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Seasonal variation, spatial distribution and source apportionment for polycyclic aromatic hydrocarbons (PAHs) at nineteen communities in Xi'an, China: The effects of suburban scattered emissions in winter☆

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ABSTRACT

Seasonal variation and spatial distribution of $PM_{2.5}$ bound polycyclic aromatic hydrocarbons (PAHs) were investigated at urban residential, commercial area, university, suburban region, and industry in Xi'an, during summer and winter time at 2013. Much higher levels of total PAHs were obtained in winter. Spatial distributions by kriging interpolations principle showed that relative high PAHs were detected in western Xi'an in both summer and winter, with decreasing trends in winter from the old city wall to the 2^{nd}-3rd ring road except for the suburban region and industry. Coefficients of diversity and statistics by SPSS method demonstrated that PAHs in suburban have significant differences ($t < 0.05$) with those in urban residential in both seasons. The positive Matrix Factorization (PMF) modeling indicated that biomass burning (31.1%) and vehicle emissions (35.9%) were main sources for PAHs in winter and summer in urban, which different with the suburban. The coal combustion was the main source for PAHs in suburban region, which accounted for 46.6% in winter and sharp decreased to 19.2% in summer. Scattered emissions from uncontrolled coal combustion represent an important source of PAHs in suburban in winter and there were about 135 persons in Xi'an will suffer from lung cancer for lifetime exposure at winter levels. Further studies are needed to specify the effluence of the scattered emission in suburban to the city and to develop a strategy for controlling those emissions and lighten possible health effects.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) bound to fine particles ($PM_{2.5}$) are ubiquitous in the ambient air, and concerns over these compounds have grown in the past 20 or more years because of their negative on human health (Mittal and Van Grieken, 2001; WHO, 2003; Yu et al., 2015; Gao et al., 2016; Ren et al., 2017; Sarti et al., 2017; Yin et al., 2017). PAHs also have been used as biomarkers to trace the origins of aerosol, terrigenous organic carbon in marine sediment, and agricultural products (soybeans) (Pongpiachan, 2015). PAHs mainly originate from the incomplete combustion of fossil fuels or wood, vehicular and domestic emissions, and emissions from ships can be important in port area (Simoneit et al., 1991a,b; Rogge et al., 1993; Shen et al., 2010; Ding et al., 2012; Alves et al., 2015, 2016; Wang et al., 2015; Pongpiachan

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et al., 2015a). China and some developing countries, such as India, Afghanistan, etc., have suffered serious air pollution from PAHs (Kong et al., 2010; Wingfors et al., 2011; Abba et al., 2012), particularly in wintertime, for the huge amount of uncontrolled or poorly controlled coal combustion and biomass burning (Xie et al., 2009; Liu et al., 2016). In China, India, South East Asia and parts of South America and Africa, abundant solid fuels (e.g., coal, wood, agricultural residue) are commonly used for daily cooking (World Health Organization, 2002). Shen et al. (2013) estimated that the combined annual emissions of PAHs from urban and rural regions in China contribute about one-fifth of the total global emissions, and this has led to high pollution levels in parts of the country as well as widespread human exposures.

The worldwide distributions of $PM_{2.5}$ bound PAHs are summarized at Supplemental Table S1, and these data and other show that industry regions, rural areas and areas with heavy traffic usually suffer heavy pollutions loadings whereas remote regions and the areas where conducted strict emission standards have better air qualities (Kong et al., 2010; Li et al., 2010; Ding et al., 2012; Chen et al., 2014a; Wang et al., 2015). The loadings of PAHs in $PM_{2.5}$ from Italy, Sweden, France, America, Japan, and Brazil were typically <20 ng/m^3 on average (Pleil et al., 2004; Bourotte et al., 2005; Tham et al., 2008; Li et al., 2009; Wingfors et al., 2011; Ringuet et al., 2012; Sarti et al., 2017). Some regions in Canada, Greece and Brazil have slightly higher levels, usually 20–50 ng/m^3 (Andreou and Rapsomanikis, 2009; Ding et al., 2009; Souza et al., 2014). Most of these researches have been made at one single site, and therefore the pollutant concentrations were likely affected by the surrounding environment and local sources (Okuda et al., 2010; Xu et al., 2016). Only a few researches have compared PAHs concentrations in different type of functional areas and also on the PAHs size distributions (Gao et al., 2016; Xu et al., 2016; Ren et al., 2017). Indeed, more data for these pollutants are better to understand the temporal and spatial trends in pollution conditions, and useful for identifying likely sources the pollutants, for assessing health risks, and for developing effective control measures.

The air quality in the city of Xi'an, which located on the Guanzhong plain, is affected by its basin-like topography, which causes the buildup of pollutants due to the very low wind speed, especially in wintertime (Cao et al., 2005; Han et al., 2010b; Gao et al., 2015; Wang et al., 2016a). A serious of studies in Xi'an has investigated the chemical components and sources apportionment of aerosol particles and gas phase in ambient environment (Cao et al., 2007, 2009; Zhang et al., 2011; Wang et al., 2006, 2012; Xu et al., 2012; Cheng et al., 2013; Bandowe et al., 2014; Li et al., 2014; Wei et al., 2015a; Xu et al., 2015; Ren et al., 2017; Wang et al., 2017). Indeed, PAHs are the obvious high loaded organic and of greatest concern for human health, and therefore, it's essential to fully understand the variability and inter-urban distributions of PAHs in Xi'an. In this study, the pollutant levels and spatial distributions of PAHs in $PM_{2.5}$ from 19 communities in Xi'an were determined for two seasons. Possible source contributions for a variety of geographical zones were estimated using a Positive Matrix Factorization (PMF) model and the inhalation incremental lifetime cancer risk (ILCR) model was applying to estimate the inhaled cancer risk.

2. Materials and methods

2.1. Sample collection

$PM_{2.5}$ samples were simultaneously collected at nineteen communities that were chosen to be representative of urban residential, university, commercial area, suburban region, and industry of Xi'an during winter and summer of 2013 (Cao et al., 2005, 2007; Han et al., 2009; Gao et al., 2015) (Supplemental Fig. S1). We expected that some of these sites would have low levels of pollution (such as the university sites), while others would be moderately polluted (urban residential), and still others heavily polluted (heavy traffic areas, the site near a power station, and the suburban site). Furthermore, the sampling sites were expected to generally from the city center to the suburbs (old city wall - the 2nd ring road - 3rd ring road - highway). Naturally, the choice of sampling sites was subject to practical limitations, such as problems caused by the noise of the sampler, and other logistical factors. Information concerning the sampler installation heights and environments surrounding the sampling sites is presented in Supplemental Table S2.

Sampling was conducted in two periods (1) summer-when filter samples were collected from 7 to 23 June 2013 and blank samples were synchronous collected on 16 June, and (2)winter-when sampling was from 2 to 15 December 2013, and blanks were collected on 11 December. The $PM_{2.5}$ samples were collected using 47 mm quartz filters (QM/A®, Whatman Inc., U.K.) from 08:30 on one day to 08:30 on the next day. $PM_{2.5}$ Mini-Volume sampler (Air metrics, Springfield, OR, USA) that operated a flow rate of 5 L/min were used for the aerosol collections. In summer, a total of 342 samples (323 aerosol loaded samples and 19 field blanks) were obtained, while in winter 285 samples (266 aerosol-loaded samples and 19 field blanks) were collected. The effective aerosol-loaded samples were 263 and 305 in winter and summer, respectively. The overall sampling strategy has been described in a previous paper (Wang et al., 2016a). After collection, the filter samples were stored in Teflon® filter bags kept in a freezer at −20 °C until they were analyzed.

2.2. Meteorological condition

Meteorological data, including temperature (T), relative humidity (H), wind speed (U), and boundary layer height (MLH) during the study are summarized in Supplemental Table S3. The concentrations of selected gas species (ozone (O_3), sulfur dioxide (SO_2), nitrogen dioxide (NO_2)) at each of the sites were also monitored using an ambient gas Ogawa passive sampler (PS-100, Florida, USA).

