higher in winter and spring than in summer and autumn, most likely due to the combustion of coal and biomass for domestic heating. Sources of PAHs were investigated by principal component analysis in combination with diagnostic ratios, which both indicated that pyrogenic sources were the main sources of PAHs in the air of Harbin, China.

Keywords PAHs · Passive air sampler · Spatial and seasonal variations · Principal component analysis

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Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent toxic substances (PTSs) in environment due to their persistent characteristic and long-range atmospheric transport. PAHs have been detected in high mountains (Wang et al. 2006) and remote polar regions (Hung et al. 2005), which indicate that atmosphere plays an important role in the transport of PAHs, as pointed out in previous studies (Motelay-Massei et al. 2005).

Passive air samplers (PASs) have been developed and utilized for sampling PTSs in atmosphere recently, which are available to be used for simultaneous investigation of PTS in a number of sites (Santiago and Cayetano 2007). Polyurethane foam (PUF) disk PAS is one of the most validated passive techniques for monitoring of PTSs for nowadays (Harner et al. 2004). In a previous study, the theory of PUF disk PAS is sufficiently studied in laboratory and field experiments (Shoeib and Harner 2002), furthermore it has been increasingly developed over the past few years for monitoring PTSs over different geographical scales, like local scales (Harner et al. 2004; Motelay-Massei et al. 2005; Wang et al. 2008), regional scales (Santiago and Cayetano 2007; Zhang et al. 2008; Chakraborty et al. 2010), continental scales (Jaward et al. 2004) and even the global scale (Pozo et al. 2006; Genualdi et al. 2010).

Located at the northeast of China, Harbin is an old industrialized city, with population of 3.8 million and urban area of 4,300 km^2. In recent years, Harbin has been undergoing fast economic development and urbanization, however, environmental problems become severe, like contamination by PAHs in soil (Ma et al. 2009). In addition to vehicle exhaust, which is the major PAHs source in most cities, coal and biomass combustion for domestic heating are the two important local PAHs sources in Harbin especially in winter and spring. Every year there are

6 months needing for domestic heating. Therefore, PUF disk PASs were deployed at eight sites along an urban–rural-background transect to study the spatial and seasonal variations of atmospheric PAHs for better understanding the urban fractionation effects and analyzing the relationship between sources and acceptors of PAHs in the region.

Materials and Methods

PUF disk PASs were deployed at eight sites simultaneously in Harbin region (Fig. 1). The three urban sites (UR1, 2, 3) are located in the center of Harbin, in high-density residential, commercial and industrial districts. The suburban site (SU1) is located in upper drift outskirt of city, in low-density residential district. The three rural sites (RU1, 2, 3) are mainly located in farming lands with villages near by. The background site (BA1) is located in a forested area.

The processes of air sampling with PUF disks PASs were described in detail in previous studies (Harner et al. 2004; Zhang et al. 2008). Briefly, prior to deployment, the PUF disks (15 cm diameter; 1.45 cm thick; surface area, 420 cm^2; mass, 5.12 g; volume, 256 cm^3; density, 0.02 g/cm^3) were cleaned with hot water followed by Soxhlet extraction with acetone for 24 h, and then hexane for another 24 h at the laboratory of International Joint Research Center for Persistent Toxic Pollutants (IJRC-PTS), Harbin Institute of Technology (HIT), Harbin, China. Before the PAS was assembled at sampling sites, PUF disks were housed inside two stainless steel chambers (pre-cleaned by acetone on field) with a 2.5 cm gap between them, which would protect the sampler from precipitation, UV sunlight, and particle direct deposition (Shoeib and Harner 2002; Jaward et al. 2004; Harner et al. 2006). The chambers can adequately buffer air flow to the PUF disk and reduce the wind effect on sampling rate, yielding approximately time-weighted air concentrations (Tuduri et al. 2006).

PUF disk PASs were deployed for four periods: period 1 (spring, February–April 2007); period 2 (summer, May–July 2007); period 3 (autumn, August–October 2007); period 4 (winter, November 2007–January 2008). After harvesting, the PUF disks were transported to IJRC-PTS laboratory, where they were stored frozen (at −20°C) until extraction. For each sampling site, one field blank was deployed during the four periods. Blanks were obtained with clean PUF disk being installed for 1 min at sampling sites and then returned to laboratory.

