

# A wintertime study of polycyclic aromatic hydrocarbons in PM<sub>2.5</sub> and PM<sub>2.5–10</sub> in Beijing: Assessment of energy structure conversion

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## Abstract

Sixteen priority polycyclic aromatic (PAHs) in PM<sub>2.5</sub> and PM<sub>2.5–10</sub> samples collected from 20 sites in Beijing, China in December 2005 and January 2006 were analyzed to determine the composition, spatial distribution and sources. Total PAHs of PM<sub>2.5</sub> and PM<sub>2.5–10</sub> ranged from 5.2 to 1062.2 ng m<sup>-3</sup> and 7.6 to 759.7 ng m<sup>-3</sup>, respectively, categorized as heavier pollution. Among five kind of functional zones involved, industrial center, commercial area and village were heavily polluted. The mean concentration of PAHs in PM<sub>2.5</sub> of 407 ng m<sup>-3</sup> was 1.67-fold of that in PM<sub>2.5–10</sub>, which was relatively high compared to the previous studies (winter in 2001 and 2002). The most evident change was the increase of Flu, BbKf and InP, which are believed to be less harmful and related to the increasing use of clean energy. However, pollution distribution was spatially heterogeneous inside the city. The most polluted sites located in the southeast of the city. Unlike previous studies, fluoranthene was the most abundant component quantified, which could be associated with increasing use of natural gas as clean energy. Compositional analysis and principal component analysis (PCA) suggested that different kinds of combustion were the main source of the PAHs in PM, though contribution of coal was still evident. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Particulate matter (PM); Polycyclic aromatic hydrocarbon (PAHs); Combustion; Principal component analysis (PCA)

## 1. Introduction

Carbonaceous species of particulate matter is often recognized as important contributors to aerosol-related consequences, including visibility, climate and human health [1]. It was reported that about one-third of total PM<sub>2.5</sub> mass in Beijing was constituted by organic carbon [2]. Among these matters, many semivolatile organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), etc., have been received utmost attention [3–4].

Polycyclic aromatic hydrocarbons are a group of persistent organic pollutants that are highly lipophilic and widely distributed in the environment. Although some natural processes can produce PAHs, the atmosphere PAHs originate mostly from vehicles, municipal incinerators, residential heating systems and various industrial processes. Many PAHs are certified carcino-

genic; moreover, some of them are reported to be mutagenic, having the capacity to form DNA and protein adducts [5]. Although the carcinogenicity of PAHs is 1/10<sup>3</sup> to 1/10<sup>4</sup> of that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) [6,7], the concentration in the atmosphere is about 10<sup>4</sup>–10<sup>6</sup> times higher than that of TCDD [8]. Hence, considering the carcinogenic risk of PAHs in the air, we must monitor the air PAHs as we would do for dioxins. Previous studies found 65–90% PAHs [9] bound to particles with diameter less than 2 μm, which can deposit in the lungs and exert their carcinogenicity over long exposure period. Therefore, it is of great importance to monitor and identify the source and behavior of PAHs in air fine particles for the sake of pollution management and control.

Coal contributed about 70% of China's primary energy. Coal combustion has been concerned as a major source of aerosol in China, especially in winter [2,10]. The large amount of coal consumption in China has led to serious air pollution. Beijing, the capital of China, is one of the megacities in the world. By 2004, the population of Beijing had reached about 15 million and annual coal consumption was 42 Mt [11]. Moreover, with rapid urbanization, industrialization and motorization, the

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energy consumption keep increasing, which leads to serious air problems consequently. Beijing is now under vigorous development because the Olympic Games will be held there in 2008. At the same time, for the purpose of urban air quality improving, the government of Beijing made detailed guidelines for energy readjustment (action plan for Beijing Olympic games 2008), which including the concrete items for coal use reduction and usage of clean energy (Chinese Olympic Committee, <http://www.beijing-2008.org>). Hence, it is necessary to monitor the air quality concurrent. Several studies on PAHs in aerosol in Beijing have been reported recently [7,12–14]. However, these reports focus on limited sites in this city, which cannot illustrate the general pollution level of Beijing. To get an overall understanding of air PAHs level and develop an effective air pollution control, it is necessary to carry out a detailed and systematic investigation in large scale.

We have performed a 1-month air particulate matter (PM<sub>2.5</sub> and PM<sub>2.5-10</sub>) sampling in winter at 20 sites that covered city zone of Beijing. It was reported that the PAHs levels was the highest in winter of most northern cities in China. Thus, the aerosol samples in winter can be regarded as representative for the worst pollution status in the city and have importance in air quality controlling. We focused on sources and spatial distribution of PAHs. The objectives of this study are: (1) to give the PAHs levels of PM in Beijing, (2) to identify the most polluted area and the health risk of PAHs in these city area, (3) to assess the effects of new energy strategy and (4) to give an advice on PAHs controlling.

## 2. Experimental

### 2.1. Sampling

The suspended particulate matters were collected onto glass fiber filters (GF/C) (Ø 90 mm, Whatman Company, UK) using

medium volume samplers (Model TH-150, Wuhan Tianhong Instrument Factory) at a flow rate of 1001 min<sup>-1</sup> in winter from 20 sites of Beijing China (Fig. 1 and Table S-1 in supporting material). The sampling times were chosen to be representative of the seasonal meteorological conditions (average temperature is about -4.6 °C). Four-hour samples (8:00–12:00 a.m. every day) were collected. Before the experiment, the filters were previously annealed for 4 h at 550 °C to remove organic material and equilibrated in desiccators, weighted and put into an envelope pretreated at 550 °C. After sampling, the filters were removed from the inlet and folded in half and returned to the envelope and transported to the laboratory as soon as possible. The filters were stored in a desiccator to equilibrate for at least 24 h before being weighed. After being weighed, the samples were stored in a refrigerator at -18 °C until analysis.

