The water-soluble ionic composition of PM2.5 in Shanghai and Beijing, China

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Abstract

A year-long field study to characterize the ionic species in PM2.5 was carried out in Shanghai and Beijing, China, in 1999–2000. Weekly samples of PM2.5 were collected using a special low flow rate (0.4 l min⁻¹) sampler. In Shanghai, \( \text{SO}_4^{2-}/\text{C}_0 \), \( \text{NO}_3^-/\text{C}_0 \) and \( \text{NH}_4^+ \) were the dominant ionic species, which accounted for 46%, 18% and 17% of the total mass of ions, respectively. Local \( \text{SO}_2 \) emissions were an important source of \( \text{SO}_4^{2-} \) in PM2.5 because the \( \text{SO}_4^{2-}/\text{C}_0 \) concentration was correlated with the \( \text{SO}_2 \) concentration \( (r = 0.66) \). The relatively stable \( \text{SO}_4^{2-}/\text{C}_0/\text{SO}_2 \) mass ratio over a large range of temperatures suggests that gas-phase oxidation of \( \text{SO}_2 \) played a minor role in the formation of \( \text{SO}_4^{2-} \). The sum of \( \text{SO}_4^{2-}/\text{C}_0 \) and \( \text{NO}_3^-/\text{C}_0 \) was highly correlated with \( \text{NH}_4^+ \) \( (r = 0.96) \), but insufficient ammonium was present to totally neutralize the aerosol. In Beijing, \( \text{SO}_4^{2-}, \text{NO}_3^- \) and \( \text{NH}_4^+ \) were also the dominant ionic species, constituting 44%, 25% and 16% of the total mass of water-soluble ions, respectively. Local \( \text{SO}_2 \) emissions were an important source of \( \text{SO}_4^{2-} \) in the winter since \( \text{SO}_4^{2-}/\text{C}_0 \) was correlated with \( \text{SO}_2 \) \( (r = 0.83) \). The low-mass \( \text{SO}_4^{2-}/\text{SO}_2 \) ratio \( (0.27) \) during winter, which had low humidity, suggests that gas-phase oxidation of \( \text{SO}_2 \) was a major route of sulfate formation. In the summer, however, much higher mass ratios of \( \text{SO}_4^{2-}/\text{SO}_2 \) \( (5.6) \) were observed and were ascribed to in-cloud sulfate formation. The annual average ratio of \( \text{NO}_3^-/\text{SO}_4^{2-} \) was 0.4 and 0.6 in Shanghai and in Beijing, respectively, suggesting that stationary emissions were still a dominant source in these two cities.

Keywords: Sulfate; Nitrate; Dicarboxylic acids; Seasonal variation; Correlation analysis

1. Introduction

Shanghai and Beijing are two of the largest cities in China. Both cities have populations of over 10 million. These two urban areas have experienced a rapid increase in the use of vehicles, concurrent with large increases in energy consumption. Particulate pollution has become a major problem. Many short-term studies on TSP and PM10 (particle size smaller than 10\( \mu \)m) have been published since the 1980s (Winchester et al., 1981; Huebert et al., 1988). However, data on PM2.5, especially regarding the semi-volatile species in PM2.5, e.g., \( \text{NO}_3^- \) and \( \text{Cl}^- \) and dicarboxylic acids, is very limited. A year-long study characterizing PM2.5 in Shanghai and Beijing, sponsored by the General Motors Co., was initiated in March 1999. The composition and seasonal trends of PM2.5 in Beijing and Shanghai have been described by He et al. (2001) and Ye et al. (2002), respectively. \( \text{SO}_4^{2-}, \text{NO}_3^- \) and \( \text{NH}_4^+ \) are the dominant ionic species in PM2.5, which account for about...
SO4 originated from primary sources. The formation of dust storms and carbonaceous species principally et al., 2001; Ye et al., 2002). In their studies, crustal species were believed to originate from local soil and/or dust storms and carbonaceous species principally originated from primary sources. The formation of SO4 and NO3 in PM2.5 was not investigated, but it should be done since an understanding of the origin of these species impacts control decisions. In Beijing, the vehicular population has grown at a rate of 15% per year since 1990. The resulting increase in NOx emissions is expected to have an impact on the PM2.5 nitrate concentration. On the other hand, clean fuels such as natural gas have replaced coal used for small domestic heating boilers in the central urban area in Beijing. This has reduced the SO2 and HCl emissions. In this paper, we focus on the composition, source, and the formation of the secondary ion species, with an emphasis on sulfate, nitrate, ammonium, chloride and dicarboxylic acids.

