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Molecular distribution and seasonal variation of hydrocarbons in $PM_{2.5}$ from Beijing during 2006

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ABSTRACT

Normal (*n*)-alkanes and polycyclic aromatic hydrocarbons (PAHs) in $PM_{2.5}$ were collected from Beijing in 2006 and analyzed using a thermal desorption-GC/MS technique. Annual average concentrations of *n*-alkanes and PAHs were 282 ± 96 and $125 \pm 150\,ng/m^3$, respectively: both were highest in winter and lowest in summer. C_{19}–C_{25} compounds dominated the *n*-alkanes while benzo[b]fluoranthene, benzo[e]pyrene, and phenanthrene were the most abundant PAHs. The *n*-alkanes exhibited moderate correlations with organic carbon (OC) and elemental carbon (EC) throughout the year, but the relationships between the PAHs, OC and EC differed between the heating and non-heating seasons. The health risks associated with PAHs in winter were more than 40 times those in spring and summer even though the $PM_{2.5}$ loadings were comparable. Carbon preference index values (<1.5) indicated that the *n*-alkanes were mostly from fossil fuel combustion. The ratios of indeno[123-cd]pyrene to benzo[ghi]pyrelene in summer and spring were 0.58 ± 0.12 and 0.63 ± 0.09, respectively, suggesting that the PAHs mainly originated from motor vehicles, but higher ratios in winter reflected an increased influence from coal, which is extensively burned for domestic heating. A comprehensive comparison showed that PAH pollution in Beijing has decreased in the past 10 years.

1. Introduction

Interest in atmospheric fine particulate matter (PM) in China has increased sharply in the past 20–30 years. No other region on Earth is as large and diverse a source of aerosols as China where millions of tons of gaseous precursors and fine particles are released into the atmosphere each year. Menon, Hansen, Nazarenko, and Luo (2002) pointed out that high loadings of carbonaceous aerosols in China may be linked to floods in the southern part of the country and droughts in the north. A study of five years of satellite images showed that the annual average loading of PM < 2.5 μm in diameter ($PM_{2.5}$) near the ground surface in northeastern China was more than $80\,\mu g/m^3$, making this among the most heavily polluted regions in the world, (van Donkelaar et al., 2010). These anthropogenic aerosols can be incorporated into clouds, and as a result, much of their water can evaporate before precipitation can occur.

Organic compounds compose a substantial fraction of the atmospheric aerosol, especially fine PM (Cao et al., 2004, 2007; Kanakidou et al., 2005; Seinfeld and Pankow, 2003). It is well known that many organic species can be used as makers for source identification. For example, diagnostic ratios of normal alkanes (*n*-alkanes) and polycyclic aromatic hydrocarbons (PAHs) can indicate whether these compounds were produced from the combustion of fossil fuels or from the release of epicuticular waxes from higher plants (Li et al., 2012; Wang, Kawamura, Xie, et al., 2009). Another characteristic of organic aerosols that has led to increased concern over their sources and loadings is their toxicity; PAHs for instance, are mutagenic and carcinogenic for humans (Wang, Jariyasopit, et al., 2011; Xie et al., 2009).

Beijing, the capital of China, is one of the world's largest cities. Rapid increases in urbanization, motor vehicle use, and energy consumption have caused severe air pollution problems in Beijing. Thus, many studies have been conducted to investigate the

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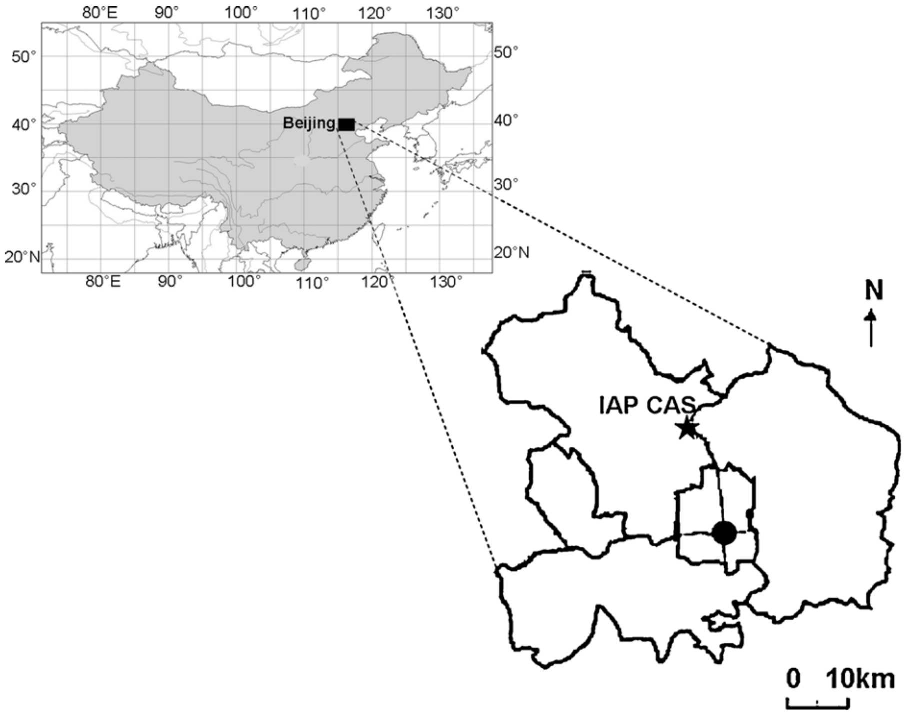

