# Distribution and Source Apportionment of Polycyclic Aromatic Hydrocarbons from Atmospheric Particulate Matter PM<sub>2.5</sub> in Beijing

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#### ABSTRACT

A total of 11 PM<sub>2.5</sub> samples were collected from October 2003 to October 2004 at 8 sampling sites in Beijing city. The PM<sub>2.5</sub> concentrations are all above the PM<sub>2.5</sub> pollution standard (65  $\mu$ g m<sup>-3</sup>) established by Environmental Protection Agency, USA (USEPA) in 1997 except for the Ming Tombs site. PM<sub>2.5</sub> concentrations in winter are much higher than in summer. The 16 Polycyclic aromatic hydrocarbons (PAHs) listed as priority pollutants by USEPA in PM<sub>2.5</sub> were completely identified and quantified by high performance liquid chromatography (HPLC) with variable wavelength detector (VWD) and fluorescence detector (FLD) employed. The PM<sub>2.5</sub> concentrations indicate that the pollution situation is still serious in Beijing. The sum of 16 PAHs concentrations ranged from 22.17 to 5366 ng m<sup>-3</sup>. The concentrations of the heavier molecular weight PAHs have a different pollution trend from the lower PAHs. Seasonal variations were mainly attributed to the difference in coal combustion emission and meteorological conditions. The source apportionment analysis suggests that PAHs from PM<sub>2.5</sub> in Beijing city mainly come from coal combustion and vehicle exhaust emission. New measures about restricting coal combustion and vehicle exhaust must be established as soon as possible to improve the air pollution situation in Beijing city.

Key words: distribution and occurrence, source apportionment, PM<sub>2.5</sub>, polycyclic aromatic hydrocarbons (PAHs), HPLC, Beijing city

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### 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are generated mainly by incomplete combustion of organic materials from both natural and anthropogenic sources (Cincinelli et al., 2003; Zeng, 2002). While the natural sources such as forest fires and volcanic eruptions may be important during specific times (e.g., dry seasons with large forest fires), in large cities like Beijing, fossil fuel combustion from industrial processes, waste incineration, residential heating, and motor vehicles have been considered as the major source of PAHs (Dan et al., 2004). Because particulate organic compounds have carcinogenic and mutagenic effects that are harmful to human life (IARC, 1991; USEPA, 1992), it has been suggested that controlling the level of atmospheric carcinogens is crucial for improving the air quality. Because one-third of the 1000 types of carcinogens are PAHs that are most harmful and are mainly produced by human activities (Dong, 2004), USEPA listed 16 PAHs as priority-controlled pollutants (USEPA, 1994).

Generally, PAH compounds with two or three aromatic rings are released mainly into the gas phase, while those containing three or more aromatic rings are associated with particulate matter (PM) emission (Liu et al., 2006). Particle-associated PAHs are primarily absorbed on fine particles, about 70%–90% of which are on PM<sub>2.5</sub> (Sikalos, 2002; Wei, 2003; Liu et al., 2003; Yang et al., 2000). For example, benzo[a]pyrene is ab-

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sorbed mainly on the particulate matter whose grain sizes are less than 1.1  $\mu$ m (Yassaa and Meklati, 2001; Ochenkuhn-Petropoulou et al., 2003; Dong, 2004). And USEPA established the corresponding pollution standard of PM<sub>2.5</sub> in 1997 (USEPA, 1997). The quantitative compositions of PAHs in air-borne particulates have been widely reported and the major emission sources are fossil fuel and biomass burning (waste incineration, firewood and straw) (Harrison et al., 1996; Wu et al., 2005). Atmospheric concentration of PAHs in the urban atmosphere is commonly higher than those in rural areas because of the emission from motor vehicle, residential heating, and domestic fuel combustion (Schnelle-Kreis et al., 2001).

In order to establish the relation between concentrations of the 16 PAHs and their temporal and spatial changes, we have studied 11  $PM_{2.5}$  samples that were collected from October 2003 to October 2004 at 8 sites across Beijing city. And the 16 PAHs were completely identified and quantified with the aid of high performance liquid chromatography (HPLC). We report here the distribution and source apportionment of the 16 PAHs from the atmospheric particulates  $PM_{2.5}$  in the city.

