





Journal of Environmental Sciences 21(2009) 142-149

JOURNAL OF ENVIRONMENTAL SCIENCES ISSN 1001-0742 CN 11-2629/X

www.jesc.ac.cn

Distribution and sources of solvent extractable organic compounds in $PM_{2.5}$ during 2007 Chinese Spring Festival in Beijing

LI Xingru^{1,2}, GUO Xueqing², LIU Xinran¹, LIU Chenshu², ZHANG Shanshan², WANG Yuesi^{1,*}

1. Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China. E-mail: lxrcc@126.com 2. Department of Chemistry, Analytical and Testing Center, Capital Normal University, Beijing 100037, China

Received 28 February 2008; revised 14 April 2008; accepted 05 May 2008

Abstract

The solvent extractable organic compounds (SEOC), including *n*-alkanes, polycylic aromatic hydrocarbons, fatty acids, and dicarboxylic acids in PM_{2.5} during the 2007 Chinese Spring Festival in Beijing, were measured via gas chromatography-mass spectrometry for determining the characteristics and sources of these organic pollutants. The concentrations of total *n*-alkanes, PAHs, and organic acids before Chinese Spring Festival Eve (1025.5, 95.9, and 543.3 ng/m³, respectively) were higher than those after (536.6, 58.9, and 331.8 ng/m³, respectively). *n*-Aalkanes and PAHs had much higher concentration in nighttime than those in daytime because of high relative humidity and low wind speed during the night. Combustion of coal and exhaust emission were major sources of *n*-alkanes. It could be concluded by the characteristic ratios that the primary source of PAHs in fine particles was the combustion of coal, but the combustion of gasoline was in the next place. The ratios of C18:0/C16 indicated the contribution of vehicular emissions to the fatty acids. Dicarboxylic and aromatic acids were abundant in daytime than in nighttime because these acids were secondary organic acid and the photochemical degradation of aromatic hydrocarbons was the main source.

Key words: aerosol; PM_{2.5}; Chinese Spring Festival; solvent extractable organic compounds

DOI: 10.1016/S1001-0742(08)62242-1

Introduction

The Spring Festival, the most important traditional festival in China, falls on the 1st day of the 1st lunar month every year. During the Spring Festival burning fireworks, one of the most typical culture, and vehicle traffic decreases since many people leave Beijing, can greatly affect the atmospheric quality of Beijing.

Aerosol fine particles (< 2.5 µm in aerodynamic diameter), which are ubiquitous in atmosphere, are environmentally important because they contribute to both climate effects (Charlson et al., 1992; Ramanathan et al., 2001; Kaufman et al., 2002) and adverse impact on human health (Wilson and Suh, 1997; Didyk et al., 2000). Atmospheric fine particles are a complicated mixture which are composed by inorganic substances (such as, metal ions, sulfate, ammonium, and nitrate) and hundreds of different organic matters (such as n-alkanes, PAHs, carboxylic, and dicarboxylic acids). Organic aerosols are the largest contributor to the atmospheric fine aerosols in highly industrialized urban areas (Xu et al., 2005; Hou, 2006). In Beijing, about 40% of the fine aerosol mass is composed of organic materials (He et al., 2001). Most of these organic materials, such as PAHs, PCBs, are carcinogenic and mutagenic (Tsai et al., 2001; Wu et al., 2005; Perera et al., 2005). The fine particles with these toxic matters can easily penetrate into the lungs and therefore are more likely to have short-term or long-term adverse effects, such as increasing respiratory symptoms and disease (Zheng et al., 2000).

Aerosols are considered as one of the most serious air pollutions in Beijing. Both anthropogenic and biogenic sources account for the atmospheric fine particulate matter. Many organic materials in atmospheric fine particles, which are confirmed as mutagenic or carcinogenic, are generated from anthropogenic sources. The monitoring results indicate that diesel vehicular exhaust and incomplete combustion of coal are the major source of organic matter in urban areas (Wild and Jones, 1995; Simcik et al., 1999; Ho et al., 2003; Li et al., 2006; Pio et al., 2001; Huang et al., 2006; Wang et al., 2007). In addition, the air can be polluted by burning fireworks during Spring Festival. Burning fireworks releases many pollutants, such as ozone, organic compounds, suspended particles and other inorganic materials, which are great threats to human health (Wang et al., 2007). During the Spring Festival, a lighter traffic may affect the atmospheric pollution in positive way. However, detailed characterization and speciation analyses of organic substances in atmospheric aerosols during the Spring Festival are still limited.

^{*} Corresponding author. E-mail: wys@mail.iap.ac.cn

Aerosol samples collected in Spring Festival, 2007 were determined for their *n*-alkanes, PAHs, and organic acid content in this study. We take the meteorological conditions (such as temperature, wind direction and relative humidity), origin of organic matters during Spring Festival into accounts to determine the sources of these organic matters and the relationships between the these organic pollutants and the meteorological conditions.