Fig. 1. Map of the sampling site. IAP CAS: Institute of Atmospheric Physics, Chinese Academy of Sciences. The circle represents the center of Beijing (Tian'anmen Square).

concentrations, chemical composition and source distributions of atmospheric PM, including $PM_{2.5}$, in the city (Huang, He, Hu, & Zhang, 2006; Wang et al., 2010; Wang, Cheng, Xu, Zhuang, & Zhao, 2008; Zhou et al., 2008). However, comprehensive studies of the seasonal variations, sources, and health risks of organic aerosols in fine PM from Beijing are limited. Here we first characterize the seasonal variations of OC, EC, *n*-alkanes and PAHs in $PM_{2.5}$ collected from Beijing during 2006, and then we discuss their sources and distributions and assess some possible health risks. A comprehensive comparison with other studies conducted in Beijing from 2001 to 2009 is also presented.

2. Experiment

2.1. Sampling

The sampling campaign was conducted in Beijing (39°58′N, 116°20′E) from the rooftop (10 m above ground) of the Chinese Academy of Sciences' Institute of Atmospheric Physics building (Fig. 1). $PM_{2.5}$ aerosol particles were collected on pre-combusted (800 °C, 3 h) quartz fiber filters with the use of a minivolume air sampler (Airmetrics, Eugene, OR, USA) which operated at a flow rate of 5 L/min. Thirty-eight 24 h ambient samples were collected in four seasons during 2006 as follows: spring (8 March to 20 May, 13 samples), summer (20 July to 21 August, 10 samples), autumn (23 October to 11 November, 10 samples) and winter (7–29 December, 5 samples). Field blanks also were collected before and after sampling by mounting filters onto the sampler but not drawing any air through them. Quartz-fiber filters were analyzed gravimetrically for mass concentrations. Meteorological conditions during the different seasons were recorded and the data are summarized in Table 1.

2.2. Measurements of elemental carbon (EC) and organic carbon (OC)

EC and OC in $PM_{2.5}$ samples were measured with the use of a DRI Model 2001 Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol (Cao et al., 2003, 2005; Chow et al., 2007). Briefly, a 0.526 cm^2 aliquot of a sample filter was placed in a quartz boat inside the analyzer and heated in a stepwise manner to temperatures of 120 °C (OC1), 250 °C (OC2), 450 °C (OC3), and 550 °C (OC4) in a non-oxidizing helium atmosphere, and 550 °C (EC1), 700 °C (EC2), and 800 °C (EC3) in an oxidizing atmosphere of 2% oxygen in helium. In addition, a pyrolized carbon (PC) fraction was determined by the reflectance and transmittance of 633 nm light. The analyzer was calibrated with known quantities of CH_4 every day of operation. One sample was randomly selected from every 10 samples and re-analyzed. Differences determined from the replicate analyses were <5% for TC and <10% for OC and EC. Average field blanks were 1.06 and 0.30 $\mu g/m^3$ for OC and EC, respectively, and were subtracted from the ambient measurements.

Table 1
Meteorological conditions during the sampling periods.

	Spring	Summer	Autumn	Winter	Annual
Temperature (°C)	15.5 ± 4.9[a]	26.1 ± 2.4	10.8 ± 2.8	−0.9 ± 2.4	15.3 ± 9.3
Relative humidity (%)	41 ± 19	71 ± 11	51 ± 18	48 ± 18	51 ± 21
Pressure (kPa)	100.7 ± 0.6	100.4 ± 0.3	101.6 ± 0.5	102.5 ± 0.5	100.4 ± 0.3
Wind speed (m/s)	2.7 ± 0.9	1.9 ± 0.6	2.1 ± 1.0	2.0 ± 1.1	2.3 ± 1.0

[a] Arithmetic mean ± standard deviation.

2.3. *n-Alkane and PAH measurements using thermal desorption-gas chromatography/mass spectrometry*

n-Alkanes and PAHs in the $PM_{2.5}$ samples were determined by a thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS) method which has been described in detail by Ho et al. (2011). Briefly, a 1.0–3.2 cm^2 punch from each sample was cut up and placed into a glass tube. The glass tube was precleaned at 450 °C for at least 5 h prior to use, and it was custom fabricated to be the same dimensions as the Agilent 7890A GC/5975C mass selective detector injector liner (Agilent Technologies, Santa Clara, CA, USA). The injector temperature was first lowered to 50 °C for sample loading. Then the temperature was set to 275 °C for desorption in a splitless mode and kept there for the entire analytical run. The GC oven program was initially held at 30 °C for 2 min, then ramped at 12 °C/min to 120 °C, ramped at 8 °C/min to 280 °C, finally ramped at 12 °C/min to 325 °C and held at that temperature for 20 min until the end of the analysis. The quadrupole mass spectrometer was operated in the electric impact mode at 70 eV. The MS detector was operated in scan mode from 50 to 650 amu at 230 °C and 70 eV for electron ionization. The GC was equipped with an Agilent Technologies HP-5MS capillary column; ultra high purity helium at a constant pressure of 8.4 psi was used as the carrier gas, and it was delivered at a flow of 1.0 mL/min.