2.3. Chemical analyses

Twenty PAHs in the filter samples were quantified using in-injection port thermal desorption (TD) unit coupled with gas chromatography/mass spectrometry (GC/MS) (Wang et al., 2015, 2016b). The procedures for the in-injection port TD-GC/MS method have described in several previous publications (Ho et al., 2008, 2011), and the methods for these analysis also are described in the supplemental materials. Briefly, an Agilent 7890A GC/5975C MS system (Santa Clara, CA, USA) was used for the instrumental analyses, and it operated in electron impact ionization (EI) mode. The $PM_{2.5}$ samples with the added internal standards were cut into small pieces and then placed into the TD tube. The inlet was sealed, and the temperature of the front inlet increased up from 50 °C to 275 °C: this caused the compounds of interest to volatilize, and then the GC temperature program began. The analytes were identified by comparing with the retention times of chromatographic peaks of standards and calibration curves were used for the quantification.

2.4. Quality assurance and control (QA/QC)

The QA/QC procedures used for this study are fundamentally the same as those described by Cao et al. (2013) and Wang et al.

(2016a), and these include (1) the analysis of laboratory and field blanks, which were used to account for any field or laboratory backgrounds; (2) analyses of internal standards, namely chrysene-d_{12} ($C_{18}D_{12}$) (98%, Sigma-Aldrich, Bellefonte, PA, USA), phenanthrene-d_{10} ($C_{14}D_{10}$) (98%, Aldrich, Milwaukee, WI, USA), and *n*-tetracosane-d_{50} (*n*-$C_{24}D_{50}$) (98%, Aldrich, Milwaukee, WI, USA), which were used to control the stability of the analysis; (3) the analysis of one duplicate for each group of ten samples (the standard deviations (SD) for the duplicates were 1.7–14.8%); and (4) the construction of a five-point calibration standard curve over a concentration range of 1–10 ng for each PAH; these were used for quantification - the limits of detection are presented in Supplemental Table S4; and (5) measurements of SRM 1649a (urban dust from the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA) were made to validate the accuracy of PAH analyses.

2.5. Health risk assessment model

A growing number of studies have highlighted the health risks of atmospheric PAHs, especially those on fine particle (Pongpiachan et al., 2015b; Pongpiachan, 2016; Zhang et al., 2016). Some of those assessments have been based on the UR_{BaP}, which is defined as the increased probability of developing cancer for people when they are continuously exposure to 1 μg/m^3 benzo[*a*]pyrene (BaP) equivalent concentration (BaP_{eq}) during the lifetime (usually was set as 70 years). Another metric for estimating cancer risk is the inhalation incremental lifetime cancer risk (ILCR), which is associated with specific inhalation and exposure parameters, and calculated from the equation:

$$\mathrm{ILCR} = \frac{(BaP_{eq} \times IR \times SF \times E_D \times cf \times EF)}{(BW \times AT)} \quad (1)$$

in which IR is the inhalation rate (m^3/day); SF is the cancer slope factor of BaP, which has a geometric mean of 3.14 (mg/kg/d)$^{-1}$ and a geometric standard deviation of 1.8 for inhalation exposure (Chen and Liao, 2006); E_D means the exposure duration (year) and EF is the exposure frequency (day/year); BW is the body weights (kg) and AT is the lifespan of carcinogens (days); and cf (mg/ng) is a unit conversion factor (10^{-6}).

In our study, ILCR for general population in Xi'an, with ages ranging from 4 to 70 years was estimated. The population was divided by gender (male and female) and then subdivided into the following four subgroups: children (4–10 years old), adolescents (11–17 years old), adults (18–60 years old), and seniors (61–70 years old). The BaP_{eq} values were calculated by multiplying the toxic PAHs species' concentrations by equivalence factor (TEF) obtained from the US EPA (2010, see Supplemental Table S5). The IR and BW data for the population groups were obtained from Xia et al. (2013), and they are listed in Supplemental Table S6. The E_D values were set at 7, 7, 43 and 10 years for children, adolescents, adults, and seniors, respectively. The EF and AT were set at 252 day/year and 25,550 days, respectively (USEPA, 2001).

3. Results and discussion

3.1. Seasonal variations of PAHs

The concentrations of PAHs for the winter and summer sampling periods are shown in Fig. 1 and summarized in Supplemental Table S7. The total PAHs concentrations in winter were almost 10 times than those in summer, ranging from 20.0 to 529.6 ng/m^3, with a median of 161.4 ng/m^3 in winter and from 2.0 to 300.4 ng/m^3 and a median of 19.2 ng/m^3 in summer. Similar findings of high PAH loadings in winter have been reported by others (Masiol et al., 2012; Sarti et al., 2017), and this is likely due to the emissions from heating systems and meteorological conditions in winter (Cincinelli et al., 2007; Sarti et al., 2017).

In winter, all the PAHs species, except fluorene (FLO), were quantified in each of the samples. Chrysene (CHR), benzo[e]pyrene (BeP), and benzo[*b*]fluoranthene (BbF) were the most abundant species (with averages of 18.8, 17.6, and 14.9 ng/m^3, respectively) in winter while FLO showed the lowest levels (with an average of 1.7 ng/m^3). In contrast, acenaphthylene (ACY) and acenapthene (ACE) were not quantified in summer when BbF was the predominant compound. The average levels of BaP were 10.0 and 1.9 ng/m^3 in winter and summer, respectively, and both of those values are higher than the standards established by the WHO and the Atmospheric Environmental Quality Standard of the People's Republic of China (annual average of 1 ng/m^3) (GB 3095-2012, 2012).

A composition of PAH concentrations grouped by ring number illustrated the following order from highest to lowest in both winter and summer: 5-ring > 4-ring > 6-ring > 3-ring. In comparison to the heavier PAHs, the 3-ring PAHs in summer (16.9%) were much higher than those in winter (3.9%), and this probably due to their relatively low vapor pressures and high emission in summer whereas compared with the stronger emissions of the higher molecular weight PAHs in winter.

One limitation of our study is that the gas phase concentrations of the PAHs were not determined. Although some models have been used to predict the gas/particle distribution for PAHs or their reactions in the gas phase and on the surface of particles (Dachs and Eisenreich, 2000; Lohmann and Lammel, 2004; Wei et al., 2015a; Zhang et al., 2017), differences in the sampling time and pollution status at the various sites have led to considerable variability in the results. Indeed, the temperature and the heterogeneous reactions of PAHs with O_3, both of them can affect gas/particle partitioning of PAHs. A previous study in Xi'an has shown that when molecular weight of PAHs is higher than 240 g/mol, the compound is mainly particle bound, and under those circumstances, the effects of the gas-phase fraction are likely minimal. Even so, information on the gas/particle distributions of PAHs is needed to fully assess health risks, and obtaining this type of data should be a goal of future studies.

The influences of meteorological conditions on the pollutants were also investigated. The results showed that relative humidity and the ventilation coefficient (VC, see Wang et al., 2016a) were the two main factors that influenced the PAHs in winter. VC is used as a direct expression of the degree of transport/dispersion of pollutants, and it was calculated by MLH multiply U. However there were no obvious correlations between PAHs and meteorological conditions were obtained in summer.

3.2. Spatial distributions of PAHs

The spatial distributions of PAHs at the 19 communities were modeled using interpolations by kriging techniques, and these are presented in Fig. 2. In winter, the average total PAHs concentrations at the 19 communities ranged from 69.8 to 279.7 ng/m^3, and relatively high levels occurred in the westerns part of the city, especially in the northwest. Although the prevailing wind direction in Xi'an in general is the westerly wind during sampling periods in this area (Fig. 3), there were no obvious different for the wind speed for each wind direction and the wind speed (U) (Supplemental Table S3 and Fig. 3) was relatively low (with an average of 1.8 m/s) during the sampling periods, and therefore, the pollution levels were probably affected most strongly by local emission.