1 Materials and methods

1.1 Sample collection

The aerosol samples were collected by quartz fiber filters (Whatman Company, UK) for 11 h using high volume air sampler (Anderson, USA) for PM_{2.5} on diurnal/nocturnal basis from Feb 11 to Feb 23, 2007 on the rooftop of a two-story building in the courtyard of the Institute of Atmospheric Physics, China. Meteorological data were recorded at each site concurrently (Table 1). The quartz fiber filters were wrapped with aluminum foil and preheated at 550°C for 4 h to remove all organic materials, and then conditioned in a constant desiccator (25°C, humidity 50%) for 24 h and weighed. After sampling, the filters were returned into the desiccator (25°C, humidity 50%) for 24 h at least, and then weighed at –18°C before analyzing.

1.2 Extraction-fraction

A half of each PM_{2.5} filter was ultrasonically extracted 20 min using 25 mL dichloromethane (DCM) (HPLC grade, Supelco, USA) for three times. The extracts were combined and filtered through glass fiber filter, and then concentrated to about 5 mL under reduced pressure at 35°C by a rotary evaporator (Buchi, Sweden), followed by drying in a gentle nitrogen stream. After that, 10 mL n-hexane was added to the tube and dried again in a gentle nitrogen stream. This extraction was transferred into the silica chromatography column (30 cm × 1 cm i.d.) filled with 5 g silica gel (80-100 mesh, activated at 180°C for 12 h) and 5 g alundum (100–200 mesh, activated at 250°C for about 12 h) to separate aliphatic hydrocarbons and PAHs. The column was sequentially eluted with 70 mL n-hexane and 70 mL mixture of hexane and DCM (1:1, V/V). The two eluted fractions were evaporated using a rotary evaporator and the final volume was adjusted to 1 mL under a gentle nitrogen stream for gas chromatography to mass spectrometry (GC-MS) analysis.

Another half of each PM_{2.5} filter was ultrasonically extracted three times with 25 mL dichloromethane for 20 min, and extracted twice with ultrapure water for 20 min. The extracts were combined, filtered with glass fiber filter, concentrated to 1 mL by rotary evaporator under reduced pressure, followed by being almost dried under a gentle stream of N₂. A 14% of BF3/methanol mixture (about 0.5 mL) was added into the reactor and sealed with Teflon tape. The samples were reacted at 100°C for 30 min to convert carboxyl groups to methyl ester. Then additional 3 mL pure water and 0.3 mL acetonitrile were added to the reaction products, and the mixture was extracted with 5 mL of *n*-hexane. The *n*-hexane layer was further washed with pure water twice and concentrated to 1 mL in *n*-hexane for GC-MS analysis.

1.3 Organic analysis

The hydrocarbons, PAHs and the derivative were identified and quantified with a trace GC-MS spectrometer (Thermo DSQ Finnigan, USA) and a HP-5MS capillary column (30 m \times 0.25 mm i.d. \times 0.25 µm film thickness). High-pure helium was used as the carrier gas at a constant flow rate of 1.0 mL/min. One micro litter of sample was injected into the GC in splitless mode. For the aliphatic hydrocarbons and PAHs fractions, the GC temperature was programed as following, from 50°C (5 min) to 180°C at 150°C/min and held for 5 min, then ramped to 280°C at 5°C/min and held at 280°C for 15 min. The temperature for fatty ester was first held at 50°C for 5 min, then ramped to 280°C at 5°C/min, and held at 280°C for 20 min.

The mass spectrometer was operated on an electron impact (EI) mode at 70 eV and fully scanned ranging from 50 to 550 amu. The identification of organic compounds was performed using the m/z mass chromatography, and the mass spectra was compared with the standards in the NIST98.

1.4 Quality control

All analytical procedures were monitored using strict quality assurance and control measures. Lab blanks and field blanks were used to determine background contam-

Table 1 Meteorological parameters during sampling periods

Date	Temperature (°C)		Humidity (%)		Wind speed (m/s)		\sum UV (MJ/m ²)	
	Day	Night	Day	Night	Day	Night	Day	Night
11-Feb	8.7	3.7	18.8	29.3	1.4	0.8	0.3	0
12-Feb	9.9	5.3	24.8	42.8	1.1	1.1	0.2	0
13-Feb	2.5	-0.4	18.8	23.0	3.9	1.4	0.3	0
14-Feb	5.3	0.1	13.3	25.5	1.9	1.0	0.4	0
15-Feb	5.9	1.4	25.0	39.3	1.4	1.1	0.2	0
16-Feb	6.5	4.0	34.3	37.3	1.2	1.1	0.2	0
17-Feb	8.5	2.7	18.0	45.6	2.4	1.2	0.4	0
18-Feb	6.9	2.0	30.3	44.6	1.4	0.9	0.3	0
19-Feb	9.1	4.1	28.7	41.5	1.4	1.0	0.3	0
20-Feb	12.2	4.1	27.0	77.1	1.0	1.2	0.3	0
21-Feb	4.5	6.6	87.8	49.7	0.5	1.5	0.04	0 ~ ((
22-Feb	10.3	7.2	9.6	28.2	2.2	0.8	0.4	0
23-Feb	1.7	5.3	18.4	14.9	1.6	2.2	0.3	CO A

ination and showed no detectable PAHs. Phthalate esters were the main contaminants found in the blanks. The mean recoveries for all the standards were greater than 72%. In this article, the data was corrected according to the recovery rates.

