Speciation of the major inorganic salts in atmospheric aerosols of Beijing, China: Measurements and comparison with model

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HIGHLIGHTS

- NH₄NO₃, NH₄Cl and (NH₄)₂SO₄ were measured in Beijing atmosphere.
- Sulfate, nitrate and chloride associated with crustal ions were important.
- ISORROPIA II was used to investigate the gas-aerosol equilibrium characteristics.
- Crustal species should be carefully considered to improve model prediction.

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ABSTRACT

In the winter and summer of 2013–2014, we used a sampling system, which consists of annular denuder, back-up filter and thermal desorption set-up, to measure the speciation of major inorganic salts in aerosols and the associated trace gases in Beijing. This sampling system can separate volatile ammonium salts (NH₄NO₃ and NH₄Cl) from non-volatile ammonium salts ((NH₄)₂SO₄), as well as the non-volatile nitrate and chloride. The measurement data was used as input of a thermodynamic equilibrium model (ISORROPIA II) to investigate the gas–aerosol equilibrium characteristics. Results show that (NH₄)₂SO₄, NH₄NO₃ and NH₄Cl were the major inorganic salts in aerosols and mainly existed in the fine particles. The sulfate, nitrate and chloride associated with crustal ions were also important in Beijing where mineral dust concentrations were high. About 19% of sulfate in winter and 11% of sulfate in summer were associated with crustal ions and originated from heterogeneous reactions or direct emissions. The non-volatile nitrate contributed about 33% and 15% of nitrate in winter and summer, respectively. Theoretical thermodynamic equilibrium calculations for NH₄NO₃ and NH₄Cl suggest that the gaseous precursors were sufficient to form stable volatile ammonium salts in winter, whereas the internal mixing with sulfate and crustal species were important for the formation of volatile ammonium salts in summer. The results of the thermodynamic equilibrium model reasonably agreed with the measurements of aerosols and gases, but large discrepancy existed in predicting the speciation of inorganic ammonium salts. This indicates that the assumption on crustal species in the model was important for obtaining better understanding on gas–aerosol partitioning and improving the model prediction.

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1. Introduction

Atmospheric particulate matter has attracted much attention due to its impacts on visibility reduction, acid deposition, climate and human health (IPCC, 2007). Inorganic soluble ions, dominated by sulfate (SO₄²⁻), nitrate (NO₃⁻) and ammonium (NH₄⁺), are the major constituents of PM₁₀ (particulate matter with aerodynamic diameter <10 μm) mass (Sun et al., 2006). These inorganic species are secondary in nature and formed through a series of chemical reactions and physical processes, which are influenced by many factors, such as the concentrations of gaseous precursors, the levels of atmospheric oxidants, the characteristics of pre-existing aerosols, the air temperature and relative humidity (Ianniello et al., 2011; Squizzato et al., 2013). Sulfate is generated through gas-phase, heterogeneous, or multi-phase oxidations of SO₂. Nitrate is mostly formed by gas to particle conversion processes involving
NOx (NO + NO2). The formation of ammonium is from the neutralization of ammonia with acid species such as, sulphuric acid (H2SO4), nitric acid (HNO3) and hydrochloric acid (HCl) (Seinfeld and Pandis, 2006). Ammonia is believed to be first taken up by H2SO4 to form ammonium sulfate (NH4+SO4) and ammonium bisulphate (NH4HSO4). Any excess ammonia could then react with HNO3 and HCl to form ammonium nitrate (NH4NO3) and ammonium chloride (NH4Cl) (Du, 2010; McMurry et al., 1983; Wang et al., 2005). The extent of sulfate neutralized by ammonia has influence on the optical properties of the aerosol (Adams et al., 2001). Moreover, as the volatile compounds in the troposphere, NH4NO3 and NH4Cl also have important influence on Earth’s radiative balance and acid deposition (Anjea et al., 2001; Harrison et al., 1990). Therefore, there is a need to accurately measure different forms of sulfate, nitrate and ammonium salts in aerosols.

Previous studies about sulfate, nitrate and ammonium in aerosols mainly focused on their concentrations, size distributions, source identifications and formation mechanisms (Kai et al., 2007; Li et al., 2013; Sun et al., 2006; Xue et al., 2014; Zhang et al., 2013). However, there are sparse data about the speciation of ammonium salts, such as (NH4)2SO4, NH4NO3 and NH4Cl. In most studies, concentrations of NH4NO3 and NH4Cl were not directly measured but were used results obtained through ion balance and regression analysis (He et al., 2012; Wang et al., 2005), which might not be accurate. In limited studies, thermal desorption techniques were applied to speciation of inorganic species (Perrino et al., 2012; Possanzini et al., 1992; Sturges and Harrison, 1988; Lun et al., 2003; Yoshizumi and Hoshi, 1983; Yoshizumi and Okita, 1983), despite the fact that the temperature to discriminate volatile and non-volatile species was not consistent in these studies and the artifacts associated with the complex gas-solid chemistry during the desorption process was also a concern. Possanzini et al. (1992) developed a thermal desorption system to separate NH4NO3 and NH4Cl from sulfate, and found that NH4NO3 and (NH4)2SO4 constituted the major species of particulate matter. Lun et al. (2003) reported the size distribution characteristics of the speciation of ammonium salts with limited sampling days. So far, there has been no comprehensive study to quantitatively determine the speciation of ammonium salts in ambient aerosols in different weather conditions.

