Archives of Environmental Contamination and Toxicology (2019) 76:102–113
https://doi.org/10.1007/s00244-018-0563-5

Atmospheric $PM_{2.5}$-Bound Polycyclic Aromatic Hydrocarbons (PAHs) in Guiyang City, Southwest China: Concentration, Seasonal Variation, Sources and Health Risk Assessment

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Received: 18 June 2018 / Accepted: 17 September 2018 / Published online: 5 October 2018

Abstract

The polycyclic aromatic hydrocarbons (PAHs) bound to fine particulate matter ($PM_{2.5}$) can cause long-term adverse health consequences and are a public concern. A total of 144 $PM_{2.5}$-bound PAHs samples collected from Guiyang City, a typical plateau montane area in southwest China, from September 2012 to August 2013 were investigated to clarify their concentration, distribution, and potential sources. The health exposure risk also was evaluated. The samplers equipped with 90-mm glass fibre filters were operated at a flow rate of 100 L min^{-1} for 24 h. The concentrations of the 16 PAHs (US EPA priority) were analysed by using ultra performance liquid chromatography equipped with photo diode array detector. Diagnostic ratios and back-trajectories were performed for the 16 PAHs sources apportionment. The results showed that the 16 PAHs ranged from 2.9 to 231 ng m^{-3} with an annual average of 41 ± 21 ng m^{-3}. The PAHs concentrations exhibited obvious seasonal variation, with higher levels in winter than in summer. Diagnostic ratios indicated that PAHs mainly originated from the combustion of coal and biomass, followed by the emission of vehicle exhaust. Cluster analyses on back-trajectories illustrated that approximately 34% of the air mass came from abroad, as far as Laos and Vietnam, in summer, whereas more than 90% of the air mass came from domestic sources in winter. The lifetime excess cancer risk from exposure to PAHs was 3.63×10^{-4}, approximately 360 times higher than the health guideline (10^{-6}) recommended by the US EPA, reflecting a high risk of cancer.

Fine particulate matter with an aerodynamic diameter less than 2.5 µm ($PM_{2.5}$) is a major environmental issue and health concern (Fan et al. 2017). $PM_{2.5}$ can cause morbidity and failure of respiratory and cardiac systems (Analitis et al. 2006). A large number of toxic compounds can be adsorbed to $PM_{2.5}$, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, and heavy metals (Ostro et al. 2000; Mar et al. 2006; Anyenda et al. 2016; Yang et al. 2017). PAHs are semivolatile organic compounds that lead to long-term adverse health consequences, such as cancer, birth defects, genetic damage, respiratory diseases, immunodeficiency, and neurological diseases (Boström et al. 2002; Choi et al. 2015; Han et al. 2015). Because of their proven carcinogenic properties (Ohura et al. 2004; Li et al. 2009a, b, c), much attention has been paid to $PM_{2.5}$-bound PAHs, even very recently (Bourotte et al. 2005; Liu et al. 2015; Yang et al. 2017).

PAHs have both natural and anthropogenic origins. The latter is the main source in the modern environment. In atmosphere, most anthropogenic PAHs are originated from the incomplete combustion of coal, petroleum, biofuels, and organic polymer compounds (Zhang and Tao 2009; Estellano et al. 2012; Cheruyiot et al. 2015). High concentrations of PAHs were found in the ambient atmosphere of industrial and commercial areas (Kim et al. 2013; Wu et al. 2014) and approximately 65–90% of PAHs in the global atmosphere

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00244-018-0563-5) contains supplementary material, which is available to authorized users.

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are bound to $PM_{2.5}$ (Poster et al. 1995; Wang et al. 2008). With the acceleration of urbanization and the increase in energy consumption, in most developing countries, emissions of PAHs have increased dramatically (Suvarapu et al. 2012; Huang et al. 2014).

Presently, characteristics, sources, and risk assessment of $PM_{2.5}$-bound PAHs were widely conducted (Li et al. 2009a, b, c; Mohanraj et al. 2012). The average concentrations of $PM_{2.5}$-bound PAHs as high as 458 ± 246 ng m^{-3} have been found in India (Etchie et al. 2018). A large number of studies showed that concentrations of $PM_{2.5}$-bound PAHs in winter and autumn were higher than those in spring and summer (Gu et al. 2010; Yang et al. 2017). The concentrations of PAHs were heavily influenced by meteorological parameters, such as temperature and humidity (Liu et al. 2016). The primary anthropogenic sources of PAHs in $PM_{2.5}$ are coal combustion and vehicle exhaust emission (Moon et al. 2006; Liu et al. 2016; Fan et al. 2017). Some studies indicated that the excess cancer risk (ECR) in Taiwan (8.4×10^{-5}), Beijing (1.1×10^{-3}), and other places exceeded the US EPA health guidelines (10^{-6}) (Li et al. 2017; Chen et al. 2017). However, most of these studies were conducted in plains (Beijing) and hilly regions (Guangzhou). There are few reports of $PM_{2.5}$-bound PAHs in highly developing plateau mountain cities in China (Liu et al. 2015; Chen et al. 2017), of which geographical and meteorological factors may affect on concentrations of PAHs and cause big differences among the regions (Kume et al. 2007; Liu et al. 2016; Yang et al. 2017).

Guiyang City, the capital of Guizhou province in Southwest China, is a typical inland plateau mountain city characterized with high sea level and unfavourable diffusion conditions. The average altitude of approximately 1100 m. It had a population of approximately 4.8 million in 2017. Guiyang has currently become a high-traffic, domestic tourism area, and its industries of coal mining, aviation manufacturing, oil processing, and nuclear fuel processing are growing fast. With the quick development, housing construction has accelerated, and the number of motor vehicles has increased dramatically in Guiyang. Several studies on $PM_{2.5}$ in ambient air in Guiyang have been conducted, suggesting high pollution level with concentrations ranging from 41 to 75 μg m^{-3} (Liu et al. 2014; Liang et al. 2015). However, $PM_{2.5}$-bound PAHs characterization and risk assessment in Guiyang has not been studied yet.