### 2.2. Material and reagents

Pesticide grade n-hexane and dichloromethane were obtained from Dikma Inc. Analytical-grade of acetone and isooctane was from Beijing Chemical Factory (China) and redistilled in all glass system. Silica gel (100–200 meshes) was purchased from Qingdao Ocean Chemical Company (China) and was heated in muffle furnace at 600 °C for 6 h and activated at 130 °C for 16 h before use. Anhydrous sodium sulfate (Beijing Chemical Factory, China) was heated at 600 °C for 6 h and kept in a desiccator until use.

16 EPA-PAHs standards of naphthalene (Na), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (InP), dibenz[*a,h*]anthracene (DBA), benzo[*g,h,i*]perylene (BghiP) were purchased from

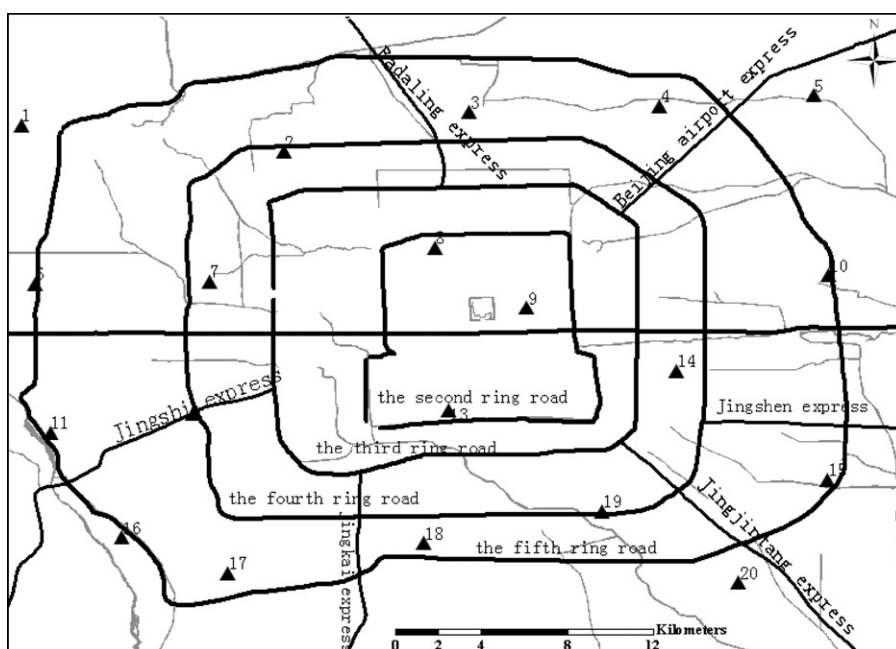


Fig. 1. Map of sampling sites in Beijing.

Aldrich (WI, USA). A series of calibration standards were prepared by diluting the mixed standard solution to final concentration of 1, 2, 10 mg l<sup>-1</sup> in isooctane and stored at 4 °C. 2-Fluorobiphenyl, the surrogate, was purchased from Supelco (Bellefonte, PA, USA).

### 2.3. Sample pretreatments

The samples were Soxhlet extracted with 120 ml acetone–hexane (1/1, v/v) for 24 h and concentrated to about 1 ml in water bath. The concentrated extract was then transferred to chromatograph column (30 cm × 10 cm i.d.) containing 10 g activated silica gel with 1 cm anhydrous sodium sulfate on the top and eluted with 40 ml hexane–dichloromethane (1/1, v/v). Then, the fraction was concentrated to 0.1 ml under a gentle stream of nitrogen.

### 2.4. PAHs determination

Agilent 6890 GC-FID was employed for quantification of PAHs. The separation was performed on a fused silica capillary column (DB-5, 30 m × 0.25 mm i.d., and 0.25 μm film thickness). Ultrapure nitrogen was used as both carrier and makeup gas. The oven temperature was programmed as follows: initial temperature 70 °C held for 1 min, then increased to 290 °C at a rate of 4 °C/min. The injector and detector temperature were 280 and 300 °C, respectively.

Agilent 6890 GC-5973 MS was also used for confirmation the identity of object compounds in some samples. A DB-5 column (30 m × 0.25 mm i.d., and 0.25 μm film thickness) was also used for separation. The ionization was performed in the electron impact mode at 70 eV and the mass range scanned was from 50 to 550 amu under full scan acquisition mode. Helium was the carrier gas. The oven program was as described above. The injector and transfer line temperature were 280 and 180 °C, respectively.

Procedural blanks (solvent), spiked matrixes (standards in filters) and spiked blanks were analyzed to assure and control the analysis quality. None of the target compounds was detected. The recovery for 16 PAHs were in the range of 73–92%.

## 3. Results and discussion

### 3.1. Meteorological conditions

Air mass backward trajectories during sampling periods were calculated using HYSPLIT model (Hybrid Single-Particle using grangian Integrated Trajectory), a comprehensive modeling system developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory [15] (Fig. 2). Results showed that air parcels arriving Beijing were mainly from north and northwest direction in sampling periods. Air parcels from northwest would bring in pollutants from industrial areas from Hebei, Inner Mongolia, Shanxi province