The extraction and clean-up of PAHs in PUF disk were described in details in previous studies (Zhang et al. 2008). Briefly, after being spiked with four surrogates recovery standards (naphthalene-D_8, fluorene-D_{10}, pyrene-D_{10}, perylene-D_{12} for PAHs) (Supelco, CO., USA), the PUF disks were then Soxhlet extracted for 24 h using mixed solvent (acetone/n-hexane, 1:1 v/v). Volume was reduced to 2 mL using a rotary evaporator, then the extracts were cleaned-up by a silica gel column [containing 2 g anhydrous sodium sulfate (activated at 600°C for 6 h before use) and 5 g silica gel (activated at 130°C for 16 h before use)]. After the column was eluted with dichloromethane/n-hexane (1:1 v/v), eluants were then concentrated with rotary evaporator and gentle stream of nitrogen to 1.0 mL.

16 EPA PAHs [naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz(a)-anthracene (BaA), chrysene (Chr), benzo(b)-fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP),

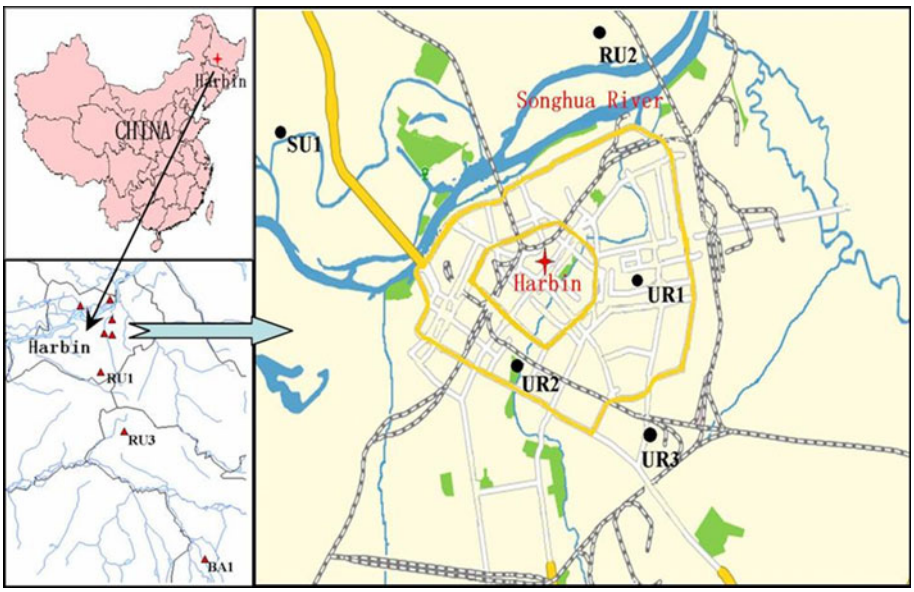

Fig. 1 Location of sampling sites in Harbin region

dibenz(a,h)anthracene (DahA), indeno(l,2,3-cd)pyrene (IcdP), benzo(g,h,i)perylene (BghiP)] were analyzed using Agilent 6890 N GC coupled with Agilent 5973 mass spectrometer detector (GC/MSD) equipped with a 60 m × 0.25 mm × 0.25 μm HP-5MS capillary column (Agilent Co., USA) in selected ion monitoring (SIM) mode. The column temperature programs were used as follows: held at 90°C for 1 min, then raised from 90 to 180°C with 10°C min^{-1}, held for 1 min, from 180 to 280°C at 3°C min^{-1}, held for 20 min. Five mixed standard solutions of 16 PAHs with different concentrations were used for the calculation of PAHs with an external standard method.

Field blanks (one blank for each sampling site) and laboratory/solvents blanks (one blank for every 10 real samples) were also extracted and analyzed in the same way as true samples. Only very low concentrations of Nap and Phe were detected in some blanks, indicating contamination was negligible during transport, storage, and process. The average recovery efficiencies of surrogates were: 74.01 ± 24.45% for naphthalene-D_8, 80.57 ± 19.78% for fluorene-D_{10}, 72.76 ± 16.31% for pyrene-D_{10}, 61.15 ± 22.99% for perylene-D_{12}, respectively. The data reported in the present study were corrected for blanks and recoveries of surrogates. The method detection limits (MDLs) ranged from 10 to 40 pg/m^3 (315 m^3 air for 3 months with PUF disk PAS) depending on different compounds. Principal component analysis were conducted using the software SPSS 13.0 for Windows.

