Science of the Total Environment 408 (2010) 5452–5460

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Polar organic and inorganic markers in PM_{10} aerosols from an inland city of China — Seasonal trends and sources

Mingjie Xie [a], Gehui Wang [a,b,*], Shuyuan Hu [a], Shixiang Gao [a], Qingyou Han [c], Yajuan Xu [c], Jianfang Feng [a]

[a] School of the Environment, State Key Laboratory of Pollution Control and Resources Reuse, Najing University, Nanjing 210093, China
[b] Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China
[c] Baoji Environment Monitoring Station, Baoji 721006, China

ARTICLE INFO

Article history:
Received 7 February 2010
Received in revised form 27 June 2010
Accepted 14 July 2010
Available online 16 August 2010

Keywords:
Biomass burning
Sugars
n-alkanoic acids
Elements
Sources

ABSTRACT

Polar organic compounds and elements were quantified in PM_{10} aerosols collected in urban and rural areas of Baoji, an inland city of China, during winter and spring 2008. Concentrations of biomass burning markers and high molecular weight *n*-alkanoic acids (HMW, $>C_{22:0}$) were heavily increased in winter. In contrast, sugars presented in higher levels in the spring, among which sucrose was the most abundant with an average of 219 ng m^{-3} in winter and 473 ng m^{-3} in spring respectively. This suggests enhanced biotic activity in the warm season, whereas no obvious trend was observed for sugar alcohols, concentrations of the three sugar alcohols in spring were only 0.94–2.3 times as those in winter, indicating a second pathway of their formation other than fungal spores in cold season. Major crustal elements (i.e., Fe, K, Mn and Ti) in PM_{10} aerosols were also observed in larger concentrations in spring samples than those in winter due to an enhancement of coarse particles from soil minerals. By using principal component analysis (PCA) and positive matrix factorization (PMF), sources and their contributions to the PM components were also investigated in this study. Four factors were extracted with both models, and the sources represented by different factors were based on the highest loaded marker species as follows: factor 1, soil and road dust (Fe, Sr and Ti); factor 2, biomass burning (levoglucosan, galactosan and syringic acid); factor 3, microbial emissions (fructose and sucrose); and factor 4, fossil fuel combustion and fungal spores influence (Pb, Zn, arabitol and mannitol). The high correlation between PM_{10} and factor 1 suggested that PM_{10} pollution in Baoji was dominated by soil and dust re-suspension.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Organic compounds consist in a significant part of atmospheric particulate matter (PM) and can have negative health and climate impacts. Numerous studies have focused on non-polar compounds such as polycyclic aromatic hydrocarbons (PAHs) due to their carcinogenic and mutagenic properties (Dockery et al., 1993). Polar constituents like sugars and *n*-alkanoic acids have been widely used as tracers for the identification of aerosol sources (e.g. biomass burning, biogenic detritus and soil re-suspension) (Cheng et al., 2006; Simoneit et al., 2004; Wang and Kawamura, 2005; Kourtchev et al., 2008). Moreover, sugars are also recognized to be active cloud condensation nuclei (CCN) as those water-soluble ions (e.g. NH_4^+, NO_3^-, SO_4^{2-}) and dicarboxylic acids (Simoneit et al., 2004; Sun and Ariya, 2006). Given the amphiphilic nature of the compounds, the hydrophobic films formed by *n*-alkanoic acids could alter the physiochemical properties of aerosols and cloud droplets (Seidl, 2000), and be transformed into a reactive hydrophilic layer by oxidative processing (Vesna et al., 2008). Besides heavy metal toxicity, water-soluble ions and elements are the most investigated inorganic components for source apportionment (Biegalski and Hopke, 2004; Wang et al., 2006b; Bi et al., 2007; Ragosta et al., 2008).

In the past several years, many studies have focused on the air pollution of mega-cities in coastal China (Guo et al., 2003; Huang et al., 2006; Duan et al., 2007; Wang et al., 2007). However, there is not much information on this problem in medium-size cities of the country, especially the inland regions, where low levels of economic development, reduced wet deposition, and more coal and biomass burning make the characteristics of air pollution different from those in the coastal regions. Therefore, it is necessary to study the aerosol pollution in the inland cities so as to fully understand air pollution in China and East Asia.

Baoji (33°35′–35°06′N, 106°18′–108°03′E) is an inland city situated in the mid-west part of China, where aerosol pollution is significant, especially in winter due to drastic enhancement of coal and biomass burning for house heating. To better understand the sources and chemical characteristics of the aerosols in Baoji, PM_{10}

---

* Corresponding author. Institute of Earth Environment, Chinese Academy of Sciences, South Fenghui Road 10#, Hi-tech Zone, Xi'an 710075, China. Tel.: +86 29 8832 9320; fax: +86 29 8832 0456.
E-mail addresses: wanggh@ieecas.cn, gehuiwang@yahoo.com.cn (G. Wang).

0048-9697/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2010.07.029

aerosols at four locations of the city were collected and comprehensively characterized including organic and inorganic species during winter and spring 2008. Here we first present the seasonal variations of polar components and element enrichment, then focus on the sources of the specified compounds using principal component analysis (PCA) and positive matrix factorization (PMF).

2. Experimental section

2.1. Site description and sample collection

The sampling campaign was conducted at four locations in urban and rural areas of Baoji City. The sites were the Environmental Monitoring Station (MS, 34º21′18.4″N, 107º08′34.7″E), Da Qing Road (DQ, 34º21′52.5″N, 107º11′47.6″E), Jing Yi Road (JY, 34º22′22.5″N, 107º08′34.1″E) and Miao Gou Village (MG, 34º17′24.0″N, 107º11′20.0″E) (Fig. 1). MS is located in a large and dense residential area, and significantly influenced by coal combustion during winter. DQ and JY are a traffic center and a downtown area respectively. MG represents a rural location, which is approximately eight kilometers from the city center.

Sampling procedures were described previously (Xie et al., 2009). Briefly, PM_{10} samples were simultaneously collected at the four sites on quartz fiber filters from 8:00 a.m. to 4:00 p.m. at a rate of 100 L/min, over a five day period in the winter (February 15–19) and for two three day periods in the spring (April 8–10 and 15–17).

2.2. Organic compound analysis by GC/MS

The GC/MS method for sample analysis was described elsewhere (Wang and Kawamura, 2005). Briefly, the filter was cut into pieces and extracted ultrasonically with a 2:1 by volume solution of dichloromethane and methanol, three times each for 10 min and then filtered through a quartz wool packed pipette. The samples were then dried using a rotary evaporator and N_2 blow-down system. The dry extracts were reacted with 50 μL of *N, O*-bis (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethyl chloride and 10 μL of pyridine for 3 h at 70 °C in order to convert COOH and OH groups into corresponding trimethylsilyl (TMS) esters and ethers. Finally, 140 μL of 1.43 ng μL^{-1} *n*-tridecane in hexane was added as an internal standard before GC–MS determination.