Besides the speciation of ammonium salts, measurements of volatile ammonium salts (NH4NO3 and NH4Cl) are also complicated since they are thermodynamically unstable and formed through reversible phase equilibrium with precursor gases such as, NH3, HNO3 and HCl (Pio and Harrison, 1987). An effective method to measure the semi-volatile inorganic salts is the use of denuders and back-up filters (Possanzini et al., 1983). Denuders absorb gases prior to particle collection and back-up filters absorb HNO3, HCl and NH3 evaporating from collected particles on the front filter. This method can avoid sampling artifacts such as gas-particle and particle-particle interactions. In field measurements, the concentration products of [NH3][HNO3] and [NH3][HCl] were compared with theoretical values predicted by thermodynamic equilibrium laws for NH4NO3 and NH4Cl formations to test the validity of equilibrium assumptions (Allen et al., 1989; Guo et al., 2010; Ianniello et al., 2011; Matsumoto and Tanaka, 1996). The thermodynamic equilibrium of a species between gas phase and particle phase depends on many factors, such as the ambient temperature, relative humidity, particle size and chemical composition of particles and gases (Mozurkewich, 1993; Stelson and Seinfeld, 1982). Some of the measurements usually agreed theoretical values well, while others were lower than the predicted ones suggesting the absence of ammonium nitrate (Allen et al., 1989; Hu et al., 2008; Ianniello et al., 2011). The reason of such deviations may be attributed to some unknown kinetic constraints on attainment of the system equilibrium (Harrison et al., 1990). A thermodynamic equilibrium model, ISORROPIA II (Fountoukis and Nenes, 2007), which is capable of simulating a comprehensive multicomponent inorganic aerosol system, can be used to investigate the gas-aerosol partitioning characteristics. This model is computationally efficient and widely used in the regional and global models (Heald et al., 2014; Sudheer and Rengarajan, 2015). However, studies on assessing the equilibrium state of the aerosol and investigating the gas-aerosol partitioning in the atmosphere of Beijing were insufficient. Therefore, investigating thermodynamic equilibrium of inorganic species and comparison between measurements and modelled results under the actual environment is desirable.

This paper presents results obtained from field measurements of the speciation of major inorganic salts and the associated trace gases in winter and summer of Beijing. Through the annular denuder, back-up filter and thermal desorption set-up, the volatile salts were separated from the non-volatile salts during sampling. The main objectives of this study are to measure the speciation of inorganic salts, to quantify their concentrations, and to study their temporal variations, size distributions characteristics and formation mechanisms in Beijing atmosphere. We use the thermodynamic equilibrium model (ISORROPIA II) to investigate gas-aerosol partitioning characteristics and further compare the modelling results with measurements to offer insights into the model predictions of inorganic salts.

2. Methods

2.1. Sampling and measurements

Measurements were performed at the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (40° 00′ 28″ N, 116° 20′ 15″ E), which is located in the northwestern urban area of Beijing. The sampling site was located on the roof of a fourth-floor building (15 m above the ground level). The measurements were conducted from 25 December 2013 to 18 January 2014 (winter) and from 21 July to 20 August 2014 (summer). The nighttime data corresponds to the period 19:00—7:00 and the daytime data to 07:00—19:00 in local time (GMT+08:00).

Ambient concentrations of some gases were measured using an annular denuder system (Possanzini et al., 1983). The denuder (22 cm in length, 16 mm and 18 mm in annulus diameter) line configuration included one denuder coated with sodium carbonate (5% Na2CO3 + 1% glycerol in 1:1 methanol/water solution) for collecting HCl, HNO3 and SO2, followed by another denuder coated with citric acid (10% citric in methanol) for NH3 removal (Nie et al., 2010; Lun et al., 2003). To determine the collection efficiency of gaseous species by annular denuder in our study, two denuders in series were arranged on days with high pollution levels and the sampling duration was 24 h. The collection efficiency was greater than 99.3%. It should be noted that the use of Na2CO3 coated denuder and the use of citric acid coated denuder may cause negative artifacts, and coating of citric acid on the denuder surface is essential. An improved denuder set-up was suggested (Perrino et al., 2001; Ianniello et al., 2010) and Perrino et al. (2001) reported the uncertainty of 8.6% and 6.1% for NH4NO3 and NH4Cl, respectively.

The sampling flow rate was 7 l min⁻¹. A cyclone was applied to remove the coarse particles (>10 μm), while particles less than 10 μm were collected on a filter pack set in series. The filter pack consisted of one Teflon filter (2 μm pore size, 47 mm diameter, Gelman, USA) on which aerosol particles were retained, and two paper filters (type 41, Whatman, USA) impregnated with Na2CO3 and phosphorous acid. The impregnating of filters and coating of denuders were treated with caution, and the filters and denuders
were sealed before sampling to avoid contamination (Perrino et al., 2001). The two back-up filters served to collect the dissociation products (HNO₃, HCl and NH₃) of ammonium nitrate and ammonium chloride (NH₄NO₃ and NH₄Cl) evaporated from the front Teflon filter. The filter pack was placed in an incubator (70 ± 0.1 °C). NH₄NO₃ and NH₄Cl were volatilized entirely from the Teflon filter under 70 °C, while sulfates were remained on the Teflon filter (Possanzini et al., 1992; Lun et al., 2003). If ammonium nitrate/sulfate double salts (such as (NH₄)₂SO₄, 2NH₄NO₃ and (NH₄)₂CO₃·3NH₄Cl) were collected, volatilization of NH₄NO₃ from the salts still occurred because of the similarities in the degree of volatilization between these compounds and their corresponding mixtures of nitrate and sulfate salts (Sturges and Harrison, 1988). Total concentrations of ammonium salts in PM₁₀ were the sum of the non-volatile ammonium salts measured on the Teflon filter and the volatile ammonium salts measured on the back-up filters.

\[
\begin{align*}
[\text{NO}_3^-]_{\text{volatile}} & = [\text{NO}_3^-]_N \\
[\text{Cl}^-]_{\text{volatile}} & = [\text{Cl}^-]_N \\
[\text{NH}_4]^+_{\text{volatile}} & = [\text{NH}_4]^+_p \\
[\text{NO}_3^-]_{\text{non-volatile}} & = [\text{NO}_3^-]_T \\
[\text{Cl}^-]_{\text{non-volatile}} & = [\text{Cl}^-]_T \\
[\text{NH}_4]^+_{\text{non-volatile}} & = [\text{NH}_4]^+_T \\
[\text{NO}_3^-]_{\text{particulate}} & = [\text{NO}_3^-]_{\text{volatile}} + [\text{NO}_3^-]_{\text{non-volatile}} \\
[\text{Cl}^-]_{\text{particulate}} & = [\text{Cl}^-]_{\text{volatile}} + [\text{Cl}^-]_{\text{non-volatile}} \\
[\text{NH}_4]^+_{\text{particulate}} & = [\text{NH}_4]^+_{\text{volatile}} + [\text{NH}_4]^+_{\text{non-volatile}}
\end{align*}
\]

The subscripts of “N”, “P” and “T” represent the Na₂CO₃ coated paper filter, phosphorous acid coated paper filter and Teflon filter, respectively.

The SO₄²⁻ is not volatile, thus its concentrations were the SO₄²⁻ measured on the Teflon filter only. The remaining species on the Teflon filter were non-volatile species, including NO₃⁻, Cl⁻ and NH₄⁺ as well as Ca²⁺, Mg²⁺, Na⁺ and K⁺.