Results and Discussion

To check for reproducibility of the method, four pairs of duplicate samples were taken at UR1 site for the four periods. Good agreement was obtained for duplicates samples with quite strong correlation ($R^2 > 0.99$), illustrating the precision of the sampling method. The reproducibility for all the 16 PAHs was very good, with the mean % normalized difference being very low, 23% for spring, 21% for summer, 17% for autumn and 18% for winter. One-way ANOVA analysis also indicated no difference between duplicate samples, verifying the reproducibility and applicability of PUF PAS to monitor PAHs in air.

The results were given as nanograms of PAHs per sample per day for comparison in this study. A summary of the 16 PAH concentrations were presented in Table 1. As expected, the highest PAHs was found at the urban sites and lowest at the background site. Generally speaking, average annual $\sum_{16}$PAHs concentrations (ng/(sample · day)) were high at urban sites (315 ± 206), followed by rural sites (222 ± 160), suburban site (142 ± 114) and background site (128 ± 107). A strong urban–rural-background transect was presented in Harbin region, which reflects the different sources. For urban sites, sources of PAHs were ubiquitous, as automobile traffic, domestic heating, thermal power and industrial emissions being the main anthropogenic origins (Motelay-Massei et al. 2005).

Table 1 Average annual concentrations of PAHs in air in Harbin region derived from PUF passive air sampler [ng/(sample·day)] (n = 4)

PAHs	UR1	UR2	UR3	SU	RU1	RU2	RU3	BA
Nap	14.2 ± 22.4	11.0 ± 12.0	15.9 ± 24.2	13.5 ± 21.2	24.6 ± 41.5	16.0 ± 22.6	17.6 ± 31.5	11.3 ± 17.3
Acy	3.5 ± 5.6	3.9 ± 4.5	7.1 ± 9.5	1.7 ± 1.9	5.6 ± 9.3	2.7 ± 3.6	2.8 ± 4.6	1.4 ± 1.5
Ace	11.2 ± 13.0	11.1 ± 11.5	22.4 ± 27.8	12.7 ± 12.4	15.3 ± 18.5	11.9 ± 11.2	13.4 ± 17.2	10.4 ± 11.9
Flu	21.5 ± 24.9	23.8 ± 26.5	37.0 ± 48.9	16.3 ± 21.0	29.8 ± 35.2	23.6 ± 24.5	17.5 ± 26.0	14.5 ± 17.7
Phe	102.8 ± 53.8	120.4 ± 64.3	188.1 ± 141.0	59.4 ± 46.2	121.8 ± 68.5	88.4 ± 52.2	76.1 ± 74.8	55.7 ± 46.9
Ant	6.6 ± 8.0	9.6 ± 11.1	15.8 ± 20.1	3.1 ± 3.8	8.9 ± 11.2	6.5 ± 7.3	4.1 ± 5.3	2.4 ± 2.5
Flua	39.6 ± 2.5	48.2 ± 12.3	67.4 ± 18.3	17.1 ± 3.5	40.6 ± 4.2	26.6 ± 4.8	23.2 ± 10.2	17.2 ± 5.0
Pyr	24.4 ± 2.1	31.1 ± 8.5	43.6 ± 15.2	11.0 ± 2.7	24.1 ± 4.1	16.7 ± 3.4	14.1 ± 6.4	9.7 ± 3.1
BaA	2.6 ± 0.8	3.9 ± 1.5	4.6 ± 2.4	1.0 ± 0.5	2.7 ± 1.2	2.0 ± 0.8	1.4 ± 0.7	0.8 ± 0.4
Chr	5.4 ± 1.3	7.4 ± 1.3	8.2 ± 0.8	2.4 ± 0.6	5.1 ± 0.8	3.3 ± 0.7	2.9 ± 0.5	2.0 ± 0.4
BbF	3.3 ± 0.9	4.8 ± 1.5	5.8 ± 3.0	1.5 ± 0.6	3.3 ± 1.3	2.2 ± 0.9	1.8 ± 0.8	1.2 ± 0.5
BkF	1.0 ± 0.3	1.4 ± 0.5	1.7 ± 1.0	0.4 ± 0.2	1.0 ± 0.4	0.6 ± 0.3	0.5 ± 0.3	0.3 ± 0.1
BaP	0.9 ± 0.7	1.4 ± 0.8	1.8 ± 1.9	0.4 ± 0.4	1.1 ± 0.9	0.8 ± 0.6	0.4 ± 0.5	0.2 ± 0.2
DahA	1.1 ± 0.5	1.6 ± 0.6	2.1 ± 1.5	0.5 ± 0.3	1.2 ± 0.6	0.8 ± 0.5	0.6 ± 0.4	0.4 ± 0.2
IcdP	0.2 ± 0.1	0.3 ± 0.1	0.4 ± 0.3	0.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.0
BghiP	1.1 ± 0.5	1.5 ± 0.5	2.0 ± 1.3	0.5 ± 0.3	1.1 ± 0.6	0.8 ± 0.4	0.5 ± 0.4	0.3 ± 0.2
Total	239.3 ± 131.8	281.5 ± 140.9	424.0 ± 304.7	141.6 ± 114.4	286.3 ± 195.0	203.2 ± 128.2	177.0 ± 174.3	128.0 ± 106.5