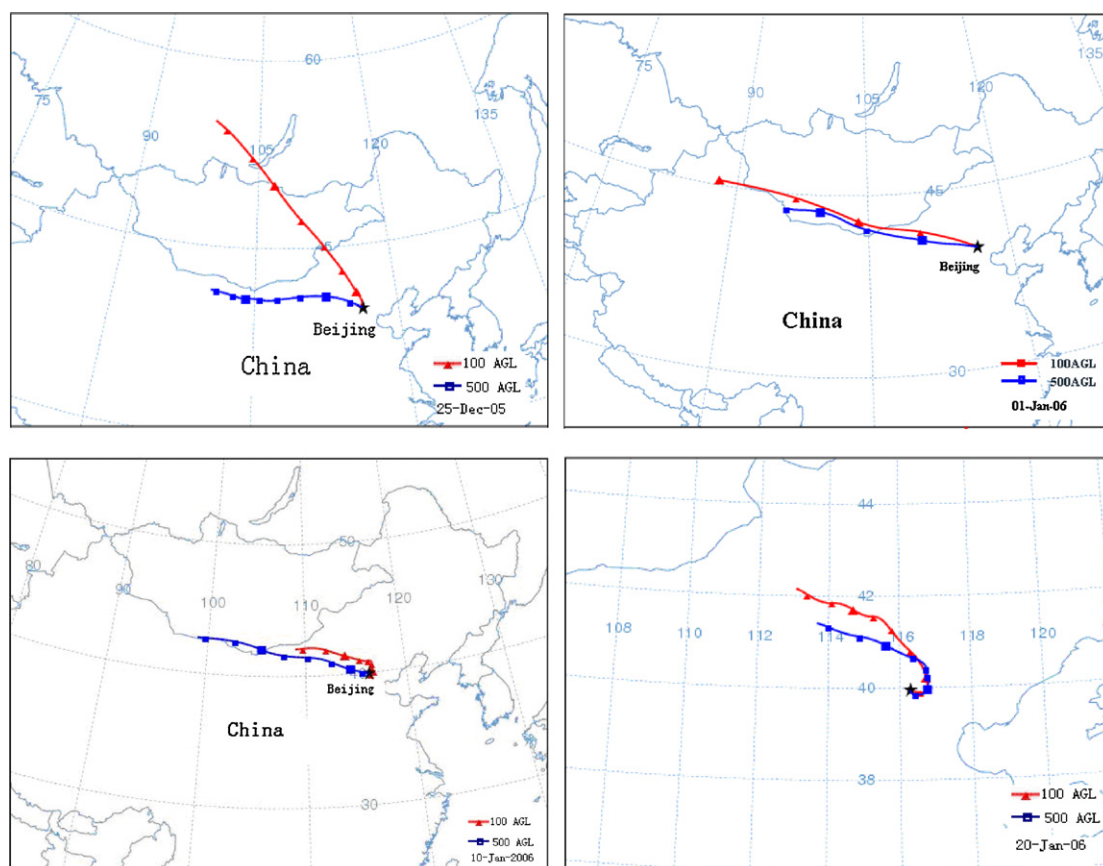


Fig. 2. Typical trajectories (48 h) during sampling periods (AGL: above ground level).

Table 1  
Compounds analyzed ( $\text{ng m}^{-3}$ )

Compounds	MW	PM <sub>2.5</sub> (mean)	FD% <sup>a</sup>	PM <sub>2.5-10</sub> (mean)	FD%
Nap	128(2) <sup>b</sup>	2.20 ± 2.63	55	2.55 ± 3.21	50
Ace	152(3)	0.53 ± 0.46	75	0.51 ± 0.38	75
Acy	154(3)	0.25 ± 0.32	55	0.38 ± 0.48	65
Fl	166(3)	3.84 ± 4.99	70	6.43 ± 7.26	85
Phe	178(3)	11.61 ± 36.28	75	4.36 ± 5.70	70
An	178(3)	1.15 ± 1.72	70	0.7 ± 0.92	70
Flu	202(4)	185.51 ± 235.59	100	96.91 ± 125.36	100
Pyr	202(4)	16.16 ± 25.34	100	13.07 ± 13.59	100
BaA	228(4)	12.34 ± 22.76	100	5.65 ± 5.30	95
Chr	228(4)	8.27 ± 14.09	95	5.58 ± 6.22	90
BbF	252(5)	35.65 ± 56.61	95	20.38 ± 26.70	95
BkF	252(5)	53.11 ± 167.24	90	37.99 ± 73.67	95
BaP	252(5)	17.83 ± 32.74	100	8.39 ± 8.99	100
InP	278(5)	27.64 ± 37.17	100	17.78 ± 18.86	95
DBA	276(6)	6.27 ± 6.85	100	4.08 ± 4.24	95
BghiP	276(6)	25.19 ± 38.70	95	19.18 ± 21.02	95
∑ PAHs		407.55 ± 468.36		243.96 ± 207.93	

<sup>a</sup> FD stands for frequency of detection.

<sup>b</sup> The numbers in brackets represent the number of rings.

or Mongolia. From December 20, 2005 to January 19, 2006, the sampling sites in northern part of Beijing were in upwind of the city. This suggests that the atmosphere in Beijing is a superposition of transported polluted air (from Hebei and Inner Mongolia or Shanxi in some cases) on locally produced pollutants. And the southern sampling site, which was in downwind of the city in sampling period, would susceptible to heavier pollution (refer to Section 3.1).

### 3.2. PAHs concentrations

The total PAHs concentrations (sum of 16 EPA priority PAHs) of PM<sub>2.5</sub> and PM<sub>2.5-10</sub> were in the range of 4.5–1042.3  $\text{ng m}^{-3}$  and 10.1–732.6  $\text{ng m}^{-3}$ , respectively. The highest concentration of PM<sub>2.5</sub> was found at an industrial center (site bj-11) in southwest of the city while that of PM<sub>2.5-10</sub> was discovered in a commercial area (bj-19) of the southeast. The lowest concentration detected was at a residential area (site bj-1) and a commercial zone (bj-2) in the northwest part for PM<sub>2.5</sub> and PM<sub>2.5-10</sub> separately. Average concentration of individual PAHs in PM<sub>2.5</sub> and PM<sub>2.5-10</sub> (Table 1) varied from 0.25 and 0.38  $\text{ng m}^{-3}$  for Acy to 185.5 and 96.9  $\text{ng m}^{-3}$  for Flu. BaP, known as the most carcinogenic PAHs, had mean value of 17.8  $\text{ng m}^{-3}$  for PM<sub>2.5</sub>, which exceeded 0.01  $\mu\text{g m}^{-3}$ , the state recommended air quality standard for BaP as day average (GB3095-1996).