#### 2. Materials and methods

#### 2.1 Sampling

We used the sampler designed by the Research Institute of Environmental Sciences of China that has the flow velocity of 77.49 L min<sup>-1</sup>. The sampler was designed to collect TSP,  $PM_{10}$  and  $PM_{2.5}$ . Filters of the sampler are made of fiberglass ( $\emptyset$ 90 mm) that was roasted in a muffle furnace at 500°C for four hours to avoid pollution from remnant organic matter. Filters were weighed in a clean lab at 50% humidity before and after sampling. The mass difference before and after sampling is the mass of the particulate matter obtained during the collection period. The glass fiber filter was weighted on a micro-balance (Sartorius) accurate to 0.001 mg.

The 11 samples were collected from October 2003 to October 2004. Eight sampling sites were selected from the entire city of Beijing (Table 1). These 8 sites were carefully chosen in order to form five distinct categories as follows: shopping centres, Zhongguancun and Qianmen; a residential area, China University of Geosciences (Beijing); industrial areas, Shougang coking and its east gate, Yanshan Petrochem; an artery, Chengfu Road Crossing; a clear band, Ming Tombs (Fig. 1). Three sampling sites (Yanshan Petrochem, Zhongguancun and Qianmen) have been chosen for seasonal variation measurements. The sampling lasted 72 hours in each site to obtain enough organic matter. During the sampling period, filters were changed every two hours. A total of 36 filters with particulate matter  $PM_{2.5}$  were collected from each site. The temperature, humidity, and wind velocity were also recorded during sampling. The filters were immediately put into refrigerators after they were conditioned in a drier at room temperature and humidity for 2 h and were weighted.

## 2.2 Sample extraction

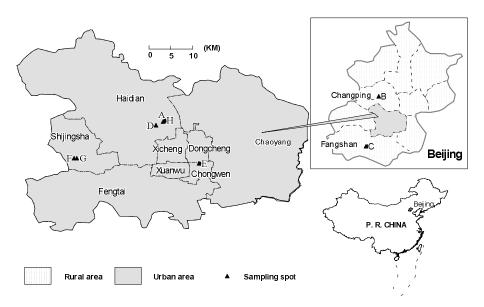
The 36 filters collected from each site were put together as a composite sample. Organic components were extracted in a soxhlet extractor with re-distilled chloroform that was put into a water bath for 72 hours at a temperature of 78°C. The extracted organic solution was condensed, dried in a nitrogen stream, and weighted to obtain the soluble organic matter. Following the standard method (SY5119-86) provided by the former Ministry of Petroleum Industry of China, extracted organic matters were precipitated to remove asphaltene with normal hexane (Liu et al., 2003). The concentrated extracts were then separated into three types (saturated hydrocarbons, aromatic hydrocarbons, and polar organics) by alumina-silica gel (60–80 mesh, activated at 130°C for at least 6 h) chromatography column and their contents were determined as the accurate weighing. For comparison, a blank filter was extracted following the same process during extraction of each sample.

Extracted aromatic hydrocarbon components were dissolved with methanol (chromatographically pure grade) to 1 mL in a brown bottle and were put into a refrigerator before the HPLC analysis.

The recovery efficiency of PAHs ranges from 85.1% (Nap) to 103.2% (Fla), and the RSD ranges from 4.31% (Flu) to 9.93% (Ind) (Gao et al., 2006). The detection limit ranges from 0.29  $\mu$ g L<sup>-1</sup> (Bkf) to 50.6  $\mu$ g L<sup>-1</sup> (Nap) (Gao et al., 2006).

#### 2.3 HPLC analysis

The 16 PAHs listed as priority pollutants by USEPA are analyzed, nine of which, Napthalene (Nap), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fla), Chrysene (Chr), Benzo[b]fluoranthene (Bbf), Benzo[k]fluoranthene (Bkf), Benzo[ghi]perylene (Bghi), and Indeno[1,2,3-cd]pyrene (Ind), were purchased from the Chinese Standards Center, three of which, Acenapthylene (Acel), Benz[a]anthracene (Baa) and Dibenzo[a,h]anthracene (Dah), were purchased from AccuStand Inc., and four of which, Acenaphthene (Ace), Fluorene (Flu), Pyrene (Pyr), and Benzo[a]pyrene (Bap), were purchased from ChemService Inc., respectively. Their purity ranges from 97.7% to 99.5%, their solvent is MeOH, except for Baa and Dah (CH<sub>2</sub>Cl<sub>2</sub>).



