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Aliphatic alkanes and polycyclic aromatic hydrocarbons in atmospheric PM_{10} aerosols from Baoji, China: Implications for coal burning

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ABSTRACT

Normal alkanes and PAHs in atmospheric PM_{10} aerosols collected during 2008 winter and spring in Baoji, a mid-scale inland city of China, were determined on a molecular level. Concentrations of *n*-alkanes ranged from 232 to 3583 ng/m^3 with an average of 1733 ng/m^3 in winter and from 124 to 1160 ng/m^3 with an average of 449 ng/m^3 in spring, while PAHs in the PM_{10} samples were 594 ± 405 and 128 ± 82 ng/m^3 in the two seasons. Molecular compositions showed that CPI (odd/even) values of *n*-alkanes were close to unity for all the samples especially in winter, and diagnostic ratios of PAHs (e.g., Phe/(Phe + Ant), CPAH/ΣPAHs and IcdP/(IcdP + BghiP)) were found similar to those in coal burning smoke with a strong linear relationship ($R^2 \geq 0.85$) between PAHs and fossil fuel derived *n*-alkanes, demonstrating that coal burning is the main source of *n*-alkanes and PAHs in the city, especially in winter due to house heating. Concentrations of the determined compounds in Baoji are much higher than those in Chinese mega-cities, suggesting that air pollution in small cities in the country is more serious and need more attention.

1. Introduction

Coal burning smoke consists of a substantial fraction of carbonaceous aerosols. These aerosols are harmful to human health, because they contain some organics such as polycyclic aromatic hydrocarbons (PAHs), which are of great mutagenicity and carcinogenicity (Dockery et al., 1993). Moreover, the carbonaceous particles influence climate directly through scattering and adsorbing solar radiation and indirectly by acting as cloud condensation nuclei (CCN) (Ghan et al., 1995; Andreae, 2001; Menon et al., 2002). China is the biggest user of coal, who combusted 38.6% of the whole world coal consumption in 2006 (Lin, 2008). Around 25% of global anthropogenic carbonaceous particles are generated from China due to coal burning and petroleum combustion (Cooke et al., 1999), which could be transported with Asian dusts to other areas (Perry et al., 1999; Huebert et al., 2003; Tamamura et al., 2007), and probably influence air quality and climate in a regional and even a global scale.

Baoji (33°35′–35°06′N, 106°18′–108°03′E) is an inland city situated in the mid-west part of China with a population of 0.75 million. Coal usage in the city was 2.2 million tons in 2007, accounting for approximately 96% of the energy consumption (Baoji Statistic Yearbook, 2008). Many studies had focused on organic aerosols from coastal mega cities in China (Bi et al., 2003; Guo et al., 2003a; Guo et al., 2003b; Wang et al., 2006a; Hong et al., 2007), where economy is much more developed than inland China with higher efficiency and lower emissions for coal burning. However, the number (275) of the cities with similar population and economically developing levels as Baoji is much bigger than those mega cities (36), accounting for over 40% of the total number of cities in China (655) (Wu, 2004). Natural gas and liquefied petroleum gas used for house heating are not so common in the economically developing cities as those in the economically developed mega-cities. Instead, coal combustion is the main method for house heating in the mid-scale

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cities, which releases a huge amount of pollutants, leading to very serious air pollution in winter. However there has been no much attention paid for the problem in these mid-scale cities. To better understand the real situation of air pollution in China and its impact on regional and global climate change, it is very necessary to know the air pollution status in these cities. In the current study, we collected PM$_{10}$ samples at four locations of Baoji and performed a detailed characterization for the organic constituents to discuss the current status of air pollution in the city.

2. Experimental section

2.1. Sampling site

Four sampling sites were selected for aerosol collection. Environmental Monitoring Station (MS, 34°21′18.4″N, 107°08′34.7″E) represents the residential region, which is located in a big residential area; Da Qing Road (DQ, 34°21′52.5″N, 107°11′47.6″E) is a traffic center in Baoji; Miao Gou Village (MG, 34°17′24.0″N,107°11′20.0″E) is located far from city center, which represents the rural environment; Jing Yi Road (JY, 34°22′22.5″N, 107°08′34.1″E) is representative of the downtown area (Fig. 1).

2.2. Aerosol collection

Aerosols were collected by KC-6120 PM$_{10}$ samplers (Laoshan Electronic Instrument Company, Qingdao, China) equipped with pre-baked (500 °C, 4 h) quartz fiber filters (Whatman, QMA Ø90 mm). All the air inlets were 1.5 m above the ground and the flow rate was set as 100 L/min. Aerosol collection was conducted for 5/6 days in winter and spring, each started from 8:00 a.m. to 4:00 p.m. After sampling, the filter was sealed in an aluminum foil and stored at −18 °C prior to analysis. Meteorological conditions during the sampling periods were summarized in Table 1.