The current concentration of 16 EPA-PAHs in PM<sub>2.5</sub> was around 1.4-fold of the reported Beijing PM<sub>2.5</sub> samples collected in winter of 2001 (228.9 ± 76.1  $\text{ng m}^{-3}$ ) [14] and 1.5–2.5-fold of that in November of 2002 (AES, suburban, 275 ± 204  $\text{ng m}^{-3}$ ; PKU, urban, 147 ± 123  $\text{ng m}^{-3}$ ) [12]. To investigate the interannual difference of individual PAHs, least significant difference (LSD) method was used. 10 PAHs of PM<sub>2.5</sub> in the three sampling years were employed for (Table 2) multiple comparison.

The results revealed An, Pyr, BaA, Chr in this study decreased statistically significant ( $p < 0.05$ ) with reference to those in

November 2001, while Flu, BbkF, InP and BghiP increased evidently. And Phe and BaP had little difference ( $p > 0.05$ ) between the two sampling durations. When compared to the results in December 2002, BaA and Chr descended notably while Flu, BbkF and InP increased markedly, the others had little difference statistically. Simcik et al. [16] pointed out that BaA, Chr, Pyr, Phe and Flu are associated with combustion of natural gas and BaA have been considered as tracer for this source. Kulkarini and Venkataraman [17] related the presence of Flu, Pyr, Chr and InP with vehicular emissions. Besides, they think Chr, BaP, Flu and Pyr could be related with wood and natural gas combustion. Park et al. [18] associated Flu, Pyr, An and Phe with industrial combustion of oil, incineration and biomass burning. According to these studies, natural gas burning, vehicular emissions and industrial combustion of oil would be the reasons for

Table 2  
Concentrations of 10 PAHs ( $\text{ng m}^{-3}$ ) in PM<sub>2.5</sub> of 3 years

	Sampling duration		
	2001.12 <sup>a</sup> Campus <sup>c</sup>	2002.11 <sup>b</sup> One urban site and one suburban site <sup>c</sup>	2005.12 (this study) Twenty sites in the city <sup>c</sup>
Phe	13a	7.5b	11.6ab
An	4a	1.75b	1.2b
Flu	32b	17c	185.5a
Pyr	28a	19b	16.2b
BaA	25a	20.5b	12.3c
Chr	19a	22a	8.3b
BbkF	39b	37.5b	88.8a
BaP	13a	14a	17.8a
InP	10b	14b	27.6a
BghiP	12c	19.5ab	25.2a

Means followed by different letters differ at  $p < 0.05$  (LSD), letters beside means refer to the difference between years.

<sup>a</sup> Huang et al. [14].

<sup>b</sup> Feng et al. [12].

<sup>c</sup> Sampling sites.

individual PAHs change in the 4 years (2001–2005), and this is also in accordance with the changes in Beijing, such as energy structure change, the increase of cars, etc. In fact, heating in Beijing changed gradually from coal to natural gas from 2001 under the city's whole layout. It is necessary to point out that concentration change of three carcinogenic PAHs, BaA and Chr decreased significantly in spite that BaP changed little between these years, which suggesting the tendency on improvement of air quality.

One of the main focuses of this study is to check the current status of PAHs pollution in different city function zones of Beijing. Five major zones (industrial center, commercial area, residential area, village and park) were divided according to surrounding environment of the sampling sites. Generally, commercial and industrial area showed high level of PAHs contamination. For  $PM_{2.5}$ , the average concentration of PAHs was in the order of industrial center > village > commercial area > park > residential area, while the order in  $PM_{2.5-10}$  was commercial area > residential area > village > park > industrial center (supporting material, Table S-2). It should be noted that the  $\Sigma 16$  PAHs of a crossroad (site 12, not included in the five zones) was 394.87 and 457.63 for  $PM_{2.5}$  and  $PM_{2.5-10}$ , respectively. Considering the typicality of the site, the PAHs concentration was followed industrial center > village > commercial area > crossroad > park > residential area for  $PM_{2.5}$  and crossroad > commercial area > residential area > village > park > industrial center for  $PM_{2.5-10}$ . Thus, the management of industrial center, commercial area, village and crossroad should be strengthened and further measures should be taken because of their high loads of PAHs.

### 3.3. PAHs profiles

Figs. S-1 and S-2 displays the relative PAHs constituent in both  $PM_{2.5}$  and  $PM_{2.5-10}$ . For  $PM_{2.5}$ , Flu was the dominant PAH, contributing about 45% of the 16 PAHs, followed by BkF (13%), BbF (9%), InP (7%) and BghiP (6%), while the order in  $PM_{2.5-10}$  was Flu (41%), BkF (16%), BbF (8%), BghiP (8%) and InP (7%). BaP consisted 4% and 3% of  $\Sigma 16$  PAHs for  $PM_{2.5}$  and  $PM_{2.5-10}$ , respectively.

According to previous studies [16–18], there are multiple sources that produce Flu, natural gas, biomass and coal combustion, vehicles, etc. In recent years, the fact that usage of coal decreased while natural gas was increasingly used as a clean energy in heating, cooking, vehicles, etc., can explain why the percentage of Flu is so high.

It was obvious that 4–6 ring PAHs were predominant in both  $PM_{2.5-10}$  and  $PM_{2.5}$ . Nevertheless,  $PM_{2.5}$  had higher value in 4–6 ring PAHs and total 16 PAHs than  $PM_{2.5-10}$ . This reflected PAHs with higher rings tend to be strongly absorbed by fine air particles, which was similar to research of Sanderson and Farant [19].

The 4–6 ring PAHs, namely BaA, Chr, BbF, BkF, BaP, InP, DBA, BghiP are considered to have carcinogenic effects [20]. The results showed  $\Sigma$ carcinogenic PAHs accounted for 45.7% and 48.8% in total PAHs of  $PM_{2.5}$  and  $PM_{2.5-10}$ , indicating a potential risk for human health.

### 3.4. Spatial distribution of PAHs

The spatial distribution of the 16 PAHs (Fig. 3) showed that both  $PM_{2.5}$  and  $PM_{2.5-10}$  levels were relatively higher in south-east sites of the city, in which laid the Beijing Coking Plant and a coal-heating residential region. This also supported previous meteorological analysis that southern part of Beijing may suffer more pollution.