Size-segregated samples were also collected using an eight-stage Anderson impactor sampler operating at a flow rate of 28.3 l min⁻¹. The 50% cut sizes for the eight stages were 0.4, 0.7, 1.1, 1.8, 2.3, 4.4, 5.6, 7.7 and 10 μm. The duration of sampling was 24 h. Nine sets of samples were collected, including three sets during winter and six sets during summer under different weather conditions and pollution levels.

After sampling, the denuders and filters were extracted and stored in −4 °C refrigerator until analysis. The samples were analyzed for NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺, Na⁺, Mg²⁺, K⁺ and Ca²⁺ by using Ion Chromatography (ICS-1100, Dionex, USA). The detection limits for these ions were about 0.01 μg m⁻³ on 12-h sampling period.

Trace gas NO₂ was continuously measured by an analyzer (42i, Thermofisher, USA) with an uncertainty of 1% (Xie et al., 2005). PM₁₀ concentrations and meteorological parameters (ambient temperature and relative humidity) were measured with a resolution of 5 min using Grimm 180 dust monitor (GRIMM aerosol technik, Germany) (Grimm and Eatough, 2009).

2.2. ISORROPIA II model

ISORROPIA II, a thermodynamic equilibrium model for inorganic gases and aerosols in the atmosphere (available at http://isorrophia.eas.gatech.edu), was applied to assess the equilibrium state of the aerosol and to investigate the model’s ability to predict the gas-aerosol partitioning. Concentrations of inorganic species (gas + aerosol concentrations of SO₂⁻, HNO₃ + NO₂⁻, NH₃ + NH₄⁺, HCl + Cl⁻, Na⁺, Mg²⁺, K⁺ and Ca²⁺) along with air temperature and relative humidity with 12 h resolution were used as input. The model was run in the “forward” mode in the thermodynamically stable state, where salts precipitate once the aqueous phase becomes saturated with respect to salts, to determine which species can exist in the gas, aerosol, or solid phases under the assumption of thermodynamic equilibrium conditions (Fountoukis and Nenes, 2007).

3. Results and discussion

3.1. General characteristics of inorganic salts and associated precursor gases

Table 1 lists the statistics summary of inorganic ions in PM₁₀ and gaseous species as well as the meteorological parameters, such as air temperature (T), and relative humidity (RH), during the winter and summer measurements. The temporal variations of the ions in PM₁₀ and gaseous species can be seen in Fig. 1.

Mean concentrations of SO₂⁻ were higher (t-test, p < 0.05) in winter (21.88 ± 24.95 μg m⁻³) than in summer (13.64 ± 11.90 μg m⁻³). The gaseous precursor SO₂ in winter (71.9 ± 43.43 μg m⁻³) was 13 times higher than that in summer (5.44 ± 4.25 μg m⁻³). Notably, the highest concentrations of SO₂⁻ (106.51 μg m⁻³) and SO₂ (192.73 μg m⁻³) were simultaneously found on 15 January 2014, suggesting the importance of direct emissions in winter. Whereas the oxidation rate of SO₂ to particulate sulfate (defined as molar ratio of [SO₄²⁻]/([SO₂⁻] + [SO₂]) was higher in summer (0.59 ± 0.29) than in winter (0.15 ± 0.09), which may due to the enhanced atmospheric oxidant (tropospheric ozone, hydrogen peroxide and hydroxyl radical) levels, sufficient ammonia for neutralization, and relatively high RH in summer.

The mean concentrations of particulate NO₃⁻ were 15.18 ± 15.96 μg m⁻³ in winter and 10.90 ± 7.93 μg m⁻³ in summer. Many previous studies suggest that particulate NO₃⁻ was mostly formed from the photochemical oxidation of precursor gases (such as NOₓ) or through the heterogeneous hydrolysis of NO₂⁻ on the pre-existing particles (Pathak et al., 2011; Wen et al., 2015). In our study, NO₃⁻ and NO₂ correlated significantly (r = 0.75, p < 0.01) in winter, suggesting that the local vehicular emissions of NO₂ might be an important source of particulate NO₃⁻. The strong correlations of NO₃⁻ with RH (r = 0.69, p < 0.01) and PM₁₀ (r = 0.74, p < 0.01) in winter indicates that the heterogeneous formation pathway could be also a potentially important contributor to particulate NO₃⁻ in winter since the heterogeneous formation generally related with RH and particulate loadings (Ianniello et al., 2011). In fact, the high RH may facilitate the absorbance of HNO₃ in humid particles to lead to the enhanced NO₃⁻ (Guinot et al., 2007; Ianniello et al., 2011; Pathak et al., 2009, 2011). In summer, we did not find the significant correlation between NO₃⁻ and NO₂, while the correlations...
between NO$_3^-$ and RH ($r = 0.60$, $p < 0.01$, exclude data in rain event) and PM$_{10}$ ($r = 0.77$, $p < 0.01$) were high. Therefore, the factors influencing the formation of NO$_3^-$ may be more complex in summer. Note that high concentrations of NH$_3$ were available to neutralize H$_2$SO$_4$ and HNO$_3$ in our study. The mean concentrations of NH$_3$ were 17.64$\mu$g m$^{-3}$ in summer, which were 4 times higher than those of winter (4.91$\mu$g m$^{-3}$) and 7.87$\mu$g m$^{-3}$ in summer. The temporal variations of NH$_4^+$ mainly originated from the neutralization of NH$_3$ and other acidic species (Ianniello et al., 2011; Sun et al., 2010). The molar concentrations of NH$_4^+$ were 5 times higher than those of SO$_2$ but lower than those of 2[SO$_2$] + [NO$_3$] + [Cl$^-$] (Fig. S1), suggesting the formation of (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and NH$_4$Cl.

We found that Cl$^-$ exhibited distinct and significant seasonal variations with high (t-test, $p < 0.01$) concentrations in winter ($7.0 \pm 5.49$ $\mu$g m$^{-3}$) and low concentrations ($0.93 \pm 0.72$ $\mu$g m$^{-3}$) in summer. Coal burning emissions during heating period may contribute to the enhanced Cl$^-$ in winter (Ianniello et al., 2011).