**Fig. 1.** Sketch map for sampling location (A: Chengfu Road Crossing; B: Ming Tombs; C: Yanshan Petrochem; D: Zhongguancun; E: Qianmen; F: East gate of Shougang; G: Shougang; H: China University of Geosciences).

 Table 1. Locations of sampling and basic characteristics.

Sampling site	Sampling time	General aspects of sampling sites
Site A: Chengfu Road Crossing	21–26 Sep. 2004	2 m away from the arterial road, heavy traffic
Site B: Ming Tombs	10–13 Oct. 2004	Fairy Farm, about 5 km away from Ming Tombs
Site C: Yanshan Petrochem	10–13 Nov. 2003	The second floor of a building belonging to
	10–13 Jun. 2004	Polypropylene Plant in Yanshan Petrochem
Site D: Zhongguancun	22–28 Oct. 2003	Close to the north gate of Zhonghai electronic
	10–13 May 2004	market, high population density, regular cooking
		in the open air, heavy traffic
Site E: Qianmen	31 Oct.–2 Nov. 2003	The third floor of the Qingxiang Hotel, high population
	28–31 May 2004	density, regular cooking in the open air
Site F: East gate of Shougang	21–24 Nov. 2003	About 100 m away from the east gate of Shougang
		Steel & Iron Co.
Site G: Shougang coking plant	14–17 Nov. 2003	At the top of a 200 kg coking oven in Shougang
		Technology Center
Site H: China University	7–10 Dec. 2003	At the top of an experimental building in the
of Geosciences (Beijing)		China University of Geosciences (Beijing) with many
		fume cupboards around it

The apparatus used in the experiment was HPLC (Agilent 1100) with two detectors, FLD and VWD. Several parameters were tested for multiple times to determine the optimal conditions for the analysis of the 16 PAHs. The optimal conditions for a complete separation and detection of the 16 PAHs are as follows.

Chromatographic column: reversed phase  $C_{18}$  column, 250 mm long and 4.6 mm i.d., column temperature 40°C; mobile phase: methanol (chromatographically pure grade) 80% and de-ionized water 20% (the optimum mobile phase attained from several experiments); flow rate: 1 mL min<sup>-1</sup>; VWD: detection wavelength 254 nm; FLD: a series of wavelength programs were set for FLD (Gao et al., 2006).

The identification and quantification of the 16 PAHs were performed using external reference standards. Five concentration gradients of mixed 16 PAHs standards were prepared and analyzed with the aid of HPLC. Based on the relation between the peak area and concentration, a standard curve can be mapped out. Since the excitation and emission maxima are different for each PAH, different detectors and detection wavelengths were adopted for optimal results. The 10 PAHs (Nap, Acel, Ace, Flu, Phe, Ant, Fla, Pyr, Baa and Chr) were chosen to be detected by VWD and the other 6 PAHs (Bbf, Bkf, Bap, Dah, Bghi and Ind) de-

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Sampling sites	$PM_{2.5}$	Soluble organics	Aromatic hydrocarbons
Site A	124.02	31.90	4.16
Site B	24.05	10.58	0.40
Site C	87.13	24.99	1.14
Site D	83.36	36.47	2.80
Site E	191.23	47.72	3.24
Site F	220.16	61.60	2.01
Site G	189.66	89.62	12.02
Site H	111.04	43.73	4.17

**Table 2.** Comparison of PM<sub>2.5</sub> with concentrations of organics in it ( $\mu$ g m<sup>-3</sup>).

tected by FLD in order to achieve the optimal effect, because the 10 PAHs can get the highest detection and resolution from VWD, while the other 6 PAHs can achieve the highest resolution from FLD after complete comparison (Gao et al., 2006). The correlation coefficients are all above 0.99.

According to the sample injection standard recommended by Agilent, injection of samples was three times the quantity intercepted by the quantitative cycle (20  $\mu$ L). Characterizing the retention time and quantifying the peak area, the 16 PAHs in PM<sub>2.5</sub> were successfully detected.