The Xi'an Thermoelectric limited company, a branch of the China Petroleum & Chemical Corporation and some manufacture

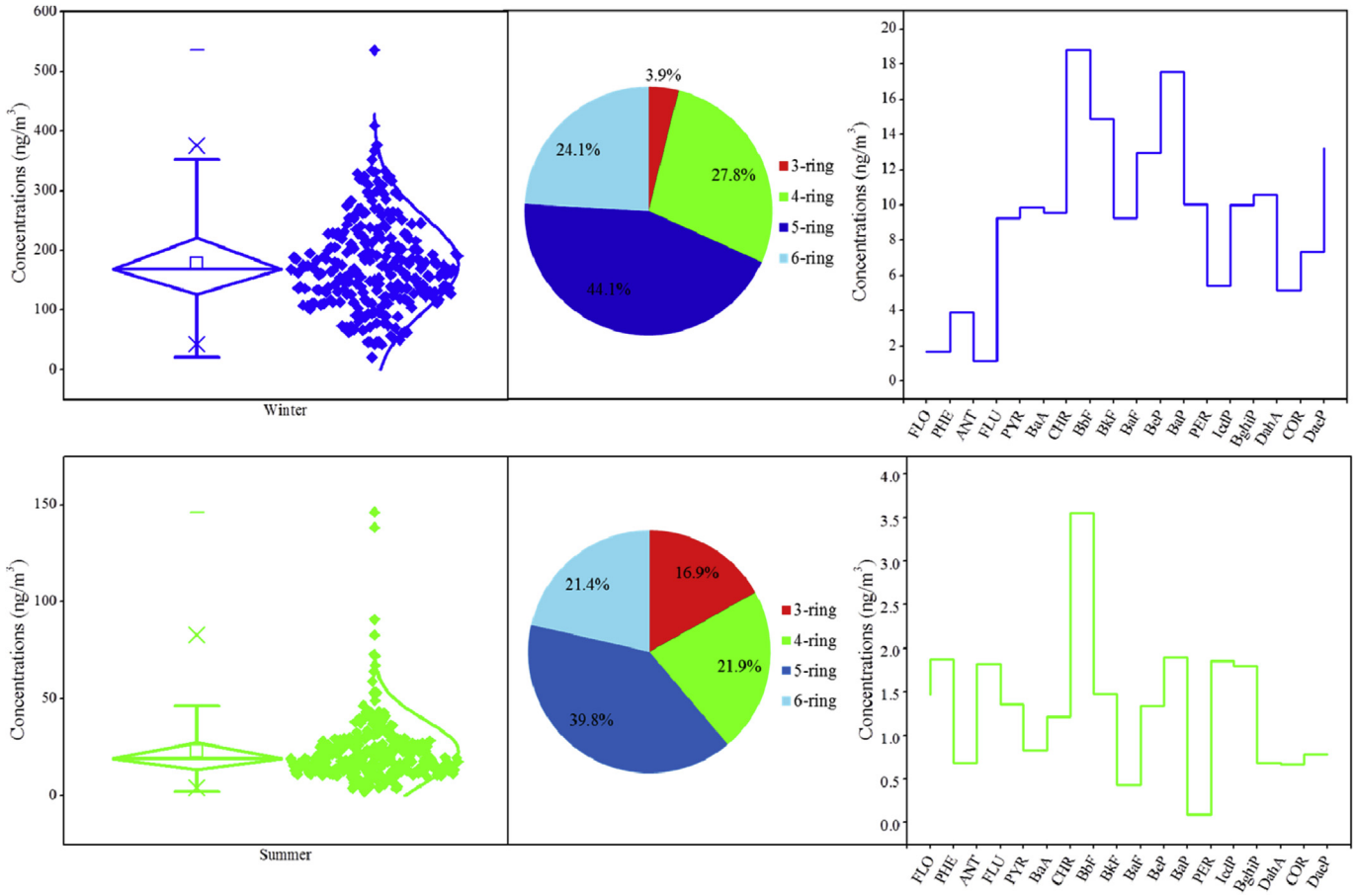

Fig. 1. Seasonal variation of polycyclic aromatic hydrocarbons (PAHs) for winter and summer $PM_{2.5}$ samples from Xi'an.

plants that emit large amounts of PAHs and other pollutants are located in the western part of Xi'an. Relatively low levels of PAHs were found in the southeastern of the city, where there are the Qujiang New District, an area that is without industry or other strong emission sources. The Xi'an Jiaotong University National Science Park, South Lake, and other famous tourist attractions located in that zone also showed relatively low PAH concentrations. Unlike the suburban and industry, the PAHs at the urban residential sites decreased from 194.0 to 174.6, and then to 132.9 ng/m^3 from the sites in the old city wall to the 2nd ring road, and then to the 3rd ring road (Fig. 4).

In summer, the average total PAHs concentrations at all of the sites were from 10.9 to 44.0 ng/m^3, and the southwestern part of the city also suffered high contaminations. Both the pollutants emission and weather conditions likely affected the PAH distributions. For example, as shown in Fig. 3, the prevailing wind direction during the summer sampling was from northeast followed by the east-northeast wind, with the wind speed were 4.8 and 6.1 m/s, respectively. Presumably as a result of this, the pollutants tend to accumulated in the western part of the city, especially in the southwest. The PAHs concentrations were 20.3 ng/m^3 at urban residential near the old city wall, 16.8 ng/m^3 at the old city wall-2nd ring road sites, for the lowest levels were found at U2 in summer, and they were 25.6 ng/m^3 at the 2nd-3rd ring road. Also very low PAHs were found at R10, which was near the Baqiao Ecological Wetland Park, where scarce habitats and environmental conditions are generally good (Xu et al., 2016).

3.3. PAHs in different geographic zones

The PAH concentrations and compositions at the different functional sites are displayed in Fig. 5. The total PAHs averages in the zones ranged from 160.9 to 268.5 ng/m^3 in winter. The urban residential sites had the lowest levels (160.9 ng/m^3), but those at the university were nearly as low (166.0 ng/m^3). The commercial area and industry had similar levels of 188.3 and 187.5 ng/m^3, respectively. The suburban region has the highest levels, 268.5 ng/m^3. In summer, the average total quantified PAHs concentrations varied from 20.1 to 42.6 ng/m^3. The industry had the highest levels of PAHs, followed by the suburban region, university, commercial area, and finally urban residential. The loading in the industry and suburban region were noticeably higher than in the other zones. Correspondingly, in winter the highest average level of BaP was again found in suburban region (15.8 ng/m^3), followed by industry (11.2 ng/m^3) and commercial area (10.3 ng/m^3). The average concentrations of BaP at university and urban residential were comparable at 9.2 and 9.1 ng/m^3, respectively. And relatively low average concentrations of BaP were found in summer (highest of 4.1 ng/m^3 in industry), indicated that more effective controls are needed to improve the air quality, especially in winter time.

The various types of sites showed generally similar characteristics in terms of the dominant PAHs ring number in both seasons. One exception was that the 3-ring PAHs was lower while the 5, 6-ring PAHs were somewhat higher at suburban and industry (especially in suburban), compared with the others (Supplemental Fig. S2).

