

# Chemical characteristics of inorganic ammonium salts in PM<sub>2.5</sub> in the atmosphere of Beijing (China)

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**Abstract.** The atmospheric concentrations of gaseous HNO<sub>3</sub>, HCl and NH<sub>3</sub> and their relative salts have been measured during two field campaigns in the winter and in the summer of 2007 at Beijing (China), as part of CARE-BEIJING (Campaigns of Air Quality Research in Beijing and Surrounding Region). In this study, annular denuder technique used with integration times of 2 and 24h to collect inorganic and soluble PM<sub>2.5</sub> without interferences from gas–particle and particle–particle interactions. The results were discussed from the standpoint of temporal and diurnal variations and meteorological effects. Fine particulate Cl<sup>−</sup>, NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2−</sup> exhibited distinct temporal variations, while fine particulate NO<sub>3</sub><sup>−</sup> did not show much variation with respect to season. Daily mean concentrations of fine particulate NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2−</sup> were higher during summer (12.30 μg m<sup>−3</sup> and 18.24 μg m<sup>−3</sup>, respectively) than during winter (6.51 μg m<sup>−3</sup> and 7.50 μg m<sup>−3</sup>, respectively). Daily mean concentrations of fine particulate Cl<sup>−</sup> were higher during winter (2.94 μg m<sup>−3</sup>) than during summer (0.79 μg m<sup>−3</sup>), while fine particulate NO<sub>3</sub><sup>−</sup> showed similar both in winter (8.38 μg m<sup>−3</sup>) and in summer (9.62 μg m<sup>−3</sup>) periods. The presence of large amounts of fine particulate NO<sub>3</sub><sup>−</sup> even in summer are due to higher local and regional concentrations of NH<sub>3</sub> in the atmosphere available to neutralize H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, which is consistent with the observation that the measured particulate species were neutralized. The composition of fine particulate matter indicated the domination of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> during winter and summer periods. In addition, the high relative humidity conditions in summer period

seemed to dissolve a significant fraction of HNO<sub>3</sub> and NH<sub>3</sub> enhancing fine particulate NO<sub>3</sub><sup>−</sup> and NH<sub>4</sub><sup>+</sup> in the atmosphere. All measured particulate species showed diurnal similar patterns during the winter and summer periods with higher peaks in the early morning, especially in summer, when humid and stable atmospheric conditions occurred. These diurnal variations were affected by wind direction suggesting regional and local source influences. The fine particulate species were correlated with NO<sub>x</sub> and PM<sub>2.5</sub>, supporting the hypothesis that traffic may be also an important source of secondary particles.

## 1 Introduction

Atmospheric particulate matter plays an important role in atmospheric visibility reduction, human health effects, acid deposition and climate (Heintzenberg, 1989; Dockery et al., 1993; Charlson and Heintzenberg, 1995; Vedal, 1997; IPCC, 2007). Fine particles, otherwise called PM<sub>2.5</sub> with an aerodynamic diameter less than 2.5 μm, contribute mainly to the above phenomena. The major inorganic particles identified in PM<sub>2.5</sub> are sulphate (SO<sub>4</sub><sup>2−</sup>), nitrate (NO<sub>3</sub><sup>−</sup>), chloride (Cl<sup>−</sup>) and ammonium (NH<sub>4</sub><sup>+</sup>), which typically comprise 25–75 % of atmospheric PM<sub>2.5</sub> mass (Gray et al., 1986; Heintzenberg, 1989). These species are secondary in nature and are formed in the atmosphere by physical processes (nucleation, condensation and evaporation), and/or chemical reactions of precursor gases (photochemical gas phase, aqueous-phase oxidation and particulate-phase processes), such as sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), nitric acid (HNO<sub>3</sub>), hydrochloric acid (HCl) and ammonia (NH<sub>3</sub>). H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are atmospheric oxidation products of gaseous sulphur dioxide (SO<sub>2</sub>) and nitrogen



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oxides ( $\text{NO}_x$ ), respectively, while  $\text{NH}_3$  is directly emitted into the atmosphere mainly by agricultural sources. Table 1 summarizes the main natural and anthropogenic sources, and formation pathways for the major inorganic constituents of secondary  $\text{PM}_{2.5}$ .

Particulate  $\text{SO}_4^{2-}$  is a product of gas to particle phase reactions involving atmospheric oxidation of  $\text{SO}_2$  by both heterogeneous and homogeneous processes. In the gas phase, the oxidation of  $\text{SO}_2$  by the hydroxyl radical ( $\text{OH}$ ) produces  $\text{H}_2\text{SO}_4$  which condenses to form  $\text{SO}_4^{2-}$  (Table 1). The majority of aqueous phase reactions with  $\text{SO}_2$  occurs in cloud-water, and once dissolved,  $\text{SO}_2$  can oxidize into  $\text{SO}_4^{2-}$  via several pathways, reacting with dissolved ozone, hydrogen and organic peroxides, hydroxyl radicals, and various oxides of nitrogen (Table 1). Particulate sulphate typically exists in one of three forms: sulphuric acid, ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4$  or ammonium bisulphate  $(\text{NH}_4\text{HSO}_4)$ . The formation of each is linked to the amount of ammonia available. If enough ammonia is present, the particulate sulphate will be found as  $(\text{NH}_4)_2\text{SO}_4$ .

Gaseous  $\text{NH}_3$  can be either wet or dry deposited, or can neutralize  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  to form ammonium sulphate salts, ammonium nitrate  $(\text{NH}_4\text{NO}_3)$  and ammonium chloride  $(\text{NH}_4\text{Cl})$  salts (Table 1) via particle gas formation and gas to particle conversion (Baek and Aneja, 2005; Aneja et al., 2009). Ammonium nitrate  $(\text{NH}_4\text{NO}_3)$  and ammonium chloride  $(\text{NH}_4\text{Cl})$  are formed via reversible phase equilibrium with precursor gases such as  $\text{NH}_3$ ,  $\text{HNO}_3$  and  $\text{HCl}$ . This thermodynamic equilibrium between gas- and particle-phase depends on the ambient temperature, relative humidity and chemical composition of particles and gases (Stelson and Seinfeld, 1982a; Pio and Harrison, 1987). Formation of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  is favoured under conditions of high relative humidity and low temperature, otherwise these ammonium salts are volatile. The affinity of sulphuric acid for ammonia is much larger than that of  $\text{HNO}_3$  and  $\text{HCl}$  for ammonia that available ammonia is first taken up by sulphuric acid to form ammonium sulphate salts. Any excess available ammonia may then react with nitric and hydrochloric acid to form ammonium nitrate and chloride. These volatile species affect Earth's radiative balance and also contribute to the long-range transport of acidic pollutants. Ammonium salts, with atmospheric lifetimes of the order of 1–15 days, will tend to deposit at larger distances from emission sources, contributing to soil acidification, forest decline and eutrophication of waterways (Aneja et al., 2000, 2001).

Particulate nitrate is formed in the atmosphere through gas to particle conversion processes starting with  $\text{NO}_x$ , and proceeding via  $\text{HNO}_3$  formation. Since this acid is subject to partitioning between gas and particle phase, the influence of  $\text{NO}_x$  extends to formation of particulate nitrate. During the daytime, the most important source of nitric acid is the homogeneous gas phase reaction of  $\text{NO}_2$  with the  $\text{OH}$  radical (Table 1) (Calvert and Stockwell, 1983; Lin and Cheng, 2007). At night, the free nitrate radical ( $\text{NO}_3$ ) is the source

of tropospheric  $\text{HNO}_3$ .  $\text{NO}_3$  either may combine with  $\text{NO}_2$  to form dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ), which reacts with water on particles, fog or cloud water droplets to produce  $\text{HNO}_3$  (Table 1), or it may form the acid by H-atom abstraction from aldehydes or hydrocarbons (Stockwell et al., 1997). When atmospheric nitric acid is available, it has a tendency to react with basic species such as  $\text{NH}_3$  to form  $\text{NH}_4\text{NO}_3$ . This reaction is believed to be the main source of fine particulate nitrate in urban air (Stockwell et al., 2000). A second path for particulate nitrate formation involves nitric acid attack on the sodium chloride ( $\text{NaCl}$ ) in sea salt particles to generate sodium nitrate ( $\text{NaNO}_3$ ) aerosol and to release hydrochloric acid to the atmosphere.

The major source of  $\text{HCl}$  in the atmosphere is biomass burning (Andreae et al., 1996), coal combustion and waste combustion (McCulloch et al., 1999), and also by the reaction of gaseous  $\text{HNO}_3$  with  $\text{NaCl}$  in sea salt particles (Keene et al., 1999). Emission fluxes of  $50 \text{ Tg Cl yr}^{-1}$ ,  $6 \text{ Tg Cl yr}^{-1}$ ,  $4.6 \text{ Tg Cl yr}^{-1}$ , and  $2 \text{ Tg Cl yr}^{-1}$  for  $\text{HCl}$  are emitted globally to the atmosphere from dechlorination of sea salt aerosols (Graedel and Keene, 1995; Keene et al., 1999), biomass burning (Lobert et al., 1999), coal combustion and waste burning (McCulloch et al., 1999), respectively. As Beijing is  $\sim 150 \text{ km}$  from the sea, it has been demonstrated that the contribution to the aerosols from the sea could be ignored here (Yuan et al., 2004). Most inorganic  $\text{Cl}$  (particulate plus gas) is principally emitted in China from both coal combustion and biomass burning. Estimated  $\text{HCl}$  emissions are  $843 \text{ Gg Cl yr}^{-1}$ ,  $480 \text{ Gg Cl yr}^{-1}$  and  $856 \text{ Gg Cl yr}^{-1}$  from coal combustion, waste combustion (McCulloch et al., 1999) and biomass burning (Lobert et al., 1999), respectively. These  $\text{HCl}$  emissions contribute about 10% of the global source strengths. Both chemical analysis of ambient  $\text{PM}_{2.5}$  and gas samples (Yao et al., 2002; Duan et al., 2006; Song et al., 2006) and source profiles measured in the laboratory (Zheng et al., 2005) indicated that the major source of  $\text{HCl}$  and  $\text{Cl}^-$  was coal combustion due to domestic heating activities and the presence of coal power plants in Beijing. Globally, release of  $\text{HCl}$  from marine aerosols by reaction with less volatile  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  or  $\text{SO}_2$  is of considerable importance. Reaction of  $\text{NO}_2$  with sodium chloride under photochemical conditions, wet and dry deposition, neutralization by gaseous ammonia to form  $\text{NH}_4\text{Cl}$  aerosol, and emissions from volcanoes may constitute other sources of  $\text{HCl}$  in the atmosphere.

The rapid industrial development and urbanization, increased vehicular population and energy consumption in Beijing ( $39^\circ 55' \text{ N}$ ,  $116^\circ 23' \text{ E}$ ), the capital city of China, have led to increased concentrations of air pollutants, especially in particulate pollution (Yao et al., 2002, 2003; Zhang et al., 2004). Dust-soil, industry emission, coal burning, vehicle exhaust emission and waste incineration have been identified as the major sources of particulate pollution in Beijing. Traffic emissions are considered to be one of the most important sources of sub-micrometer particles in the urban area of Beijing (He et al., 2001; Zheng et al., 2005; Song et al.,

**Table 1.** Summary of the main natural and anthropogenic sources, and formation pathways for the major inorganic constituents of secondary PM<sub>2.5</sub>. <sup>a</sup> means “day”; <sup>b</sup> means “day and night”; <sup>c</sup> means “night”.

Species	Transformation Processes	Chemical Reactions	Natural Sources	Anthropogenic Sources
SO <sub>4</sub> <sup>2-</sup>	1. Gas phase oxidation of SO <sub>2</sub> followed by condensation H <sub>2</sub> SO <sub>4</sub> <sup>a</sup> and gaseous NH <sub>3</sub> neutralizing acids	SO <sub>2</sub> + OH → HSO <sub>3</sub> HSO <sub>3</sub> + O <sub>2</sub> → SO <sub>3</sub> + HO <sub>2</sub> SO <sub>3</sub> + H <sub>2</sub> O → H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> SO <sub>4</sub> + NH <sub>3</sub> → NH <sub>4</sub> HSO <sub>4</sub> NH <sub>4</sub> HSO <sub>4</sub> + NH <sub>3</sub> → (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Volcanic and fire emissions, marine phytoplankton degradation of dimethyl sulfide (DMS)	Biomass burning, fossil fuel combustion, gas to particle conversion
	2. SO <sub>2</sub> dissolution in cloud, fog, or rain water <sup>b</sup> and subsequent aqueous phase oxidation to H <sub>2</sub> SO <sub>4</sub>	SO <sub>2</sub> + H <sub>2</sub> O → H <sub>2</sub> SO <sub>3</sub> H <sub>2</sub> SO <sub>3</sub> → SO <sub>3</sub> <sup>2-</sup> + 2H <sup>+</sup> SO <sub>3</sub> <sup>2-</sup> + O <sub>3</sub> (or H <sub>2</sub> O <sub>2</sub> ) → sulphates		
NO <sub>3</sub> <sup>-</sup>	3. Gas phase oxidation of NO <sub>x</sub> <sup>a</sup> and gaseous NH <sub>3</sub> neutralizing acids	NO <sub>2</sub> + OH → HNO <sub>3</sub> HNO <sub>3</sub> + NH <sub>3</sub> ↔ NH <sub>4</sub> NO <sub>3</sub>	Soil, lighting	Biomass burning, fossil fuel combustion, vehicle exhaust, gas to particle conversion
	4. Gas phase oxidation of NO <sub>x</sub> <sup>c</sup> and gaseous NH <sub>3</sub> neutralizing acids	NO <sub>2</sub> + O <sub>3</sub> → NO <sub>3</sub> + O <sub>2</sub> NO <sub>2</sub> + NO <sub>3</sub> ↔ N <sub>2</sub> O <sub>5</sub> N <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O → 2HNO <sub>3</sub>		
Cl <sup>-</sup>	5. Gaseous NH <sub>3</sub> neutralizing acids	HCl + NH <sub>3</sub> ↔ NH <sub>4</sub> Cl	Volcanic activity	Biomass burning, fossil fuel combustion, gas to particle conversion
NH <sub>4</sub> <sup>+</sup>	6. Gaseous NH <sub>3</sub> neutralizing acids	H <sub>2</sub> SO <sub>4</sub> + NH <sub>3</sub> → NH <sub>4</sub> HSO <sub>4</sub> NH <sub>4</sub> HSO <sub>4</sub> + NH <sub>3</sub> → (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> HNO <sub>3</sub> + NH <sub>3</sub> ↔ NH <sub>4</sub> NO <sub>3</sub> HCl + NH <sub>3</sub> ↔ NH <sub>4</sub> Cl	Ocean, microbial activity, crop, soils, wild animals, and vegetation	Biomass burning, fossil fuel combustion, sewage, fertilized lands, vehicle exhaust, gas to particle conversion

2006). Zheng et al. (2005) and Song et al. (2006) indicated that, as a primary source, traffic emissions in Beijing contributed 6–7 % to PM<sub>2.5</sub> concentrations while the respective contribution from road dust resuspension was estimated to be 7–9 %. Gaseous pollutants are also vehicular sources, such as NO<sub>x</sub>, which are essential for the atmospheric photochemical processes and the gas-to-particle conversions. NO<sub>x</sub> is also related to the formation of secondary particulate matter such as secondary particulate ammonium, sulphate and nitrate. These particulate species contribute over 35 % of PM<sub>2.5</sub> in Beijing. Coal dominated energy structure is one of the major causes of air pollution in Beijing. Beijing's power plants emit 49 % and 27 % of the total SO<sub>2</sub> and NO<sub>x</sub> emissions, respectively (He et al., 2003).

