



Characterization of parent and oxygenated-polycyclic aromatic hydrocarbons (PAHs) in Xi'an, China during heating period: An investigation of spatial distribution and transformation



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H I G H L I G H T S

- PAHs and oxygenated-PAHs (OPAHs) were widely detected in 19 sites in PM_{2.5} from Xi'an at 2013.
- Secondary formation was the main source for OPAHs.
- Biomass burning accounted for 37.1% of the total PAHs in Xi'an during heating period.

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Polycyclic aromatic hydrocarbons (PAHs) and its oxygenated derivatives (OPAHs) are toxins in PM_{2.5}. Little information has been known for their transformation in the ambient airs. In this study, PM_{2.5} samples were collected at 19 sampling sites in Xi'an, China during the heating period, which is classified into: urban residential, university, commercial area, suburban region, and industry. Organic compounds including PAHs, OPAHs, hopanes and cholestanes were quantified. The average of total quantified PAHs and OPAHs concentrations were 196.5 ng/m³ and 29.4 ng/m³, respectively, which were consistent with other northern cities in China. Statistical analyses showed that there were significant differences on the distributions of PAHs between urban and suburban regions. The industry also had distinguishable profiles compared with urban residential and commercial area for OPAHs. The greater diversity of OPAHs than PAHs might be due to different primary emission sources and transformation and degradation pathways. The ratios of OPAHs to the corresponding parent PAHs, including 9-fluorenone/fluorene, anthraquinone/anthracene, benz[a]anthracene-7,12-dione/benzo[a]anthracene were 6.2, 12.7, and 1.4, respectively, which were much higher than those for the fresh emissions from coal combustion and biomass burning. These prove the importance of secondary formation and transformation of OPAHs in the ambient airs. Biomarkers such as retene, cyclopenta[CD]pyrene and α -homohopane were characterized for the source apportionment. With Positive Matrix Factorization (PMF) model analysis, biomass burning was recognized as the most dominant pollution sources for PAHs during the heating period, which accounted for a contribution of 37.1%. Vehicle emission (22.8%) and coal combustion (22.6%) were also contributors in Xi'an.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) disperse on particulate matters, especially fine particles (PM_{2.5}), which have been attracting widespread public concern on their adverse human health impacts (Yu et al., 2015; Wincent et al., 2015). PM_{2.5} bounded PAHs have been quantified in mega-cities in China (Feng et al., 2006; Wang et al., 2006, 2011; Kong et al., 2010; Xu et al., 2013). Recent study also highlights the bioaccumulation of PAHs in agricultural products (soybean) (Pongpiachan, 2015). The importance of PAH emission sources in tropical environment have been well demonstrated (Pongpiachan, 2013a, 2013b; Pongpiachan et al., 2013; Pongpiachan et al., 2015). Moreover high levels of PAHs in PM_{2.5} were often obtained while the places suffered from severe air pollution, particularly in wintertime regularly. Oxygenated-PAHs (OPAHs) are derivatives of PAHs with hydrogen on the aromatic ring substituted by carbonyl groups, which include polycyclic aromatic quinones and ketones, and are frequently found at similar levels as the parent PAHs in the environment (Walgraeve et al., 2010). Measurement of OPAHs is a hot topic in recent years (Wang et al., 2011; Bandowe et al., 2014; Li et al., 2015). Toxicological studies showed that OPAHs might be more potently mutagenic or carcinogenic than the parent PAHs (Franco et al., 2010; Wei et al., 2012; Souza et al., 2014). As a group of species in the formation of reactive oxygen species (ROS), OPAHs such as polycyclic aromatic quinones can directly cause oxidative damage in biological molecules such as DNA and proteins, while the PAHs require an initial enzymatic activation to induce toxicity (Chung et al., 2006; Walgraeve et al., 2010; Dasgupta et al., 2014; Souza et al., 2014; Lin et al., 2015).

OPAHs are mainly released and/or formed from the incomplete combustion of fossil fuels and biomass burning (Ding et al., 2012; Huang et al., 2014a; Wei et al., 2015a). The fuel types, properties, and combustion conditions can affect the direct OPAHs and PAHs emissions. The lower combustion efficiencies and higher combustion temperature can induce relatively higher OPAHs productions in the enclosed residential stoves (Shen et al., 2011; Wei et al., 2015a). They can be also formed in the atmosphere through direct photolysis of parent-PAHs or homogeneous and heterogeneous reactions between parent-PAHs and atmospheric oxidants (e.g., ozone (O₃), hydroxyl radical (·OH)) (Lundstedt et al., 2007; Huang et al., 2014b; Wei et al., 2015b). Extremely high concentrations of OPAHs can be seen in the kitchen of a rural household, showing the significances in primary emissions from biomass fuel combustion (Ding et al., 2012). However, atmospheric formations were found to be the dominant sources of OPAHs in some environments (Kojima et al., 2010; Lin et al., 2015). Currently little information is known about the contribution of the primary emission and secondary transformation for OPAHs (Lin et al., 2015). More relative researches need to be done for their identifications.

Xi'an is the capital city of Shaanxi Province and is a popular tourist destination in central China. However, it is also one of the most polluted mega-cities (Cao et al., 2005; Han et al., 2010b). The comprehensive and systematic studies of organic carbon (OC), element carbon (EC), elements, and inorganic and organic ions have been developed here. Limited researches regarding to the organic species have been conducted or most were restricted to a single sampling point in Xi'an (Wei et al., 2015a; Bandowe et al., 2014). In this study, PM_{2.5} samples were collected at 19 sampling sites simultaneously to pursue the actual pollutant statues in Xi'an. The aims of this work are to determine variations of the concentrations of PAHs and OPAHs in Xi'an during the heating period and to investigate the influences from meteorological conditions. The phenomenon of the formation and transformation of OPAHs were also discussed. In addition, the source contributions to the area were identified using the biomarkers and statistical modeling.

2. Materials and methods

2.1. Sampling

Xi'an (33.29°N–34.44°N and 107.4°E–109.49°E) is the largest city in northwestern China. It is located on the Guanzhong Plain at the south edge of the Loess Plateau. The city had the worst air quality in record in China (Okuda et al., 2010), especially during the heating periods in the wintertime. Biomass burning and the meteorology (e.g., low wind speeds) exacerbate poor air quality (Gao et al., 2015).

PM_{2.5} samples were simultaneously collected at 19 different sites in Xi'an (Fig. 1). The details of the sampling environment were listed in Table S1. These sites could be classified into five categories including (1) urban residential, (2) university, (3) commercial area, (4) suburban region, and (5) industrial. The sampling period was from 2nd December to 15th December 2013. Daily sample (from 08:30 to 08:30 next day) were collected onto 47 mm quartz filters (QM/A[®], Whatman Inc., U.K.) with a PM_{2.5} Mini-Volume sampler (Airmetrics, Springfield, OR, USA) at a flow rate of 5 L/min. The samplers were calibrated using a Defender 510 Volumetric Primary Flow Standard (Bios international Corporation, Butler, NJ, USA) and the variance in flow was approximately ± 2%. A blank sample was taken at each site as well. A total of 285 samples (266 aerosol-loaded samples and 19 field blanks) were collected in this study. All of the samples were properly stored in a freezer at –20 °C before analysis.