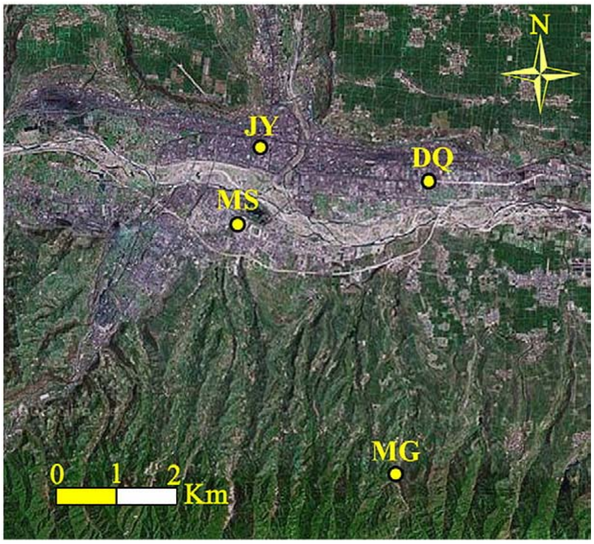

Fig. 1. Locations of four sampling sites: Environmental Monitoring Station (MS), Da Qing Road (DQ), Miao Gou Village (MG) and Jing Yi Road (JY) (http://earth.google.com/).

Table 1
Meteorological condition during sampling campaign.

Sampling date	Sample number[a]	RH[b], %	T, °C	p[c], hPa	Wind speed, m/s
Winter (February 15–19, 2008)	20	60–87	2–12	953–961	0.7–1.5
Spring (April 8–10, 5–17, 2008)	24	57–81	16–27	933–943	1.3–1.9

[a] Sample number: sum of the four sites.
[b] RH: relative humidity.
[c] p: atmospheric pressure.

2.3. Sample extraction and derivatization

Extraction and derivatization procedures were described elsewhere (Wang and Kawamura, 2005), here we only give a brief introduction. One fourth of each filter was cut into pieces, extracted ultrasonically with dichloromethane/methanol (2:1, v/v) three times each for 10 min, and filtered through quartz wool packed in a Pasteur pipette. Afterward, the extracts were concentrated using a rotary evaporator under a vacuum condition and blown down to dryness with a gentle stream of pure nitrogen, then reacted with 50 µL of N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) with 1% trimethyl chloride and 10 µL of pyridine to derivatize the compounds containing carboxyl and hydroxyl groups into the corresponding trimethylsilyl esters and ethers. Finally, 140 µL of hexane containing 1.43 ng/µL C$_{13}$ *n*-alkane as an internal standard was added to dilute the derivatives prior to determination. Here we only report *n*-alkanes and PAHs, and other components such as sugars and fatty acids will be reported later.

2.4. Gas chromatography–mass spectrometry quantification

All the derivatized extracts were quantified by Trace GC coupled with DSQ II mass spectrometer operated in electron impact mode (70 eV). The GC separation was carried out on a DB-5MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with the GC oven temperature programmed from 50 °C (2 min) to 120 °C at 15 °C min^{-1} and then to 300 °C at 5 °C min^{-1} with final isothermal hold at 300 °C for 16 min. The sample was injected on a splitless mode at an injector temperature of 280 °C. Identifications of individual compounds were conducted by comparing mass spectra with library data and authentic standards, and their GC-MS response factors were calculated based on the standards.

2.5. Quality assurance

Field blanks were collected at each site in both seasons, and treated by the same procedures for regular samples to determine any potential contamination. The results showed that the major contaminants were low molecular weight *n*-alkanes (C$_{15}$–C$_{21}$) and PAHs (MW = 178, 202), of which the abundances were less than 5% of those in the real samples.

Additionally, 100–200 ng of the standards was spiked onto a clean filter and analyzed to determine their recoveries. The triplicate experiments showed that the average recoveries of *n*-alkanes, PAHs were in the range of 70–110%, except for the lighter *n*-alkanes (C_{15}–C_{18}), whose recoveries were lower than 70%. All the data reported here were corrected for field blanks but not for the recoveries.

3. Results and discussion

3.1. n-alkanes

3.1.1. General results

Concentrations of *n*-alkanes (C_{18}–C_{33}) of PM_{10} in Baoji are listed in Table 2. The total concentrations varied from 232 to 3583 ng/m^3 with an average of 1733 ng/m^3 in the winter, and from 124 to 1160 ng/m^3 with an average of 449 ng/m^3 in the spring.

Lower molecular weight (LMW) *n*-alkanes (<C_{23}) are mainly derived from emissions of incomplete combustion of fossil fuels with a carbon preference index (CPI, a mass ratio of *n*-alkanes with odd carbon numbers to those with even carbon numbers) close to unity, whereas high molecular weight (HMW) *n*-alkanes (>C_{25}) are mostly derived from higher plant waxes with a CPI value far beyond 1.0 (Rogge et al., 1993a; Rogge et al., 1993b; Rogge et al., 1997; Schauer et al., 1999; Simoneit 2002; Cheng et al., 2006; Bi et al., 2008). In this study, concentrations of LMW *n*-alkanes (C_{18}–C_{25}, 1191 ± 788 ng/m^3) were much higher than those of HMW *n*-alkanes (C_{26}–C_{33}, 465 ± 259 ng/m^3) in winter, but an odd/even predominance could still be observed in the range of C_{26}–C_{33}, which might be resulted from the biomass burning in the city and/or other biogenic sources. CPI values in winter ranged from 1.1 to 1.5 with an average of 1.3, being similar to those in other Chinese cities such as Nanjing (1.2–1.4, average 1.3) (Wang and Kawamura, 2005) and Qingdao (1.2–1.8, average 1.4) (Guo et al., 2003b). In spring, abundances of the LMW *n*-alkanes (231 ± 126 ng/m^3) were equivalent to the HMW ones (218 ± 156 ng/m^3) with the highest concentration in the range of C_{22}–C_{25}. CPI values of the springtime *n*-alkanes were 1.6 ± 0.2 at the four sites, being

Table 2
Concentrations of *n*-alkanes and PAHs in PM_{10} during winter and spring in Baoji (ng/m^3).