2 Results and discussion

2.1 Variation of aerosol mass concentration

Figure 1 shows the variations of $PM_{2.5}$ mass concentrations during Spring Festival from 11 Feb to 23 Feb in 2007. The average concentration of $PM_{2.5}$ varied from 58 to 224 $\mu g/m^3$, where it was higher at the night (150 $\mu g/m^3$) than in the day time (112 $\mu g/m^3$). There is only slight change in the average concentrations before (130 $\mu g/m^3$) and after (132 $\mu g/m^3$) Spring Festival Eve.

The mass concentrations of PM_{2.5} were influenced by meteorological conditions (Wang *et al.*, 2004, 2005, 2006; Song *et al.*, 2003). Therefore, it is necessary to investigate the relationships between mass concentrations of fine particles and the meteorological parameters. As shown in Fig. 2, a positive correlation between the mass concentrations of PM_{2.5} and the relative humidity was found (R = 0.69), while a less obvious negative correlation between the mass concentrations of PM_{2.5} and the wind speed was observed (R = 0.52) (95% probability confidence).

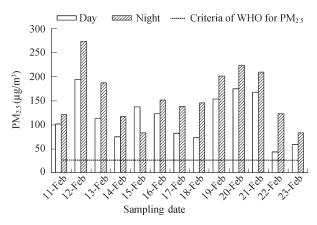


Fig. 1 Variations of PM_{2.5} during 2007 Spring Festival in Beijing.

2.2 n-Alkanes

Twenty four kinds of n-alkanes (ranging from C_{10} to C₃₃) were detected on the PM_{2.5} aerosols with mean total concentrations of 588.7 ng/m³ (ranged from 196.3 to 2303.1 ng/m³) in daytime and 943.5 ng/m³ (ranging from 298.6 to 3128.2 ng/m³) at night (Table 2). The high concentrations of alkanes at night can be contributed by both the low ambient temperature and high relative humidity at night, which lead to the conversion from the gas phase to the particle phase. The total concentrations of *n*-alkane before Spring Festival Eve with mean value 1025.5 ng/m³ were higher than those after the Eve with mean value 536.6 ng/m³. These change could be explained in terms of the decrease of industrial and vehicular transport pollutants during the festival. The average concentrations of n-alkane were significantly decreased after Spring Festival Eve (Fig. 2). C₂₃ was the most abundant followed by C₂₄ and C₂₅. Carbon preference index (CPI) which stand for the relative abundance of compounds containing odd or even number of carbon atoms is usually used to distinguish two main resources of *n*-alkane, biogenic and anthropogenic activities (fossil fuels and biomass combustion) (Simoneit et al., 1986, 1991; Rogge et al., 1993; Azevedo et al., 1999; Chen et al., 2006; Feng et al., 2006). It is recognized that the carbon number profiles of *n*-alkanes derived from natural sources (primarily cuticular waxes of higher plants) show high CPI value (higher than three), whereas CPI about 1 implies anthropogenic influences (combustion of fossil fuels) (Simoneit, 1984). The *n*-alkanes in Beijing displayed little odd-even preference with a CPI in the range of 0.90-1.42, and with carbon number maximum (C_{max}) at C_{23} , indicating a dominance of anthropogenic nalkanes from automobile exhaust and combustion of coal (Kalaitzoglou et al., 2004). The contribution from plant can be calculated by $WaxC_n$ (Simoneit *et al.*, 1991):

WaxC_n =
$$\sum (C_n - 0.5(C_{n-1} + C_{n+1})) / \sum C_n \times 100\%$$
 (1)

where, $WaxC_n$ was plant wax concentrations for n-alkanes, Negative values of C_n were taken as zero. The calculation results (Table 2) revealed that the contribution of biogenic wax n-alkanes ranged from 16.32% to 47.94% (mean 24.7%) for day time and from 13.2% to 35.1% (mean = 18.6%) for night time, respectively. These results indicated

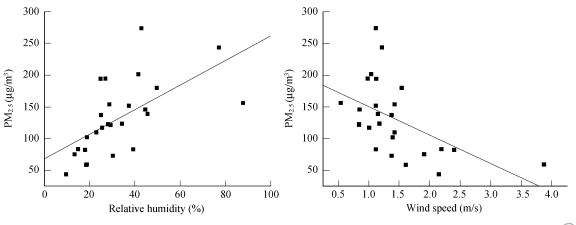


Fig. 2 Variation of PM_{2.5} mass concentration and relative humidity and wind speed

Table 2 Concentrations and compositions of solvent extractable organic compounds (ng/m³)