## 3. Results and discussions

# 3.1 Concentration and composition of organics from $PM_{2.5}$

As is shown in Table 2, the PM<sub>2.5</sub> concentrations are all above the PM<sub>2.5</sub> pollution standard (65  $\mu$ g m<sup>-3</sup>) established by USEPA in 1997, except for the Ming Tombs site. The sum of soluble organics in PM<sub>2.5</sub> ranged from 10.58 to 89.62  $\mu$ g m<sup>-3</sup>. However, the total soluble organics from TSP in Beijing city in 1999 ranged from 2.7 to 48  $\mu$ g m<sup>-3</sup> (Zeng et al., 2001), which indicates that the pollution situation is still serious in Beijing city.

Table 3 shows that asphaltene is most prominent in the four components, followed by saturated hydrocarbons and polar organics, while aromatic hydrocarbons are the least. Many studies have shown that harmful matters are mostly in polar organics and aromatic hydrocarbons. These two components are the least in the Ming Tombs site, indicating that the urban pollution sources including industrial pollution and vehicle exhaust etc. (Wu et al., 2005), significantly influence the contents of harmful matter in  $PM_{2.5}$ .

# 3.2 Content and distribution of PAHs from $PM_{2.5}$

Aromatic Hcs concentration varies from 0.4 to

12.02  $\mu$ g m<sup>-3</sup> (Table 3), but the sum of 16 PAHs concentrations ranges from 22.17 to 5366 ng  $m^{-3}$  (Table 4). Nap was not detected in all the samples, suggesting that Nap is possibly a gaseous phase in the atmosphere and little is absorbed on PM, and losses during sample preparation or chromatographic interferences are the most likely reasons for not finding Nap in the samples. The other 15 PAHs were all detected in various degrees. The concentrations of heavier PAHs are enriched in the airborne particulate matter in comparison to compounds of lower molecular weight. Although many researchers emphasized the importance of aerosol to the concentration of Bap (Schnelle-Kreis et al., 2001; Yassaa and Meklati, 2001; Yang et al., 2002; Zeng, 2002) and China has established the relevant pollution standard on the basis of Bap concentration (GB3095-1996, 10 ng  $m^{-3}$ ) (NEPBC, 1996), the concentration data in Table 4 suggest that Bap is not the major component of the PAHs. Except for Shougang and its east gate sites, the Bap concentrations are all below 10 ng m $^{-3}$ . Measured Bap concentrations in the crossroad of Chengfu Rd, Ming Tombs, Zhongguancun (summer) and Qianmen (summer) are all lower than the air criteria of WHO (1 ng  $m^{-3}$ ) (WHO, 1987). Beijing city government has conducted ten stages of measures to control the air pollution since 1998. The above data shows that the measures are very effective. However, the Bap concentrations in Shougang and its east gate sites exceed the standard of GB3095-1996 by 30 and 2.5 times respectively. The air pollution of PAHs in the Shougang district of Beijing was very serious (Liu et al., 2003) and is still in urgent need of government concern. The measured Bap concentration in Site H was 7.61 ng m<sup>-3</sup> in winter owing to domestic heating in Beijing city.

Dah is the same carcinogenic and mutagenic as Bap in the 16 PAHs (Wei, 2003). Besides Shougang and its east gate sites, high concentrations of Dah are also detected in Qianmen and Zhongguancun sites. The two sites are characterized by high population density and regular cooking in the open air. We suggest that regular cooking and cigarette smoking are the possible pollution sources of Dah, which needs to be tested thoroughly.

#### 3.3 Seasonal difference of PM<sub>2.5</sub> and PAHs

The  $PM_{2.5}$  concentrations varied hourly, and five peaks were present at different times from 7 December to 8 December 2003, at the top of experimental building in the China University of Geosciences (Beijing) (Site H); the first peak occurred between 0730 LST and 0930 LST, coinciding with the hours for people going to work because this building is very close to the Xueyuan Highway; the second and third peaks

Sampling sites	Saturated hydrocarbons	Aromatic hydrocarbons	Polar organics	Asphaltene	
Site A	4.42	13.03	21.81	57.73	
Site B	21.04	1.60	11.18	66.18	
Site C	20.39	4.75	36.18	38.68	
Site D	19.96	7.50	24.19	48.35	
Site E	25.11	10.23	20.56	44.10	
Site F	24.24	6.53	16.40	52.83	
Site G	17.09	26.82	15.14	40.95	
Site H	25.39	10.15	34.23	30.23	

**Table 3.** Group components of organic pollutants in some areas of Beijing (%).

Table 4. Concentrations of 16 PAHs characterized by USEPA from  $PM_{2.5}$  detected by HPLC (ng m<sup>-3</sup>).