Measurements of semi-volatile species are complicated by sampling artifacts, resulting from gas–particle and particle–particle interactions (Sickles et al., 1999). Denuders for absorbing gases prior to particle collection and back filters for absorbing HNO3, HCl and NH3 evaporated from collected particles have been widely accepted as effective tools to minimize sampling artifacts (Chow and Watson, 1998). In this study, a special low flow rate sampler equipped with three parallel cassettes (one cassette equipped with an Na2CO3-coated denuder and a nylon back filter) was used to collect PM2.5. Correlation analysis along with seasonal variation in ratios will be examined to provide insight into the formation of secondary species and the relative importance of stationary and mobile sources of nitrogen and sulfur in PM2.5.

Dicarboxylic acids and/or their salts are important constituents in the water-soluble organic fraction of PM (Kawamura and Kaplan 1987; Kerminen et al., 2000) and are expected to be useful in source apportionment. Kawamura and Kaplan (1987) proposed that vehicle exhaust is an important source of dicarboxylic acids in PM. Given that organic carbon was the most abundant species in PM2.5 in Shanghai and Beijing (He et al., 2001; Ye et al., 2002), obtaining more information on its source is very important for control purposes. In this study, the composition of dicarboxylic acids in PM2.5 was determined only for samples collected after December 1999. Correlation analyses between dicarboxylic acids and other species, such as organic carbon, sulfate and nitrate in PM2.5 and O3, was performed to understand the source of dicarboxylic acids and the formation of secondary species.

2. Method

2.1. Sampling and chemical analysis

PM2.5 sampling in Shanghai was conducted by Tongji University. The two sampling sites in Shanghai were both downtown and were 5 km apart. One was inside the Tongji University campus and the other was on Hainan Road. The sampler at the Tongji University campus was placed on the roof of a three-story building, 16 m above ground level. About 150 m northwest from this site is a heavily trafficked road. The sampler at the Hainan Road site was also placed on the roof of a building, 18 m above the ground level, and 150 m from a main road. The Hainan site was next to an air quality monitoring station, where the meteorological conditions and the concentrations of SO2, NOx, and O3 were measured. PM2.5 sampling in Beijing was conducted by Tsinghua University and the sampling sites have been described in detail by He et al. (2001). While the Tsinghua site was in a suburban area, the Chegongzhuang site was in Beijing's urban area and was also located next to an air quality monitoring station. The air pollution index at this station was often the highest in Beijing. Wind data was available in Beijing, but not in Shanghai.

The sampler and chemical analyses employed in this study were the same as described by He et al. (2001). Concurrent weekly (7 days) samples were collected at the two sites in each city. The sampler was a special low flow rate sampler equipped with three cassettes for collecting PM2.5, each at a flow rate of 0.41 min-1 (Aerosol Dynamics, USA). The low flow rate enables continuous sampling during a week without overloading the filters so that a year-long data set could be readily obtained. The sampler has three parallel sampling cassettes for sampling aerosols for (1) gravimetric and elemental analyses, (2) elemental carbon/organic carbon (EC/OC) analysis and (3) ionic analysis. Elemental analyses by X-ray fluorescence (XRF) and EC/OC analyses by thermal optical reflection (TOR) were performed at the Desert Research Institute, USA. Ionic analysis by ion chromatography (IC) was performed at the Hong Kong University of Science and Technology (HKUST). The cassette for ionic analysis included a denuder coated with Na2CO3 to remove acidic gases prior to particle collection and a back nylon filter to absorb the HNO3 and HCl evaporated from the collected particles on the Teflon filter. Sampling artifacts of NH4+ could be present because neither an NH3 denuder nor a back filter coated with citric acid was used. The cassette for gravimetric and metal analysis did not have a denuder or a back filter. After sampling, the Teflon and nylon filters were put in Petri dishes, sealed with Parafilm and stored in a refrigerator before they were put in an icebox for express delivery to HKUST for...
ionic analysis. Results for the elemental and EC/OC analysis in Shanghai are reported by Ye et al. (2002).