2.2. Meteorological condition

Concentrations of gas pollutants (O₃ and sulfur dioxide (SO₂)) were measured by ambient gas Ogawa passive sampler (PS-100, Florida, USA) in each sampling site. The meteorological parameters including temperature and relative humidity were received from the National Oceanic and Atmospheric Administration (NOAA) while the wind data was obtained from the National Meteorological Information Center (<http://data.cma.gov.cn>). The data of boundary layer height was achieved from the European Center for Medium-Range Weather Forecasts (<http://apps.ecmwf.int/datasets/>).

2.3. Chemical analyses

Organic species (including twenty-five parent- and alkyl-PAHs, three OPAHs, eight hopanes and nine cholestanes) in the filter samples were quantified using in-injection port thermal desorption (TD) coupled with gas chromatography/mass spectrometry (GC/MS) (Ho and Yu, 2004; Ho et al., 2008, 2011; Wang et al., 2015a; 2016). Without sample pretreatment, it minimizes potential contaminations and offers lower detection limits, that has been used as an alternative method of traditional solvent extraction followed by GC/MS detection (Bi et al., 2008; Wang et al., 2015b).

The details of in-injection port TD-GC/MS method have been described in our previous publications (Ho and Yu, 2004; Ho et al., 2008, 2011). In this study, 0.526 or 1.052 cm² of filter punches was used for each sample analysis, subjected to its aerosol loadings. The filters were cut into small pieces and inserted into the TD tube, which has the identical dimension as the default GC injector liner. An Agilent 7890A GC/5975C MS system (Santa Clara, CA, USA) was applied which was operated in electron impact ionization (EI) mode. The temperature of the injector port was lowered to 50 °C before loading of the sample tube, and then raised to 275 °C for desorption in a splitless mode while the GC oven temperature was kept at 30 °C. After the injector temperature reached 275 °C, the GC temperature program began. The analytes separation was performed on an Agilent HP-5MS (30 m × 0.250 mm i.d., 0.25 μm film

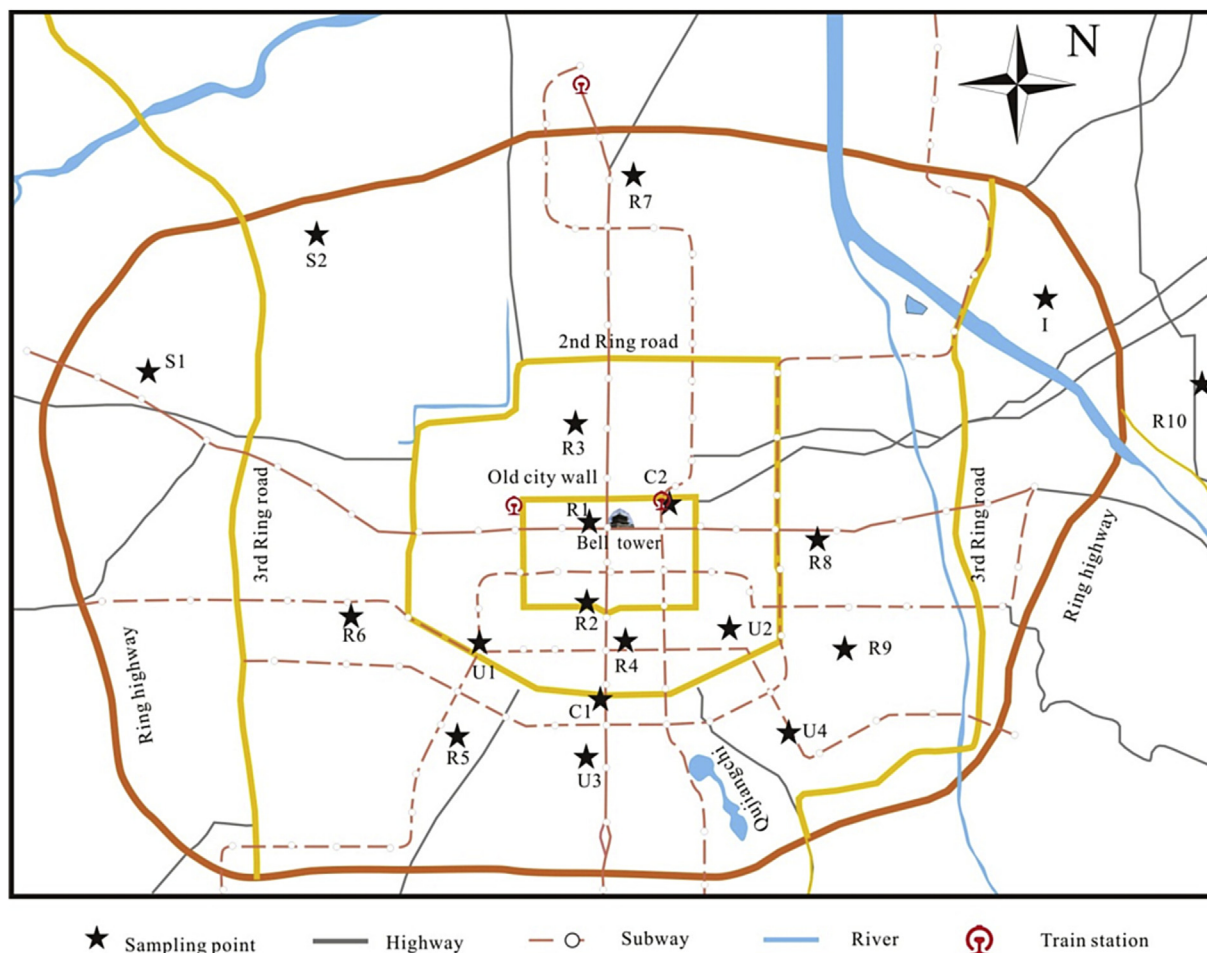


Fig. 1. The map of sampling sites in Xi'an (R means residential; U means university; C means commercial area; S means suburban region; I means industry).

thickness) column. The constant flow rate of carrier gas helium (99.999% purity) was 1.2 mL/min. The mass selective detector was scanned from 50 to 550 amu. The EI voltage was 70 eV and selected ion mode was used for quantification. Identification was achieved by characteristic ion and comparing the retention times of the chromatographic peaks with those of standards.

2.4. Quality assurance and control (QA/QC)

Previous studies which used the same procedures as in this study have detailed the QA/QC procedures (Ho et al., 2011; Cao et al., 2013; Xu et al., 2013; Wang et al., 2015a), that concluded the sampling and analysis. In brief, the aerosol sampler was checked and calibrated regularly during the sampling periods, and the field blank filters were collected to correct for backgrounds.