$\Sigma 16$  EPA-PAHs distribution in PM was similar to that in soil of Beijing [20], which somewhat approved the PAHs in soils come from atmospheric deposition, but need further research. Besides, distribution of BaP had resemblance to distribution of 16 PAHs. Correlation analysis (Tables S-3 and S-4) between BaP and  $\Sigma 16$  EPA-PAHs revealed the correlation between them is significant at 0.01 level.

Because the proportion of 4–6 ring PAHs in total PAHs can reflect the carcinogenic risk of the region, we compared percentage of 4–6 ring PAHs in different regions. The results revealed the southern part of the city had rather higher percentage of 4–6 ring PAHs in both  $PM_{2.5}$  (97.2%) and  $PM_{2.5-10}$  (94.9%) than the northern part (87.6% and 92.5% for  $PM_{2.5}$  and  $PM_{2.5-10}$ ), which suggested more health risk lies in the southern part. On the other hand, this maybe related with the energy strategy switch from coal to natural gas and liquefied petroleum gas, etc., in the northern part. However, the coking plant stopped production on July 4th 2006. This will reduce 2.96 Mt coal consumptions each year and help improve air quality of southern part.

### 3.5. Source apportionment

In general, petrogenic and pyrolytic sources are considered the two main origins of PAHs released into the environment. The former refers to processes related to petroleum products, such as oil spills, etc. [21], while the later include combustion courses like fossil fuel combustion, forest fires, biomass burning, smelters, automobile exhaust, etc. [20]. Concretely, PAHs originated from combustion contains more 4–6 ring PAHs [22], and those comes from petroleum contains relative higher proportion of 2–3 ring PAHs [23]. It should be noted that of the combustion derived PAHs, low-molecular-weight PAHs were mostly from low to moderate temperature while high-molecular-weight PAHs produced at high temperatures. Based on the knowledge, there are two common means to discriminate the origins of emissions of PAHs in the atmospheric samples, compositional analysis and principal component analysis (PCA).

#### 3.5.1. Compositional analysis

The ratio of anthracene to anthracene plus phenanthrene ( $An/(An + Phe)$ ) and fluoranthene to fluoranthene plus pyrene ( $Flu/(Flu + Pyr)$ ) are commonly suggested indexes for identifying the petroleum or combustion sources of PAHs. In detail, the value of  $An/(An + Phe)$  less than 0.1 and  $Flu/(Flu + Pyr)$  less than 0.4 are characteristic of petroleum, and the opposite is the combustion [20,22]. For  $PM_{2.5}$ ,  $An/(An + Phe)$  ratio was between 0 and 1, with an average value of 0.3 and  $Flu/(Flu + Pyr)$  ranged from 0.07 to 0.99 with mean of 0.66. For  $PM_{2.5-10}$ ,  $An/(An + Phe)$  was in the range of 0–1 with average of 0.34 and

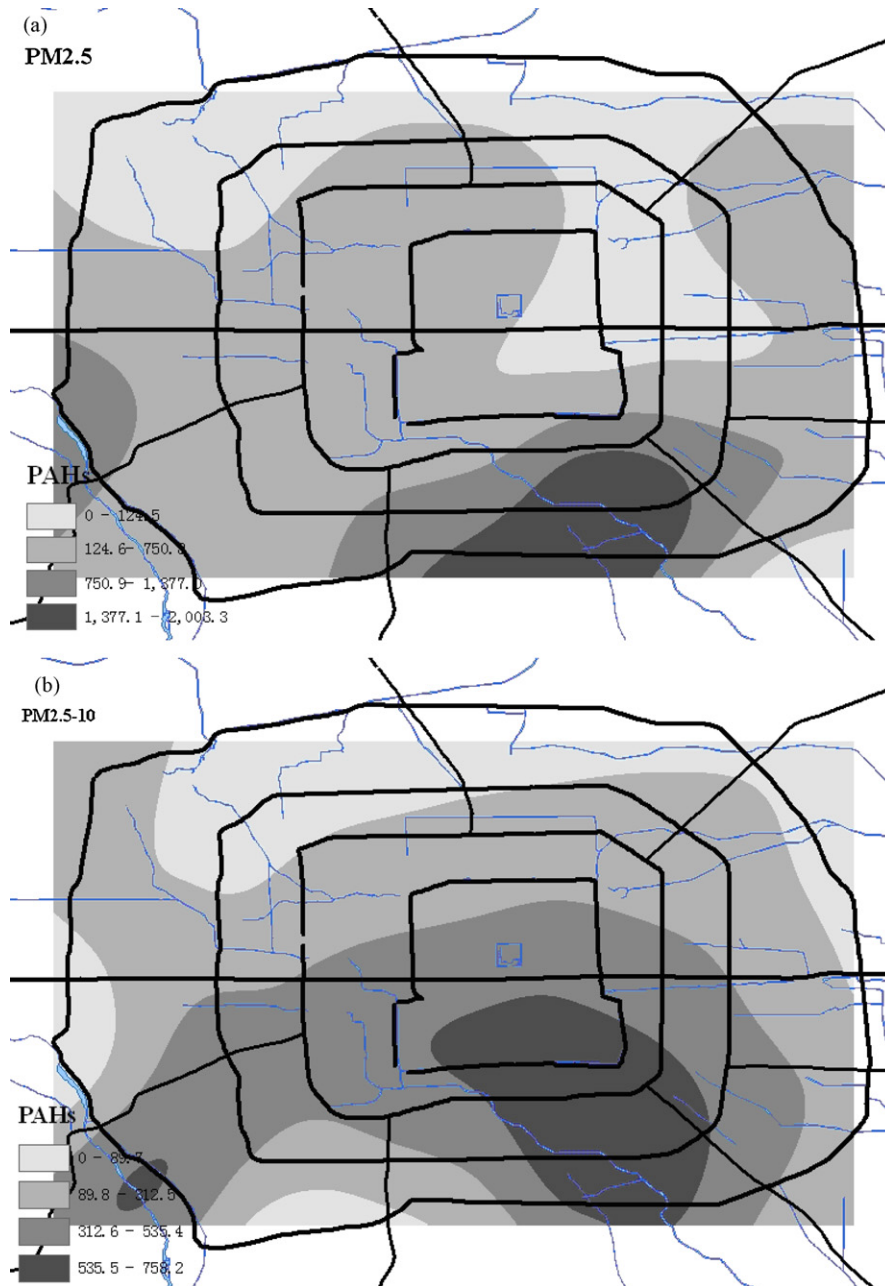


Fig. 3. The spatial distribution of 16 EPA-PAHs in PM<sub>2.5</sub> (a) and PM<sub>2.5-10</sub> (b) in Beijing.