The filters were extracted using ultra-pure water. Ion chromatography was used to determine the concentrations of $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, $\text{K}^+$ and $\text{NH}_4^+$. More information on the extraction and ionic analysis is available in Yao et al. (2002) and He et al. (2001). The detection limits in neq m$^{-3}$ were 0.2 for $\text{SO}_4^{2-}$, 0.1 for $\text{NO}_3^-$, 0.2 for $\text{Cl}^-$, 0.2 for $\text{Ca}^{2+}$, 0.4 for $\text{Mg}^{2+}$, 0.2 for $\text{Na}^+$, 0.1 for $\text{K}^+$ and 0.4 for $\text{NH}_4^+$. The uncertainties were 5% for $\text{SO}_4^{2-}$ and $\text{NH}_4^+$, 6% for $\text{NO}_3^-$, $\text{Cl}^-$, $\text{K}^+$, and 12% for $\text{Ca}^{2+}$, $\text{Mg}^{2+}$. In the first ten months of sampling, the nylon filters had high $\text{Cl}^-$ blanks of 4.5 $\mu$g m$^{-3}$ on average, but negligible $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ blanks. Because of the high nylon $\text{Cl}^-$ blank levels, only the $\text{Cl}^-$ found on the Teflon filter was counted as PM2.5 $\text{Cl}^-$ in this study. For samples collected after December 1999, a Dionex AS11 column (4 mm) with an AG11 guard column and an anion trap column (4 mm) were also used for organic anion detection (Kerminen et al., 2000). The eluent for the organic anion analysis was 0.4–6 mM NaOH (gradient), which is lower than the concentration used by Kerminen et al. (2000). This concentration gave better separation of the different dicarboxylic acids. The detection limits in neq m$^{-3}$ were 0.2 for oxalate and 0.1 for both malonate and succinate in aqueous extracts. Uncertainties were ±10% for oxalate, ±20% for malonate, ±25% for succinate.

2.2. Data quality assurance

The mass concentrations of all ions except $\text{NO}_3^-$ were calculated based on the particles collected on the Teflon filter alone. $\text{NO}_3^-$ concentrations included the contributions from both the Teflon and the nylon filters. In some (about 25%) Beijing samples, $\text{SO}_4^{2-}$ was found on the nylon filter. This was suspected to be due to leaks because some black particles were found on those nylon filters. Including the S on the nylon filter significantly improved the correlation between $\text{SO}_4^{2-}$ and sulfur measured by XRF in another cassette. Therefore, the total $\text{SO}_4^{2-}$ mass concentration on the Teflon and nylon filter was used in Beijing. Sampling artifacts for $\text{Cl}^-$ were possible. We found that the high $\text{Cl}^-$ blank present on nylon filters was due to contamination by the Petri dishes (Becton Dickinson Company, USA) used for storing the samples. The Petri dishes did not affect the Teflon filter $\text{Cl}^-$ blank. Similar high $\text{Cl}^-$ blanks on nylon filters have been reported by other researchers (Eldering et al., 1991; Koutrakis et al., 1992). Subsequently, the Petri dishes were washed in an ultrasonic bath for 20 min and then rinsed with ultra-pure water (specific resistance $\geq 18.1$ M$\Omega$ cm$^{-1}$) before use. The $\text{Cl}^-$ blank on the nylon filter was then reduced to below 0.25 $\mu$g m$^{-3}$ in samples collected during the last 2 months of the study.

The $\text{Cl}^-$ concentration determined by IC from samples collected in the denuded cassette with a back filter was compared to the XRF measurement of chlorine from the sample collected in the cassette without the denuder and back filter. Good agreement was expected since atmospheric particulate chloride is generally found to be completely water-soluble (Kasahara et al., 1996). In Shanghai, $\text{Cl}^-$ measured by IC was significantly lower (26% on average) than that by XRF, which suggests that the $\text{Cl}^-$ concentration in PM2.5 was underestimated. In Beijing, $\text{Cl}^-$ measured by IC agreed well with Cl measured by XRF except for some samples with the leak problem.

3. PM2.5 ionic species in Shanghai

3.1. The concentration of PM2.5 ions

The minimum, annual average and maximum weekly concentrations of the inorganic ions in PM2.5 are listed in Table 1. The annual average $\text{SO}_4^{2-}$ concentration was 15.9 $\mu$g m$^{-3}$ at Hainan Road and 15.2 $\mu$g m$^{-3}$ at Tongji in Shanghai. Hence, sulfate alone would exceed the US NAAQS annual PM2.5 standard of 15 $\mu$g m$^{-3}$. Sulfate accounted for 46% (on average) of the total mass of inorganic ions. The annual average $\text{NO}_3^-$ concentrations at the two sites in Shanghai were 6.8 and 6.5 $\mu$g m$^{-3}$. Nitrate accounted for 18% of the total mass of the inorganic ions. The annual average ammonium concentrations were 6.4 $\mu$g m$^{-3}$ in Shanghai. The sum of $\text{Cl}^-$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$ and $\text{K}^+$ accounted for 18% of the total mass of the inorganic ions in these two cities.