The objectives of this study were (1) to elucidate characteristics and distribution patterns of $PM_{2.5}$-bound PAHs in an inland plateau mountain city, (2) to identify potential sources of PAHs in Guiyang, and (3) to assess the associated health risk.

Materials and Methods

Study Area

Guiyang is located in Southwestern China and has a subtropical, humid, and mild climate, with an annual average temperature of 15.3 °C. The annual average relative humidity in Guiyang is 77%, and the total annual precipitation is 1129.5 mm. According to statistical data, the number of motor vehicles, including private cars and taxis, increased from 310,000 to 700,000 between 2007 and 2012. The energy structure of Guiyang is dominated by coal, which is mainly used for industry and domestic heating. The former generally uses coal in nonferrous metal smelting and cement plant, whereas the latter mostly uses it for heating in the winter. The Yunyan district is a major urban area within the city. By the end of 2016, the total population was approximately 1.0 million in the Yunyan region. Several nonferrous heavy metal facilities and an airport are adjacent to Yunyan. The Baiyun district is the geographical centre of Guiyang City. It is the largest aluminum industrial center in China because of its abundant bauxite sources. The Huaxi district is an ecological district of Guiyang. It is a tourism area with no apparent emission sources.

Sampling and Preparation

Considering geographical, economic, and social development information of Guiyang, three sampling sites were selected for $PM_{2.5}$ collection, consisting of a site YY (26°35′31.26″N, 106°43′12.02″E) in Yunyan district, a site BY (26°43′01.51″N, 106°37′21.27″E) in Baiyun district, approximately 23 km northwest of YY, and a site HX (26°25′44.74″N, 106°40′19.65″E) in Huaxi district, approximately 21 km southwest of YY (Fig. 1).

All sites were located on a rooftop, approximately 15 m above the ground. At each site, a middle-volume $PM_{2.5}$ sampler (TH-150A, China) equipped with $PM_{2.5}$ cut cyclones and 90-mm glass fibre filters (Whatman, USA) was operated at a flow rate of 100 L min^{-1} for 24 h. Five samples at each sampling site were continually collected per month. The overall sampling period was from September 2012 to August 2013. A total of 144 valid samples were selected for further analysis. Glass fibre filters were preheated at 500 °C for 5 h before sample collection to remove any organic contaminants. An average of quadruplicate filter weighing was determined using an analytical balance (AX120, SHIMADZU, Japan) after equilibration, with initial filter weighing 24 h prior under preconditional temperature (25 ± 2 °C) and humidity ($50 \pm 5\%$)

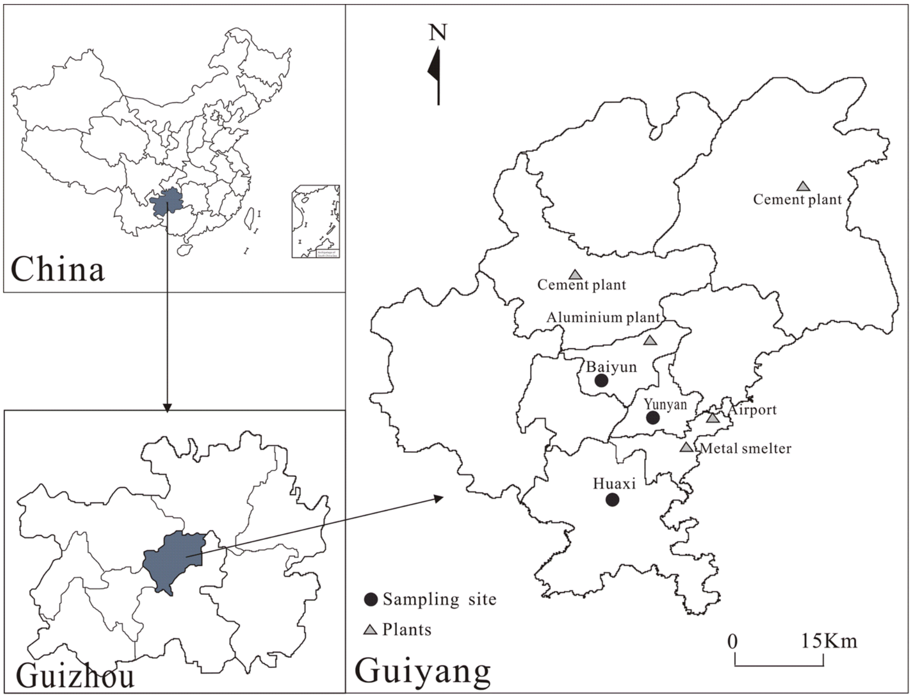

Fig. 1 Map of sampling sites

in a controlling chamber (HWS-250BX, Nernst, Tianjin, China). Each membrane was weighed again after 2 h in the constant temperature and humidity chamber, and the difference between four repeated weighing values was not greater than 0.4 mg. All weighed membranes were placed in self-sealing bags with the corresponding recorded total mass and then placed in a drying box for sampling.

After sampling, the filter membrane was folded in half by using tweezers and then loaded into the original sample bag. All sampled filter membranes were reweighed four times. The mass of the samples was determined by using a weight reduction method. To ensure the accuracy of the analytical results, all samples for PAHs analysis were weighed and stored in a refrigerator at − 18 °C. Measurements of PAHs in filters were conducted within 7 days.

PAHs in $PM_{2.5}$ were extracted with a mixed solvent of acetone and *n*-hexane (1:1, v/v) using an accelerated solvent extraction ASE 150 (DIONEX, USA) (Johansen et al. 1994). The extraction was duplicated at a temperature of 100 °C and a pressure of 1500 psi. The extract was concentrated to approximately 5.0 mL using a rotary evaporator (EYALA, Japan) and then reduced to 0.5–1.0 mL under a gentle nitrogen stream. The concentrated extracts were sequentially purified in the chromatography column filled with 6-cm length activated neutral alumina (Al_2O_3) and 12-cm length Silica gel (SiO_2) and eluted with 70 mL of Hexane/dichloromethane (1:1, v:v). After that, the purified extract was concentrated to approximately 5.0 mL using a rotary evaporator (EYALA, Japan) and then reduced to 1.0 mL under a gentle nitrogen for analysis.