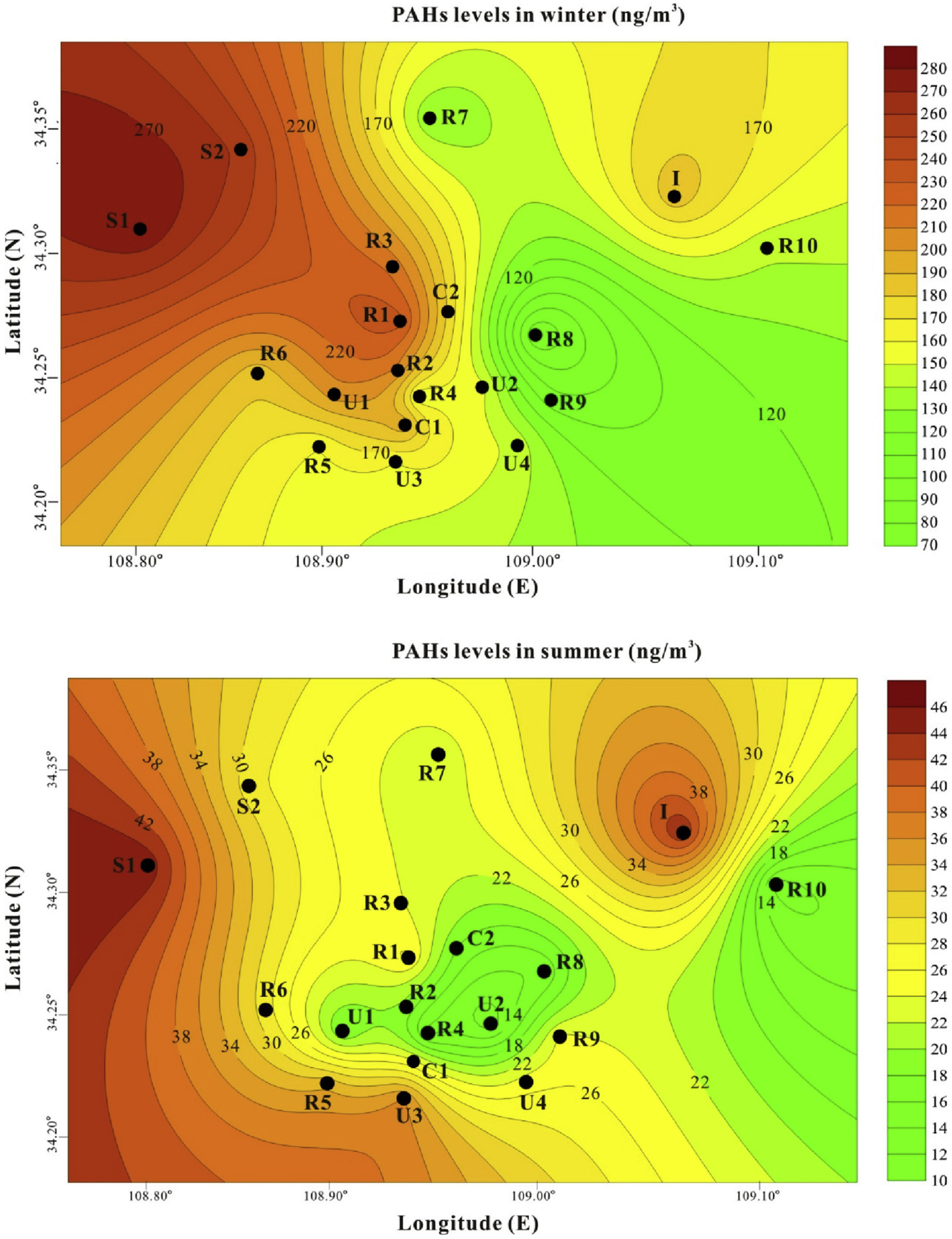

Fig. 2. Kriging interpolations of PAHs concentrations in winter and summer in Xi'an.

The coefficient of diversity (CD) is commonly used to compare the similarities of different sites or profiles. Here, CD was calculated as:

$$CD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{X_{ij}-X_{ik}}{X_{ij}+X_{ik}}\right)^2}$$

where j and k denote the sampling sites, p is the number of target components (total PAHs species), x_{ij} and x_{ik} mean the average concentrations of chemical component i (each PAHs species) at each of the j and k sites (Wongphatarakul et al., 1998). The CD_{jk} calculated in this way varies from 0 to 1, and higher values show larger differences between the two sites or sources (Han et al., 2010a; Pongpiachan and Iijima, 2016). A CD value of 0.269 was set here as the boundary between similarity and differences for PAHs collected at pairs of sites (Wang et al., 2016a).

The CDs for the pairs of function sites in both winter and summer are summarized in Supplemental Table S8. In winter, the CD values were from 0.051 to 0.277 for PAHs, and all the CD values were <0.269 except for those between the suburban and urban residential (0.272) and between the suburban and university (0.277), which indicates significant differences for their compositions or sources. And the statistical analysis by SPSS method also indicated that the PAHs composition for suburban sites have significant differences ($t < 0.05$) with that in urban residential and university sites. Differences in heating methods for the functional zones may have been responsible for that in the heating period, because in most urban residential, central heating is used, whereas uncontrolled scattered emissions from coal and biomass burning are prevalent in suburban regions (Wang et al., 2016a).

In summer, the CD values ranged from 0.087 to 0.463 for the PAHs, and the urban residential and commercial area pair had the minimum CD value of 0.087. The CD value between industry and suburban was 0.219; however, both of these area had higher CD values with the other function zones, which was from 0.397 to 0.463, 0.287 to 0.360, respectively. This indicates that in summer, the industry and suburban may have different sources for PAHs compared with the other function zones. The correlation coefficients between the pairs of different zones are displayed in Supplemental Table S8, and they show a much narrower range in winter (0.892–0.993) compared with summer (0.266–0.908). This is probably because the pollution in winter was heavier, due in part to the meteorological conditions that led to stagnant air, but also because the PAH sources were more widespread. During summer, in contrast, the PAHs were more strongly affected by local sources and the differences between sites were greater.

3.4. Source apportionment

3.4.1. Diagnostic ratios of PAHs

Diagnostic ratios of PAHs (e.g., anthracene (ANT)/(ANT + phenanthrene (PHE)), benzo[*a*]anthracene (BaA)/(BaA + CHR), indeno[1,2,3-*cd*]pyrene (IcdP)/(IcdP + benzo[ghi]perylene (BghiP)), and fluoranthene (FLU)/(FLU + pyrene (PYR)), BaP/BghiP have become widely used for the source apportionment studies (Yunker et al., 2002; Bi et al., 2005; Gao et al., 2012; Tobiszewski and Namieśnik, 2012; Wang et al., 2015; Xu et al., 2016). The diagnostic ratios measured in our study are presented in Supplemental Table S9 along with data for representative emissions. The oxidation and biodegradation of PAHs can affect the ratios after emission, and therefore, the boundaries between different sources can become blurred and results are at times inconclusive (Biache et al., 2014). Even so, from Supplemental Table S9, it can be seen that pyrogenic sources, that is, coal combustion, biomass burning and vehicle emissions, were more than likely the main source for PAHs in Xi'an.

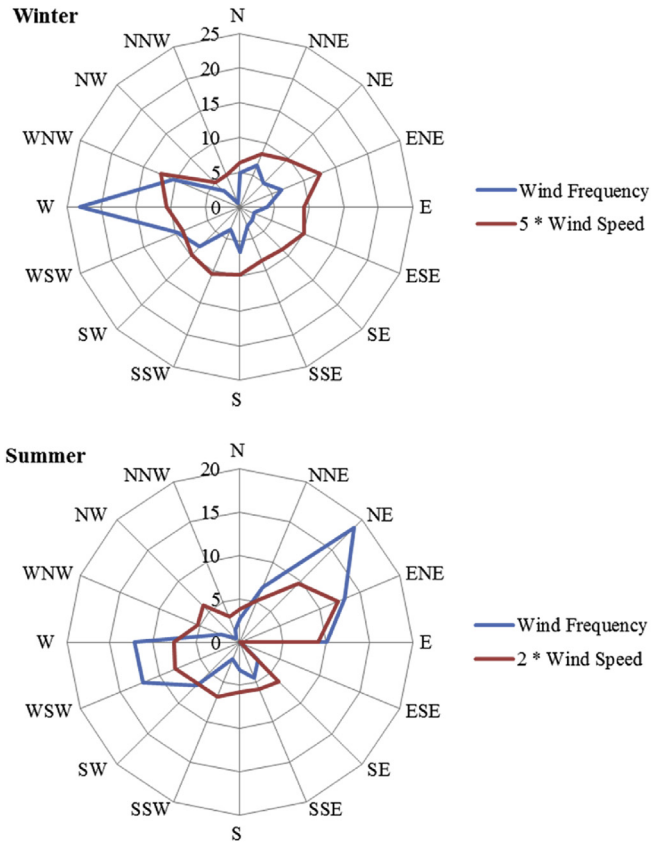

Fig. 3. Wind direction and wind speed in Xi'an during the winter and summer sampling periods.

To help identify the likely PAH sources for the different functions zones, scatter diagrams of FLU/PYR, IcdP/BghiP were prepared, and they are displayed in Fig. 6, along with the corresponding ratios for selected emission sources (Sheesley et al., 2003; Zhang et al., 2008; He et al., 2008; Yu and Yu, 2011). Unlike the case in summer, the wintertime plots show good linearity for FLU/PYR and IcdP/BghiP.