Calibration standards were prepared by spiking known amounts of liquid standard mixtures onto pre-combusted quartz-fiber filters. Calibration curves were constructed by plotting the peak areas versus the amount of each species in the standards. Eighteen *n*-alkanes (C_{19}–C_{36}) and 17 PAHs were identified and quantified in this study; the PAHs were phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]-fluoranthene (BaF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Per), indeno[1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBA), benzo[ghi]perylene (BghiP), coronene (Cor), and dibenzo[a,e]pyrene (DBP).

2.4. *Quality assurance and quality control (QA/QC) for the TD-GC/MS analyses*

National Institute of Standards and Technology (NIST) Standard Reference Material® (SRM) 1649b was used to validate the accuracy of PAH concentrations in this study. The relative error between the certified values in SRM 1649b and the calibration standard concentrations was <9.6%. The limit of detection (LOD) for the method was defined as the minimum amount of an *n*-alkane or a PAH that generated the minimum detectable signal plus three times the standard deviation of the blank signals. No peaks were detected for either *n*-alkanes or PAHs in the blank calibration samples. As a result, we approximated the mean blank signal with the calibration line intercept and the blank signal standard deviation with the standard error for the peak area estimate. Using this approach, the LODs in nanograms per sample were calculated to be in the range of 0.016–0.075 ng for the *n*-alkanes and 0.025–0.560 ng for the PAHs. Replicate analyses were conducted on every tenth sample. The relative standard deviations for the samples were 1.5–9.3% for targeted compounds. Additional information on QA/QC procedures may be found in Ho et al. (2011).

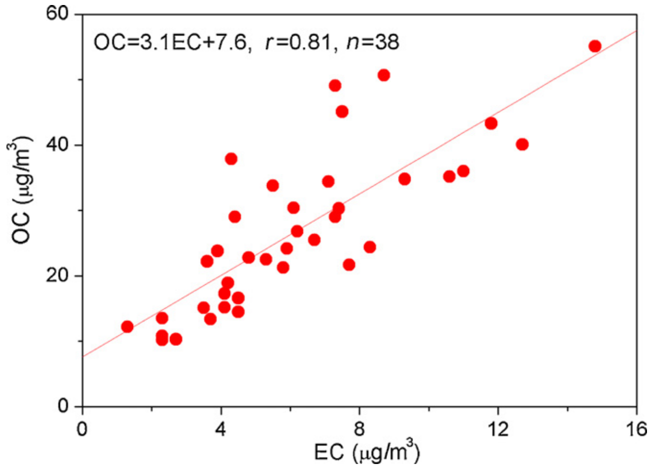

Fig. 2. Relationship between organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$.

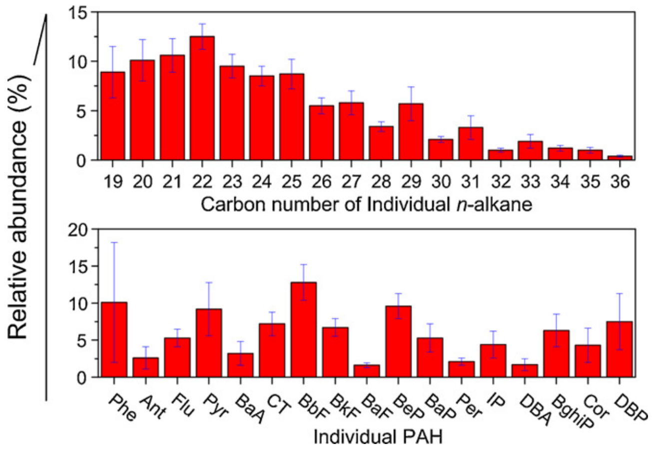

Fig. 3. Relative abundances of individual *n*-alkanes and PAHs in $PM_{2.5}$ from Beijing during 2006.

3. Results and discussion

3.1. *Concentrations*

The concentrations of $PM_{2.5}$, OC, EC, *n*-alkanes and PAHs in Beijing during 2006 are shown in Table 2. The observed annual average $PM_{2.5}$ mass concentration was 176 ± 34 μg/m^3; this is more than five times the Chinese annual $PM_{2.5}$ standard (35 μg/m^3). The loadings of OC and EC were 29 ± 9.7 and 6.4 ± 1.8 μg/m^3, respectively, and these concentrations are comparable with the results of previous studies conducted in Beijing (Feng et al., 2006; He et al., 2001). OC and EC showed, in Fig. 2, a significant linear correlation ($r = 0.81$), suggesting they are emitted by common sources (Cao et al., 2003; Li et al., 2011), most likely coal combustion and motor vehicle exhausts.

The annual average concentration of total *n*-alkanes in $PM_{2.5}$ was 282 ± 96 ng/m^3. As shown in Fig. 3, the most abundant *n*-alkanes were C_{19} to C_{25} compounds. This finding is quite different from what has been observed in some mountainous areas where heavier (C_{29} to C_{31}) *n*-alkanes were found to dominate (Li et al., 2012; Wang, Kawamura, Xie, et al., 2009). Simoneit et al. (2004) found that *n*-alkanes from fossil fuel combustion were mostly low molecular-weight (LMW, carbon number <25) species while those derived from plant waxes were heavier; these authors also noted that plant waxes had preferentially odd carbon numbers.

Thus, the dominance of the LMW *n*-alkanes in this study is evidence that anthropogenic emissions are the main source for straight-chain hydrocarbons in Beijing. In addition, the odd carbon number predominance in the HMW *n*-alkanes indicates some influences from biomass burning or plant waxes or both.