Compound	Abbreviation	Winter ($n = 20$)				Spring ($n = 24$)			
		Max	Min	Mean	Std	Max	Min	Mean	Std
I. n-alkanes									
Octadecane	C_{18}	54.8	18.8	36.9	10.0	30.7	8.8	15.6	4.9
Nonadecane	C_{19}	62.8	9.3	33.9	15.7	18.4	4.5	9.7	3.2
Eicosane	C_{20}	188	11.3	85.7	55.0	22.6	5.2	12.5	5.4
Heneicosane	C_{21}	395	14.9	175	117	42.9	5.5	19.2	10.8
Docosane	C_{22}	505	24.4	241	153	53.2	7.6	25.1	15.8
Tricosane	C_{23}	568	27.8	266	171	95.4	10.6	46.7	28.7
Tetracosane	C_{24}	463	20.5	209	133	107	10.8	47.9	29.7
Pentacosane	C_{25}	429	24.1	200	127	126	13.3	54.5	31.7
Hexacosane	C_{26}	226	14.7	107	66.0	81.7	8.5	33.7	20.6
Heptacosane	C_{27}	206	15.2	102	56.4	139	14.3	51.4	33.6
Octacosane	C_{28}	90.7	9.7	44.2	24.9	60.4	<LOD	19.1	13.8
Nonacosane	C_{29}	192	22.9	103	42.1	148	10.7	47.9	32.2
Tricontane	C_{30}	65.6	3.0	23.0	15.0	41.7	<LOD	11.6	10.1
Hentriacontane	C_{31}	123	13.6	69.9	30.2	135	<LOD	33.5	28.6
Dotriacontane	C_{32}	35.5	<LOD	13.2	10.9	34.5	<LOD	7.4	9.4
Tritriacontane	C_{33}	50.7	<LOD	23.1	14.7	57.5	<LOD	13.6	15.8
Subtotal		3583	232	1733	999	1160	124	449	268
II. PAHs									
Phenanthrene	Phe	75.3	10.5	38.0	15.7	20.2	3.9	10.2	4.1
Anthracene	Ant	9.1	<LOD	3.0	2.2	1.1	<LOD	0.5	0.3
Fluoranthene	Flu	185	8.5	82.3	50.3	26.4	4.2	12.2	6.2
Pyrene	Pyr	119	6.6	56.8	34.9	19.0	4.2	10.7	4.5
Benzo[b]fluorine	BF	83.1	1.6	25.1	22.1	5.0	0.5	2.2	1.3
Benzo[a]anthracene	BA	123	1.8	39.5	33.5	11.0	0.5	5.1	3.7
Chrysene/triphenylene	CT	140	3.4	52.3	37.2	28.3	1.7	10.5	7.1
Benzo[b]fluoranthene	BbF	290	5.8	107	76.2	84.6	3.8	27.7	20.3
Benzo[k]fluoranthene	BkF	68.2	1.2	25.7	19.0	23.8	0.7	7.5	5.7
Benzo[e]pyrene	BeP	82.4	1.8	31.3	21.6	29.7	1.2	9.3	6.8
Benzo[a]pyrene	BaP	68.2	1.3	24.6	19.0	15.8	0.6	5.7	4.0
Perylene	Per	27.7	<LOD	8.2	7.0	5.2	<LOD	1.9	1.6
Indeno[1,2,3-cd]pyrene	IcdP	91.6	1.9	34.6	25.2	24.2	1.2	8.3	6.1
Dibenzo[a,h]anthracene	DBA	24.4	<LOD	6.8	6.4	6.1	<LOD	1.4	1.5
Benzo[ghi]perylene	BghiP	84.1	1.86	33.1	23.7	29.5	1.2	10.2	7.8
Anthanthrene	Anta	33.3	<LOD	7.9	9.4	4.4	<LOD	0.8	1.4
Coronene	Cor	53.0	<LOD	18.5	15.8	11.4	<LOD	4.1	3.6
Subtotal		1517	46	594	405	335	30	128	82
Total, ng/m^3		4908	278	2327	1383	1495	153	578	347
PM_{10}, μg/m^3		574	207	402	100	691	158	410	160
Total/PM_{10}, ‰		11.2	1.4	5.4	2.6	2.5	0.6	1.4	0.5

LOD: limit of detection.

Table 3
Concentration and diagnostic ratio of *n*-alkanes in the PM_{10} samples from Baoji.

Location	Urban site						Rural site	
	MS		DQ		JY		MG	
	Winter	Spring	Winter	Spring	Winter	Spring	Winter	Spring
$\sum$n-alkanes(ng/m^3)	1598 ± 864	314 ± 199	1914 ± 539	552 ± 209	2828 ± 240	684 ± 240	592 ± 337	246 ± 91
$C_n$max[a]	C_{23}	$C_{25,\ 27,\ 29}$	$C_{22,\ 23}$	$C_{23,\ 24,\ 25}$	C_{23}	$C_{25,\ 27,\ 29,\ 31}$	$C_{23,\ 29,\ 31}$	$C_{27,\ 29}$
CPI[b]	1.3 ± 0.1	1.7 ± 0.2	1.2 ± 0.1	1.4 ± 0.1	1.3 ± 0.1	1.6 ± 0.2	1.4 ± 0.1	1.7 ± 0.3
Plant wax C_n (%)[c]	15.8 ± 2.2	27.4 ± 5.4	10.6 ± 2.2	17.1 ± 2.4	14.9 ± 2.8	23.5 ± 4.4	22.1 ± 2.1	29.7 ± 6.8

[a] $C_n$max: maximal peak of *n*-alkanes.
[b] CPI: carbon preference index ($\sum C_{19}$–C_{33}/$\sum C_{18}$–C_{32}).
[c] Plant wax C_n: calculated as the excess odd homologues — adjacent homologues average.

similar to those in Hong Kong (1.3–1.9, average 1.6) (Zheng et al., 2000) and Beijing (average 1.6) (Huang et al., 2006) but higher than those in Guangzhou (1.0–1.2, average 1.1) (Bi et al., 2003).

