



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



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## HIGHLIGHTS

- $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$  and  $(\text{NH}_4)_2\text{SO}_4$  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 ( $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ ) from non-volatile ammonium salts ( $(\text{NH}_4)_2\text{SO}_4$ ), 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  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  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  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  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 ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and ammonium ( $\text{NH}_4^+$ ), are the

major constituents of  $\text{PM}_{10}$  (particulate matter with aerodynamic diameter  $<10\ \mu\text{m}$ ) 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  $\text{SO}_2$ . Nitrate is mostly formed by gas to particle conversion processes involving

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NO<sub>x</sub> (NO + NO<sub>2</sub>). The formation of ammonium is from the neutralization of ammonia with acid species such as, sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), nitric acid (HNO<sub>3</sub>) and hydrochloric acid (HCl) (Seinfeld and Pandis, 2006). Ammonia is believed to be first taken up by H<sub>2</sub>SO<sub>4</sub> to form ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) and ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>). Any excess ammonia could then react with HNO<sub>3</sub> and HCl to form ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) and ammonium chloride (NH<sub>4</sub>Cl) (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, NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl also have important influence on Earth's radiative balance and acid deposition (Aneja 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 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl. In most studies, concentrations of NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl were not directly measured but were usually estimated through the 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, 1985; 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 NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl from sulfate, and found that NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 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 (NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl) are also complicated since they are thermodynamically unstable and formed through reversible phase equilibrium with precursor gases such as NH<sub>3</sub>, HNO<sub>3</sub> 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 HNO<sub>3</sub>, HCl and NH<sub>3</sub> 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 [NH<sub>3</sub>][HNO<sub>3</sub>] and [NH<sub>3</sub>][HCl] were compared with theoretical values predicted by thermodynamic equilibrium laws for NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl 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 measurement results 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 formations 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% Na<sub>2</sub>CO<sub>3</sub> + 1% glycerol in 1:1 methanol/water solution) for collecting HCl, HNO<sub>3</sub> and SO<sub>2</sub>, followed by another denuder coated with citric acid (10% citric in methanol) for NH<sub>3</sub> 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 Na<sub>2</sub>CO<sub>3</sub> coated denuder may cause positive artifacts of HNO<sub>3</sub> (Perrino et al., 1990) and the use of citric acid coated denuder may cause negative artifacts of NH<sub>3</sub> (Perrino and Gherardi, 1999). 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 HNO<sub>3</sub> and NH<sub>3</sub>, respectively.

The sampling flow rate was 7 l min<sup>-1</sup>. 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 Na<sub>2</sub>CO<sub>3</sub> and phosphorous acid. The impregnating of filters and coating of denuders were treated with caution, and the filters and denuders

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