During the analysis, the QA/QC procedures contain experiment blank filter analysis, internal standard (IS), and replicate analysis. Experiment blank was done everyday to evaluate experimental backgrounds. The National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) SRM 1649a urban dust was employed to validate the accuracy of PAH analyses. Internal standard (IS) was added in each samples which contains chrysene-d₁₂ (C₁₈D₁₂) (98%, Sigma-Aldrich, Bellefonte, PA, USA), *n*-tetracosane-d₅₀ (n-C₂₄D₅₀) (98%, Aldrich, Milwaukee, WI, USA), phenanthrene-d₁₀ (C₁₄D₁₀) (98%, Aldrich, Milwaukee, WI, USA) and d₂ C₂₇ ααα (20R)-Cholestane (98%, Chiron AS, Trondheim, Norway). A five-point calibration over a concentration range of 1–10 ng for each

PAH and OPAHs (Sigma-Aldrich, Bellefonte, PA, USA), and of 0.5–5 ng for hopanes and cholestanes from a standard mixture was established. The correlation coefficients (R^2) 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 from 1.7 to 14.8% for PAHs, from 3.9 to 10.6% for OPAHs, from 0 to 8% for hopanes, and from 8.4 to 12.7% for cholestanes. All data were corrected for the average value of the blanks.

3. Results and discussion

3.1. Target organic levels

Table 1 summarizes the concentrations of target organic compounds in PM_{2.5} and atmospheric gases including SO₂ and O₃ during the sampling periods. The sum of quantified PAHs ranged from 23.5 to 574.3 ng/m³ with an average of 196.5 ng/m³. The concentrations were comparable with the data recorded in Xi'an, Beijing, Shanghai, Guangzhou and Qingdao (Feng et al., 2006; Wang et al., 2008; Guo et al., 2009; Wei et al., 2015a), but much higher than other areas being governed by better emission control (e.g., Hong Kong) or less influenced by local or regional pollution such as Sanya and Tibetan Plateau (Chen et al., 2014; Wang et al., 2015a). The average level was also higher than that in most developing countries (Tham et al., 2008; Andreou and Rapsomanikis, 2009; Li et al., 2009; Wingfors et al., 2011).

Except the alkyl-PAHs, the total concentration of 21 aliphatic

Table 1
Summary the concentrations of target compounds in PM_{2.5} of Xi'an.

Pollutants (abbreviation)	Winter (n = 263)				
	Min ^b	Max ^b	Med ^b	Mean	SD ^b
sulfur dioxide (SO ₂)	19.8	57.1	40.4	40.0	8.5
O ₃	6.5	16.6	12.0	11.8	2.2
acenaphthylene(ACY)	0.06	26.5	2.9	5.1	5.5
acenaphthene (ACE)	0.03	14.2	1.6	1.9	1.5
Fluorene (FLO)	LOD ^b	19.3	1.0	1.7	1.8
phenanthrene (PHE)	0.07	71.3	3.4	3.9	4.6
anthracene (ANT)	0.06	2.7	1.1	1.1	0.40
fluoranthene (FLU)	0.66	29.7	8.6	9.2	4.7
pyrene (PYR)	0.66	38.2	9.1	9.9	5.3
benzo[a]anthracene (BaA)	0.23	39.6	8.5	9.6	5.3
chrysene (CHR)	0.88	59.0	17.3	18.8	9.7
benzo[b]fluoranthene (BbF)	1.1	50.1	13.6	14.9	7.5
benzo[k]fluoranthene (BkF)	0.81	21.6	8.6	9.2	4.0
benzo[a]fluoranthene (BaF)	1.72	65.3	11.9	13.0	7.1
benzo[e]pyrene (BeP)	1.8	46.1	16.6	17.6	8.0
benzo[a]pyrene (BaP)	1.2	25.5	9.3	10.0	4.6
perylene (PER)	1.8	13.3	5.3	5.4	1.8
indeno[1,2,3-cd]pyrene (IcdP)	1.3	32.8	9.4	10.0	4.5
cyclopenta[cd]pyrene (PcdP)	0.20	7.9	1.7	1.8	1.0
benzo[g,h,i] perylene (BgHiP)	1.2	30.7	10.1	10.6	4.6
dibenzo[a,h]anthracene (DahA)	1.5	10.6	5.0	5.2	1.7
coronene (COR)	1.5	17.8	7.3	7.4	2.5
dibenzo[a,e]pyrene (DaeP)	2.6	67.4	12.3	13.2	6.7
2,6-dimethylnaphthalene (2,6-di-ME-NAP)	0.03	5.5	2.5	2.3	1.3
9-methylanthracene (9-Me-ANT)	1.5	24.6	4.5	4.5	3.5
retene (RETENE)	0.42	24.1	7.3	7.8	4.0
2-methylfluoranthene (2-ME-FLU)	0.30	8.6	2.2	2.4	1.1
Σ4alkyl-PAHs ^a	2.3	52.4	16.3	17.0	7.8
ΣLMW-PAHs ^a	1.3	73.5	11.4	13.7	8.6
ΣHMW-PAHs ^a	20.0	531.8	155.7	165.7	75.0
ΣComb-PAHs ^a	15.4	466.7	135.7	145.3	67.4
Σ21PAHs ^a	21.2	543.6	169.8	179.4	78.3
Σ25PAHs ^a	23.5	574.3	186.6	196.5	84.8
9-fluorenone (9FLO)	1.1	15.6	4.7	5.2	2.2
Anthraquinone (ANTQ)	0.24	26.2	13.7	13.7	5.4
Benz[a]anthracene-7,12-dione (BaAQ)	0.37	42.1	8.4	10.5	7.7
Σ30PAHs ^a	3.2	73.2	28.1	29.4	12.1
17α(H)-22,29,30-trisnorhopane(Tm)	0.24	5.6	1.8	2.0	0.9
17α(H)-21β(H)-30-norhopane(αβ-NH)	0.18	10.3	3.6	3.7	1.7
17β(H)-21α(H)-30-norhopane(βα-NH)	0.28	5.5	2.4	2.5	0.95
ΣNorhopanes ^a	0.70	19.8	8.1	8.2	3.3
17α(H)-21β(H)-hopane(αβ-HH)	0.43	11.2	4.3	4.4	1.8
17α(H)-21α(H)-hopane(αα-HH)	0.12	1.3	0.60	0.61	0.20
17β(H)-21α(H)-hopane(βα-HH)	0.33	3.7	1.8	1.9	0.60
ΣHopanes ^a	0.91	15.2	6.9	6.8	2.5
17α(H)-21β(H)-(22S)-Homohopane(αβ-S-HH)	0.09	3.7	1.4	1.5	0.63
17α(H)-21β(H)-(22R)-Homohopane(αβ-R-HH)	0.12	5.2	2.1	2.1	0.92
ΣHomohopanes ^a	0.28	9.0	3.5	3.6	1.5
Σ8Hopanes ^a	1.9	44.0	18.3	18.6	7.2
ααα(20S)-Cholestane(ααα-S-C)	0.01	28.1	2.0	4.0	5.4
ααα(20R)-Cholestane(ααα-R-C)	0.06	13.5	1.2	1.9	1.9
ααα(20R,24R)-24-Methylcholestane(ααα-RR-MC)	LOD	4.4	1.0	1.3	0.94
ααα(20S,24RS)-24-Ethylcholestane(ααα-SR-EC)	LOD	4.2	1.4	1.6	0.8
ααα(20R,24R)-24-Ethylcholestane(ααα-RR-EC)	0.31	3.0	1.4	1.4	0.5
αββ(20R)-Cholestane(αββ-R-C)	0.25	12.6	2.5	3.1	2.4
αββ(20R,24S)-24-Methylcholestane(αββ-RS-MC)	0.03	6.0	2.0	2.3	1.3
αββ(20R,24R)-24-Ethylcholestane(αββ-RR-EC)	0.12	18.7	4.3	5.9	4.4
αββ(20R,24RS)-24-Ethylcholestane(αββ-RS-EC)	0.03	3.5	1.2	1.3	0.83
ΣCholestanes ^a	2.5	61.8	18.5	22.7	13.3