PM<sub>2.5</sub> mass and chemical compositions in Beijing have been widely studied since the last decade (He et al., 2001; Yao et al., 2002, 2003; Sun et al., 2004; Chan et al., 2005; Wang et al., 2005; Duan et al., 2006; Guinot et al., 2006; Chan et al., 2008). The sources of particulate matter in Beijing include local primary emissions, secondary formation and regional transport (Yao et al., 2003; Wang et al., 2005; Chen et al., 2007; Street et al., 2007). Duan et al. (2007) reported that SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were the major water soluble ions in wintertime in Beijing, with the average concentrations of 30.8 ± 25.4, 10.8 ± 8.0 and 6.7 ± 5.4 μg m<sup>-3</sup>, respectively. In these studies the maximum concentrations appeared on 4 January 1999, 114, 31 and 27 μg m<sup>-3</sup> for above three ions, respectively. Yao et al. (2002) found that a large part of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in PM<sub>2.5</sub> might be formed through the

direct emissions of their precursor gases, such as SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub>. However, data on PM<sub>2.5</sub>, especially regarding the semi-volatile species in PM<sub>2.5</sub>, e.g., NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> are very limited. In a polluted urban environment, the volatile ammonium salts (NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl) account for 10–30 % of the fine aerosol mass, and the total inorganic salts account for 25–30 % of the fine aerosol mass.

Different field measurements of concentrations of NH<sub>3</sub>, HCl, and HNO<sub>3</sub> observed that the concentration products of [HCl] [NH<sub>3</sub>] and [HNO<sub>3</sub>] [NH<sub>3</sub>] were in agreement with theoretical values predicted by thermodynamic equilibrium laws for NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> formations, respectively, (Harrison and Pio, 1983; Chang et al., 1986). In other cases experimental products were different from theoretical predictions mainly at relative humidity below 60 % and above 90 % (Cadle et al., 1982; Allen et al., 1989; Harrison and MacKenzie, 1990; Pio et al., 1992; Harrison and Msibi, 1994; Mehlmann and Warneck, 1995), some of them lower and others higher than theoretical values. They also found that gas-particle equilibrium conditions were not attained instantaneously in the atmosphere at temperatures lower than 15 °C, requiring several minutes for the achievement of the system equilibrium. They attributed the departures from experimental data to unknown kinetic constraints on attainment of the system equilibrium. These kinetic constraints on the evaporation of ammonium containing aerosols have been restricted to chemical reaction and mass-transfer-limited particle evaporation.

Measurements of semi-volatile fine particulate species, such as inorganic ammonium salts ( $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ ), are complicated by the existence of the thermodynamic equilibrium between precursor gases ( $\text{HCl}$ ,  $\text{HNO}_3$  and  $\text{NH}_3$ ) and particulate ammonium salts. The concentrations of these fine particulate species will be significantly underestimated in urban environments because of the loss of the semi-volatile material from particles collected on the filters during and after sampling, resulting from gas-particle and particle-particle interactions (Sickles et al., 1999a). The underestimation of the semi-volatile inorganic ammonium salts will tend to overemphasize the importance of non-volatile fine particulate species such as sulfate. For this reason, there is a need for representative and reliable methods for measuring atmospheric concentrations of the semi-volatile inorganic ammonium salts without disturbing atmospheric equilibrium conditions during sampling. Denuders for absorbing gases prior to particle collection and back-up filters for absorbing  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$  evaporated from collected particles have been widely accepted as effective tools to avoid sampling artifacts (gas-particle and particle-particle interactions). In this study, annular denuder and filter pack technique was used to accurately measure inorganic and soluble  $\text{PM}_{2.5}$  without disturbing the partition equilibrium existing in the atmosphere. Following this, as part of the international collaborative research CAREBEIJING (Campaigns of Air Quality Research in Beijing and Surrounding Region), the main objectives of the present work were to measure experimentally and accurately the formation of inorganic ammonium salts and their chemical associations, to provide quantitative information on their concentrations, to investigate their temporal and diurnal variations, and to examine the contributions of local and regional sources to their observed concentrations in the atmosphere of Beijing.

## 2 Experimental

Atmospheric measurements were performed at Peking University ( $39^\circ 59' 23'' \text{N}$ ,  $116^\circ 18' 19'' \text{E}$ ), located in the north-western urban area of Beijing and outside of the fourth ring road. The sampling site was located on the roof of a fifth-floor academic building, 15 m a.g.l. There are two major roads at the east and south of the sampling site, which are 200 and 600 m away from the sampling site, respectively. Measurements were carried out on a 24-h basis, starting at midnight from 23 January to 14 February 2007 and from 2 to 31 August 2007. The air samples on a 2-h basis (intensive measurements) were carried out on 9–10 February during the winter period and on 17–21 August during the summer period. Problems occurred on 9 February between 10:00 and 12:00 in the morning and on 19 August between 22:00 and 00:00, thus data from these events were not considered.

Ambient concentrations of gases and particles were measured using the annular denuder system (Possanzini et al.,

1983; Allegrini et al., 1987; Febo et al., 1989; Perrino et al., 1990, 2001; Perrino and Gherardi, 1999; Beine et al., 2001; Ianniello et al., 2002, 2007). The denuder line configuration used in this study included two sodium fluoride (1 % NaF in 9:1 ethanol/water solution) coated denuders for the simultaneous collection of  $\text{HCl}$  and  $\text{HNO}_3$ , followed by two sodium carbonate plus glycerol (1 %  $\text{Na}_2\text{CO}_3$  + 1 % glycerol in 1:1 ethanol/water solution) coated denuders for the collection of  $\text{HONO}$  and  $\text{SO}_2$ . A fifth denuder was coated with phosphorous acid (1 %  $\text{H}_3\text{PO}_4$  in 9:1 ethanol/water solution) for the collection of  $\text{NH}_3$  (Perrino and Gherardi, 1999; Perrino et al., 2001; Ianniello et al., 2010). Downstream of the denuder train a cyclone collected coarse particles ( $>2.5 \mu\text{m}$  aerodynamic diameter cut size at flow rate of  $15 \text{ l min}^{-1}$ ), while fine particles ( $<2.5 \mu\text{m}$  at flow rate of  $15 \text{ l min}^{-1}$ ) were collected on a filter pack set in series. The filter pack included a Teflon filter (Gelman Teflon, 47-mm, 1- $\mu\text{m}$  pore size) for the collection of fine particles, a Nylon filter (Nylosorb Gelman, 47 mm, 1- $\mu\text{m}$  pore size) and one phosphorous acid coated paper filter (Whatman 41). These last two back-up filters separately collected  $\text{NO}_3^-$  as  $\text{HNO}_3$ ,  $\text{Cl}^-$  as  $\text{HCl}$ , and  $\text{NH}_4^+$  as  $\text{NH}_3$ , which evolved from the front Teflon filter as a result of ammonium salt dissociations ( $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ ) (Possanzini et al., 1992; Masia et al., 1994; Perrino and Gherardi, 1999; Perrino et al., 2001; Ianniello et al., 2010). The evaporation of volatile ammonium salts from the fine particles collected on the front Teflon filter is due to fluctuations in temperature and relative humidity and/or pressure drop across this filter, which perturb the gas-particle equilibrium (Appel et al., 1984; Pathak et al., 2004, 2009; Pathak and Chan, 2005). Total concentrations of ammonium salts in  $\text{PM}_{2.5}$  are estimated as the sum of the measurements both on the Teflon filter for non-volatile fine particulate species (unevolved particulate species) and on the back-up filters for volatile fine particulate species (evolved particulate species):

$$[\text{NO}_3^-]_{\text{evolved}} = [\text{NO}_3^-]_{\text{N}} \quad (1)$$

$$[\text{Cl}^-]_{\text{evolved}} = [\text{Cl}^-]_{\text{N}} \quad (2)$$

$$[\text{NH}_4^+]_{\text{evolved}} = [\text{NH}_4^+]_{\text{N}} + [\text{NH}_4^+]_{\text{PA}} \quad (3)$$

$$[\text{NO}_3^-]_{\text{unevolved}} = [\text{NO}_3^-]_{\text{T}} \quad (4)$$

$$[\text{Cl}^-]_{\text{unevolved}} = [\text{Cl}^-]_{\text{T}} \quad (5)$$

$$[\text{NH}_4^+]_{\text{unevolved}} = [\text{NH}_4^+]_{\text{T}} \quad (6)$$

$$[\text{NO}_3^-]_{\text{fine}} = [\text{NO}_3^-]_{\text{unevolved}} + [\text{NO}_3^-]_{\text{evolved}} \quad (7)$$

$$[\text{Cl}^-]_{\text{fine}} = [\text{Cl}^-]_{\text{unevolved}} + [\text{Cl}^-]_{\text{evolved}} \quad (8)$$

$$[\text{NH}_4^+]_{\text{fine}} = [\text{NH}_4^+]_{\text{unevolved}} + [\text{NH}_4^+]_{\text{evolved}} \quad (9)$$

where subscripts N, PA and T stand for the Nylon filter, phosphorous acid coated paper filter and Teflon filter, respectively. The concentration of evolved  $\text{NH}_4^+$  is the sum of its

amounts measured both on the Nylon filter, which absorbs a small fraction of evolved  $\text{NH}_3$  (Masia et al., 1994), and on the coated paper filter. The remaining fine particulate species recovered on the Teflon filter are indicated with term of un-evolved particulate species. Thus, the total concentrations of the fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  were determined without disturbing the partition equilibrium existing in the atmosphere between gaseous  $\text{NH}_3$  and the particulate components ( $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ ).

The fine particulate  $\text{SO}_4^{2-}$  is not volatile and, therefore, its concentration was taken as that on the Teflon filter only.

Thus, the particulate chloride, nitrate, sulphate, sodium, ammonium, potassium, magnesium and calcium in the coarse and fine fractions were measured. After sampling, the denuders and filters were extracted and samples were analyzed within 24-h at the PKU laboratories by using Ion Chromatography (IC) (Dionex DX 120 connected with autosampler DX AS50 for anions and DX ICS90 connected with autosampler DX AS40 for cations).

The sampling flow rate was  $151\text{ min}^{-1}$ . The sampling volume was about  $23.10\text{ m}^3$  for a 24-hour sampling period. In these operative conditions the collection efficiency for all species was higher than 99%. The detection limits on 24-h measurement period were  $0.020\text{ }\mu\text{g m}^{-3}$  for  $\text{NH}_4^+$ ,  $0.0093\text{ }\mu\text{g m}^{-3}$  for  $\text{Na}^+$ ,  $0.0051\text{ }\mu\text{g m}^{-3}$  for  $\text{K}^+$ ,  $0.0082\text{ }\mu\text{g m}^{-3}$  for  $\text{Mg}^{2+}$ ,  $0.015\text{ }\mu\text{g m}^{-3}$  for  $\text{Ca}^{2+}$ ,  $0.0013\text{ }\mu\text{g m}^{-3}$  for  $\text{SO}_4^{2-}$ ,  $0.0014\text{ }\mu\text{g m}^{-3}$  for  $\text{NO}_3^-$  and  $0.0073\text{ }\mu\text{g m}^{-3}$  for  $\text{Cl}^-$ .

Information about the mixing properties of the lower boundary layer were obtained by means of a Stability Monitor (OP SIS SM200) during the summer period. These measurements were described in detail in Ianniello et al. (2010). The Stability Monitor instrument collects atmospheric particles and determines their short life radioactivity due to Radon decay products, providing 1-h interval radioactivity data. From the study of the temporal trend of natural radioactivity and of its time derivative one can gather important information about the mixing properties of the lower atmosphere and about its ability to dilute atmospheric pollutants.

### 3 Results and discussion

#### 3.1 Temporal variation

Summary statistics for fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , and gaseous  $\text{HNO}_3$  and  $\text{HCl}$  determined by means of the annular denuder technique during the winter and summer periods at Beijing are listed in Table 2.

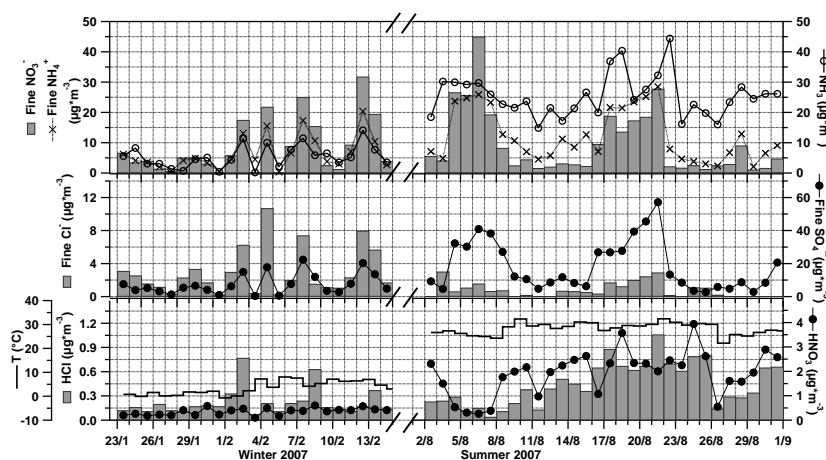
The temporal patterns of these measured fine particulate and gas-phase species during the two sampling periods are reported in Fig. 1. The temporal variations are evaluated applying the paired *t*-test to determine the significance at the 0.05 level ( $p \leq 0.05$ ) of differences among the mean of com-

**Table 2.** Statistics of concentrations ( $\mu\text{g m}^{-3}$ ) of some gas species and ions in  $\text{PM}_{2.5}$ , measured on a 24-h basis, during the winter and the summer periods at Beijing.

Species	N	Min	Max	Median	Mean	SD
Winter						
$\text{HNO}_3$	23	0.10	0.60	0.40	0.35	0.14
$\text{HCl}$	23	0.07	0.77	0.17	0.22	0.10
$\text{Cl}^-$	23	0.23	10.69	1.96	2.94	0.79
$\text{NO}_3^-$	23	0.25	31.80	5.06	8.38	3.00
$\text{SO}_4^{2-}$	23	0.40	22.37	5.38	7.50	2.34
$\text{NH}_4^+$	23	0.32	20.38	4.50	6.51	2.51
$\text{Na}^+$	23	0.04	3.60	0.41	0.59	0.73
$\text{K}^+$	23	0.03	4.13	0.61	1.07	0.95
$\text{Mg}^{2+}$	23	0.01	0.46	0.09	0.14	0.13
$\text{Ca}^{2+}$	23	0.05	0.99	0.40	0.44	0.28
Summer						
$\text{HNO}_3$	30	0.26	3.94	2.08	1.92	0.91
$\text{HCl}$	30	0.40	1.06	0.38	0.45	0.27
$\text{Cl}^-$	30	0.06	3.02	0.57	0.79	0.10
$\text{NO}_3^-$	30	1.09	44.96	4.28	9.62	2.37
$\text{SO}_4^{2-}$	30	2.70	57.13	11.15	18.24	2.01
$\text{NH}_4^+$	30	2.11	28.46	8.78	12.30	2.48
$\text{Na}^+$	30	0.14	1.89	0.47	0.57	0.42
$\text{K}^+$	30	0.13	6.52	1.23	1.74	1.36
$\text{Mg}^{2+}$	30	0.02	1.00	0.09	0.15	0.10
$\text{Ca}^{2+}$	30	0.11	2.47	0.44	0.58	0.49

ponents by examining the amount of variation between the samples. Fine particulate  $\text{Cl}^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  exhibited distinct and significant ( $p < 0.001$ ,  $p = 0.004$ ,  $p = 0.002$ , respectively) temporal variations (Yao et al., 2002; Duan et al., 2003), while fine particulate  $\text{NO}_3^-$  did not show much variation with respect to season (Duan et al., 2006; Lin et al., 2006).

Specifically, the mean concentrations of fine particulate  $\text{NO}_3^-$  were  $8.38 \pm 3.00\text{ }\mu\text{g m}^{-3}$  and  $9.62 \pm 2.37\text{ }\mu\text{g m}^{-3}$  during winter and summer periods, respectively, and reached the maximum peak of  $44.96\text{ }\mu\text{g m}^{-3}$  on 6 August 2007. Similar variation of  $\text{NO}_3^-$  concentrations has been reported by other studies (Erduran and Tuncel, 2001; Gupta et al., 2003). Particulate  $\text{NO}_3^-$  is mostly formed through gas to particle conversion and, therefore, through the oxidation of precursor gases, such as  $\text{NO}_x$ , to nitrate. In winter, local  $\text{NO}_2$  emissions, which are mainly from the vehicular emissions in big cities (Hao et al., 2005; Chak and Yao, 2008; Meng et al., 2008), were an important source of fine particulate  $\text{NO}_3^-$  because  $\text{NO}_3^-$  and  $\text{NO}_2$  correlated significantly ( $R^2 = 0.58$ ,  $p < 0.001$ , at the 99.9% confidence level). Thus,  $\text{NO}_2$  was converted to  $\text{NO}_3^-$  principally through photochemical processes in Beijing during the winter season (Wang et al., 2006; Kai et al., 2007; Hu et al., 2008; Pathack et al., 2009, 2011).



