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Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation

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Abstract. Dicarboxylic acids (C_2–C_{10}), metals, elemental carbon (EC), organic carbon (OC), and stable isotopic compositions of total carbon (TC) and total nitrogen (TN) were determined for PM_{10} samples collected at three urban and one suburban sites of Baoji, an inland city of China, during winter and spring 2008. Oxalic acid (C_2) was the dominant diacid, followed by succinic (C_4) and malonic (C_3) acids. Total diacids in the urban and suburban areas were 1546 ± 203 and $1728 \pm 495\,\mathrm{ng\,m^{-3}}$ during winter and 1236 ± 335 and $1028 \pm 193\,\mathrm{ng\,m^{-3}}$ during spring. EC in the urban and the suburban atmospheres were 17 ± 3.8 and $8.0 \pm 2.1\,\mathrm{\mu g\,m^{-3}}$ during winter and 20 ± 5.9 and $7.1 \pm 2.7\,\mathrm{\mu g\,m^{-3}}$ during spring, while OC at the urban and suburban sites were 74 ± 14 and $51 \pm 7.9\,\mathrm{\mu g\,m^{-3}}$ in winter and 51 ± 20 and $23 \pm 6.1\,\mathrm{\mu g\,m^{-3}}$ in spring. Secondary organic carbon (SOC) accounted for $38 \pm 16\%$ of OC in winter and $28 \pm 18\%$ of OC in spring, suggesting an enhanced photochemical production of secondary organic aerosols in winter under an inversion layer development. Total metal elements in winter and spring were 34 ± 10 and $61 \pm 27\,\mathrm{\mu g\,m^{-3}}$ in the urban air and 18 ± 7 and $32 \pm 23\,\mathrm{\mu g\,m^{-3}}$ in the suburban air. A linear correlation ($r^2 > 0.8$ in winter and $r^2 > 0.6$ in spring) was found between primary organic carbon (POC) and Ca^{2+}/Fe, together with a strong dependence of pH value of sample extracts on water-soluble inorganic carbon, suggesting fugitive dust as an important source of the airborne particles. Polycyclic aromatic hydrocarbons (PAHs), sulfate, and Pb in the samples well correlated each other ($r^2 > 0.6$) in winter, indicating an importance of emissions from coal burning for house heating. Stable carbon isotope compositions of TC (δ^{13}C) became higher with an increase in the concentration ratios of C_2/OC due to aerosol aging. In contrast, nitrogen isotope compositions of TN (δ^{15}N) became lower with an increases in the mass ratios of NH_4^+/PM_{10} and NO_3^-/PM_{10}, which is possibly caused by an enhanced adsorption and/or condensation of gaseous NH_3 and HNO_3 onto particles.

1 Introduction

Coal is a major energy source in China, accounting for around 70% of the total energy consumption. In 2007, China produced 2.5 billion tons of coal, of which around 50% was burned for generating electricity. A substantial fraction of the remaining is used for domestic heating and cooking. The latter emits a huge amount of carbonaceous aerosols due to low combustion efficiency. These carbonaceous particles, together with sulfate, nitrate and ammonium, can be transported into the North Pacific region and even into North America, causing an inter-continental pollution (Heald et al., 2006).

Very few studies have been performed for air pollution problems in western regions of China, which are characterized by semi-arid/arid climate, intensive usage of coal and relatively lower level of economic development. These situations cause the concentration levels of airborne particulate matter much higher than those in the coastal region of China (Shen et al., 2009; Wang et al., 2006a, b). High concentration

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of fugitive dust frequently occurs in the western area due to the proximity of dust source regions. Annual average pH values of rainwater were observed with the highest ($pH = 8.20$) in Jiayuguan, a mid-scale city in Northwestern China, and the lowest ($pH = 3.05$) in Jieshou, a mid-scale city in Southern China (China Ministry of Environment Protection, 2006), suggesting that the atmospheric environment in the northwest is different from that in other regions of the country.

Baoji is a mid-scale city (33°35′ ∼35°06′ N, 106°18′ ∼108°03′ E, population 0.8 million) located in the semi-arid region of Northwest China, where high loading of particles has been a persistent air pollution problem because of emissions from coal burning and dust. In order to better understand the impact of coal burning and fugitive dust on the atmosphere over in inland regions of China, an intensive aerosol (PM_{10} and size-segregated particles) sampling was simultaneously conducted at four sites in Baoji city during 2008 winter and spring (Wang et al., 2010, 2009; Xie et al., 2009). Here we report the chemical compositions of the PM_{10} samples (i.e. dicarboxylic acids, water-soluble inorganic and organic carbon, elemental and organic carbon, and metals) and their stable carbon and nitrogen isotopic compositions, and discuss the characteristics and sources of those airborne particulate matters in the inland region.

2 Experimental section

2.1 Sample collection

PM_{10} aerosols were simultaneously collected at three urban sites and one suburban site in Baoji city onto a pre-baked (450 °C for 12 h) quartz fiber filter (Φ 90 mm, Whatman) using a mid-volume air sampler (Laoshan Company, China) at a flow rate of $100\,L\,min^{-1}$. The sampling was performed on 10–15 February and 1–6 April 2008 for 8h on each day from 8:30 a.m. to 16:30 p.m. Field blank was mounted onto the sampler for a few minutes without sucking the air. The blank samples were collected before and after sampling at each site in each season. A total of 20 and 24 samples were collected in the winter and spring, respectively, along with 8 blanks in each season. After sampling, the sample and blank filters were sealed in an aluminum foil and stored at −20 °C prior to analysis.