^a Σ4alkyl-PAHs is sum of 2,6-dimethylnaphthalene, 9-methylanthracene, 2-methylfluoranthene and retene. ΣLMW-PAHs is sum of acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene. ΣHMW-PAHs is sum of fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[g,h,i] perylene, dibenzo[a,h]anthracene, coronene, dibenzo[a,e]pyrene, and cyclopenta[cd]pyrene. ΣComb-PAHs is the ΣHMW-PAHs minus pyrene, dibenzo[a,e]pyrene, and cyclopenta[cd]pyrene. Σ21PAHs is sum of the ΣLMW-PAHs and ΣHMW-PAHs mentioned above. Σ25PAHs is sum of the Σ21PAHs and Σ4alkyl-PAHs. Σ30PAHs is sum of the three detected OPAH: 9-fluorenone, anthraquinone, benz[a]anthracene-7,12-dione. ΣNorhopanes is sum of 17α(H)-22,29,30-trisnorhopane, 17α(H)-21β(H)-30-norhopane, and 17β(H)-21α(H)-30-norhopane. ΣHopanes is sum of 17α(H)-21β(H)-hopane, 17α(H)-21α(H)-hopane, and 17β(H)-21α(H)-hopane. ΣHomohopanes is sum of 17α(H)-21β(H)-(22S)-Homohopane and 17α(H)-21β(H)-(22R)-Homohopane. Σ8Hopanes is sum of ΣNorhopanes, ΣHopanes and ΣHomohopanes. Σcholestanes is sum of ααα(20S)-Cholestane, ααα(20R)-Cholestane, ααα(20R,24R)-24-Methylcholestane, ααα(20S,24RS)-24-Ethylcholestane, ααα(20R,24R)-24-Ethylcholestane, αββ(20R)-Cholestane, αββ(20R,24S)-24-Methylcholestane, αββ(20R,24R)-24-Ethylcholestane, and αββ(20R,24RS)-24-Ethylcholestane.

^b min, max, med, SD mean of minimum, maximum, median, standard deviation of the data. LOD is lower than the limited line.

Table 2
PAHs and OPAHs in particulate matters in different regions of the worldwide (ng/m³).

Region	Sampling year	Size	PAHs		OPAH		Reference
			Species	Concentration	Species	Concentration	
Beijing, China ^[u]	2012/2013	PM _{2.5}	23	3.5–904(143) ^a	5	0.47–610 (55.2)	Lin et al., 2015
Zhuanghu, China ^[r]	2010	PM _{2.5}	22	7500 ± 4100	4	8400 ± 9200	Ding et al., 2012
Xi'an, China ^[u]	2008/2009	PM _{2.5}	28	7–387	15	5–208	Bandowe et al., 2014
Qingyuan, China ^[l]	2009/2010	PM _{2.5}	17	7.38–113	6	0.519–1.246	Wei et al., 2012
Wuwei, China ^[u]	2010/2011	PM ₁₀	ND ^b	ND	4	0.8–50.0	Li et al., 2015
Yinchuan, China ^[u]	2010/2011	PM ₁₀	ND	ND	4	0.01–15.9	Li et al., 2015
Taiyuan, China ^[u]	2010/2011	PM ₁₀	ND	ND	4	0.3–50.0	Li et al., 2015
Beijing, China ^[u]	2010/2011	PM ₁₀	ND	ND	4	0.7–23.3	Li et al., 2015
Dezhou, China ^[u]	2010/2011	PM ₁₀	ND	ND	4	0.02–10.8	Li et al., 2015
Yantai, China ^[u]	2010/2011	PM ₁₀	ND	ND	4	0.08–3.9	Li et al., 2015
Dalian, China ^[u]	2010/2011	PM ₁₀	ND	ND	4	0.2–79.0	Li et al., 2015
Wuwei, China ^[v]	2010/2011	PM ₁₀	ND	ND	4	0.5–21.0	Li et al., 2015
Yinchuan, China ^[v]	2010/2011	PM ₁₀	ND	ND	4	0.7–77.0	Li et al., 2015
Taiyuan, China ^[v]	2010/2011	PM ₁₀	ND	ND	4	0.5–24.1	Li et al., 2015
Dezhou, China ^[v]	2010/2011	PM ₁₀	ND	ND	4	0.2–34.4	Li et al., 2015
Yantai, China ^[v]	2010/2011	PM ₁₀	ND	ND	4	0.2–55.6	Li et al., 2015
São Paulo, Brazil ^[r]	2010	PM _{2.5}	12	0.61–53	3	LOD-6	Souza et al., 2014
Chiang Mai, Thailand ^[u]	2011	PM ₁₀	15	3.4 ^c	10	1.1 ^c	Walgraeve et al., 2015
Kabul, Afghanistan ^[u]	2009	PM _{2.5}	15	21–466	12	5.1–210	Wingfors et al., 2011
Umea, Sweden ^[T]	2009	PM _{2.5}	15	0.94–7.9(2.5) ^a	12	0.09–1.8(0.48)	Wingfors et al., 2011
Paris, France ^[u]	2009/2010	PM ₁₀	17	0.53–7.05	9	0.1–1.4	Ringuet et al., 2012
Athens, Greece ^[u]	2003/2004	PM _{2.5}	18	1.2 ± 1.5–32 ± 29	14	3.5 ± 2.6–7 ± 11	Andreou and rapsomanikis,2009
Xi'an, China ^[c]	2013	PM _{2.5}	25	23.5–574.3	3	3.2–73.2	This study

^[u]Means urban areas.

^[r]Means rural areas in kitchen.

^[v]Means rural village.

^[T]Means traffic reference location.

^[c]Means complex regions.

^a The figure between brackets was the mean values.

^b ND means no data was available.

^c Means median of the data. ^a the data was selected in kitchen in wintertime.

PAHs ranged from 21.2 to 543.6 ng/m³ with a median of 169.8 ng/m³. The average sum of low molecular weight PAHs (Σ PAH_{LMW}, with 2–3 aromatic rings) was 13.7 ng/m³, much lower than that of high molecular weight PAHs (Σ PAH_{HMW}, with aromatic rings \geq 4 rings) of 165.7 ng/m³. The ratio of Σ PAH_{HMW}/ Σ PAH_{LMW} was 15.4 ± 9.0. This is comparable with the values obtained from previous studies conducted in Guangzhou and Xi'an (Wei et al., 2015a; Li et al., 2005). However, the ratio of Σ PAH_{HMW}/ Σ PAH_{LMW} in gas phase in Xi'an was much smaller, which was 0.08 and 0.114 in spring and fall seasons, respectively, resulting in the ratio of Σ PAH_{HMW}/ Σ PAH_{LMW} in total gas and particle phases was of 0.26 and 0.25, respectively. This was mainly due to the higher vapor pressure for lower molecular weight PAHs, which tend to occur in gaseous phase, whereas the high molecular weight components mostly bound with particulate (Wei et al., 2015a). Epidemiological study evidenced that >4-rings PAHs can penetrate deeply into lungs when inhaled, resulting in greater bio-accessibility than LMW-PAHs (Yu et al., 2015). It was thus proposed that PAHs in the particulate phase can pose greater adverse health impacts on the human.