**Fig. 1.** Temporal trends of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , and gaseous  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$ , and temperature ( $T$ ) during the winter and summer measurements, carried out on a 24-h basis, at Beijing.

The nitrate formation might be also ascribed to heterogeneous processes such as the condensation or absorption of  $\text{NO}_2$  in moist aerosols in addition to  $\text{N}_2\text{O}_5$  oxidation and  $\text{HNO}_3$  condensation (Wang et al., 2006). The heterogeneous formation generally relates to relative humidity (RH) and the particulate loading. In summer, the correlation between fine particulate  $\text{NO}_3^-$  and  $\text{NO}_2$  did not occur, while significant correlation between fine particulate  $\text{NO}_3^-$  and RH was the highest ( $R^2 = 0.43$ ,  $p < 0.001$  and  $R^2 = 0.20$ ,  $p = 0.04$  in summer and in winter, respectively).  $\text{PM}_{2.5}$  was not collected during the winter period but there is a good and significant linear correlation ( $R^2 = 0.62$ ,  $p < 0.001$ ) between particulate  $\text{NO}_3^-$  and  $\text{PM}_{2.5}$  in summer period showing the possible heterogeneous formation of particulate nitrate at Beijing. The presence of large amounts of fine particulate  $\text{NO}_3^-$  even in summer is surprising since  $\text{NH}_4\text{NO}_3$  is volatile and tends to dissociate and remain in gas phase under high temperatures. The mean concentration of  $\text{NH}_3$  was  $31.84 \pm 16.70 \mu\text{g m}^{-3}$  in summer period at Beijing, which was 6 times higher than in winter period of  $5.22 \pm 3.75 \mu\text{g m}^{-3}$  (Ianniello et al., 2010). In addition, the temperatures ranged between 1 and  $14^\circ\text{C}$  and 22 and  $35^\circ\text{C}$  in winter and summer periods, respectively. Thus, the high concentrations of fine particulate  $\text{NO}_3^-$  in summer period might be due to higher concentrations of  $\text{NH}_3$  in the atmosphere available to neutralize  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , which is consistent with the observation that the measured particulate species seemed to be neutralized (see below). In addition, the high relative humidity conditions (daily mean 35%–90%) in summer period might dissolve a significant fraction of  $\text{HNO}_3$  and  $\text{NH}_3$  in humid particles, therefore enhancing fine particulate  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the atmosphere (Hesterberg et al., 1996; Krupa, 2003; Trebs et al., 2004, 2005; Guinot et al., 2007; Sciare et al., 2007; Hu et al., 2008; Pathack et al., 2009, 2011; Ianniello et al., 2010; Sun et al., 2010).

As shown in Fig. 1 and in Table 2, the mean concentrations of fine particulate  $\text{Cl}^-$  were higher during the winter period ( $2.94 \pm 0.79 \mu\text{g m}^{-3}$ ) than during the summer period ( $0.79 \pm 0.10 \mu\text{g m}^{-3}$ ) and reached the maximum peak of  $10.69 \mu\text{g m}^{-3}$  on 4 February 2007. The major sources of particulate  $\text{Cl}^-$  in Beijing might be associated to coal burning activities, which could explain the higher  $\text{Cl}^-$  concentrations in winter because of the enhanced burning activities in this season (Yao et al., 2002; Wang et al., 2005), and the formation of  $\text{NH}_4\text{Cl}$ .

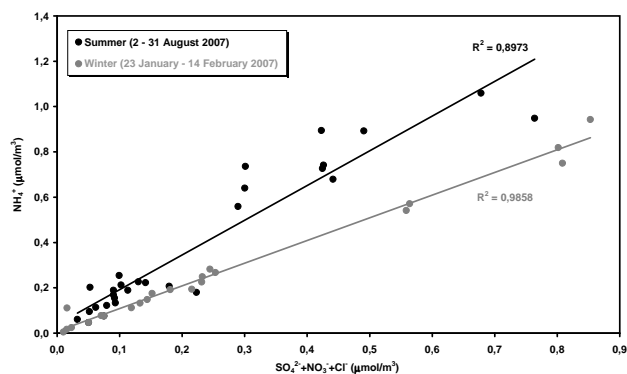
Mean concentrations of fine particulate  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  were higher during summer ( $12.30 \pm 2.48 \mu\text{g m}^{-3}$  and  $18.24 \pm 2.01 \mu\text{g m}^{-3}$ , respectively) than during winter ( $6.51 \pm 2.51 \mu\text{g m}^{-3}$  and  $7.50 \pm 2.34 \mu\text{g m}^{-3}$ , respectively). Similarly to  $\text{NH}_3$  (Ianniello et al., 2010), particulate  $\text{NH}_4^+$  concentrations showed higher values during warm months (Sickles, 1999b; Walker et al., 2000, 2004; Whittall and Paerl, 2001; Robarge et al., 2002; Street et al., 2007; Ianniello et al., 2010), as shown in Table 2 and in Fig. 1. The temporal variations of fine particulate  $\text{NH}_4^+$  basically coincided with those of fine particulate  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , indicating that  $\text{NH}_4^+$  largely originated from the neutralization between ammonia and acidic species (Wang et al., 2006). The very similar patterns of sulfate, nitrate, chloride and ammonium suggest that they were likely internally mixed and came from similar gas-to-particle processes (Huang et al., 2010).

The highest concentrations of particulate  $\text{SO}_4^{2-}$  during the summer period at Beijing were attributed to the higher temperatures and solar radiation, which enhance the photochemical activities and the atmospheric oxidation (higher concentrations of ozone, hydrogen peroxide and hydroxyl radical) and, thus, the oxidation rate of  $\text{SO}_2$  to particulate sulphate (Puxbaum et al., 1993; Robarge et al., 2002; Bari et al., 2003; Gupta et al., 2003; Plessow et al., 2005; Wang et al., 2005; Duan et al., 2006; Street et al., 2007). Sulphate showed

also a strong correlation with fine particulate  $K^+$ , the most abundant cation after  $NH_4^+$ , during the winter ( $R^2 = 0.95$ ,  $p < 0.001$ ) and summer periods ( $R^2 = 0.80$ ,  $p = 0.001$ ), indicating the presence of potassium sulphate ( $K_2SO_4$ ). Agricultural biomass burning and its impacts on the regional brown hazes in northern China, especially in Beijing, were reported by previous studies (Duan et al., 2004; Li et al., 2010). They showed that the agricultural biomass burning consisted mostly of fine potassium salts ( $K_2SO_4$ ,  $KNO_3$  and  $KCl$ ), and they were internally mixed.

It is worth pointing out that  $[NH_3]$  in units of  $\mu\text{mol m}^{-3}$  was always in same time scale higher than that of  $[HNO_3] + [HCl]$  in gas phase. The ratio of  $[NH_3]$  to  $[HNO_3] + [HCl]$  was  $27.90 \pm 12.70$  in the winter period and  $54.06 \pm 20.60$  in the summer period, respectively. It implied that the atmosphere was ammonia-rich in gas phase during the winter and summer periods in Beijing. The evaluation of the chemical composition of fine particulate species collected on annular denuder/filter pack system can be used to calculate the  $NH_4^+$  neutralization factor, defined as the molar ratio of  $NH_4^+$  to the theoretical one, assuming complete conversion to  $(NH_4)_2SO_4$ ,  $NH_4NO_3$  and  $NH_4Cl$ . Thus, the ionic composition of  $PM_{2.5}$  has been evaluated with regard to the balance between the major anions ( $NO_3^-$ ,  $Cl^-$ ,  $SO_4^{2-}$ ) and ammonium (Fig. 2) in the winter and summer periods.

During the winter period the strong correlation between  $\mu\text{mol m}^{-3}$  concentrations of fine particulate  $NH_4^+$  and  $\mu\text{mol m}^{-3}$  concentrations of fine particulate  $SO_4^{2-}$  ( $R^2 = 0.85$ ,  $p = 0.001$ ) collected on the Teflon filters and a slope of this regression line of 3.82, higher than 2, suggested the complete neutralization of  $H_2SO_4$  by  $NH_3$  and a predominance of particulate  $(NH_4)_2SO_4$  during the winter period (Possanzini et al., 1999; Walker et al., 2004). Thus, the excess of  $NH_4^+$  was inferred to be associated with fine particulate  $Cl^-$  and  $NO_3^-$ . In addition, the ionic composition of  $PM_{2.5}$  has been also evaluated with regard to the balance between the major anions ( $NO_3^-$ ,  $SO_4^{2-}$ ,  $Cl^-$ ) and ammonium. The  $\mu\text{mol m}^{-3}$  concentrations of fine particulate ammonium compared to the sum of the  $\mu\text{mol m}^{-3}$  concentrations of fine particulate nitrate, chloride and sulphate collected on Teflon filters (Fig. 2) improved the correlation between ammonium and measured anions ( $R^2 = 0.98$ ,  $p < 0.001$ ). The correlation showed an ion charge balance with a slope of 1.00, confirming that sufficient  $NH_3$  was present to completely neutralize all acidic components ( $H_2SO_4$ ,  $HNO_3$  and  $HCl$ ) to form  $(NH_4)_2SO_4$ ,  $NH_4NO_3$  and  $NH_4Cl$ . The scattering of some data could be attributed to the minor influences of other atmospheric processes, such as the formation of non volatile nitrate and chloride salts (e.g.  $NaNO_3$ ,  $KNO_3$ ,  $NaCl$ ,  $KCl$ ). In addition, our denuder data showed that on average 33.05 %, 23.65 % and 34.71 % of the fine particulate nitrate, chloride and ammonium, respectively, evaporated from the Teflon filters during the winter period at Beijing (Fig. 3). A comparison between  $\mu\text{mol m}^{-3}$  amount of  $NH_4^+$  with sum of



**Fig. 2.** Relationship between molar concentrations of fine particulate ammonium ( $NH_4^+$ ) and the sum of the molar concentrations of fine particulate sulphate ( $SO_4^{2-}$ ), nitrate ( $NO_3^-$ ) and chloride ( $Cl^-$ ) on the Teflon filters during the winter and summer measurements, carried out on a 24-h basis, at Beijing.

$\mu\text{mol m}^{-3}$  amounts of anions ( $NO_3^- + Cl^-$ ) determined on the back-up filters showed a good and significant correlation between these ions ( $R^2 = 0.90$ ,  $p < 0.001$ ). The slope of this regression line was 1.65, indicating an excellent ion balance and the presence on Nylon filters of  $NH_4NO_3$  and  $NH_4Cl$  as constituent of the total fine particles. In addition, using the approach of Ansari and Pandis (1998) and of Blanchard et al. (2000) it is possible to calculate the excess  $NH_3$ , which represents the quantity of  $NH_3$  that would remain after complete neutralization of available aerosol and acid gases, is defined as:

$$\text{Excess ammonia} = [NH_3] + [NH_4^+] - 2[SO_4^{2-}] - [NO_3^-] - [HNO_3] - [HCl] - [Cl^-] \quad (10)$$

where all concentrations are in units of  $\mu\text{mol m}^{-3}$ . Our results showed that excess  $NH_3$  existed with a mean value of  $0.30 \mu\text{mol m}^{-3}$  ( $5.10 \mu\text{g m}^{-3}$ ) during the winter period, indicating that the atmosphere contained sufficient ammonia to form ammonium nitrate and chloride. Furthermore, there might be also the presence of other nitrate and chloride containing species, which are less volatile than  $NH_4NO_3$  and  $NH_4Cl$ . Hence, a part of the fine particulate nitrate and chloride might be bound as a relatively non-volatile salts of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$  or  $Na^+$ . Therefore, we have calculated the free nitrate and chloride concentrations (Hildemann et al., 1984; Gaidajis, 2002), defined as the fractions of nitrate and chloride in excess which are not bound with the alkali or alkaline earth metals, expressed in  $\mu\text{mol m}^{-3}$ , from data collected on the Teflon filters during the winter period:

$$\text{Free nitrate} = [NO_3^-] - \left\{ 2[Ca^{2+}] + 2[Mg^{2+}] + [K^+] + [Na^+] - [Cl^-] \right\} \quad (11)$$

$$\text{Free chloride} = [\text{Cl}^-] - \left\{ 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+] \right\} \quad (12)$$

Zero or negative values of free nitrate and chloride imply that  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  are not present. The free nitrate and chloride concentration were found to be present with a mean value of  $0.13 \mu\text{mol m}^{-3}$  ( $8.06 \mu\text{g m}^{-3}$ ) and  $0.01 \mu\text{mol m}^{-3}$  ( $0.35 \mu\text{g m}^{-3}$ ), respectively, indicating the presence of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  during winter period. Besides,  $\text{NO}_3^-$  showed significant correlations with cations  $\text{K}^+$  ( $R^2 = 0.91$ ,  $p < 0.001$ ) and  $\text{Na}^+$  ( $R^2 = 0.40$ ,  $p = 0.002$ ), indicating possible formation of non-volatile  $\text{KNO}_3$  and  $\text{NaNO}_3$  salts along with  $\text{NH}_4\text{NO}_3$ .  $\text{Cl}^-$  had also good correlations with cations  $\text{K}^+$  ( $R^2 = 0.75$ ,  $p < 0.001$ ), suggesting the possible formation of  $\text{KCl}$  along with  $\text{NH}_4\text{Cl}$ . The presence of  $\text{K}^+$  suggests biomass burning emissions, including most likely house-hold combustion of agricultural residues and firewood in Beijing, and road and soil dust emissions (Duan et al., 2004; Wang et al., 2005, 2007, 2008). However, the observed  $\text{K}^+$  concentrations were low (mean values of  $1.07 \mu\text{g m}^{-3}$ ) and might not play a significant role in the formation of these particles in Beijing during winter period (Wang et al., 2005; Behera and Sharma, 2010).

During the summer period the correlation between particulate  $\text{NH}_4^+$  with  $\text{SO}_4^{2-}$  collected on Teflon filters was also very strong ( $R^2 = 0.85$ ,  $p < 0.001$ ). The mean value of  $\text{NH}_4^+/\text{SO}_4^{2-}$  molar ratio was 2.10, indicating the complete neutralization of  $\text{H}_2\text{SO}_4$  by  $\text{NH}_3$  and a predominance of  $(\text{NH}_4)_2\text{SO}_4$  aerosol during the summer season. In addition, the molar concentrations of fine particulate ammonium compared to the sum of the molar concentrations of fine particulate nitrate, chloride and sulphate collected on Teflon filters (Fig. 2) showed a very strong correlation ( $R^2 = 0.90$ ,  $p < 0.001$ ) and an ion charge balance (Possanzini et al., 1999; Walker et al., 2004). The slope of this regression line was higher than unity (1.53), confirming that abundant  $\text{NH}_3$  was present to neutralize the acidic components ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$ ) to form  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ . Our results show also that excess  $\text{NH}_3$  exists with a mean value of  $1.60 \mu\text{mol m}^{-3}$  ( $27.20 \mu\text{g m}^{-3}$ ) during the sampling period, indicating that ammonium salts formation occurred. In addition, our denuder data showed that on average 83.33 %, 74.64 % and 53.07 % of the fine particulate nitrate, chloride and ammonium, respectively, evaporated from the Teflon filters during the summer period at Beijing (Fig. 4). A comparison between  $\mu\text{mol m}^{-3}$  amount of  $\text{NH}_4^+$  with sum of  $\mu\text{mol m}^{-3}$  amounts of anions ( $\text{NO}_3^- + \text{Cl}^-$ ) determined on the back-up filters showed a good and significant correlation between these ions ( $R^2 = 0.70$ ,  $p = 0.001$ ) indicating the presence of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  as constituent of the total fine particles. Furthermore, free nitrate and chloride concentrations were also present with mean values of  $0.10 \mu\text{mol m}^{-3}$  ( $6.20 \mu\text{g m}^{-3}$ ) and  $0.06 \mu\text{mol m}^{-3}$

( $2.13 \mu\text{g m}^{-3}$ ), respectively. Besides,  $\text{NO}_3^-$  showed significant correlation with cationic species such as  $\text{K}^+$  ( $R^2 = 0.24$ ,  $p < 0.001$ ), indicating possible presence of non-volatile  $\text{KNO}_3$  salt along with  $\text{NH}_4\text{NO}_3$ . However, the observed  $\text{K}^+$  concentrations were also low (mean values of  $1.74 \mu\text{g m}^{-3}$ ) and might not play a significant role in the formation of these particles in Beijing during summer period.