Mean concentrations of NH$_4^+$ were $12.08 \pm 12.57$ $\mu$g m$^{-3}$ in winter and $7.87 \pm 6.55$ $\mu$g m$^{-3}$ in summer. The temporal variations of NH$_4^+$ agreed well with SO$_2$ and NO$_3^-$ and Cl$^-$, suggesting that NH$_4^+$ mainly originated from the neutralization of NH$_3$ and other acidic species (Ianniello et al., 2011; Sun et al., 2010). The molar concentrations of NH$_4^+$ were 2 times higher than those of SO$_2$ but lower than those of 2[SO$_2$] + [NO$_3$] + [Cl$^-$] (Fig. S1), suggesting the formation of (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$ and NH$_4$Cl.

The predominant form of sulfate neutralized by NH$_3$ was identified and quantified from SO$_2^-$/NH$_3$ ratio on the front Teflon filter. The excess of SO$_2^-$ on the front Teflon filter was then inferred to be associated with crustal species such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$. Therefore, the excess of SO$_2^-$ (hereinafter referred to as “other sulfate”) was the total concentrations of SO$_2^-$ subtract SO$_2^-$ in (NH$_4$)$_2$SO$_4$.

**Table 1** Summary of ions in PM$_{10}$ and some gaseous species (HNO$_3$, HCl, NH$_3$, SO$_2$, NO$_2$) and meteorological parameters during the winter and summer in Beijing. The meteorological parameters were reported with 12-h average.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Winter (N = 52)</th>
<th>Summer (N = 60)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$ (µg m$^{-3}$)</td>
<td>1.05 ± 0.22</td>
<td>1.12 ± 0.27</td>
</tr>
<tr>
<td>SO$_2$ (µg m$^{-3}$)</td>
<td>2.57 ± 0.72</td>
<td>0.90 ± 0.21</td>
</tr>
<tr>
<td>Cl$^-$ (µg m$^{-3}$)</td>
<td>1.30 ± 0.42</td>
<td>0.23 ± 0.07</td>
</tr>
<tr>
<td>NH$_4^+$ (µg m$^{-3}$)</td>
<td>1.83 ± 0.56</td>
<td>0.56 ± 0.15</td>
</tr>
<tr>
<td>Na$^+$ (µg m$^{-3}$)</td>
<td>0.45 ± 0.15</td>
<td>1.05 ± 0.30</td>
</tr>
<tr>
<td>Cl$^-$ (µg m$^{-3}$)</td>
<td>0.06 ± 0.02</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Mg$^{2+}$ (µg m$^{-3}$)</td>
<td>0.10 ± 0.05</td>
<td>0.12 ± 0.05</td>
</tr>
<tr>
<td>Ca$^{2+}$ (µg m$^{-3}$)</td>
<td>0.90 ± 0.31</td>
<td>1.20 ± 0.05</td>
</tr>
<tr>
<td>PM$_{10}$ (µg m$^{-3}$)</td>
<td>40.16 ± 10.53</td>
<td>16.30 ± 7.19</td>
</tr>
<tr>
<td>NH$_3$ (µg m$^{-3}$)</td>
<td>0.17 ± 0.05</td>
<td>5.19 ± 7.95</td>
</tr>
<tr>
<td>HCl (µg m$^{-3}$)</td>
<td>0.14 ± 0.06</td>
<td>4.33 ± 7.95</td>
</tr>
<tr>
<td>HNO$_3$ (µg m$^{-3}$)</td>
<td>0.11 ± 0.06</td>
<td>0.12 ± 0.07</td>
</tr>
<tr>
<td>SO$_2$ (µg m$^{-3}$)</td>
<td>9.62 ± 2.92</td>
<td>0.29 ± 0.18</td>
</tr>
<tr>
<td>NO$_2$ (µg m$^{-3}$)</td>
<td>16.93 ± 3.92</td>
<td>4.33 ± 7.95</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>8.64 ± 7.95</td>
<td>17.59 ± 7.95</td>
</tr>
<tr>
<td>RH (%)</td>
<td>61.77 ± 27.01</td>
<td>21.81 ± 43.36</td>
</tr>
</tbody>
</table>

**Fig. 1.** Temporal trends of the particulate Cl$^-$, NO$_3^-$, SO$_2^-$ and NH$_4^+$, gaseous HNO$_3$, HCl, NH$_3$ and SO$_2$ and air temperature.

The predominant form of sulfate neutralized by NH$_3$ was identified and quantified from SO$_2^-$/NH$_3$ ratio on the front Teflon filter. The excess of SO$_2^-$ on the front Teflon filter was then inferred to be associated with crustal species such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$. Therefore, the excess of SO$_2^-$ (hereinafter referred to as “other sulfate”) was the total concentrations of SO$_2^-$ subtract SO$_2^-$ in (NH$_4$)$_2$SO$_4$.

**Fig. 2.** Shows the temporal variations of different forms of sulfate. On the whole, the SO$_2^-$ in (NH$_4$)$_2$SO$_4$ was the dominant form of SO$_2^-$ in both seasons. As listed in Table 2, the SO$_2^-$ in form of (NH$_4$)$_2$SO$_4$ was $17.63 \pm 22.30$ $\mu$g m$^{-3}$ and the other SO$_2^-$ was $4.25 \pm 4.68$ $\mu$g m$^{-3}$ in winter. In summer, the former was $12.20 \pm 11.07$ $\mu$g m$^{-3}$, while the latter was $1.44 \pm 1.07$ $\mu$g m$^{-3}$.

Different forms of sulfate may reflect their different sources and formation pathways. It is believed that (NH$_4$)$_2$SO$_4$ is formed through reactions of ammonia and sulphuric acid, and thisformation pathway is relatively well understood (Guo et al., 2010). In contrast, the other sulfate can originate from both direct emissions such as fly ash of coal burning (Lun et al., 2003) or biomass burning (Guo et al., 2010; Huang et al., 2006), and secondary formations such as heterogeneous reaction of sulfate on alkaline surfaces of aerosols. For instance, previous studies (Guo et al., 2010; Zhuang et al., 1999; Huang et al., 2006; Liu et al., 2005) suggested that the SO$_2$ or H$_2$SO$_4$ could react with aqueous carbonates (dissolved CaCO$_3$ and MgCO$_3$) on soil particles to form MgSO$_4$. CaSO$_4$. In our study, other SO$_2^-$ showed significant correlations with Mg$^{2+}$ ($r = 0.71$), Ca$^{2+}$ ($r = 0.68$) and K$^+$ ($r = 0.63$) in winter.
K2SO4 salts. In summer, other SO2 variation. One the one hand, the other sulfate might be from the summer (11%). The following two reasons may lead to the seasonal other sulfate to the total sulfate was higher in winter (19%) than in seasons at Beijing. Percentages of SO4 2- in (NH4)2SO4 to total SO4 2- in different species of NH4, SO4 2- , NO3 - and Cl - by thermal speciation.