For FLU/PYR, the samples collected at the industry and suburban apparently were impacted by vehicle emissions and bituminite coal (Fig. 6a), and high mixing ratios of SO_2 at site S1 and NO_2 at S2 also were evident in winter (Fig. 7a). For IcdP/BghiP, samples from suburban sites were consistent with biomass burning emissions, and the PAHs in industry apparently were from brown coal. The PAH ratios in urban residential, commercial area and university were consistent with biomass burning and coal combustion.

A comparison of FLU/PYR ratios measured in summer, suggests that the samples from industry were mainly affected by bituminite coal combustion, and the relatively low level of SO_2, thete may have been related to the high level of O_3 (Fig. 7b). The diagnostic ratios of FLU/PYR indicate that the PAHs in the commercial areas were mainly from vehicle emissions, and this is consistent with the high levels of NO_2 found at C1 and C2 (Fig. 7b). The IcdP/BghiP ratios indicate that mixtures of source affected the urban residential, while the industry samples were also mainly affected by coal combustion.

Though for IcdP/BghiP, vehicle emission was not significant in either season, the BaP/BghiP and BaA/(BaA + CHR) ratios showed strong correlations with vehicle emission (Supplemental Table S9).

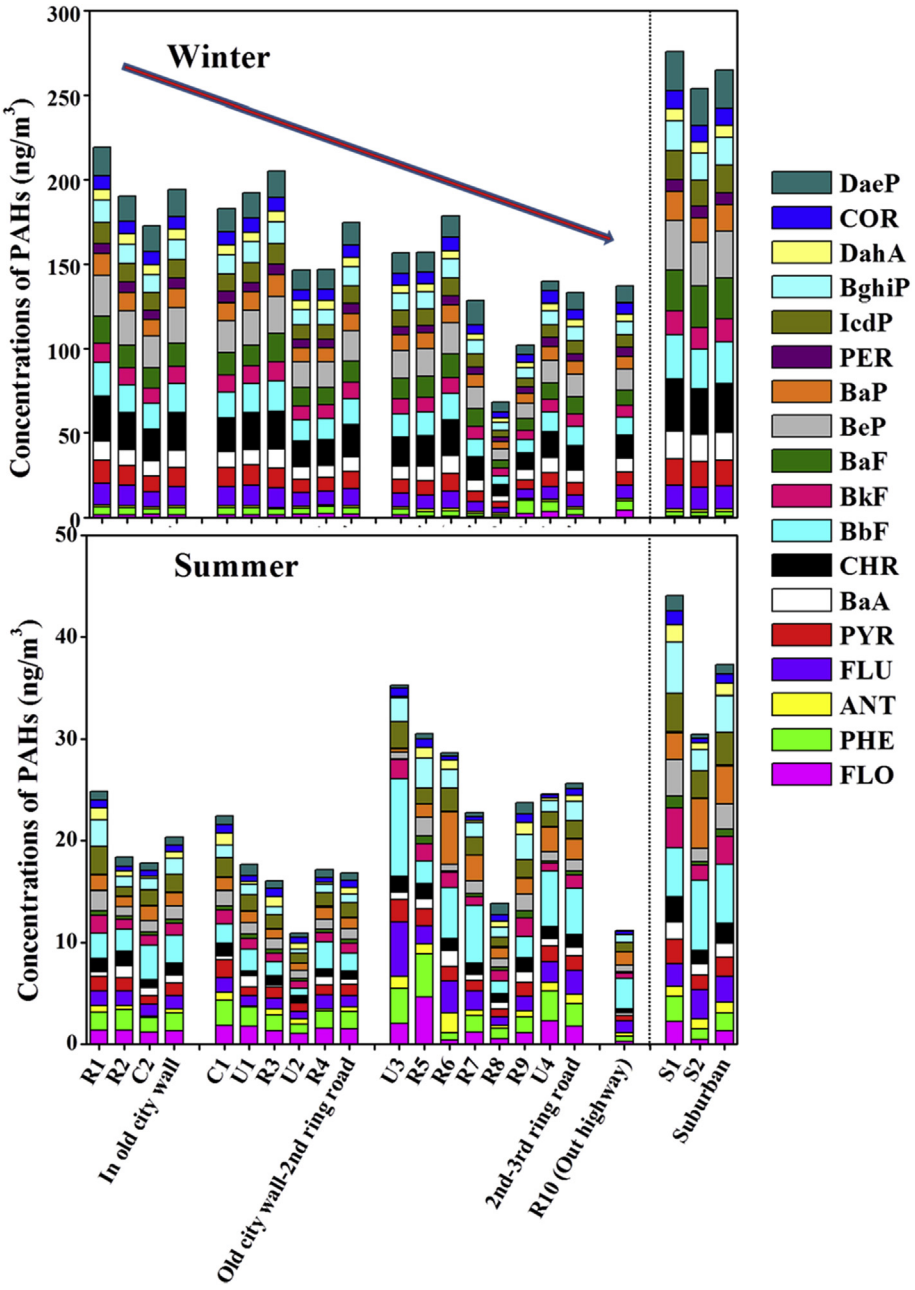

Fig. 4. Concentrations and compositions of PAHs from city center to the suburban Xi'an.

Overall, these results indicate that in winter, coal combustion and biomass burning are main sources for PAHs, especially in suburban and industry. In summer, the most important PAH source apparently is vehicle emission, especially in commercial area, where heavy traffic is common. However, at industry, impacts from coal combustion also were evident.

3.4.2. PMF analysis

To estimate the relative contributions of PAHs sources, Positive Matrix Factorization (PMF) (EPA PMF 5.0 version) modeling was applied. Details regarding the methodology we used have been described in previous papers (Ma et al., 2010; Gao et al., 2012; Chen et al., 2014b; Callen et al., 2014; Lin et al., 2015), but briefly the concentrations and uncertainties of eighteen PAHs in the samples from each function zone were input into the model. The uncertainties were calculated using the fraction of concentration and method detection limit (MDL) and they were from 0.004 to 0.352 and from 0.013 to 0.358 in winter and summer, respectively. The model settings were summarized in Supplemental Table S10. There were no missing data and only a few data in urban residential, university, commercial and suburban regions in summer were below detection limit (BDL). They were used as reported and have no modification or censoring. The sample number × number of species was used as matrix. The signal-to- noise ratios of all the eighteen species were higher than 1 and defined as strong in all zones.

Brown et al. (2015) detailed the uncertainty of PMF solutions and sofowote et al. (2011) described it for the PAHs source apportionment. In this study, PMF was run on all the eighteen species. The $Q_{robust}/Q_{expected}$ of the three factors (three-to five-factor