Table 2
Molecular distribution of n-alkanes and PAHs (ng/m^3) in $PM_{2.5}$ in Beijing during 2006.

Species	Non-heating seasons				Heating season	
	Spring (n = 13)	Summer (n = 10)	Autumn (n = 10)	Mean (n = 23)	Winter (n = 5)	Annual
$PM_{2.5}$ (μg/m^3)	222 ± 83[a]	129 ± 49	184 ± 56	182 ± 77	169 ± 36	176 ± 34
OC (μg/m^3)	26 ± 7.0	15 ± 3.7	32 ± 12	25 ± 11	42 ± 8.1	29 ± 9.7
EC (μg/m^3)	5.2 ± 2.2	4.1 ± 1.6	8.8 ± 3.7	6.0 ± 3.2	7.3 ± 0.8	6.4 ± 1.8
I. n-Alkanes						
Nonadecane (C_{19})	20 ± 14	25 ± 26	21 ± 10	22 ± 18	26 ± 11	23 ± 2.6
Icosane (C_{20})	24 ± 17	20 ± 8.3	25 ± 11	23 ± 14	32 ± 8.8	25 ± 4.2
Henicosane (C_{21})	24 ± 16	22 ± 11	26 ± 11	24 ± 13	40 ± 13	28 ± 7.4
Docosane (C_{22})	26 ± 18	24 ± 13	33 ± 13	27 ± 16	56 ± 15	35 ± 13
Tricosane (C_{23})	17 ± 13	17 ± 11	29 ± 14	21 ± 14	48 ± 15	28 ± 13
Tetracosane (C_{24})	16 ± 12	16 ± 9.9	27 ± 13	19 ± 13	41 ± 11	25 ± 10
Pentacosane (C_{25})	15 ± 11	14 ± 10	30 ± 15	19 ± 14	47 ± 13	27 ± 13
Hexacosane (C_{26})	11 ± 8.9	8.7 ± 6.7	19 ± 11	13 ± 9.9	28 ± 6.4	17 ± 7.7
Heptacosane (C_{27})	11 ± 8.8	7.3 ± 5.2	23 ± 10.6	14 ± 11	26 ± 6.8	17 ± 7.9
Octacosane (C_{28})	8.2 ± 8.3	4.7 ± 3.0	13 ± 7.3	8.6 ± 7.5	14 ± 3.4	10 ± 3.8
Nonacosane (C_{29})	11 ± 7.7	6.2 ± 4.0	25 ± 11	14 ± 11	21 ± 5.9	16 ± 7.6
Triacotane (C_{30})	5.1 ± 5.3	2.8 ± 2.0	8.0 ± 4.7	5.3 ± 4.8	8.3 ± 2.0	6.0 ± 2.3
Hentriacotane (C_{31})	6.3 ± 4.5	3.9 ± 2.9	17 ± 8.4	8.7 ± 7.8	12 ± 3.3	9.6 ± 4.9
Dotriacotane (C_{32})	2.3 ± 2.3	1.3 ± 1.1	4.9 ± 3.2	2.8 ± 2.8	4.0 ± 1.1	3.1 ± 1.4
Tritriacotane (C_{33})	3.4 ± 2.1	2.2 ± 1.6	9.9 ± 5.5	5.0 ± 4.7	6.8 ± 2.1	5.6 ± 3.0
Tetratriacotane (C_{34})	2.6 ± 1.5	1.6 ± 0.9	5.6 ± 3.6	3.2 ± 2.8	4.6 ± 1.0	3.6 ± 1.6
Pentatriacotane (C_{35})	2.0 ± 1.1	1.2 ± 0.8	5.2 ± 3.0	2.7 ± 2.5	3.7 ± 1.0	3.0 ± 1.5
Hexatriacontane(C_{36})	0.7 ± 0.4	0.4 ± 0.3	1.9 ± 1.3	1.0 ± 1.0	1.8 ± 0.6	1.2 ± 0.7
Subtotal	205 ± 128	179 ± 112	323 ± 130	233 ± 138	420 ± 110	282 ± 96
Fossil fuel n-alkanes	192 ± 125	156 ± 85	275 ± 120	206 ± 122	379 ± 88	206 ± 86
Plant wax n-alkanes	13 ± 7.5	22 ± 29	48 ± 20	27 ± 25	41 ± 24	31 ± 14
II. PAHs						
Phenanthrene (Phe)	2.3 ± 1.5	1.9 ± 1.5	3 ± 1.3	2.4 ± 1.5	4.2 ± 1.5	2.9 ± 0.9
Anthracene (Ant)	0.6 ± 0.3	0.4 ± 0.3	0.8 ± 0.4	0.6 ± 0.4	3.1 ± 1.4	1.2 ± 1.1
Fluoranthene (Flu)	1.4 ± 1.3	0.7 ± 0.7	3 ± 1.8	1.7 ± 1.6	18.9 ± 6.8	6 ± 7.5
Pyrene (Pyr)	2.5 ± 1.8	1.2 ± 1	4.3 ± 2.3	2.7 ± 2.2	22.3 ± 8.5	7.6 ± 8.6
Benz(a)anthracene (BaA)	0.4 ± 0.4	0.2 ± 0.2	3 ± 1.9	1.1 ± 1.6	22.7 ± 10.9	6.6 ± 9.4
Chrysene (Chr)	1.7 ± 1.8	0.6 ± 0.7	8 ± 5.4	3.3 ± 4.5	35 ± 15	11 ± 14
Benzo(b)fluoranthene (BbF)	3.0 ± 2.8	1.3 ± 1.4	15 ± 9.7	6.1 ± 8.2	50 ± 22	17 ± 20
Benzo(k)fluoranthene (BkF)	1.4 ± 1.2	0.7 ± 0.6	8.5 ± 6.3	3.3 ± 4.9	25.3 ± 9.4	9.0 ± 9.9
Benzo(a)fluoranthene (BaF)	0.2 ± 0.1	0.2 ± 0.1	1.2 ± 0.9	0.5 ± 0.7	6.8 ± 3.4	2.1 ± 2.7
Benzo(e)pyrene (BeP)	2.0 ± 1.7	0.8 ± 0.7	11.6 ± 7.6	4.6 ± 6.3	37.3 ± 17	13 ± 15
Benzo(a)pyrene (BaP)	0.6 ± 0.4	0.4 ± 0.2	6.2 ± 4.8	2.2 ± 3.7	31 ± 16	9.5 ± 13
Perylene (Per)	0.5 ± 0.4	0.3 ± 0.2	1.5 ± 1.1	0.7 ± 0.8	6.4 ± 3.5	2.2 ± 2.5
Indeno[123-cd]pyrene (IP)	1.1 ± 1.0	0.5 ± 0.6	6.4 ± 4.6	2.9 ± 3.9	20 ± 9.2	7.0 ± 7.9
Dibenz(a,h)anthracene (DBA)	0.4 ± 0.3	0.2 ± 0.2	2.2 ± 2.1	1.0 ± 1.6	8.6 ± 3.3	2.8 ± 3.4
Benzo(ghi)perylene (BghiP)	1.7 ± 1.3	0.9 ± 0.8	7.7 ± 4.9	3.7 ± 4.3	25 ± 13	8.9 ± 9.9
Coronene (Cor)	1.4 ± 0.9	1.2 ± 0.4	5.2 ± 2.3	2.2 ± 2.1	27.7 ± 10.9	8.9 ± 11
Dibenzo[a,e]pyrene (DBP)	3.1 ± 1.6	2.3 ± 1.1	9.7 ± 2.4	4.5 ± 3.4	35.7 ± 15.4	13 ± 14
Subtotal	24 ± 17	10 ± 8.7	88 ± 52	39 ± 45	379 ± 159	125 ± 150

