



Microscale spatial distribution and health assessment of PM_{2.5}-bound polycyclic aromatic hydrocarbons (PAHs) at nine communities in Xi'an, China[☆]



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ARTICLE INFO

Article history:

Received 12 May 2016

Received in revised form

23 August 2016

Accepted 24 August 2016

Available online 28 August 2016

Keywords:

PAHs

Spatial distribution

PM_{2.5}

Health assessment

Cancer risk

ABSTRACT

Spatial variability of polycyclic aromatic hydrocarbons (PAHs) associated with fine particulate matter (PM_{2.5}) was investigated in Xi'an, China, in summer of 2013. Sixteen priority PAHs were quantified in 24-h integrated air samples collected simultaneously at nine urban and suburban communities. The total quantified PAHs mass concentrations ranged from 32.4 to 104.7 ng m⁻³, with an average value of 57.1 ± 23.0 ng m⁻³. PAHs were observed higher concentrations at suburban communities (average: 86.3 ng m⁻³) than at urban ones (average: 48.8 ng m⁻³) due to a better enforcement of the pollution control policies at the urban scale, and meanwhile the disorganized management of motor vehicles and massive building constructions in the suburbs. Elevated PAH levels were observed in the industrialized regions (west and northwest of Xi'an) from Kriging interpolation analysis. Satellite-based visual interpretations of land use were also applied for the supporting the spatial distribution of PAHs among the communities. The average benzo[a]pyrene-equivalent toxicity (Σ[BaP]_{eq}) at the nine communities was 6.9 ± 2.2 ng m⁻³ during the sampling period, showing a generally similar spatial distribution to PAHs levels. On average, the excess inhalation lifetime cancer risk derived from Σ[BaP]_{eq} indicated that eight persons per million of community residents would develop cancer due to PM_{2.5}-bound PAHs exposure in Xi'an. The great in-city spatial variability of PAHs confirmed the importance of multiple points sampling to conduct exposure health risk assessment.

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1. Introduction

Fine particulate matter (PM_{2.5}, particulate matter with aerodynamic diameters ≤ 2.5 μm) strongly affects air quality, human health, and climate (Dockery and Pope, 1996; Seinfeld and Pandis,

2006). China has one of the highest PM_{2.5} levels in the world (Van Donkelaar et al., 2010). In the past ten years (i.e., 2003–2013), the average annual PM_{2.5} concentration of 167 μg m⁻³ in Xi'an, a heavily polluted northwestern Chinese city, was 4.8 times exceeded the China's annual Ambient Air Quality Standards (AAQS, 35 μg m⁻³; GB3095-2012, 2012), 14 times the annual average standard recommended by the United States Environmental Protection Agency (U.S. EPA) (12 μg m⁻³), or 17 times the World Health Organization (WHO) standard (10 μg m⁻³) (Cao, 2014).

Among all of chemical organic components in PM_{2.5}, polycyclic aromatic hydrocarbons (PAHs) show the most consistent

[☆] This paper has been recommended for acceptance by David Carpenter.

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association with adverse health outcomes and therefore are of great public health concern. PAHs are ubiquitous in the environment and some can be cytotoxic, mutagenic, teratogenic, or carcinogenic for humans (WHO, 1998). Measurements of PAHs can provide information on sources apportionment, determination of potential health impacts to human, and knowledge on the air quality (Dockery et al., 1993; Jacobson et al., 2000; Turpin et al., 2000; Mauderly and Chow, 2008). PAHs can be generated from various natural sources such as forest fires and volcanic eruptions, but are mainly produced from anthropogenic sources including motor vehicle exhaust, incomplete combustion of fossil fuels for heating or power generation, and fugitive emissions from industries (Simoneit et al., 1991; Schauer et al., 1996). In addition, PAHs are also produced from indoor activities (e.g., cooking, wood and coal burning for house warming) (Peng et al., 2012).

In an urbanized region, people spend roughly 80%–90% of their time indoors (Castro et al., 2011). Community PM_{2.5} and its chemical compositions can greatly influence the indoor air quality, potentially resulting in a variety of health impacts to the residents. To the best of our knowledge, very limited data were reported for the communal PM and its conventional components (e.g., organic carbon (OC), elemental carbon (EC), and trace elements) in ambient air of different communities in a city (Viana et al., 2007; Hammond et al., 2008; Krudysz et al., 2008; Ward and Lange, 2010; Zhou et al., 2012; Hasheminassab et al., 2014). More particularly, there was a lack of such study on the PM_{2.5}-bound PAHs done in any Chinese communities, which has been published on peer-reviewed scientific literature. The characteristics of environment factors and emission sources vary spatially and therefore greatly influence the PAHs levels. However, most current PAHs measurements were conducted at a single sampling point (Okuda et al., 2010; Li et al., 2016; Wang et al., 2016a). In-city scale spatial variations on the pollutants concentration and the influences from more local or regional pollution sources are thus unknown or cannot be identified.

Investigations of the PM_{2.5}-bound PAHs in the atmosphere of urban communities can offer insights on their chemical characteristics and variations, and subsequently on their health implications to the residents. Hence, the objectives of this study were to (1) determine the concentrations of communal PM_{2.5} and PAHs and investigate their in-city spatial distribution in Xi'an, (2) identify the local pollution sources and interpret the impacts from regional sources, and (3) conduct health risk assessment for the exposure to the PAHs by the estimation of excess inhalation lifetime cancer risk at the communities of this major in-land city of northern China.