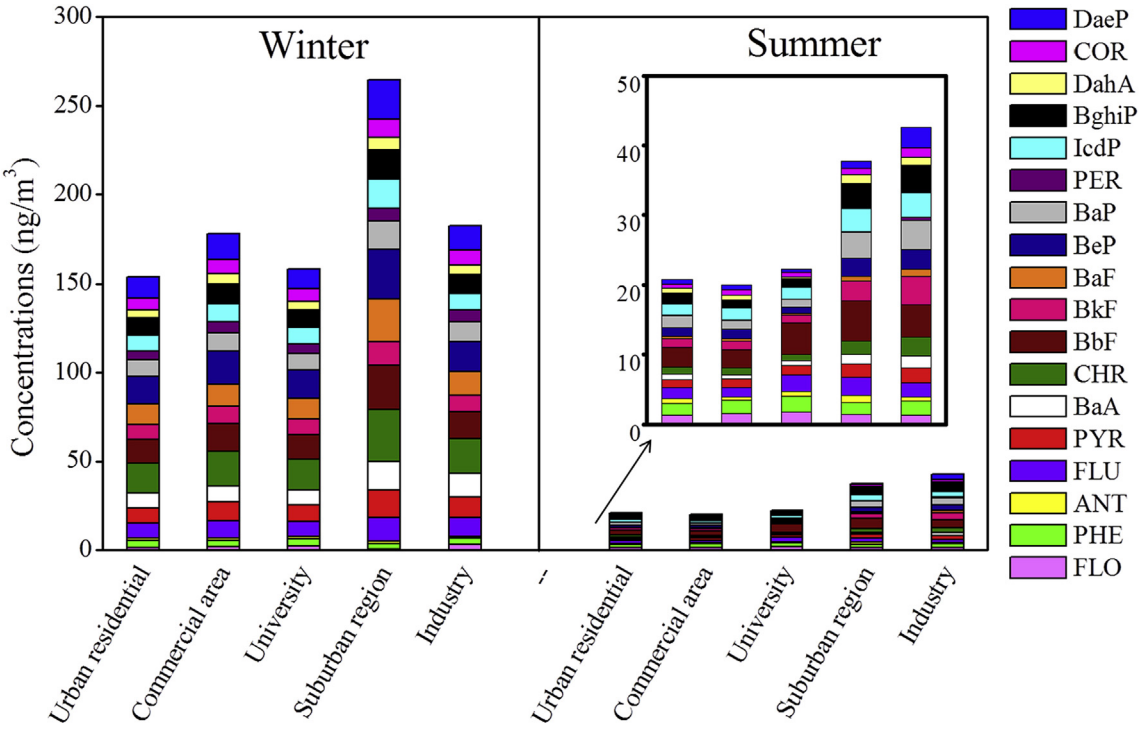

Fig. 5. Concentrations and compositions of PAHs in different function zones in Xi'an.

solution) was displayed in Supplemental Table S11. The number of runs was set 20 and start seed number 1 with four-factor solution. Here 100 random bootstrapping with a minimum correlation R-value of 0.7. The Fpeak, which were 0.5, −0.5, 1.0, −1.0, and 1.5, was used to sharpen the differences of the factor contributions. And for different function zones, default data was selected. Then Fpeak model bootstrap method was run when number of bootstrap was set 20 and minimum correlation R-Value was 0.6 with the default block size. Mapping over 80% was appropriate for each factor. And the %dQ(Robust) was defined fine when it was smaller than 5. The correlations between the measured and modeled PAHs for all samples were 0.9569–0.9999. The error estimations were summarized in Supplemental Table S12. And in industry, because of the less sample size, the statistical data displayed not very well.

The factor which was abundant loaded with high molecular weight PAHs (5- to 6-ring PAHs), such as indeno[1,2,3-*cd*]pyrene (IcdP), coronene (COR), benzo[ghi] perylene (BghiP), dibenzo[a,h] anthracene (DahA) and dibenzo[a,e]pyrene (DaeP), can be linked to vehicle emission (Wang et al., 2015, 2016a). The factor that was strongly loaded of 3-ring PAHs had a profile similar to that of biomass burning (Lin et al., 2015). The factor representing coal combustion was mainly loaded with FLU, CHR, PYR, BbF, and benzo [*a*]fluoranthene (BaF) (Chen et al., 2014a; Wang et al., 2016a). The contributions of the PMF factors are summarized in Fig. 8 and their PAHs concentration profiles and % species contributions are shown in Supplemental Table S13 and Fig. S3. It is regret that there were no other external validations for PAHs source apportionment, for the biomarkers for different sources cannot be got here, such as K^+ and levoglucan are biomarkers for the biomass burning, hopanes for vehicle emission and picene for coal combustion. And it is also difficult to identify the other contributions of emission source, because of the missing source spectrum data. So more works need to done for the supplement of sources apportionment in the future.

In urban residential at winter, PMF results are generally consistent with the diagnostic ratios, that biomass burning, vehicle emission, and coal combustion were the main sources for PAHs, with the contribution from biomass burning slightly higher than the other two sources (31.1% versus 25.0% for vehicle emissions and 23.9% for coal combustion). For the commercial area in winter, the contributions of biomass burning, vehicle emission, and coal combustion were 24.9%, 23.7% and 26.3%, respectively. However, in summer, vehicle emission was the main source for PAHs at urban residential (35.9%) and commercial area (37.8%), followed by coal combustion and then biomass burning. For university, vehicle emission evidently was the largest PAH source (38.7%) in winter, whereas coal combustion was the strongest source (40.1%) in summer. This last finding was somewhat puzzling, but coal is used in summer as a fuel for cooking in the dining hall and for the small boiler for the bathhouse, but more studies would need to be done to confirm this.

In suburban region and industry, coal combustion was the main source for PAHs, and that accounted for 46.6% and 31.5% of the totals, respectively in winter. Coal combustion (34.3%) at industry in summer was comparable with that in winter, suggesting that emissions from coal combustion at thermal power plant may have been comparatively stable. However, the contribution of coal combustion at suburban in summer sharply decreased to 19.2%, and this could be explained by large quantities of coal burned for heat in winter but not in the warmer parts of the year. This raises the question of the impacts of the scattered wintertime emission for the entire city, but more researches will be needed to determine this.

3.5. Health risk assessment

Table 1 shows the ILCR for the four age groups in the different function zones in Xi'an during both winter and summer. Previous studies (Xia et al., 2013) have showed that when the ILCR values are $\geq 10^{-4}$, serious health risks may exist whereas ILCR values $< 10^{-6}$ are generally considered acceptable or

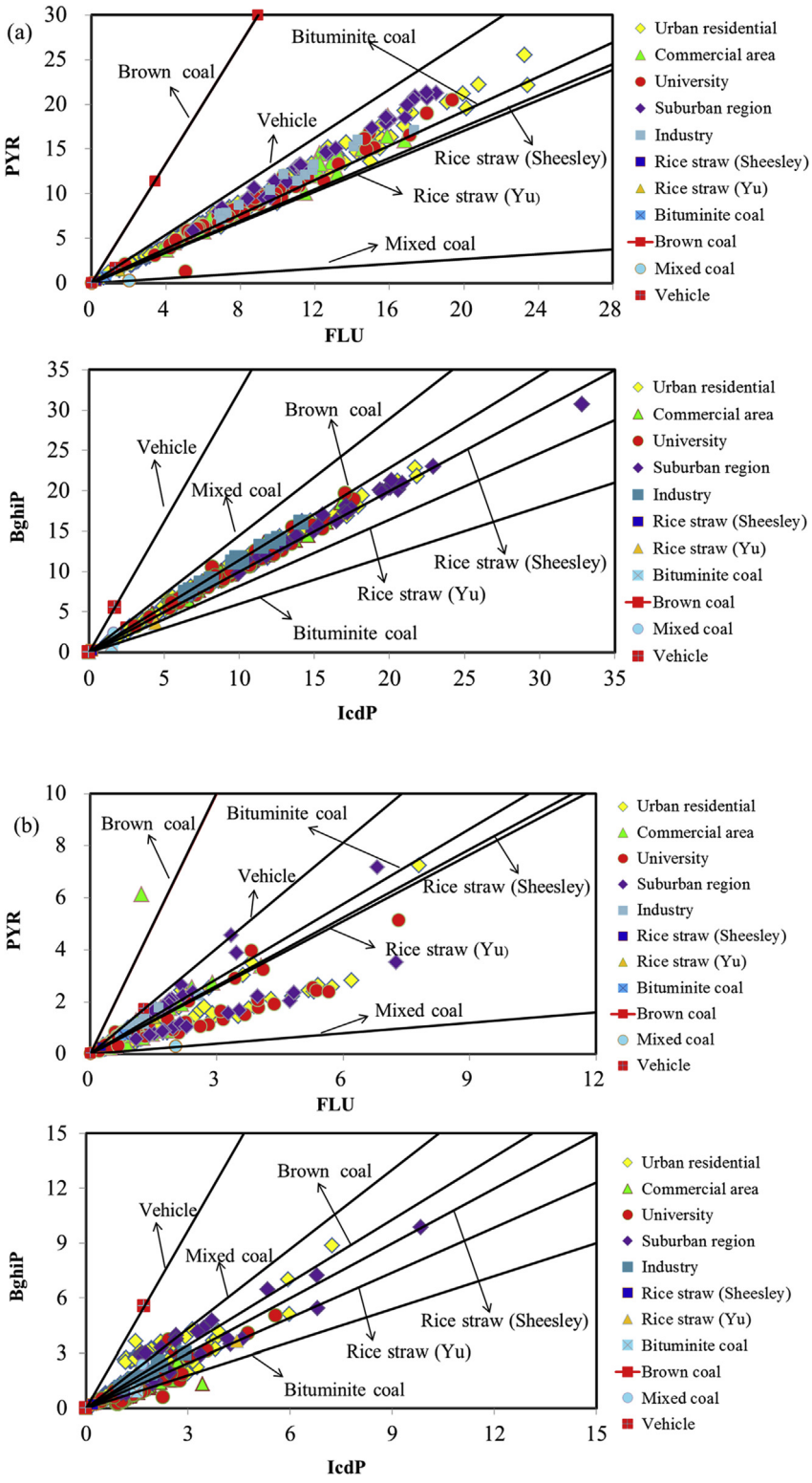

Fig. 6. Scatter diagrams for the ratios of FLU/PYR and IcdP/BghiP at different function zones in $PM_{2.5}$ in Xi'an (a) winter, (b) summer.