Date	<i>n</i> -Alkane								PAHs	
	Day			Night						
	TC (ng/m ³)	CPI	C_{\max}	$WaxC_n$	TC (ng/m ³)	CPI	C_{\max}	$WaxC_n$	Day	Night
11-Feb	889.1	1.17	25	19.62	813.2	1.07	25	18.93	48.3	134.2
12-Feb	2303.1	1.05	24	33.10	3128.2	0.96	24	17.36	114.2	152.4
13-Feb	279.4	1.42	23	28.56	492.7	1.02	23	19.56	48.4	108.4
14-Feb	460.2	1.11	30	22.55	1225.4	1.08	23	20.74	41.0	179.1
15-Feb	385.8	1.37	23	26.89	795.8	1.06	23	19.88	109.8	182.8
16-Feb	581.4	1.23	23	16.32	952.1	1.15	23	13.25	81.2	222.5
17-Feb	541.3	1.19	31	22.77	926.6	1.11	29	14.42	30.6	25.6
18-Feb	196.3	1.22	23	18.84	307.1	1.27	23	15.90	50.6	115.8
19-Feb	264.7	1.33	24	17.56	846.8	1.07	23	16.46	39.9	212.4
20-Feb	864.6	1.23	25	22.51	1351.1	1.16	25	20.79	34.4	89.2
21-Feb	296.3	1.06	23	21.66	315.9	0.90	23	14.05	41.6	48.6
22-Feb	393.6	1.31	23	47.94	811.5	0.90	24	35.01	32.5	50.0
23-Feb	198.4	1.27	27	23.50	298.6	1.17	27	16.08	35.8	81.6

TC: total concentration; CPI: carbon preference index, odd-to-even for n-alkanes; C_{max} : carbon number maximum, the carbon number with the highest concentration in that fraction.

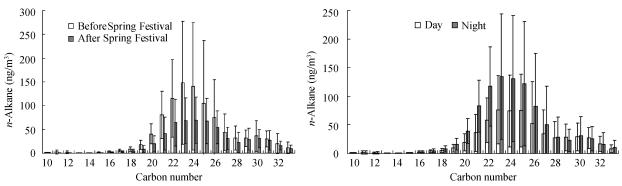


Fig. 3 Distribution diagrams of *n*-alkanes average concentration.

that the fossil fuel is the major contributor to the air pollution in Beijing in winter.

2.3 PAHs

Seventeen PAHs were quantified in all samples with total concentrations of 95.9 ng/m³ before and 58.9 ng/m³ after Spring Festival Eve (Table 2). This result revealed that there was little influence of burning fireworks on the PAHs concentration. The changes of the PAHs' concentration can be rationalized in the terms of the decrease of industrial and vehicular transport pollutants during the festival. PAHs were much more abundant at night than those in the daytime, which is due to the accumulation process caused by inversion layers at night. Fuloranthene is the most abundant PAHs followed by pyrene and chrysene (Fig. 4). All measured BaP concentrations exceeded the air criteria of World Health Organization (1 ng/m³) which indicated that the air pollution of PAHs in Beijing was serious. Figure 5 illustrates the mass distribution of different ring PAH. It was concluded that PAH (4) contributed most to the total concentrations of PAHs.

The molecular composition profiles and characteristic ratios of PAHs have been used to distinguish different resources. The ratios of IP/BghiP close to 0.22, 0.50, and 1.3 are typically indicative of gasoline, diesel, and petroleum combusting, respectively (Yassaa, 2001). In this study, IP/BghiP was in the range of 0.09–1.2 (mean 0.31), indicating that gasoline burning was the major source of

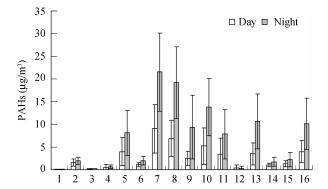


Fig. 4 Average concentration of individual PAH. (1) naphthalene (Nap); (2) acenaphthylene (Acy); (3) acenaphthene (Ace); (4) fluorene (Flu); (5) phenanthrene (Phe); (6) anthracene (Ant); (7) fluoranthene (Fluor); (8) pyrene (Pyr); (9) benzo[a]anthr acene (BaA); (10) chrysene (Chry); (11) benzo[b]fluorant hene (BbF) + benzo[k]fluoranthene (BkF); (12) benzo[e]pyrene (BeP); (13) benzo[a]pyrene (BaP); (14) indeno[1,2,3-cd]pyrene (IP); (15) dibenzo[a,h]anthracene (DBahA); (16) benzo[ghi]perylene (BghiP).

PAHs. The results of Fluor/(Pyr + Flu) close to 0.4, between 0.4 and 5, and > 0.5 are characteristic of petroleum, exhaust emission, and combustion of grass or wood or coal, respectively (Yunker *et al.*, 2002). In current study, Fluor/(Pyr + Flu) was in the range of 0.51–0.67 (mean 0.56), indicating that the combustion of biomass or coal might be an primary source of PAHs. Sawicki (1962) used the Bap/BghiP ratio of 0.3–0.4 and 0.7–6.6 to identify the vehicular and coal combustion sources. For samples in this

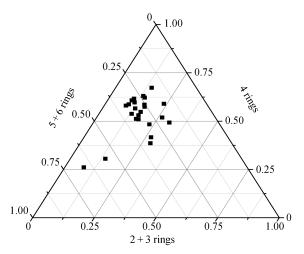


Fig. 5 Triangular diagram of percentage concentrations of 17 PAHs.

study, the Bap/BghiP ratio were ranged from 0.43 to 4.02, with mean value 1.05, indicating a mixture of exhaust and coal burning emissions and coal burning was the main sources of PAHs in Beijing during Spring Festival. In addition, the BeP/(BaP + BeP) ratio was 0.12 and 0.02 in the daytime and nighttime respectively, indicating less degradation of PAHs, especially in nighttime (Pistikopoulos et al., 1990).