The total concentrations of quantified alkyl-PAHs (Σ alkyl-PAHs) ranged from 2.3 to 52.4 ng/m³. The alkyl-PAHs can originate from both natural processes and anthropogenic inputs associated with PAHs (Rabodonirina et al., 2015). The petrogenic emissions include more alkylated PAHs than their parent homologues (Li et al., 2010).

The total quantified of norhopanes, hopanes, and homohopanes (Σ Norhopanes, Σ Hopanes, and Σ Homohopanes) were 8.2 ± 3.3, 6.8 ± 2.5, and 3.6 ± 1.5 ng/m³, respectively. Cholestanes were also detected in this study with a sum (Σ Cholestanes) of 2.5–61.8 ng/m³. These are common molecular markers of motor vehicle exhaust and are found in crude oil, source rocks and refinery petroleum products (Choi et al., 2012).

Few biomarker-PAHs are useful tools to differentiate the source contributions (Table 1). Retene, a tracer for biomass burning, ranged from 0.42 to 24.1 ng/m³ in all of the samples. It had a good correlation with the total quantified combustion-related PAHs (Σ Comb-PAHs) ($R^2 = 0.73$, $P < 0.001$) (Wei et al., 2015b), representing the significance of biomass burning to the combustion activities to this area. Cyclopenta[CD]pyrene (PcdP), ranging from 0.20 to 7.9 ng/m³, is considered as a marker for gasoline-fuelled engine exhaust (Caricchia et al., 1999). It has been shown a good correlation with Σ Hopanes ($R^2 = 0.60$, $P < 0.001$), which are well-known biomarkers for fossil fuels (e.g., petroleum) (Bi et al., 2002; Huang et al., 2014c). This can be ascribed to the similar sources for both PcdP and hopanes.

Previous study reported that the sources of OPAHs were mainly derived from primary emission from biomass fuel combustions and secondary atmospheric formation (Huang et al., 2014a). The sum of OPAHs (Σ 3OPAHs, 9-fluorenone (9FLO), anthraquinone (ANTQ), and benz[a]anthracene-7,12-dione (BaAQ)) was 29.4 ng/m³ on average. ANTQ had the highest concentration, followed by BaAQ and 9FLO. Table 2 compares the particulate-OPAHs quantified in other studies. Both generally demonstrated the levels of the pollutants were higher in wintertime than summertime (Wei et al., 2012; Bandowe et al., 2014). Residential in rural can be greatly influenced by biomass burning related activities such as cooking and house warming, especially in cold climate seasons (Ding et al., 2012). The levels in this study were comparable with those measured in industrial regions in northern China and Kabul, Afghanistan (Wingfors et al., 2011; Li et al., 2015), but much higher than many cities in foreign countries, such as Chiang Mai, Sao Paulo, Umea, Paris, and Athens (Andreou and Rapsomanikis, 2009; Wingfors et al., 2011; Ringuet et al., 2012; Souza et al., 2014; Walgraeve et al., 2015).

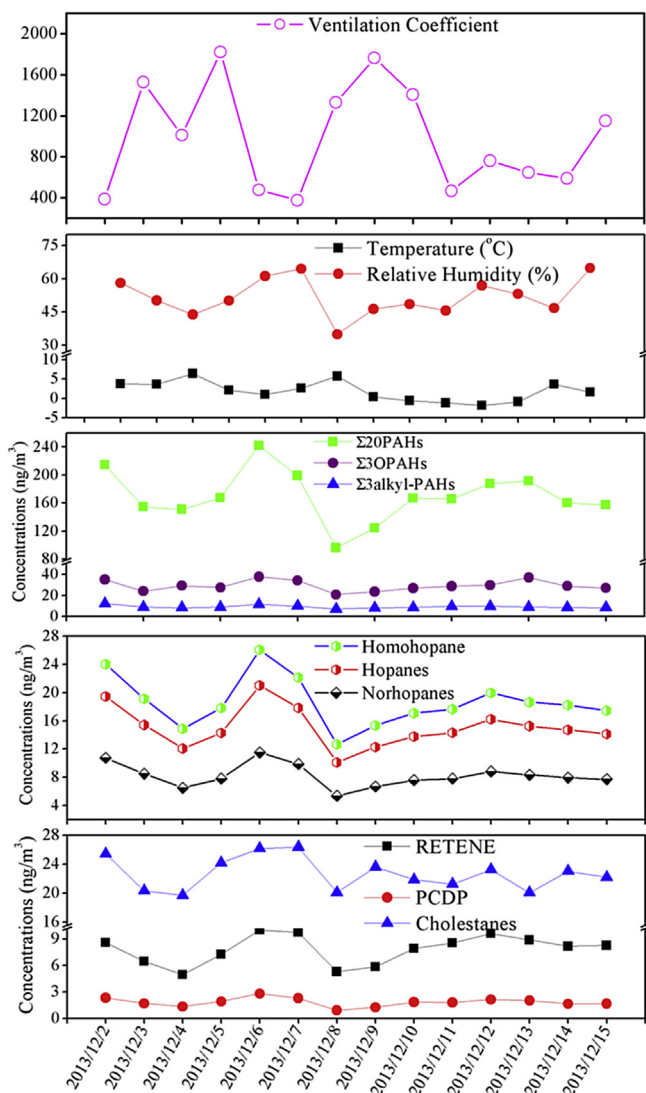


Fig. 2. Climate parameters and concentrations of organic compounds during sampling time.

3.2. Meteorological effects

The temporal trends of meteorological parameters and concentrations of targeted organic compounds were plotted in Fig. 2. The highest levels of PAHs, OPAHs, hopanes, and cholestanes were both seen on 6th December, 2013. This might be due to the accumulation of pollutants, which has relatively low wind speed (1.1 m/s) and high relative humidity (61.2%) in 6th December.

The impacts of meteorological conditions including temperature (T), relative humidity (H), boundary layer height (MLH) and horizontal wind speed (U) on the PAHs levels were assessed. Ventilation coefficient (VC) is used as a direct measure to characterize the degree of transport/dispersion of the pollutants taking place within convective boundary layer. The higher values of VC indicate effective dispersion (Kompalli et al., 2014). VC is calculated by:

$$VC = MLH \times U$$

Basing on the plots of meteorological parameters and concentrations of PAHs (Fig. S1), it can be concluded that H and VC were the two main factors influenced to the area. The correlation

coefficient (R^2) of the PAHs concentrations with H and VC were 0.57 and 0.43, respectively. The equation of linear regression for the two factors was $y = 2.5x_1 - 0.029x_2 + 69.6$ ($R^2 = 0.66$, $F = 13.5$, $P = 0.0011$) where x_1 and x_2 represents H and VC, respectively.