The total extracts were quantified by a Trace GC-Polaris II mass spectrometer (electron impact mode, 70 eV). GC separation was carried out with a DB-5 fused silica capillary column. The GC oven temperature was programmed from 50 °C (2 min) to 120 °C at 15 °C per minute, then to 300 °C at 6 °C per minute and held at 300 °C for 16 min. GC–MS response factors were acquired using previously authenticated standards. Recovery experiments showed that average recoveries for all the compounds were better than 80%. No significant contamination was found in the field and laboratory blanks. All the data reported here were corrected for field blanks, but not for recoveries.

2.3. Inorganic elemental analysis

One fourth of each sample was digested in an 8 mL mixture of concentrated nitric acid, hydrochloric acid and hydrofluoric acid (2:1:1 ratio by volume) at 110 °C for 3–4 h. After digestion, the solution was evaporated to dryness at 70 °C and re-dissolved with 2% nitric acid and brought to a final volume of 15 mL with de-ionized (18 MΩ) water. A Perkin Elmer 5300 ICP-AES was used to quantify the concentrations of eighteen elements. Blank filters were analyzed by the same method in order to blank-correct the samples. The average contents of most metals in the blanks were 5–20 times lower than those in the real samples. Certified reference material from NIST (particulate matter 1648) was used to evaluate the recovery of the entire analytical procedure, which ranged from 91% for Fe to 103% for Zn. In this study, we only report the enrichment of Ba, Cd, Cu, Fe, K, Mn, Ni, Pb, Sr, Ti, V and Zn in the PM_{10} samples for source apportionment. Their seasonal and spatial variations and relationship with primary and secondary organic aerosols in the samples have been presented elsewhere (Wang et al., 2010).

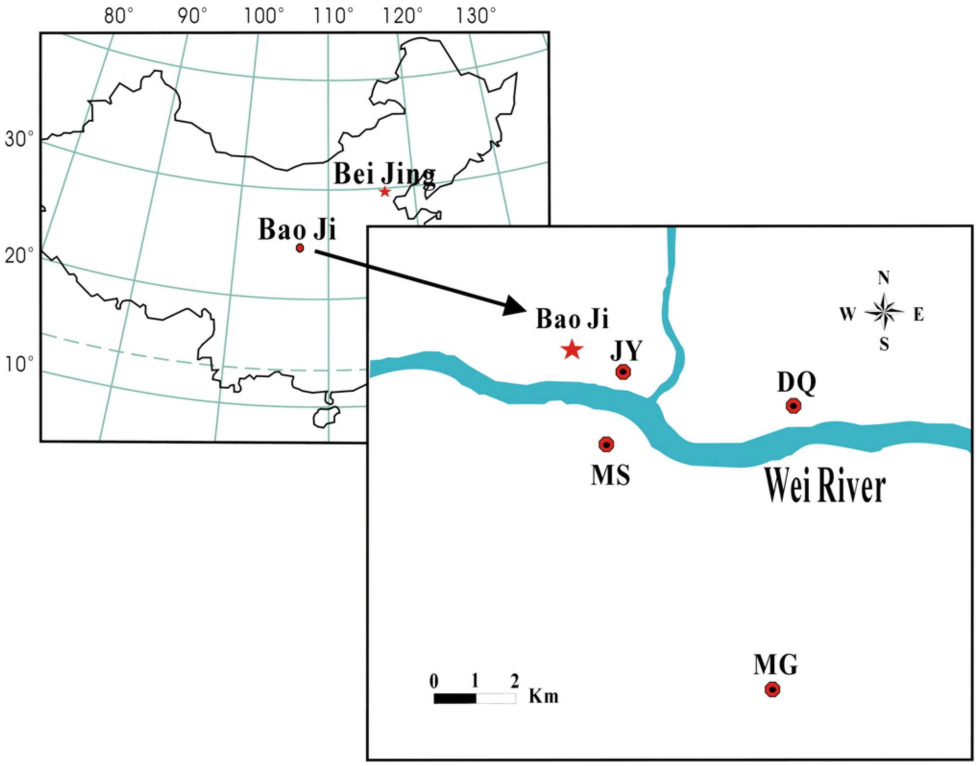

Fig. 1. Locations of four sampling sites: Environmental Monitoring Station (MS), Da Qing Road (DQ), Jing Yi Road (JY), Miao Gou Village (MG).

Table 1

PM loadings in Baoji and other Chinese mega-cities.

City	Time period of measurement	Particles	Site number	Sample number	Average concentrations ($\mu g\ m^{-3}$)	Reference
Baoji	02/2008	PM_{10}	4	20	402	This study
	04/2008	PM_{10}	4	24	410	
Beijing	03/2001–03/2006	PM_{10}	12	1746	154	Okuda et al. (2008)
Nanjing	02–12/2001	PM_{10}	5	40	316	Wang et al. (2003)
Shanghai	11/2001–02/2002	PM_{10}	7	7	152	Zheng et al. (2004)
Guangzhou	07–09/2004	TSP	4	23	212	Yu et al. (2006)
	07/2006–04/2007	TSP	3	30	224	Ma et al. (in press)
Hong Kong	11/2000–02/2001	PM_{10}	3	70	79	Ho et al. (2003)

2.4. Factor analysis

In order to investigate the relationship between the elements and polar organic components measured in this work, principal component analysis (PCA) was applied on the database of all 44 samples. 18 species were selected according to their data quality and importance for specific sources. Varimax rotated factor loading matrix were calculated with SPSS 11.0, and only factors with eigenvalues higher than 1.0 were retained. Due to the small sample size in this study, positive matrix factorization (PMF) analysis were also performed with the same database, so as to compare with the results of PCA and estimate the source contributions to different species. For current analysis, PMF 1.1 was run 20 times in robust mode, and the number of factors was based on the sum of the squared weight residuals (Q value), and the plausibility and interpretability of different solutions (3–10 factors).

3. Results and discussion

3.1. General comments on previous studies in Baoji City

PM_{10} loadings in Baoji were 1–2 times higher than the National Ambient Air Quality Standard (NAAQS) of USA ($150\ \mu g\ m^{-3}$ for a 24 hour period), with the highest level at the site DQ ($461 \pm 56\ \mu g\ m^{-3}$) in winter and at JY ($556 \pm 125\ \mu g\ m^{-3}$) in spring; while the lowest was observed at the MG location (winter $308 \pm 84\ \mu g\ m^{-3}$, spring $296 \pm 134\ \mu g\ m^{-3}$) during both seasons (Hu et al., 2010). The

Table 2

Concentrations of polar organic tracers in PM_{10} from Baoji and aerosols from other cities ($ng\ m^{-3}$).