2.4 Organic acids

Thirty-eight organic acids were identified and quantified in the PM_{2.5} samples of Beijing. The major compound classed included fatty acids, dicarboxylic acids, and aromatic acids with the total concentration of 284.9, 110.1 and 46.8 ng/m³, respectively, including Benzoic acid, Salicylic acid, p-Phthalic acid, and o-Phthalic acid. The total concentrations of organic acids before Spring Festival Eve were higher than those after with the mean concentration of 550.0 and 331.8 ng/m³, respectively. Fatty acids were the most abundant class, which contributed 66% of the total quantified organic acids (Table 3).

Figure 6 shows the average concentrations of individual fatty acid during Spring Festival. The concentrations were in the range of 120.3–765.6 ng/m³ and the averages were 294.5 and 275.3 ng/m³ for the daytime and nighttime, respectively. The C16 saturated acid was the most abundant acid followed by the C18. Even carbon number predominance was found of the < 20 homologues which were considered to be derived in part from microbial activities and meat cooking (Simoneit, 1986; Rogge et al., 1991), while the homologues > 22 which were from vascular plant wax (Simoneit and Mazurek, 1982). Even carbon number predominance can not be found in this study.

Table 3	Total concentration	of solvent extractab	le organic compounds
Table 3	Total Concentration	or sorvent extractat	ic organic compounds

Date		Fatty acid				Dicarboxylic acid		Aromatic acid	
	Day		Night		TC (ng/m ³)		TC (ng/m ³)		
	TC (ng/m ³)	C18:1/C18	TC (ng/m ³)	C18:1/C18	Day	Night	Day	Night	
11-Feb	293.3	0.90	237.2	0.54	136.9	156.6	43.9	48.5	
12-Feb	259.9	0.11	604.7	1.04	115.8	142.3	82.0	80.3	
13-Feb	309.9	1.37	276.7	0.86	106.9	71.2	50.4	33.6	
14-Feb	128.3	0.54	391.9	0.87	101.2	163.6	67.8	52.5	
15-Feb	765.6	1.23	272.5	0.32	186.7	90.1	67.4	75.5	
16-Feb	237.7	1.38	415.7	0.40	105.7	59.7	44.4	39.7	
17-Feb	490.7	0.34	141.5	1.02	168.9	120.4	86.9	36.3	
18-Feb	195.2	1.12	193.8	0.77	86.6	81	22.8	22.1	
19-Feb	216.6	0.04	127.4	0.80	128.1	77.5	73.7	30.6	
20-Feb	149.6	0.79	315.7	0.31	132.2	145.8	31.6	36.1	
21-Feb	458.7	0.78	309.7	1.17	85.7	78.5	39.8	33.1	
22-Feb	150.8	1.63	120.3	1.72	58	46.5	21.9	20.8	
23-Feb	172.8	2.07	171.2	1.23	63.2	66.1	22.0	29.4	

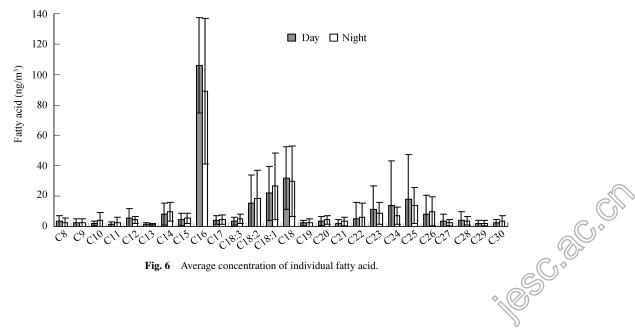


Fig. 6 Average concentration of individual fatty acid.

Besides saturated fatty acids, three unsaturated fatty acids, oleic (C18:1), linoleic (C18:2), and eleostearic acid (C18:3), were also abundant in the $PM_{2.5}$ samples of Beijing. Linoleic and oleic acids are unstable and can be rapidly degraded in the atmosphere (Kawamura and Gagosian, 1987). Thus the oleic acid to stearic acid ratio is often used as an indicating the ageing of aerosol. The average ratios (C18:1/C18) of 0.98 for daytime and 0.85 for nighttime in this study were much higher than those in summer (Feng et al., 2005) and dust samples (Hou et al., 2006). These suggested that there were fresh aerosols and/or little degradation of the fatty acids (Guo et al., 2003). The ratio of C18:1/C16 has been used as a qualitative tool for source assessment (Oliveira et al., 2007). The ratio lower than 0.25, between 0.25 and 0.5, in the interval of 0.5–1 were attribute to foliar vegetation combustion and wood smoke, car and diesel trucks exhausts, paved and unpaved road dust and charbroiling, respectively (Rogge et al., 2006). In this study, the ratios of C18:1/C16 were in the range of 0.059-0.47 (mean=0.36), indicating that beside the contribution of vehicular emissions, a stronger input from cooking operations can not be neglected.