The molecular distribution pattern in winter suggests that emission from fossil fuel combustion is the major source of *n*-alkanes in the Baoji atmosphere. Compared to those in spring the three times higher concentration of *n*-alkanes in the wintertime samples are most likely due to the sharp increase of coal burning for house heating, although the meteorological conditions in winter are favorable to accumulate the pollutants (Kadowaki, 1994).

3.1.2. Spatial and seasonal variations

At the downtown site JY, total concentrations of *n*-alkanes were significantly higher than those at other three sites with an average of 2828 ± 633 and 684 ± 240 ng/m^3 in winter and spring respectively, which is mainly caused by the emission from domestic coal burning of the restaurants without any emission control and the crowded buildings that prevent the dilution of the pollutants. CPI value at the site in winter is 1.3 ± 0.1 (Table 3) with the concentrations of *n*-alkanes peaking at C_{23} (Fig. 2 a). In contrast, the molecular distributions of *n*-alkanes in spring were characterized by significant odd/even predominance in the range of C_{26}–C_{33}, although a slightly higher CPI value (1.6 ± 0.2) was found for the total homologues, indicating somewhat increase in the contribution from biological sources.

MS site, which is located in a residential area, had 1598 ± 864 and 314 ± 199 ng/m^3 of total *n*-alkanes in winter and spring separately. As seen in Fig. 2 b and Table 3, molecular

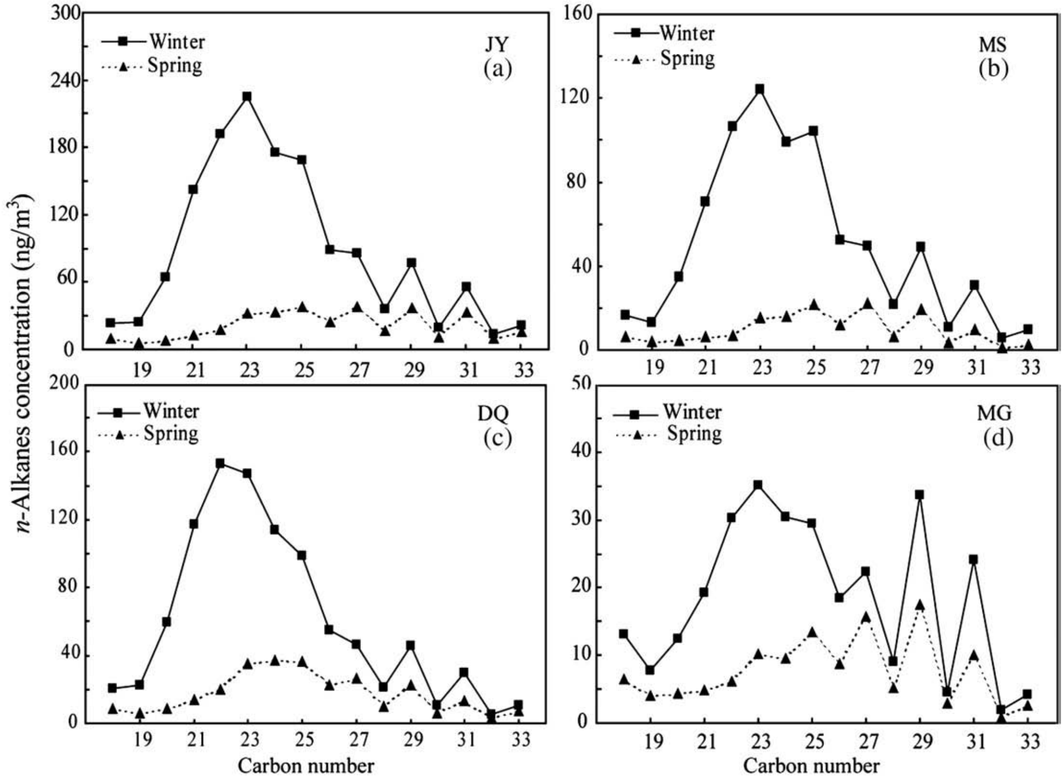

Fig. 2. Molecular distributions of *n*-alkanes in the PM_{10} aerosols collected in winter ($n = 5$) and spring ($n = 6$) at the 4 sampling sites: (a) Jing Yi Road (JY), (b) Environmental Monitoring Station (MS), (c) Da Qing Road (DQ), and (d) Miao Gou Village (MG).

distributions, CPI values and relative abundances of plant wax derived *n*-alkanes were similar to JY site in both seasons, suggesting the similarity in the sources of the ambient particle associated *n*-alkanes at the two sites.