2. Materials and methods

2.1. Site description

Xi'an (E 108°09', N 34°02') is the capital city of Shaanxi Province as well as the largest city in northwest China. It is located at an elevation of 400 m above sea level and situated between the Yellow River valley and the centre of the Guanzhong Plain. The city borders the northern foot of the Qin Mountain to the south, and the banks of the Wei River to the north. Xi'an has a temperate climate with humid/hot summers and dry/cold winters influenced by the East Asian monsoon. The monthly 24-h average temperature ranges from the lowest of freezing mark in January to the highest of 26.6 °C in July. Monthly sunshine potentials range from a minimum of 31% in December to a maximum of 47% in August, which leads to an average of 1646 h of bright sunshine annually. The annual precipitation in Xi'an is 553 mm.

Xi'an is in a sub-provincial status, the municipality administers nine districts and four counties. It has a total area of

9983 km² and a population size of approximately 8.6 millions inhabitants. According to the 2013 data (Xi'an Statistical Yearbook, 2014), its urban area itself accounts for 3581 km² with a 5.8 million permanent population. A network of nine sampling locations was established to assess the PAHs concentrations at different communities (Supplemental Fig. S1), involving six central districts of Lianhu, Beilin, Weiyang, Yanta, Xincheng, and Baqiao. Table 1 lists the details of each sampling locations such as potential PM_{2.5} pollution sources and traffic intensities. The sites were selected to capture environments with different sources and atmospheric conditions. The sampling heights ranged from 1 to 10 m, subjected to the installation of sampling device at a safe and accessible location.

2.2. PM_{2.5} collection and gravimetric analysis

24-h integrated samples (from 8:00 a.m. to 8:00 a.m. local time of next day) were collected simultaneously at the nine community sites between 15th and 21st June 2013. The PM_{2.5} was collected onto pre-fired (780 °C, 4-h) 47-mm quartz-fiber filters (QM/A, Whatman, U.K.) using mini-volume air samplers (Airmetrics, USA) at a flow rate of 5 L min⁻¹. One field blank was collected at each site, which was used to account for any artifacts caused by gas absorption. A total of 72 samples (63 samples and 9 field blanks) were collected. Meteorological parameters (downloaded from the China Meteorological Data Centre, <http://data.cma.gov.cn/>) at the nine sites were highly correlated during the sampling period, with an average temperature of 29.5 °C, relative humidity (RH) of 62.4%, wind speed of 1.5 m s⁻¹, and prevailing winds from the east and northeast. The aerosol samples were stored in a refrigerator at < -18 °C before chemical analysis to prevent the evaporation of volatile components.

Gravimetric measurements were performed using an electronic microbalance with a sensitivity of ±1 µg (ME 5-F, Sartorius, Germany). The quartz filters were weighed before and after the sampling with 24-h equilibration in a chamber maintained at a temperature between 20 and 23 °C and a RH between 35% and 45% (Cao et al., 2007; Huang et al., 2014). The absolute error between duplicate weights were <0.015 mg for blank filters and <0.020 mg for aerosol-loaded samples.

2.3. PAHs analysis

An in-injection port thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) method was used to quantify the PAHs. The approach has the advantages of shorter sample preparation time (<1 min), minimizing of contaminations from solvent impurities, and higher sensitivity, compared with the traditional solvent extraction-GC/MS method (Chow et al., 2007). The detail analytical procedures have been reported in our previous publications (Ho and Yu, 2004; Chow et al., 2007; Ho et al., 2008, 2011; Xu et al., 2013a). The Agilent 7890A GC/5975C MS system used (Agilent Technology, USA) was operated in electron impact (EI) ionization mode. A total of sixteen PAHs was identified and quantified (Supplemental Table S1). Briefly, aliquots of the sample filter (1.0 cm²) was cut into small pieces and transferred into a TD tube. The sample-loaded tube was placed into the GC injection port at 50 °C. The injection port temperature was then raised to 275 °C for desorption in a splitless mode while the GC oven temperature was kept at 30 °C. Separation of organic compounds was performed with a HP-5MS (30 m × 0.250 mm i.d., 0.25 µm film thickness, Agilent Technologies, USA) capillary column. The constant flow rate of carrier gas helium (ultra high purity (UHP) grade, 99.999% purity) was 1.2 mL min⁻¹. The mass spectrometry detector (MSD) was scanned from 50 to 550 amu. The EI voltage was 70 eV and selected

Table 1
Characteristics of nine sampling communities (sites) in Xi'an in this study.

Communities (sites) (abbreviation)	District	Latitude (N) (°)	Longitude (E) (°)	No of sample	Surrounding environment (sampling height)
Chengnei (CN)	Lianhu	34.2745	108.9379	8	Urban, within the old city wall, downtown area (1 m)
Zhonglou (ZL)	Beilin	34.2547	108.9373	8	Urban, within the old city wall, downtown area (10 m)
Wenjing (WJ)	Weiyang	34.2963	108.9337	8	Urban, between the north old city wall and the second ring road (1 m)
Wenyi (WY)	Beilin	34.2444	108.9480	8	Urban, between the south old city wall and the second ring road (3 m)
Bowen (BW)	Yanta	34.2233	108.9000	8	Urban, between the southwest second and third ring road, high-tech industrial zone (1 m)
Changle (CL)	Xincheng	34.2700	109.0034	8	Urban, between the east second and third ring roads (1 m)
Jiangong (JG)	Xincheng	34.2440	109.0116	8	Urban, between the southeast second and third ring roads (6 m)
Guangyuntan (GY)	Baqiao	34.3268	109.0691	8	Suburban, the northeast of Xi'an, farmland and village, Xi'an International Horticultural Exposition (10 m)
Sanqiao (SQ)	Weiyang	34.3093	108.8114	8	Suburban, the northwest of Xi'an, industrial and heavy transport area (3 m)

ion mode was applied for the quantification. Identification was achieved by characteristic ion and comparing the retention times of the chromatographic peaks with those of standards. The field blank filters were analyzed using these same procedures. The results of the blank analyses showed only trace contamination levels (<5.0% of the concentrations of samples).