[a] Arithmetic mean ± standard deviation.

Benzo(b)fluoranthene (BbF) was the most abundant compound in the PAH class, and it was followed by benzo(e)pyrene (BeP) and phenanthrene (Phe).

3.2. Seasonal variations

The $PM_{2.5}$ mass loadings and the concentrations of OC, EC and organic markers in $PM_{2.5}$ all showed obvious seasonal variations in Beijing. $PM_{2.5}$ exhibited a spring > winter > autumn > summer distribution, and this is different from OC whose concentrations decreased in the following manner: winter > autumn > spring > summer. The high $PM_{2.5}$ concentrations in spring can be attributed to the annual influx of mineral dust from Inner Mongolia and the Xinjiang Autonomous Region (He et al., 2001). In contrast, the burning of coal and biomass for residential heating in winter likely causes the OC concentrations to be much higher than those in the non-heating seasons (Cao et al., 2007). The EC concentration in winter was lower than in autumn, however, and the seasonal differences between OC and EC may be explained not only by differences in their sources but also by the high wind speeds in winter which can disperse the aerosols around the city.

The total n-alkane concentrations in $PM_{2.5}$ were highest in winter (420 ± 110 ng/m^3), followed by autumn (323 ± 130 ng/m^3), spring (205 ± 128 ng/m^3) and then summer (179 ± 112 ng/m^3). n-Alkanes in aerosols mainly originate from two sources: fossil fuel combustion and plant wax emissions (Fu et al., 2008; Simoneit et al., 2004), and Simoneit et al. (1991) proposed that the concentrations of plant wax n-alkanes could be calculated by formula (1) because of the odd-even carbon number predominance of the compounds from that source:

$$Wax\quad C_n = \frac{C_n - (C_{n-1} + C_{n+1})}{2}, \tag{1}$$

where $Wax\ C_n$ is the concentration of the plant wax n-alkane with carbon number n and C_{n-1}, C_n and C_{n+1} are the concentrations of n-alkanes with the specified carbon numbers. Note that negative values of $Wax\ C_n$ are taken as 0. The n-alkanes that are attributable to fossil fuels can then be calculated as the difference between the total n-alkane sum and the sum of the plant wax alkanes.

