Chemical characteristics of inorganic ammonium salts in PM$_{2.5}$ in the atmosphere of Beijing (China)

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Abstract

The atmospheric concentrations of gaseous HNO$_3$, HCl and NH$_3$ 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 CAREBEIJING (Campaigns of Air Quality Research in Beijing and Surrounding Region). In this study, annular denuder technique was used with integration times of 2 and 24 h to collect inorganic and soluble PM$_{2.5}$ 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$^-$, NH$_4^+$ and SO$_4^{2-}$ exhibited distinct temporal variations, while fine particulate NO$_3^-$ did not show much variation with respect to season. Daily mean concentrations of fine particulate NH$_4^+$ and SO$_4^{2-}$ were higher during summer (12.30 µg m$^{-3}$ and 18.24 µg m$^{-3}$, respectively) than during winter (6.51 µg m$^{-3}$ and 7.50 µg m$^{-3}$, respectively). Instead, daily mean concentrations of fine particulate Cl$^-$ were higher during winter (2.94 µg m$^{-3}$) than during summer (0.79 µg m$^{-3}$), while fine particulate NO$_3^-$ showed similar variations both in winter (8.38 µg m$^{-3}$) and in summer (9.62 µg m$^{-3}$) periods. However, the presence of large amounts of fine particulate NO$_3^-$ even in summer are due to higher local and regional concentrations of NH$_3$ in the atmosphere available to neutralize H$_2$SO$_4$ and HNO$_3$, which is consistent with the observation that the measured particulate species were neutralized. Indeed, the composition of fine particulate matter indicated the domination of (NH$_4$)$_2$SO$_4$ during winter and summer periods. In addition, the high relative humidity conditions in summer period seemed to dissolve a significant fraction of HNO$_3$ and NH$_3$ enhancing fine particulate NO$_3^-$ and NH$_4^+$ 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 nearly by wind direction suggesting regional and local source influences. Indeed, the fine particulate species were also correlated with NO$_x$ and PM$_{2.5}$, supporting the hypothesis that the 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$_{2.5}$ with an aerodynamic diameter less than 2.5 µm, contribute mainly to the above phenomena. The major inorganic particles identified in PM$_{2.5}$ are sulphate (SO$_4^{2-}$), nitrate (NO$_3^-$), chloride (Cl$^-$) and ammonium (NH$_4^+$), which typically comprise 25–75 % of atmospheric PM$_{2.5}$ mass (Gray et al., 1986; Heitzenberg, 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, oxidation aqueous-phase oxidation and particulate-phase processes), such as sulphuric acid (H$_2$SO$_4$), nitric acid (HNO$_3$), hydrochloric acid (HCl) and ammonia (NH$_3$). H$_2$SO$_4$ and HNO$_3$ are atmospheric oxidation products of gaseous sulphur dioxide (SO$_2$) and nitrogen oxides (NO$_x$), respectively, while NH$_3$ is directly emitted into the atmosphere mainly by agricultural source.

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

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Gaseous NH$_3$ can be either wet or dry deposited, or can neutralize H$_2$SO$_4$, HNO$_3$ and HCl to form ammonium sulphate salts, and ammonium nitrate (NH$_4$NO$_3$) and ammonium chloride (NH$_4$Cl) salts via particle gas formation and gas to particle conversion (Baek and Aneja, 2005; Aneja et al., 2009). Ammonium nitrate (NH$_4$NO$_3$) and ammonium chloride (NH$_4$Cl) are formed via reversible phase equilibrium with precursor gases as NH$_3$, HNO$_3$ and 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 NH$_4$NO$_3$ and NH$_4$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 HNO$_3$ and 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. As a matter of fact, 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 NO$_x$, and proceeding via HNO$_3$ formation. Since this acid is subject to partitioning between gas and particle phase, the influence of 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 NO$_2$ with the OH. At night, the free nitrate radical (NO$_3$) is the source of tropospheric HNO$_3$. NO$_3$ either may combines with NO$_2$ to form dinitrogen pentoxide (N$_2$O$_5$), which reacts with water on particles, fog or cloud water droplets to produce HNO$_3$, 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 NH$_3$ to form NH$_4$NO$_3$. This reaction is believed to be the main source of fine particulate nitrate.
in urban air (Stockwell et al., 2000). A second frequent path for particulate nitrate formation involves nitric acid attach on the sodium chloride (NaCl) in sea salt particles to generate sodium nitrate (NaNO₃) aerosol and to release hydrochloric acid to the atmosphere.

The major source of HCl in the atmosphere is probably coal combustion. Globally, release of HCl from marine aerosols by reaction with less volatile HNO₃, H₂SO₄ or SO₂ is of considerable importance. Reaction of NO₂ with sodium chloride under photochemical conditions, emissions from volcanoes, and refuse incineration may constitute other sources of HCl in the atmosphere. Besides wet and dry deposition, a major sink for HCl will be neutralization by gaseous ammonia to form NH₄Cl aerosol.

The rapid industrial development and urbanization, increased vehicular population and energy consumption in Beijing (39°55′ N, 116°23′ E), the capital city of China, have led to an 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., 2006). Zheng et al. (2005) and Song et al. (2006) indicated that, as a primary source, traffic emissions in Beijing contributed 6–7 % to PM₂.₅ concentrations while the respective contribution from road dust resuspension was estimated to be 7–9 %. However, gaseous pollutants are also emitted by vehicular sources, such as NOₓ, which are essential for the atmospheric photochemical processes and the gas-to-particle conversions. NOₓ 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 PM₂.₅ in Beijing. Coal dominated energy structure is one of the major causes of air pollution in Beijing. Beijing’s power plants take about one third of the total coal consumptions emitting 49 % and 27 % of the total SO₂ and NOₓ emissions, respectively (He et al., 2003), which contribute to formation of atmospheric inorganic fine particles (nitrates and sulphates),
as said above.