The identification of eight kinds of dicarboxylic acids (C3di-C10di) and four kinds of aromatic acids were detected in this study. Figure 7 shows the diurnal variation and contrast of the average concentrations of before and after Spring Festival Eve. Unlike previously mentioned hydrocarbon, the average concentrations of these acids were abundant in daytime than in the nighttime. Moreover, the total concentrations of these acids before Spring Festival Eve were higher than those after the Eve. This variation trend was the same to n-alkanes and PAHs. The most abundant acids of PM_{2.5} are azelaic acid, followed by Phthalic acids. Although oxalic acid is usually considered as the most abundant atmospheric dicarboxylic acid species (Chebbi and Carlier, 1996; Wang et al., 2002), it was considered too volatile to be quantified using methyl esterification (Ray and McDow, 2005).

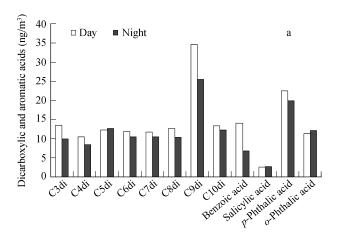
Aliphatic dicarboxylic acids have several sources including primary emissions from burning of biomass and fossil fuel, as well as photochemical oxidation of organic precursors. The C_3/C_4 ratio has been reported in the

range of 0.3–0.5 from vehicular emissions (Kawamura and Kaplan, 1987), and its mass ratio in secondary atmospheric particles is much larger than unity (Kawamura and Sakaguchi, 1999; Yao *et al.*, 2002). The samples collected during Spring Festival had an average C₃/C₄ ratio of 1.2, which indicated that secondary formation of dicarboxylic acids in PM_{2.5} was important.

Benzoic and phthalic acids have been proposed as secondary organic acid. Photochemical degradation of aromatic hydrocarbons such as benzene, and toluene may be a possible source of benzoic acid. A significant concentration increase was observed in daytime, possibly with relevance to stronger photochemical reaction. Phthalic acids which may be derived from the oxidation of naphthalene or other polycyclic aromatic hydrocarbons (Fine *et al.*, 2004a), can be used as a surrogate for the contribution of Second organic aerosol (SOA) to an ambient sample (Oliveira *et al.*, 2007).

3 Conclusions

The samples of PM_{2.5} aerosol in daytime and nighttime were analyzed to study the composition of solvent extractable organic compounds including *n*-alkanes, PAHs, and organic acids during Chinese Spring Festival of 2007. The concentrations of solvent extractable organic compounds (SEOC) showed a strong variation trends that the total concentrations before Spring Festival Eve were higher than those after the Eve as a result of vehicle traffics decrease during the festival. At the same time, the concentrations of semi-volatile species such as alkanes and PAHs were much higher in nighttime than that in daytime due to the lower ambient temperature and higher relative humidity at night and the dominant source was fossil fuel combustion. Fatty acids had weak diurnal variation and were mostly from vehicular emissions and cooking operations. Dicarboxylic and aromatic acids were abundant in daytime than in nighttime. Dicarboxylic acids with both primary and secondary origin. The ratio of C3di/C4di indicated that secondary formation of dicarboxylic acids in PM_{2.5} was more important. Benzoic and phthalic acids, as secondary organic acids, may be derived from the



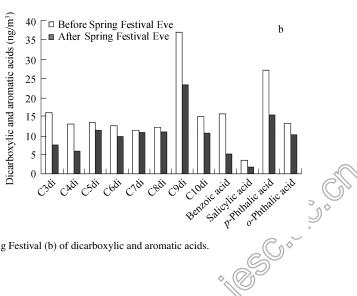


Fig. 7 Diurnal variation (a) and variation during Spring Festival (b) of dicarboxylic and aromatic acids.

oxidation of aromatic hydrocarbon. The results also indicated that the burning of fireworks has no influence to the SEOC in fine particles.

Acknowledgments

This work was supported by the National Basic Research Program (973) of China (No. 2007CB407303), the National Natural Science Foundation of China (No. 40525016), and the Hi-Tech Research and Development Program (863) of China (No. 2006AA06A301). The authors appreciate Assistant Professor Yingfeng Wang of Capital Normal University for the support of GC/MS, and also appreciate Dr. Bo Hu for the providing of meteorological data.