These results indicate that  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{KNO}_3$  were formed preferentially in Beijing during winter and summer seasons.

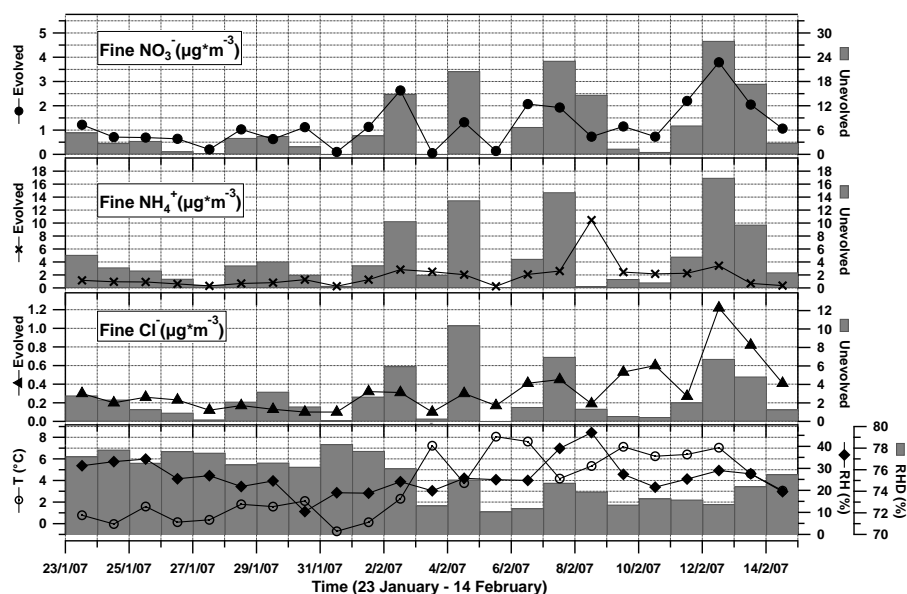
Following similar studies on equilibria of inorganic trace gases with related ionic aerosol compounds, we have tested if thermodynamic equilibrium was attained for the pure  $\text{NH}_3/\text{HNO}_3/\text{NH}_4\text{NO}_3$  ( $\text{HNO}_3(\text{g}) + \text{NH}_3(\text{g}) \leftrightarrow \text{NH}_4\text{NO}_3(\text{s or aq})$ ) and  $\text{NH}_3/\text{HCl}/\text{NH}_4\text{Cl}$  ( $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \leftrightarrow \text{NH}_4\text{Cl}(\text{s or aq})$ ) systems under the meteorological conditions in Beijing during the winter and summer periods. The theoretical equilibrium dissociation constants for solid  $\text{NH}_4\text{NO}_3$  ( $K_n$ ) and for solid  $\text{NH}_4\text{Cl}$  ( $K_c$ ) were calculated and compared to the measured concentration products of  $\text{NH}_3$  and  $\text{HNO}_3$  ( $K_{\text{mn}} = [\text{HNO}_3][\text{NH}_3]$ ) and of  $\text{NH}_3$  and  $\text{HCl}$  ( $K_{\text{mc}} = [\text{HCl}][\text{NH}_3]$ ). The measured concentration product  $K_{\text{mn}}$  in units of  $\text{ppb}^2$  was determined using the measured data for 24-h sampling time while the theoretical equilibrium constant  $K_n$  in units of  $\text{ppb}^2$  was calculated according to the method in Stelson and Seinfeld (1982a), when the ambient relative humidity (RH) is less than relative humidity of deliquescence (RHD) at any absolute temperature ( $T$ ) recorded in Kelvin (Hammer and Wu, 1972):

$$\ln K_n = 84.6 - 24220/T - 6.1 \ln (T/298) \quad (13)$$

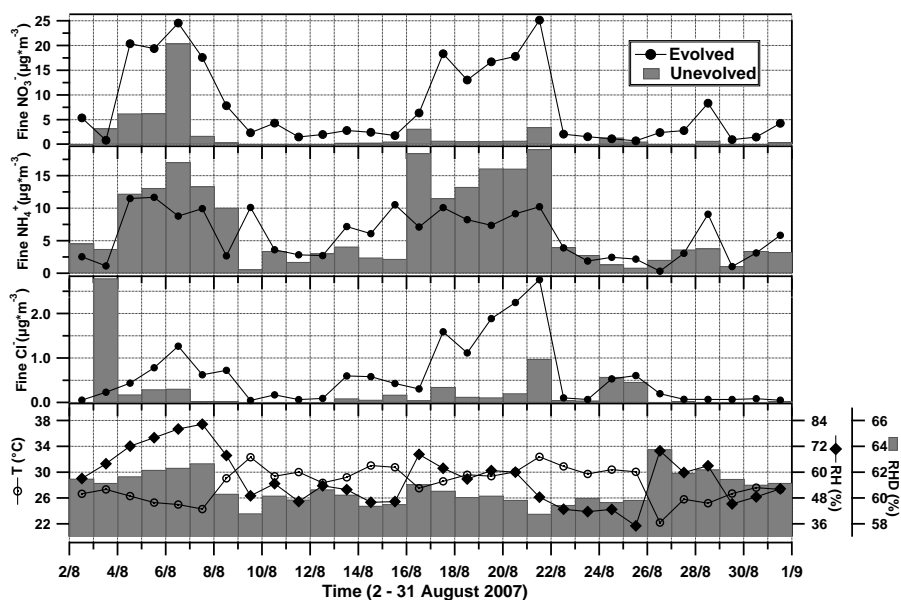
$$\ln (\text{RHD}) = 723.7/T + 1.7037 \quad (14)$$

Several laboratory and field studies have given attention to the relative humidity (RH) at which solid particles liquefy (deliquescence point), and the RH at which liquid particles form solids (crystallization point), because the phase (wet or dry) of the atmospheric aerosol particles can affect both their optical and radiative properties and gas-aerosol reactions (Wexler and Seinfeld, 1991; Kim and Seinfeld, 1993; Tang et al. 1995; Dougle et al., 1998). Cizco et al. (1997) carried out laboratory and field experiments on ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ) and ammonium bisulphate ( $\text{NH}_4\text{HSO}_4$ ) aimed to determine the phase of the particles as the relative humidity (RH) with which they are in equilibrium is changed. Their results showed that  $(\text{NH}_4)_2\text{SO}_4$  at room temperature uptakes water (deliquesces) at a relative humidity (RH) of  $79 \pm 1\%$  that there is no kinetic inhibition to the uptake of water by dry  $(\text{NH}_4)_2\text{SO}_4$  particles on the timescales of a few seconds and longer.  $(\text{NH}_4)_2\text{SO}_4$  aerosol particles remain liquid phase, forming a “metastable” liquid state (supersaturated state), until a very low RH ( $33 \pm 2\%$ , crystallization point) is reached, at which point a highly concentrated liquid aerosol particle nucleates to form a solid.  $\text{NH}_4\text{HSO}_4$  particles deliquesce at a 39 % RH, but solid  $\text{NH}_4\text{HSO}_4$  particles





**Fig. 3.** Temporal trends of temperature ( $T$ ), relative humidity (RH), deliquescent relative humidity (RHD), and evolved and unevolved fine particulate ammonium ( $\text{NH}_4^+$ ), sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and chloride ( $\text{Cl}^-$ ) during the winter measurements, carried out on a 24-h basis, at Beijing.



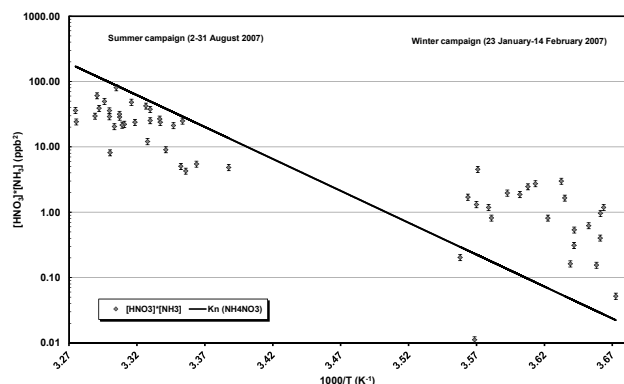
**Fig. 4.** Temporal trends of temperature ( $T$ ), relative humidity (RH), deliquescent relative humidity (RHD), and evolved and unevolved fine particulate ammonium ( $\text{NH}_4^+$ ), sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ) and chloride ( $\text{Cl}^-$ ) during the summer measurements, carried out on a 24-h basis, at Beijing.

are difficult to form (Cizco et al., 1997). Pure ammonium nitrate deliquesces at 62 % RH (298 K), but laboratory experiments show that they don't reach crystallization point also at 8 % RH (Dougle et al., 1998). The deliquescence relative humidity (RHD) for pure  $\text{NH}_4\text{NO}_3$  varies with air temperature

and can be modified by particle size and composition under real ambient conditions (Seinfeld and Pandis, 1998). If the ambient RH is less than the RHD, then the equilibrium state of  $\text{NH}_4\text{NO}_3$  is modeled as a solid. At relative humidity above that of deliquescence,  $\text{NH}_4\text{NO}_3$  is modeled in the aqueous

**Table 3.** Mean values  $\pm$  standard deviation of some components, such as theoretical equilibrium constant ( $K_n$ ) and measured concentration product ( $K_{mn}$ ) of  $\text{NH}_4\text{NO}_3$  formation and theoretical equilibrium constant ( $K_c$ ) and measured concentration product ( $K_{mc}$ ) of  $\text{NH}_4\text{Cl}$  formation in the winter and summer periods at Beijing.

Time	N	$\text{HNO}_3$ (ppb)	HCl (ppb)	$\text{NH}_3$ (ppb)	$K_n$ (ppb <sup>2</sup> )	$K_{mn}$ (ppb <sup>2</sup> )	$K_c$ (ppb <sup>2</sup> )	$K_{mc}$ (ppb <sup>2</sup> )	$1000/T$ (K <sup>-1</sup> )
Winter									
2 h	24	$0.18 \pm 0.11$	$0.10 \pm 0.12$	$7.21 \pm 1.50$	$0.35 \pm 0.19$	$1.49 \pm 0.40$	$0.60 \pm 0.40$	$0.78 \pm 0.25$	$3.58 \pm 0.04$
24 h	23	$0.14 \pm 0.05$	$0.14 \pm 0.11$	$7.88 \pm 1.40$	$0.11 \pm 0.08$	$1.25 \pm 1.13$	$0.36 \pm 0.27$	$1.41 \pm 1.00$	$3.62 \pm 0.04$
Summer									
2 h	47	$1.15 \pm 1.12$	$0.43 \pm 0.23$	$45.89 \pm 13.87$	$116.26 \pm 85.97$	$51.35 \pm 23.49$	$267.01 \pm 86.45$	$18.72 \pm 10.25$	$3.30 \pm 0.03$
24 h	30	$0.75 \pm 0.35$	$0.30 \pm 0.17$	$36.59 \pm 9.96$	$73.51 \pm 20.23$	$27.79 \pm 17.33$	$172.65 \pm 40.07$	$11.75 \pm 9.28$	$3.32 \pm 0.02$



**Fig. 5.** Thermodynamically predicted equilibrium dissociation constant  $K_n$  (black solid line) for pure  $\text{NH}_4\text{NO}_3$  and measured concentration product  $K_{mn} = [\text{HNO}_3][\text{NH}_3]$  as a function of temperature for winter (right side) and summer (left side) seasons at Beijing. The  $K_n$  and  $K_{mn}$  constants have been determined by data collected on a 24-h basis.

state. During the winter the ambient RH was always lower than RHD (Fig. 3), thus,  $\text{NH}_4\text{NO}_3$  will exist in equilibrium with the solid phase. Instead, during the summer the ambient RH was not always lower than RHD (Fig. 4), thus,  $\text{NH}_4\text{NO}_3$  will be also in equilibrium with the aqueous phase and deliquescent particles. The explanation could be that  $\text{NH}_4\text{NO}_3$  in the atmosphere exists as a mixture of other components such as ammonium sulphate/bisulphate, elemental carbon (soot), organic carbon, crustal material. Impurities can initiate crystallization in bulk salts, inducing crystallization at a higher RH than the crystallization point of the pure salt aerosols. Douglas et al. (1998) found that soot is highly unlikely to promote crystallization in ambient aerosols, and suggested that the crystallization in the ambient aerosols might have been induced by the more abundant organic carbon. The relationship between  $K_{mn}$  and  $K_n$ , when RH was lower than RHD, is shown in Fig. 5 for winter and summer periods. The solid line indicates the theoretical equilibrium constant  $K_n$  for solid  $\text{NH}_4\text{NO}_3$  calculated as a function of temperature (Stelson and Seinfeld, 1982a). Concentration products  $K_{mn}$

are plotted on a logarithmic scale against a reciprocal average absolute temperature ( $1000/T$ ) and compared with the constant dissociations for both seasons.  $1000/T$  values varied from  $3.6$  to  $3.7 \text{ K}^{-1}$  and from  $3.3$  to  $3.4 \text{ K}^{-1}$  in the winter and summer, respectively, during the 24-h sampling periods in both seasons. The percentage relative error associated to  $K_{mn}$  was 10.54 % (Taylor, 1982; Perrino et al., 2001). In order for solid  $\text{NH}_4\text{NO}_3$  to be formed in the atmosphere, the concentration products of  $\text{HNO}_3$  and  $\text{NH}_3$  must exceed the theoretical equilibrium dissociation constant  $K_n$  (Stelson and Seinfeld, 1982a).

According to this, during the winter period the results of these thermodynamic calculations (Fig. 5 and Table 3) showed that the measured concentration products were higher than the theoretical predictions at low temperatures (Walker et al., 2006), with the exception of two days, 3 and 5 in February, where the  $K_{mn}$  are lower than  $K_n$ . Thus, almost on all days  $\text{NH}_4\text{NO}_3$  would be expected to be formed at Beijing site under winter conditions, in agreement with other results (Harrison and Pio, 1983; Allen et al., 1989; Harrison and Mackenzie, 1990; Pio et al., 1992; Possanzini et al., 1992; Mehlmann and Warneck, 1995; Danalatos and Glavas, 1999; Gupta et al., 2003). This could be due to the presence of excess  $\text{NH}_3$  even during the winter.