2.2 Dicarboxylic acid determination

Analytical method for diacids was reported elsewhere (Kawamura and Ikushima, 1993; Wang et al., 2002). Briefly, an aliquot of the filter was cut in pieces and extracted with pure water. The extracts were concentrated in dryness using a rotary evaporater under a vacuum and then reacted with 10% of BF_3 in butanol at 100 °C for 30 min to convert the carboxyl group into butyl esters. *n*-Hexane was added to the reaction products and the derivatives were washed with pure water 3 times. Finally, the derivatives in hexane were concentrated into 100 µL and quantified by GC/MS and GC.

2.3 Water-soluble organic carbon (WSOC), water-soluble inorganic carbon (WSIC), elemental carbon (EC), organic carbon (OC) and metal element measurements

One fourth of the filter was cut in pieces and sonicated with 10 mL of fresh Millipore pure water (>18 MΩ) for 15 min in an ice bath to keep the sample at a low temperature in order to prevent evaporation. After filtered through a PTFE filter to remove the particles and quartz residue, pH of the extracts was determined using a pH meter (HANNA HI8424, US), and then measured for WSOC and WSIC using a Shimazdu TOC-5000 analyzer (Wang et al., 2003). For the determination of metals, one eighth of the filter was cut in pieces and digested by $HClO_4$ and HF. Metals in the solution were determined using inductively coupled plasma spectroscopy – AES (ICP-AES) (Wang et al., 2003).

EC and OC in the samples were measured by a Sunset Lab Carbon Analyzer following the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal protocol (Wang et al., 2005). Briefly, a small disk (area $\sim 1.5\,cm^2$) of the sample filter was put in a quartz boat inside the analyzer. OC was determined in a helium atmosphere at 120, 250, 450 and 550 °C. Afterwards, oxygen (2%) was introduced and EC was determined from 550 to 900 °C. A He-Ne laser was used to monitor and correct for pyrolytic conversion of OC to EC. Primary organic carbon (POC) and secondary organic carbon (SOC) was calculated using the EC tracer method (Castro et al., 1999; Chu, 2005; Yu et al., 2009)

$$\mathrm{POC{=}EC} \times \left(\frac{\mathrm{OC}}{\mathrm{EC}}\right)_{\min} \tag{1}$$

$$\mathrm{SOC{=}OC{-}POC} \tag{2}$$

where the $(OC/EC)_{min}$ is the minimum ratio of OC/EC for all the urban and suburban samples in each season.

2.4 Total carbon (TC), total nitrogen (TN) and stable isotopic compositions of TC and TN

For TC and TN measurements, a small disk of sample filter was placed in a tin cup and combusted at 1400 °C using an elemental analyzer (EA) (Carlo Erba, EA 1500). The derived NO was converted into N_2 in a reduction column. N_2 and CO_2 gases were isolated on a GC in EA and determined with a thermal conductivity detector (Kawamura et al., 2004). Stable isotope composition of TC and TN were determined using the same EA interfaced to isotope ratio mass spectrometer (IRMS) (ThermoQuest, Delta Plus) (Narukawa et al., 1999). Inorganic ions in the samples are reported elsewhere (Wang et al., 2010) and cited here for calculating organic nitrogen (ON) in PM_{10}. NO_3^- and NH_4^+ are the major

Table 1. Concentrations of major components and C and N isotopic compositions of PM_{10} in Baoji City, China ($\mu g\,m^{-3}$).

	Winter		Spring	
	Urban ($n = 15$)	Suburban ($n = 5$)	Urban ($n = 18$)	Suburban ($n = 6$)
PM_{10}	433 ± 85	333 ± 71	448 ± 153	296 ± 134
pH^a	-1.6 ± 0.4	-2.4 ± 0.8	-1.3 ± 0.4	-2.1 ± 0.2
$WSIC^b$	1.3 ± 0.4	0.9 ± 0.3	1.8 ± 0.7	1.0 ± 0.3
$WSOC^c$	31 ± 6.9	31 ± 3.4	22 ± 11	19 ± 6.3
OC^d	74 ± 14	51 ± 7.9	51 ± 20	26 ± 8.4
EC^e	17 ± 3.8	8.0 ± 2.1	20 ± 5.9	7.1 ± 2.7
TC^f	87 ± 14	54 ± 5.9	73 ± 24	31.2 ± 9.6
TN^g	54 ± 28	56 ± 19	25 ± 6.3	25 ± 8.3
ON^h	22 ± 15	22 ± 8.7	5.2 ± 2.3	5.2 ± 3.6
$\delta^{13}C$, ‰	-23.4 ± 0.4	-22.5 ± 0.2	-24.4 ± 0.5	-23.9 ± 0.7
$\delta^{15}N$, ‰	23.1 ± 8.3	8.8 ± 5.7	22.5 ± 1.7	17.5 ± 2.0

[a] ΔpH= pH of sample-pH of blank, [b] WSIC: water-soluble inorganic carbon, [c] WSOC: water-soluble organic carbon; [d] OC: organic carbon; [e] EC: elemental carbon; [f] TC: total carbon; [g] TN: total nitrogen; [h] ON: organic nitrogen.