References

- Azevedo D A, Moreira L S, Siqueira D S, 1999. Composition of extractable organic matter in aerosols from urban areas of Rio de Janeiro city, Brazil. *Atmospheric Environment*, 33: 4987–5001.
- Charlson R J, Schwartz S E, Hales J M, Cess R D, Coakley Jr J A, Hansen J E, 1992. Climate forcing by anthropogenic aerosols. *Science*, 25: 423–430.
- Chebbi A, Carlier P, 1996. Carboxylic acids in the troposphere, occurrence, sources and sinks: a review. Atmospheric Environment, 24: 4233–4249.
- Chen Y, Li S M, Leithead A, Brook J R, 2006. Spatial and diurnal distributions of *n*-alkanes and *n*-alkan-2-ones on PM_{2.5} aerosols in the Lower Fraser Valley, Canada. *Atmospheric Environment*, 40: 2706–2720.
- Didyk B M, Simoneit B R T, Pezoa L A, Riveros M L, Flores A A, 2000. Urban aerosol particles of Santiago, Chile: organic content and molecular characterization. *Atmospheric Environment*, 33: 783–795.
- Fine P, Chakrabarti B, Krudysz M, Schauer J J, Sioutas C, 2004a. Diurnal variations of individual organic compound constituents of ultrafine and accumulation mode particulate matter in the Los Angeles Basin. *Environmental Science & Technology*, 38: 1296–1304.
- Feng J L, Chan C K, Fang M, Hu M, He L Y, Tang X Y, 2006. Characteristics of organic matter in PM_{2.5} in Shanghai. *Chemosphere*, 64: 1393–1400.
- Guo Z G, Sheng L F, Feng J L, Feng M, 2003. Seasonal variation of solvent extractable organic compounds in the aerosols in Qingdao, China. Atmospheric Environment, 37: 1825–1834.
- He K B, Yang F M, Ma Y L, Zhang Q, Yao X H, Chan C K, Cadle S H, Chan T, Mulawa P A, 2001. The characteristics of PM_{2.5} in Beijing, China. *Atmospheric Environment*, 35: 4959–4970.
- Ho K F, Lee S C, Chan C K, Yu J C, Chow J C, Yao X H, 2003. Characterization of chemical species in PM_{2.5} and PM₁₀ aerosols in Hong Kong. *Atmospheric Environment*, 37: 31–39.
- Hou X M, Zhuang G S, Sun Y L, An Z S, 2006. Characteristics and sources of polycyclic aromatic hydrocarbons and fatty acids in PM_{2.5} aerosols in dust season in China. *Atmospher-ic Environment*, 40: 3251–3262.
- Huang X F, He L Y, Hu M, Zhang Y H, 2006. Annual variation of particulate organic compounds in PM_{2.5} in the urban atmosphere of Beijing. *Atmospheric Environment*, 40: 2449–2458.

- Kalaitzoglou M, Terzi E, Samara C, 2004. Patterns and sources of particle-phase aliphatic and polycyclic aromatic hydrocarbons in urban and rural sites of western Greece. *Atmospheric Environment*, 38: 2545–2560.
- Kaufman Y J, Tanre D, Boucher O, 2002. A satellite view of aerosols in the climate system. *Nature*, 419: 215–223.
- Kawamura K, Kaplan I R, 1987. Motor exhaust emission as a primary source for dicarboxylic acids in Los Angeles Ambient Air. *Environmental Science & Technology*, 21: 105–110.
- Kawamura K, Sakaguchi F, 1999. Molecular distribution of water soluble carboxylic acids in marine aerosols over the Pacific Ocean including tropics. *Journal of Geophysical Research*, 104: 3501–3509.
- Kawamura K, Gagosian R B, 1987. Implications of ωoxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids. *Nature*, 325: 330–332.
- Li J, Zhang G, Li X D, Qi S H, Liu G Q, Peng X Z, 2006. Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Science of the Total Environment*, 355: 145–155.
- Oliveira C, Pio C, Alves C, Evtyugina M, Santos P, Gonçalves V, Nunes T, Silvestre A J D, Palmgren F, Wåhlin P, Harrad S, 2007. Seasonal distribution of polar organic compounds in the urban atmosphere of two large cities from the North and South of Europe. *Atmospheric Environment*, 41: 5555–5570.
- Perera F, Tang D L , Whyatt R, 2005. DNA damage from polycyclic aromatic hydrocarbons measured by benzo[a]pyrene-DNA adducts in mothers and newborns from Northern manhattan, The World Trade Center area, Poland, and China. Cancer Epidemiology Biomarkers and Prevention, 14: 709–714.
- Pistikopoulos P, Wortham H M, Gomes L, Masclet-Beyne S, Nguyen E B, Masclet P A, Mouvier G, 1990. Mechanism of formation of particulate polycyclic aromatic hydrocarbons in relation to the particle size distribution: effects on mesoscale transport. *Atmospheric Environment*, 24a: 2573–2584.
- Pio C A, Alves C A, Duarte A C, 2001. Identification, abundance and origin of atmospheric organic particulate matter in a Portuguese rural area. *Atmospheric Environment*, 35: 1365– 1375.
- Ramanathan V, Crutzen P J, Kiehl J T, Rosenfeld D, 2001. Aerosols, climate and the hydrological cycle. *Science*, 294: 2119–2124.
- Ray J , McDow S R , 2005. Dicarboxylic acid concentration trends and sampling artifacts. Atmospheric Environment, 39: 7906–7919.
- Rogge W F, Medeiros P M, Simoneit B R T, 2006. Organic marker compounds for surface soil and fugitive dust from open lot dairies and cattle feedlots. *Atmospheric Environment*, 40: 27–49.
- Rogge W F, Hildemann L M, Mazured M A, Cass G R, Simoneit B R T, 1991. Sources of fine organic aerosol.1. Charbroilers and meat cooking operations. *Environmental Science & Technology*, 25: 1112–1125.
- Rogge W F, Hildemann L M, Masurek M A, Cass G R, Simoneit B R T, 1993. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. *Environmental Science & Technology*, 7: 2700–2711.
- Sawicki E, 1962. Analysis for airborne particulate hydrons, their relative proportion affected by different types of pollution. *National Cancer Institute Monograph*, 9: 201–208