Flu/(Flu + Pyr) was 0.01–0.99 with 0.66 as the mean. This denoting predominant of combustion sources in PM of Beijing. When referenced the two ratios (An/(An + Phe) and Flu/(Flu + Pyr)), of the five city zones mentioned above, they all suffered from combustion and the crossroad showed dependency on the nature of petroleum (Table 3).

The ratios of BaA/Chr, BbF/BkF and InP/BghiP are considered as indicators to discriminate between pyrogenic PAH [24]. However, no clear tendency on sources is found from the mean BaA/Chr ( $5.14 \pm 11.49$  and  $2.35 \pm 3.63$  for PM<sub>2.5</sub> and PM<sub>2.5-10</sub>), BbF/BkF ( $4.93 \pm 10.67$  and  $4.66 \pm 8.39$  for PM<sub>2.5</sub> and PM<sub>2.5-10</sub>) and InP/BghiP ( $4.69 \pm 13.17$  and  $2.75 \pm 6.91$  for PM<sub>2.5</sub> and PM<sub>2.5-10</sub>) values. These values are relatively close to recommended values for coal/coke combustion (BaA/Chr

1.0–1.3, BbF/BkF 3.8–4.2, InP/BghiP 1.0–1.2) according to the ratios of different city zones (Table 3). Because the ratios have big variation in 20 sampling sites, it is not realistic to relate PM PAHs with one or two sources but a mixture of sources that are not well defined. Thus, we could preliminary conclude there exist different origins of PAHs due to the energy structure change of the city though coal weighs most. In addition, the ratio of InP/(InP + BghiP) has been widely used to distinguish PAHs emission from traffic and coal burning. Ratios of 0.18, 0.37 and 0.56 were reported for gasoline vehicles, diesel vehicles and coal burning, respectively [12,13,25]. In this study, the ratio of InP/(InP + BghiP) was between 0.34 and 1 with mean of 0.6 for PM<sub>2.5</sub>, 0.29 to 0.97 with 0.51 as average for PM<sub>2.5-10</sub>, indicating a mixed emission of engine exhaust and coal burning in winter

Table 3  
Ratios for PAHs attributed to specific sources

	An/(An + Phe)	Flu/(Flu + Pyr)	BaA/Chr	BbF/BkF	InP/BghiP	InP/(InP + BghiP)
Petrogenic	<0.1 <sup>a,b</sup>	<0.4 <sup>b</sup>				<0.2 <sup>b</sup>
Heavy fuel combustion	>0.1 <sup>a,b</sup>	>0.4 <sup>b</sup>				
Liquid fossil fuel combustion		0.4–0.5 <sup>b</sup>				0.2–0.5 <sup>b</sup>
Automobiles						
Diesel		0.6–0.7 <sup>b</sup>	0.53 ± 0.06 <sup>f</sup>	1.26 ± 0.19 <sup>f</sup>	0.33 ± 0.06 <sup>f</sup>	0.37 <sup>c,d,e</sup>
Gasoline	0.4 <sup>a</sup>					0.18 <sup>c,d,e</sup>
Coal/coke		>0.5 <sup>b</sup>	1.11 ± 0.06 <sup>f</sup>	3.70 ± 0.17 <sup>f</sup>	1.09 ± 0.33 <sup>f</sup>	0.56 <sup>c,d,e</sup>
Wood		0.74 <sup>b</sup>	0.79 ± 0.13 <sup>f</sup>	0.92 ± 0.16 <sup>f</sup>	0.28 ± 0.05 <sup>f</sup>	
Smelters			0.60 ± 0.06 <sup>f</sup>	2.69 ± 0.20 <sup>f</sup>	1.03 ± 0.15 <sup>f</sup>	
Industrial center						
PM <sub>2.5</sub>	0.13	0.96	1.15	10.10	1.07	0.52
PM <sub>2.5–10</sub>	0.24	0.93	1.14	0.96	0.75	0.75
Residential						
PM <sub>2.5</sub>	0.13	0.95	1.16	1.85	1.11	0.53
PM <sub>2.5–10</sub>	0.06	0.89	1.38	1.29	1.44	1.44
Village						
PM <sub>2.5</sub>	0.36	0.83	1.24	2.98	1.23	0.55
PM <sub>2.5–10</sub>	0.11	0.93	0.88	1.50	0.50	0.50
Park						
PM <sub>2.5</sub>	0.05	0.95	3.56	2.53	1.31	0.57
PM <sub>2.5–10</sub>	0.29	0.64	0.69	0.10	1.10	1.10
Commercial						
PM <sub>2.5</sub>	0.23	0.73	1.68	0.02	0.95	0.49
PM <sub>2.5–10</sub>	0.18	0.92	1.52	0.12	0.80	0.80
Crossroad						
PM <sub>2.5</sub>	0	0.95	0.83	6.58	0.96	0.49
PM <sub>2.5–10</sub>	0.04	0.89	0.71	4.19	0.68	0.41

<sup>a</sup> Budzinski et al. [22].

<sup>b</sup> Li et al. [20].

<sup>c</sup> Grimmer et al. [25].

<sup>d</sup> Feng et al. [12].

<sup>e</sup> Hou et al. [13].

