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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Received: 4 February 2010 – Published in Atmos. Chem. Phys. Discuss.: 11 March 2010
Revised: 22 June 2010 – Accepted: 30 June 2010 – Published: 6 July 2010

Abstract. Dicarboxylic acids (C₂–C₁₀), metals, elemental carbon (EC), organic carbon (OC), and stable isotopic compositions of total carbon (TC) and total nitrogen (TN) were determined for PM₁₀ samples collected at three urban and one suburban sites of Baoji, an inland city of China, during winter and spring 2008. Oxalic acid (C₂) was the dominant diacid, followed by succinic (C₄) and malonic (C₃) acids. Total diacids in the urban and suburban areas were 1546±203 and 1728±495 ng m⁻³ during winter and 1236±335 and 1028±193 ng m⁻³ during spring. EC in the urban and the suburban atmospheres were 17±3.8 and 8±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. Secondary organic carbon (SOC) accounted for 38±16% of OC in winter and 28±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±27 µg m⁻³ in the urban air and 18±7 and 32±23 µg m⁻³ in the suburban air. A linear correlation (r² > 0.8 in winter and r² > 0.6 in spring) was found between primary organic carbon (POC) and Ca²⁺/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 (r² > 0.6) in winter, indicating an importance of emissions from coal burning for house heating. Stable carbon isotope compositions of TC (δ¹³C) became higher with an increase in the concentration ratios of C₂/OC due to aerosol aging. In contrast, nitrogen isotope compositions of TN (δ¹⁵N) became lower with an increases in the mass ratios of NH₄⁺/PM₁₀ and NO₃⁻/PM₁₀, which is possibly caused by an enhanced adsorption and/or condensation of gaseous NH₃ and HNO₃ 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
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 inland regions of China, an intensive aerosol (PM10 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 PM10 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

PM10 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 8 h 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 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 Shimadzu TOC-5000 analyzer (Wang et al., 2003). For the determination of metals, one eighth of the filter was cut in pieces and digested by HClO₄ 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 ~1.5 cm²) 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)

POC=EC × \left(\frac{OC}{EC}\right)_{\text{min}} \quad (1)

SOC=OC−POC \quad (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 N₂ in a reduction column. N₂ and CO₂ 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 PM10. NO₃⁻ and NH₄⁺ are the major
inorganic species containing nitrogen while NO$_2^-$ is negligible, thus ON concentration can be calculated as follow:

$$\text{ON}=\text{TN} - 14 \times \left( \frac{[\text{NO}_3^-]}{62} + \frac{[\text{NH}_4^+]}{18} \right)$$  (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 ± 0.6) than in spring (pH = 7.0 ± 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 ± 6.9 µg m$^{-3}$) and suburban (31 ± 3.4 µg 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 ± 3.8 µg m$^{-3}$ in winter and 20 ± 5.9 µg m$^{-3}$ in spring, being 2–3 times higher than those at the suburban sites.

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
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 ± 11 µg m⁻³ at the urban sites, which is approximately two times higher than that (23 ± 6 µg 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 ± 10 µg m⁻³ in the urban air and 14 ± 5 and 9 ± 3 µg 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 increased 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 ± 172 ng m⁻³ in the urban samples and 984 ± 373 ng m⁻³ in the suburban samples during winter, while its spring concentration was 532 ± 247 ng m⁻³ at the urban sites and 413 ± 154 ng m⁻³ at the suburban site (Table 2). These values are comparable to those reported in Nanjing (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$^{-3}$.