Compounds	Baoji				Ghent (Belgium)[a]		Elverum (Norway)[b]		Nanjing (China)[c]	
	Winter ($N=20$)		Spring ($N=24$)		Winter	Summer	Winter	Summer	Winter	Summer
	Range	Mean	Range	Mean	PM_{10}		PM_{10}		$PM_{2.5}$	
Cellulosic products										
Levoglucosan	430–1894	901	87–644	261	420	19	605	47	267	151
1,6-anhydroglucо-furanose	24–133	58	5.7–63	21	32	1.6				
Galactosan	30–186	96	7.2–85	30	25	1	4	3		
Manosan	22–134	54	3.8–37	15	61	3	167	10		
M/G[d]	0.41–0.72	0.55	0.34–0.78	0.54						
Resin and lignin products										
Dehydroabietic acid	4.3–220	44	1.8–115	28					17	7.9
Vanillic acid	3.2–21	12	0.3–6.7	2.3					5.1	0.9
Syringic acid	1.6–13	6.9	n.d.[e]–3.9	1.2					3.3	0.6
Sugars and sugar alcohols										
Fructose	5.7–422	73	9.3–654	120	37	193	11	11	13	25
Glucose	2.4–304	55	8.0–537	112	73	270	22	19	14	19
Sucrose	0.9–1736	219	4.0–2709	473	48	100	95	110	13	11
Trehalose	n.d.–18	7.9	2.5–77	20			13	30	2.8	3.8
Mannitol	1.0–11	5	2.9–34	13	26	97	4.2	18	3.8	5.7
Arabitol	5.3–27	17	4.8–27	16	26	105	5.3	20	7.7	4.4
Inositol	0.4–19	5.1	0.7–39	7.6	4.3	40	3.4	2.5	2.1	1.8
Fatty acids										
$C_{12:0}$–$C_{30:0}$	407–3962	2020	120–3743	1104					233	277
Global CPI[f]	6.4–14	9.4	10–22	14					6.6	7.6
Plant wax %[g]	22–50	39	10–38	21					31	59
$>C_{22:0}/<C_{20:0}$	0.3–1.2	0.8	0.1–0.7	0.3					0.5	1.7
$C_{18:0}/C_{18:1}$	4.1–14	7.7	4.6–14	7.1					1.5	2.0
Total polar organics	1062–6851	3573	486–8694	2404					582	508
Particle mass ($\mu g\ m^{-3}$)	207–574	402	158–691	410					119	132
Total polar organics/PM, %	0.39–1.65	0.86	0.23–1.36	0.51					0.49	0.38

[a] Pashynska et al.(2002).

[b] Yttri et al.(2007).

[c] Wang and Kawamura, 2005.

[d] Ratios of mannosan to galactosan.

[e] Not detected.

[f] Global CPI: carbon preference index ($\sum C_{12:0} + C_{14:0} + \ldots + C_{28:0} + C_{30:0} / \sum C_{13:0} + C_{15:0} + \ldots + C_{27:0} + C_{29:0}$).

[g] Plant wax %: ($\sum C_{23:0} - C_{30:0} / \sum C_{12:0} - C_{30:0}$) * 100%.

increased vehicle emissions, road dust and re-entrainment of soil particles along with other anthropogenic activities lead to the high PM_{10} levels at the DQ and JY sites. The size-resolved particles collected at the MS site showed that fractions of coarse particles (>2.1 μm) increased by approximately 20% from winter to spring (Wang et al., 2009). Table 1 shows that average particle mass concentrations in Baoji were higher than in more studied Chinese mega-cities. Similar trends were also observed for PM_{10}-associated *n*-alkanes and PAHs in a previous study (Xie et al., 2009), which may indicate that air pollution in mid-scale cities like Baoji is a more serious problem than previously thought.

3.2. Polar organic compounds

3.2.1. Cellulose, resin and lignins

Table 2 shows the strong seasonal trends observed for all biomass burning tracers with higher levels in winter, which suggested an enhancement from biomass fuel use during the colder weather. Levoglucosan was the most abundant cellulose product, followed by galactosan, 1,6-anhydrogluco-furanose and mannosan, and had concentrations from 430 to 1894 ng m^{-3} with an average of 901 ng m^{-3} in winter, and from 87 to 261 ng m^{-3} with an average of 261 ng m^{-3} in spring. These concentrations are much higher than the average concentrations (winter 671 ng m^{-3}, summer 105 ng m^{-3}) observed in the 14 mega-cities of China (Wang et al., 2006a). Levoglucosan is a key maker for biomass burning for its stability and ubiquity in ambient aerosols (Simoneit et al., 1999), but mannosan and galactosan have been demonstrated as better specific tracers because levoglucosan also presents in high levels in brown coal pyrolysates (Fabbri et al., 2008). A strong association between levoglucosan and the two species was obtained for all samples in both winter and spring (Fig. 2a), suggesting that levoglucosan was mostly generated from cellulose burning in this study. Moreover, average ratios of mannosan to galactosan (M/G 0.55 in winter and 0.54 in spring) were close to those observed in deciduous tree combustion (0.52) (Oros and Simoneit, 2001b), which indicated greater contribution of anhydrosugars from angiosperms burning than gramineae (M/G 0.23, Oros et al., 2006) and gymnosperms (M/G 0.94, Oros and Simoneit, 2001a).

Dehydroabietic acid is a key tracer for coniferous wood combustion, which also contributes minor amounts of vanillic and syringic acids (Simoneit et al., 1999). Concentrations of vanillic acid and syringic acid were highly correlated in the two periods, with less correlation between vanillic and dehydroabietic acids (Fig. 2b). These results can likely be explained by their different precursors and formation processes. Vanillic and syringic acids are lignin pyrolysis products, while dehydroabietic acid is a variation derived from resin acids (Simoneit, 2002). Along with conifers, deciduous trees and grass combustion also contained vannilic and syringic acids, but no dehydroabietic acid (Simoneit et al., 1999). Compared with those mega-cities in China, biomass was still an important fuel resource in Baoji and widely used for cooking and heating, resulting in high concentrations of the biomass tracers in this area.