2.4. Quality assurance and quality control (QA/QC)

QA and QC establish the precision, accuracy and validity of the experimental data, and details of the QA/QC procedures were the same as those in previously studies (Ho and Yu, 2004; Chow et al., 2007; Ho et al., 2008, 2011; Cao et al., 2013; Xu et al., 2013a; Wang et al., 2015a, 2016b) and one Chinese patent (No.: 2013 2 0470244.7). In brief, the aerosol samplers were checked and calibrated regularly during the sampling period, and the field blank filters were collected to correct for backgrounds. In addition, *n*-alkanes (C₁₇–C₄₀) were determined at the same time for the source apportionment supporting information. Chrysene-d₁₂ (C₁₈D₁₂) (98%, Sigma-Aldrich, USA) was added as internal standard (IS) for the PAHs and *n*-tetracosane-d₅₀ (n-C₂₄D₅₀) (98%, Aldrich, Milwaukee, WI, USA) for the *n*-alkanes. A five-point calibration over a concentration range of 0.5–5.0 ng for each of the target compounds from a standard mixture (Sigma-Aldrich, USA) was established, and the correlation coefficients (R²) for linear regressions of the calibration curves were >0.99. For each ten samples, one replicate analysis was done; the relative standard deviation of these replicates was 5.7%–19.5%. All data were corrected for the average value of the blanks. The minimum detection limits (MDLs) for the targeted PAHs are listed in Supplemental Table S1.

3. Results and discussion

3.1. PM_{2.5} and PAH concentrations at Xi'an community

The average PM_{2.5} concentration at the nine communities was 84.1 ± 6.9 μg m⁻³. It should be noted that only the level at CL (70.0 μg m⁻³ on average) met the 24-h AAQS of 75 μg m⁻³ in China during the sampling period (Supplemental Fig. S2). And, all of the samples exceeded the 24-h WHO PM_{2.5} guideline of 25 μg m⁻³. PM_{2.5} concentrations were considerably consistent among those communities (70.0–94.1 μg m⁻³ on average) (Supplemental Fig. S2), potentially suggesting that the regional sources dominated the PM_{2.5} pollution in Xi'an (Wang et al., 2015b). The total quantified PAH concentrations ranged from 32.4 to 104.7 ng m⁻³, with an average of 57.1 ± 23.0 ng m⁻³. The highest and lowest PAHs levels were detected at CL and SQ, respectively (Supplemental Fig. S2). The highest average concentration was twice of the lowest value. The PAH levels followed a similar trend than the PM_{2.5}

mass at all of the communities, but with a greater scattering. This can be ascribed to the fact that the abundances of PAHs can be lightly influenced by particular local pollution sources, human activity and other environmental conditions within each community. The total PAHs accounted for 0.04%–0.11% of the PM_{2.5} mass. More abundant PAHs were observed at SQ than at the other communities, while the lowest value was found at WJ.

The average PAH concentration in this study was 60% lower than the value of 136.7 ± 56.7 ng m⁻³ in total suspended particulates (TSP) in southeast downtown of Xi'an measured in summer of 2005–2007 (Okuda et al., 2010). Cao (2014) reported that the PAH concentration in PM_{2.5} was 13.7 ± 10.2 ng m⁻³ in summer of 2008, which was only one fifth of our average value in 2013. Such discrepancies can be attributed to the differences in the sampling locations. For the study conducted in 2008 (Cao, 2014), there was only a single sampling point in the southwest of the city centre, characterized by a mixture of urban/industrial/commercial activities (no other particular pollution sources around) and thus had no significant persuasion and indication on the spatial distribution. Besides, the lower pollutant levels could be attributed to the favorable meteorological conditions and the held of 29th Summer Olympics Games in Beijing. The Beijing Municipal Government and peripheral provinces authorities (including Shaanxi) had implemented various measures to reduce emissions of air pollutants and improve the air quality, aiming to achieve the goal of "Green Olympic Games" in 2008 (Wang and Xie, 2009; Wang et al., 2010). A large reduction in PM_{2.5} mass and other pollutants were thus seen in northern China during the period. In short, multiple point sampling was conducted in this study, and presumably yielded to more reliable and representative data from the communities.