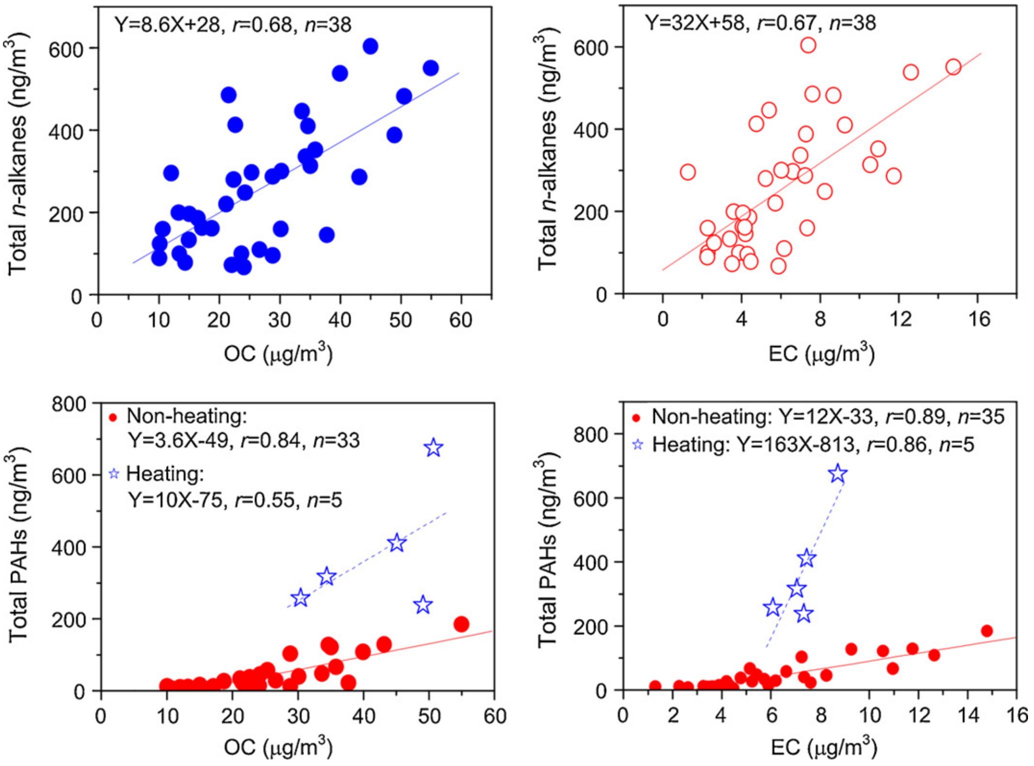

Fig. 4. Relationship between *n*-alkanes and organic carbon (OC) and elemental carbon (EC) and PAHs and OC and EC in $PM_{2.5}$.

As shown in Table 2, the $PM_{2.5}$ *n*-alkanes in Beijing are predominantly produced by fossil fuel combustion. Total *n*-alkanes showed moderate correlations with OC and EC (Fig. 4), suggesting that they are produced from some of the same emission sources. The concentrations of fossil-fuel derived *n*-alkanes in winter were nearly double those in the non-heating seasons, and this was presumably caused by the large quantities of coal burned for home heating. The lowest concentrations of fossil fuel *n*-alkanes occurred in summer, and that is probably due, at least in part, to the removal of these compounds from the atmosphere by precipitation scavenging because rainstorms are relatively common during that part of the year.

Although the contributions of plant waxes to the total *n*-alkane loadings were relatively small in the Beijing urban area, as one might expect, higher contributions of plant wax *n*-alkanes occurred in autumn and winter compared with spring and summer. This could be due to relatively large quantities of plant materials, especially crop residues, burned in outlying areas during autumn and winter.

PAHs are formed during incomplete combustion, coal burning, emissions from motor vehicle exhausts and burning plastics are the most important sources for this group of hydrocarbons (Gaga & Ari, 2011; Hanedar et al., 2011). The concentrations of total PAHs during spring and summer were much lower than in autumn, but the concentrations of PAHs during the winter heating season were an order-of-magnitude higher than in the other seasons. The differences in PAHs concentrations among the three non-heating seasons are likely caused by the combined effects of meteorological cycles and patterns in human activities. That is, during the spring and summer, high wind speeds and precipitation scavenging reduce aerosol loadings; in autumn, on the other hand, the burning of crop residues raises the concentrations of PAHs and other combustion-related materials in the atmosphere.

It is well known that most PAHs are mutagenic and carcinogenic to humans (Wang, Jariyasopit, et al., 2011; Xie et al., 2009). The health risks of PAHs can be assessed by calculating BaP-equivalent (BaPE) concentrations as follows:

$$\text{BaPE} = 0.06\text{BaA} + 0.07(\text{BbF} + \text{BkF}) + \text{BaP} + 0.6\quad\text{DBA} + 0.08\text{IP}. \qquad (2)$$

The BaPE concentrations in Beijing during spring and summer were 1.3 ± 0.9 and 0.6 ± 0.5 ng/m^3, respectively, as shown in Fig. 5, and these low values indicate that the health risks associated PAHs during those seasons should be small. Nonetheless, the BaPE values increased more than 40 times in winter despite the fact that the $PM_{2.5}$ mass concentrations then were comparable with those in the other seasons. As shown in Fig. 4, the slope of relationship between

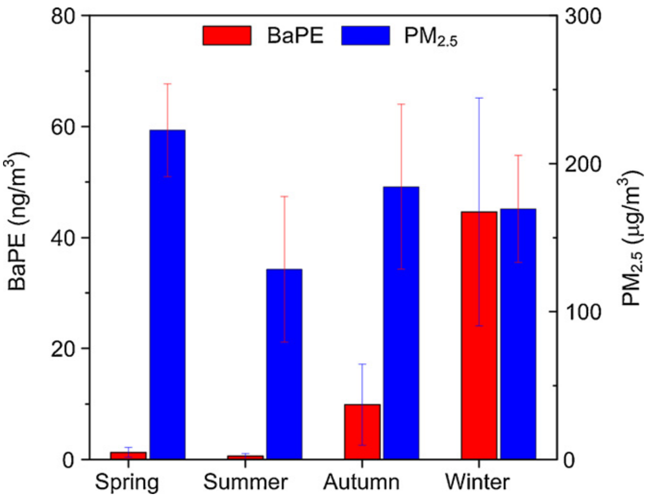

Fig. 5. Benzo(a)pyrene-equivalent (BaPE) concentrations in $PM_{2.5}$ during four seasons.