3.2.2. Sugars and sugar alcohols

Primary sugars mainly originate from soil dust, microorganisms, pollen, and fragments of plants and animals (Bieleski, 1995; Simoneit et al., 2004; Medeiros et al., 2006), and are associated mostly with coarse aerosols (>2.0 μm) (Graham et al., 2003; Yttri et al., 2007). In this study, sucrose was found to be the most abundant sugar with 219 ng m^{-3} (0.9–1736 ng m^{-3}) in winter and 473 ng m^{-3} (4.0–2709 ng m^{-3}) in spring (Table 2), 2–3 times higher than fructose and glucose. Fig. 3 shows examples of GC/MS data for sugar compounds (m/z 217 ion tracers) in winter and spring, and a relatively higher presence of mono- and disaccharides were found in spring. Similar seasonal variation was also obtained in Belgium (Pashynska et al., 2002), the increment of coarse particles and biotic activities in the warmer season are the most important reasons for the higher concentration of primary sugars. Quantitative relationships have been established between the number of fungal spores and the concentrations of arabitol and mannitol (Bauer et al., 2008). However, sugar alcohols emitted by fungal spores with a diameter range of 2–50 μm are mainly associated with coarse aerosols (Carvalho et al., 2003), and should have higher concentrations in warm seasons. Here, concentrations of the three sugar alcohols in spring were only 0.94–2.3 times as those in winter, comparable with the levels in Elverum (Norway) and Nanjing (China) (Wang and Kawamura, 2005; Yttri et al., 2007), and a second source for sugar alcohols might be inferred from the slightly higher concentration of arabitol in winter.

3.2.3. Fatty acids

The total concentration of saturated fatty acids ($C_{12:0}$–$C_{30:0}$) ranged from 407 to 3962 ng m^{-3} with an average of 2020 ng m^{-3} in winter and from 120 to 3743 ng m^{-3} with an average of 1104 ng m^{-3} in spring (Table 2), higher than the results obtained in coastal cities of China such as Hong Kong (winter 134 ng m^{-3}, spring 58 ng m^{-3}) (Zheng et al., 2000), Beijing (winter 426 ng m^{-3}, spring 255 ng m^{-3}) (Huang et al., 2006) and Qingdao (winter 925 ng m^{-3}, spring 247 ng m^{-3}) (Guo et al., 2003). Hexadecanoic acid ($C_{16:0}$) and octadecanoic acid ($C_{18:0}$) were the most abundant *n*-alkanoic acids in all samples. Octadecenoic acid ($C_{18:1}$) is chemically unstable and $C_{18:0}/C_{18:1}$ is a useful marker to gauge the age of the aerosols. In this work, the similar values of $C_{18:0}/C_{18:1}$ in the winter and spring samples suggested that the aerosols collected had a similar degradation rate in both seasons (Guo et al., 2003). The global CPI

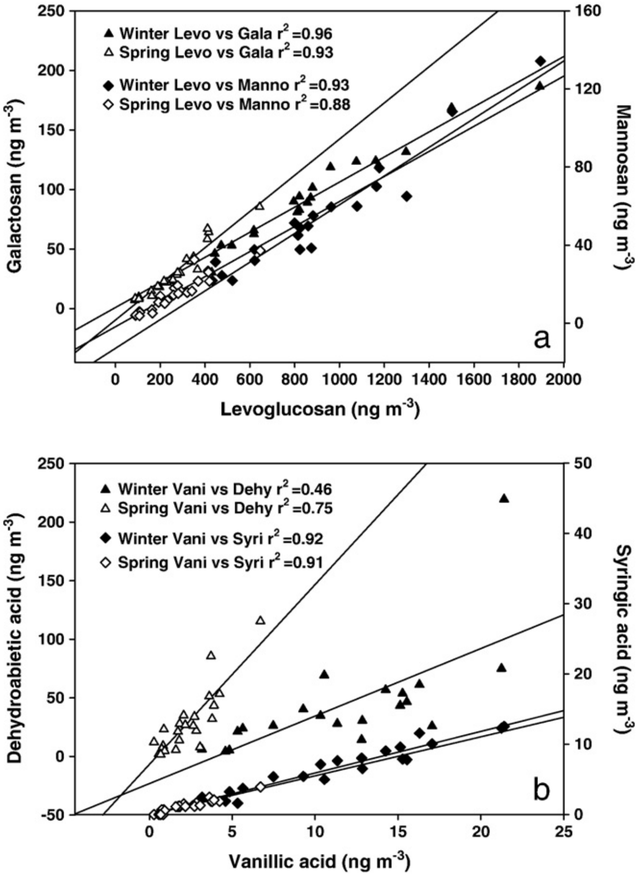

Fig. 2. Scatter plot of biomass tracer concentration, (a) levoglucosan vs. galactosan and mannosan; (b) vanillic acid vs. dehydroabietic and syringic acids.