inorganic species containing nitrogen while NO_2^- is negligible, thus ON concentration can be calculated as follow:

$$ON = TN - 14 \times \left(\frac{[NO_3^-]}{62} + \frac{[NH_4^+]}{18} \right) \quad (3)$$

3 Results and discussion

3.1 Particle mass, EC, OC, TC and TN

Table 1 shows the seasonal variations of major species in the samples at the urban and suburban sites. It should be noted that TC concentration was underestimated about 10% compared with that of (EC+OC), which is resulted from the two different measurement methods (Kawamura et al., 2004). Thus here we used EC and OC instead of TC for the related discussion. A similar level of PM_{10} concentrations was observed in winter and spring, but pH of the water-extracted solution was lower in winter ($pH = 6.1 \pm 0.6$) than in spring ($pH = 7.0 \pm 0.4$), indicating the wintertime PM_{10} is more acidic. Moreover, the suburban samples showed lower pH values compared to those of urban samples due to an enhanced deposition of dust, being consistent with the spatial distribution of water-soluble inorganic carbon (WSIC). A strong correlation was found between pH of the water-extracts and WSIC in the samples; the pH values increase when WSIC concentrations increase in both seasons (Fig. 1). Such a strong relation, however, was not observed between the pH and sulfate at the same sites (Wang et al., 2010), suggesting that the acidity of airborne particles in inland China is controlled by dust-/soil- derived species rather than sulfate. Water-soluble organic carbon (WSOC) showed a similar level at the urban ($31 \pm 6.9\,\mu g\,m^{-3}$) and suburban ($31 \pm 3.4\,\mu g\,m^{-3}$) sites during winter, which are 1.5 times higher than those during spring (Table 1). Organic carbon (OC) is more abundant in winter than in spring, and also more abundant in the urban regions than in the suburban area. It may be due to more emissions of fossil fuel combustion at the urban area, especially in winter when burning coal for house heating is very common. Elemental carbon (EC) in the urban aerosols is $17 \pm 3.8\,\mu g\,m^{-3}$ in winter and $20 \pm 5.9\,\mu g\,m^{-3}$ in spring, being 2–3 times higher than those at the suburban sites.

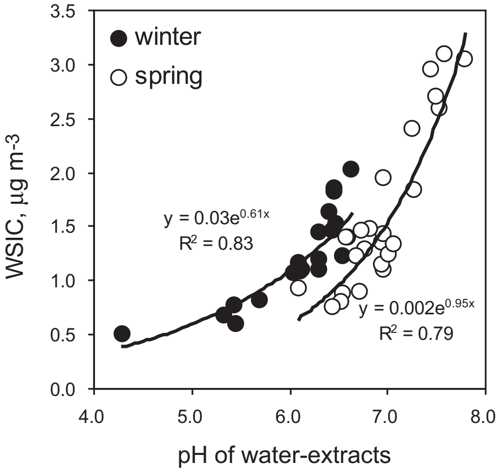

Fig. 1. Correlation of water-soluble inorganic carbon (WSIC) and pH of water-extracts of the PM_{10} samples during winter and spring.

During winter OC/EC ratios are 4.5 ± 0.9 in the urban and 6.5 ± 0.9 in the suburban sites. On the other hand, OC/EC ratios in spring are 2.7 ± 0.7 and 3.4 ± 0.7 in the urban and suburban areas, respectively (Fig 2). The higher OC/EC

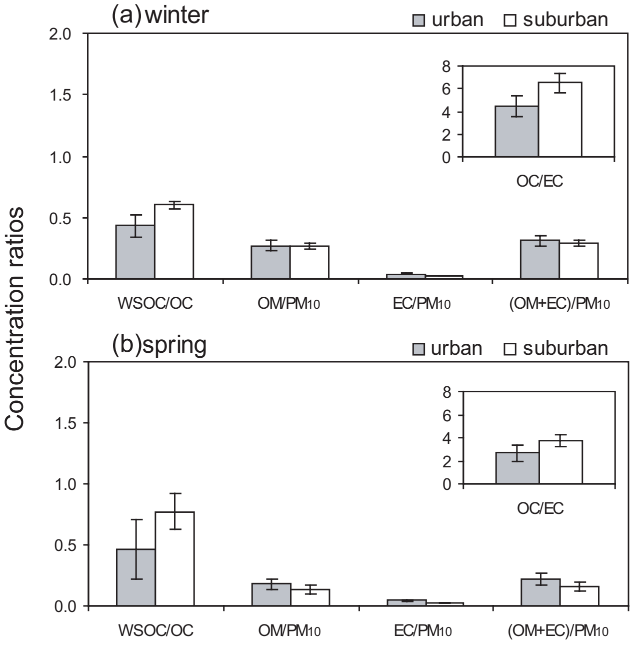

Fig. 2. Relative abundance of major species in the urban and suburban areas of Baoji City during winter and spring.