All glassware was soaked in potassium dichromate sulfuric acid solution for 5 h, were rinsed with distilled water and Milli-Q water (Merck Millipore, France), and then were baked in a muffle furnace at 450 °C for 4 h. Silica gel and alumina used in the chromatographic column were extracted by soxhlet extractor with methanol and dichloromethane for 24 h, both of which were baked for 12 h at 180 °C for silica and 250 °C for alumina. Then, silica gel and alumina were activated by 3% water and soaked in *n*-hexane before usage.

Analysis

Sixteen PAHs mixed standards, including Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (Bap), Indeno(1,2,3-cd)pyrene (IcdP), Dibenzo(a,h)anthracene (DBA), and Benzo(g,hi)perylene (Bghip), were used for the quantitative determination (Supelco, USA).

Analyses of PAHs were performed by ultra performance liquid chromatography (UPLC) (ACQUITY, Waters, USA), equipped with photo diode array (PDA) detector, and Empower chromatography work station. The chromatographic separation was performed on a Waters Acquity UPLC BEH C18 column (100 mm × 2.1 mm × 1.7 mm) maintained at 25 °C (Mirivel et al. 2011). The detection wavelengths were 254 nm and 220 nm. The injection volume was 2 μL, and the mobile phase consisted of water (A) and acetonitrile (B). The gradient elution procedure was as follows: solvent B 65–89% at 0–5 min, 89% at 5–7 min, 89–100% at 7–9 min, 100% at 9–16 min, and 65% at 16–18 min. The flow rate was 0.15 mL min^{-1}.

Date Analysis

The proportion of PAHs in $PM_{2.5}$, the seasonal variation of PAHs, and the correlation between $PM_{2.5}$ and PAHs were analyzed by Origin 8.5 (OriginLab, USA). Pearson's and Spearman correlation coefficients were used to report the association between PAHs and meteorological factors by SPSS 22 (IBM, USA). One-way ANOVA analysis was used to analyze significant differences in different seasons by SPSS 22 (IBM, USA).

Quality Control

The linearity, detection limit, relative standard deviation, and recovery of 16 PAHs were determined by referring to the US EPA-610 method (Dejean et al. 2009). The external method was applied in the present study, following with duplicate analyses every ten samples, and spiked recovery tests of treatment with standard samples for each batch during measurements. The target compound in the regent and blank filter membrane was not detectable. Prior to each sample analyzed, the detector UPLC-PDA was rinsed for 30 min. The PAHs recoveries of the standard-spiked matrix ranged from 67 to 102%, and the relative standard deviation (RSD) was in the range of 0.25–7.2% ($n = 10$). The method detection limit (MDLs) of PAHs was between 0.50 and 2.0 μg L^{-1}. All correlation coefficients of the standard curves of each target compound were greater than 0.999. Detail information of quality control was shown in Table S1 in Supplemental Materials.

Source Apportionment

According to their properties and sources, the 16 PAHs are divided into low-molecular-weight PAHs (LMW-PAHs: 2–3 rings), middle-molecular-weight PAHs (MMW-PAHs: 4rings), and high-molecular-weight PAHs (HMW-PAHs: 5–6 rings). PAHs of 3–4 rings are mainly derived from coal combustion, whereas those of 5–6 rings are mainly derived from gasoline vehicles (Ravindra et al. 2006; Wu et al. 2014).

Diagnostic Ratios

The ratios of Phe/(Ant + Phe), Flu/(Flu + Pyr), BaA/(BaA + Chr), and IcdP/(IcdP + BghiP) were widely used to estimate various sources of PAHs contamination in the environment (Grimmer et al. 1983; Larsen and Baker 2003; Wang et al. 2014), which were employed in the present study for sources apportionment as well. Each interval value and reference of diagnostic ratios were shown in Table S2 in Supplemental Materials.

Air Mass Trajectories Analysis

The HYSPLIT Trajectory model, developed by NOAA (https://ready.arl.noaa.gov/HYSPLIT_traj.php), was employed to identify pollutants sources using the direction of air mass movement. Because the sampling sites are closed, the backward trajectory analyses are the same. Therefore, YY was selected to analyze and calculate the clustering backward trajectory during the summer and winter sampling campaigns. Considering the altitude of Guiyang, a height of 1000 m was selected as the starting point to track the changes in both summer and winter.

Estimation of Distance from Emission Sources

The low ring PAHs can migrate over a long distance with the circulation of the atmosphere. Based on differences in photochemical decomposition of Ant and Phe isomers that can be used as the geochemical tracers showing the anthropogenic activities, Li et al. (2014) established a model to estimate PAHs migration distance in the atmosphere, and the calculation is Eq. (1) as follows:

$$D_{\mathrm{t}} = -\frac{6 \times 10^{6}}{C_{\mathrm{OH}}} \times S_{\mathrm{w}} \times \ln\left(\frac{C_{\mathrm{st}}^{\mathrm{A}}}{C_{\mathrm{st}}^{\mathrm{P}}} \times \frac{C_{\mathrm{g0}}^{\mathrm{P}}}{C_{\mathrm{g0}}^{\mathrm{A}}}\right) \quad (1)$$

where D_{t} (km) is the longest distance that PAHs may transport in the atmosphere, C_{OH} (mol cm^{-3}) is the concentration of OH radicals in the atmosphere, S_{w} (m s^{-1}) is wind speed, $C_{\mathrm{g0}}^{\mathrm{P}}/C_{\mathrm{g0}}^{\mathrm{A}}$ is the ratio of Phe and Ant at the emission site, $C_{\mathrm{st}}^{\mathrm{A}}/C_{\mathrm{st}}^{\mathrm{P}}$ is the ratio of Ant and Phe in samples.