<table>
<thead>
<tr>
<th></th>
<th>Winter</th>
<th></th>
<th>Spring</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Urban (n = 15)</td>
<td>Suburban (n = 5)</td>
<td>Urban (n = 18)</td>
<td>Suburban (n = 6)</td>
</tr>
<tr>
<td>I. Dicarboxylic and keto acids</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic acid (C$_2$)</td>
<td>816$\pm$ 172</td>
<td>984$\pm$ 373</td>
<td>532$\pm$ 247</td>
<td>413$\pm$ 154</td>
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<tr>
<td>Malonic acid (C$_3$)</td>
<td>219$\pm$ 26</td>
<td>209$\pm$ 11</td>
<td>198$\pm$ 25</td>
<td>191$\pm$ 22</td>
</tr>
<tr>
<td>Succinic acid (C$_4$)</td>
<td>255$\pm$ 40</td>
<td>288$\pm$ 78</td>
<td>216$\pm$ 30</td>
<td>202$\pm$ 24</td>
</tr>
<tr>
<td>Glutaric acid (C$_5$)</td>
<td>109$\pm$ 13</td>
<td>111$\pm$ 15</td>
<td>101$\pm$ 11</td>
<td>93$\pm$ 3</td>
</tr>
<tr>
<td>Adipic acid (C$_6$)</td>
<td>26$\pm$ 29</td>
<td>30$\pm$ 35</td>
<td>53$\pm$ 21</td>
<td>44$\pm$ 22</td>
</tr>
<tr>
<td>Azelaic acid (C$_9$)</td>
<td>120$\pm$ 32</td>
<td>106$\pm$ 25</td>
<td>136$\pm$ 57</td>
<td>85$\pm$ 6</td>
</tr>
<tr>
<td>Glyoxylic acid (ωC$_2$)</td>
<td>283$\pm$ 135</td>
<td>289$\pm$ 58</td>
<td>95$\pm$ 30</td>
<td>101$\pm$ 41</td>
</tr>
<tr>
<td>Subtotal</td>
<td>1829$\pm$ 304</td>
<td>2107$\pm$ 541</td>
<td>1332$\pm$ 354</td>
<td>1129$\pm$ 229</td>
</tr>
<tr>
<td>II. Metals</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>8678$\pm$ 2521</td>
<td>4841$\pm$ 2314</td>
<td>13840$\pm$ 6319</td>
<td>8352$\pm$ 6715</td>
</tr>
<tr>
<td>Ba</td>
<td>174$\pm$ 39</td>
<td>86$\pm$ 26</td>
<td>240$\pm$ 92</td>
<td>108$\pm$ 65</td>
</tr>
<tr>
<td>Ca</td>
<td>9779$\pm$ 4071</td>
<td>3610$\pm$ 1606</td>
<td>22566$\pm$ 11193</td>
<td>8661$\pm$ 7159</td>
</tr>
<tr>
<td>Cd</td>
<td>9$\pm$ 5</td>
<td>5$\pm$ 1</td>
<td>3$\pm$ 7</td>
<td>3$\pm$ 7</td>
</tr>
<tr>
<td>Co</td>
<td>6$\pm$ 1</td>
<td>2$\pm$ 1</td>
<td>5$\pm$ 3</td>
<td>3$\pm$ 3</td>
</tr>
<tr>
<td>Cr</td>
<td>16$\pm$ 25</td>
<td>20$\pm$ 24</td>
<td>11$\pm$ 22</td>
<td>14$\pm$ 34</td>
</tr>
<tr>
<td>Cu</td>
<td>62$\pm$ 20</td>
<td>63$\pm$ 49</td>
<td>56$\pm$ 26</td>
<td>70$\pm$ 22</td>
</tr>
<tr>
<td>Fe</td>
<td>5340$\pm$ 1302</td>
<td>2351$\pm$ 749</td>
<td>10106$\pm$ 4484</td>
<td>4684$\pm$ 3517</td>
</tr>
<tr>
<td>K</td>
<td>4016$\pm$ 880</td>
<td>3015$\pm$ 783</td>
<td>5800$\pm$ 2221</td>
<td>3659$\pm$ 2001</td>
</tr>
<tr>
<td>Mg</td>
<td>1795$\pm$ 517</td>
<td>974$\pm$ 271</td>
<td>3299$\pm$ 1918</td>
<td>2176$\pm$ 2070</td>
</tr>
<tr>
<td>Mn</td>
<td>199$\pm$ 72</td>
<td>120$\pm$ 24</td>
<td>312$\pm$ 121</td>
<td>166$\pm$ 89</td>
</tr>
<tr>
<td>Na</td>
<td>2508$\pm$ 1356</td>
<td>1737$\pm$ 1266</td>
<td>1565$\pm$ 2037</td>
<td>1887$\pm$ 2031</td>
</tr>
<tr>
<td>Ni</td>
<td>16$\pm$ 13</td>
<td>7$\pm$ 1</td>
<td>21$\pm$ 13</td>
<td>5$\pm$ 5</td>
</tr>
<tr>
<td>Pb</td>
<td>612$\pm$ 251</td>
<td>445$\pm$ 172</td>
<td>616$\pm$ 218</td>
<td>469$\pm$ 211</td>
</tr>
<tr>
<td>Sr</td>
<td>101$\pm$ 25</td>
<td>44$\pm$ 10</td>
<td>110$\pm$ 55</td>
<td>55$\pm$ 38</td>
</tr>
<tr>
<td>Ti</td>
<td>515$\pm$ 111</td>
<td>243$\pm$ 50</td>
<td>742$\pm$ 307</td>
<td>447$\pm$ 259</td>
</tr>
<tr>
<td>V</td>
<td>13$\pm$ 3</td>
<td>7$\pm$ 2</td>
<td>14$\pm$ 7</td>
<td>11$\pm$ 8</td>
</tr>
<tr>
<td>Zn</td>
<td>791$\pm$ 340</td>
<td>511$\pm$ 75</td>
<td>1208$\pm$ 271</td>
<td>745$\pm$ 208</td>
</tr>
<tr>
<td>Subtotal, µg m$^{-3}$</td>
<td>34$\pm$ 10</td>
<td>18$\pm$ 7</td>
<td>61$\pm$ 27</td>
<td>32$\pm$ 23</td>
</tr>
</tbody>
</table>