It is interesting to note that the $\sum_{16}$PAHs was higher in rural sites near villages than the suburban one (see Table 1), which was consistent with the PAHs in soil in the same region (Ma et al. 2009). Liu et al. (2007) also found no significant difference of PAH concentrations between the urban and the rural areas in the Chinese Northern Plain, due to predominant sources of biomass and domestic coal combustion widely spread in rural areas in China.

The estimated air concentration of PAHs (mass per volume of air) can be derived if the effective air sample volume (V_{AIR}) is known for PUF PAS. According to passive sampling theory and many experimental evidences, different values of the linear sampling rates of PAHs were estimated, such as 3.5 m^3/d by Motelay-Massei et al. (2005), and 2.94 m^3/d by Santiago and Cayetano (2007). The sampling rate of 3.5 m^3/d was used in this study, and the estimated levels of $\sum_{16}$PAHs (ng/m^3) ranged from 25 to 120 in spring, from 13 to 50 in summer, from 22 to 74 in autumn, from 81 to 240 in winter. For winter and summer, both concentrations of total PAHs were higher than those in Dalian, China, collected by the similar PUF PAS (Wang et al. 2008). In Toronto, Canada, the $\sum_{17}$PAHs concentrations ranged from 3.5 to 61 ng/m^3 which was lower than those measured in Harbin (Motelay-Massei et al. 2005). Santiago and Cayetano (2007) reported that the air concentrations of $\sum_{13}$PAHs ranged from 41 to 170 ng/m^3 for urban and rural in Philippines, similar to the value obtained in this study. Phe was the most predominant PAH, followed by Flu and Pyr in Harbin air. The same results were also found in Dalian air, where the same three PAHs consisted more than 65% of all PAH concentrations in summer and winter (Wang et al. 2008). A slight difference was observed in urban sites outside of China. However, in Paris, Ollivon et al. (2002), Flu were the most predominant PAH, followed by Pyr and Phe.

Decreasing concentrations with rising molecular weight were observed in all sites (Table 1). Fourteen air samples were collected by an active air sampler from 7 to 20 May, 2008 at the UR1 site, and the PAHs profiles for both gas phase and particle phase were study in order to compare with those of samples sequestered by PUF PAS. Figure 2 presents the PAHs profiles for air samples sequestered by PUF PAS (average for UR1, UR2, UR3) and that obtained by active air sampler. The predominant PAHs sequestered by PUF PAS were low-molecular-weights (LMW) PAHs (2–3 ring), accounting for more than 60%, which are easily associated with gas phase. The dominant LMW compound was Phe, which accounted for more than 43% for total PAHs concentration. High-molecular-weights (HMW) PAHs (5–6 ring, such as BbF, BghiP, IcdP, BaP, BkF) with low vapor pressure mainly associated with particulate phase were also sequestered by PUF PAS but with smaller amount (<4%). Four-ring PAHs accounted for 36% in all samples, with Flu