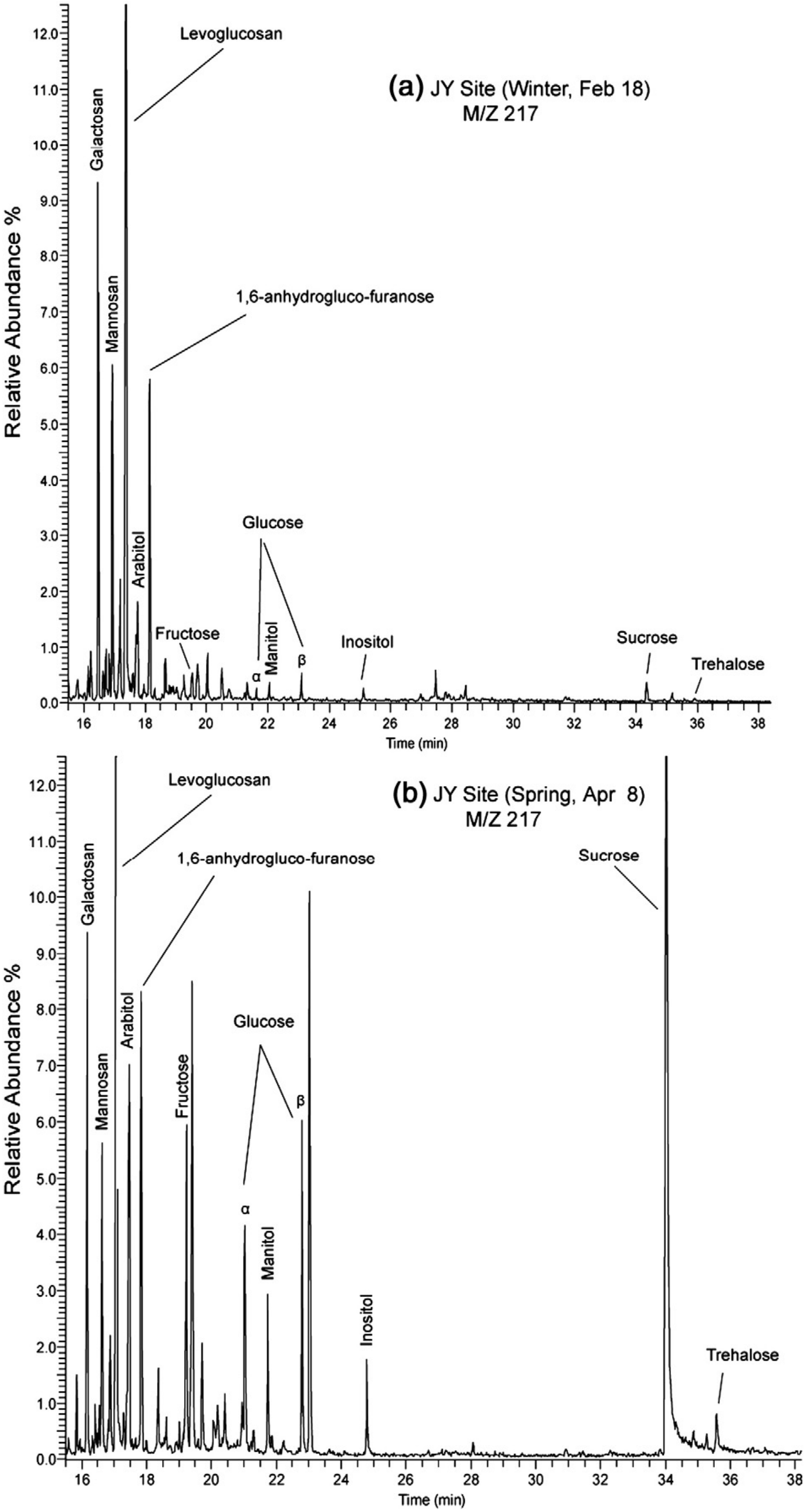

Fig. 3. Representative examples of GC–MS data for m/z 217ion tracers: anhydrosugars, mono-, disaccharides and sugar alcohols in (a) winter and (b) spring.

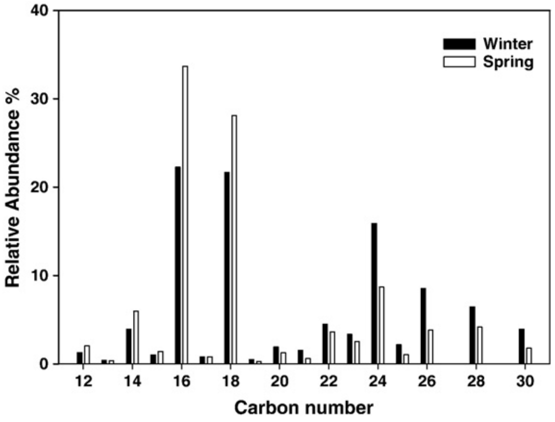

Fig. 4. Molecular pattern of *n*-alkanoic acids during winter and spring.

values on average were 9.4 ± 1.7 and 14 ± 3.0 in winter and spring respectively, indicating an important contribution from biogenic sources in Baoji.

Low molecular weight (LMW) fatty acids ($<C_{20:0}$) are mainly from microbial activities, fossil fuel combustion and cooking (Oliveira et al., 2007), while high molecular weight (HMW) fatty acids ($>C_{22:0}$) are derived primarily from terrestrial higher plant wax by direct emission or biomass burning (Radzi Bin Abas et al., 2004). Fig. 4 shows that LMW fatty acids were dominant in both periods, especially in spring with an average of 0.3 ± 0.1 for $>C_{22:0}/<C_{20:0}$ ratios. C_{max} of $>C_{22:0}$ homologue series was tetracosanoic acid ($C_{24:0}$) for all samples. Concentrations of HMW fatty acids ($>C_{22:0}$) increased by 236% from spring to winter, much more abundant than LMW acids (31%). Consequently, $>C_{22:0}/<C_{20:0}$ ratios and plant wax portion in winter were respectively 2.7 and 1.9 times of their corresponding values in spring (Table 2), which can also be observed from Fig. 4 and probably due to the enhancement in biomass fuel use during winter.

3.3. Enrichment of various elements and their sources

Fe was the most abundant element, accounting for 1.1% and 2.1% of the PM_{10} mass in winter and spring respectively, followed by K, Zn, Pb and Ti (Table 3). All crustal elements (Fe, K, Sr, Ti) presented in higher contributions in spring due to the increase of coarse particles (>2.1 μm). Most elements detected were less enriched in this PM_{10} mass than Beijing, Shanghai and Hangzhou (%PM, Table 3), especially for Pb and Zn, whose concentrations, however, were comparable with these mega-cities. Possible reasons are as follows. First, since the three urban sites were close to busy roads, Zn and Pb from engine exhaust should be an important source, and the two elements from tire and brake wear and oil leakage are likely resuspended with road dust (Harrison et al., 2003; McKenzie et al., 2009; Wang et al., 2006b). Second, coal usage (2.16 million tons per year) accounted for approximately 96% of the fossil fuel energy in Baoji, which also contributes great amount of Zn and Pb. Finally, high Zn and Pb levels can partially be attributed to the metallurgical industry for the rich Zn and Pb minerals in Baoji.

Enrichment factor (EF) analysis is a useful tool to assess the primary source of elements and has been calculated using Fe as the reference. The mean abundance of the target elements in the crust is cited from Taylor (1964), and an enrichment factor of 10 is taken as the critical value to judge true anthropogenic influences. Here, EFs of K, Ti, Sr, Ba, Mn, Ni, V generally fell below 5 in both seasons indicating no enrichment (Table 3), even though diverse anthropogenic sources had been observed for Ba, Mn, Ni and V (Godoy et al., 2005; Wang et al., 2006b). The EFs of Cu were slightly higher with an average of 10 and 15 in winter and spring respectively, while Cd, Pb and Zn were mostly from human activities due to their relatively high values (>100). Unlike that seen in mega-cities, Ba and Cu in Baoji had less anthropogenic contribution as determined from their low EFs.

3.4. Source apportionment

Four factors were resolved by both PCA and PMF analysis. Factors in PCA interpret 92% of the total data variability; and the minimum Q_{robust} reported from PMF results is only 0.4% larger than theoretical value. Despite those inherent problems of receptor models described by Schnelle-Kreis et al. (2007), the factors separated by means of PCA and PMF presented a similar loading pattern of the investigated compounds (Fig. 5), and could be clearly assigned to dominant sources.

Factor 1 is characterized by high loadings of elements such as Fe, Ti, and Sr. Zn presented the second highest loading on this factor, which is due to the similar component pattern between road dust and soil, and they could not be distinguished in this study. Factor 2 appears to represent biomass burning. Loadings on this profile are highest for

Table 3
Elemental compositions and enrichment factors (EFs) of PM_{10} in Baoji and other cities in China.