3.2. The seasonal variations of the $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ concentrations

The $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ seasonal variations are shown in Fig 1(a). The maximum $\text{SO}_4^{2-}$ peak occurred at the end of January 2000. On average, $\text{SO}_4^{2-}$ in the winter was 80% higher than in the summer. $\text{SO}_4^{2-}$ at the Hainan site and the Tongji site was similar, suggesting that sulfate may be from regional sulfate formation or long-range transport (Tanner et al., 1981; Keeler et al., 1991). The $\text{NO}_3^-$ concentrations at the two Shanghai sites were also similar to each other. The maximum $\text{NO}_3^-$ concentration (18.1 $\mu$g m$^{-3}$) occurred in mid-November, 6 weeks earlier than the maximum $\text{SO}_4^{2-}$ peak. The minimum $\text{NO}_3^-$ concentration (0.6 $\mu$g m$^{-3}$) occurred at the end of August. The partition of $\text{NO}_3^-$ between the gas and particulate phases strongly depends on temperature ($T$), relative humidity (RH) and ammonia concentration. Although the seasonal variation of RH was not large in Shanghai, the temperature decreased from above 20°C in summer to below 0°C in winter (Fig. 2a), resulting in a large seasonal variation of $\text{NO}_3^-$ in PM2.5. The
concentration of sulfate, in general, was about twice that of nitrate. NO₃⁻ and SO₄²⁻ were highly correlated with a correlation coefficient of 0.91–0.92. This can result if they exist as internal mixtures or their concentrations are governed by common meteorological conditions. Size distribution data of SO₄²⁻/C₀ and NO₃⁻/C₀ is required to understand the formation of these species (John et al., 1990; Zhuang et al., 1999). For example, the condensation mode (mode diameter = 0.2 μm) and the droplet mode (0.7 μm) are associated with the gas-to-particle interactions and in-cloud processes, respectively.

### 3.3. The source of SO₄²⁻ and NO₃⁻ in PM2.5

The mass ratio of [NO₃⁻]/[SO₄²⁻] has been used as an indicator of the relative importance of stationary vs mobile sources of sulfur and nitrogen in the atmosphere (Arimoto et al., 1996). In China, gasoline and diesel fuel contain 0.12% and 0.2% sulfur (by weight), respectively (Kato, 1996). The estimated ratios of SOₓ to NOₓ from the emission of gasoline and diesel fuel burning are 1:13 and 1:8, respectively. The sulfur content in coal is 1% in Shanghai and the estimated ratio of SO₂ to NOₓ is 2:1 from coal burning. High [NO₃⁻]/[SO₄²⁻] mass ratios of 2 and 5 in downtown Los Angeles and in Rubidoux in Southern California, USA have been reported (Kim et al., 2000)—part of the reason is that Southern California does not use coal. Arimoto et al. (1996) ascribed high [NO₃⁻]/[SO₄²⁻] mass ratios to the predominance of mobile source over stationary source of pollutants. However, lower ratios (0.3–0.5) have usually been found in China (Huebert et al., 1988) because of the wide use of sulfur-containing coal. The seasonal variation of the [NO₃⁻]/[SO₄²⁻] mass ratio in Shanghai is shown in Fig. 2(a). The ratio varied between 0.1 and 0.7 with an annual average of 0.4. The minimum ratio occurred in September and the maximum ratio occurred in December. The measured ratios are, in general, in agreement with the literature values for PM2.5, e.g., 0.4–1.0 in Nanjing (about 300 km from Shanghai; Wang et al., 2002) and 0.5–0.7 in Cheshan (about 30 km from Shanghai) and Changshu (about 80 km from Shanghai) (Xu et al., 2002). The low-mass ratios suggest that stationary source emissions were more important than the vehicle emissions in the source areas.

### 3.4. The formation of SO₄²⁻ and NO₃⁻

The [SO₄²⁻]/[SO₂] ratio is an indication of the formation route and/or the source of sulfate (Sievering et al., 1991). Since the concentration of SO₂ was available only at the Hainan Road site, correlations between SO₄²⁻/C₀ and SO₂ were analyzed using the Hainan Road data. As shown in Fig. 3(a), the linear regression equation was [SO₄²⁻]=0.23[SO₂]+6.1 with a correlation coefficient (r) of 0.66. The [SO₄²⁻]/[SO₂] mass ratio varied from 0.16 to 0.79. Since the gas-phase oxidation of SO₂ to sulfate by OH radical is a strong function of temperature (Seinfeld, 1986), a low [SO₄²⁻]/[SO₂] mass ratio in the winter was expected. However, a significant decrease in the [SO₄²⁻]/[SO₂] mass ratio was not observed in the winter, indicating that local gas-phase oxidation of SO₂ was not important. This suggests an impact of long-range transport and/or aqueous transformation processes such as the metal catalyzed oxidation of sulfur, in-cloud processes, etc. during the winter. 