PAHs	Site A	Site B	Site $C_1$	Site $C_2$	Site $D_1$	Site $D_2$	Site $E_1$	Site $E_2$	Site F	Site G	Site H
Nap	_	_	_	_	_	_	_	_	_	_	_
Acel	_	8.52	_	_	12.15	19.15	_	_	220.3	_	_
Ace	11.97	5.37	13.80	6.42	12.74	17.00	34.14	10.64	_	_	9.77
Flu	6.83	2.99	7.04	2.10	2.66	5.37	10.99	2.65	50.42	484.8	6.66
Phe	4.19	1.37	3.64	1.76	2.32	3.15	8.42	2.75	12.41	77.94	7.29
Ant	0.41	0.21	0.39	0.24	0.31	0.31	0.39	0.21	0.87	1.49	1.04
Fla	10.88	4.20	6.86	2.75	4.73	7.38	22.55	2.50	49.86	782.4	6.60
Pyr	11.84	4.51	5.45	3.61	5.46	4.18	26.94	2.24	58.22	625.8	13.98
Baa	2.32	1.22	1.55	1.66	1.91	1.31	3.71	0.18	20.25	394.9	4.45
Chr	1.91	2.15	1.44	1.53	1.92	2.23	2.41	1.47	25.96	556.2	4.53
Bbf	0.73	3.50	5.56	0.12	3.62	2.78	15.66	2.37	13.83	472.0	12.87
Bkf	_	1.03	1.60	0.45	1.31	1.15	3.32	0.91	20.51	240.8	5.80
Bap	0.63	0.49	1.24	1.18	1.67	0.32	5.10	0.16	24.39	307.4	7.61
Bghi	_	1.05	3.22	0.35	5.18	1.48	9.66	1.57	22.51	232.6	_
Dah	_	_	_	_	33.31	_	45.14	23.62	831.6	1190	7.18
Ind	_	_	1.18	_	_	_	31.25	_	88.0	_	_
Sum	51.71	36.61	52.97	22.17	89.29	65.81	219.68	51.27	1439	5366	87.78

Note: A: Chengfu Road Crossing, B: Ming Tombs, C<sub>1</sub>: Yanshan Petrochem (winter), C<sub>2</sub>: Yanshan Petrochem (summer), D<sub>1</sub>: Zhongguancun (winter), D<sub>2</sub>: Zhongguancun (summer), E<sub>1</sub>: Qianmen (winter), E<sub>2</sub>: Qianmen (summer), F: East gate of Shougang, G: Shougang coking plant, H: China University of Geosciences.

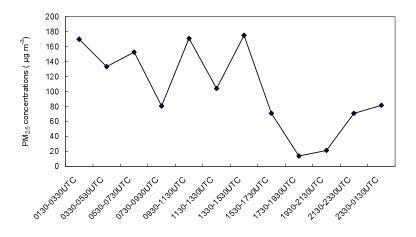


Fig. 2. Hourly variation of  $PM_{2.5}$  concentrations at the top of experimental building in China University of Geosciences (Beijing) (Site H) from 7 December to 8 December 2003.

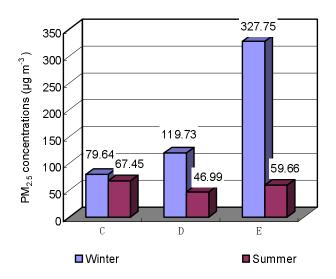


Fig. 3. Comparison of average concentrations of  $PM_{2.5}$  in winter and summer (C: Yanshan Petrochem; D: Zhongguancun; E: Qianmen).