To obtain the maximum transmission distance of PAHs between emission sources and sampling location, the maximum wind speed of 60 m s^{-1} (Gatey and Miller 2007) and the lowest concentration of OH radical of 0.3×10^{6} mol cm^{-3} (Hewitt and Harrison 1985) were referred in the calculation. For low ring PAHs are mainly derived from coal combustion; hence, the $C_{\mathrm{g0}}^{\mathrm{P}}/C_{\mathrm{g0}}^{\mathrm{A}}$ ratio was referred to coal burning, which is 5.67 (Li et al. 2014; Yu et al. 2018).

Health Risk Assessment

BaP was used as a marker of total carcinogenicity of PAHs (Guerreiro et al. 2014). The equivalent concentration of BaP (BaPeq) is commonly used to assess the carcinogenicity of PAHs (Zhu et al. 2015), and it is calculated by multiplying the mass concentration of specific PAHs species with their corresponding toxic equivalent factor (TEF), as Eq. (2) (Nisbet and Lagoy 1992; Pongpiachan 2016). The toxic equivalence quotient (TEQ) represents the toxic equivalent of target compounds and can be estimated by the sum of the BaPeq concentrations of each PAH (Li et al. 2017). The lifetime excess cancer risk (ECR) can be obtained by the resultant BaPeq (in ng m^{-3}) and the unit risk (UR) of 8.7×10^{-5} ng m^{-3} (WHO 2000). Its calculation Eq. (3) is as follows:

$$\mathrm{TEQ} = \sum \mathrm{BaPeq}_i = \sum \mathrm{PAH}_i \times \mathrm{TEF}_i \tag{2}$$

$$\mathrm{ECR} = \mathrm{BaPeq} \times \mathrm{UR} \tag{3}$$

Results and Discussion

PAHs Concentrations

The annual average concentration of PAHs in all $PM_{2.5}$ samples was 41 ± 21 ng m^{-3} ($n = 144$). At the three sampling sites, slight variations were observed, with the highest average of 43 ± 25 ng m^{-3} recorded at YY, followed by (average: 36 ± 16 ng m^{-3}) and HX (average: 35 ± 26 ng m^{-3}) (Table 1). These values were higher than those observed in other cities worldwide, such as Tuscany, Italy (Martellini et al. 2012), Shizuoka, Japan (Kume et al. 2007), Madrid, Spain (Barrado et al. 2012), and Atlanta, GA, USA (Li et al. 2009a, b, c) (Table 2). Compared with those in Hong Kong (Ma et al. 2016), Kunming (Bi et al. 2015), and Guangdong (Liu et al. 2015), PAH levels in Guiyang were high.

Generally, for all samples, the percentages of PAHs with different rings were in the following order: LMW-PAHs (55.1%) > HMW-PAHs (32.1%) > MMW-PAH (12.8%). For each site, the same order for three categories of PAHs was found (Fig. 2). The highest percentage of LMW-PAHs observed in the present study was different from those previously reported, where PAHs in $PM_{2.5}$ were dominated by HMW-PAHs (Eiguren-Fernandez et al. 2004; Kume et al. 2007; Li et al. 2010; Wang et al. 2014, 2017; Yang et al. 2017). This difference may be related to low-temperature combustion of coal, which can cause a sharp increase in emission of LMW-PAHs (Wu et al. 2014; Samburova et al. 2016).

During the study period, the total average concentrations of $PM_{2.5}$-bound PAHs combined with three sites in Guiyang among the four seasons were in the order of spring > winter > autumn > summer (Fig. S1). The highest average of 49 ± 18 ng m^{-3} was observed in spring, with a similar average of 46 ± 35 ng m^{-3} in winter, and the lowest average of 26 ± 16 ng m^{-3} was recorded in summer. Among three sampling sites, Fig. 3 showed that the seasonal variation in YY was different from both BY and HX (ANOVA, $p < 0.05$). Those differences observed in the present study might be related to the unclear seasonal changes in Guiyang caused by its meteorological parameters. Seasonal variations at the three sites showed that the average concentrations of PAHs in winter were 2.1, 1.1, and 2.6 times of those in summer for YY, BY, and HX, respectively. The highest concentrations of PAHs observed in winter may be attributed to domestic coal combustion. An alternative explanation is the slow degradation of PAHs during winter, due to the low temperature and little rain. In contrast, in summer, the degradation rate of PAHs increased with high temperature, strong radiation, and abundant rainwater (Eiguren-Fernandez et al. 2004; Moon et al. 2006), which resulted in low concentrations of PAHs in the present study. Our results were in agreement with previous studies, in which the concentrations of PAHs in winter were high and up to 5.6 times of those in summer in Dekalb, USA (Li et al. 2009a, b, c). Yi et al. (2013) also reported that the concentration of PAHs in winter was approximately 2 times than that in summer in Fuzhou, China.

Influencing factors

$PM_{2.5}$ mass concentrations

The annual average mass concentration of $PM_{2.5}$ (66 ± 31 μg m^{-3}) exceeded the air quality guideline of 25 μg m^{-3} recommended by WHO (2008) but was lower than the secondary standard concentration of 75 μg m^{-3} in China. As shown in Fig. 4, PAHs were positively correlated with $PM_{2.5}$ ($R = 0.43$, $p < 0.001$), which was similar to the findings reported by Yang et al. (2017). Previous studies indicated that HMW-PAHs and MMW-PAHs were more likely to associate with particulate matter (Krugly et al. 2014; Fan et al. 2017), whereas in the present study, the correlation between $PM_{2.5}$ and HMW-PAHs ($R = 0.48$, $p < 0.001$) was stronger than that of $PM_{2.5}$ and MMW-PAHs ($R = 0.35$, $p < 0.001$) as well as $PM_{2.5}$ and LMW-PAHs ($R = 0.26$, $p < 0.001$), which indicates the higher molecular rings of PAHs the easier combined to $PM_{2.5}$ (Kume et al. 2007; Yang et al. 2017).