\[
([SO₄²⁻]+[NO₃⁻]) \text{ was linearly correlated with } [NH₄⁺] \text{ at the two sampling sites. The linear fits of the data}
\]

<table>
<thead>
<tr>
<th>Site</th>
<th>SO₄²⁻ (µg/m³)</th>
<th>NO₃⁻ (µg/m³)</th>
<th>Cl⁻ (µg/m³)</th>
<th>Ca²⁺ (µg/m³)</th>
<th>Mg²⁺ (µg/m³)</th>
<th>Na⁺ (µg/m³)</th>
<th>K⁺ (µg/m³)</th>
<th>NH₄⁺ (µg/m³)</th>
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<tr>
<td>Min.</td>
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<td>0.6</td>
<td>0.1</td>
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<td>BDL</td>
<td>BDL</td>
<td>0.2</td>
<td>2.4</td>
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<tr>
<td>Ave.</td>
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<td>6.8</td>
<td>1.8</td>
<td>0.6</td>
<td>0.3</td>
<td>0.6</td>
<td>2.0</td>
<td>6.6</td>
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<td>Max.</td>
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<td>5.3</td>
<td>3.5</td>
<td>0.8</td>
<td>1.9</td>
<td>7.0</td>
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<td>0.1</td>
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<td>1.7</td>
<td>0.3</td>
<td>0.3</td>
<td>0.7</td>
<td>1.9</td>
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<td>1.4</td>
<td>5.7</td>
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<td>Min.</td>
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<td>1.6</td>
<td>0.1</td>
<td>BDL</td>
<td>BDL</td>
<td>BDL</td>
<td>0.6</td>
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<td>0.7</td>
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<td>1.9</td>
<td>3.6</td>
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</tr>
</tbody>
</table>

BDL: below detection limit.
are described as
\[ [\text{NO}_3^-] + [\text{SO}_4^{2-}] = 1.25 \times [\text{NH}_4^+] - 15.2, \quad r = 0.96 \]
(Hainan Road),
\[ [\text{NO}_3^-] + [\text{SO}_4^{2-}] = 1.33 \times [\text{NH}_4^+] + 9.9, \quad r = 0.94 \]
(Tongji).

The slopes of the regression fits between ([SO$_4^{2-}$] + [NO$_3^-$]) and [NH$_4^+$] at the two sites are all larger than 1, indicating an incompletely neutralized system. The extent of SO$_4^{2-}$ and NO$_3^-$ neutralization was possibly underestimated because the evaporated ammonium was not considered.

3.5. Dicarboxylic acids in PM2.5

The concentrations of dicarboxylic acids in PM2.5 were determined for samples collected after 22 November 1999. The minimum, average and maximum concentrations of dicarboxylic acids in PM2.5 are listed in Table 2. Due to the lack of data on dicarboxylic acids in PM2.5 in the literature, the concentrations of dicarboxylic acids in TSP were used for comparison in Table 2. This comparison is reasonable because oxalate and succinate, but not malonate, principally exist in fine particles (Kerminen et al., 2000, Yao et al., 2002). Among these acids, oxalate was the dominant species, followed by malonate. This trend is consistent with observations in Tokyo, Falkenberg and Leipzig, but different from observations in Hong Kong and Los Angeles where succinate was more abundant than malonate (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Röhrl and Lammel, 2001; Yao et al., 2002). Kawamura and Kaplan (1987) proposed that the larger succinate concentration in Los Angeles is associated with vehicle exhaust. The maximum mass ratio of dicarboxylic-carbon to organic carbon was 1.3% in Shanghai, and the sum of the three dicarboxylic acids only account for 0.3–2% of the total mass of the water-soluble ions. Although these species are not...
significant contributors to the PM2.5 mass, their determination is useful since it can help us to better understand the formation of sulfate and nitrate.