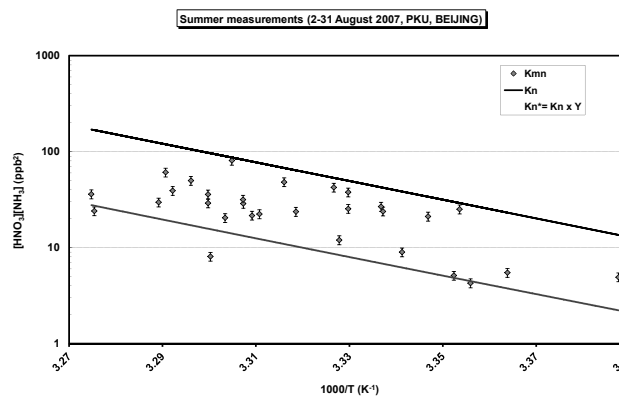
During the summer period, the results of thermodynamic calculations (Fig. 5) showed that almost on all days  $\text{NH}_4\text{NO}_3$  would not be expected to be formed at Beijing site under summer conditions. The measured concentration product values are below the thermodynamically predicted dissociation constants (Table 3), despite the fact that our measurements showed that the fine particulate ammonium nitrate was present at Beijing in the summer period (Fig. 1), as showed by other studies (Hildemann et al., 1984; Yao et al., 2002; Gupta et al., 2003; Trebs et al., 2005; Pathak et al., 2009; Guo et al., 2010). This disagreement can be understood by the fact that the theoretical predictions are achieved on the assumption that ammonium nitrate and chloride exist as pure solids or liquid particles. However, previous studies (Wu et al., 1987; Matsumoto and Tanaka, 1996; Zhang et al., 2000) confirmed that, for deliquescent particles, most of the

fine particulate nitrate exists as an internal mixture with sulphate, so that  $\text{HNO}_3$  can easily be absorbed into the droplets. This coexistence of sulphate considerably reduces the thermodynamic dissociation constant  $K_n$  for  $\text{NH}_4\text{NO}_3$ . Thus, the fine particulate nitrate can be formed from  $\text{HNO}_3$  and  $\text{NH}_3$  through heterogeneous reactions on fully neutralized fine particulate sulphate, which is abundantly present in an urban area. A strong and significant correlation between sulphate and nitrate was observed ( $R^2 = 0.80$ ,  $p < 0.001$ ), and a high concentrations of sulphate and nitrate were found at high levels of RH (35–83 %). Significant correlations between sulphate and RH ( $R^2 = 0.40$ ,  $p = 0.002$ ), and nitrate and RH ( $R^2 = 0.43$ ,  $p < 0.001$ ) were observed. These results can be interpreted as nitrate being produced on preexisting sulfate aerosols, which could provide sufficient surface area and aerosol water content for the heterogeneous reactions. In this case, at high RH, the amounts of the gaseous precursors, such as  $\text{NH}_3$  and  $\text{HNO}_3$ , have relatively less influence on the formation of the fine particulate nitrate (Zhang et al., 2010; Markovic et al., 2011). Accordingly, to include the coexistence of  $\text{SO}_4^{2-}$ , the  $\text{NH}_4\text{NO}_3$  ionic strength fraction  $Y = [\text{NH}_4\text{NO}_3]/([\text{NH}_4\text{NO}_3] + 3[(\text{NH}_3)_2\text{SO}_4])$  was calculated according to Stelson and Seinfeld (1982c) resulting in a mean value of  $Y = 0.20$  at Beijing site during the summer period, as seen in previous studies where fine particulate  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  were observed under high temperatures (33–36 °C) and high relative humidities (40–100 %) (Yao et al., 2003; Gupta et al., 2003; Trebs et al., 2005; Guo et al., 2010). Then, the new equilibrium dissociation constant  $K_n^*$  was derived by multiplying  $K_n$  with  $Y$ , providing a  $K_n^*$  value significantly lower than  $K_n$  at 25 °C (Fig. 6), with the exception of three days, 6, 9 and 11 in August, where  $K_n^*$  was higher than  $K_{mn}$ . This, almost on all days the meteorological conditions favour the formation of  $\text{NH}_4\text{NO}_3$  at Beijing site in summer period.

Another possible explanation can be provided by recent studies on the solid phase changes of  $\text{NH}_4\text{NO}_3$ , leading to appreciable  $\text{NH}_4\text{NO}_3$  concentrations in the troposphere even at high temperatures (>30 °C). Furthermore, potassium ions, such as  $\text{KNO}_3$ , were found to co-exist with fine particulate  $\text{NH}_4\text{NO}_3$ , and they changed the phase transition behaviors of solid  $\text{NH}_4\text{NO}_3$ . The presence of potassium ions into particulate  $\text{NH}_4\text{NO}_3$  widened its stable temperature range (32–84 °C) (Chan and Chan, 2004; Wu and Chan, 2008).

These results indicate that both  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  are formed in the urban of Beijing during summer season.

As far as the formation of solid  $\text{NH}_4\text{Cl}$  is concerned, the same procedure was applied. It is well known that the thermodynamic equilibrium conditions for the formation of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  aerosols are similar and depend on humidity and temperature, with  $\text{NH}_4\text{Cl}$  showing a volatility 2–3 times higher than that of  $\text{NH}_4\text{NO}_3$  (Stelson and Seinfeld, 1982a; Pio and Harrison, 1987; Casimiro and Nunes 1992; Matsumoto and Tanaka, 1996). At humidity lower than 75–85 % the particulate  $\text{NH}_4\text{Cl}$  exists in the solid phase in equi-



**Fig. 6.** Thermodynamically predicted equilibrium dissociation constant  $K_n$  (black solid line) for pure  $\text{NH}_4\text{NO}_3$ ,  $K_n^*$  (grey solid line) for  $\text{NH}_4^+/\text{NO}_3^-/\text{SO}_4^{2-}$  mixtures, and measured concentration product  $K_{mn} = [\text{HNO}_3][\text{NH}_3]$  as a function of temperature for summer period at Beijing. The  $K_n$ ,  $K_n^*$  and  $K_{mn}$  constants have been determined by data collected on a 24-h basis.

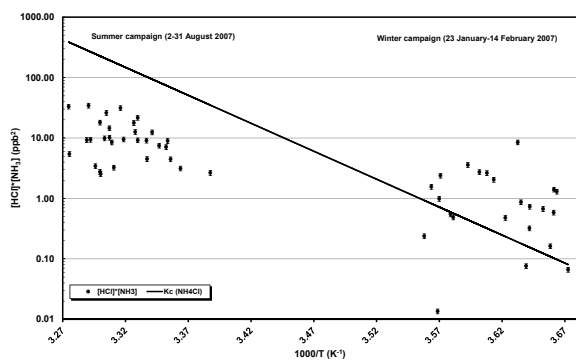
librium with the gaseous products. The theoretical equilibrium constant  $K_c$  in units of  $\text{pbb}^2$  for solid  $\text{NH}_4\text{Cl}$  was calculated by Pio and Harrison (1987), when the ambient relative humidity is below the respective deliquescence relative humidity (DRH):

$$\ln K_c = 2.23581 \ln T - 2.13204 \times 10^4 T^{-1} + 65.4375 - 8.167 \times 10^{-3} T + 4.644 \times 10^{-7} T^2 - 1.105 \times 10^{-10} T^3 \quad (15)$$

Fig. 7 presents the measured concentration products,  $K_{mc}$ , for both winter and summer periods in Beijing, compared with  $K_c$ . The measured concentration products are plotted on a logarithmic scale against a reciprocal average absolute temperature. The percentage relative error associated to  $K_{mc}$  was 8.91 % (Taylor, 1982; Perrino et al., 2001). Since  $\text{HCl}$  is more volatile than  $\text{HNO}_3$ ,  $K_c$  for  $\text{NH}_4\text{Cl}$  was higher than the theoretical value for  $\text{NH}_4\text{NO}_3$  (Table 3), as seen in previous papers (Allen et al., 1989). The behaviour of ammonium chloride is also similar to that ammonium nitrate, thus  $K_{mc}$  exhibited a similar behaviour to  $K_{mn}$  during both winter and summer periods.

During the winter period, the results of these thermodynamic calculations (Fig. 7) showed that almost on all days  $\text{NH}_4\text{Cl}$  will be formed in the winter because the measured  $[\text{NH}_3][\text{HCl}]$  products are above the predicted equilibrium constant for  $\text{NH}_4\text{Cl}$ , as seen for  $\text{NH}_4\text{NO}_3$ . Some of the data points in Fig. 7 of 28 and 31 January and of 3, 5, 10 and 11 February appeared to indicate an insufficient gas phase concentration product to form  $\text{NH}_4\text{Cl}$  aerosol. However, our denuder data showed the presence of fine particulate chloride during these days.

During the summer period, the results of thermodynamic calculations (Fig. 7) showed that on all days  $\text{NH}_4\text{Cl}$  would



**Fig. 7.** Thermodynamically predicted equilibrium dissociation constant  $K_c$  (black solid line) for pure  $\text{NH}_4\text{Cl}$  and measured concentration product  $K_{mc} = [\text{HCl}][\text{NH}_3]$  as a function of temperature for winter (right side) and summer (left side) seasons at Beijing. The  $K_c$  and  $K_{mc}$  constants have been determined by data collected on a 24-h basis.

not be formed (Allen, 1989; Matsumoto and Tanaka, 1996). In fact, the measured concentration product values are below the thermodynamically predicted equilibrium constants (Table 2). Instead, our denuder data are in disagreement compared with theory because our denuder data showed that, on average, more than 70% of the fine particulate chloride is recovered on back-up filters (Fig. 4) in the summer season indicating the presence of  $\text{NH}_4\text{Cl}$  as constituent of atmospheric particulate chloride. Thus, ammonium chloride was also generated in the high temperature range, despite the fact that these particles should be volatilized according the thermodynamic predictions. This disagreement can be understood taking into account the same interpretation for  $\text{NH}_4\text{NO}_3$  in the summer concerning the internal mixture of the volatile ammonium salts (Wu et al., 1987; Matsumoto and Tanaka, 1996). A strong and significant correlation between sulphate and chloride was observed ( $R^2 = 0.75$ ,  $p < 0.001$ ), and a high concentrations of sulphate and chloride were found at high levels of RH (35–83%). A significant correlation between fine particulate chloride and RH ( $R^2 = 0.35$ ,  $p < 0.001$ ) were observed. In this case, the amount of the gaseous precursors has relatively less influence on the formation of the fine particulate chloride. This will minimise the thermodynamic constant dissociation  $K_c$  for  $\text{NH}_4\text{Cl}$  which can be generated from HCl and  $\text{NH}_3$  through heterogeneous reactions on neutralized sulphate particles.

These results indicate that  $\text{NH}_4\text{Cl}$  is formed in the urban atmosphere of Beijing during winter and summer seasons.

### 3.2 Diurnal variation

#### 3.2.1 Winter

The diurnal variations of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and gaseous  $\text{HNO}_3$ , HCl and  $\text{NH}_3$  along with meteorologi-

cal parameters (temperature,  $T$ , relative humidity, RH, wind speed and direction) during the intensive winter measurements are reported in Fig. 8.

The weather conditions during this study were described in detail in Ianniello et al. (2010). Both the temperature and relative humidity exhibited strong diurnal variation patterns during the entire sampling period. The mean temperature was  $6.67^\circ\text{C}$  and increased at 08:00 reaching maxima values of about  $13.98^\circ\text{C}$  between 12:00 and 16:00, while the relative humidity peaked between 04:00 and 08:00 with a maximum value of 40.10%. The mean wind speed was  $2.18\text{ m s}^{-1}$  ( $0.02\text{--}8.85\text{ m s}^{-1}$ ) and blew mainly from northwest, southwest and southeast.

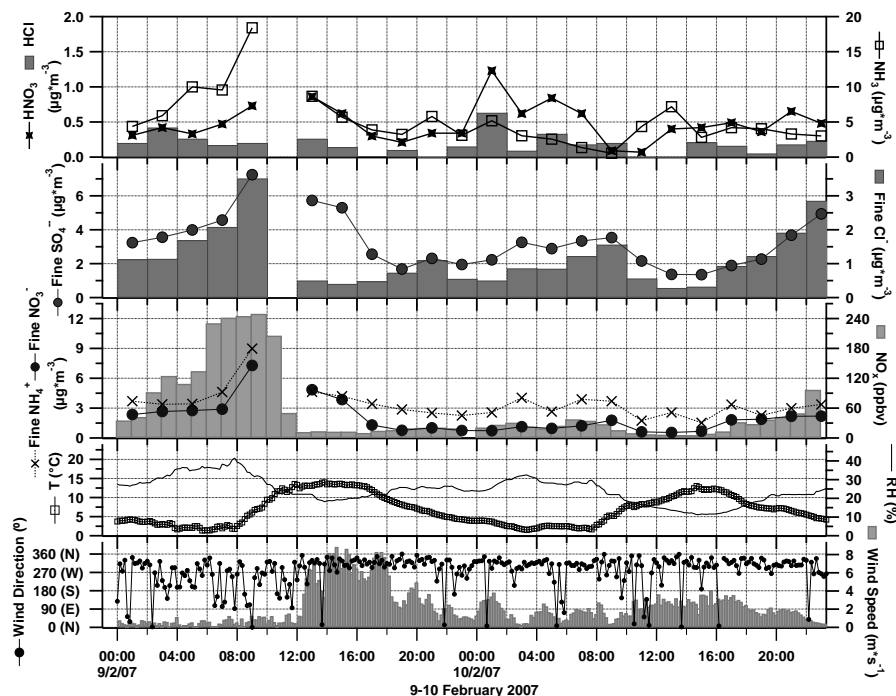
The mean concentrations of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  for the entire data ( $N = 23$ ) were  $1.14 \pm 0.82\ \mu\text{g m}^{-3}$ ,  $2.01 \pm 1.09\ \mu\text{g m}^{-3}$ ,  $3.26 \pm 1.50\ \mu\text{g m}^{-3}$  and  $3.42 \pm 1.47\ \mu\text{g m}^{-3}$ , respectively. The concentration ranges were  $0.28\text{--}3.22\ \mu\text{g m}^{-3}$ ,  $0.55\text{--}7.28\ \mu\text{g m}^{-3}$ ,  $1.35\text{--}7.25\ \mu\text{g m}^{-3}$  and  $1.53\text{--}8.98\ \mu\text{g m}^{-3}$  for fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ , respectively.

The diurnal variations are evaluated applying the paired  $t$ -test ( $p \leq 0.05$ ) to day and night samples. Data were grouped into sunrise (between 06:00 and 18:00) and sunset (between 18:00 and 06:00) times during the intensive winter and summer measurements at Beijing. On applying paired  $t$  test to day and night samples, fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  exhibited significant diurnal variations ( $p = 0.034$ ,  $p = 0.008$ ,  $p = 0.013$  and  $p = 0.016$ , respectively) in the winter period.

The diurnal variation of fine particulate  $\text{Cl}^-$  showed broad peaks in the morning (between 08:00 and 10:00) and in the evening (between 20:00 and 22:00). The mean chloride concentrations ranged from  $0.28$  to  $3.51\ \mu\text{g m}^{-3}$  during the day and from  $0.50$  to  $2.85\ \mu\text{g m}^{-3}$  during the night.

The ammonium concentrations followed the chloride, nitrate and sulphate concentrations in time (Fig. 8) with higher peaks between 08:00 and 10:00, indicating the presence of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{NO}_3$ , and ammonium sulphate salts. In addition, the similar diurnal variations of these measured species are consistent with the strong correlations between  $\text{NH}_4^+$  and  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The correlation coefficients were 0.86 ( $p < 0.001$ ) for  $\text{NH}_4^+\text{--Cl}^-$ , 0.90 ( $p < 0.001$ ) for  $\text{NH}_4^+\text{--NO}_3^-$ , and 0.96 ( $p < 0.001$ ) for  $\text{NH}_4^+\text{--SO}_4^{2-}$ .

Furthermore, the nitrate, sulphate and ammonium concentrations reached maxima values of  $7.30\ \mu\text{g m}^{-3}$ ,  $7.25\ \mu\text{g m}^{-3}$  and  $8.98\ \mu\text{g m}^{-3}$ , respectively, at daytime and of  $2.76\ \mu\text{g m}^{-3}$ ,  $4.94\ \mu\text{g m}^{-3}$  and  $4.04\ \mu\text{g m}^{-3}$ , respectively, at nighttime. The highest daytime concentrations of these species measured on 9 February might be related to the weather conditions and to emissions from Friday traffic during this day (Ianniello et al., 2010). Lower wind speeds between 00:00 and 12:00 ( $0.02\text{--}1.53\text{ m s}^{-1}$ ) and southeasterly and southwesterly wind directions (60%) on 9 February, in combination with higher  $\text{NO}_x$  concentrations and relative



**Fig. 8.** Diurnal trends of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , and gaseous  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$ , and temperature ( $T$ ), relative humidity ( $\text{RH}$ ), wind speed and direction during the intensive winter measurements, carried out on a 24-h basis, at Beijing.

humidities, and lower temperatures during this time period, resulted in higher peaks of all four species between 08:00 and 10:00 (Ianniello et al., 2010). Obviously,  $\text{NH}_4^+$  was strongly influenced by its gas phase precursor, such as  $\text{NH}_3$ , peaking between 08:00 and 10:00 in the morning and revealing much higher concentrations than the anionic species. Possible evaporation of  $\text{NH}_3$  from wet surfaces at sunrise, when relative humidities were still high might have caused a significant fraction of gaseous ammonia to dissolve in still humid particles, therefore enhancing particulate  $\text{NH}_4^+$  (Trebs et al., 2004; Ianniello et al., 2010).