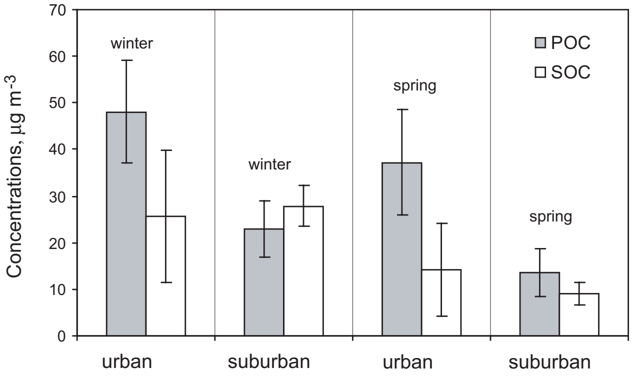

Fig. 3. Concentrations of primary organic carbon (POC) and secondary organic carbon (SOC) in the urban and suburban atmosphere.

ratios in winter mainly resulted from emissions from residential coal burning for house heating, which contain more organic pollutants compared with vehicle exhausts (Cao et al., 2005). Biomass burning for house heating and cooking is still common in rural area of inland China, which releases more organics compared to fossil fuel combustions. In addition, our previous study showed that biogenic emission is more significant at the suburban site than at the urban sites especially in spring (Xie et al., 2009). Therefore, ratios of OC/EC in the suburban samples are higher than in the urban samples, which is consistent with the results reported for India aerosols (Ram and Sarin, 2010). Relative abundances of WSOC in OC are 43 ± 9% at the urban sites and 60 ± 3% at the suburban site in winter, whereas they are 46 ± 24% and 73 ± 25% in both regions in spring (Fig. 2). Organic matter (OM), which was calculated by multiplying OC by a factor of 1.6 (Turpin and Lim, 2001), accounted for more than 25% of PM_{10} mass in winter and less than 20% of the particle mass in spring due to an enhanced input of dust in the warm season. Compared to OM, EC is relatively minor, accounting for less than 5% of the particle mass. The sum of OM and EC accounts for 30% of PM_{10} in winter and 20% of PM_{10} in spring, suggesting that inorganic components are the major fraction of the particles in inland China.

Figure 3 shows the seasonal and spatial variations of POC and SOC in the city. Wintertime POC is $48 \pm 11\,\mu g\,m^{-3}$ at the urban sites, which is approximately two times higher than that ($23 \pm 6\,\mu g\,m^{-3}$) at the suburban site. In contrast, SOC of the urban samples is equivalent to that of the suburban particles. In spring, POC and SOC are 37 ± 11 and $14 \pm 10\,\mu g\,m^{-3}$ in the urban air and 14 ± 5 and $9 \pm 3\,\mu g\,m^{-3}$ in the suburban atmosphere, respectively. SOC/POC ratios for the urban and suburban samples are 0.6 ± 0.3 and 1.3 ± 0.3 during winter and 0.4 ± 0.4 and 0.8 ± 0.3 during spring. The higher SOC/POC ratios in winter suggest an enhanced photooxidation of organics under favorable meteorological conditions (e.g., a development of inversion layer) (Yu et al., 2009). Furthermore, the higher SOC/POC ratios at the suburban site also indicate an increased photochemical production during the transport process of organic pollutants from the urban to the suburban.

Total nitrogen (TN) and organic nitrogen (ON) showed a similar concentration level in the urban and suburban samples, respectively, with 38 ± 5% of TN in winter and 20 ± 6% of TN in spring being organic, suggesting that organic nitrogen species are an important component of particulate nitrogen in inland China especially in winter, which is different from that in Jeju Island, Korea, where particulate organic nitrogen is less than 5% TN (Kawamura et al., 2004). Organic nitrogen compounds like alkyl amines are volatile (McGregor and Anastasio, 2001), thus they are preferable to stay in solid phase in wintertime due to low temperature, which might be the factor resulting in ON of PM_{10} more abundant in winter than in spring in addition to the seasonal difference in the source (Table 2).

3.2 Dicarboxylic and keto acids and metals

Homologous dicarboxylic acids (C_2–C_9) were detected in the samples with oxalic acid (C_2) being most abundant followed by succinic (C_4) and malonic (C_3) acids. Concentration of oxalic acid (C_2) was $816 \pm 172\,ng\,m^{-3}$ in the urban samples and $984 \pm 373\,ng\,m^{-3}$ in the suburban samples during winter, while its spring concentration was $532 \pm 247\,ng\,m^{-3}$ at the urban sites and $413 \pm 154\,ng\,m^{-3}$ at the suburban site (Table 2). These values are comparable to those reported in Nanjng (178–1388 $ng\,m^{-3}$, av. 790 $ng\,m^{-3}$)

Table 2. Concentrations of dicarboxylic and keto acids and metals in PM_{10} of Boaji city, ng m^{-3}.