In-cloud or heterogeneous formation of oxalate is expected to yield a good correlation between oxalate and sulfate (Kerminen et al., 2000, Yao et al., 2002). On the other hand, photochemical formation would yield a good correlation between oxalate and O₃ (Kawamura and Ikushima, 1993). Dicarboxylic acids can also originate directly from vehicle exhaust (Kawamura and Kaplan, 1987), in which case, oxalate may be correlated with CO. As shown in Fig. 4(a), oxalate was reasonably well correlated with sulfate (r = 0.7) but oxalate and nitrate were poorly correlated (r = 0.45). Recall that NO₃⁻ and SO₄²⁻ were highly correlated with a correlation coefficient of 0.91–0.92 and the gas-phase oxidation of SO₂ was not important for SO₄²⁻ formation. If SO₄²⁻, NO₃⁻ and oxalate totally originated from the in-cloud processes, more NO₃⁻ than oxalate would be released from the cloud droplet as water evaporated because nitrate is more volatile than oxalate. A better correlation between oxalate and SO₄²⁻ than NO₃⁻ and SO₄²⁻ is expected, but not found in our study. Since oxalate principally exists in the droplet mode (Kerminen et al., 2000; Blando and Turpin, 2000; Yao et al, 2002) and oxalate in the droplet mode is believed to originate from in-cloud processes like sulfate (Blando and Turpin, 2000; Yao et al, 2002), we infer that NO₃⁻ did not originate from in-cloud processes. The possible pathway to form an internal mixture of NO₃⁻ and SO₄²⁻ is the formation of SO₄²⁻ and oxalate, followed by HNO₃ and possibly NH₃ absorption into SO₄²⁻ aerosol droplets. Since the mass of SO₄²⁻ is much higher than the mass of oxalate, the liquid water content of aerosol droplets, an important parameter for the aqueous phase reactions, will be determined by the mass of SO₄²⁻, not by the mass of oxalate. This can explain the good correlation between NO₃⁻ and SO₄²⁻. The correlation coefficient between oxalate and O₃ concentrations was <0.1, which suggests that photochemical reactions are not important.
possibly NH3 absorption in heterogeneous reactions. Nitrate accounted for 25% of the total mass of the ions, whereas chloride was close to the US NAAQS 24-h PM2.5 standard of 65 µg m\(^{-3}\) for 44% of the total mass of ions. Sulfate alone also exceeds the US NAAQS annual PM2.5 standard of 6.5 µg m\(^{-3}\) for 16% of the total mass of the inorganic ions. The annual average ammonium concentrations were 6.2–6.5 µg m\(^{-3}\) in Beijing, which accounted for 16% of the total mass of the inorganic ions. The sum of Cl\(^{-}\), Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\) and K\(^{+}\) accounted for 15% of the total mass of the inorganic ions.

4. Ionic species of PM2.5 in Beijing

4.1. The composition of PM2.5 ions

As listed in Table 1, the annual average SO\(_4^{2-}\) concentrations were 18.4 µg m\(^{-3}\) at Chegongzhuang and 16.9 µg m\(^{-3}\) at Tsinghua in Beijing, which accounted for 44% of the total mass of ions. Sulfate alone also exceeds the US NAAQS annual PM2.5 standard of 15 µg m\(^{-3}\). The maximum SO\(_4^{2-}\) concentration was 62.4 µg m\(^{-3}\) at Chegongzhuang and 55.7 µg m\(^{-3}\) at Tsinghua, which was close to the US NAAQS 24-h PM2.5 standard of 65 µg m\(^{-3}\). The annual average NO\(_3^-\) concentrations at the two sites were 9.9 and 10.3 µg m\(^{-3}\). Nitrate accounted for 25% of the total mass of the inorganic ions. The annual average ammonium concentrations were 6.2–6.5 µg m\(^{-3}\) in Beijing, which accounted for 16% of the total mass of the inorganic ions. The sum of Cl\(^{-}\), Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\) and K\(^{+}\) accounted for 15% of the total mass of the inorganic ions.

4.2. The seasonal variations of the SO\(_4^{2-}\) and NO\(_3^-\) concentrations

As shown in Fig 1(b), the average SO\(_4^{2-}\) concentrations in summer and fall were about 20% higher than in winter, although there were four sulfate episodes in winter, which will be discussed later. The SO\(_4^{2-}\) concentrations at the Chegongzhuang site and at the Tsinghua site were similar most of the time, which can be explained by regional sulfate formation or long-range transport during those seasons. However, large differences in SO\(_4^{2-}\) concentrations were found in some cases, e.g., from July to September (the rainy season in Beijing), which may be associated with local sources. The NO\(_3^-\) concentration was generally higher in winter than in summer, probably due to a combination of lower temperatures and meteorology. The maximum NO\(_3^-\) concentration occurred at the end of November. The sharp decrease in the NO\(_3^-\) and SO\(_4^{2-}\) concentrations for the week 25/11/99–02/12/99 was due to snowfall. NO\(_3^-\) and SO\(_4^{2-}\) were moderately correlated at the two sites (r = 0.70 & 0.73) and they had several concurrent peaks in winter, especially during the four high NO\(_3^-\) and SO\(_4^{2-}\) episodes. Although sulfate was generally more abundant than nitrate, they were quite comparable at times.