Meteorology Parameters

Meteorological conditions, such as pressure (P), temperature (T), relative humidity (RH), precipitation, and wind speed (WS), may affect PAHs (Cortes et al. 2000; Li et al. 2010). In this study, correlations between PAHs and meteorological parameters were obtained with the results in YY. The meteorological data of YY were collected by HOBO-U30 (Onset, USA). As known, the degradation rate of PAHs is high at high temperatures, and high wind speed can disperse pollutants in the atmosphere. Weak and negative correlations between PAHs and

Table 1 Concentrations of $PM_{2.5}$ (μg m^{-3}) and PAHs (ng m^{-3}) collected from three sites of YY, BY, and HX during a whole year period

	YY (*N* = 48)					BY (*N* = 48)				
	Spring	Summer	Autumn	Winter	Annual	Spring	Summer	Autumn	Winter	Annual
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Npa	3.1 ± 2.4	0.87 ± 0.92	0.48 ± 0.68	3.9 ± 1.9	2.1 ± 2.2	1.9 ± 0.83	0.73 ± 0.72	1.2 ± 1.4	2.5 ± 0.6	1.6 ± 1.1
Acy	11 ± 6.1	5.9 ± 6.3	2.6 ± 1.5	3.4 ± 1.8	5.7 ± 5.5	8.2 ± 5.5	6.3 ± 7.3	5.9 ± 4.1	2.3 ± 0.38	5.7 ± 5.4
Ace	7.0 ± 2.6	6.5 ± 4.4	2.6 ± 2.9	7.9 ± 4.4	6.0 ± 4.2	3.5 ± 1.6	5.4 ± 4.2	12.3 ± 9.8	4.0 ± 0.52	6.3 ± 6.4
Flu	1.7 ± 0.76	0.41 ± 0.16	0.26 ± 0.28	1.6 ± 0.8	1.0 ± 0.85	1.2 ± 0.21	0.37 ± 0.13	1.3 ± 0.46	0.79 ± 0.19	0.91 ± 0.45
Phe	11 ± 2.7	3.2 ± 2.2	2.6 ± 1.5	11.8 ± 7.0	7.1 ± 5.8	4.9 ± 0.68	3.2 ± 2.24	7.6 ± 2.5	6.2 ± 2.0	5.5 ± 2.6
Ant	2.3 ± 0.35	1.4 ± 0.29	2.9 ± 0.68	1.1 ± 0.29	1.9 ± 0.84	1.8 ± 0.46	1.2 ± 0.58	1.4 ± 1.3	0.88 ± 0.17	1.3 ± 0.80
Fla	1.1 ± 0.41	0.20 ± 0.12	0.11 ± 0.12	2.1 ± 1.0	0.88 ± 1.0	0.65 ± 0.06	0.27 ± 0.20	0.48 ± 0.49	0.66 ± 0.23	0.51 ± 0.33
Pyr	3.3 ± 1.3	0.45 ± 0.20	0.75 ± 0.22	1.5 ± 0.49	1.5 ± 1.3	1.9 ± 0.53	0.47 ± 0.21	1.4 ± 0.03	1.5 ± 0.80	1.3 ± 0.73
BaA	2.7 ± 0.46	0.81 ± 0.14	0.58 ± 0.15	1.5 ± 0.11	1.4 ± 0.87	3.1 ± 2.5	0.74 ± 0.12	2.1 ± 1.2	1.1 ± 0.16	1.8 ± 1.7
Chr	1.7 ± 0.76	0.44 ± 0.18	0.75 ± 0.18	2.5 ± 2.0	1.3 ± 1.4	1.4 ± 0.52	0.51 ± 0.20	1.5 ± 0.43	1.5 ± 0.39	1.2 ± 0.57
BbF	4.6 ± 1.1	1.4 ± 0.86	1.8 ± 0.13	4.9 ± 3.1	3.2 ± 2.3	3.3 ± 0.86	1.0 ± 0.37	3.2 ± 1.3	3.3 ± 1.2	2.7 ± 1.4
BkF	1.7 ± 0.88	0.57 ± 0.54	0.70 ± 0.17	2.2 ± 1.5	1.3 ± 1.1	1.4 ± 0.39	0.50 ± 0.35	1.2 ± 0.52	1.3 ± 0.29	1.1 ± 0.53
BaP	2.8 ± 1.6	0.14 ± 0.05	0.92 ± 0.19	3.1 ± 2.3	1.7 ± 1.9	1.3 ± 0.48	0.24 ± 0.24	1.1 ± 0.58	1.2 ± 0.12	1.0 ± 0.58
IcdP	2.0 ± 0.60	0.93 ± 0.89	0.82 ± 0.65	4.3 ± 2.5	2.0 ± 2.0	1.3 ± 0.31	0.67 ± 0.21	1.2 ± 1.2	2.1 ± 0.85	1.3 ± 0.92
DBA	2.7 ± 0.75	0.63 ± 0.15	1.5 ± 0.08	4.6 ± 2.3	2.3 ± 1.9	1.5 ± 0.48	0.40 ± 0.16	1.8 ± 0.73	2.7 ± 0.17	1.6 ± 0.93
BghiP	6.3 ± 2.7	0.79 ± 0.18	3.7 ± 1.0	5.4 ± 1.4	4.0 ± 2.6	2.3 ± 1.2	0.48 ± 0.16	2.5 ± 0.29	3.4 ± 1.2	2.2 ± 1.4
∑PAHs	65 ± 2.7	25 ± 16	23 ± 6.1	62 ± 27	43 ± 25	40 ± 10	22 ± 15	46 ± 20	36 ± 6.0	36 ± 16
$PM_{2.5}$	76 ± 5.8	39 ± 16	53 ± 13	80 ± 51	62 ± 32	94 ± 34	63 ± 15	74 ± 14	68 ± 33	75 ± 29