	Winter		Spring	
	Urban ($n = 15$)	Suburban ($n = 5$)	Urban ($n = 18$)	Suburban ($n = 6$)
I. Dicarboxylic and keto acids				
Oxalic acid (C_2)	816 ± 172	984 ± 373	532 ± 247	413 ± 154
Malonic acid (C_3)	219 ± 26	209 ± 11	198 ± 25	191 ± 22
Succinic acid (C_4)	255 ± 40	288 ± 78	216 ± 30	202 ± 24
Glutaric acid (C_5)	109 ± 13	111 ± 15	101 ± 11	93 ± 3
Adipic acid (C_6)	26 ± 29	30 ± 35	53 ± 21	44 ± 22
Azelaic acd (C_9)	120 ± 32	106 ± 25	136 ± 57	85 ± 6
Glyoxylic acid (ωC_2)	283 ± 135	289 ± 58	95 ± 30	101 ± 41
Subtotal	1829 ± 304	2107 ± 541	1332 ± 354	1129 ± 229
II. Metals				
Al	8678 ± 2521	4841 ± 2314	13840 ± 6319	8352 ± 6715
Ba	174 ± 39	86 ± 26	240 ± 92	108 ± 65
Ca	9779 ± 4071	3610 ± 1606	22566 ± 11193	8661 ± 7159
Cd	9 ± 5	5 ± 1	3 ± 7	3 ± 7
Co	6 ± 1	2 ± 1	5 ± 3	3 ± 3
Cr	16 ± 25	20 ± 24	11 ± 22	14 ± 34
Cu	62 ± 20	63 ± 49	56 ± 26	70 ± 22
Fe	5340 ± 1302	2351 ± 749	10106 ± 4484	4684 ± 3517
K	4016 ± 880	3015 ± 783	5800 ± 2221	3659 ± 2001
Mg	1795 ± 517	974 ± 271	3299 ± 1918	2176 ± 2070
Mn	199 ± 72	120 ± 24	312 ± 121	166 ± 89
Na	2508 ± 1356	1737 ± 1266	1565 ± 2037	1887 ± 2031
Ni	16 ± 13	7 ± 1	21 ± 13	5 ± 5
Pb	612 ± 251	445 ± 172	616 ± 218	469 ± 211
Sr	101 ± 25	44 ± 10	110 ± 55	55 ± 38
Ti	515 ± 111	243 ± 50	742 ± 307	447 ± 259
V	13 ± 3	7 ± 2	14 ± 7	11 ± 8
Zn	791 ± 340	511 ± 75	1208 ± 271	745 ± 208
Subtotal, µg m^{-3}	34 ± 10	18 ± 7	61 ± 27	32 ± 23

(Wang et al., 2002) and other 14 Chinese mega-cities (151–1437 ng m^{-3}, av. 558 ng m^{-3}) (Ho et al., 2007). Concentrations of glutaric (C_5), adipic (C_6) and azelaic (C_9) acids were relatively small with averages in the range of 26–136 ng m^{-3} (Table 2). Concentration of glyoxylic acid, a smallest keto-carboxylic acid, is 283 ± 135 and 289 ± 58 ng m^{-3} in the urban and suburb samples in winter and 95 ± 30 and 101 ± 41 ng m^{-3} in spring, around 10 times more abundant than that (38 ± 20 ng m^{-3} in winter) in Chinese mega-cities (Ho et al., 2007). Coal burning emission is an important source of benzene, toluene, ethene, and acetylene, which can be photochemically oxidized into glyoxylic and pyruvic acids (Huang et al., 2005; Warneck, 2000). Thus the higher concentration of glyoxylic acid in the samples may be ascribed to coal combustion in the region. As shown in Fig. 4, C_3/C_2 ratio linearly correlated with that of C_4/C_2 in both seasons ($r^2 = 0.86$ and 0.98 in winter and spring, respectively). Such a strong correlation suggests that C_3 and C_4 may be the major precursors of C_2, both can be further oxidized into the smallest dicaroboxylic acid (Wang and Kawamura, 2006).

A total of 18 metals were determined in the samples with Ca being the most abundant, followed by Al, Fe, K, Mg and Na. Other metals such as Cd, Co, Cu, Ni and V are minor (Table 2). A strong correlation was found for the crustal elements, i.e., Al, Ba, Ca, Fe, K, Mg and Ti ($r \geq 0.76$ for the winter samples and $r \geq 0.83$ for the spring samples, Tables 3 and 4). Those components are also significantly correlated with Ca^{2+} (Tables 3 and 4). Total metals determined are 34 ± 10 and 18 ± 7 µg m^{-3} in the urban and suburban atmospheres during winter, respectively. These values are around 50% of those in springtime (Table 2), demonstrating an increased input of dust in the inland city during spring.

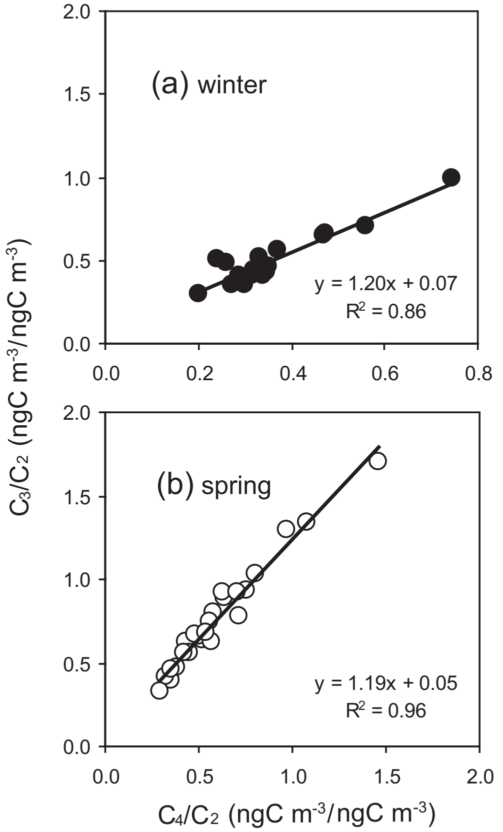

Fig. 4. Concentration ratios of malonic (C_3) and succinic (C_4) acids to oxalic acid (C_2) in PM_{10} from Baoji City during winter and spring (Data including the urban and suburban samples).