Table 2
Summary of different species of sulfate (SO4 2- ), ammonium (NH4 + ), nitrate (NO3 - ) and chloride (Cl - ) by thermal speciation during daytime (D) and nighttime (N) in different seasons at Beijing. Percentages of SO4 2- in (NH4)2SO4 to total SO4 2- , volatile NH4+ (NH4+ in NH4NO3 + NH4Cl) to total NH4+ , volatile NO3- (NO3- in NH4NO3) to total NO3- and volatile Cl- (Cl- in NH4Cl) to total Cl- were also calculated.

<table>
<thead>
<tr>
<th></th>
<th>SO4 2- (%)</th>
<th>NH4+ (%)</th>
<th>NO3- (%)</th>
<th>Cl- (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>16.78 ± 20.83</td>
<td>84.5</td>
<td>6.29 ± 7.81</td>
<td>6.71</td>
</tr>
<tr>
<td>N</td>
<td>18.48 ± 24.06</td>
<td>77.3</td>
<td>6.93 ± 9.02</td>
<td>5.47</td>
</tr>
<tr>
<td>All</td>
<td>17.63 ± 22.30</td>
<td>80.6</td>
<td>8.36</td>
<td>6.74</td>
</tr>
<tr>
<td>Summer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>12.30 ± 11.32</td>
<td>89.9</td>
<td>4.60 ± 4.24</td>
<td>67.6</td>
</tr>
<tr>
<td>N</td>
<td>12.10 ± 11.00</td>
<td>89.3</td>
<td>4.12 ± 4.12</td>
<td>70.1</td>
</tr>
<tr>
<td>All</td>
<td>12.20 ± 11.07</td>
<td>89.4</td>
<td>4.14</td>
<td>67.8</td>
</tr>
</tbody>
</table>

(Table 3), indicating the possible formation of MgSO4, CaSO4 and K2SO4 salts. In summer, other SO4 2- only showed a slight correlation (r = 0.47) with K+ (Table 3), indicating the possible formation of K2SO4.

Table 2 shows that other sulfate was high and the percentage of other sulfate to the total sulfate was higher in winter (19%) than in summer (11%). The following two reasons may lead to the seasonal variation. One the one hand, the other sulfate might be from the direct emissions of coal burning (Lun et al., 2003) and/or their secondary formations of heterogeneous reaction (Zhuang et al., 1999; Huang et al., 2006; Liu et al., 2005). On the other hand, NH3 was more efficient in summer than in winter to react with SO2 to form (NH4)2SO4.

There were no clear diurnal variations of SO2 in summer; in contrast, nighttime had higher values than daytime in winter (Table 2). Possible reasons might be that relatively high RH in night enhanced the heterogeneous formation of particulate sulfate and the variation of atmospheric mixing height in winter.

The measurements of size distribution of inorganic ions could provide information for understanding the sources and formation mechanisms of sulfate. Table 3 shows the size distributions of inorganic ions in winter and summer. The result shows that most of sulfate dominated in the fine mode in the whole measurements. And a predominant fine mode was also observed for NH4+ suggesting the formation of (NH4)2SO4 was mainly in the fine mode. As previous studies showed that the formation processes of sulfate in the fine mode include homogeneous gas phase photochemical oxidation of SO2 followed by gas-to-particle conversion, and aqueous oxidation of SO2 in clouds/fogs droplets followed by water evaporation and NH3 neutralization to form (NH4)2SO4 (Seinfeld and Pandis, 2006). K+ was also dominated in the fine mode. Many studies reported that the presence of K+ was mainly
3.3. Speciation of nitrate and chloride

As mentioned in the Introduction, the artifacts associated with biomass burning emissions (K$_2$SO$_4$, KNO$_3$ and KCl) in Beijing (Duan et al., 2004; Zhang et al., 2008; Li et al., 2010). Therefore, K$_2$SO$_4$ was mainly existed in fine mode and associated with biomass burning. Ca$^{2+}$ and Mg$^{2+}$ were predominant in the coarse mode, reflecting their origin in crustal CaCO$_3$, MgCO$_3$ followed by reactions with H$_2$SO$_4$ since coarse mode sulfate may be attributed to heterogeneous reactions of SO$_2$ on soil particles.

The contributions of different formation pathways of sulfate, especially heterogeneous reactions, are still unknown and have not been quantified yet (Lun et al., 2003) because different formation pathways of sulfate cannot be quantitatively separated only by the measurement. Despite this, our work provides information about speciation of sulfate and suggests the important role of heterogeneous reactions for sulfate formations. Further research is necessary to investigate how heterogeneous reactions happen and their contributions to the sulfate formations.

3.3. Speciation of nitrate and chloride

As mentioned in the Introduction, the artifacts associated with the complex gas-solid chemistry during the sampling and desorption process is a concern. In our sampling system, denuders were equipped to remove gaseous species to avoid the gas-particle reactions of aerosols on the filter, while the cyclone before the filter pack removed the coarse particles (>10 μm) to reduce the possible chloride and nitrate artifacts due to reactions on the aerosols already collected, which may occur between NaCl particles and HNO$_3$ produced by NH$_4$NO$_3$ dissociation (Possanzini et al., 1992). The effects of such reactions were observed with pure salts (Sturges and Harrison, 1988). However, the fact that the sodium chloride levels are very low in real aerosol samples decreases the risks associated with the complex gas-solid chemistry. This is consistent with the study of Perrino et al. (2012), who suggested that heating real atmospheric samples to discriminate inorganic salts were feasible though interconversion were observed when heating mixtures of pure salts. Perrino et al. (2012) suggested that low contact surface among individual particles in real samples might be the reason. Therefore, the speciation of nitrate and chloride by thermal desorption method was feasible.

There were strong positive correlations between the molar concentrations of NH$_4^+$ with the sum of molar concentrations of NO$_3^-$ and Cl$^-$ on the back-up filters in summer (slope = 1.02, r = 0.98) and winter (slope = 1.02, r = 0.95). The excellent ion balance indicates the possible absence of sampling artifacts and suggests the volatilization of NH$_4$NO$_3$ and NH$_4$Cl from the front Teflon filter. Furthermore, we used the method of Hildemann et al. (1984) to calculate the free nitrate and chloride concentrations in the front Teflon filter. The results showed negative values in both seasons, indicating that NH$_4$NO$_3$ and NH$_4$Cl was absent in the front Teflon filter after thermal decomposition.