The second highest level of *n*-alkanes was obtained at site DQ, a traffic center in the city, with 1914 ± 539 and 552 ± 209 ng/m^3 in winter and spring. During both seasons *n*-alkanes were dominated by LMW *n*-alkanes with a C_{max} at C_{22}–C_{25} (Fig. 2 c). CPI values were on average 1.2 ± 0.1 and 1.4 ± 0.1 in winter and spring with the lowest contribution from plant wax (10.6 ± 2.2% in winter and 17.1 ± 2.5 in spring, Table 3) probably due to more contributions from traffic exhausts at the site.

MG is a background site and located in rural area about 8 km far away from the urban center. Concentrations of *n*-alkanes at MG were 592 ± 337 and 246 ± 91 ng/m^3 in winter and spring with slightly higher levels of CPI values (1.4 ± 0.1 and 1.7 ± 0.3 in winter and spring, respectively, Table 3) and plant wax emissions (22.1 ± 2.1% in winter and 29.7 ± 6.8% in spring, Table 3). A bimodal distribution was found with two major peaks at C_{23} and C_{29} in winter and a unimodal distribution was observed in spring peaking at C_{29} (Fig. 2d), suggesting the enhancement of springtime biogenic emissions.

3.2. PAHs

3.2.1. General results

Seventeen PAHs were detected for all the samples with ΣPAHs concentrations of 594 ± 405 ng/m^3 in winter and 128 ± 82 ng/m^3 in spring (Table 2). The decreased concentration in spring is largely due to the shutting down of coal burning for house heating. Benzo(b)flouranthene (BbF) was found to be the most abundant PAH in all the samples, accounting for 22% and 18% of the total PAHs in winter and spring, respectively, followed by fluoranthene (Flu), pyrene (Pyr) and chrysene/triphenylene (CT). Such a molecular distribution is consistent with those reported by Wang et al. (2007) and Yang et al. (2005) for the samples from Nanjing in eastern China.

3, 4-Ring, 5-ring and 6,7-ring PAHs accounted for 50%, 33% and 17% of the total PAHs in winter and 40%, 41% and 19% of the total in spring with an increase in the relative abundance of wintertime 3,4-ring PAHs (Fig. 3). Most of LMW molecular PAHs (MW ≤ 228) are present in the gas phase due to their high volatility (Jenkins et al., 1996; Bi et al., 2003; Chen et al., 2005), and tend to partition more into aerosols under a lower ambient temperature. Moreover, emission factors of these LMW PAHs are much higher than HMW PAHs for coal burning (Oros and Simoneit, 2000; Chen et al., 2005; Bi et al., 2008). Therefore, more LMW PAHs in the winter samples are probably resulted from the enhancement of coal burning and the lower temperature.

Though large-scale residential heating was stopped in spring, the total concentration of PM_{10} associated PAHs was still far beyond the levels in many other mega-cities in China (Wang et al., 2006b), which should primarily be attributed to the large amount of coal burned in the season with less emission control. In winter, total consumption of coal for residential heating was 0.35 million ton (Baoji Statistic Yearbook, 2008), accounting for about 13% of the annual usage, adding an additional source for PAHs in the air, which is associated with the lower temperature and calm wind, resulting in PAHs four times more abundant in winter (594 ± 405 ng/m^3, Table 2) than in spring (128 ± 82 ng/m^3).

3.2.2. Spatial and seasonal variations

Total PAHs presented the highest concentrations at the site JY and the lowest at the site MG in both seasons (Fig. 4), being consistent with the spatial distribution of *n*-alkanes. Unlike its isomer benzo(e)pyrene (BeP), benzo(a)pyrene (BaP) is liable to photochemical decomposition, thus ratio of BeP/(BeP + BaP) is an indicator for photochemical degradation (Nielsen, 1988; Spitzer and Kuwatsuka, 1993). The ratios (0.57 ± 0.05, Table 4) of BeP/(BeP + BaP) in winter were found to be lower than that (0.62 ± 0.04) in spring, indicating

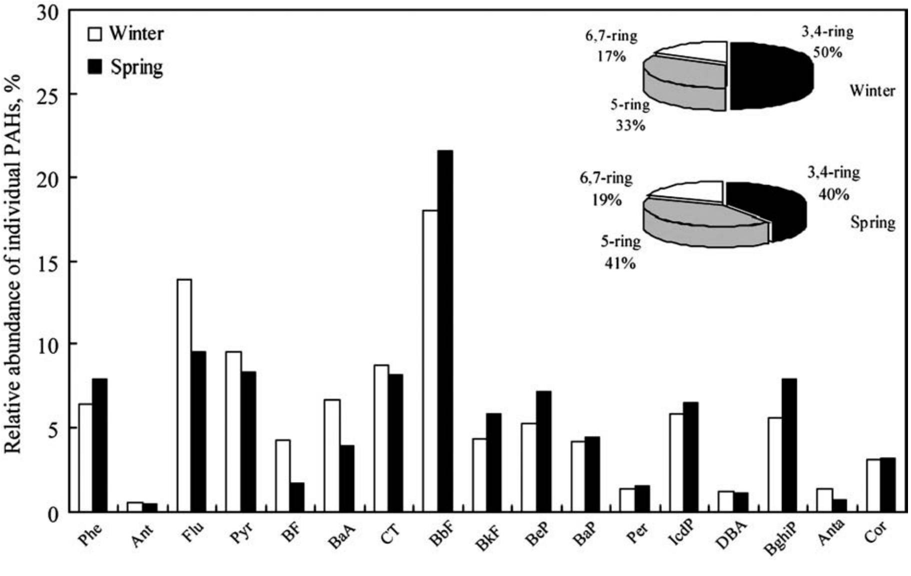

Fig. 3. Relative abundance of PAHs with different molecular weight in winter and spring. (For compound abbreviations, see Table 2).