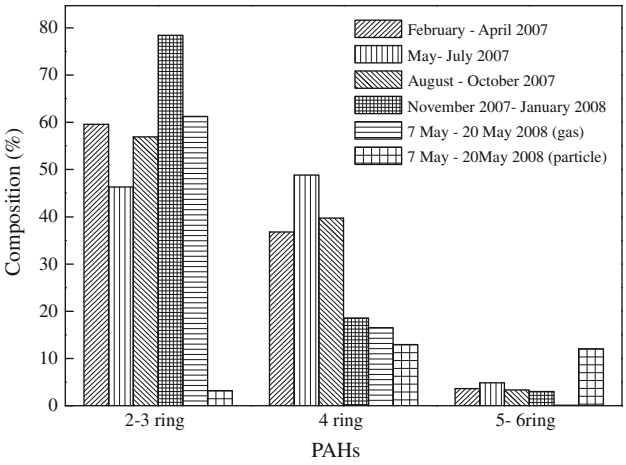

Fig. 2 Comparison of PAHs profiles in air collected by PUF PAS and active air sampler

(18%) followed by Pyr (12%). The similar profile was observed for the gas phase PAHs in the samples collected by active air sampler, in which LMW PAHs accounting for 61%. Our study showed that the PUF PAS collect major PAHs in gas phase, with only a little PAHs in particle phase, which was consistent with other previous studies (Liu et al. 2007; Santiago and Cayetano 2007).

In general, higher concentrations were found in urban sites, the lowest in the background site, reflecting a strong urban–rural-background gradient, which indicates the urban influences in the study region. This can be explained by the dominant emission activities in Chinese urban cities, where biomass burning, domestic coal combustion and coking industry are the three dominate emission sources (Xu et al. 2006). Besides the industrial emission at site UR3, other PAHs sources from a nearby railway were also possible. The sampling site UR1 is a typical urban residential area in Harbin where little industry sources nearby, but the vehicle traffic and domestic heating may be the two main sources of PAHs. The sampling site UR2 is located in a business area and there is a cloverleaf junction within 1 km distance, so the dense traffic may result in the higher concentration of PAHs. The suburban site is located in upwind from the outskirt of Harbin with low-density resident and surrounded by open space, so the lower PAHs concentration in this site might be attributed to the dilution by wind and the dispersion in neighboring areas. So the PAHs in this site may be influenced by the potential local sources other than the city emissions. The three rural sites (RU1, 2, 3) are located in farm lands with villages near by, where dispersed domestic heating are adopted and automobile traffic, thermal power and industrial emissions are on small scale. The reason for the high concentrations measured in rural samples may be associated with the local sources, such as domestic heating and cooking using coal,

biomass and other organic matters. The background site (BA1) is located in a forested land far from anthropogenic sources, so the long-range atmospheric transport may play an important role to the atmospheric PAHs levels as discussed in other studies (Harner et al. 2004; Wilcke et al. 2006).

Along the urban–rural-background transect, not only the air concentration decreased, but the composition of PAHs changed as well, which was indicated by Fig. 3. Obvious trend along the transect can be observed with proportions of LMW PAHs increasing and those of HMW PAHs decreasing. This was influenced by the urban fractionation effect, which was first demonstrated by analyzing PCBs (Harner et al. 2004) and PAHs (Motelay-Massei et al. 2005) in Toronto air collected by the similar PUF PAS, and followed by investigating PCBs in soil in Shanghai region (Ren et al. 2007).

The highest concentration was found in winter, followed by spring, autumn and lowest in summer, showing the obvious seasonal variation. Such seasonal variation has also been found in previous studies. In Dalian, Wang et al. (2008) also found clear seasonal trend of atmospheric PAHs, with high levels in heating period and relatively lower concentration in non-heating period. In the Pearl River Delta in Southern China, Liu et al. (2006) also found PAHs to be higher in winter than in summer. The similar seasonal variation of PAHs was also observed in BA1, which may also indicate the urban influences to the background area even approximate 115 km far away from the city centre. In Harbin, there are 6 months (from 1 January to 15 April and from 15 October to 31 December) every year needing for domestic heating. The ratios of the mean air concentrations of PAHs between heating and non-heating periods were 2.5 for urban samples, 2.4 for sub-urban sample, 2.7 for rural samples and 3.1 for background sample, which indicated an important input of PAHs from domestic heating in the study region.