As shown in Fig. 2, the heated front filter exhibited a high extent depletion of nitrate. As listed in Table 2, most of nitrate was volatile in winter (66.5%) and summer (85.2%). And this form of NO$\text{_x}$ was predominant in the front filter, while the cyclone before the back-up filter after thermal decomposition.

\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \quad (\text{R1}) \]

\[ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 \quad (\text{R2}) \]

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad (\text{R3}) \]

Different forms of nitrate may reflect their sources and formation pathways. In coastal area, natural sources such as sea-salts are an important contributor to the non-volatile NO$_3^-$ (Allen et al., 2015; Perrino et al., 2009). Some studies used the non-volatile nitrate and the volatile nitrate to discriminate natural and secondary source of nitrate (Perrino et al., 2012), however, heterogeneous reactions of HNO$_3$ on alkaline surfaces of aerosols could also form nitrate in continental urban areas. Table 3 shows that the non-volatile NO$_3^-$ exhibited significant correlations with K$^+$ (r = 0.83) and Mg$^{2+}$ (r = 0.71) in winter, and with Mg$^{2+}$ (r = 0.89), Ca$^{2+}$ (r = 0.78) and K$^+$ (r = 0.70) in summer, indicating the possible formation of Mg(NO$_3$)$_2$, Ca(NO$_3$)$_2$ and KNO$_3$ salts in our site. This is agreement with many studies (Guo et al., 2010; Pakkanen et al.,...
that crustal aerosol like CaCO$_3$ can react with nitric acid to form Ca(NO$_3$)$_2$ and the formation of other salts such as NaNO$_3$ and KNO$_3$.

Size distributions of inorganic ions can offer further information to understand their sources and formation pathways. As shown in Fig. 3, NO$_3^-$ dominated in the fine mode in winter. The formation of NH$_4$NO$_3$ was mainly in fine mode as confirmed by the dominant fine mode of NH$_3^-$. The coarse mode nitrate in this study could be attributed to heterogeneous reactions of HNO$_3$ on soil particles since dust concentrations were high in winter of Beijing.

We found that the characteristics of size distribution of NO$_3^-$ in summer (Fig. 4) were different from those of winter. In fact, three patterns of the size distributions of NO$_3^-$ were identified in summer: two sets of samples were dominated by the fine mode, two sets were dominated by the coarse mode, and the remaining two sets were bi-modally distributed in the fine mode and coarse mode. These different patterns could be attributed to the semi-volatile nature of NH$_4$NO$_3$, which exists in reversible phase equilibrium with gaseous HNO$_3$ and NH$_3$ (R2). Dissociation of NH$_4$NO$_3$ is easily influenced by temperature and RH; increase of temperature or decrease of RH may cause the release of HNO$_3$, which could react with coarse soil and sea-salts particles (R4 and R5) (Xue et al., 2014). Therefore, nitrate could be shifted from fine mode to coarse mode and from the volatile nitrate to the non-volatile nitrate, especially in summer with high temperature.

To identify factors influencing the size distribution and speciation of nitrate, the weather conditions (temperature and RH) and chemical compositions of gases and aerosols in different days were investigated (Table S1). The molar ratio of NH$_3$ to HCl and HNO$_3$ in the gas phase was first investigated. Although fine nitrate-dominated samples tended to have high ratios, there was no direct link between NO$_3^-$ size distributions and the ratio. Instead, environmental factors (temperature and RH) seem to be important in regulating the relative abundance of fine and coarse mode nitrate. During the days with the coarse mode dominated, relatively high temperature (28.0 and 28.8 °C) and low RH (32.4 and 42.6%) were observed. Note that the highest molar ratios of [NH$_3$]/[HCl]+[$\text{HNO}_3$] (33.2) were found on 7 August, however, a significant coarse mode of NO$_3^-$ was observed at the same time (Fig. 4). On this day, the relatively high temperature (28.8 °C) and low RH (40.8%) were recorded. This indicates that the abundance of NH$_3$ in the gas phase alone would not lead to a dominated fine mode of NO$_3^-$.

The chemical compositions of the gas phase and weather conditions influenced the size distribution and speciation of nitrate and these influences may be finally reflected in the molar ratio of $[\text{NH}_3]/[2\text{SO}_4^{2-}]+[\text{NO}_3^-]+[\text{Cl}^-]$ (R$_{fl}$/species) in our aerosol samples. As illustrated in Fig. 4, in two sets of fine-dominated samples, the R$_{fl}$/species were high (0.66 and 0.77), suggesting the formation of (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, NH$_4$Cl. In contrast, low R$_{fl}$/species were found (0.35 and 0.38) in the coarse nitrate-dominated samples. The low R$_{fl}$/species suggests the lack of NH$_3$ to neutralize HNO$_3$ and HCl. Therefore, more HNO$_3$ and HCl were available for reactions with dust particles to form the non-volatile nitrate and chloride. The other samples had the middle R$_{fl}$/species (0.52 and 0.58), which may explain their bimodal size distribution. Similar results were also found when we investigated R$_{fl}$/species of particles in different size (Fig. 3 and Fig. S2).

Distinct characteristics were found for different forms of NO$_3^-$ in the whole measurements. Volatile NO$_3^-$ had slightly higher concentrations in winter than in summer, whereas non-volatile NO$_3^-$ in winter was three times higher than in summer (Table 2). The reason might be that more non-volatile NO$_3^-$ was formed through heterogeneous reactions since dust particles were high in winter. In addition, higher percentages of non-volatile nitrate to total nitrate were found in winter (33%) than in summer (15%) (Table 2). This seems to be unexpected since the coarse mode of nitrate was obviously observed in summer. There are two reasons to explain this phenomenon. First, non-volatile NO$_3^-$ was high in winter, of which an important contributor KNO$_3$ existed in fine mode of nitrate as demonstrated in our study. Another study in Beijing (Guo et al., 2010) also provided evidence that NO$_3^-$ associated with crustal species were important in fine particles. Second, the contributions of coarse mode nitrate might be underestimated by using Anderson sampler in summer since that the impactor sampler may experience loss of particulates due to evaporation during high temperature and low RH (<70%) environment (Huang et al., 2004; Nie et al., 2010). Our results also showed that a significant nitrate loss (15%) was observed with the Anderson sampler in summer (Fig. S3). Therefore, the NH$_4$NO$_3$ in fine mode may be underestimated and the contribution of coarse mode nitrate may be overestimated by using Anderson sampler in summer. There were diurnal variations with higher NH$_4$NO$_3$ in nighttime than daytime in both seasons. This may be jointly influenced by the low temperature, high RH and low atmospheric mixing height in the nighttime (Seinfeld and Pandis, 2006).