(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 ketocarboxylic acid, is 283$\pm$ 135 and 289$\pm$ 58 ng m$^{-3}$ in the urban and suburban samples in winter and 95$\pm$ 30 and 101$\pm$ 41 ng m$^{-3}$ in spring, around 10 times more abundant than that (38$\pm$ 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; Warneke, 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 dicarboxylic 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$\pm$ 10 and 18$\pm$ 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 (C₃) and succinic (C₄) acids to oxalic acid (C₂) in PM₁₀ from Baoji City during winter and spring (Data including the urban and suburban samples).

Fig. 5. Concentrations of major components determined in the PM₁₀ of Baoji City (Data of inorganic ions are cited from Wang et al. (2010)).

3.3 Mass closure of PM₁₀

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 PM₁₀ mass in winter and one sixth of the particle mass in spring, followed by SO₄²⁻, NO₃⁻, NH₄⁺, 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 PM₁₀ 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 Ca²⁺ (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 Ca²⁺ in the samples largely originated from
Thus the concentration ratio of C2/OC can be largely attributed to aerosol photochemical aging, although initial δ13C values of the carbonaceous aerosols depend on their sources. Such an enrichment in 13C 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).

Solid-phase NH4+ and NO3− are formed via adsorption/condensation of gaseous NH3 and HNO3 onto pre-existing particles (Seinfeld and Pandis, 1998), favoring an enrichment of light 14N in particles (Hoefs, 1997; Yeatman et al., 1998).
et al., 2001). Thus, a clear trend of decrease in $\delta^{15}$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 $\delta^{15}$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. $\delta^{13}$C of TC increased with an increase in the concentration ratio...
of C$_2$/OC because of aerosol aging. In contrast, $\delta^{15}$N 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.

Acknowledgements. This work was financially supported by National Natural Science Foundation (No. 40873083), the Knowledge Innovation Program of Chinese Academy Sciences, China (No. kckx2-yw-148), and in part supported by the Environment Research and Technology Development Fund (B-0903) of the Ministry of the Environment, Japan.

Edited by: N. Mihalopoulos

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