<sup>f</sup> Dickhut et al. [24].

aerosol of Beijing. Referenced the four ratios, industrial center, residential area, village and park had been influenced by coal combustion while the crossroad affected much by automobiles (Table 3). The ratio also suggested that coal burning had heavier influence on the city. Thus, reduction of coal consumption especially its shift to clean energy may be work in air PAHs controlling of the city. And the industrial center, villages and crossroad should be monitored at emphasis.

### 3.5.2. PCA

To get further insight of the data, PCA was performed. Four principal components (PC1, PC2, PC3, PC4) were identified based on PAH loadings and accounted for 87.7% and 82.2% of the total variances for PM<sub>2.5</sub> and PM<sub>2.5–10</sub> (Tables S-5 and S-6), respectively.

**3.5.2.1. PCA for PM<sub>2.5</sub>.** For the particulate fraction, PC1 was dominated by high-molecular-weight PAHs and had high load of Pyr, BaA, Chr, BkF, BaP, InP, DBA and BghiP. These compounds gave strong correlation with the total ΣPAHs concentration ( $r^2 > 0.75$ ). Among these compounds, Pyr are components of

fossil fuels (especially coal and diesel oil) and a portion of them related with combustion. BaP is often resulted from catalyst and noncatalyst automobiles. BaA and Chr are often resulted from the combustion of both diesel and natural gas. InP and BghiP are usually associated with indicator of traffic emission. However, BaA, Pyr and Chr are also considered as the character of coal combustion. Thus, PC1 reflected the character of high temperature combustion and illustrated the PAHs originate from coal, natural gas and traffic emission. PC2 were represented by low-molecular-weight PAHs and had strong significant correlation with Na, Ace, Flu, therefore it could be ascribed as low to moderate temperature combustion and petrogenic sources. PC3 was explained by Phe and An while PC4 was characterized by BbF.

PC1 and PC2 collectively accounted for 69% of the total variance, and representing 54% and 15% of the variances. PC1 and PC2 score plots (Fig. 4(1)) for sampling sites display that most of samples except those from open area (site bj-8, bj-10, bj-11 and bj-19) are gathered near the origin, suggesting a relative identical compositional patterns among the samples and displayed both high temperature and low to moderate temper-

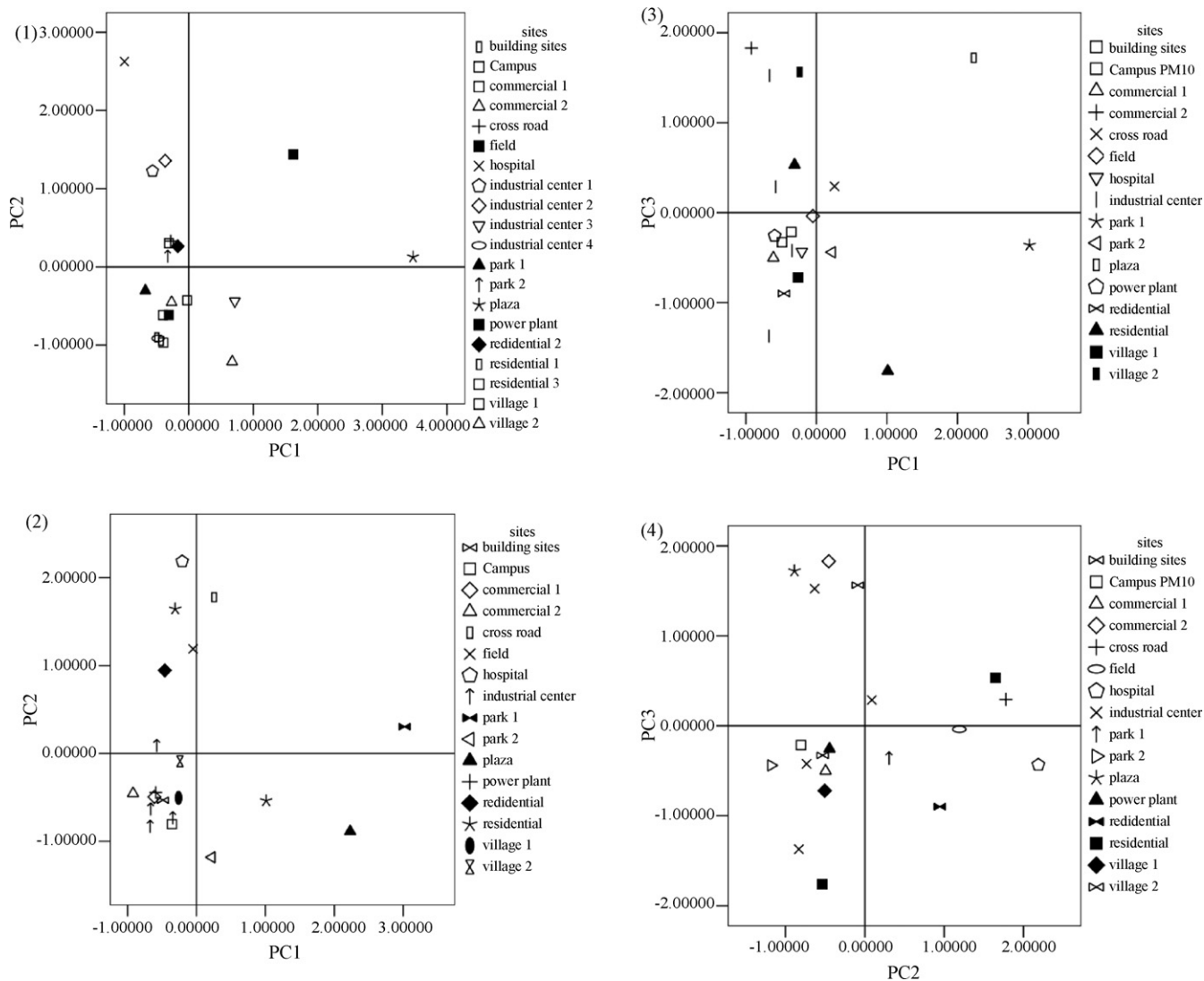


Fig. 4. Comparison of principal components, PC1 (high temperature combustion) and PC2 (low to moderate temperature combustion and petrogenic) in  $PM_{2.5}$  (1) and PC1 vs. PC2 (2), PC1 vs. PC3 (3) and PC2 vs. PC3 (4) in  $PM_{2.5-10}$  for different type of sampling sites.

ature combustion sources for the  $PM_{2.5}$  PAHs in Beijing. The results also agreed with previous analysis by different ratios of PAHs isomers.  $PM_{2.5}$  samples collected from hospital yard and two industrial centers had high PC2 values, reflecting contributions from low to moderate combustion or petroleum. Instead, those from a plaza contributed much to PC1, indicating high temperature sources.