Elements	Baoji				Beijing[a]		Shanghai[b]		Hangzhou[c]		Hong Kong[d]	
	Winter		Spring		Winter		Winter		Annual		Winter	
	%PM [e]	EF [f]	%PM	EF	%PM	EF	%PM	EF	%PM	EF	%PM	EF
Ba	0.037	4.4	0.05	3.3	–	–	1.63	125	0.40	29	–	–
Cd	0.002	517	n.d.[g]	–	0.007	1250	0.007	1286	0.008	1285	–	–
Cu	0.015	15	0.015	10	0.042	28	0.11	57	0.11	61	0.048	52
Fe	1.1	1.0	2.1	1.0	1.54	1.0	1.8	1.0	1.84	1.0	0.96	1.0
K	0.91	2.4	1.3	1.8	–	–	2.2	3.6	3.49	5.1	1.50	4.2
Mn	0.044	2.4	0.067	2	0.067	2.6	0.12	4.2	0.11	3.5	0.029	1.8
Ni	0.003	1.8	0.004	1.8	0.043	21	0.009	3.3	0.017	6.9	0.011	8.7
Pb	0.14	613	0.14	398	0.17	506	0.34	674	0.31	761	0.11	519
Sr	0.021	2.7	0.024	1.7	0.034	3.3	0.022	1.8	–	–	–	–
Ti	0.11	1	0.16	0.8	0.12	0.8	0.15	0.8	0.14	0.8	0.022	0.2
V	0.003	1.1	0.003	0.7	0.007	1.9	0.012	2.3	0.017	3.8	0.006	2.6
Zn	0.18	136	0.27	133	0.35	184	0.93	288	0.46	202	0.39	329
PM_{10} mass (μg m^{-3})	402		410		255		152		119		79	

[a] Sun et al. (2004).
[b] Zheng et al. (2004).
[c] Cao et al. (2009).
[d] Ho et al. (2003).
[e] %PM = (element concentration / PM_{10} mass) * 100%.
[f] EF: enrichment factor = $(X/R)_{Atmosphere}/(X/R)_{Crust}$.
[g] Not detected.

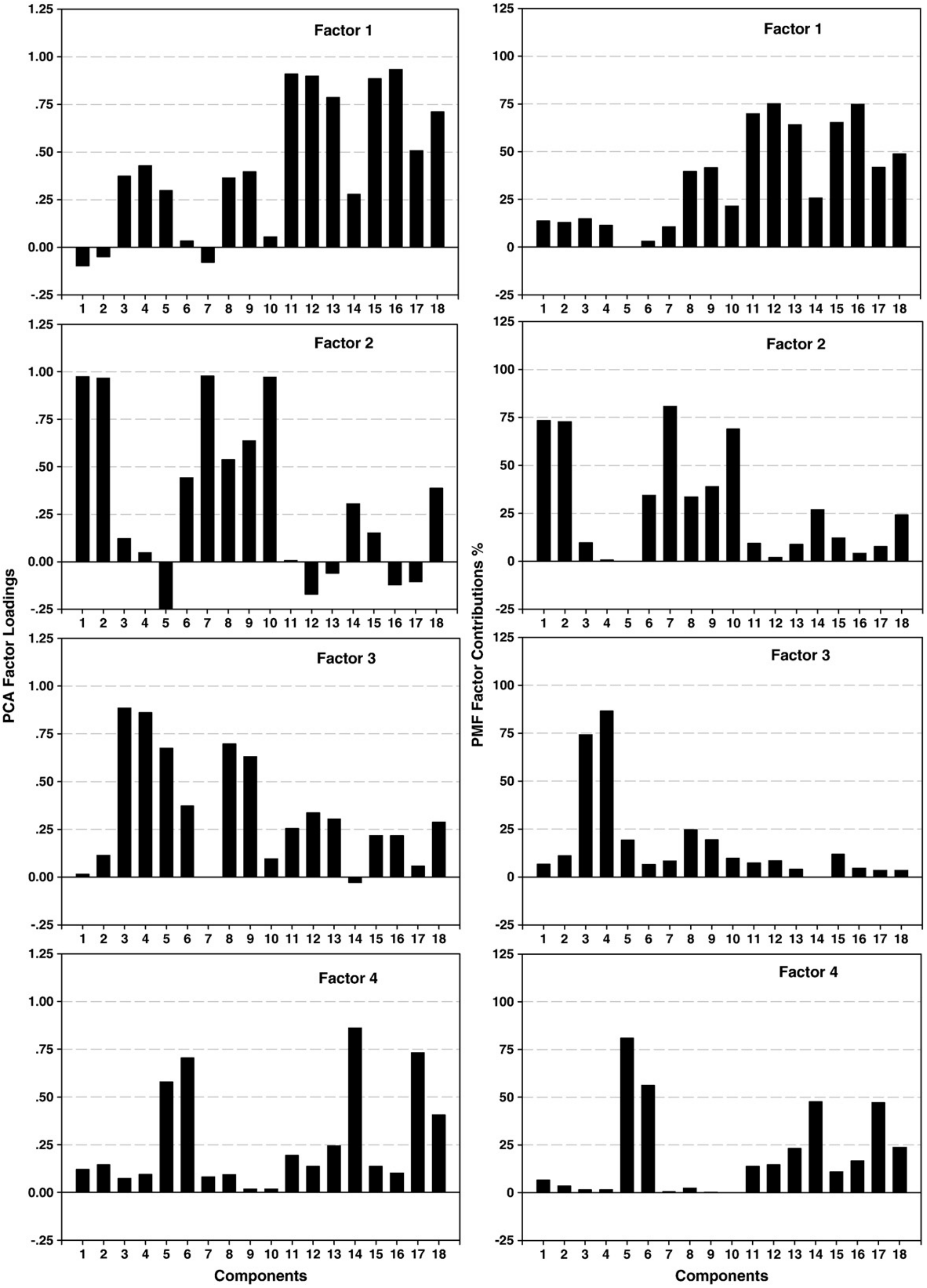

Fig. 5. Results of PCA and PMF analysis. 1.Levoglucosan 2. Galactosan 3. Fructose 4. Sucrose 5. Mannitol 6. Arabitol 7. Vannilic acid 8. Hexadecanoic acid ($C_{16:0}$) 9. Octadecanoic acid ($C_{18:0}$) 10. Tetracosanoic acid ($C_{24:0}$) 11. Ba 12. Fe 13. Mn 14. Pb 15. Sr 16. Ti 17. Zn 18. PM_{10} mass.