- Simcik M F, Eisenreich S J, Lioy P J, 1999. Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment*, 33: 5071–5079.
- Simoneit B R T, 1986. Characterization of organic constituents in aerosols in relation to their origin and transport: A review. *International Journal of Environmental Analytical Chemistry*, 23: 207–237.
- Simoneit B R T, Sheng G Y, Chen X, Fu J M, Zhang J, Xu Y, 1991. Molecular marker study of extractable organic matter in aerosols from urban areas of China. *Atmospheric Environment*, 25a: 2111–2129.
- Simoneit B R T, 1984. Organic matter of the troposphere III: Characterization and sources of petroleum and pyrogenic residues in aerosols over the Western United States. *Atmospheric Environment*, 18: 51–67.
- Simoneit B R T, Crisp P T, Mazurek M A, Standley L J, 1991. Composition of extractable organic matter of aerosols from the blue mountains and southeast coast of Australia. *Environmental Internationas*,17: 405–419.
- Simoneit B R T, Mazurek M A, 1982. Organic matter of the troposphere-II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmospheric Environment*, 16: 2139–2159.
- Song Y, Tang X Y, Zhang Y H, 2003. The study of the status and degradation of visibility in Beijing. *Research of Environmental Sciences*, 16: 10–12.
- Tsai P J, Shieh H Y, Lee W J, Lai S O, 2001. Health-risk assessment for workers exposed to polycyclic aromatic hydrocarbons (PAHs) in a carbon black manufacturing industry. *Science of the Total Environment*, 278: 137–150.
- Wang G H, Kawamura K, Zhao X, Li Q G, Dai Z X, Niu H Y, 2007. Identification, abundance and seasonal variation of anthropogenic organic aerosols from a mega-city in China. *Atmospheric Environment*, 41: 407–416.
- Wang G H, Niu S L, Liu C, Wang L S, 2002. Identification of dicarboxylic acids and aldehydes of PM₁₀ and PM_{2.5} aerosols in Nanjing, China. *Atmospheric Environment*, 36: 1941–1950.

- Wang J L, Zhang Y H, Shao M, Liu X L, Zeng L M, Cheng C L, Xu X F, 2004. Chemical composition and quantitative relationship between meteorological condition and fine particles in Beijing. *Journal of Environmental Sciences*, 16(5): 860–864.
- Wang Y, Zhuang G S, Sun Y L, An Z S, 2005. Water-soluble part of the aerosol in the dust storm season-evidence of the mixing between mineral and pollution aerosols. *Atmospheric Environment*, 39: 7020–7029.
- Wang Y, Zhuang G S, Sun Y L, An Z S, 2006. The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing. *Atmospheric Environment*, 40: 6579–6591.
- Wild S R, Jones K C, 1995. Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environmental Pollution*, 88: 91–108.
- Wilson W E, Suh H H, 1997. Fine particles and coarse particles: concentration relationship to epidemiological studies. Water, Air, and Soil Pollution, 47: 551–581.
- Wu S P, Tao S, Zhang Z H, Lan T, Zuo Q, 2005. Distribution of particle-phase hydrocarbons, PAHs and OCPs in Tianjin, China. Atmospheric Environment, 39: 7420–7432.
- Xu D D, Dan M, Song Y, Chai Z F, Zhuang G S, 2005. Concentration characterizations of extractable organohalogens in PM_{2.5} and PM₁₀ in Beijing, China. *Atmospheric Environment*, 39: 4119–4128.
- Yao X, Fang M, Chan C K, 2002. Size distributions and formation of dicarboxylic acids in atmospheric particles. *Atmospheric Environment*, 6: 2099–2107.
- Yassaa N, Meklati B Y, Cecinato A, Marino F, 2001. Particulate *n*-alkanes, *n*-alkanoic acid and polycyclic aromatic hydrocarbons in the atmosphere of Algiers City. *Atmospheric Environment*, 35: 1843–1851.
- Yunker M B, Macdonald R W, Vingarzan R, Mitchell R H, Goyette D, Sylvestre S, 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Geochemistry*, 33: 489–515.
- Zheng M, Fang M, Wang F, To K L, 2000. Characterization of the solvent extractable organic compounds in PM_{2.5} aerosols in Hong Kong. *Atmospheric Environment*, 34: 2691–2702.