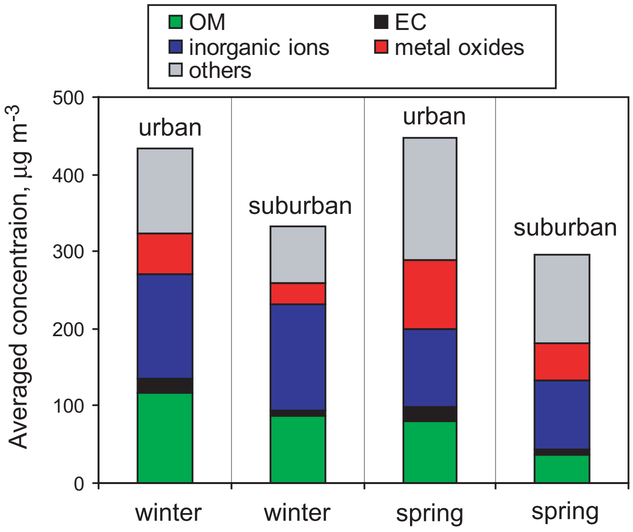

Fig. 5. Concentrations of major components determined in the PM_{10} of Baoji City (Data of inorganic ions are cited from Wang et al. (2010)).

Table 3. Correlation coefficients of dust-derived species in PM_{10} during winter ($n = 20$, $p = 0.01$).

	Ca^{2+}	Al	Ba	Ca	Fe	K	Mg	Ti
Ca^{2+}	1.00							
Al	0.85	1.00						
Ba	0.92	0.95	1.00					
Ca	0.88	0.89	0.91	1.00				
Fe	0.91	0.94	0.98	0.95	1.00			
K	0.79	0.80	0.87	0.76	0.79	1.00		
Mg	0.87	0.92	0.95	0.96	0.95	0.83	1.00	
Ti	0.87	0.91	0.91	0.89	0.95	0.67	0.87	1.00

Table 4. Correlation coefficients of dust-derived species in PM_{10} during spring ($n = 24$, $p = 0.01$).

	Ca^{2+}	Al	Ba	Ca	Fe	K	Mg	Ti
Ca^{2+}	1.00							
Al	0.83	1.00						
Ba	0.85	0.87	1.00					
Ca	0.90	0.93	0.94	1.00				
Fe	0.85	0.93	0.92	0.92	1.00			
K	0.87	0.97	0.92	0.96	0.96	1.00		
Mg	0.78	0.98	0.84	0.89	0.90	0.96	1.00	
Ti	0.86	0.97	0.90	0.93	0.95	0.97	0.92	1.00

3.3 Mass closure of PM $_{10}$

To reconstruct the sample mass balance, the metals were converted as their oxide forms while OC was converted into OM as mentioned above. The reconstructed concentrations and percentages of the determined species are shown in Fig. 5 and Table 5. The most abundant species in the particles are OM, accounting for around one fourth of PM_{10} mass in winter and one sixth of the particle mass in spring, followed by SO_4^{2-}, NO_3^-, NH_4^+, metal oxides and EC (Table 5). The sum of all the quantified components including EC, OM, inorganic ions and metal oxides accounted for more than 70% of the PM_{10} mass in winter and 60% of the particle mass in spring with the remaining mostly being silicon-related components (Table 5).

3.4 Implications for dust and coal burning emission and secondary aerosol formation

A strong linear correlation was found for POC, Fe and Ca^{2+} (Fig. 6) ($r^2 > 0.8$ in winter and $r^2 > 0.6$ in spring). Our previous studies showed that coal burning is the major source of sulfate and PAHs in Baoji city (Xie et al., 2009; Wang et al., 2010). Here we further observed intermediate linear correlation of POC with PAHs and fossil fuel derived *n*-alkanes ($r^2 < 0.6$ in winter and $r^2 < 0.4$ in spring). As mentioned above Fe and Ca^{2+} in the samples largely originated from

Table 5. Percentages of major species in particle mass, %.

	Winter		Spring	
	Urban	Suburban	Urban	Suburban
OM	27±3.2	25±2.1	19±3.8	13±3.1
EC	3.9±0.7	2.4±0.3	4.5±0.9	2.5±0.2
NO_3^-	9.3±3.2[a]	14±2.4[a]	7.4±2.[a]	11±3.6[a]
SO_4^{2-}	11±3.5[a]	14±2.2[a]	7.0±1.9[a]	10±2.1[a]
NH_4^+	6.6±1.6[a]	9.1±0.6[a]	4.0±1.5[a]	6.7±2.1[a]
Ca^{2+}	1.5±0.4[a]	0.8±0.2[a]	2.2±0.4[a]	1.7±0.5[a]
$F^-+Cl^-+Na^++K^++Mg^{2+}$	2.7±0.8[a]	2.9±0.7[a]	3.2±3.0[a]	2.9±1.7[a]
Metal oxides	8.1±2.1	5.5±1.7	13±2.7	10±5.0
Total	70±5.5	73±3.1	60±6.1	58±8.6

[a] Data were calculated from Wang et al. (2010)