PAHs and OC for the winter heating season was nearly three times higher than those for the other seasons, and the heating versus non-heating season differences for PAHs versus EC loadings were also dramatic. These results highlight the increased health risks associated with the high PAH loadings during the winter heating season. This information on seasonality is vitally important for developing effective environmental health protection measures.

3.3. *Implications for sources*

Certain characteristics and diagnostic ratios of organic markers, including the *n*-alkanes and PAHs, can be used to identify presumptive emission sources. As noted above, Simoneit et al. (1991) found that *n*-alkanes from plant waxes exhibited an odd carbon number preference while those from fossil fuel emissions showed no odd/even carbon number preference. More specifically, the carbon preference index (CPI, the sum of the odd carbon number *n*-alkanes divided by the sum of the even carbon number *n*-alkanes) approaches unity for fossil-fuel derived *n*-alkanes, but it is >5 for those from plant waxes. The seasonally averaged CPI values in our study ranged from 1.18 to 1.44, and the annual average CPI was 1.26 ± 0.10 (Table 3); these low values show that the aerosol *n*-alkanes in Beijing were mainly produced from the combustion of fossil fuels. Our results are also similar to the CPI values of 1.2–1.8 for samples collected in 2001 reported by Huang et al. (2006).

Grimmer, Jacob, Naujack, and Dettbarn (1981) proposed that IP/BghiP ratios could be used to distinguish among certain anthropogenic emissions; for example, values of 0.2, 0.5, and 1.3 were said to be diagnostic for emissions from gasoline, diesel, and coal combustion, respectively. In our study, the ratios of IP/BghiP in summer (0.58 ± 0.12) and spring (0.63 ± 0.09) were much closer to the diesel and gasoline combustion ratios than that characteristic of coal burning, suggesting that PAHs in Beijing are dominated by motor vehicle exhaust emissions in those seasons. However, the IP/BghiP ratio increased to 0.82 ± 0.10 in winter due to the sharp increase in the burning of coal for home heating.

In comparison to our results, Feng et al. (2006) reported that IP/BghiP ratios in summer and winter in Beijing during 2002 were 0.85 and 0.89. Wang et al. (2008) performed a 1-month study of $PM_{2.5}$ in Beijing from December 2005 to January 2006, and they found that the mean IP/BghiP ratio was 1.10. The lower ratios observed in the present study suggest that amount of coal burned in Beijing was lower during the winter of 2006 compared with the 1 year earlier, and this may have been due to the implementation of environmental protection measures in preparation for the Olympic Games in 2008.

The ratio of BaP/BeP has used an indicator of aerosol aging because BaP is more susceptible to photochemical degradation than its isomer BeP (Wang, Kawamura, Xie, et al., 2009; Wang, Kawamura, & Lee, 2009). The lowest BaP/BeP values in our study occurred in spring (Table 3) and that may have been due to the large quantities of aerosols delivered to the region by long-range transport. On the other hand, the high BaP/BeP values in winter may be explained by the reduced levels of solar insolation and the low air temperatures at that time of year. Both of these factors would tend to reduce the photodegradation of BaP, thereby increasing the BaP/BeP ratios.

3.4. *Comparison with other studies in Beijing*

A comprehensive comparison of atmospheric particulate *n*-alkanes and PAHs in Beijing for 2001–2009 is presented in Fig. 6. In our study, the total *n*-alkanes in $PM_{2.5}$ showed a winter > autumn > spring > summer seasonal distribution, and this pattern is consistent with results for 2001 reported by Huang et al. (2006). However, Zhou et al. (2009) indicated that concentrations of *n*-alkanes in PM_{10} in 2003–2004 were highest in winter, followed by spring, summer and autumn. The apparent discrepancy may have been caused by differences in the particle sizes sampled in the studies. That is, the HMW plant wax *n*-alkanes (such as C_{29} and C_{31}) tend to be concentrated in coarse aerosols (Bi, Simoneit, Sheng, Ma, & Fu, 2008; Simoneit et al., 2004), and therefore, the relative contributions of plant waxes versus combustion emissions is likely to differ for $PM_{2.5}$ versus PM_{10}, with more of the former in larger particles. No clear decreasing trend in *n*-alkanes in Beijing can be seen in the figure, and that may be because the sources of *n*-alkanes are diverse and therefore not easily controlled.