It is interesting to note that in the two domestic heating seasons (spring and winter), the PAH level in the spring of 2008 was only half of that in the winter of 2007. The result is expected since in spring, the quantity of coal combustion and automobile exhaust are less than those in winter, due to higher temperature in spring than in winter. Besides, the wind speed is faster in spring than that in winter, which can dispel the PAHs in air from urban area to suburban/rural and background areas, so the measured PAHs in other areas also showed a clear seasonal variation similar to the urban area. In addition, meteorological conditions of the lower boundary layer height and decreased photochemical oxidation also enhanced the PAHs pollutions in winter (Park et al. 2002).

Source distinguish and control are important to study the fate and transport of PAHs in air and to reduce the

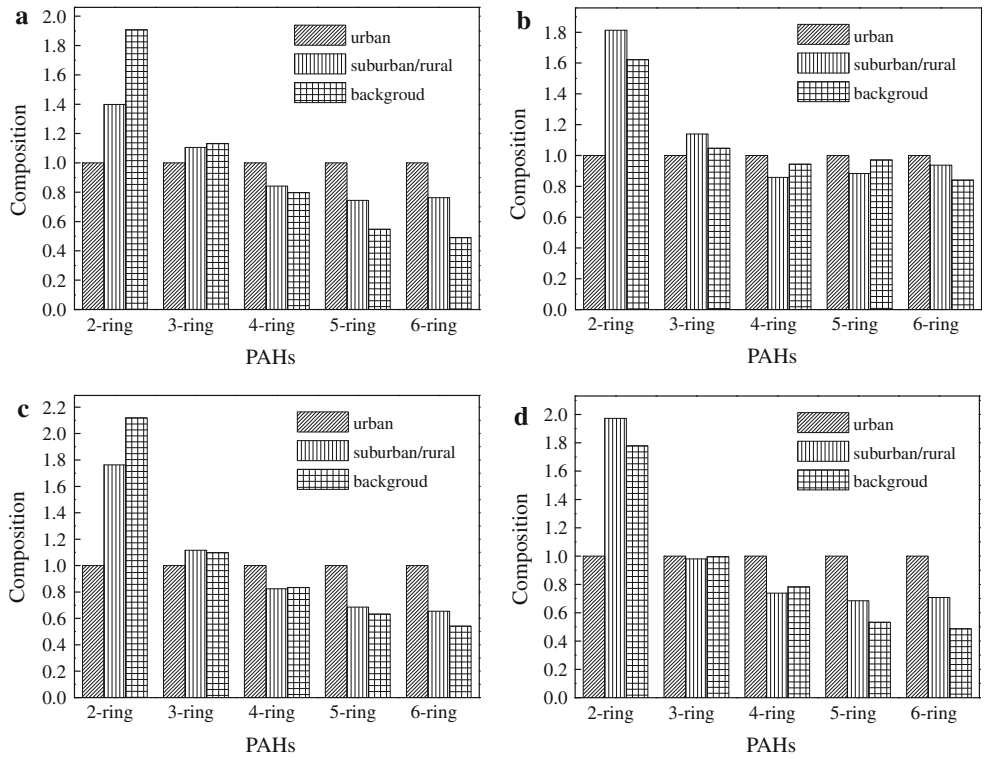

Fig. 3 Composition of PAHs in air samples for different seasons in Harbin normalized to the percent composition for urban sites where all values are equal to 1 (**a** spring, **b** summer, **c** autumn, **d** winter)

environmental risk caused by PAHs. The possible sources of PAHs in air may be identified by diagnostic ratios of individual PAH compounds. The ratio values of Flu/(Flu + Pyr) and IcdP/(IcdP + BghiP) are always used for identifying petrogenic (PAHs are derived from petroleum spills) and pyrogenic sources (PAHs are generated by incomplete combustion of fossil fuel (coal, petroleum and natural gas) and biomass). Flu and Pyr were considered as typical pyrogenic products derived from high temperature combustion of lower molecular weight aromatic compounds (Morillo et al. 2007).