There is no regulatory standard or guideline for particulate PAHs in China. And, there is a lack of related assessment in the community environment. Our results were thus compared with the findings from other worldwide cities. Both communal PM_{2.5} and associated PAHs in Xi'an were much higher than those in three retirement communities in Los Angeles, U.S. (PM_{2.5}: 49.5–51.3 μg m⁻³; PAHs: 2.9–4.3 ng m⁻³ in 2005–2006) (Hasheminassab et al., 2014). For a subsite study conducted with this work, three identical PM_{2.5} air samplers were situated (i) outside the Shaanxi Provincial Library (downtown commercial district), (ii) in the Xi'an railway station square (high population density and heavy traffic flow), and (iii) on an university campus (urban background) in Xi'an, respectively. The aerosol samples were synchronously collected. The highest average PAH concentration of 120.2 ng m⁻³ was observed in the railway station, due to intense traffic emissions. The value was twice higher than the communal values. The average PAH concentration in the Shaanxi Provincial Library was 64.5 ng m⁻³, much closer to our average value. The lowest level was seen on the university campus

(15.2 ng m⁻³), where pollution sources were the fewest, while traffic lines stand far away. The findings support that there should be a reasonable concern on human exposure to PAHs at the communities in Xi'an. More representative (e.g., seasonal effect) and frequent assessment should consequently be conducted.

3.2. Spatial distribution of PAHs

3.2.1. PM_{2.5}-bound PAH concentrations distribution

The estimated spatial distributions of PAHs at the nine communities obtained from the Kriging interpolation principle were represented in Fig. 1. Relatively high concentrations of the 16 priority PAHs were found in the west and northwest regions, where the Xi'an western suburb thermal power plant stands. The Xi'an western suburb thermal power plant is one of the largest scale power plants in China, but is equipped with the most backward purification system in Xi'an, and can consequently emit enormous amounts of PAHs and other pollutants to the atmosphere. Moreover, it is worth mentioning that the west areas of Xi'an are located under the wind, where suffer more serious air pollution.

Lower PAHs levels were observed in the north and northeast parts of the city. Xi'an Economic and Technological Development Zone is a state-level economic development district, which has been established in north gate of Xi'an with an area of 4.9 km² in 2000. Its pillar industries include the sectors of mechanical electronics, foods processing, bio-pharmaceuticals, new materials designs and new high-tech products. With a new economic development pattern, more efficient air pollution purification equipment and advanced management technology have been remedied, resulting in a better air quality to the north. In addition, the Xi'an International Horticultural Expo Garden and Ecological District probably contributed to lower PAHs abundances measured in the north and northeast areas. The Expo Garden, covering a total area of 4.2 km² (including 1.9 km² of water), is located in the northeast of Xi'an. It is also close to the Chan-Ba Ecological District, which is a mix of residential, office, gardens, farms, open waters and open spaces. Its surrounding ecological environment is improved by comprehensive management of the river and the reconstruction of the valley, which thus increase the overall urban bearing capacity. Those settings overall favor a clean air environment to north and northeast areas.

Fig. 2 illustrates a suburban-urban declining trend of PAH

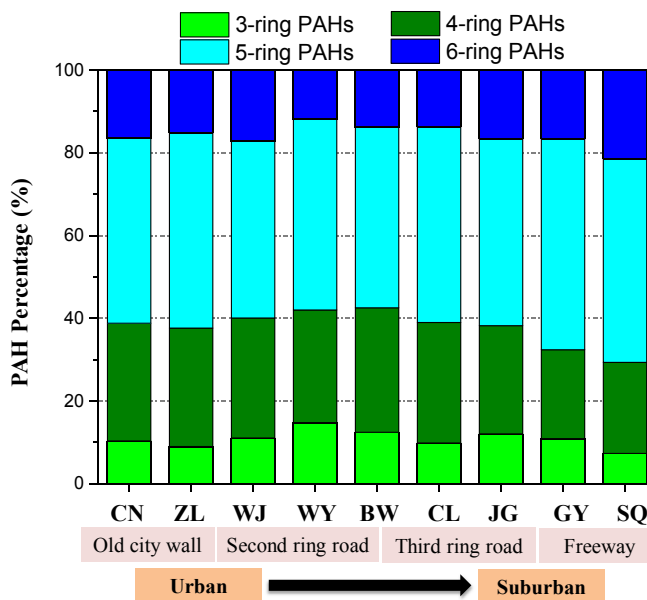


Fig. 2. Percentages of PAH ring concentrations at the nine Xi'an communities.

concentrations in Xi'an, showing an elevation of high molecular weight (HMW) (MW ≥ 252 or defined as compounds with 5- and 6-aromatic rings) at the suburban sites. This can be possibly ascribed with the co-existence of petroleum and biomass/coal combustion sources. It should be noted that generally the mobile sources differ in PAH profiles, with the heavy diesel vehicles being characterized by low molecular weight (LMW, MW < 252 or defined as compounds with 3- and 4-aromatic rings) components than gasoline vehicles. However, per driven kilometer, total emissions from a gasoline-fuelled car are much lower than emissions from a diesel-fuelled car (Rogge et al., 1993). The HMW PAHs accounted for 67.6% and 70.7% of total quantified PAHs at GY and SQ (two suburban sites), respectively, which were higher than the average of 60.3% (in a range of 57.5%–62.4%) measured at the seven urban communities. The lower contribution of HMW PAH in the urban might be due to the enforcement of the traffic restriction scheme within the second ring road and selected areas within the third ring road of Xi'an