	HX (*N* = 48)				
	Spring	Summer	Autumn	Winter	Annual
	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD	Mean ± SD
Npa	2.5 ± 1.8	0.64 ± 0.56	1.3 ± 1.6	2.0 ± 0.93	1.6 ± 1.5
Acy	7.3 ± 1.3	3.5 ± 4.6	5.5 ± 6.4	1.0 ± 0.74	4.4 ± 4.6
Ace	4.5 ± 2.0	4.1 ± 3.4	12.3 ± 16.0	2.8 ± 0.19	5.9 ± 9.1
Flu	1.1 ± 0.57	0.26 ± 0.20	0.80 ± 0.89	0.77 ± 0.41	0.73 ± 0.65
Phe	6.8 ± 2.7	2.3 ± 1.7	4.6 ± 6.2	5.1 ± 2.5	4.7 ± 4.0
Ant	1.5 ± 0.23	0.78 ± 0.40	1.5 ± 1.0	0.72 ± 0.29	1.1 ± 0.69
Fla	0.9 ± 0.58	0.20 ± 0.17	0.89 ± 1.0	2.3 ± 0.84	1.1 ± 1.1
Pyr	1.8 ± 0.04	0.34 ± 0.05	1.0 ± 0.56	1.5 ± 1.2	1.1 ± 0.88
BaA	1.9 ± 0.54	0.53 ± 0.22	1.9 ± 2.3	1.6 ± 0.43	1.5 ± 1.3
Chr	0.91 ± 0.25	0.26 ± 0.14	1.4 ± 0.66	1.4 ± 0.63	1.0 ± 0.67
BbF	2.6 ± 0.93	0.83 ± 0.68	3.1 ± 1.5	3.5 ± 2.2	2.5 ± 1.8
BkF	1.2 ± 0.39	0.50 ± 0.47	1.4 ± 0.68	1.8 ± 1.1	1.2 ± 0.85
BaP	1.7 ± 0.79	0.23 ± 0.11	1.4 ± 0.87	2.3 ± 1.7	1.4 ± 1.3
IcdP	1.7 ± 0.82	0.64 ± 0.56	1.4 ± 1.6	3.5 ± 1.6	1.8 ± 1.6
DBA	1.9 ± 0.85	0.66 ± 0.51	2.0 ± 0.95	3.8 ± 0.89	2.1 ± 1.4
BghiP	3.1 ± 1.6	0.86 ± 0.53	2.9 ± 1.5	5.1 ± 3.0	3.0 ± 2.4
∑PAHs	41 ± 11	17 ± 14	43 ± 39	39 ± 18	35 ± 26
$PM_{2.5}$	83 ± 29	32 ± 1.4	53 ± 29	83 ± 11	63 ± 31

SD Standard deviation

temperature ($R = -0.15$) and between PAHs and wind speed ($R = -0.12$) were observed, which was in agreement with previous results (Eiguren-Fernandez et al. 2004; Moon et al. 2006; Teixeira et al. 2013; Kim et al. 2015). However, we obtained a positive correlation ($R = 0.25$) between PAHs and humidity, which was in agreement with results reported by Gu et al. (2010) and Li et al. (2009a, b, c).

Table 2 Comparison of concentrations of $PM_{2.5}$-bound PAHs measured in this study with those reported from worldwide

Country	Location	$\sum$PAHs (ng m^{-3})	Sampling period	References
USA	Atlanta	3.16	2003.12–2004.6	Li et al. (2009a, b, c)
	Chapel Hill	1.91	2002.9–2003.2	Pleil et al. (2004)
Italy	Tuscany	0.92–13.0	2009.3–2010.3	Martellini et al. (2012)
	Turin	8.24 ± 6.30	2001.11–2004.12	Gilli et al. (2007)
Spain	Madrid	0.18–2.13	2008.1–2008.11	Barrado et al. (2012)
	Zaragoza	2.14 ± 2.18	2011.6–2012.5	Callén et al. (2014)
Japan	Shizuoka	1.00–8.40	2001.12–2002.1	Kume et al. (2007)
Korea	Chongju	12.9	1998.10–1999.10	Park et al. (2006)
Turkey	Izmir	8.30 ± 3.10	2006.4–2006.5	Odabasi et al. (2015)
Greece	Thessaloniki	12.8	2011.6–2012.5	Tolis et al. (2015)
China	Hong Kong	4.59	2011.9–2012.8	Ma et al. (2016)
	Beijing	9.1–200	2003.9–2004.7	Chen et al. (2017)
	Shanghai	16.9 ± 9.00	2011.11–2012.8	Wang et al. (2015)
	Guangdong	33.9	2012.6–2013.5	Liu et al. (2015)
	Qingdao	87.5	2001.6–2002.5	Guo et al. (2003)
	Kunming	28.3	2013.4–2014.1	Bi et al. (2015)
	Guiyang	41 ± 21	2012.9–2013.8	This study

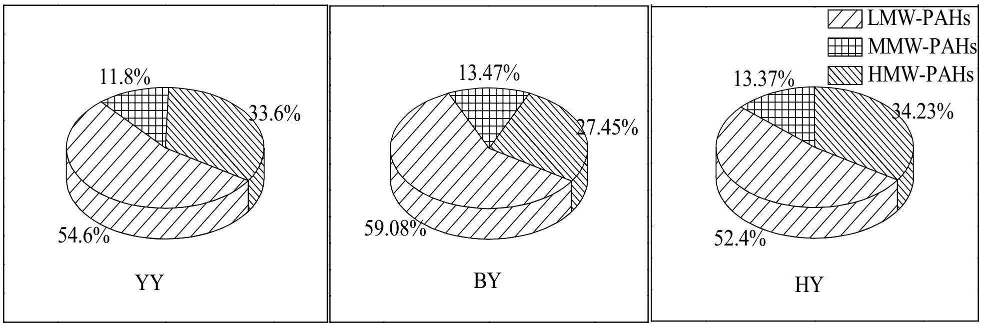

Fig. 2 Percentages of LMW-PAHs, MMW-PAHs, and HMW-PAHs in total PAHs

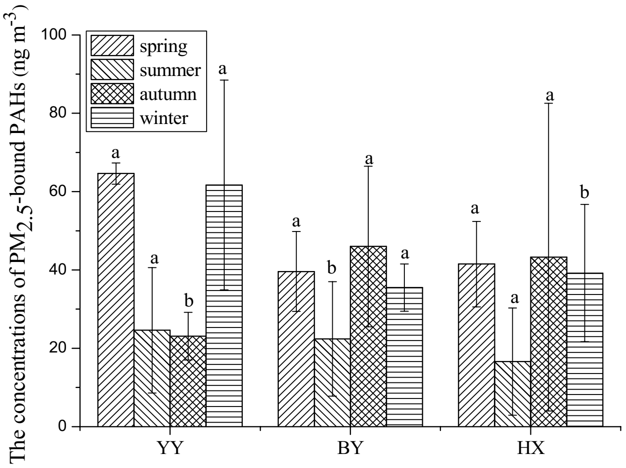

Fig. 3 Seasonal variation of $PM_{2.5}$ bound PAHs (a and b represent different significant difference)

Potential Sources of PAHs

Diagnostic Ratios of PAHs

In the present study, the ratios of Ant/(Ant + Phe) were mainly greater than 0.1, indicating PAHs mainly originated from combustion. Most ratios of BaA/(BaA + Chr) were greater than 0.35, which indicated that the main source of PAHs was of pyrolytic origin (Simcik et al. 1999; Soclo et al. 2000).