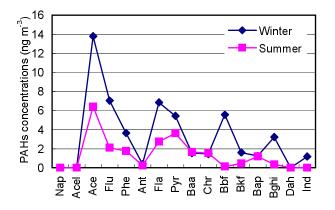


Fig. 4. Comparison of PAHs concentrations from  $PM_{2.5}$  at Yanshan Petrochem in winter and summer.

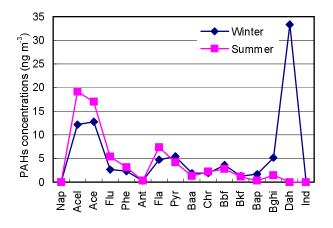


Fig. 5. Comparison of PAHs concentrations from  $PM_{2.5}$  at Zhongguancun in winter and summer.

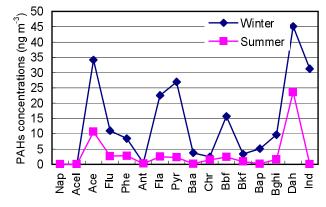


Fig. 6. Comparison of PAHs concentrations from  $PM_{2.5}$  at Qianmen in winter and summer.

occurred between 0930 LST and 1130 LST, 1330 LST and 1530 LST, respectively, corresponding to the heating time; the fourth peak occurred between 1730 LST and 1930 LST corresponding to the time of people returning home; the fifth peak occurred between 2130 LST and 2330 LST owing to the passage of heavy trucks through the city after 2200 LST at night (Fig. 2). Through the comparison of the PM<sub>2.5</sub> concentrations sampling from Yanshan Petrochem, Zhongguancun and Qianmen, it was found that PM<sub>2.5</sub> concentrations in winter were much higher than those in summer (Fig. 3).

The concentrations of the heavier molecular weight PAHs and the lower PAHs have a different pollution trend (Fig. 4–Fig. 6). The concentrations of the lower PAHs are higher with the rising of temperature and the heavier PAHs show the opposite trend, especially at Zhongguancun (Fig. 5). Similar results have been mentioned in the research of Zeng (2002). A possible reason is that it is easier for the lower PAHs to volatilize into the air from natural and anthropogenic emission in summer and absorbed on particulate matter. On the contrary, the heavier PAHs may be degraded under high temperature and strong light. However, the concentrations of both heavier and lower PAHs are higher in winter than those in summer at Yanshan Petrochem and Qianmen (Fig. 4 and Fig. 6), which indicates the atmospheric pollution in winter is more serious than in summer in Beijing city owing to the influence of temperature, humidity, and air flow (Liu et al., 2005). The seasonal trend has also been reported in literature (Bae et al., 2002; Kalaitzoglou et al., 2004) and the concentrations of PAHs in winter are generally higher than those in other seasons. Three meteorological parameters (wind speed, mixing height, and ventilation index) were medium or low negative values for air pollutants in Northern Taiwan (Yu

Sampling site	$\operatorname{Bap}/\operatorname{Bghi}$	$\operatorname{Baa/Chr}$	Pollution sources		
Site A	_	1.21	Gasoline motor car		
Site B	0.47	0.57	Diesel car, gasoline motor car		
Site $C_1$ (winter)	0.39	1.08	Gasoline combustion, coal combustion		
Site $C_2$ (summer)	3.37	1.08	Coal combustion		
Site $D_1$ (winter)	0.33	0.99	Gasoline motor car, coal combustion		
Site $D_2$ (summer)	0.22	0.59	Gasoline motor car		
Site $E_1$ (winter)	0.53	1.54	Gasoline motor car		
Site $E_2$ (summer)	0.07	0.12	_		
Site F	2.12	0.78	Coal combustion, coking		
Site G	1.32	0.71	Coal combustion, coking		
Site H	-	0.98	Gasoline motor car, coal combustion		

Table 5. Source identification of PAHs from  $PM_{2.5}$  in Beijing city.

and Chang, 2006). Analysis of the  $PM_{10}$  and  $PM_{2.5}$ data from Belgrade city also indicated a marked difference between the season without heating (summer; mean value 56  $\mu g m^{-3}$ ) and the heating season (winter; mean value 96  $\mu$ g m<sup>-3</sup>) (Rajsic et al., 2004). The research result by Zeng (2002) also indicated a marked difference between winter and summer in Beijing, the content of organic pollutants from TSP in Beijing in winter was as ten times as that in summer. Yu et al. (2006) found out that there were differences between organic carbon (OC) and elemental carbon (EC) in  $PM_{2.5}$  in Beijing during winter and summer, and the higher OC/EC ratio in summer indicated the formation of secondary organic matter. Zhang et al. (2004) showed that there were obvious differences in chemical compositions of aerosols between the dust period and the non-dust period in Beijing as well. In Beijing, the significant difference between winter and summer can be attributed to coal combustion for domestic heating, lack of precipitation, and a relative stagnant atmosphere in winter.