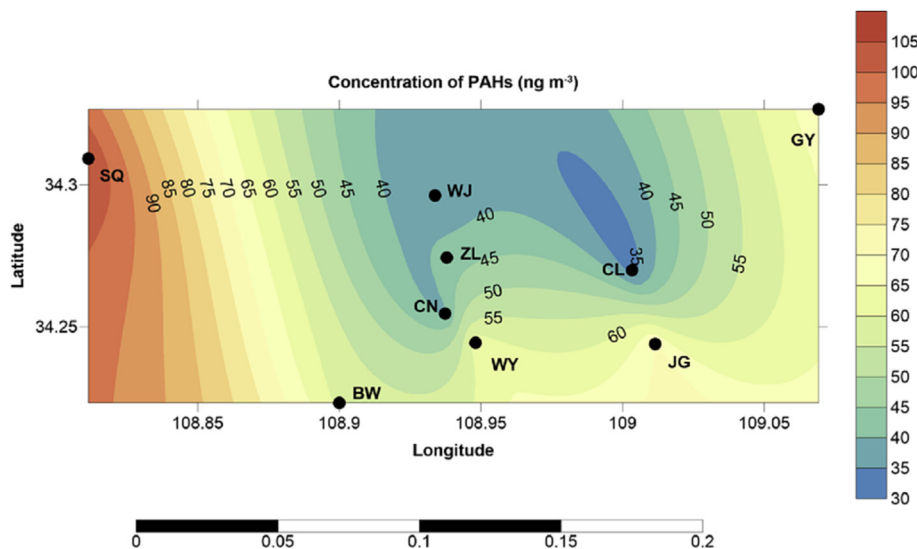


Fig. 1. Kriging interpolation of PAH concentrations in Xi'an.

(road with a smaller order of ring means the area is closer to the city centre). Since 2007, the “Government Circular on Strengthening Management of the Motor Vehicle Traffic in Xi'an City” has banned all diesel-fuelled vehicles, especially heavy-duty trucks, within the second ring road from 7:00 a.m. to 10:00 p.m., as well as on some important road arteries between the second and third ring roads during rush hours. In addition, from 2012, small coal-fired boilers (<20 t) have been step-by-step forbidden to operate within the second ring road. The combined pollution reduction regulations resulted in the differences on PAHs abundances and distributions between the urban and suburban sites. This further suggests that the pollution sources in the suburban could be more significant than those in the urban Xi'an. The sources contributing to emit PAHs at the suburban scale should not be overlooked during the summertime.

3.2.2. Coefficient of divergence of PAHs

The coefficient of divergence (CD) of the average concentrations of PAH individual species between any two sampling sites was adopted to assess the spread and difference of PAH species between two communities (Shen et al., 2011). As a self-normalizing parameter, the CD is calculated as follows:

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

where x_{ij} represents the concentration of individual PAH specie i at site j , j and k represent the two sampling sites (two communities), and p is the number of PAH individual species in this study. Here p equals 16. If all PAH individual species at any two sampling sites are similar, the CD approaches zero; if the CD is close to unity, it shows an inconsistency of PAH individual species at these two selected sampling sites. In general, CD value < 0.2 proves the existence of similarity (Shen et al., 2011; Wang et al., 2015b).

Table 2 shows the average CD values of the PAHs for individual communities. In general, the CD values ranging from 0.251 to 0.361 indicated a lack of uniformity for the PAHs over the spatial scale of this study. The highest CD (0.361 ± 0.120) was observed at SQ, suggesting that its distribution of individual species were dissimilar with those in other sites. Among all pair-wise comparisons, the maximal and minimal CD values were found between SQ and CL (0.522) and WY and JG (0.136), respectively (Fig. 3). Fig. 3A indicates that all of the measured PAHs drifted from the 1:1 line, especially for DahA (15), IcdP (14), BghiP (16), BaA (6), and BaP (12) (in the red circle of Fig. 3A). It is known that the combustions of fuels on a gasoline engine can elevate the emissions of BaA (6), BaP (12), and BghiP (16) by ~20% (Pedersen et al., 1980). These drifts not only suggest the high levels of PAHs at SQ during the sampling period, but also point out that traffic-related PAHs and their sources were more serious than those in other sites (e.g., CL). Furthermore, the

distance between SQ and CL was approximately 20 km. There could be a diversity of surrounding environments, major vehicular fuel types and quality, and life-style of the residents. In addition, the CD value between SQ and CL was approximately four times of that of WY and JG pair (Fig. 3B), demonstrating the similarity of PAHs at WY and JG. The distance between WY and JG sites was only 7 km and both were located in the south part of the city centre, considered as a commercial/residential region.

3.2.3. Visual interpretation

High spatial resolution images released from the Google Earth can provide great support for the traditional land use/cover mapping (Mering et al., 2010). The Google Earth images were used as a visualization tool (Kaimaris et al., 2011) to support the understanding of potential air pollution sources in this study (Long et al., 2016). The maps of land use derived from the Google Earth imagery for communities of SQ and CL are presented in Fig. 4a and b, where the highest and lowest PAH levels were observed, respectively. Referring to the features of their surrounding environments, it can be seen that the largest land use located type in the study area was the build-up areas with values of 15.6 km² at SQ and 17.4 km² at CL, accounting for 70% at SQ and 78% at CL of each selected area (22.2 km²). Construction area at SQ (1.87 km²) (Fig. 4a) was much wider than that at CL (0.86 km²) (Fig. 4b). SQ was also located nearby a large vehicles centre (Fig. 4c). More construction sites and higher number of motor vehicles were found at SQ. On the contrary, CL had no particular air pollution sources.