Wind speed was an important factor affecting the SO\(_4^{2-}\) concentration in Beijing, as shown in Fig. 5(a). At Chegongzhuang, SO\(_4^{2-}\) concentrations decreased with increasing weekly average wind speed. In the four high SO\(_4^{2-}\) and NO\(_3^-\) episodes in November and January, the daily average wind speed was significantly lower than the annual average value of 2.5 m s\(^{-1}\), with some days below 1.0 m s\(^{-1}\), as shown in Fig. 5(b). On the other hand, dust storms led to the low SO\(_4^{2-}\) and NO\(_3^-\) concentrations but high Si concentration in PM2.5. For example, during 23–30 March 2000, the Si concentration in PM2.5 increased by eight times but the SO\(_4^{2-}\) concentrations decreased by 60% to 4.0 and 2.9 µg m\(^{-3}\) at Tsinghua, respectively. For this sample, the mass ratio of elemental Ca to sulfate was 1:2, while the mass ratio of water-soluble Ca to sulfate was only 1:6. Similarly, during 20–27 April, the Si concentration increased by three times and the SO\(_4^{2-}\) and NO\(_3^-\) concentrations decreased by 70% to 5.1 and 2.3 µg m\(^{-3}\) at Tsinghua, respectively. Overall, the SO\(_4^{2-}\) and NO\(_3^-\) concentrations during the periods of the dust storms were only about one-third of the annual average concentrations.
4.3. The sources of $SO_4^{2-}$ and $NO_3^-$

As in Shanghai, the mass ratio of $[NO_3^-]/[SO_4^{2-}]$ was used as an indicator of stationary vs mobile sources of sulfur and nitrogen in the PM. As shown in Fig. 2(b), the ratios at the two sites were almost the same although the $NO_3^-$ and $SO_4^{2-}$ concentrations at the two sites were different in some cases (Fig 1(b)). The ratio varied from 0.1 to 1.5 with an annual average of 0.58. The minimum ratio occurred in August and the maximum ratio occurred at the end of October. The maximum ratio of 1.5 was comparable to the value (2.0) in downtown Los Angeles (Kim et al., 2000). The second highest ratio occurred at the beginning of April. The partitioning of $NO_3^-$ between the gas and particulate phases and among the different sized particles is affected by temperature,
relative humidity, $\text{SO}_4^{2-}$ concentration and the abundance of crustal species in the particles (PM2.5 and coarse particle; Zhang et al., 2000). In Beijing, the complicated seasonal variations of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ may be due to a combination of all these potential factors because of the city’s large seasonal variations in $T$, RH and the $\text{SO}_4^{2-}$ concentrations (Fig. 1(b) and Fig. 2(b)) and high Ca concentrations in the coarse particles (Zhou et al., 1998). Zhou et al. (1998) reported that the mass ratios of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ in the PM1.5 and PM10 were 0.28 and 0.27 in the winter in 1994, 0.71 and 0.70 in the spring of 1995, 0.03 and 0.14 in the summer of 1995, 0.67 and 0.74 in the fall of 1995 and 0.28 and 0.29 in the winter of 1995 in Beijing. Compared with the data reported by Zhou et al. (1998), our measured mass ratios of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ are about 20% higher in the spring and 60% higher in the fall and winter. This is probably related to both the increase in vehicle population and the decreased usage of coal. The difference may also be due to $\text{NO}_3^-$ sampling artifacts in the Zhou et al. study, in which a dichotomous sampler was used. Since RH is usually lower than 60% in winter in Beijing, particles are expected to be dry and no particle–particle interactions in the collected particles occur. Low temperature in winter in Beijing also favors the partition of ammonium nitrate in the particulate phase. Hence, sampling artifacts probably were not a major problem in winter.

High $\text{Cl}^-$ concentrations (>1 $\mu$g m$^{-3}$) were observed from November to March. The maximum concentration reached 9.3 $\mu$g m$^{-3}$ (Table 1). This chloride is believed to be associated with coal burning. The contribution from sea-salt particles is not important because the sampling sites in Beijing are about 200 km from the sea. The $\text{Na}^+$ concentrations (on average 0.7 $\mu$g m$^{-3}$ in Table 1) were generally lower than 1 $\mu$g m$^{-3}$ during the year-long sampling and the mole ratio of measured $\text{Cl}^-$ to $\text{Na}^+$ in the winter was 2.3, much higher than the ratio in sea water of 1.17. A significant seasonal variation in the mass ratio of $\text{Cl}^-/\text{NO}_3^-$ was observed in Beijing (not shown). It varied from 0.28 to 0.90 (on average 0.51) in December through January and from 0.06 to 0.21 (on average 0.12) in September through October. House heating started at the middle of November. The mass ratio of $\text{Cl}^-/\text{NO}_3^-$ increased from 0.02 at the beginning to 0.55 at the end of November although a lot of small boilers have converted to natural gas recently in Beijing, some larger boilers still used coal for house-heating and were possibly the major source of air pollutants. The increase of the mass ratio of $\text{Cl}^-/\text{NO}_3^-$ in December to January is consistent with coal burning being the major source of $\text{Cl}^-$.  