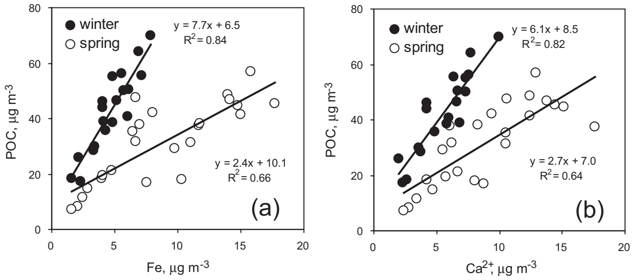

Fig. 6. Correlation of primary organic carbon (POC) with Fe and Ca^{2+} in the PM_{10} of Baoji City.

soil dust. Thus the relationship between POC and those inorganic and organic tracers suggest that POC in the PM_{10} largely resulted from soil dust and coal burning emission. Moreover, the linear correlation in turn demonstrates that the approach we used for the differentiation of POC and SOC from OC is useful. Pb also positively correlated with sulfate (Fig. 7a and b) and PAHs (Fig. 7c and d). Like sulfate Pb is largely derived from coal burning, thus the linear correlation of Pb with sulfate and PAHs again confirms the importance of coal-burning smoke as their major source.

Oxalic acid (C_2) is mostly formed via photo-oxidation of various organic precursors including glyoxylic acid, although a small fraction of C_2 can be directly emitted from vehicle exhaust (Kawamura and Kaplan, 1987; Kawamura and Yasui, 2005). Thus the concentration ratio of C_2/OC can be thought as an indicator of aerosol aging. In the current study we found that $\delta^{13}C$ of TC became higher with an increase in the ratio of C_2/OC (Fig. 8a and b). During the atmospheric oxidation process organic compounds release CO_2/CO by reaction with OH radical, and result in the evolved species enriched with lighter isotope (^{12}C) and the remaining substrate enriched in ^{13}C due to kinetic isotope effects (KIEs) (Hoefs, 1997; Sakugawa and Kaplan, 1995). Thus the ^{13}C increase can largely be attributed to aerosol photochemical aging, although initial $\delta^{13}C$ values of the carbonaceous aerosols depend on their sources. Such an enrichment in ^{13}C caused by photochemical aging was also observed for dicarboxylic acid aerosols from remote marine (Wang and Kawamura, 2006) and East Asia continent (Aggarwal and Kawamura, 2008).

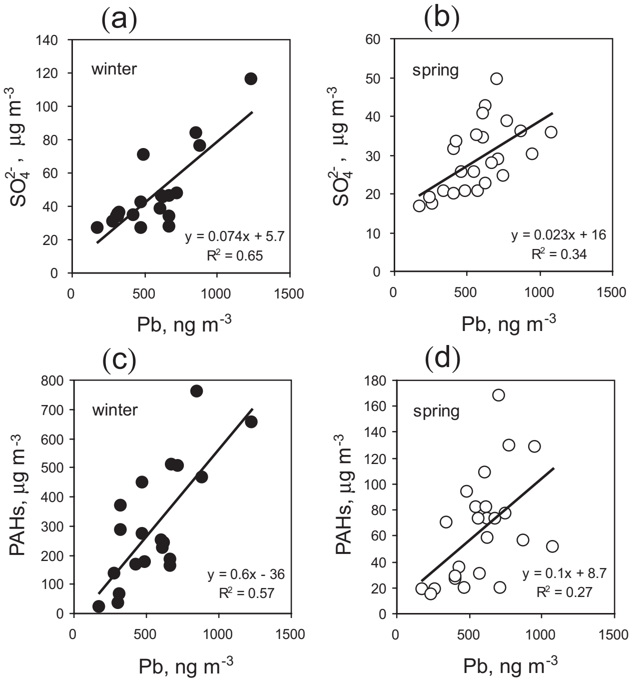

Fig. 7. Correlation of Pb with sulfate and PAHs in the PM_{10} of Baoji city during winter and spring (Sulfate data are cited from Wang et al. (2009a), and PAH data are cited from Xie et al. (2009)).

Solid-phase NH_4^+ and NO_3^- are formed via adsorption/condensation of gaseous NH_3 and HNO_3 onto preexisting particles (Seinfeld and Pandis, 1998), favoring an enrichment of light ^{14}N in particles (Hoefs, 1997; Yeatman