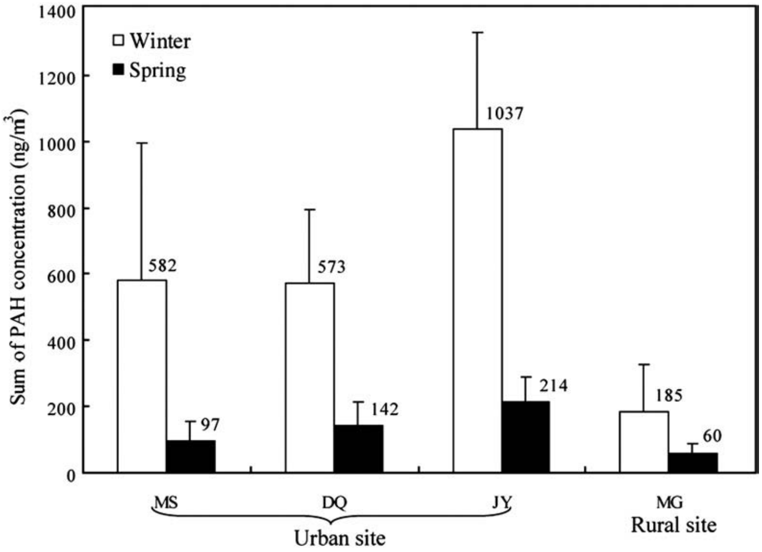

Fig. 4. Concentrations of total PAHs at the four locations.

a slight enhancement of photochemical oxidation in the warm season.

To further assess the origins of PAHs present in the samples, diagnostic ratios of PAHs that are relevant to the specific sources are calculated and showed in Table 4. Phe/(Phe + Ant) and Flu/(Flu + Pyr) were usually taken as indicators of petroleum or combustion (Sicre et al., 1987; Budzinski et al., 1997). In this study, Phe/(Phe + Ant) ranged from 0.91 ± 0.01 to 0.98 ± 0.01 in winter and from 0.94 ± 0.01 to 0.97 ± 0.01 in spring at the four sites, being higher than the transition point of petroleum/combustion (0.90) (Budzinski et al., 1997) and implying a dominance of combustion. As reported by Yunker et al. (2002), Flu/(Flu + Pyr) ratios in the range of 0.40–0.50 and >0.50 represent liquid fossil fuel and solid fuel (i.e., grass, wood, and coal) combustions, respectively. The average values for Flu/(Flu + Pyr) in this study were 0.59 ± 0.03 and 0.52 ± 0.04 in winter and spring, further suggesting a solid fuel combustion source in Baoji.

The nine major compounds (Flu, Pyr, BaA, Chry, BkF, BbF, BaP, IcdP, BghiP) are mainly produced through combustion processes (Prahl et al., 1984; Takada et al., 1990). The ratio of total concentration of the nine PAHs (CPAHs) to the whole (CPAHs/∑PAH) ranged from 0.30 to 0.51 for vehicle emissions (Rogge et al., 1993a). In this work, the average ratios were 0.76 and 0.75 during the two periods, indicating that particle associated PAHs in Baoji were less related to vehicle exhausts. The mean BghiP/BeP ratio was 1.06 in both seasons, which is far below the characteristic value (2.02 ± 0.17) for traffic emission but close to that (0.80) of non-traffic sources (Nielsen, 1996), again confirming the weak contribution from

Table 4
Diagnostic ratios of PAHs in the PM_{10} samples from Baoji.

Location	This study, Urban site						Rural site		Non-combustion	Source signature		Reference
	MS		DQ		JY		MG			Combustion sources		
	Winter	Spring	Winter	Spring	Winter	Spring	Winter	Spring		Vehicle emission	Coal burning	
Phe/(Phe + Ant)	0.92 ± 0.03	0.96 ± 0.02	0.93 ± 0.01	0.95 ± 0.01	0.91 ± 0.01	0.94 ± 0.01	0.98 ± 0.01	0.97 ± 0.01	<0.90	>0.90		Budzinski et al., 1997
Flu/(Flu + Pyr)	0.59 ± 0.02	0.50 ± 0.05	0.58 ± 0.01	0.52 ± 0.03	0.59 ± 0.01	0.54 ± 0.02	0.62 ± 0.04	0.53 ± 0.06	<0.40	0.40–0.50	>0.50	Yunker et al., 2002
BeP/(BeP + BaP)	0.54 ± 0.05	0.59 ± 0.03	0.56 ± 0.04	0.62 ± 0.04	0.57 ± 0.04	0.64 ± 0.03	0.62 ± 0.03	0.62 ± 0.06				
CPAH/∑PAH	0.77 ± 0.01	0.77 ± 0.02	0.76 ± 0.01	0.75 ± 0.03	0.78 ± 0.01	0.77 ± 0.02	0.73 ± 0.03	0.73 ± 0.05		0.30–0.51		Rogge et al., 1993a
IcdP/(IcdP + BghiP)	0.51 ± 0.01	0.49 ± 0.03	0.50 ± 0.01	0.44 ± 0.04	0.52 ± 0.02	0.44 ± 0.02	0.50 ± 0.03	0.46 ± 0.04			0.51 ± 0.08	Bi et al., 2008
BghiP/BeP	1.13 ± 0.15	0.99 ± 0.28	1.06 ± 0.13	1.07 ± 0.12	1.04 ± 0.07	1.22 ± 0.12	1.02 ± 0.08	0.98 ± 0.13		2.02 ± 0.17		Nielsen, 1996