**3.5.2.2. PCA for  $PM_{2.5-10}$ .** For this fraction, PC1 explains about 51% of the variance with a high load of Pyr, Chr, BkF, BaP, InP, DBA and BghiP, which are in particulate phase. According to what discussed above, it is not possible to associate PC1 with one or two sources but to a mixture of combustion sources. However, it is more appropriate that these compounds are attributed to coal combustion and biomass burning. PC2 representing 13% of the variances and has a high load for BbF and Fl. The diesel emission is characterized by the presence of BbF and Fl [26]. Thus, PC2 is better related with vehicular emissions. PC3 was represented by Flu and BaA, which are tracers for natural gas

combustion [16] and PC4 was characterized by Na, Ace and Acy.

PC1 and PC2 accounted for 63% of the total variance, their score plots for sampling sites (Fig. 4(2)) showed most sites influenced by both two sources. Plaza and park had high PC1 values, indicating the coal and biomass burning sources while crossroad, hospital, one of residential area had high PC2 values showing the influence of vehicle emissions.

Score plots of PC1 versus PC3 (Fig. 4(3)) showed both coal and biomass combustion and natural gas sources of  $PM_{2.5-10}$  in most sites except for two industrial centers, a residential area, a village and a commercial center, which suffered more from natural gas, and a plaza and a park impact much by coal and wood burning.

PC2 and PC3 score plots (Fig. 4(4)) displayed the sampling sites clustered into three groups, most of them gathered near the origin, indicating both automobile and natural gas origin. Another group represented by industrial center, commercial center, village and plaza showed the natural gas source. Crossroad



and hospital reflected the impact of vehicle. Besides, two residential areas showed the impact of the two sources, respectively, and this in accordance with the fact natural gas used for heating and increasing vehicles of residential areas in Beijing.

It is reported that persistent organic pollutants (POPs) including PAHs were subject to atmospheric long-range transport, which lead to the pollution of remote sites like Arctic [27,28]. Thus, we need to think whether the PAHs observed in Beijing was from long-range transport.

In fact, 5–6 ring PAHs are nonvolatile organics and exist only particle phase, while 4 ring PAHs are semivolatile and occur in both particle and gas phase. Some research reported that particle bound PAH were difficult in long-range transport than low particle bound ones [29]. It was found in three Arctic sampling sites 3–4 ring PAHs (Fl, Phe, Flu and Pyr) were predominant, while 5–6 ring PAHs would have been removed before reaching the Arctic [27,29]. Simoneit et al. [30] hypothesized that semivolatile PAH (4 ring PAHs) were the predominant components in the distribution of PAH from long distance transport. Hou et al. [13] reported using the ratio of 4 ring PAHs (Flu, Pyr, BaA and Chr) to 5–6 ring PAHs (BbF, BkF, BaP, DBA, BghiP and InP) to evaluate the sources of PAH, i.e., the higher the ratio indicated longer distance of transport while the lower ratio implied the PAH might mostly from local emission. Fig. S-3 displays the ratio of PAH (4)/PAH (5,6) in PM<sub>2.5</sub> and PM<sub>2.5–10</sub>, and the average value was in the range 0.07–18.06 and 0.14–34.6, respectively. Among 20 sampling sites, most had ratio of PAH (4)/PAH (5, 6) less than 1 in PM<sub>2.5</sub> and PM<sub>2.5–10</sub>, indicating their local sources of PAHs. The sites had much higher the ratios were in campus, park, residential area for PM<sub>2.5</sub> and villages and newly developed industrial center for PM<sub>2.5–10</sub>, which were dominated by 4 ring PAH and relatively remote sites in comparison with city center. Hence, according to the conclusion of Hou et al., we can preliminary deduce that PAH in these sites were likely from atmospheric transport of city plumes or other industrial centers outside Beijing. Although PM<sub>2.5</sub> statistically significant ( $p < 0.01$ ) correlated with PM<sub>2.5–10</sub> in Beijing aerosol samples, their PAH (4)/PAH (5, 6) at some sites had much difference (Fig. S-3). This is probably the result of 5–6 ring PAHs easier bound to fine particles than 4 ring PAHs.

#### 4. Conclusions

The investigation showed PAHs levels in PM were relatively high in comparison with previous study on Beijing. We compared concentrations of 10 PAHs (Phe, An, Flu, Pyr, BaA, Chr, BbF, BaP, InP, BghiP) in PM<sub>2.5</sub> between the winter of 2001–2002 and 2005–2006. The results showed significant increase of Flu, BbF and InP, decrease of BaA and Chr but no evident changes on the others, which reflect the influence of natural gas, vehicular emission, etc. This also indicates the effect of Beijing's energy structure change from mainly on coal to cleaner energy. Although, PM<sub>2.5</sub> had higher PAHs concentrations than PM<sub>2.5–10</sub>, they had similar spatial distribution of total PAHs and BaP concentrations. The PAHs concentrations in southeast part were higher than other parts of the city, and the northern part had lowest values. Concentrations in different city zones showed

industrial center, commercial area, village and crossroad were four heavily PAHs polluted areas. Flu was predominant in PM PAHs compared with previous studies, which could be associated with increasing use of natural gas as clean energy. The result of compositional analysis and PCA displayed the contribution of combustion, not one or two types but a mixture, on PAHs in PM though coal still had heavier impact.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jbiotec.2007.12.013.

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