The heated front filter also exhibited a high extent depletion of chloride (Fig. 2). The volatile Cl$^-$ was the major form of Cl$^-$.
accounting for 67.8% and 93.3% of the total Cl− in winter and summer, respectively. The correlations between non-volatile Cl− and crustal species suggest the possible formations of KCl, MgCl2 and CaCl2 (Table 3). The size distributions of inorganic ions show that the volatile Cl− might mainly exist in fine mode, while the non-volatile Cl− such as MgCl2 and CaCl2 might mainly exist in coarse mode and KCl mainly in fine mode.

The temporal variations of the volatile and non-volatile NH4+ were closely related with nitrate, chloride and sulfate (Fig. 2), since the volatile NH4+ was in the form of NH4NO3 and NH4Cl and the non-volatile NH4+ were in form of (NH4)2SO4. We found that 45.3% and 42.0% of NH4+ were volatile in winter and summer, respectively (Table 2).

The above results showed that volatile ammonium salts were the dominate form of nitrate and chloride in Beijing and mainly existed in the fine mode. The non-volatile ammonium salts were also an important contributor. In fact, we found that the non-volatile nitrate accounted for about 33% and 15% of the total nitrate in winter and summer, respectively. Our results highlight the importance of heterogeneous reactions in nitrate formations on the existing sulfate particles in both seasons of Beijing.

In summary, the behavior of sulfate, nitrate and chloride in aerosols were influenced not only by direct emissions, the abundance of gaseous species, the chemical composition of particles, but also by atmospheric conditions such as temperature and RH (Matsumoto and Tanaka, 1996; Lun et al., 2003). Indeed, the volatile parts of these salts were easily affected by temperature and RH. We thus investigated the behavior of the volatile species from the perspective of thermodynamic equilibrium in the next section.

### 3.4. Thermodynamic equilibrium for NH4NO3 and NH4Cl

NH4NO3 and NH4Cl, which are thermodynamically unstable under the normal atmospheric condition, exist in the reversible phase equilibrium with gaseous precursors (Pio and Harrison, 1987). From this viewpoint, we investigated whether these two volatile species could be formed stably by comparing the measured concentration products of their corresponding gases with the theoretical dissociation constant.

To assess if solid phase of NH4NO3 could exist, we compared the measured [NH4+][HNO3] / [NH4][HNO3] (Kmn) with theoretical dissociation constant (Kn) when RH was lower than RHD. The Kmn in winter was calculated according to Pio and Harrison (1987). The volatility of NH4NO3 in the fine mode was dissociated, nitric acid could react with alkaline particles such as CaCO3, MgCO3 or K2CO3 to form Ca(NO3)2, Mg(NO3)2 and KNO3. The coexistence of sulfate considerably reduces the stable temperature range of NH4NO3 (Wu and Chan, 2008).

Relative humidity is an important factor that influences the existence of aqueous phase on aerosols (Dougle et al., 1998; Gupta et al., 2015; Martin, 2000). If the ambient RH is lower than the relative humidity of deliquescence (RHD) (followed the study of Stelson and Seinfeld, 1982), then the equilibrium state of NH4NO3 is relative humidity of deliquescence (RHD) (followed the study of Stelson and Seinfeld, 1982) for NH4NO3, the formed NH4NO3 can be stable.

To determine the new equilibrium dissociation constant Kn* for NH4+/NO2−/SO42− system, the NH4NO3 ionic strength fraction Y = |NH4NO3| / |NH4NO3| + 3| (NH4)2SO4| was calculated according to Stelson and Seinfeld (1982). Kn* was derived by multiplying Kn with Y. As shown in Fig. 6, nearly all of nighttime samples (except for two days) had lower Kn* than Knm, suggesting the existence of NH4NO3. In contrast, nearly all of daytime samples (except for one day) had higher Kn* than Knm. The daytime data seem to indicate insufficient precursors to form NH4NO3, however, our back up filter data showed the presence of particulate NH4NO3 (Fig. 2). Thus, there were other factors that might influence the formation of NH4NO3 during the daytime. The complex mixture of aerosols (soot, organic carbon and crustal material) is one possible factor because they could change the behavior of pure salts. For instance, as discussed in Section 3.3, we found that when NH4NO3 in the fine mode was dissociated, nitric acid could react with alkaline particles such as CaCO3, MgCO3 or K2CO3 to form Ca(NO3)2, Mg(NO3)2 and KNO3. The coexistence of KNO3 with NH4NO3 could alter the phase transition behaviors of solid NH4NO3 and widen the stable temperature range of NH4NO3 (Wu and Chan, 2008).

Similar procedure was applied to study the formation of solid NH4Cl. The theoretical equilibrium constant Kc for solid NH4Cl was calculated according to Pio and Harrison (1987). The volatilities of NH4Cl was 2–3 times higher than that of NH4NO3 (Pio and Harrison, 1987; Stelson and Seinfeld, 1982). The behavior of ammonium chloride is similar to that of ammonium nitrate. Our results show that NH4Cl would be formed in most of days in winter,

![Fig. 5. Measured concentration product Kmn = [NH4+][HNO3] as a function of temperature for winter and summer, as well as daytime (open symbols) and nighttime (solid symbols). Theoretical dissociation constants Kn for pure NH4NO3 is shown as black solid line.](image-url)
whereas NH$_4$Cl would not be formed on nearly all days (except for one day) in summer (Fig. 7). The measured concentration product Kmc was below the predicted equilibrium constants Kc in summer (Table 4). However, measurements from back-up samples showed that the formation of NH$_4$Cl in both seasons. Similar with the case of NH$_4$NO$_3$, this disagreement can be explained when internal mixtures, and measured concentration product Kmn = [HCl][NH$_3$] as a function of temperature for summer. Daytime data were shown with open symbols and nighttime with solid symbols.