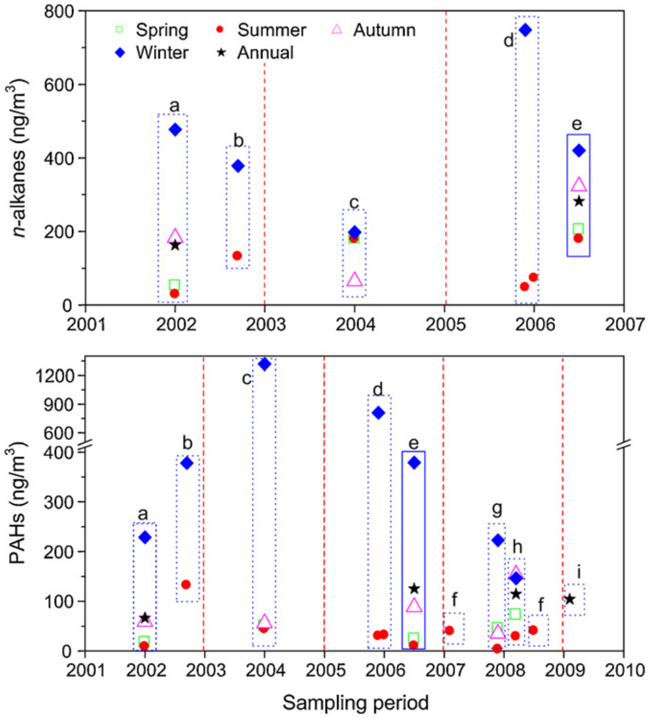

Fig. 6. Comparison of atmospheric particulate *n*-alkanes and PAHs (ng/m^3) in Beijing from 2001 to 2009. (a) $PM_{2.5}$ (Huang et al., 2006); (b) $PM_{2.5}$ (Feng et al., 2006); (c) PM_{10} (Zhou et al., 2009); (d) $PM_{2.5}$ (Wang, Shao, Zhang, et al., 2009); (e) $PM_{2.5}$ (this study); (f) $PM_{2.5}$ (Okuda et al., 2011); (g) PM_{10} (Wang, Simonich, Wang, et al., 2011); (h) passive particulate samplers (Wang, Simonich, Giri, et al., 2011); (i) TSP (Ma et al., 2011).

PAHs are useful indicators of air pollution because they mainly originate from combustion processes and they are concentrated in fine particles. As shown in Fig. 6, the highest total PAH concentrations in all of the studies included occurred in winter, followed by autumn, spring and summer. PAH concentrations in winter initially increased from 2001 to 2004 in Beijing but then decreased almost an order-of-magnitude from 2004 to 2008. The PAH concentrations in summer showed a similar tendency, but the highest value occurred in 2002. The annual average concentration of PAHs in $PM_{2.5}$ in our study (125 ± 150 ng/m^3) is roughly double what was reported for 2001 (66.2 ± 93.5 ng/m^3) (Huang et al., 2006). On the other hand, Ma et al. (2011) reported that the annual concentration of PAHs in TSP from September 2008 to July 2009 was 104.1 ± 129.9 ng/m^3, and one would assume that the PAH concentrations in $PM_{2.5}$ would be even lower. Okuda et al. (2011) reported that during the period of the Olympic Games, the water-soluble ions in TSP, except for nitrogen-containing species, declined by 43–79%, and they also found a decrease in the concentrations of HMW (5–7 ring) PAHs. Thus it can be concluded that the PAH levels in Beijing have decreased since the mid-2000s, and this implies

Table 3
Diagnostic ratios of *n*-alkanes and PAHs in $PM_{2.5}$ in different seasons.

Sampling season	CPI[a]		IP/BghiP[b]		BaP/BeP	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
Spring, *n* = 13	1.00–1.65	1.20 ± 0.15	0.41–0.75	0.63 ± 0.09	0.14–0.87	0.34 ± 0.18
Summer, *n* = 10	1.08–1.53	1.18 ± 0.13	0.35–0.72	0.58 ± 0.12	0.29–1.13	0.58 ± 0.29
Autumn, *n* = 10	1.18–2.48	1.44 ± 0.37	0.25–1.19	0.75 ± 0.24	0.27–0.69	0.50 ± 0.14
Winter, *n* = 5	1.15–1.34	1.20 ± 0.07	0.73–1.00	0.82 ± 0.10	0.72–0.93	0.81 ± 0.09
Annual, *n* = 38	1.00–2.48	1.26 ± 0.10	0.25–1.00	0.69 ± 0.10	0.14–1.13	0.56 ± 0.17

[a] CPI stands for carbon preference index (sum of the odd carbon number *n*-alkanes divided by the sum of the even carbon number *n*-alkanes).

[b] Abbreviations are as follows: IP = indeno[123-cd]pyrene, BghiP = benzo[ghi]pyrelene, BaP = benzo(a)pyrene, and BeP = benzo(e)pyrene.

that their major sources are known and that the environmental protection measures implemented in the past 10 years have been effective.

4. Conclusions

The annual average concentration of $PM_{2.5}$ in Beijing during 2006 was much higher than the Chinese $PM_{2.5}$ air quality standard, attesting to the severe fine particle pollution in the city. The concentrations of *n*-alkanes, OC, and EC in $PM_{2.5}$ exhibit moderate correlations throughout the year, suggesting that they originate from similar or related sources. Correlations of PAHs with OC and EC are very different for the non-heating versus heating seasons, however. A much higher slope for the relationship between PAHs with OC and EC in winter compared with the other seasons can be explained by patterns in energy usage, or more specifically, by the burning of coal for domestic heating in winter. Health risks associated with PAHs in winter are more than 40 times those in spring and summer even though the $PM_{2.5}$ concentrations in these seasons are comparable. The CPI values for *n*-alkanes in all seasons are less than 1.5, indicating that they are mostly produced during fossil fuel combustion. Relatively low values for the IP/BghiP ratio showed that PAHs in Beijing are dominated by motor vehicle exhaust emissions in summer and spring, but the contribution from coal burning increased in the winter heating season. A comprehensive comparison showed that PAH pollution in Beijing has decreased since the mid 2000s, suggesting that the recent implementation of environmental protection measures has been effective.

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