SQ is located in the suburban area and downwind position of Xi'an. It is close to a freeway (2.1 km) and to the third ring road (2.7 km), and very close to the “western suburb international vehicle sales city” (1.9 km) (outlined as green box in Fig. 4a and enlarged in Fig. 4c). There were two major traffic arteries crossing themselves in the vicinity of the SQ community (0.5 km and 0.8 km), which had very large traffic flows (Fig. 4a), especially for the commercial trucks and long-distance buses. In addition, direct emissions of unburned fuel from diesel engines can contribute to high PAHs abundances (Williams et al., 1989). Besides, a large amount of construction sites (as shown in red box in Fig. 4a) at SQ may lead to increase in uses of non-road mobile machinery, including construction vehicles, building materials transportation vehicles, and excavators. Densely covered traffic communication networks and mass running vehicles are the essential characteristics at SQ.

BghiP, mainly emitted from light-duty gasoline motor vehicle (Rogge et al., 1993; Ravindra et al., 2006), accounted for 11% of the total quantified PAHs at SQ, which was ~1.7 times of the average value for the other communities and compared with only 7% at CL. The average contribution of 6-ring PAHs was 22% at SQ, which was higher than that of 13% at CL. This can be supported by the fact that PAHs at SQ were associated to pyrogenic sources and gasoline-fuelled vehicle emissions, in consistent with our previous conclusion.

3.2.4. Implication for PAH pollution sources

Diagnostic ratios of PAHs have been widely used in source identification (Yunker et al., 2002; Tobiszewski and Namiesnik, 2012). In our study, the average values of IcdP/(IcdP + BghiP) and FLU/(FLU + PYR) were 0.53 and 0.49, respectively, indicating the strong mixed influences from both pollution sources such as grass, wood, coal, and petroleum combustion (Okuda et al., 2010; Xu et al., 2013b). Furthermore, the ratios indicated that the PAHs at BW, JG, and SQ were mainly produced from motor vehicle emissions, while grass, wood and coal combustions were more dominant at ZL, WY, and WJ (Fig. 5).

The motor vehicle emissions dominated sites (BW, JG, and SQ)

Table 2

Average coefficient of divergence (CD) values of the PAHs at the nine communities in Xi'an.

Communities	CD	STDEV
CN	0.251	0.082
ZL	0.272	0.089
WJ	0.284	0.111
WY	0.254	0.081
BW	0.280	0.051
CL	0.282	0.115
JG	0.259	0.094
GY	0.278	0.093
SQ	0.361	0.120

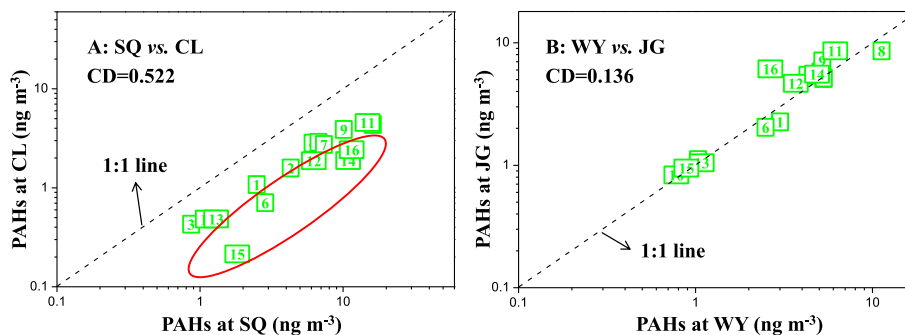


Fig. 3. Comparison of coefficient of divergence (CD) values of individual PAHs between (A) SQ vs. CL (maximum CD value) and (B) WY vs. JG (minimum CD value). (Green colour small boxes for PAHs identification: 1: FLO; 2: PHE; 3: ANT; 4: FLU; 5: PYR; 6: BaA; 7: CHR; 8: BbF; 9: BkF; 10: BaF; 11: BeP; 12: BaP; 13: PER; 14: IcdP; 15: DahA; 16: BghiP). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