3.5. Equilibrium model simulation

The theoretical equilibrium considerations above are restricted to NH$_4$O$_3$/NO$_3$/SO$_4$$_2$ systems which may not completely explain gas–aerosol partitioning and formation processes of inorganic aerosol compositions in Beijing. It has been shown that the consideration of crustal material in predicting the partitioning of nitrate and ammonium, especially in areas where dust comprises a significant portion of total PM, is of great importance and can greatly improve model predictions (Allen et al., 2015; Fountoukis and Nenes, 2007). As shown by thermal speciation of inorganic aerosol in Sections 3.2 and 3.3, crustal species were very important in the formation of sulfate, nitrate and chloride. Therefore, in this section, the equilibrium model (ISORROPIA II) that considers the crustal species in the modelling framework was applied. This model is capable of simulating a comprehensive multicomponent inorganic gas/liquid/solid aerosol system.

The comparison of the model and measurement results of the partitioning between particle and gases was shown in Fig. 8. The model predictions and measurements were in reasonable agreement, and the agreement on the aerosol phase was better than the gas phase. According to Fig. 8 and Table 5, except that aerosol NH$_4$ was underestimated and gaseous NH$_3$ was overestimated in both seasons, in most cases the model tended to over-predict aerosols and under-predict gaseous compounds in summer, and the opposite trend was found in summer. The partitioning of aerosol and gas predicted by model is sensitive to temperature and RH. The difference may be the use of average RH and temperature in the model calculation which could not capture the evolution of gas/particle partitioning.

The model we used is also capable to calculate equilibrium concentrations of species in solid and liquid phase. When modelled sulfate solely existed as solid phase and no liquid sulfate phase existed, we were able to compare the modelled and measured SO$_4$$_2$ as the measured concentration product Kmn = [HCl][NH$_3$] as a function of temperature for summer. Daytime data were shown with open symbols and nighttime with solid symbols. Theoretical dissociation constants Kc for pure NH$_4$Cl is shown as black solid line.

![Fig. 6. Theoretical dissociation constant Kn (black solid line) for pure NH$_4$NO$_3$, Kn* (black dotted line) for NH$_4$/NO$_3$/SO$_4$$_2$ mixtures, and measured concentration product Kmn (black dot) as a function of temperature for summer. Daytime data were shown with open symbols and nighttime with solid symbols.](image)

![Fig. 7. Measured concentration product Kmc = [HCl][NH$_3$] as a function of temperature for winter and summer, as well as daytime (open symbols) and nighttime (solid symbols). Theoretical dissociation constants Kc for pure NH$_4$Cl is shown as black solid line.](image)
those of modelling, whereas the observed volatile nitrate and volatile chloride were lower than those of modelling. This may be due to the model’s assumption that the crustal species (such as Na$^+$ and K$^+$) is preferentially associated with sulfate to form Na$_2$SO$_4$ and K$_2$SO$_4$ before they are bound with nitrate and chloride (Fountoukis and Nenes, 2007). With this assumption, the amount of sulfate balanced by crustal cations was over-estimated and the sulfate neutralized by ammonia was under-estimated, and this trend was the opposite for nitrate and chloride. It may be premature to ascribe the discrepancies to the only one reason, and other possible factors cannot be ruled out, such as the faster uptake of HNO$_3$ than the attainment of equilibrium (Trebs et al., 2005), the influence of mass transport of species between gas and aerosol phase (Wexler and Seinfeld, 1992), the long duration of sampling time (Fountoukis et al., 2009), the mixing of the organic components especially water-soluble organic acids (Trebs et al., 2005) and the uncertainty of our sampling methods. However, we believe that our findings provide evidence that the model’s assumption about crustal species was an important factor. In fact, the important formation of the non-volatile nitrate should be taken into better consideration as suggested in our measurements and other studies (Parmar et al., 2001; Allen et al., 2015). More importantly, the modelled salts in different forms also have influences on calculating the pH, liquid water content and activity coefficients which are used in regional

Table 5

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<th>Winter</th>
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<th>Summer</th>
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<td>NMB (%)</td>
<td>NME (%)</td>
<td>NMB (%)</td>
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<td>73.7</td>
<td>30.6</td>
</tr>
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Table 5 Statistical evaluation of observed and modelled aerosol NH$_4$$^+$, NO$_3$ -$^-$, Cl$^-$, NH$_3$, HNO$_3$, and HCl by ISORROPIA II.

Fig. 8. Observed and modelled concentrations of NO$_3$, HNO$_3$, NH$_4$, Cl$^-$, and HCl.

Fig. 9. Comparison of the SO$_4$$^{2-}$ in the form of (NH$_4$)$_2$SO$_4$ in solid phase from model with SO$_4$$^{2-}$ in (NH$_4$)$_2$SO$_4$ from measurements. The modelled nitrate in the form of solid phase NH$_4$NO$_3$ and modelled chloride in the form of solid phase NH$_4$Cl were also compared with their observed value in winter. The 1:1 line is shown with dotted gray line.
model. Therefore, the deviations from the equilibrium model can lead to large uncertainty in chemical transport model outputs (Sudheer and Rengarajan, 2015). More research is needed to obtain better understanding on gas–aerosol partitioning and improve the prediction of model.

4. Conclusions

Measurements of speciation of major inorganic salts in aerosols and associated trace gases were carried out by annular denuder, back-up filter and thermal desorption set-up in winter and summer of 2013–2014 at Beijing (China) and gas–aerosol equilibrium characteristics were investigated. Results showed that (NH4)2SO4, NH4NO3 and NH4Cl were the major species of inorganic salts in aerosols. Sulfate, nitrate and chloride associated with crustal ions were also the important contributor in Beijing where dust concentrations were high. Our results suggest the important role of heterogeneous reactions in Beijing.

Comparison of measurement results with theoretical equilibrium dissociation constants for volatile ammonium salts (NH4NO3 and NH4Cl) suggests the internally mixing of sulfates and crustal species were important for the formation of volatile ammonium salts. Furthermore, modelling results of ISORROPIA II were reasonably consistent with measurements of aerosols, while large discrepancy existed in predicting the speciation of inorganic ammonium salts. The deviation may be attributed to the assumption of the model about some crustal species. This suggests that the role of crustal species should be carefully considered in thermodynamic equilibrium model in the future. Further measurements focused on inorganic salts speciation are important to obtain better understanding on gas–aerosol partitioning and improve the prediction of model.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2016.03.013.

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