4.4. The formation $\text{SO}_4^{2-}$ and $\text{NO}_3^-$

Correlations between $\text{SO}_4^{2-}$ and $\text{SO}_2$ were performed only for the Chegongzhuang site because $\text{SO}_2$ data were
not available at the Tsinghua site. Considering all the samples as a whole, SO$_4^{2-}$ and SO$_2$ were poorly correlated as shown in Fig. 3(b). However, much better correlations were obtained when the data was grouped by season because of the seasonal variation in the mechanism of sulfate formation. For example, SO$_4^{2-}$ was well correlated with [SO$_3$] in the winter with a linear regression equation of [SO$_4^{2-}$] = 0.37[SO$_3$]−8.4 and a correlation coefficient of 0.83. The average RH in the winter was generally lower than 60% as shown in Fig. 2(b), in which case aqueous heterogeneous reactions and in-cloud processes are less likely to be important. Alternatively, slow gas-phase SO$_2$ oxidation followed by condensation or absorption into the particle phase leads to the low [SO$_4^{2-}$]/[SO$_3$] mass ratio (0.27±0.15) in winter. The good correlation between SO$_2$ and sulfate in the winter supports this hypothesis. In the summer, the [SO$_4^{2-}$]/[SO$_3$] mass ratios were significantly higher, with an average value of 5.6 (molar ratio = 3.7) and a maximum value of 11.6 (molar ratio = 7.6), which were 20 times and 40 times larger than the ratios in the winter. Furthermore, SO$_2$ plus nitrogen oxide emissions were 20 times and 40 times larger than the ratios in the non-heating season. This is due to the low ambient temperature (and low photophysical flux) during the heating season, lowering the possibility of photochemical oxidation formation (Kawamura and Ikushima, 1993). The correlation coefficients between oxalate and nitrate and between oxalate and organic carbon were 0.5 and 0.1, respectively. Hence, vehicle exhaust is not a dominant source of oxalate.

5. Conclusion

Overall, SO$_4^{2-}$ NO$_3^-$ and NH$_4^+$ were dominant ionic species in PM2.5 in both Shanghai and Beijing. In Shanghai, the annual average SO$_4^{2-}$ NO$_3^-$ and NH$_4^+$ concentrations were 15.5, 6.6 and 6.4 µm$^{-3}$, which account for 46%, 18% and 17% of the total mass of ions, respectively. In Beijing, the annual average SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ concentrations were 17.7, 10.1 and 6.4 µm$^{-3}$, which account for 44%, 25% and 16% of the total mass of ions, respectively.

In Shanghai, the SO$_4^{2-}$ concentration was moderately correlated with the ambient SO$_2$ concentration with a correlation coefficient of 0.66. Local SO$_2$ emissions were an important source of sulfate in PM2.5. Since different SO$_4^{2-}$/SO$_2$ mass ratios were observed in summer and winter, we inferred that the gas-phase oxidation of SO$_2$ played only a minor role in the sulfate formation. NO$_3^-$ and SO$_4^{2-}$ were highly correlated with a correlation coefficient of 0.91–0.92. In Beijing, local SO$_2$ emissions were an important source of PM2.5 in the winter, when the SO$_4^{2-}$ concentration was well correlated with the ambient SO$_2$ ($r = 0.83$). Gas-phase oxidation of SO$_2$ was an important route of sulfate formation. In the summer, in-cloud processes became dominant.

The annual average ratio of NO$_3^-$/SO$_4^{2-}$ was 0.4 and 0.6 in Shanghai and in Beijing, respectively, suggesting
that stationary emissions were still the dominant source in these two cities. In both cities, \( \text{(SO}_4^{2-} + \text{NO}_3^-) \) was highly associated with \( \text{NH}_4^+ \) and was incompletely neutralized by \( \text{NH}_3 \) as indicated by an equivalence ratio of \( \text{(SO}_4^{2-} + \text{NO}_3^-) / \text{NH}_4^+ > 1 \). The PM2.5 in these two cities are likely to be acidic.

Oxalate was the dominant dicarboxylic acid species, followed by malonate in these two cities. Oxalate was better correlated with sulfate than with organic carbon or \( \text{O}_3 \). The principal source of dicarboxylic acids is from secondary reaction, not from primary vehicular exhaust.

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References


composition of PM2.5 in Shanghai for a 1 yr period. 