In addition, thermodynamic calculations obtained by 2-h samplings over the 9–10 February in winter showed the same results to that obtained during 24-h samplings. The only difference was that the measured concentration products and the equilibrium constants tend to be higher on the average than those derived from longer sampling periods (Table 3). The mean values of  $K_{\text{mn}}$  and  $K_n$  for  $\text{NH}_4\text{NO}_3$  were 1.49  $\text{ppb}^2$  and 0.35  $\text{ppb}^2$ , respectively, and the mean values of  $K_{\text{mc}}$  and  $K_c$  for  $\text{NH}_4\text{Cl}$  were 0.78  $\text{ppb}^2$  and 0.60  $\text{ppb}^2$ , respectively, during the intensive winter measurements. As discussed above, the atmosphere is ammonia rich in Beijing during winter period and ammonium nitrate and chloride formations were permitted.

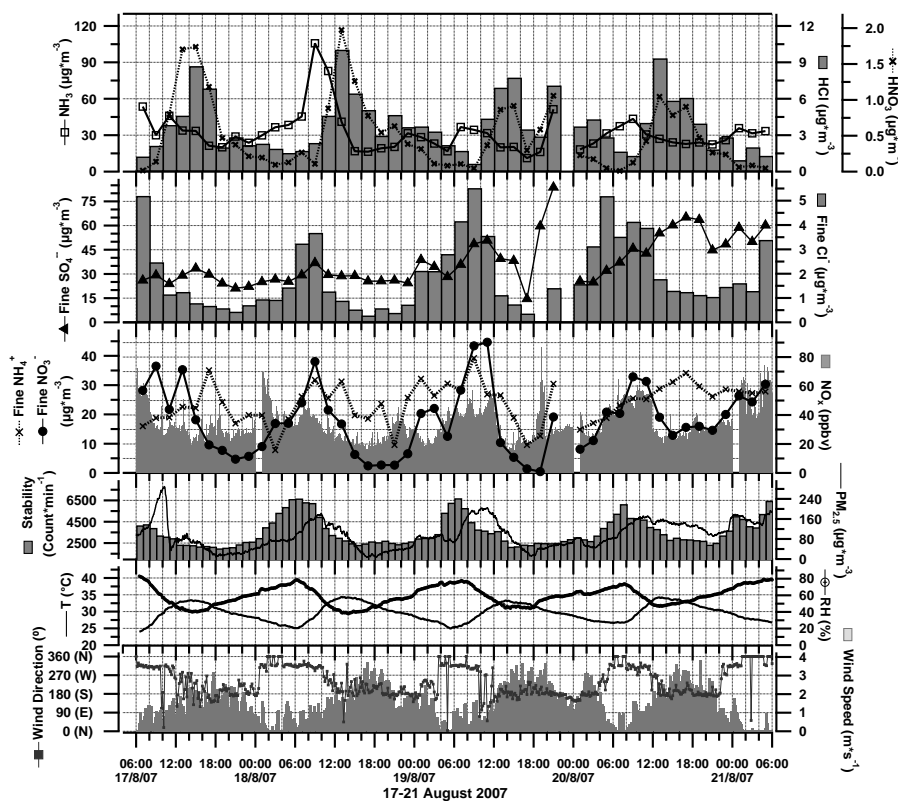
To gain an insight into the impact of regional transport on  $\text{NH}_3$  at Beijing, 24-h backward trajectories were calculated by using NOAA ARL HYSPLIT trajectory model

(<http://ready.arl.noaa.gov/Hysplit.php>) for winter and summer intensive measurements in Ianniello et al. (2010). The dominant transport of air masses in the winter period originated in the northwest (83 %) of Beijing, coinciding with the direction of Inner Mongolia and Hebei province. These air masses arrived at higher speeds (8.17–15.70  $\text{m s}^{-1}$ ), which results in less accumulation of air pollutants. Instead, the local wind speeds, coming mainly from southeast and southwest of Beijing, arrived slower (0.02–8.85  $\text{m s}^{-1}$ ), especially on 9 February between 00:00 and 12:00 (0.02–1.29  $\text{m s}^{-1}$ ), which results in more accumulation of air pollutants. This implies that local emissions contributed greatly to the fine particulate matter in Beijing, where morning peaks of these fine particulate species correlated with morning traffic emissions such as with higher  $\text{NO}_x$  concentrations in rush hours.

### 3.2.2 Summer

The diurnal variations of fine particulate species  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , and gaseous  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$  along with meteorological parameters (temperature,  $T$ , relative humidity,  $\text{RH}$ , wind speed and direction, and natural radioactivity) during the intensive summer measurements are reported in Fig. 9.

The weather conditions during this time period were described in detail in Ianniello et al. (2010). Both the temperature and relative humidity exhibited strong diurnal variation patterns during the entire sampling period. The temperature



**Fig. 9.** Diurnal trends of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ , and gaseous  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$ , and temperature ( $T$ ), relative humidity ( $\text{RH}$ ), wind speed and direction, and natural radioactivity (Stability) during the intensive summer measurements, carried out on a 24-h basis, at Beijing.

ranged between  $23.86^\circ\text{C}$  and  $33.22^\circ\text{C}$  reaching maxima between 12:00 and 14:00, while the relative humidity varied from 40 % to 80.77 % peaking between 04:00 and 06:00. The wind speed reached a maxima value of  $3\text{ m s}^{-1}$  at 18:00 and blew mainly from south, northwest and southwest.

The mean concentrations of fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$  for the entire data ( $N = 47$ ) were  $1.87 \pm 1.05\ \mu\text{g m}^{-3}$ ,  $17.92 \pm 8.38\ \mu\text{g m}^{-3}$ ,  $37.40 \pm 10.80\ \mu\text{g m}^{-3}$  and  $23.81 \pm 6.95\ \mu\text{g m}^{-3}$ , respectively. The concentration ranges were  $0.07\text{--}5.52\ \mu\text{g m}^{-3}$ ,  $0.45\text{--}44.65\ \mu\text{g m}^{-3}$ ,  $14.56\text{--}83.71\ \mu\text{g m}^{-3}$  and  $7.80\text{--}39.23\ \mu\text{g m}^{-3}$  for fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NH}_4^+$ , respectively. The presence of substantial amounts of fine particulate matter such as fine particulate  $\text{NO}_3^-$  in summer period is interesting since fine particulate ammonium salts ( $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ ) are volatile and tends to dissociate and remain in the gas phase under high temperatures. The possible explanation for the detection of high concentrations of fine particulate  $\text{NO}_3^-$  in August is that there was abundant  $\text{NH}_3$  to neutralize  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  and  $\text{HCl}$ , which is consistent with the results obtained from our measurements on the predominance of overall neutralized particles, such as  $(\text{NH}_4)_2\text{SO}_4$  (see Sect. 3.1). In addition, the particulate mat-

ter in Beijing was likely humid due to high  $\text{RH}$  conditions, which might favor the absorption of  $\text{NH}_3$  and  $\text{HNO}_3$  (He et al., 2001; Yao et al., 2003; Chan and Yao, 2008; Sun et al., 2010).

All four measured species showed broadly similar patterns but only fine particulate  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  exhibited significant diurnal variations ( $p = 0.030$ ,  $p = 0.021$  and  $p = 0.025$ , respectively) in the summer in Beijing (Fig. 9). In addition, the similar diurnal variations of these measured species are consistent with the strong correlations between  $\text{NH}_4^+$  and  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ . The correlation coefficients were 0.80 ( $p = 0.001$ ) for  $\text{NH}_4^+\text{--Cl}^-$ , 0.85 ( $p < 0.001$ ) for  $\text{NH}_4^+\text{--NO}_3^-$ , and 0.90 ( $p < 0.001$ ) for  $\text{NH}_4^+\text{--SO}_4^{2-}$ . The variation of  $\text{NH}_4^+$  coincided with those of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ , indicating that  $\text{NH}_4^+$  largely originated from the neutralization between ammonia and acidic species.  $\text{NH}_4^+$  concentration peaked at around 08:00 due to its accumulation under humid conditions within the stable nocturnal boundary layer between 06:00 and 08:00. This can be explained by a significant fraction of  $\text{NH}_3$  dissolved in humid particles under high  $\text{RH}$  conditions which increases  $\text{NH}_4^+$  formation (Stelson and Seinfeld, 1982b, 1982c; Baek and Aneja, 2004). The observed diurnal pattern of fine particulate  $\text{NO}_3^-$  also peaked

at around 08:00 within a thermally stable nocturnal boundary layer. After 08:00,  $\text{NO}_3^-$  concentrations dropped and remained at low levels between 12:00 and 18:00 due to the gas to particle partitioning of  $\text{NH}_4\text{NO}_3$  precursors ( $\text{HNO}_3$  and  $\text{NH}_3$ ), which is favored by the lower temperature and high RH during night and early morning. In addition, the low concentrations of fine particulate  $\text{NO}_3^-$  were also due to when the convective mixing of the atmosphere occurred between the late morning (12:00–13:00) of previous day and the early morning (03:00–04:00) of the subsequent day (Fig. 9). The  $\text{NO}_3^-$  concentration peaked at around 08:00 as a result of the accumulation under high RH conditions. As for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , after 08:00, the observed diurnal pattern of fine particulate  $\text{Cl}^-$  showed a decrease trend during daytime due to increase of the boundary layer height and dissociation of  $\text{NH}_4\text{Cl}$  at high temperatures (Fig. 9).

Fine particulate  $\text{SO}_4^{2-}$  concentrations did not show a pronounced diurnal variation as that of other fine particulate species ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ), being relatively stable throughout day and night. This might be explained by a more regional formation originating from distant sources. High sulphate concentrations occurred between 08:00 and 14:00 in combination with high RH conditions and high peaks of  $\text{NO}_x$  and  $\text{PM}_{2.5}$ , supporting the hypothesis that the traffic was also an important mobile source of fine particulate matter. These results are consistent with the significant correlations between  $\text{SO}_4^{2-}$  and RH,  $\text{NO}_x$  and  $\text{PM}_{2.5}$ . The correlation coefficients were 0.52 ( $p = 0.001$ ) for  $\text{SO}_4^{2-}$ -RH, 0.35 ( $p = 0.001$ ) for  $\text{SO}_4^{2-}$ - $\text{NO}_x$ , and 0.50 ( $p < 0.001$ ) for  $\text{SO}_4^{2-}$ - $\text{PM}_{2.5}$ .

In addition, thermodynamic calculations obtained by 2-h samplings over the 17–21 August in summer showed the same results to that obtained during 24-h samplings. The only difference was that the equilibrium constants tend to be higher on the average than those derived from longer sampling periods (Table 3). The mean values of  $K_{\text{mn}}$  and  $K_n$  for  $\text{NH}_4\text{NO}_3$  were 51.35  $\text{ppb}^2$  and 116.26  $\text{ppb}^2$  for  $K_{\text{mn}}$  and  $K_n$ , respectively, and the mean values of  $K_{\text{mc}}$  and  $K_c$  for  $\text{NH}_4\text{Cl}$  were 18.72  $\text{ppb}^2$  and 267.01  $\text{ppb}^2$ , respectively, during the intensive summer measurements. As discussed above, even if the atmosphere is ammonia rich in Beijing during summer period, ammonium nitrate and chloride would not be expected to be formed but the meteorological conditions favoured their formations at Beijing site in summer period.

As in winter, to identify the impact on the regional transport of air masses on the sampled pollutants, 24-h backward trajectories were calculated for summer intensive measurements in Ianniello et al. (2010). The dominant transport of air masses in the summer period originated in the south (53 %) and southeast (15 %) of Beijing, coinciding with the direction of Hebei province and Tianjing municipality, which are highly industrialized and polluted areas. These polluted air masses from southern directions arrived slower (1.63–

3.85  $\text{m s}^{-1}$ ) and had much time to accumulate air pollutants in the Beijing area. This suggests that the high concentrations of fine particulate species, such as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , were due to the impact of regional sources in Beijing during the summer period. Thus, the presence of high concentration of primary precursors in the southern regions, such as  $\text{NH}_3$ ,  $\text{SO}_2$  and  $\text{NO}_x$ , led to the high particulate ammonium, sulfate and nitrate concentrations in the atmosphere of Beijing. The indication that the areas to the south of Beijing are major sources of particulate matter for Beijing have been reported in other studies (Xia et al., 2007; Streets et al., 2007; Wehner et al., 2008; Zhao et al., 2009; Wu et al., 2009). In addition, the urban area itself is a major source for traffic emission. The local wind speeds, coming mainly from south and northwest of Beijing, arrived also slowly (0.02–3.83  $\text{m s}^{-1}$ ), especially between 06:00 and 10:00 (0.02–1.30  $\text{m s}^{-1}$ ) during all days, in combination with northwesterly wind direction, boundary layer variations and daytime traffic emissions in rush hours such as with highest concentrations of  $\text{NO}_x$  and  $\text{PM}_{2.5}$  between 06:00 and 10:00 (morning rush hour) for all days. In Beijing 74 % of ground  $\text{NO}_x$  originates from vehicular emissions (Hao et al., 2005; Xu et al., 2011), while  $\text{PM}_{2.5}$  accounted for 90 % of total PM emissions from vehicle exhaust emissions (Zheng et al., 2005). The observed morning peaks of  $\text{NO}_x$  and  $\text{PM}_{2.5}$  were due to enhanced anthropogenic activity during rush hours and this suggests that the atmosphere of Beijing received regional polluted air from southern urban regions on locally produced particulate species.

These results indicate that reducing the concentrations of precursor gases, such as  $\text{NH}_3$  and  $\text{NO}_x$ , could be an effective method for alleviating secondary inorganic  $\text{PM}_{2.5}$  pollution in the urban atmospheres as in Beijing.

#### 4 Conclusions

The atmospheric concentrations of gaseous  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{NH}_3$  and their chemically related fine particulate species  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  have been measured at an urban site (Peking University) in Beijing (China) in the winter and summer of 2007. These measurements were carried out by means of annular denuder and filter pack in order to determine the fine particulate inorganic ammonium salts without disturbing the partition equilibrium existing in the atmosphere between gaseous  $\text{NH}_3$  and the particulate components ( $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ ). All data were analyzed to investigate temporal and diurnal variations in fine particulate species and meteorological effects, and to examine the contribution of local and regional sources to fine particulate species. According to the results, the following conclusions were reached:

1. Fine particulate  $\text{Cl}^-$ ,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  exhibited distinct temporal variations, while fine particulate  $\text{NO}_3^-$  did not show much variation with respect to season.

- All measured particulate species showed diurnal patterns during the winter and summer periods with higher peaks in the early morning, especially in summer, when humid and stable atmospheric conditions occurred.
- The atmosphere of Beijing was ammonia-rich during the winter and summer periods. Thus, abundant  $\text{NH}_3$  was present to neutralize the acid components, such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$ , and to form fine particulate ammonium salts, such as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ , in winter and summer periods at Beijing.
- Significant amounts of fine particulate nitrate even in summer were found in disagreement with theoretical values predicted by thermodynamic equilibrium laws for  $\text{NH}_4\text{NO}_3$  formation. In the summer the presence of large amounts of  $\text{NH}_3$ , the domination of  $(\text{NH}_4)_2\text{SO}_4$ , the high relative humidity conditions seemed to dissolve a significant fraction of  $\text{HNO}_3$  and  $\text{NH}_3$  enhancing fine particulate  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the atmosphere of Beijing.
- Moderate correlations were obtained between fine particulate species and pollutants emitted by motor-vehicle exhausts, such as  $\text{NO}_x$  and  $\text{PM}_{2.5}$ , indicating influence traffic emissions at Beijing.
- Emissions from regional sources contributed to the atmospheric levels of fine particulate species in winter and summer seasons at Beijing.