inconsequential. The ILCR values for the PAHs in winter (from 1.0×10^{-6} to 7.2×10^{-5}) were much higher than those in summer (from 1.1×10^{-8} to 5.2×10^{-5}) for all groups, and the ILCR value decreased in order adults > children > seniors ~ adolescent for males and females in both seasons. This sequence likely is the result of several factors, (1) adult have the highest inhalation rate and longest exposure than the other groups; (2) children have lower inhalation rate and exposure than seniors; however their much lower body weight increase their ILCRs; (3) adolescent had a bit higher inhalation rate than the senior while lower exposure time and body weight. In both seasons and all age groups-except adult, females showed slightly higher or comparable ILCR values

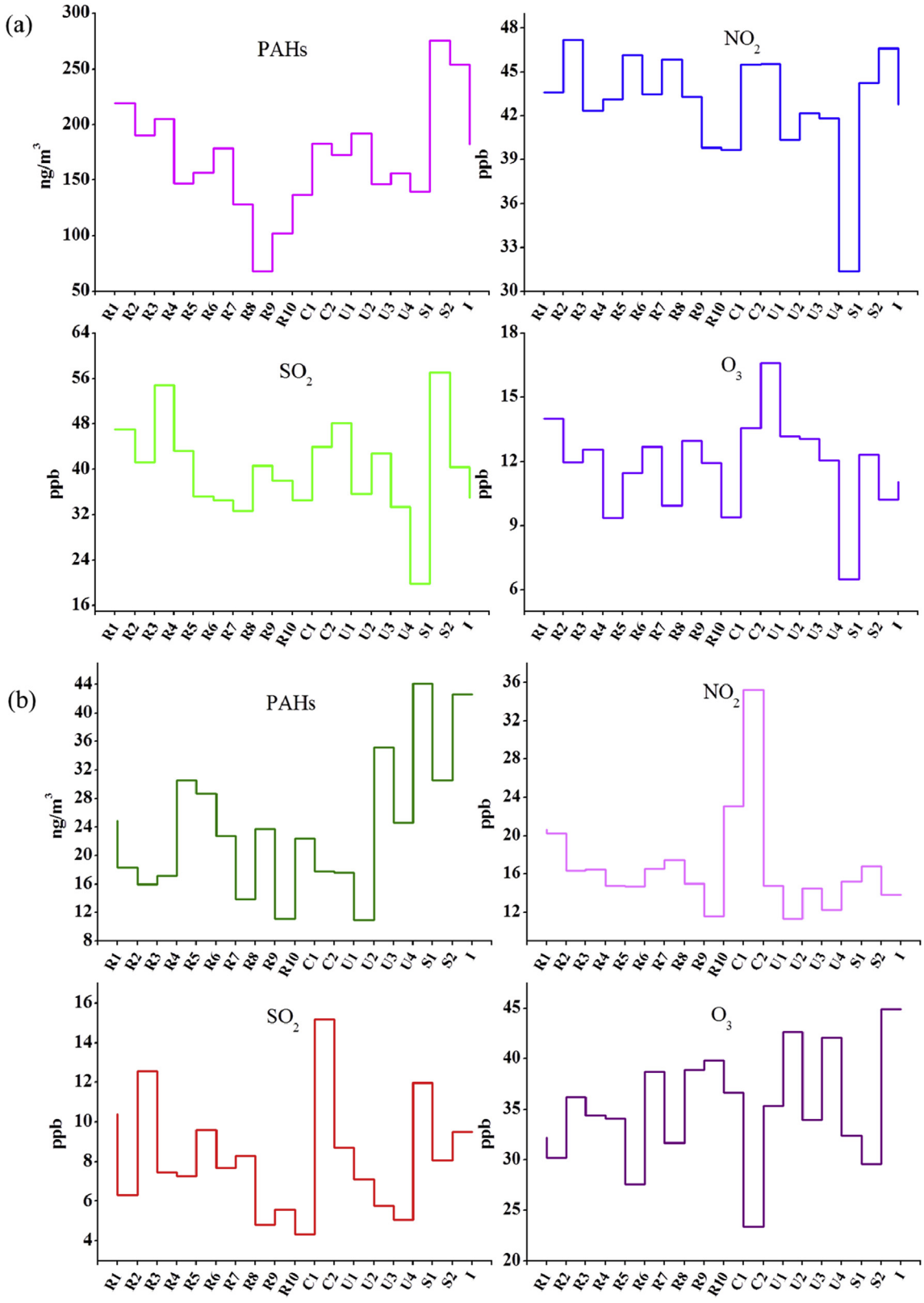

Fig. 7. The spatial distributions of PAHs and gas pollutants (NO_2, SO_2, O_3) in winter and summer.

compared with males. This can be explained by the fact that the ratios of IR_{male}/IR_{female} were higher than the corresponding ratios of BW_{male}/BW_{female} for adult only while the other aging groups have the opposite trends.

As far as the wintertime results for the different functional zones, people in suburban region have the highest risks from PAH