3.3. OPAHs

Most combustion studies demonstrated that 9FLO was often the most abundant OPAHs in the fresh emission airs while ANTQ and BaAQ are the second largest contributors. However, in the ambient atmospheres, their levels were more equivalent in general (Shen et al., 2011). In comparison with their parent PAHs (pPAHs), the OPAHs mostly occur in the particulate phase due to their lower vapor pressure (Albinet et al., 2008; Shen et al., 2011).

The concentrations of 9FLO, ANTQ, and BaAQ ranged from 1.1 to 15.6, 0.24 to 26.2, and 0.37–42.1 ng/m^3 , respectively, in this study. ANTQ was the most dominated OPAHs which accounted for 47% of the total quantified OPAHs, followed by BaAQ and 9FLO, which accounted for 33% and 20%, respectively. The relative high OPAHs can be partly derived by the primary incomplete combustions of solid fuels such as coal, firewood, and crop residues (Li et al., 2015; Shen et al., 2011). The good correlations between Σ OPAHs and the total concentration of corresponding pPAHs (Σ pPAHs, $R^2 = 0.64$, $P = 0$) (Fig. 3a) potentially suggests either from the primary fuel incomplete combustion or the significances of the secondary formation by radical reactions with pPAHs (Walgraeve et al., 2010; Shen et al., 2013a, 2013b; Li et al., 2015). However, different coefficients were observed for the individual pairs of OPAH vs pPAH (i.e., 9FLO vs FLO, ANT vs ANTQ, and BaAQ vs BaA), representing a diversity of rates in secondary formation or degradation and gas-particle conversion for each PAH or OPAH.

Currently it is still a challenge to apportion the contributions from secondary formation and primary emissions for OPAHs. The emission factor experiments supplied some perspective and systematic determinations of the ratios of OPAHs and their corresponding pPAHs. Previous studies demonstrated that the oxygenation rate (R_o) for 9FLO/FLO, ANTQ/ANT, and BaAQ/BaA, were 0.40 ± 0.18 , 0.89 ± 0.41 , and 0.16 ± 0.05 , respectively, from crop residue burning; 0.25 ± 0.25 , 0.14 ± 0.08 , and 0.03 ± 0.02 , respectively, from coal combustion; and 2.06 ± 0.84 , 0.79 ± 0.23 , and $6.6 \pm 0.0075 \times 10^{-2}$, respectively, from residential fuel wood and brushwood combustions (Shen et al., 2011, 2012). The average ratios of 9FLO/FLO, ANTQ/ANT, and BaAQ/BaA were 6.2, 12.7, and 1.4, respectively, in this study (as shown in Fig. 3b), and a comparison to other regions was displayed in Table S2. The ratios in this study were consistent with the data obtained in most field measurements (Wang, 2010; Shen et al., 2011), but much higher than those found in UK and Afghanistan. The much greater R_o than those from the freshly emitted combustion sources illustrated that atmospheric formation of OPAHs can play an important role in the ambient air, though it is difficult to quantify their contributions from primary and secondary sources accurately with the limited data and resources. In our study, no statistical correlation was seen between the concentrations levels of pPAHs, OPAHs and other gases such as SO_2 and O_3 in air. However, the air reductants and oxidants might participate in the transformations of OPAHs with complex atmospheric reactions. It is well known that BeP has a relatively long atmospheric life time (i.e., higher persistence for chemical and/or biological degradation). A low ratio of PAH to BeP could indicate the high susceptibility of corresponding PAH to any possible decompositions. Even though the chemical stability can be demonstrated by the certain concentration ratios of PAH to B[e]P (Nielsen et al., 1996; Dickhut et al., 2000; Fraser et al., 1999), it is still difficult to thoroughly interpret and correlate the aging process of pPAHs with the transformation of OPAHs. In order to have better

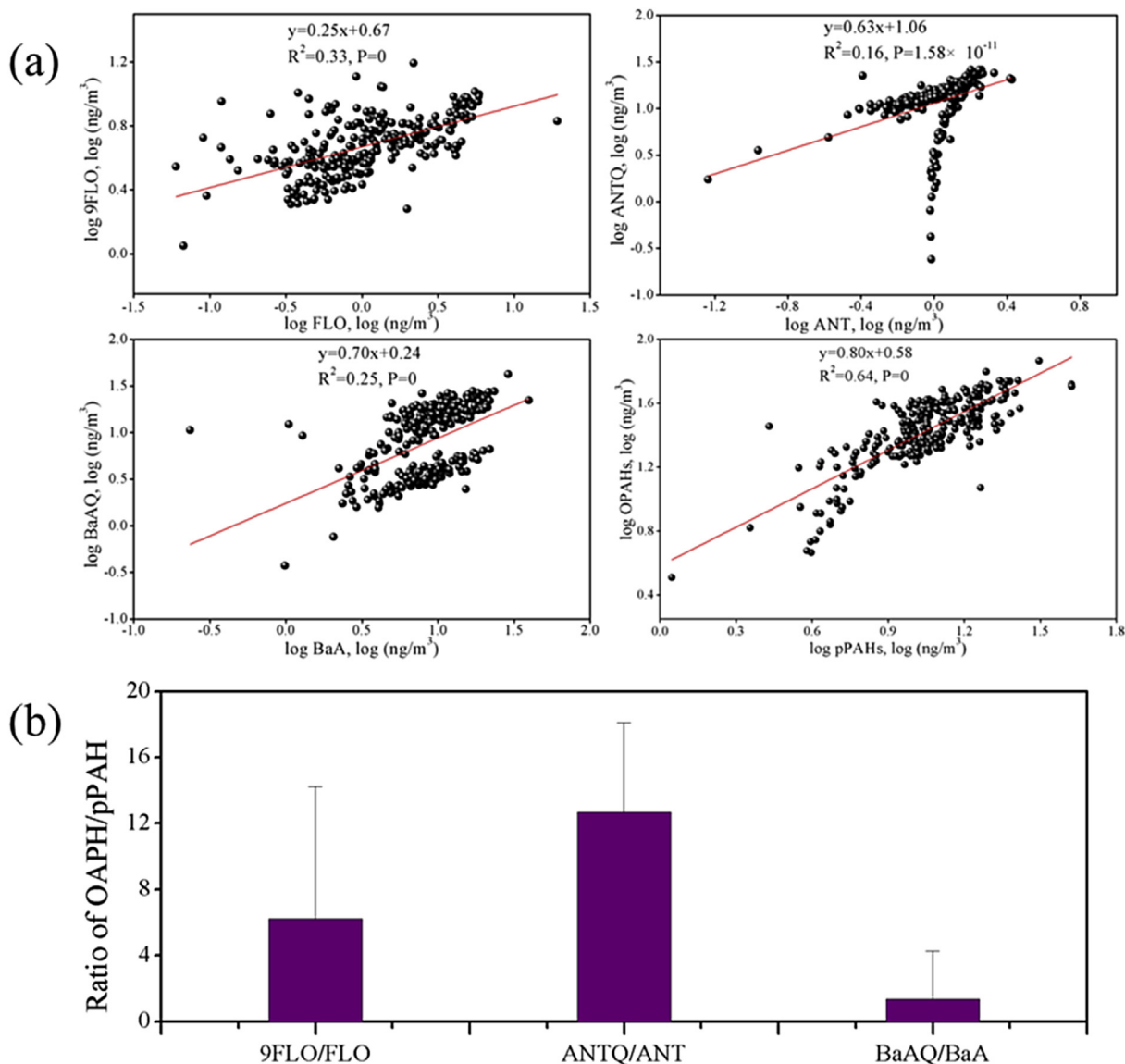


Fig. 3. (a) Relationship between OPAHs and its corresponding PAHs in $\text{PM}_{2.5}$ of Xi'an. The data are log-transformed. (b) The ratio of OPAHs to corresponding parent PAHs in all of the samples.

understanding of the secondary formation mechanism for OPAHs in the ambient environment, further field and chamber studies are thus required.