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## References

- Allegrini, I., De Santis, F., Di Palo, V., Febo, A., Perrino, C., Posanzini, M., and Liberti, A.: Annular denuder method for sampling reactive gases and aerosols in the atmosphere, *Sc. Total Environ.*, 67, 1–16, 1987.
- Allen, A. G., Harrison, R. M., and Erisman, J. W.: Field measurements of the dissociation of ammonium nitrate and ammonium chloride aerosols, *Atmos. Environ.*, 23, 1591–1599, 1989.
- Andreae, M. O., Atlas, E., Harris, G. W., Helas, G., de Koc, A., Koppmann, R., Maenhaut, W., Manø, S., Pollock, W. H., Rudolph, J., Scharffe, D., Schebeske, G., and Welling, M.: Methyl halide emissions from savanna fires in southern Africa, *J. Geophys. Res.*, 101, 23603–23613, doi:10.1029/95JD01733, 1996.
- Aneja, V. P., Chauhan, J. P., and Walker, J. T.: Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons, *J. Geophys. Res.*, 105, 11535–11545, 2000.
- Aneja, V. P., Roelle, P. A., Murray, G. C., Southerland, J., Erisman, J. W., Fowler D., Asman, W. A. H., and Patni N.: Atmospheric nitrogen compounds: II. Emissions, transport, transformation, deposition and assessment, *Atmos. Environ.*, 35, 1903–1911, 2001.
- Aneja, V. P., Schlesinger, W. H., and Erisman, J. W.: Effects of agriculture upon the air quality and climate: research, policy, and regulations, *Environ. Sci. Technol.*, 43, 4234–4240, 2009.
- Ansari, A. S. and Pandis, S.: Response of inorganic PM to precursor concentrations, *Environ. Sci. Technol.*, 32, 2706–2714, 1998.
- Appel, B. R., Tokiwa, Y., Haik, M., and Kothny, E. L.: Artifact of particulate sulfate and nitrate formation on filter media, *Atmos. Environ.*, 18, 409–416, 1984.
- Baek, B. H. and Aneja, V. P.: Measurement and Analysis of the Relationship between Ammonia, Acid Gases, and Fine Particles in Eastern North Carolina, *J. Air Waste Manage. Assoc.*, 54, 623–633, 2004.
- Baek, B. H. and Aneja, V. P.: Observation based analysis for the determination of equilibrium time constant between ammonia, acid gases, and fine particles, *Int. J. Environ. Pollut.*, 23, 239–247, 2005.
- Bari, A., Ferraro, V., Wilson, L. R., Luttinger, D., and Husain L.: Measurements of gaseous HONO,  $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{NH}_3$ , particulate sulfate and  $\text{PM}_{2.5}$  in New York, NY, *Atmos. Environ.*, 37, 2825–2835, 2003.
- Behera, S. N. and Sharma, M.: Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment, *Sc. Total Environ.*, 408, 3569–3575, 2010.
- Beine, H. J., Allegrini, I., Sparapani, R., Ianniello, A., and Valentini, F.: Three years of springtime trace gas and particle measurements at Ny-Alesund, Svalbard, *Atmos. Environ.*, 35, 3645–3658, 2001.
- Blanchard, C. L., Roth, P. M., Tanenbaum, S. J., Ziman, S. D., and Seinfeld, J. H.: The use of ambient measurements to identify which precursor species limit aerosol nitrate formation, *J. Air Waste Manage. Assoc.*, 50, 2073–2084, 2000.
- Cadle, S. H., Countess, R. J., and Kelly, N. A.: Nitric acid and ammonia in urban and rural locations, *Atmos. Environ.*, 16, 2501–2506, 1982.
- Calvert, J. G. and Stockwell, W. R.: Acid generation in the troposphere by gas-phase chemistry, *Environ. Sci. Technol.*, 17, 428–443, 1983.
- Casimiro, P. and Nunes, T. V.: Kinetic and thermodynamic behaviour of volatile ammonium compounds in industrial and marine atmospheres, *Atmos. Environ.*, 26, 505–512, 1992.
- Chak, C. K. and Yao, X.: Air pollution in mega cities in China – A review, *Atmos. Environ.*, 42, 1–42, 2008.
- Chan, C. K. and Chan, M. N.: New Directions: Polymorphic transformation of ammonium nitrate in atmospheric aerosols, *Atmos. Environ.*, 38, 1387–1388, 2004.
- Chan, C. Y., Xu, X. D., Li, Y. S., Wong, K. H., Ding, G. A., Chan, L. Y., and Cheng, X. H.: Characteristics of vertical profiles and sources of  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$  and carbonaceous species in Beijing, *Atmos. Environ.*, 39, 5113–5124, 2005.
- Chan, C. K. and Yao, X.: Air pollution in mega cities in China,



- Atmos. Environ., 42, 1–42, 2008.
- Chang, Y. S., Carmichael, G. R., Kurita, H., and Ueda, H.: An investigation of the formation of ambient  $\text{NH}_4\text{NO}_3$ , Atmos. Environ., 20, 1969–1977, 1986.
- Charlson, R. J. and Heintzenberg, J.: Aerosol Forcing of Climate, Wiley, England, 363–382, 1995.
- Chen, D. S., Cheng, S. Y., Liu, L., Chen, T., and Guo, X. R.: An integrated MM5-CMAQ modeling approach for assessing trans-boundary  $\text{PM}_{10}$  contribution to the host city of 2008 Olympic summer games – Beijing, China, Atmos. Environ., 41, 1237–1250, 2007.
- Cizco, D. J., Nowak, J. B., Hu, J. H., and Abbatt, J. P. D.: Infrared spectroscopy of model tropospheric aerosols as a function of relative humidity: observation of deliquescence and crystallization, J. Geophys. Res., 102, 18843–18850, 1997.
- Wexler, A. S. and Seinfeld, J. H.: Second generation inorganic aerosol model, Atmos. Environ. 25A, 12, 2731–2748, 1991.
- Danalatos, D. and Glavas, S.: Gas phase nitric acid, ammonia and related particulate matter at a Mediterranean coastal site, Patras, Greece, Atmos. Environ., 33, 3417–3425, 1999.
- Dockery, D. W., Pope III, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris Jr., B. G., and Speizer, F. E.: An association between air pollution and mortality in six US cities, New Engl. J. Med., 29, 1753–1759, 1993.
- Dougle P. G., Veeffkind J. P. and Ten Brink H. M.: Crystallisation of mixtures of ammonium nitrate, ammonium sulphate and soot, J. Aerosol Sci., 29, 3, 375–386, 1998.
- Duan, F. K., Liu, X. D., He, K. B., Lu, Y. Q., and Wang, L.: Atmospheric aerosol concentration level and chemical characteristic of its water soluble ionic species in wintertime in Beijing, China, J Environ. Monit., 5, 569–573, 2003.
- Duan, F. K., Liu, X. D., Dong, S. P., Lu, Y. Q., Yu, T., and Cachier H.: Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentration in Beijing, Atmos. Environ., 38, 1275–1282, 2004.
- Duan, F. K., He, K., Ma, Y. L., Yang, F. M., Yu, X. C., Cadle, S. H., Chan, T., and Mulawa, P. A.: Concentration and chemical characteristics of  $\text{PM}_{2.5}$  in Beijing, China: 2001–2002, Sci. Total Environ., 55, 264–275, 2006.
- Duan, F. K., Liu, X. D., He, K. B., Li, Y. W., and Dong, S. P.: Characteristics and source identification of particulate matter in wintertime in Beijing, Water Air Soil Poll., 180, 171–183, 2007.
- Erduran, M. S. and Tuncel, S. G.: Gaseous and particulate air pollutants in the Northeastern Mediterranean Coast, Sci. Total Environ., 281, 205–215, 2001.
- Febo, A., De Santis, F., Perrino, C., and Giusto, M.: Evaluation of laboratory and field performance of denuder tubes: a theoretical approach, Atmos. Environ., 23, 1517–1530, 1989.
- Gaidajis, G.: Considerations on the dissociation of ambient ammonium aerosols based on field measurements of atmospheric gases and aerosols, J. Environ. Prot. Ecol., 3, 361–369, 2002.
- Graedel, T. E. and Keene, W. C.: The tropospheric budget of reactive chlorine, Global Biogeochem. Cycles, 9, 47–78, 1995.
- Gray, H. A., Cass, G. R., Huntzicker, J. J., Heyerdahl, E. K., Rau, J. A.: Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles, Environ. Sci. Technol., 20, 580–589, 1986.
- Guinot, B., Roger, J.-C., Cachier, H., Pucai, W., Bai, J., and Yu, T.: Impact of vertical atmospheric structure on Beijing aerosol distribution, Atmos. Environ., 40, 5167–5180, 2006.
- Guinot, B., Cachier, H., Sciare, J., Tong, Y., Xin, W., and Jianhua, Y.: Beijing aerosol: Atmospheric interactions and new trends, J. Geophys. Res., 112, D14314, doi:10.1029/2006JD008195, 2007.
- Guo, S., Hu, M., Wang, Z. B., Slanina, J., and Zhao, Y. L.: Size-resolved aerosol water-soluble ionic compositions in the summer of Beijing: implication of regional secondary formation, Atmos. Chem. Phys., 10, 947–959, doi:10.5194/acp-10-947-2010, 2010.
- Gupta, A., Kumar, R., Maharaj Kumari, K., and Srivastava, S. S.: Measurement of  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{NH}_3$  and  $\text{SO}_2$  and related particulate matter at a rural site in Rampur, India, Atmos. Environ., 37, 4837–4846, 2003.
- Hammer, W. J. and Wu, Y. C.: Osmotic coefficients and mean activity coefficients of univalent electrolytes in water at 25 °C, J. Phys. Chem. Ref. Data, 1, 1047–1099, 1972.
- Hao, J., Wang, L., Li, L., Hu, J. N., and Yu, X. C.: Air pollutants contribution and control strategies of energy-use related sources in Beijing, Sci. China, Ser. D 48, (Suppl. II), 138–146, 2005.
- Harrison, R. M. and MacKenzie, A. R.: A numerical simulation of kinetic constraints upon achievement of the ammonium nitrate dissociation equilibrium in the troposphere, Atmos. Environ., 24A, 91–102, 1990.
- Harrison, R. M. and Msibi, I. M.: Validation of techniques for fast response measurement of  $\text{HNO}_3$  and  $\text{NH}_3$  and determination of the  $[\text{NH}_3][\text{HNO}_3]$  concentration product, Atmos. Environ., 28, 247–255, 1994.
- Harrison, R. M. and Pio, C. A.: An investigation of the atmospheric  $\text{HNO}_3$ - $\text{HN}_3$ - $\text{NH}_4\text{NO}_3$  equilibrium relationship in a cold humid climate, Tellus, 35B, 155–159, 1983.
- He, K. B., Yang, F., Ma, Y., Zhang, Q., Yao, X. H., Chan, C. K., Cadle, S. H., Chan, T., and Mulawa, P. A.: The characteristics of  $\text{PM}_{2.5}$  in Beijing, China, Atmos. Environ., 35, 4959–4970, 2001.
- He, K. B., Yu, X. C., Lu, Y. Q., Hao, J. M., and Fu, L. X.: Characterization of urban air pollution sources, Urban Environment and Urban Ecology, 16, 269–271, 2003.
- Heintzenberg, J.: Fine particles in global troposphere: A review, Tellus, 41B, 149–160, 1989.
- Hesterberg, R., Blatter, A., Fahrni, M., Rosset, M., Neftel, A., Eugster, W., and Wanner, H.: Deposition of nitrogen-containing compounds to an extensively managed grassland in central Switzerland, Environ. Pollut., 91, 21–34, 1996.
- Hildemann, L. M., Russell, A. G., and Cass, G. R.: Ammonia and nitric acid concentrations in equilibrium with atmospheric aerosols: experiments vs. theory, Atmos. Environ., 18, 1737–1750, 1984.
- Hu, M., Wu, Z., Slanina, J., Lin, P., Liu, S., and Zeng, L.: Acidic gases, ammonia and water-soluble ions in  $\text{PM}_{2.5}$  at a coastal site in the Pearl River Delta, China, Atmos. Environ., 42, 6310–6320, 2008.
- Huang, X.-F., He, L.-Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L.-W., Liu, X.-G., Zhang, Y.-H., Jayne, J. T., Ng, N. L., and Worsnop, D. R.: Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos. Chem. Phys., 10, 8933–8945, doi:10.5194/acp-10-8933-2010, 2010.
- Ianniello, A., Beine, H. J., Sparapani, R., Di Bari, F., Allegrini, I., and Fuentes, J. D.: Denuder measurements of gas and aerosol