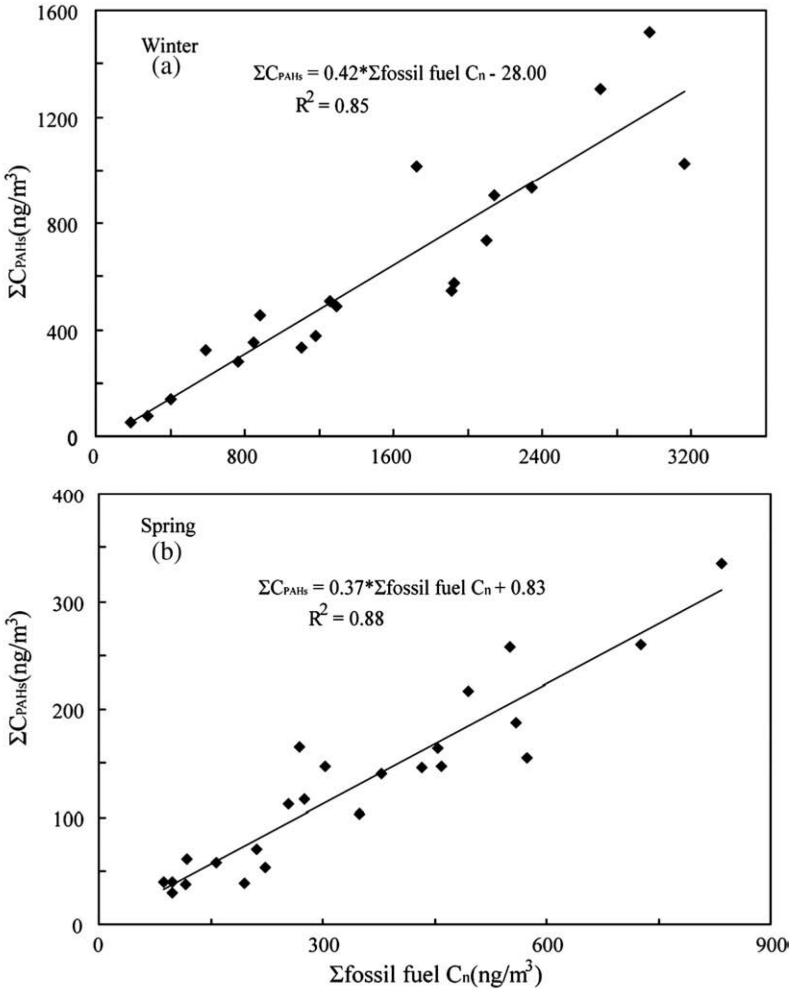

Fig. 5. Relationship of PAHs versus fossil fuels derived *n*-alkanes during the two seasons: (a) winter and (b) spring (ΣC_{PAHs} = total concentration of PAHs in each PM_{10} sample; Σfossil fuel C_n = Concentration of total *n*-alkanes − concentration of plant wax derived *n*-alkanes).

vehicle emissions. In contrast, IcdP/(BghiP + IcdP) was 0.51 ± 0.02 in winter versus 0.46 ± 0.04 in spring, which is in agreement with the diagnostic ratio for coal burning smoke (0.51 ± 0.08) (Bi et al., 2008). Such molecular compositions of PAHs, therefore, clearly demonstrate that coal burning is the major source of PAHs in the city, which is consistent with that reported for the fourteen Chinese cities (Wang et al., 2006b). No significant differences in the PAHs ratios were observed among the four sites, suggesting the common source. Additionally, the seasonal variation of the diagnostic ratios was not obvious at the sites. Coal is the major energy source in Baoji throughout the whole year, and wintertime house heating is only one of many sections (e.g. power generation, metal smelting) that are dominated by coal burning, thus the diagnostic ratios of PAHs in spring are still characteristic of emissions of coal combustion.

3.2.3. Fossil fuel derived *n*-alkanes versus PAHs relationships

As mentioned in Section 3.1.1, high plant wax is an important source of *n*-alkanes, which could be calculated as the excess odd homologues-adjacent even homologues average, and the difference from the total *n*-alkanes is the fossil fuel-derived amount (Simoneit et al., 1991). In this study, the fossil fuel derived *n*-alkanes contributed from 75.7% to 92.5% with an average of 84.2% in winter and from 60.1% to 86.7% with an average of 75.6% in spring. Additionally, a strong positive linear correlation was found between total PAHs and the fossil fuel derived *n*-alkanes in both seasons (Fig. 5 a and b), suggesting the similarity of sources for the two classes of compounds. According to the diagnostic ratios, combustion of coal is the dominant source of PAHs, thus most of the fossil fuel derived *n*-alkanes should also be ascribed to coal burning in the city.

3.3. The current situation and trend of atmospheric pollution in China

As shown in Table 5, the concentrations of *n*-alkanes and PAHs in the atmosphere of Chinese cities except Hong Kong are 1–2 orders of magnitude higher than those in other

Table 5
Comparison of *n*-alkanes and PAHs concentrations in Baoji with those in other international cities (ng/m^3).