3.4. Functional zone distributions

Based on the characteristics of population, traffic density and industry distribution, the sampling sites were classified into five function zones, which are (i) urban residential ($n = 10$, R1-R10), (ii) university ($n = 4$, U1-U4), (iii) commercial area ($n = 2$, C1-C2), (iv) suburban region ($n = 2$, S1-2) and (v) industry ($n = 1$, I). As showed in Fig. 4, the total quantified PAHs concentrations were varied from 178.0 to 292.7 ng/m^3 . Suburban had the highest PAHs concentration on average, followed by commercial district and industry, while the lowest concentrations were seen in urban residential. The total concentrations of quantified OPAHs ranged from 25.0 to 42.6 ng/m^3 on average, has a descending order of industry > suburban region > university > urban residential > commercial area. The average concentrations of BaP in

sub-urban region was 15.8 ng/m^3 , followed by industry (11.2 ng/m^3), commercial area (10.3 ng/m^3), university (9.2 ng/m^3), and residential (9.1 ng/m^3). The values in all of the zones were exceeded than the level recommended by World Health Organization (WHO) of an annual average of 1 ng/m^3 and new environmental standards of 1 ng/m^3 for annual average and 2.5 ng/m^3 for daily average in China effective on 1st January, 2016. This represents that more effective controls are required to improve the ambient air quality.

The coefficient of diversity (CD) in this study was used to compare the similarities between each site or each function zone. The CD was calculated by the formula of:

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

where j and k stand for the two different sampling sites, species or fractions, p is the number of target components, x_{ij} and x_{ik} represent the average mass concentrations of chemical component i for j

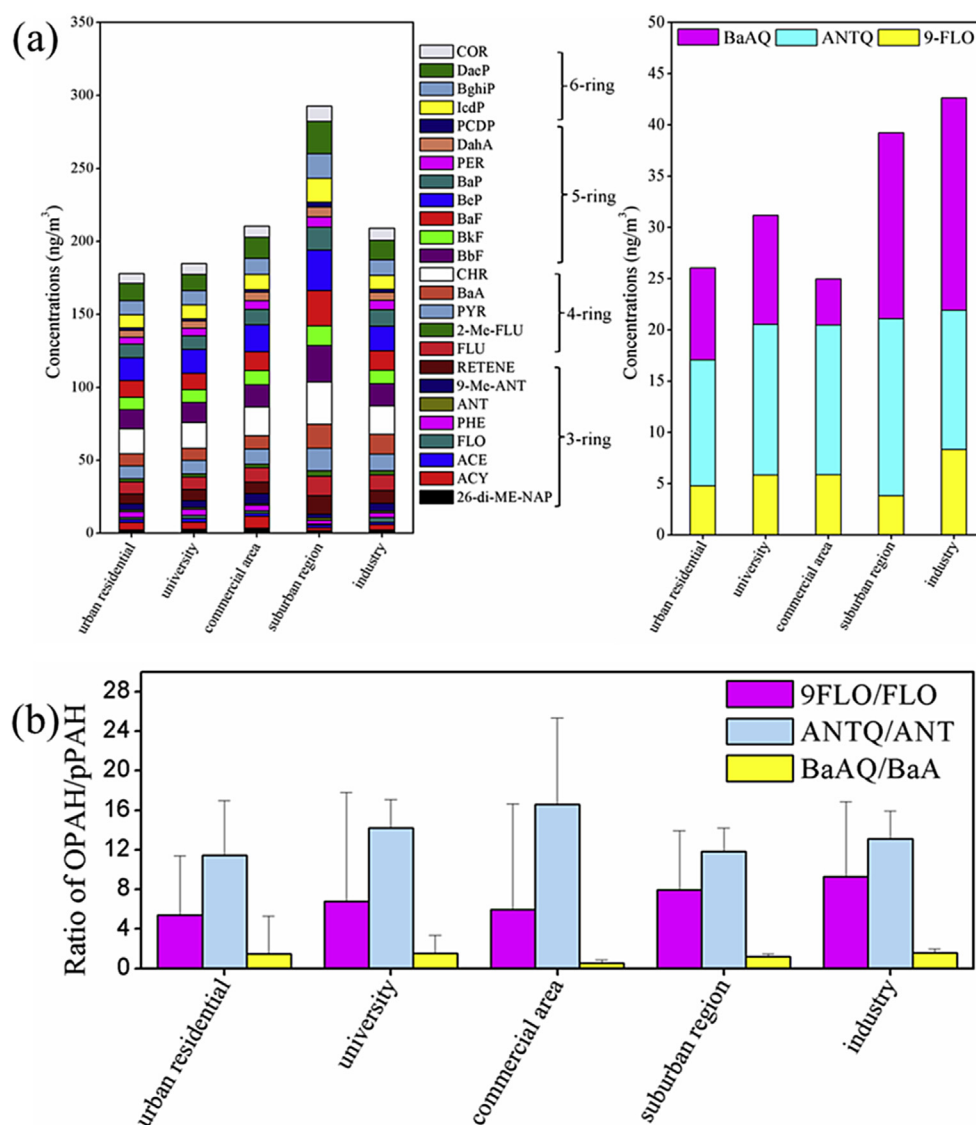


Fig. 4. (a) Concentrations of PAHs and OPAHs in different function zone in PM_{2.5} of Xi'an. (b) The ratio of OPAHs to corresponding parent PAHs in different function zones in PM_{2.5} of Xi'an.

and k (Wongphatarakul et al., 1998; Kong et al., 2010). When CD_{jk} approaches zero, it determines that sources j and k are similar; while approaches one, it means there are significantly different between the two sources (Pongpiachan and Iijima, 2016; Han et al., 2010a). The CDs between the function zones in this study were summarized in Table S3. The CD values ranged from 0.051 to 0.277 and 0.092 to 0.386 for PAHs and OPAHs, respectively. Wongphatarakul et al. (1998) pointed out that CD value of 0.269 reflected the similarity between particles collected in the two cities. Pongpiachan and Iijima (2016) considered that when the CD values were <0.3 , they were predominantly affected by comparable sources. The university and urban residential had the minimum CD values for PAHs and OPAHs, which illustrated that the sources contributions were similar to these two areas.