levoglucosan, galactosan, fatty acids, and vannilic acids. No other factors show high loading for tetracosanoic acid ($C_{24:0}$), supporting the theory that biomass burning caused the observed higher plant wax portion of fatty acids in cold season. The third factor from PCA is dominated by monosaccharides, LMW fatty acids and mannitol, which is somewhat inconsistent with the third factor pattern of PMF analysis. This might have been caused by the innate difference of these two models. The factor loading in PCA only represents the correlation between variables and factors, while PMF model uses non-negativity constraints to estimate factor contributions. However, fructose and sucrose are the most characteristic compounds in factor 3 for both models, indicating microorganism activities as the major source in this factor. This also corresponds to the other highly correlated variables in factor 3 of PCA. Factor 4 was determined to be representative of fossil fuel combustion since Pb and Zn were highest loaded on this factor. Moreover, there are also clear indications for fungal spore influence, due to the high concentrated arabitol and mannitol in this factor, and no other emission sources for these two components have been reported (Bauer et al., 2008). Therefore, factor 4 combines fossil fuel combustion and fungal spore emissions, and the lack of separation might be caused by the limitation in sample number. According to PMF model results, factor 1 contributes the largest part of PM_{10} mass (49%), followed by factor 2 and 4, both account for 24%, and factor 3 has the lowest quota, suggesting that soil and road dust are the most important sources for PM_{10} mass, and biomass fuel use do relate to the high concentrations of PM_{10} aerosols in this area.

4. Conclusion

Polar organic compounds comprising cellulose, resin products, sugars, sugar alcohols and fatty acids, along with inorganic elements were examined in PM_{10} aerosols at four sites of Baoji during winter and spring of 2008. Biomass tracers and HMW *n*-alkanoic acids exhibited higher concentrations in winter due to increased biomass fuel use for the heating season, contrasted against the seasonal variation of sugars and crustal elements, which had higher loadings in spring due to an enhancement in coarse particle fraction. Sucrose was the most abundant sugar type with an average value of 219 ng m^{-3} and 473 ng m^{-3} in winter and spring, followed by fructose (73 ng m^{-3} in winter and 120 ng m^{-3} in spring) and glucose (55 ng m^{-3} in winter and 112 ng m^{-3} in spring). The non-uniform seasonal trend of sugar alcohols might be attributed to a secondary source other than fungal spores. Most elements were less enriched in the PM_{10} samples than in those more heavily polluted areas in China, and only Cd, Pb and Zn were clearly associated with anthropogenic activities based on their high enrichment factors. Source apportionment analysis was conducted by using Principal Component Analysis and EPA PMF1.1 models. Both models identified four factors that were consistent with each other, and the sources represented were soil and road dust, biomass burning, microbial emissions and a mixture of fossil fuel combustion and fungal spores, among which soil and road dust accounted for most of the PM_{10} mass. This study is one of the few source apportionment results for an inland mid-scale city in China, and shows a variety of source influences other than coal burning as were reported in a previous study (Xie et al., 2009).

Acknowledgments

This work was financially support by the China Natural Science Foundation (nos. 40873083 and 40475050) and the Knowledge Innovation Program of Chinese Academy of Sciences (no. KZCX2-YW-148).

References

Bauer H, Claeys M, Vermeylen R, Schueller E, Weinke G, Berger A, et al. Arabitol and mannitol as tracers for the quantification of airborne fungal spores. Atmos Environ 2008;42:588–93.

Bi XH, Feng YC, Wu JH, Wang YQ, Zhu T. Source apportionment of PM10 in six cities of northern China. Atmos Environ 2007;41:903–12.

Biegalski SR, Hopke PK. Total potential source contribution function analysis of trace elements determined in aerosol samples collected near Lake Huron. Environ Sci Technol 2004;38:4276–84.

Bieleski RL. Onset of phloem export from senescent petals of Daylily. Plant Physiol 1995;109:557–65.

Cao J, Shen Z, Chow JC, Qi G, Watson JG. Seasonal variations and sources of mass and chemical composition for PM10 aerosol in Hangzhou, China. Particuology 2009;7:161–8.

Carvalho A, Pio C, Santos C. Water-soluble hydroxylated organic compounds in German and Finnish aerosols. Atmos Environ 2003;37:1775–83.

Cheng Y, Li SM, Leithead A, Brook JR. Spatial and diurnal distributions of n-alkanes and n-alkan-2-ones on PM2.5 aerosols in the Lower Fraser Valley, Canada. Atmos Environ 2006;40:2706–20.

Dockery DW, Pope CA, Xu XP, Spengler JD, Ware JH, Fay ME, et al. An association between air-pollution and mortality in 6 U.S. cities. N Engl J Med 1993;329:1753–9.

Duan J, Bi X, Tan J, Sheng G, Fu J. Seasonal variation on size distribution and concentration of PAHs in Guangzhou city, China. Chemosphere 2007;67:614–22.

Fabbri D, Marynowski L, Fabiańska MJ, Zatoń M, Simoneit BRT. Levoglucosan and other cellulose markers in pyrolysates of Miocene lignites: geochemical and environmental implications. Environ Sci Technol 2008;42:2957–63.

Godoy MLDP, Godoy JM, Artaxo P. Aerosol source apportionment around a large coal fired power plant—Thermoelectric Complex Jorge Lacerda, Santa Catarina, Brazil. Atmos Environ 2005;39:5307–24.

Graham B, Guyon P, Taylor PE, Artaxo P, Maenhaut W, Glovsky MM, et al. Organic compounds present in the natural Amazonian aerosol: characterization by gas chromatography-mass spectrometry. J Geophys Res Atmos 2003;108(D24):4766.

Guo ZG, Sheng LF, Feng JL, Fang M. Seasonal variation of solvent extractable organic compounds in the aerosols in Qingdao, China. Atmos Environ 2003;37:1825–34.

Harrison RM, Tilling R, Romero MSC, Harrad S, Jarvis K. A study of trace metals and polycyclic aromatic hydrocarbons in the roadside environment. Atmos Environ 2003;37:2391–402.

Ho KF, Lee SC, Chan CK, Yu JC, Chow JC, Yao XH. Characterization of chemical species in PM2.5 and PM10 aerosols in Hong Kong. Atmos Environ 2003;37:31–9.

Hu S, Xie M, Wang G, Han Q, Zhao Y. Component and characteristics of water-soluble species in PM10 aerosol of Baoji. Environ Pollut Contr 2010;32:34–8 (In Chinese).

Huang XF, He LY, Hu M, Zhang YH. Annual variation of particulate organic compounds in PM2.5 in the urban atmosphere of Beijing. Atmos Environ 2006;40:2449–58.

Kourtchev I, Warnke J, Maenhaut W, Hoffmann T, Claeys M. Polar organic marker compounds in PM2.5 aerosol from a mixed forest site in western Germany. Chemosphere 2008;73:1308–14.