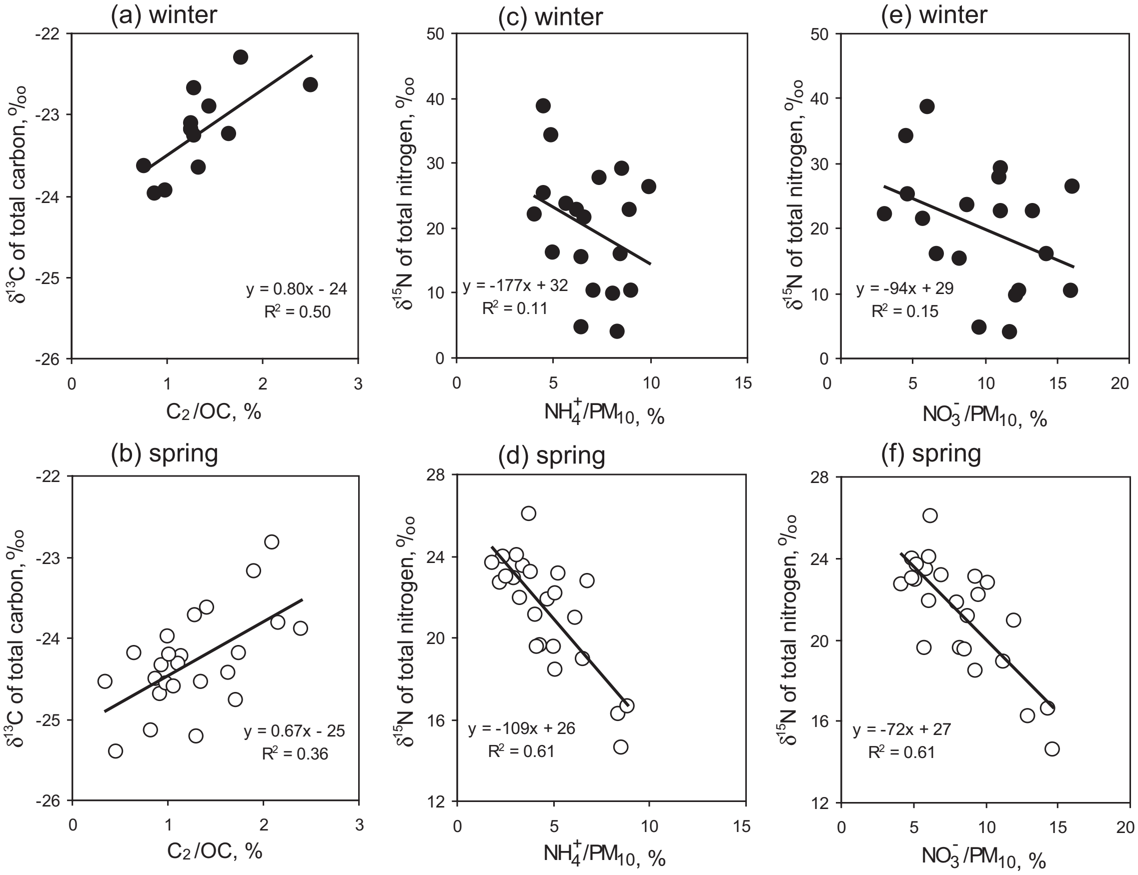

Fig. 8. Correlations of δ^{13}C of TC with C_2/OC (**a** and **b**) and δ^{15}N of TN with NH_4^+/PM_{10} (**c** and **d**) and NO_3^-/PM_{10} (**e** and **f**) during winter and spring (Data points including urban and suburban samples in each season. Due to instrument problem, the δ^{13}C data for a few winter samples are unavailable).

et al., 2001). Thus, a clear trend of decrease in δ^{15}N of TN with an increase in the ratios of NH_4^+/PM_{10} and NO_3^-/PM_{10} was observed in spring, although such a pattern was not so significant in winter (Fig. 8c–f). Around 40% TN in winter are organic (Table 2), in contrast to 20% of TN being organic in spring, resulting in the nitrogen isotopic composition being less influenced by NH_4^+ and NO_3^- in winter than in spring. Therefore the correlations between δ^{15}N of TN and the ratios of NH_4^+/PM_{10} and NO_3^-/PM_{10} in winter were not as well as those in spring.

4 Summary and conclusion

Winter and spring PM_{10} samples from Baoji, an inland city of China, were chemically characterized for water-soluble organic species, EC, OC, metals and isotopic compositions of TC and TN. Oxalic acid (C_2) was the most abundant diacid, followed by succinic (C_4) and malonic (C_3) acids. Concentrations of dicarboxylic and glyoxylic acids were 1776 ± 543 and 1185 ± 316 ng m^{-3} in winter and spring with no significant difference between the urban and suburban sites. EC in the urban and the suburban atmospheres were 17 ± 3.8 and 8.0 ± 2.1 µg m^{-3} during winter and 20 ± 5.9 and 7.1 ± 2.7 µg m^{-3} during spring, while OC at the urban and suburban sites were 74 ± 14 and 51 ± 7.9 µg m^{-3} in winter and 51 ± 20 and 23 ± 6.1 µg m^{-3} in spring. SOC/POC ratios were higher in winter than in spring, indicating an enhanced photochemical oxidation in the cold season under a development of inversion layer. pH of water-extracted solution of the samples showed a strong correlation ($r^2 > 0.8$) with WSIC, suggesting that fugitive dust is an important source of airborne particles in the city. Moreover, POC also showed a strong correlation ($r^2 > 0.8$ in winter and $r^2 > 0.6$ in spring) with Ca^{2+} and Fe and an intermediate correlation with PAHs and fossil fuel derived *n*-alkanes ($r^2 < 0.6$ in winter and $r^2 < 0.4$ in spring), further indicating the importance of fugitive dust and coal burning emission. C_3/C_2 ratio positively correlated with C_4/C_2 ratio, probably suggesting C_3 and C_4 as the precursors of C_2. PAHs, sulfate, and Pb in the samples well correlated each other in winter, again confirming the importance of coal burning emission due to house heating. δ^3C of TC increased with an increase in the concentration ratio of C_2/OC because of aerosol aging. In contrast, δ^5N of TN decreased with an increase in the ratios of NH_4^+/PM_{10} and NO_3^-/PM_{10}, possibly due to the absorption/condensation of gaseous NH_3 and HNO_3 onto pre-existing particles

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