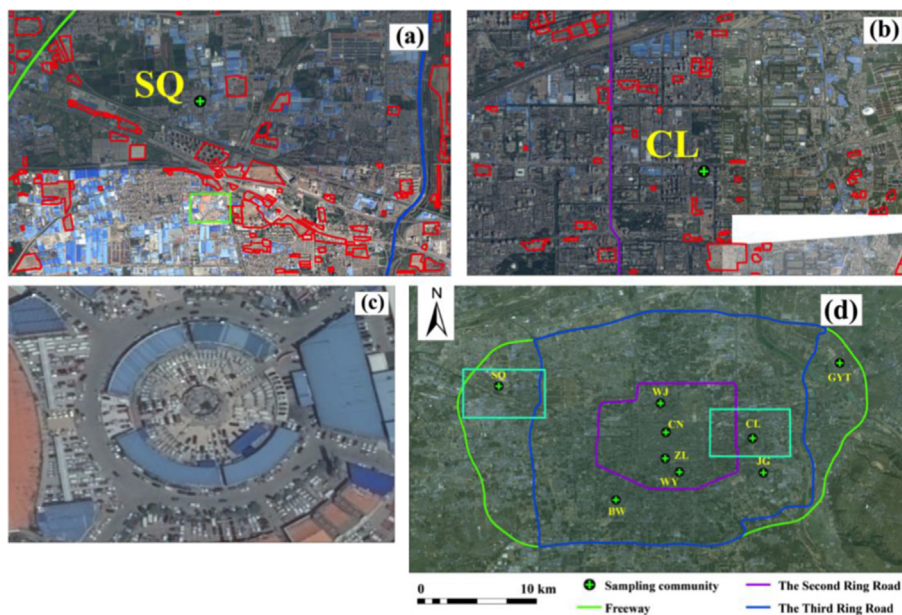


Fig. 4. Satellite-based visual interpretation result of land use at (a) SQ and (b) CL. The vehicle sales centre near SQ is framed in green in panel (a) and zoomed in panel (c). The construction sites are highlighted by red bold lines in panel (a) and panel (b). The selected areas of SQ and CL were framed in cyan in panel (d). The background images were very-high resolution satellite data with 0.5 m, which were described by Long et al., 2016. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were located outside the second ring road in Xi'an. The PAH diagnostic ratios at SQ were consistent with our previous discussion that vehicle emission was the most critical pollution. For BW and JG, heavy traffic flows, even with a relatively low population density, led to a strong PAHs contribution from petroleum combustion. On the contrary, the sites dominated by coal combustion (ZL, WY, and WJ) were located inside the second ring road. It must be noted that there was a large amount of breakfast stalls and eating houses in the city centre, providing ordinary and convenient foods for the citizens. Although the use of small inefficient coal-fired boiler has been banned within the second ring road, honeycomb briquette and chunk-anthracitic coals were still used as the majority of the fuels at such small-scale food shops in Xi'an.

The carbon preference index (CPI, the relative quantities of odd/even carbon number) of *n*-alkanes has been used to evaluate the contributions of biogenic versus anthropogenic sources (Peltzer and Gagosian, 1989; Simoneit, 1985), acting as supporting information for the spatial distribution of PAHs. The CPI values (range: 1.1–2.4, average: 1.7) were near unity, accounting for a strong

contribution from anthropogenic pollution sources, such as coal combustion, diesel residues, and gasoline emissions. The average CPI values at the motor vehicle emissions- and coal combustion-dominated sites were 1.4 and 1.8, respectively. The average CPI value at SQ was the lowest and close to unity (CPI = 1.1), suggesting the strongest influence from anthropogenic sources among these sites. In addition, the lowest wax mass contribution (wax $C_{n\%}$) of *n*-alkanes at SQ also demonstrated that any impact from biogenic sources was comparatively lower.

3.3. Health risk assessment

BaP is of the greatest concern among PAHs because it has been used as an indicator of carcinogenicity (Bi et al., 2003; Wang et al., 2006). The average BaP concentration was 3.4 ng m^{-3} (range: $1.9\text{--}6.2 \text{ ng m}^{-3}$) at the nine communities, which was more than three times exceeded the limit established by the EU (European Union) air quality annual mean guideline of 1.0 ng m^{-3} (EU, 2004). Referred to the 24-h AAQS (GB3095-2012, 2012) in China, the

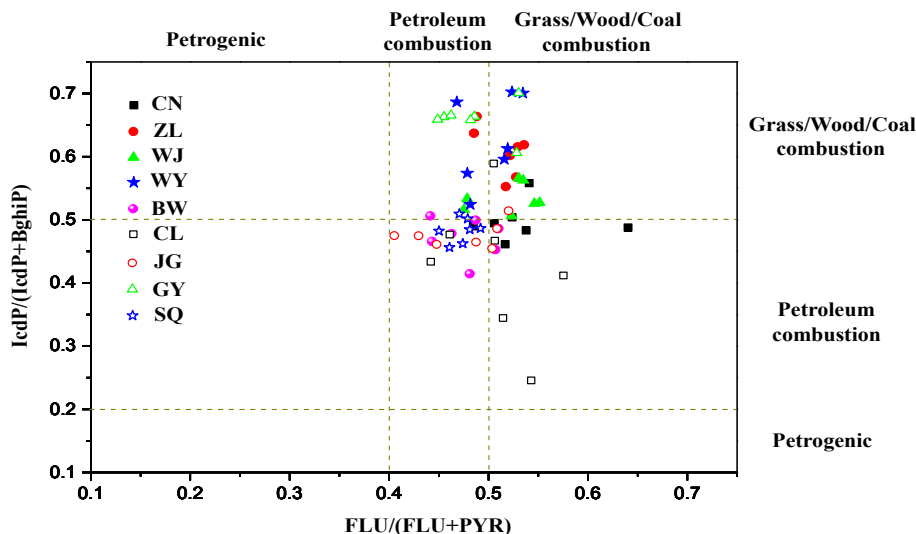


Fig. 5. Correlations between PAHs diagnostic ratios (FLU/(FLU + PYR) and IcdP/(IcdP + BghiP)) at the nine communities.

average BaP concentration in this study was still higher than the standard of 2.5 ng m⁻³ in PM₁₀. The maximum BaP level was observed at SQ, which was twice of the average value measured at the other eight communities (3.1 ng m⁻³) (Fig. 6). Both of the PAH abundances and their potential carcinogenicity in suburban sites were worse than those in urban sites.