Ma S., Peng P., Song J., Bi X., Zhao J., He L., Sheng G., Fu J. in press. Seasonal and spatial changes of free and bound organic acids in total suspended particles in Guangzhou, China. Atmos Environ. doi:10.1016/j.atmosenv.2010.03.013.

McKenzie ER, Money JE, Green PG, Young TM. Metals associated with stormwater-relevant brake and tire samples. Sci Total Environ 2009;407:5855–60.

Medeiros PM, Conte MH, Weber JC, Simoneit BRT. Sugars as source indicators of biogenic organic carbon in aerosols collected above the Howland Experimental Forest, Maine. Atmos Environ 2006;40:1694–705.

Okuda T, Katsuno M, Naoi D, Nakao S, Tanaka S, He K, et al. Trends in hazardous trace metal concentrations in aerosols collected in Beijing, China from 2001 to 2006. Chemosphere 2008;72:917–24.

Oliveira C, Pio C, Alves C, Evtyugina M, Santos P, Gonçalves V, et al. Seasonal distribution of polar organic compounds in the urban atmosphere of two large cities from the North and South of Europe. Atmos Environ 2007;41:5555–70.

Oros DR, Simoneit BRT. Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 1. Temperate climate conifers. Appl Geochem 2001a;16:1513–44.

Oros DR, Simoneit BRT. Identification and emission factors of molecular tracers in organic aerosols from biomass burning Part 2. Deciduous trees. Appl Geochem 2001b;16:1545–65.

Oros DR, Abas MRB, Omar NYMJ, Rahman NA, Simoneit BRT. Identification and emission factors of molecular tracers in organic aerosols from biomass burning: Part 3. Grasses. Appl Geochem 2006;21:919–40.

Pashynska V, Vermeylen R, Vas G, Maenhaut W, Claeys M. Development of a gas chromatographic/ion trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols. Application to urban aerosols. J Mass Spectrom 2002;37:1249–57.

Radzi Bin Abas M, Rahman NA, Omar NYMJ, Maah MJ, Abu Samah A, Oros DR, et al. Organic composition of aerosol particulate matter during a haze episode in Kuala Lumpur, Malaysia. Atmos Environ 2004;38:4223–41.

Ragosta M, Caggiano R, Macchiato M, Sabia S, Trippetta S. Trace elements in daily collected aerosol: level characterization and source identification in a four-year study. Atmos Res 2008;89:206–17.

Schnelle-Kreis J, Sklorz M, Orasche J, Stölzel M, Peters A, Zimmermann R. Semi volatile organic compounds in ambient PM2.5. seasonal trends and daily resolved source contributions. Environ Sci Technol 2007;41:3821–8.

Seidl W. Model for a surface film of fatty acids on rain water and aerosol particles. Atmos Environ 2000;34:4917–32.

Simoneit BRT. Biomass burning? — a review of organic tracers for smoke from incomplete combustion. Appl Geochem 2002;17:129–62.

Simoneit BRT, Schauer JJ, Nolte CG, Oros DR, Elias VO, Fraser MP, et al. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmos Environ 1999;33:173–82.

Simoneit BRT, Elias VO, Kobayashi M, Kawamura K, Rushdi AI, Medeiros PM, et al. Sugars dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter. Environ Sci Technol 2004;38:5939–49.

Sun J, Ariya PA. Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): a review. Atmos Environ 2006;40:795–820.

Sun Y, Zhuang G, Wang Y, Han L, Guo J, Dan M, et al. The air-borne particulate pollution in Beijing—concentration, composition, distribution and sources. Atmos Environ 2004;38:5991–6004.

Taylor SR. Abundance of chemical elements in the continental crust: a new table. Geochim Cosmochim Acta 1964;28:1273–85.

Vesna O, Sjogren S, Weingartner E, Samburova V, Kalberer M, Gäggeler HW, et al. Changes of fatty acid aerosol hygroscopicity induced by ozonolysis under humid conditions. Atmos Chem Phys J1-ACP 2008;8:4683–90.

Wang G, Kawamura K. Molecular characteristics of urban organic aerosols from Nanjing: a case study of a mega-city in China. Environ Sci Technol 2005;39:7430–8.

Wang G, Wang H, Yu Y, Gao S, Feng J, Gao S, et al. Chemical characterization of water-soluble components of PM10 and PM2.5 atmospheric aerosols in five locations of Nanjing, China. Atmos Environ 2003;37:2893–902.

Wang G, Kawamura K, Lee S, Ho KF, Cao JJ. Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. Environ Sci Technol 2006a;40: 4619–25.

Wang X, Sato T, Xing B. Size distribution and anthropogenic sources apportionment of airborne trace metals in Kanazawa, Japan. Chemosphere 2006b;65:2440–8.

Wang G, Kawamura K, Zhao X, Li Q, Dai Z, Niu H. Identification, abundance and seasonal variation of anthropogenic organic aerosols from a mega-city in China. Atmos Environ 2007;41:407–16.

Wang G, Kawamura K, Xie M, Hu S, Gao S, Cao J, et al. Size-distributions of n-alkanes, PAHs and hopanes and their sources in the urban, mountain and marine atmospheres over East Asia. Atmos Chem Phys J1-ACP 2009;9:8869–82.

Wang G, Xie M, Hu S, Tachibana E, Kawamura K. Dicarboxylic acids, elements and isotope compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation. Atmos Chem Phys Discuss J1-ACPD 2010;10:6895–921.

Xie M, Wang G, Hu S, Han Q, Xu Y, Gao Z. Aliphatic alkanes and polycyclic aromatic hydrocarbons in atmospheric PM10 aerosols from Baoji, China: implications for coal burning. Atmos Res 2009;93:840–8.

Yttri KE, Dye C, Kiss G. Ambient aerosol concentrations of sugars and sugar–alcohols at four different sites in Norway. Atmos Chem Phys 2007;7:4267–79.

Yu L, Mai B, Meng X, Bi X, Sheng G, Fu J, et al. Particle-bound polychlorinated dibenzo-p-dioxins and dibenzofurans in the atmosphere of Guangzhou, China. Atmos Environ 2006;40:96-108.

Zheng M, Fang M, Wang F, To KL. Characterization of the solvent extractable organic compounds in PM2.5 aerosols in Hong Kong. Atmos Environ 2000;34:2691–702.

Zheng J, Tan M, Shibata Y, Tanaka A, Li Y, Zhang G, et al. Characteristics of lead isotope ratios and elemental concentrations in PM10 fraction of airborne particulate matter in Shanghai after the phase-out of leaded gasoline. Atmos Environ 2004;38: 1191–200.