- species above Arctic snow surfaces at Alert 2000, *Atmos. Environ.*, 36, 5299–5309, 2002.
- Ianniello, A., Beine, H. J., Landis, M. S., Stevens, R. K., Esposito, G., Amoroso, A., and Allegrini, I.: Comparing field performances of denuder techniques in the high Arctic, *Atmos. Environ.*, 41, 1604–1615, 2007.
- Ianniello, A., Spataro, F., Esposito, G., Allegrini, I., Rantica, E., Ancora, M. P., Hu, M., and Zhu, T.: Occurrence of gas phase ammonia in the area of Beijing (China), *Atmos. Chem. Phys.*, 10, 9487–9503, doi:10.5194/acp-10-9487-2010, 2010.
- IPCC: Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon S., Qin D., Manning M., Chen Z., Marquis M., Averyt K. B., Tignor M., Miller H. L., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 996 pp., 2007.
- Kai, Z., Yuesi, W., Tianxue, W., Yousef, M., and Frank, M.: Properties of nitrate, sulfate and ammonium in typical polluted atmospheric aerosols (PM<sub>10</sub>) in Beijing, *Atmos. Res.*, 84, 67–77, 2007.
- Keene, W. C., Khalil, M. A. K., Erickson, D. J., McCulloch, A., Graedel, T. E., Lobert, J. M., Aucott, M. L., Gong, S.-L., Harpe, D. B., Kleiman, G., Midgley, P., Moore, R. A., Seuzaret, C., Sturges, W. T., Benkovitz, C. M., Koropalov, V., Barrie, L. A., Li, Y.-F.: Composite global emissions of reactive chlorine from anthropogenic and natural sources: The reactive chlorine emissions inventory, *J. Geophys. Res.*, 104, 8429–8440, 1999.
- Kim, Y. P. and Seinfeld, J. H.: Atmospheric gas-aerosol equilibrium I. Thermodynamic model, *Aerosol Sci. Technol.*, 19, 157–181, 1993.
- Krupa, S. V.: Effects of atmospheric ammonia (NH<sub>3</sub>) on terrestrial vegetation: A review, *Environ. Pollut.*, 124, 179–221, 2003.
- Li, W. J., Shao, L. Y., and Buseck, P. R.: Haze types in Beijing and the influence of agricultural biomass burning, *Atmos. Chem. Phys.*, 10, 8119–8130, doi:10.5194/acp-10-8119-2010, 2010.
- Lin, Y. C. and Cheng, M. T.: Evaluation of formation rates of NO<sub>2</sub> to gaseous and particulate nitrate in the urban atmosphere, *Atmos. Environ.*, 41, 1903–1910, 2007.
- Lin, Y.-C., Cheng, M.-T., Ting, W.-Y., and Yeh, C.-R.: Characteristics of gaseous HNO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub> and particulate ammonium nitrate in an urban city of Central Taiwan, *Atmos. Environ.*, 40, 4725–4733, 2006.
- Lobert, J. M., Keene, W. C., Logan, J. A., and Yevich, R.: Global chlorine emissions from biomass burning: The reactive chlorine emissions inventory, *J. Geophys. Res.*, 8373–8389, 1999.
- Markovic, M. Z., Hayden, K. L., Murphy, J. G., Makar, P. A., Ellis, R. A., Chang, R. Y.-W., Slowik, J. G., Mihele, C., and Brook, J.: The effect of meteorological and chemical factors on the agreement between observations and predictions of fine aerosol composition in southwestern Ontario during BAQS-Met, *Atmos. Chem. Phys.*, 11, 3195–3210, doi:10.5194/acp-11-3195-2011, 2011.
- Masia, P., Di Palo, V., and Possanzini, M.: Uptake of ammonia by nylon filters in filter pack systems, *Atmos. Environ.*, 28, 365–366, 1994.
- Matsumoto, K. and Tanaka, H.: Formation and dissociation of atmospheric particulate nitrate and chloride: an approach based on phase equilibrium, *Atmos. Environ.*, 30, 639–648, 1996.
- McCulloch, A., Aucott, M. L., Benkovitz, C. M., Graedel, T. E., Kleiman, G., Midgley, P., and Li, Y.-F.: Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration, and industrial activities: The reactive chlorine emissions inventory, *J. Geophys. Res.*, 104, 8417–8428, 1999.
- Mehlmann, H. and Warneck, P.: Atmospheric gaseous HNO<sub>3</sub>, particulate nitrate and aerosol size distribution of major ionic species at a rural site in Western Germany, *Atmos. Environ.*, 29, 2359–2373, 1995.
- Meng, Z. Y., Ding, G. A., Xu, X. B., Xu, X. D., Yu, H. Q., and Wang, S. F.: Vertical distributions of SO<sub>2</sub> and NO<sub>2</sub> in the lower atmosphere in Beijing urban areas, China, *Sci. Total Environ.*, 390, 456–465, 2008.
- Pathak, R. K. and Chan, C. K.: Inter-particle and gas-particle interactions in sampling artifacts of PM<sub>2.5</sub> in filter-based samplers, *Atmos. Environ.*, 39, 1597–1607, 2005.
- Pathak, R. K., Yao, X. H., and Chan, C. K.: Sampling artifacts of acidity and ionic species in PM<sub>2.5</sub>, *Environ. Sci. Technol.*, 38, 254–259, 2004.
- Pathak, R. K., Wu, W. S., and Wang, T.: Summertime PM<sub>2.5</sub> ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere, *Atmos. Chem. Phys.*, 9, 1711–1722, doi:10.5194/acp-9-1711-2009, 2009.
- Pathak, R. K., Wang, T., and Wu, W. S.: Nighttime enhancement of PM<sub>2.5</sub> nitrate in ammonia-poor atmospheric conditions in Beijing and Shanghai: Plausible contributions of heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub> and HNO<sub>3</sub> partitioning, *Atmos. Environ.*, 45, 1183–1191, 2011.
- Perrino, C. and Gherardi, M.: Optimization of the coating layer for the measurement of ammonia by diffusion denuders, *Atmos. Environ.*, 33, 4579–4587, 1999.
- Perrino, C., De Santis, F., and Febo, A.: Criteria for the choice of a denuder sampling technique devoted to the measurement of atmospheric nitrous and nitric acids, *Atmos. Environ.*, 24A, 617–626, 1990.
- Perrino, C., Ramirez, D., and Allegrini, I.: Monitoring acidic air pollutants near Rome by means of diffusion lines: development of a specific quality control procedure, *Atmos. Environ.*, 35, 331–341, 2001.
- Pio, C. A. and Harrison, R. W.: Vapour pressure of ammonium chloride aerosol: effect of temperature and humidity, *Atmos. Environ.*, 21, 2711–2715, 1987.
- Pio, C. A., Nunes, T. V., and Leal, R. M.: Kinetic and thermodynamic behaviour of volatile ammonium compounds in industrial and marine atmosphere, *Atmos. Environ.*, 26A, 505–512, 1992.
- Plessow, K., Spindler, G., Zimmermann, F., and Matschullat, J.: Seasonal variations and interactions of N-containing gases and particles over a coniferous forest, Saxony, Germany, *Atmos. Environ.*, 39, 6995–7007, 2005.
- Possanzini, M., Febo, A., and Liberti, A.: New design of a high performance denuder for the sampling of atmospheric pollutants, *Atmos. Environ.*, 17, 2605–2610, 1983.
- Possanzini, M., Masia, P., and Di Palo, V.: Speciation of ammonium-containing species in atmospheric aerosols, *Atmos. Environ.*, 26A, 1995–2000, 1992.
- Possanzini, M., De Santis, F., and Di Palo, V.: Measurements of nitric acid and ammonium salts in lower Bavaria, *Atmos. Environ.*, 33, 3597–3602, 1999.
- Puxbaum, H., Haumer, G., Moser, K., and Ellinger, R.: Seasonal

- variation of  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$  and particulate matter at a rural site in north eastern Austria (Wolkersdorf, 240 m a.s.l.), *Atmos. Environ.*, 27A, 2445–2447, 1993.
- Robarge, W. P., Walker, J. T., McCulloch, R. B., and Murray, G.: Atmospheric concentrations of ammonia and ammonium at an agricultural site in the southeast United States, *Atmos. Environ.*, 36, 1661–1674, 2002.
- Sciare, J., Cachier, H., Sarda-Estève, R., Yu, T., and Wang, X.: Semi-volatile aerosols in Beijing (R.P. China): Characterization and influence on various  $\text{PM}_{2.5}$  measurements, *J. Geophys. Res.*, 112, D18202, doi:10.1029/2006JD007448, 2007.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics*, edited by: John Wiley & Sons, New York, USA, I., 1326 pp., 1998.
- Sickles, J. E., Hodson, L. L., and Vorburger, L. M.: Evaluation of the filter pack for long-duration sampling of ambient air, *Atmos. Environ.*, 33, 2187–2202, 1999a.
- Sickles II, J. E.: A summary of airborne concentrations of sulfur and nitrogen-containing pollutants in the north-eastern United States, *J. Air Waste Manage. Assoc.*, 49, 882–893, 1999b.
- Song Y., Zhang Y., Xie S., Zeng L., Zheng M., Salmon L. G., Shao M., and Slanina S.: Source apportionment of  $\text{PM}_{2.5}$  in Beijing by positive matrix factorization, *Atmos. Environ.*, 40, 1526–1537, 2006.
- Stelson, A. W. and Seinfeld, J. H.: Relative humidity and temperature dependence of the ammonium nitrate dissociation constant, *Atmos. Environ.*, 16, 983–992, 1982a.
- Stelson, A. W. and Seinfeld, J. H.: Relative Humidity and pH Dependence of the Vapor Pressure of Ammonium Nitrate-Nitric Acid and Solutions at 25 Degree Celsius; *Atmos. Environ.*, 16, 993–1000, 1982b.
- Stelson, A. W. and Seinfeld, J. H.: Thermodynamic prediction of the water activity,  $\text{NH}_4\text{NO}_3$  dissociation constant, density and refractive index for the  $\text{NH}_4\text{NO}_3$ – $(\text{NH}_4)_2\text{SO}_4$ – $\text{H}_2\text{O}$  System at 25 °C, *Atmos. Environ.*, 16, 2507–2514, 1982c.
- Stockwell, W. R., Krichner, F., Kuhn, M., and Seinfeld, J. H.: A new mechanism for regional atmospheric chemistry modeling, *J. Geophys. Res.*, 102, 25,847–25,879, doi:10.1029/97JD00849, 1997.
- Stockwell, W. R., Watson, J. G., Robinson, N. F., Steiner, W., and Sylte, W.: The ammonium nitrate particle equivalent of  $\text{NO}_x$  emissions for wintertime conditions in Central California's San Joaquin Valley, *Atmos. Environ.*, 34, 4711–4717, 2000.
- Streets, D. G., Fu, J. H. S., Jang, C. J., Hao, J. M., He, K. B., Tang, X. Y., Zhang, Y. H., Wang, Z. F., Li, Z. P., Zhang, Q., Wang, L. T., Wang, B. Y., and Yu, C.: Air quality during the 2008 Beijing olympic games, *Atmos. Environ.*, 41, 480–492, 2007.
- Sun, Y., Zhuang, S., Wang, Y., Han, L., Guo, J., Dan, M., Zhang, W., Wang, Z., and Hao, Z.: The air-borne particulate pollution in Beijing – concentration, composition, distribution and sources, *Atmos. Environ.*, 38, 5991–6004, 2004.
- Sun, J., Zhang, Q., Canagaratna, M. R., Zhang, Y., Ng, N. L., Sun, Y., Jayne, J. T., Zhang, X., Zhang, X., and Worsnop, D. R.: Highly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol Mass Spectrometer, 44, 131–140, *Atmos. Environ.*, 2010.
- Tang, I. N., Fung, K. H., Irnre, D. G., and Munkelwitz, H. R.: Phase transformation and metastability of hygroscopic microparticles, *J. Aerosol Sci.*, 23, 443–453, 1995.
- Taylor, J. R.: *An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements*, University Science Books, Mill Valley, CA, 1982.
- Trebs, I., Meixner, F. X., Slanina, J., Otjes, R., Jongejan, P., and Andreae, M. O.: Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin, *Atmos. Chem. Phys.*, 4, 967–987, doi:10.5194/acp-4-967-2004, 2004.
- Trebs, I., Metzger, S., Meixner, F. X., Helas, G., Hoffer, A., Andreae, M. O., Moura, M. A. L., da Silva Jr., R. S., Rudich, Y., Falkovich, A. H., Artaxo, P., and Slanina, J.: The  $\text{NH}_4^+$ – $\text{NO}_3^-$ – $\text{Cl}^-$ – $\text{SO}_4^{2-}$ – $\text{H}_2\text{O}$  aerosol system and its gas phase precursors at a pasture site in the Amazon Basin: How relevant are mineral cations and soluble organic acids?, *J. Geophys. Res.*, 110, D07303, doi:10.1029/2004JD005478, 2005.
- Vedal, S.: Critical review – ambient particles and health: Lines that divide, *J. Air Waste Manage. Assoc.*, 47, 551–581, 1997.
- Walker, J. T., Nelson, D., and Aneja, V. P.: Trends in ammonium concentration in precipitation and atmospheric ammonia emissions at a Coastal Plain site in North Carolina, USA, *Environ. Sci. Technol.*, 34, 3527–3534, 2000.
- Walker, J. T., Whitall, D. R., Robarge, W., and Paerl, H. W.: Ambient ammonia and ammonium aerosol across a region of variable ammonia emission density, *Atmos. Environ.*, 38, 1235–1246, 2004.
- Walker, J. T., Robarge, W., Shendrikar, A., and Kimball, H.: Inorganic  $\text{PM}_{2.5}$  at a U.S. agricultural site, *Environ. Pollut.*, 139, 258–271, 2006.
- Wang, Y., Zhuang, G., Tang, A., Yuan, H., Sun, Y., Chen, S., and Zheng, A.: The ion chemistry and the source of  $\text{PM}_{2.5}$  aerosol in Beijing, *Atmos. Environ.*, 39, 3771–3784, 2005.
- Wang, Y., Zhuang, G., Zhang, X., Huang, K., Xu, C., Tang, A., Chen, J., and Zheng, A.: The ion chemistry, seasonal cycle, and sources of  $\text{PM}_{2.5}$  and TSP aerosol in Shanghai, *Atmos. Environ.*, 40, 2935–2952, 2006.
- Wang, Y., Zhuang, G., Tang, A., Zhang, W., Sun, Y., Wang, Z., and An, Z.: The evolution of chemical components of aerosols at five monitoring sites of China during dust storms, *Atmos. Environ.*, 41, 1091–1106, 2007.
- Wang, H., Zhuang, Y., Wang, Y., Sun, Y., Yuan, H., Zhuang, G., and Hao, Z.: Long-term monitoring and source apportionment of  $\text{PM}_{2.5}/\text{PM}_{10}$  in Beijing, China, *J. Environ. Sci.*, 20, 1323–1327, 2008.
- Wehner, B., Birmili, W., Ditas, F., Wu, Z., Hu, M., Liu, X., Mao, J., Sugimoto, N., and Wiedensohler, A.: Relationships between submicrometer particulate air pollution and air mass history in Beijing, China, 2004–2006, *Atmos. Chem. Phys.*, 8, 6155–6168, doi:10.5194/acp-8-6155-2008, 2008.
- Wexler, A. S. and Seinfeld, J. H.: Second generation inorganic aerosol model, *Atmos. Environ.*, 25A, 2731–2748, 1991.
- Whitall, D. R. and Paerl, H. W.: Spatiotemporal variability of wet atmospheric nitrogen deposition to the Neuse River Estuary, NC, *J. Environ. Qual.*, 30, 1508–1515, 2001.
- Wu, P.-M., Ono, A., and Okada, K.: On the mixture of submicrometer nitrate-containing particles in the urban atmosphere, *J. Meteorol. Soc. Japan*, 65, 1005–1010, 1987.
- Wu, H. B. and Chan, C. K.: Effects of potassium nitrate on the solid phase transitions of ammonium nitrate particles, *Atmos. Environ.*, 42, 313–322, 2008.

- Wu, Z., Hu, M., Shao, K., and Slanina, J.: Acidic gases,  $\text{NH}_3$  and secondary inorganic ions in  $\text{PM}_{10}$  during summertime in Beijing, China and their relation to air mass history, *Chemosphere*, 76, 1028–1035, 2009.
- Xia, X., Chen, H., and Zhang, W.: Analysis of the dependence of column-integrated aerosol properties on long-range transport of air masses in Beijing, *Atmos. Environ.*, 41, 7739–7750, 2007.
- Xu, W. Y., Zhao, C. S., Ran, L., Deng, Z. Z., Liu, P. F., Ma, N., Lin, W. L., Xu, X. B., Yan, P., He, X., Yu, J., Liang, W. D., and Chen, L. L.: Characteristics of pollutants and their correlation to meteorological conditions at a suburban site in the North China Plain, *Atmos. Chem. Phys.*, 11, 4353–4369, doi:10.5194/acp-11-4353-2011, 2011.
- Yao, X., Chan, C. K., Fang, M., Cadle, S., Chan, T., Mulawa, P., He, K., Ye, B.: The water-soluble ionic composition of  $\text{PM}_{2.5}$  in Shanghai and Beijing, China, *Atmos. Environ.*, 36, 4223–4234, 2002.
- Yao, X., Lau, A. P. S., Fang, M., Chan, C. K., and Hu, M.: Size distributions and formation of ionic species in atmospheric particulate pollutants in Beijing, China: 1-inorganic ions, *Atmos. Environ.*, 37, 2991–3000, 2003.
- Yuan, C. S., Sau, C. C., and Chen, M. C.: Influence of Asian Dusts On the Physiochemical Properties of Atmospheric Aerosols in Taiwan District Using the Penchu Islands as an Example, *China Part.*, 2, 144–152, 2004.
- Zhang, D., Shi, G.-Y., Iwasaka, Y., and Hu, M.: Mixture of sulfate and nitrate in coastal atmospheric aerosols: individual particle studies in Qingdao ( $36^{\circ}04' \text{N}$ ,  $120^{\circ}21' \text{E}$ ), China, *Atmos. Environ.*, 34, 2669–2679, 2000.
- Zhang, Y., Zhu, X., Slanina, S., Shao, M., Zeng, L., Hu, M., Bergin, M., and Salmon, L.: Aerosol pollution in some chinese cities (IUPAC Technical report), *Pure Appl. Phys.*, 76, 1227–1239, 2004.
- Zhao, X., Zhang, X., Xu, X., Xu, J., Meng, W., and Pu, W.: Seasonal and diurnal variations of ambient  $\text{PM}_{2.5}$  concentration in urban and rural environments in Beijing, *Atmos. Environ.*, 43, 2893–2900, 2009.
- Zhao, Q., He, K., Rahn, K. A., Ma, Y., Jia, Y., Yang, F., Duan, F., Lei, Y., G, Chen, Cheng, Y., H, Liu, and Wang, S.: Dust storms come to Central and Southwestern China, too: implications from a major dust event in Chongqing, *Atmos. Chem. Phys.*, 10, 2615–2630, doi:10.5194/acp-10-2615-2010, 2010.
- Zheng, M., Salmon, L. G., Schauer, J. J., Zeng, L., Kiang, C. S., Zhang, Y., and Cass, G. R.: Seasonal trends in  $\text{PM}_{2.5}$  sources contributions in Beijing, China, *Atmos. Environ.*, 39, 3967–3976, 2005.