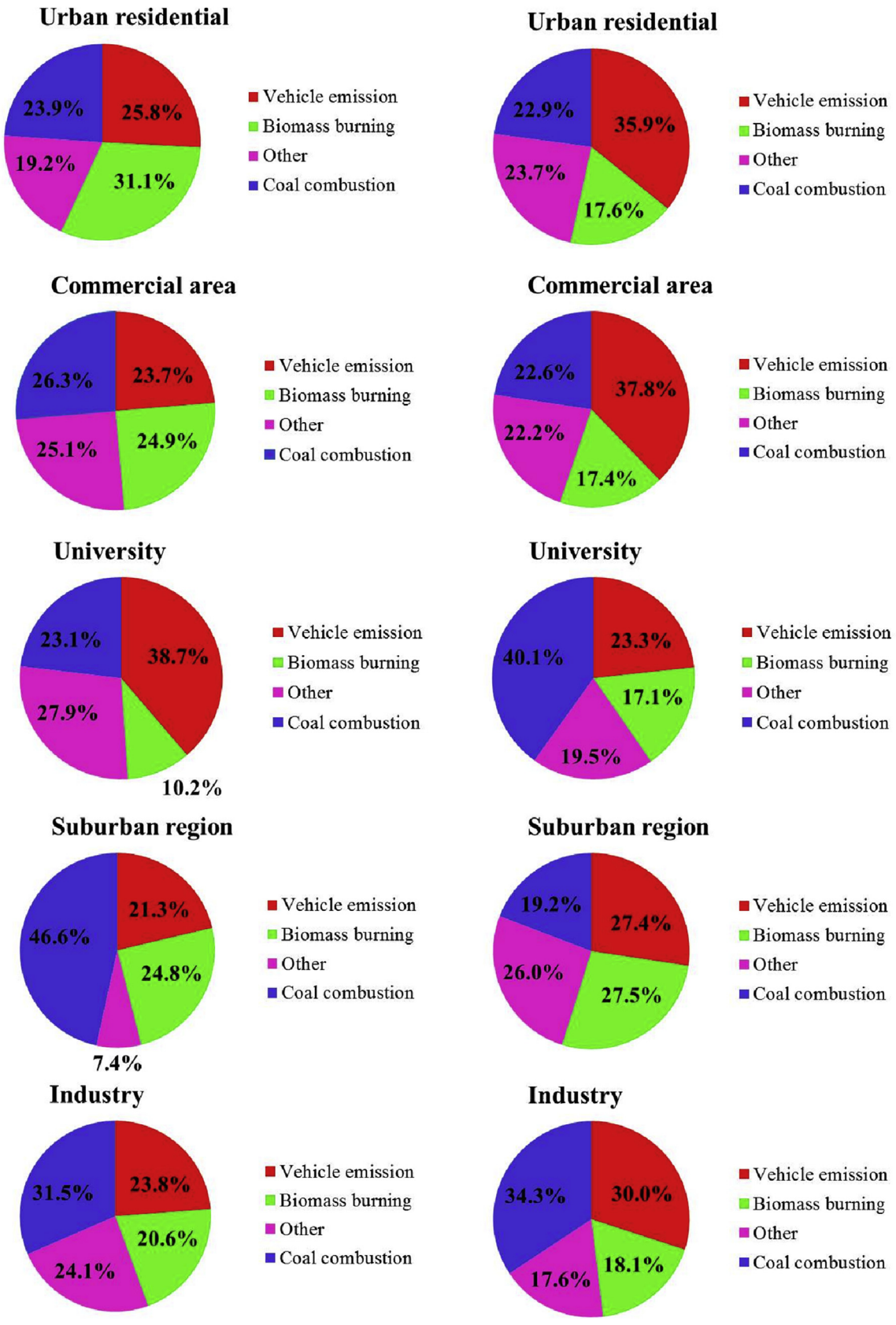

Fig. 8. Contributions of each PAH source obtained from PMF model for the different function zone in winter and summer.

Table 1
The inhalation incremental lifetime cancer risks (mean ± standard deviation) from PAHs for people living in Xi'an.

Winter								
Zone	Male				Female			
	Boys	Adolescents	Adults	Seniors	Girls	Adolescents	Adults	Seniors
	$\times10^{-6}$	$\times10^{-6}$	$\times10^{-5}$	$\times10^{-6}$	$\times10^{-6}$	$\times10^{-6}$	$\times10^{-5}$	$\times10^{-6}$
Urban residential	5.4 ± 2.2	4.0 ± 1.7	2.7 ± 1.1	4.1 ± 1.7	5.6 ± 2.3	4.1 ± 1.7	2.4 ± 1.0	4.3 ± 1.8
University	5.6 ± 1.6	4.2 ± 1.2	2.8 ± 0.8	4.2 ± 1.2	5.8 ± 1.6	4.2 ± 1.2	2.5 ± 0.7	4.5 ± 1.3
Commercial area	6.6 ± 1.4	4.9 ± 1.0	3.3 ± 0.7	5.0 ± 1.0	6.8 ± 1.4	4.9 ± 1.0	2.9 ± 0.6	5.2 ± 1.1
Suburban region	8.4 ± 2.2	6.3 ± 1.6	4.2 ± 1.1	6.4 ± 1.6	8.6 ± 2.2	6.3 ± 1.6	3.7 ± 1.0	6.7 ± 1.7
Industry	6.3 ± 1.5	4.7 ± 1.2	3.2 ± 0.7	4.8 ± 1.1	6.5 ± 1.5	4.8 ± 1.1	2.8 ± 0.6	5.1 ± 1.2
All	5.9 ± 2.2	4.4 ± 1.6	3.0 ± 1.1	4.5 ± 1.7	6.1 ± 2.3	4.5 ± 1.7	2.6 ± 1.0	4.7 ± 1.8
Summer								
Zone	Male				Female			
	Boys	Adolescents	Adults	Seniors	Girls	Adolescents	Adults	Seniors
	$\times10^{-7}$	$\times10^{-7}$	$\times10^{-6}$	$\times10^{-7}$	$\times10^{-7}$	$\times10^{-7}$	$\times10^{-6}$	$\times10^{-7}$
Urban residential	8.7 ± 5.2	6.5 ± 3.9	4.4 ± 2.6	6.6 ± 4.0	8.9 ± 5.4	6.5 ± 4.0	3.8 ± 2.3	6.9 ± 4.2
University	6.2 ± 4.9	4.6 ± 3.6	3.2 ± 2.5	4.7 ± 3.7	6.4 ± 5.0	4.7 ± 3.7	2.8 ± 2.2	5.0 ± 3.9
Commercial area	7.8 ± 4.3	5.8 ± 3.2	4.0 ± 2.2	5.9 ± 3.3	8.1 ± 4.4	5.9 ± 3.2	3.5 ± 1.9	6.3 ± 3.4
Suburban region	16 ± 13	12 ± 9.0	8.0 ± 6.4	12 ± 10	16 ± 13	12 ± 10	7.0 ± 5.6	13 ± 10
Industry	15 ± 25	12 ± 19	7.8 ± 13	12 ± 19	16 ± 26	12 ± 19	6.8 ± 11	12 ± 20
All	9.1 ± 8.6	6.8 ± 6.4	4.6 ± 4.3	6.9 ± 6.5	9.4 ± 8.8	6.9 ± 6.4	4.0 ± 3.8	7.3 ± 6.8

exposure while commercial and industry residents apparently have higher health impacts compared with those in the urban and university. In summer, however, people in university have lowest exposure levels and health risks, whereas residents in suburban and industry regions have relatively higher exposure levels. This was similar with the patterns in PAHs levels in different function zones during the two seasons.

In winter, all that ILCR values were higher than 10^{-6}, which reflected potentially serious health problems in that season, and in summer, 90% of ILCR values for adults were higher than10^{-6}; however ~70% of ILCR values for children and 85% of those for adolescent and senior were $<10^{-6}$. According to the census in Xi'an, there were 6.2 million persons living in Xi'an in 2013: people who were between 0 and 14 years accounted for 12.9% of the total population, those between 15 and 64 accounted for 78.6%, and those older than 65 were about 8.5% (Xi'an Statistical Yearbook, 2015), and we assumed those values for our analysis. Here we get a conservative estimate of the risks by set that children and adolescent were about 12.9% of the total persons. The adult were about 78.6% and senior were about 8.5% of total persons. Basing on these assumptions, we calculate that there are about 4 persons (0–14 years old) who have the potential risk for suffering from lung cancer for lifetime exposure at the pollution levels. For persons from 15 to 64, the model indicates that about 128 of them will suffer from lung cancer for lifetime exposure at winter levels. For senior older than 65, about 3 person would develop lung cancer risk for a lifetime exposure during winter. Even though the ILCRs were lower in summer, there still were about 19 persons ageing from 15 to 64 who would have the potential risk of developing lung cancer.

4. Conclusions

Our studies of PAHs bound to $PM_{2.5}$ at nineteen sites in Xi'an showed concentrations in winter about eight times those in summer (170.6 vs 23.8 ng/m^3 on average), and the average BaP levels also showed strong differences: 10.0 ng/m^3 in winter versus 1.9 ng/m^3 in summer. In both seasons, the suburban had relatively high levels of PAHs compared with the urban residential, and this can be explained by differences in the PAH sources between these sites. That is, biomass burning is dominant source for the PAHs in urban residential while coal combustion is the main source at suburban regions in winter. The results of our study demonstrated that in winter (1) PAHs are regional pollutants of PAHs and biomass burning and coal combustion were main sources; (2) widely scattered emission from uncontrolled coal combustion impact the suburban sites; (3) the emission from coal burned in a thermal power plant were likely treated and the impacts from the power plant were relatively stable. In summer, vehicle emission was dominant source in most communities. In summary, it appears that implementing and enforcing controls on the widespread coal combustion sources in winter and the motor vehicle emissions in summer would be the most effective ways to reduce the emission of PAHs and mitigate possible health effects. To more accurately assess the effects of the scattered emission from suburban on the overall air quality of the city, more studies will need to be done in the future. On the other hand, in order to acquire accurate output, elaborate spectrum data are also needed to develop in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.08.106.

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