In Fig. 5, approximately 42% of Flu/(Flu+Pyr) ratios were greater than 0.5, and approximately 40% of ratios were less than 0.4, indicating that the main source of PAHs in this area was combustion of biomass/coal and oil (Yunker et al. 2002; Liu et al. 2007). Most of the IcdP/(Bghi + IcdP) ratios were less than 0.5 (approximately

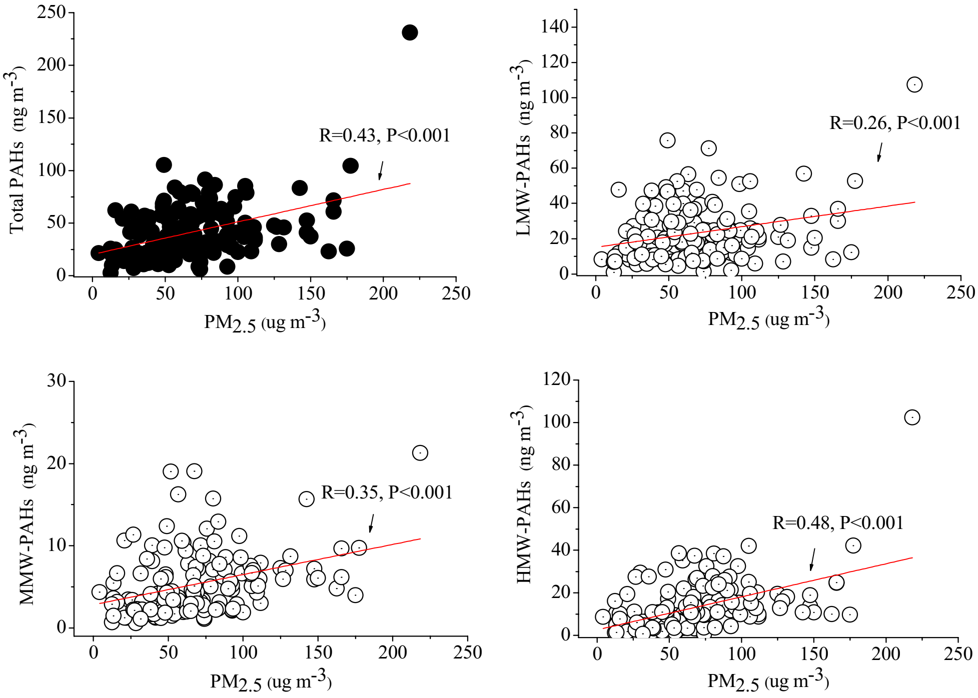

Fig. 4 Correlations among different molecular weight PAHs and PM$_{2.5}$

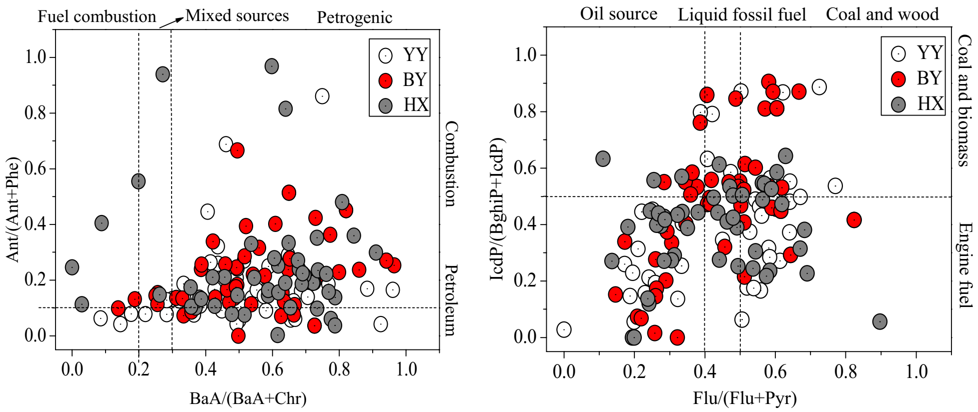

Fig. 5 Diagnostic ratios of PM$_{2.5}$ bound PAHs in four seasons at Guiyang

67%), and the rest were greater than 0.5, indicating that the PAHs were from mixed sources of engine fuel and coal/biomass combustion (Yunker et al. 2002).

Above all, the results suggested that sources of the PM$_{2.5}$ in PAHs in Guiyang were mainly from the combustion of coal and biomass, followed by the emission of vehicle exhaust. The coal combustion in Guiyang might be responsible for the high concentrations of PAHs in PM$_{2.5}$. Moreover, the unfavourable diffusion conditions in Guiyang due to its plateaued and montane landscape might be an alternative explanation.