The ratio of Flu/(Flu + Pyr) > 0.5 suggests pyrogenic sources, whereas <0.5 indicates petrogenic sources (Yunker et al. 2002). The ratio of IcdP/(IcdP + BghiP) can also be used to identify pyrogenic and petrogenic sources. IcdP/(IcdP + BghiP) ratio <0.20 likely implies petroleum (petrogenic sources), between 0.20 and 0.50 for liquid fossil fuel (vehicle and crude oil) combustion (pyrogenic sources), and ratio >0.50 implies grass, wood and coal combustion (pyrogenic sources) (Yunker et al. 2002). The values of IcdP/(IcdP + BghiP) ranged from 0.48 to 0.58 higher than 0.2, indicating a predominant contribution of pyrogenic sources in Harbin. In addition, the values of Flu/(Flu + Pyr) were higher than 0.5, with average value of 0.62 ± 0.02, also indicating the pyrogenic sources may be the most important sources of PAHs in Harbin. According to other study (Kavouras et al. 2001), the average value of 0.62 ± 0.02 indicates that the diesel engines emission is also an origin of PAHs in air. It is not surprising since there were 4.24×10^5 vehicles in 2007 in Harbin, so automobile exhaust is also an important source of PAHs, especially in urban region. From the above discussion, the pyrogenic sources are the main source of PAHs in air in Harbin.

Principal component analysis (PCA) is a useful data analysis technique for examining factors to reveal relationships and patterns within datasets. PCA with varimax rotation and retention of principal components having eigenvalues >1 was used to extract the possible sources. Three principal components (PCs) were extracted for all samples. The accumulative variances accounted for 94.4% of the total variance (Table 2).

As presented in Table 2, the first factor PC1 was related to HMW PAHs (BaA, BkF, BaP, DahA, IcdP and BghiP), which explained 42.8% of the total variance. Among these HMW PAHs, BkF, IcdP and BghiP were considered to be the tracers of vehicle exhaust (Harrison et al. 1996). This profile of PAH was consistent with pyrogenic sources, especially coal/biomass combustion and vehicle exhaust (Chen et al. 2005). So, pyrogenic sources (including coal/biomass combustion and automobile exhaust) may be the most important sources of PAHs in air in Harbin.

PC 2, accounted for 36.8% of the total variance, was dominated by some moderate-weight PAHs (Flua, Pyr and Chr), which has strong similarity to natural gas emissions. In natural gas combustion, Chr is expected to be present with Flua and Pyr (Lee et al. 2004). Actually, in Harbin city, most families use natural gas for cooking, encouraged by the government as the environment friendly energy, so natural gas combustion is supposed to be a responsible source of PAHs in Harbin.

Table 2 Factor pattern for PAHs in air in Harbin

PAHs	PC1	PC2	PC3
Nap	−0.49	−0.77	0.11
Acy	−0.34	−0.39	**0.83**
Ace	−0.62	−0.67	−0.07
Flu	−0.28	−0.89	0.29
Phe	0.30	−0.71	0.46
Ant	−0.14	−0.39	0.88
Flua	0.20	**0.92**	−0.31
Pyr	0.17	**0.94**	−0.20
BaA	**0.89**[a]	0.43	−0.02
Chr	0.22	**0.86**	−0.43
BbF	0.63	0.64	−0.35
BkF	**0.94**	0.26	−0.22
BaP	**0.99**	0.05	0.01
DahA	**0.95**	0.23	−0.20
IcdP	**0.98**	0.01	−0.14
BghiP	**0.94**	0.25	−0.20
Explained variance (%)	42.8	36.8	14.8

[a] Boldfaced type indicates PCA loading values higher than 0.8

PC 3 (explained 14.8% of the total variance), had high loadings on LMW PAHs (Acy and Ant), which can be attributed to petrogenic sources (volatilization and leak of petroleum and petroleum products) (Soclo et al. 2000; Morillo et al. 2007). So the PCA revealed that pyrogenic sources and petrogenic sources were the main contributors of PAHs in air in Harbin.

Overall, the results from both methods (diagnostic ratios and PCA) were in good agreement, which suggested that the PAHs in air of Harbin mainly generated from pyrogenic sources, such as coal/biomass and natural combustion, especially for HMW PAHs, while the petrogenic sources (petroleum spills) were responsible for the presence of LMW PAHs. It must be kept in mind that the successful source apportionment depends on the basic emission source profiles. So source profile identification for both local sources and external sources should be taken into consideration for more exact source apportionment of PAHs in atmosphere in future study.

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