City	Year	Size	Season				Reference
			Spring	Summer	Fall	Winter	
I. n-alkanes							
Baoji, China	2008	PM_{10}	449 ± 268			1733 ± 999	This study
Nanjing, China	2001	$PM_{2.5}$			145(4–350)	607(118–1407)	(Yang et al., 2005)
	2004–2005	$PM_{2.5}$		69 ± 32		225 ± 113	(Wang and Kawamura 2005)
Beijing, China	2001–2002	$PM_{2.5}$	52 ± 19	39 ± 17	183 ± 130	477 ± 168	(Huang et al., 2006)
	2002	$PM_{2.5}$		133(57–267)		514(112–1312)	(Feng et al., 2005)
	2002–2003	$PM_{2.5}$		51(24–78)	333(143–749)	375(102–651)	(He et al., 2006)
Guangzhou, China	2001	PM_{10}	390 ± 262	71 ± 29			(Bi et al., 2002)
Qingdao, China	2001–2002	TSP	73	53	90	371	(Guo et al., 2003b)
Hong Kong, China	1996–1997	$PM_{2.5}$	20 ± 9	24 ± 11	26 ± 18	27 ± 5	(Zheng et al., 2000)
Auckland, New Zealand	1998–1999	PM_{10}	75(51–92)	66(14–142)	60(44–79)		(Yassaa et al., 2001)
Huston, USA	1997–1998	$PM_{2.5}$	30(15–34)	24(11–37)		42(26–72)	(Fraser et al., 2002)
II. PAHs							
This study	2008	PM_{10}	128 ± 82			594 ± 405	
Nanjing, China	2001	$PM_{2.5}$			105(66–175)	244(34–433)	(Yang et al., 2005)
	2004–2005	$PM_{2.5}$		40 ± 30		87 ± 42	(Wang et al., 2007)
Beijing, China	2001–2002	$PM_{2.5}$	17 ± 8.0	8.4 ± 5.2	59 ± 52	229 ± 76	(Huang et al., 2006)
	2002	$PM_{2.5}$		30(15–51)		212(33–547)	(Feng et al., 2005)
	2002–2003	$PM_{2.5}$		16(2.3–32)	119(36–309)	259(45–494)	(He et al., 2006)
	2003–2005	PM_{10}		42 ± 32Non-heating season)		305 ± 279	(Okuda et al., 2006)
Guangzhou, China	2001	PM_{10}	107 ± 44	19 ± 11			(Bi et al., 2002)
	2002–2003	PM_{10}	31(8.1–62)	19(9.3–27)	32(11–99)	57(8.4–106)	(Tan et al., 2006)
	2003–2004	TSP	32 ± 13	16	79 ± 12	84 ± 49	(Duan et al., 2007)
Qingdao, China	2001–2002	TSP	13	12	28	177	(Guo et al., 2003b)
Hong Kong, China	1996–1997	$PM_{2.5}$	2.5 ± 1.5	1.6 ± 0.4	2.1 ± 1.2	7.8 ± 3.5	(Zheng et al., 2000)
	2000–2001	PM_{10}		5.3(1.9–10)		47(3.8–297)	(Guo et al., 2003a)
Tokyo, Japan	1997	TSP		14 ± 3.7		36 ± 18	(Tang et al., 2005)
Santiago, Brazil	2000	PM_{10}	5.6(1.4–12)			25(5.3–60)	(Del Rosario Sienra et al., 2005)

regions/countries, among which the pollutants in Baoji are comparable and even more abundant than those in heavily polluted mega-cities. Such a severe air pollution problem in mid-scale cities like Baoji is mainly due to the increasing use of coal without strict emission controls.

Chinese government has made great efforts in dealing with the acid rain, planning a cut in SO_2 emission by 10% from 2005 to 2010. In the past three years, with the help of desulfurization before coal burning in power plant and other rigid controls, acid rain pollution in China has been mitigated with an decrease in total emission of SO_2 by 3.2%, but the air quality in more than 40% cities in the country are still in bad situation (China Environmental Bulletin, 2007). As seen in Table 5, no significant decrease could be found in the concentrations of *n*-alkanes and PAHs in Bejing and Guangzhou, and more serious pollution is observed in mid-scale cities like Baoji, thus a solution for carbonaceous aerosol pollution is in great need for now and the future.

4. Conclusion

In this study, 16 *n*-alkanes (C_{18}–C_{33}) and 17 PAHs of PM_{10} in four sites of Baoji, a mid-scale city in China, were characterized on a molecular level with a GC/MS technique. Concentrations of *n*-alkanes were 1733 ± 990 ng/m^3 for winter and 449 ± 268 ng/m^3 for spring respectively, while concentrations of PAHs were 594 ± 405 and 128 ± 82 ng/m^3 in both seasons. The much more abundant organic aerosols in winter are mainly due to the sharp increase in coal use for house heating. *n*-Alkanes and PAHs had similar spatial distributions in both seasons with the highest level at the downtown area and the lowest at the rural area. CPI values of *n*-alkanes, diagnostic ratios of PAHs and the strong correlation between the concentrations of PAHs and fossil fuel derived *n*-alkanes suggest that the PM_{10} associated organics in the city are mainly originated from coal burning, especially in heating season. Compared to those in the mega cities, air pollution in mid-scale cities in China such as Baoji is much more serious and need more attention.

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