# 3.4 Source apportionment of PAHs from $PM_{2.5}$

The concentrations of the PAHs acquired by the experiment are all absolutely quantitative, which provide convincing guarantee for us to identify the sources of PAHs. Ratio method was applied to the source identification, which depends on the characteristic concentration ratio of different PAHs. The preliminary results of source identification are shown in Table 5. The results depend on the characteristic ratio (Bap/Bghi, Baa/Chr) summarized by Yang et al. (2002). The Bap/Bghi and Baa/Chr ratios from coal combustion are 0.9–6.6 and 1.0–1.2, respectively, 0.3–0.4 and 0.28– 1.2, respectively, from gasoline motor cars, 0.46–0.81 and 0.17–0.36, respectively, from diesel cars, and 5.1 and 0.7, respectively, from coking (Yang et al., 2002). According to Table 5, coal combustion and vehicle exhaust are still the main sources of PAHs from  $PM_{2.5}$  in Beijing city. Zeng (2002) also got the similar conclusions, the Bap/Bghi ratio at Qianmen and Shijingshan Beijing in spring was 0.61 and 0.61, respectively, indicating the diesel car source, while it's 0.85 and 1.06, respectively, in winter, indicating the coal combustion source. Among the study areas, the PAHs pollution at Shougang coking plant and its east gate is most serious, secondly at Qianmen and Zhongguancun, lowest at Ming Tombs. The main pollution source in summer and winter in Beijing is different at each area, with PAHs in summer mainly coming from gasoline cars and diesel cars, while it's mainly from coal combustion in winter. Yu and Chang (2006) revealed that mobile sources (anthropogenic emission sources) were dominant factors affecting ambient air quality in southwest Taipei City. The relatively consistent distribution of PAHs seemed to indicate the similar combustion source of PAHs at both of rural and urban sites in Tianjin City (Wu et al., 2006). Chetwittayachan et al. (2002) measured particulate PAH concentration at traffic and normal sites in Tokyo, Japan, showing its sharp increase in the early morning. The high PAH concentration peaks in the early morning were strongly associated with an increase in traffic during the early morning rush hours. Park et al. (2002) collected PAHs at an urban site in Seoul, showing that seasonal trends in atmospheric PAH concentrations were highly influenced by fossil fuel usage for domestic heating, boundary layer height, and air temperature.

New measures about restricting coal combustion and vehicle exhaust must be established as soon as possible to accelerate the structural transformation of energy and to improve the pollution situation in Beijing city.

#### 4. Conclusions

(1) The 16 PAHs were completely identified and quantified in  $PM_{2.5}$  with the aid of HPLC in proper conditions.

(2) The PM<sub>2.5</sub> concentrations are all above the PM<sub>2.5</sub> pollution standard (65  $\mu$ g m<sup>-3</sup>) established by USEPA in 1997 except for the Ming Tombs site. It is clear that the pollution situation is still serious in Beijing.

(3) Except for Shougang and its east gate sites, the benzo[a]pyrene concentrations are all below 10 ng m<sup>-3</sup>. But the benzo[a]pyrene concentrations in Shougang and its east gate sites exceed GB3095-1996 by 30 and 2.5 times, respectively.

(4)  $PM_{2.5}$  concentrations vary hourly and five peaks are present at different times in a day, which are much higher in winter than those in summer. The concentrations of the heavier molecular weight PAHs and the lower PAHs have a different pollution trend.

(5) Coal combustion and vehicle exhaust are still the main sources of PAHs from  $PM_{2.5}$  in Beijing city. New measures about restricting coal combustion and vehicle exhaust must be established as soon as possible to improve the air pollution situation in Beijing city.

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