Cluster Analysis on Back-Trajectories

Figure 6 exhibited cluster backward trajectory diagram of YY in summer and winter. During the summer sampling period, most of Guiyang's polluted air mass came from China, with small amounts from Vietnam and Laos. Approximately 67% of the air mass mainly came from Gansu province via Sichuan province and Chongqing, 21% came from Vietnam via Guangxi, and 13% came from Laos via Yunnan. During the winter sampling period, the polluted air mass was mainly domestic. The polluted air

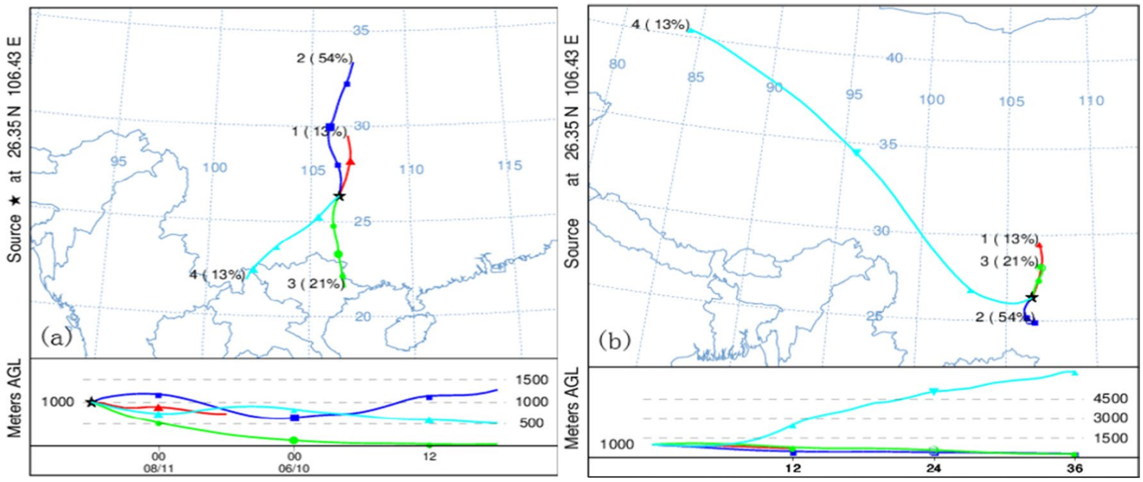

Fig. 6 Cluster analysis on back-trajectories for PAHs during summer (**a**) and winter (**b**)

mass transferred from Guangxi to Guiyang is the largest, accounting for 54% of the total, followed by 13% from Chongqing, 13% from Xinjiang with the longest transmission path via Qinghai and Sichuan provinces, and 21% from the Guizhou province.

Estimation of Distance from Emission Sources

In the present study, the average value of $C_{\mathrm{st}}^{\mathrm{A}}/C_{\mathrm{st}}^{\mathrm{P}}$ was calculated as 1.31. The maximum distance between emission sources and sampling location was estimated to be 2406 km. This estimated maximum distance was in agreement with back-trajectories results, which indicated that PAHs primarily came from domestic regions, such as Xinjiang (2323 km), Gansu (1469 km), Sichuan (649.2 km), Guangxi (550.9 km), and minor from abroad of Vietnam (482.5 km) and Laos (887.9 km). Those emission sources are all at distances of less than 2406 km.

Health Risk Assessment

The TEQ values of PAHs in particulate matter were in Table 3. The TEQ of PAHs in Guiyang was 4.2 ng m^{-3}, which was higher than the standard formulated by WHO (1 ng m^{-3}) and lower than the national standard of China (10 ng m^{-3}) (WHO 1987; Li et al. 2017). The ECR values in all three sites of YY (4.3×10^{-4}), BY (3.7×10^{-4}), and HX (2.9×10^{-4}) exceeded the health guideline (10^{-6}) provided by USEPA (Chithra and Shiva Nagendra 2013). The average ECR value obtained in Guiyang was of 3.6×10^{-4}, which was 360 times higher than the health guideline, indicating a high potential risk of cancer.

Table 3 TEF values and BaPeq concentrations (10^{-2}) (ng m^{-3}) of individual PAHs' compounds

Compounds	TEF	BaPeq (YY)	BaPeq (BY)	BaPeq (HX)
Nap	0.001	0.2080	0.1624	0.1589
Acy	0.001	0.5667	0.4355	0.5670
Ace	0.001	0.6003	0.5926	0.6296
Flu	0.001	0.0974	0.0729	0.0905
Phe	0.001	0.7096	0.4703	0.5453
Ant	0.01	1.941	1.118	1.319
Fla	0.001	0.0876	0.1077	0.0515
Pyr	0.001	0.1498	0.1148	0.1339
BaA	0.1	14.11	14.98	17.72
Chr	0.01	1.348	0.9881	1.210
BbF	0.1	31.76	24.99	26.83
BkF	0.1	12.84	12.23	11.12
BaP	1	172.7	141.3	96.4
IcdP	0.1	20.33	18.22	13.4
DBA	1	234.4	208.5	158.3
BghiP	0.01	4.039	3.003	2.194
∑BaPeq		495.9	330.7	427.2

TEF toxic equivalent factor; *BaPeq* BaP equivalent concentration

Conclusions

The PM$_{2.5}$-bound PAHs concentration on average in Guiyang was of 41 ± 21 ng m^{-3}, which was higher than that of most cities in China and abroad. The highest percentage of LMW-PAHs observed in the present study probably related to the low-temperature combustion of coal in the study region. Seasonal variations of the highest PAHs concentrations in spring, followed by winter, autumn, and summer might attribute to the unclear seasonal changes in Guiyang due to its meteorological parameters. Source apportionment results showed that coal/biomass combustion and vehicle emission were the two dominant sources of $PM_{2.5}$-bound PAHs. The cluster backward trajectory analysis indicated that PAHs also was influenced by air masses from other domestic provinces of Sichuan, Guangxi, and Yunnan, as well as abroad countries of Laos and Vietnam. The maximum distance between emission sources and sampling location was estimated to be 2406 km, which was in agreement with back-trajectories results. The ECR value in Guiyang (3.6×10^{-4}) exceeded the health guideline (10^{-6}), reflecting high potential risks of cancer. Both particulate and gaseous phase of PAHs as well as their transformation and bioaccumulation are necessary to investigate in the montane city in the future.

Acknowledgements Financial support for this work was provided by the National Natural Science Foundation of China (NSFC: 21767007) and the Technology Program of Guizhou (QianKeHe[2018]1111). The authors gratefully acknowledge assistants from all persons involved in the project.

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