It is well known that most PAHs are mutagenic and carcinogenic to human bodies, and its health risk can be assessed by BaP-equivalent toxicity ([BaP]_{eq}) concentration (Yassaa et al., 2001). The recommended guideline from the Office of Environmental Health Hazard Assessment (OEHHA) of the California Environmental Protection Agency (CalEPA) were used to calculate the inhalation lifetime cancer risk (Hickox, 2003; Yu et al., 2008). The [BaP]_{eq} is calculated from the individual PM_{2.5}-bound PAH concentrations in each sample and the toxicity equivalency factor (TEF) of target compounds (Nisbet and Lagoy, 1992; Petry et al., 1996) with the equation of:

$$\sum [BaP]_{eq} = \sum (C_i \times TEF_i) \quad (2)$$

where C_i is the concentration of the target PAH compound i (ng m⁻³) and TEF_i is the TEF of i. Excess inhalation lifetime cancer risk is

calculated by:

$$\text{Inhalation lifetime cancer risk} = \sum [BaP]_{eq} \times UR[BaP] \quad (3)$$

where UR[BaP] is the inhalation cancer unit risk factor of BaP and is defined as the number of people at risk of contracting cancer from inhalation a BaP equivalent concentration of 1 ng m⁻³ within their lifetime of 70 years. The UR[BaP] value from the CalEPA is 1.1 × 10⁻⁶ (Hickox, 2003; Yu et al., 2008). The averaged [BaP]_{eq} level was dominated by BaP, followed by DahA, BbF, BkF, and IcdP (accounting for 92.2% of Σ[BaP]_{eq}). The contributions of 5- and 6-ring PAHs to Σ[BaP]_{eq} reached up to 94.8%, suggesting a distinctly higher human health risk from HMW PAHs (~two orders of magnitude higher) compared with that of LMW PAHs.

The average Σ[BaP]_{eq} at the nine communities was 6.9 ± 2.2 ng m⁻³ (range: 3.5–12.9 ng m⁻³), with the highest and lowest values at SQ and CL, respectively. The average excess total inhalation lifetime cancer risk was 7.6 × 10⁻⁶ (range: 3.9 × 10⁻⁶–1.4 × 10⁻⁵), while its median was 5.5 × 10⁻⁶, with 6.5 × 10⁻⁶ and 8.7 × 10⁻⁶ at the 5th and 95th percentile, respectively. An estimated average of eight (range: 4–14) cancer cases per million of residents in Xi'an communities could be attributable to the inhalation of PM_{2.5}-bound PAHs. According to Xi'an Statistical Yearbooks (2014), the total number of the permanent residents in Xi'an city was approximately 5.8 million at the end of 2013. Therefore, there was an estimation of a total of 46 cancer cases for its residents caused by the inhalation of PM_{2.5}-bound PAHs. It should be noted that such estimation is most likely to be underestimated since PAHs concentrations were usually lower in summer than in other seasons (Wang et al., 2006; Cao, 2014). These extremely high Σ[BaP]_{eq} values and the corresponding health risks should not be neglected in Xi'an.

4. Conclusions

The concentrations of 16 PAHs in PM_{2.5} were determined at the nine communities in Xi'an during the summertime in 2013. Higher concentrations of PAHs were found at the suburban than the urban communities, presumably related to the local and regional economic development and vehicle emission control measures. Anthropogenic sources including vehicle emission and coal combustion had strong impacts on the atmosphere of the communities.

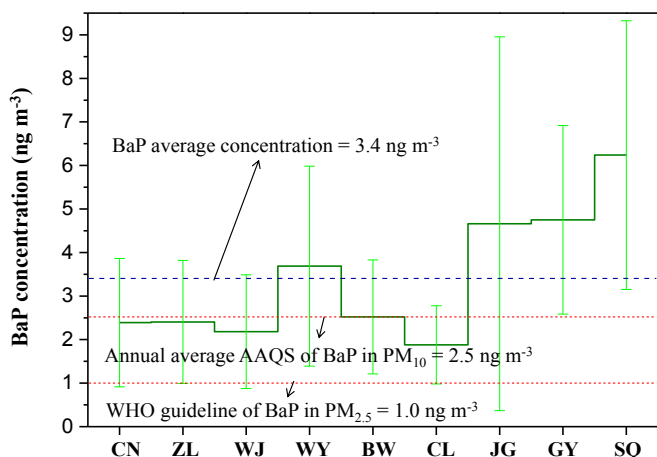


Fig. 6. Comparison of the communal BaP concentrations with the guidelines.

The excess inhalation lifetime cancer risk derived from $\Sigma[\text{BaP}]_{\text{eq}}$ estimated that eight persons per million of community residents would develop cancer due to exposure to $\text{PM}_{2.5}$ -bound PAHs in Xi'an. Our findings suggest that there are needs for efficient motor vehicle emission controls, better management on road operations, and a stricter enforcement of regulations for the coal combustion-related activities. In addition, green plans such as development of ecological protection areas in either urban or rural regions can be benefited for the air quality. Cleaner fuels should be used for motor vehicles and industries to reduce the emission of toxic compounds into the air.

We do acknowledge that the current one-week sampling campaign may not sufficiently collect the best representatives expressed the air pollutions for the communities in Xi'an. More future works such as extension of the sampling duration, re-run the identical sampling campaign in winter or other seasons, measurement of other toxic components (e.g., heavy metals), and further investigations of indoor-outdoor PAHs distribution and relationship are to be conducted in the future to assist our knowledge of the health risks associated for the residents.

Acknowledgments

This study was supported by the Natural Science Foundation of China (NSFC) (Grant No. 41503096), and Shaanxi Postdoctoral Science Foundation. And it was also supported by the University of California Berkeley Wood-Calvert Chair grant, and the United States Fulbright fellowship. And also supported by the "Strategic Priority Research Program" of the Chinese Academy of Sciences (Grant No. XDB05060500).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2016.08.058>.

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