The CD values of suburban region vs urban residential (0.272) and suburban vs university (0.277) were slightly higher than the decision point of 0.269 but lower than 0.3. In addition with the statistical analysis results using SPSS, the PAHs in sub-urban showed significant differences ($P < 0.05$) from those in urban

residential and university. This represents distinguish pollution sources between urban (urban residential and university) and suburban environments. During the heating period, this can be also recognized due to different energy sources used for household warming. Central warming was supplied in most urban districts whereas more uncontrollable coal and natural biomass burning were widely found in suburban. The maximum CD value for PAHs was found between suburban region and university, whereas the commercial area vs industry had the maximum CD value for OPAHs. The industry generally had greater CD values with the other function zones, reflecting that the emissions of PAHs and OPAHs from factories had their characteristic distributions and patterns from other common pollution sources (e.g., automobile exhausts, coal combustion, and biomass burning) in either urban or sub-urban. It must be also noted that higher CD values and lower correlation coefficients were seen for OPAHs than their corresponding pPAHs among all of the function zones. The results further support that rather than primary emissions, there were a potential diversity of transformation pathway of OPAHs in the environments.

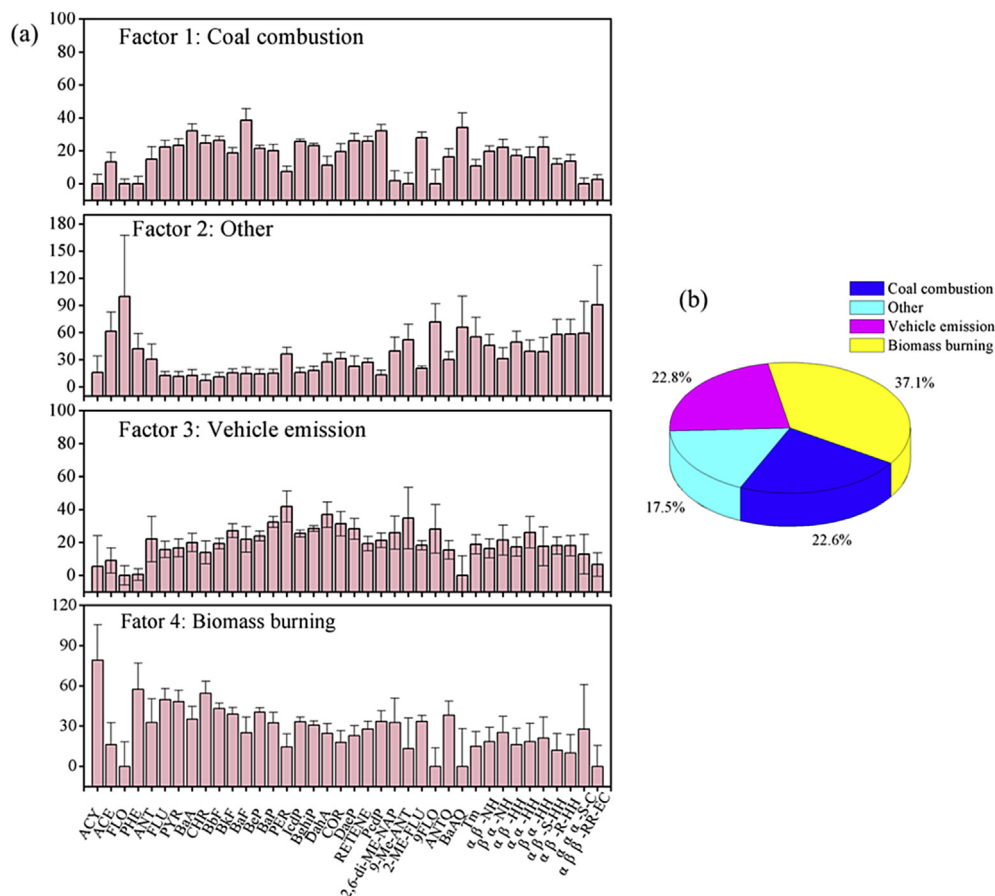


Fig. 5. PMF analysis results of (a), profiles of four PAHs factors. The error bars represent the standard deviation. (b), pie chart of contributions of four possible factions in PM_{2.5} of Xi'an.

3.5. Source apportionment

In order to conduct the source apportionment for the entire Xi'an city, the organic constituents from different sites were considered and averaged. In this study, Positive Matrix Factorization (PMF) (EPA PMF 3.0 version) modeling was applied to identify and assess probable sources and contributions with the particulate PAHs. PMF has been widely used in atmospheric source characterization and the details of the methodology were described elsewhere (Moon et al., 2008; Ma et al., 2010; Okuda et al., 2010; Lin et al., 2015). Twenty-five PAHs, three OPAHs, eight hopanes, and two cholestanes were input in the model with their concentrations and uncertainties. The profiles of each factor and their contributions are summarized in Fig. 5.

In factor 1 (22.6% of the contribution), it is similar to that of the industrial coal combustion in power plants and thus refers to coal burning emission which is heavily loaded with fluoranthene (FLU), pyrene (PYR), chrysene (CHR) and BaA (Chen et al., 2014). Benzo[*a*]fluoranthene (BaF) and benzo[*b*]fluoranthene (BbF) were also abundant in this factor. Factor 2 (17.5%) is highly loaded by 3-ring PAHs (i.e., acenaphthene (ACE) and FLO), OPAHs, and cholestanes. It represents pyrogenic emissions such as cooking activities and the transformations and secondary organic formations. Factor 3 accounted for 22.8% of the total organic constituents. It acts as a representative for the vehicle emission which mainly consists of high MW PAHs (5- to 6-ring PAHs, such as indeno[1,2,3-*cd*]pyrene (IcdP), coronene (COR), benzo[*g,h,i*]perylene (BghiP), dibenzo[*a,h*]anthracene (DahA) and dibenzo[*a,e*]pyrene (DaeP)) (Wang et al., 2009), additional with high portion of $\alpha\alpha$ -homohopane. The

$S/(S + R)$ of homohopane ranged from 0.25 to 0.58, with an average of 0.41, which was higher than that of the coal rank (0.05–0.35) (Oros and Simoneit, 2000), further supporting the contribution of vehicle emission. In factor 4, both 3- and 4-ring PAHs were the dominant that was similar to that of profile of biomass burning (Lin et al., 2015; Wang et al., 2015b). This is consistent with the fact that biomass burning was a significant pollution source in Xi'an during the heating period. As a result, the highest contribution of 37.1% of the total organic constituents was found in factor 4. The PMF results prove that the significance of biomass burning for the heating in wintertime, followed by the influences of vehicle emission and coal combustion.

4. Conclusions

Particulate PAHs and OPAHs were quantified at 19 locations in Xi'an during the heating period in 2013. Their concentrations were comparable with those measured in polluted areas in China. H and VC were the two main meteorological factors, which influenced the levels of pollutants to the sites. Compared with the primary emission spectrum, the ratios of 9FLO/FLO, ANTQ/ANT, and BaAQ/BaA proved significant transformations from pPAHs in the ambient airs. The CD values showed that there were statistical differences between suburban and urban areas. Biomass burning was the most dominant pollution source for PAHs in Xi'an during the heating period, followed by vehicle emission and coal combustion. Proper and efficient control measures should be considerably applied to limit heavy pollution.

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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.chemosphere.2016.06.033>.

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