PM$_{2.5}$ 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, 2008; Wang et al., 2005; Duan et al., 2006; Guinot et al., 2006). The sources of particulate matter in Beijing include the 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$_4^{2-}$, NO$_3^-$ and NH$_4^+$ 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$^{-3}$, respectively. In these studies the maximum concentrations appeared on 4 January 1999, 114, 31 and 27 µg m$^{-3}$ for above three ions, respectively. Yao et al. (2002) found that a large part of SO$_4^{2-}$ and NO$_3^-$ in PM$_{2.5}$ might be formed through the direct emissions of their precursor gases, such as SO$_2$, NO$_x$ and NH$_3$. However, data on PM$_{2.5}$, especially regarding the semi-volatile species in PM$_{2.5}$, e.g., NO$_3^-$ and Cl$^-$ are very limited. In a polluted urban environment, the volatile ammonium salts (NH$_4$NO$_3$ and NH$_4$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 simultaneous concentrations of NH$_3$, HCl, and HNO$_3$ observed that the concentration products of [HCl] [NH$_3$] and [HNO$_3$] [NH$_3$] were in agreement with theoretical values predicted by thermodynamic equilibrium laws for NH$_4$Cl and NH$_4$NO$_3$ 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 of 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 (NH$_4$NO$_3$ and NH$_4$Cl), are complicated by the existence of the thermodynamic equilibrium between precursor gases (HCl, HNO$_3$ and NH$_3$) and relative 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 HNO$_3$, HCl and 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 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 the 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 the Peking University (39°59′23″ N, 116°18′19″ E), located in the northwestern 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 HCl and HNO₃, followed by two sodium carbonate plus glycerol (1% Na₂CO₃ + 1% glycerol in 1:1 ethanol/water solution) coated denuders for the collection of HONO and SO₂. A fifth denuder was coated with phosphorous acid (1% H₃PO₄ in 9:1 ethanol/water solution) for the collection of NH₃ (Perrino and Gherardi, 1999; Perrino et al., 2001; Ianniello et al., 2010). Downstream of the denuder train a cyclone collected coarse particles (>2.5 µm aerodynamic diameter cut size at flow rate of 15 l/min), while fine particles (<2.5 µm at flow rate of 15 l min⁻¹) were collected on a filter pack set in series. The filter pack included a Teflon filter (Gelman Teflon, 47-mm, 1-µm pore size) for the collection of fine particles, a Nylon filter (Nylosorb Gelman, 47 mm, 1-µm pore size) and one phosphorous acid coated paper filter (Whatman 41). These last two back-up filters separately collected NO₃⁻ as HNO₃, Cl⁻ as 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). The dissociation products recovered on the back-up filters are indicated with term of evolved particulate species, estimating their concentrations from the nitrate, chloride and ammonium amounts measured on the back-up filters, as follows:

\[
\begin{align*}
[\text{NO}_3^-]_{\text{evolved}} &= [\text{NO}_3^-]_N \\
[\text{Cl}^-]_{\text{evolved}} &= [\text{Cl}^-]_N \\
[\text{NH}_4^+]_{\text{evolved}} &= [\text{NH}_4^+]_N + [\text{NH}_4^+]_{\text{PA}}
\end{align*}
\]

where subscripts N and PA stand for the Nylon filter and phosphorous acid coated paper filter, respectively. The concentration of $\text{NH}_4^+$ 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 unevolved particulate species. Thus, adding the amounts of $\text{Cl}^-$, $\text{NO}_3^-$ and $\text{NH}_4^+$ found on the Teflon filter (unevolved fine particles) to the respective amounts found on back-up filters (evolved fine particles), 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 $\text{NH}_4\text{NO}_3$), as follows:

\[
\begin{align*}
[\text{NO}_3^-]_{\text{fine}} &= [\text{NO}_3^-]_{\text{unevolved}} + [\text{NO}_3^-]_{\text{evolved}} \\
[\text{Cl}^-]_{\text{fine}} &= [\text{Cl}^-]_{\text{unevolved}} + [\text{Cl}^-]_{\text{evolved}} \\
[\text{NH}_4^+]_{\text{fine}} &= [\text{NH}_4^+]_{\text{unevolved}} + [\text{NH}_4^+]_{\text{evolved}}
\end{align*}
\]
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 15 l min\(^{-1}\). The sampling volume was about 23.10 m\(^3\) for a 24-h 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 µg m\(^{-3}\) for \( \text{NH}_4^+ \), 0.0093 µg m\(^{-3}\) for \( \text{Na}^+ \), 0.0051 µg m\(^{-3}\) for \( \text{K}^+ \), 0.0082 µg m\(^{-3}\) for \( \text{Mg}^{2+} \), 0.015 µg m\(^{-3}\) for \( \text{Ca}^{2+} \), 0.0013 µg m\(^{-3}\) for \( \text{SO}_4^{2-} \), 0.0014 µg m\(^{-3}\) for \( \text{NO}_3^- \) and 0.0073 µg m\(^{-3}\) for \( \text{Cl}^- \).

Information about the mixing properties of the lower boundary layer were obtained by means of a Stability Monitor (OPSIS 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 Cl\(^{-}\), NO\(_3\)^{−}, SO\(_4\)^{2−}, NH\(_4\)^{+}, Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), and Ca\(^{2+}\), and gaseous HNO\(_3\) and HCl determined by means of the annular denuder technique during the winter and summer periods at Beijing are listed in Table 1.

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 components by examining the amount of variation between the samples. Fine particulate Cl\(^{-}\), NH\(_4\)^{+} and 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 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 NO\(_3\)^{−} were 8.38 ± 3.00 µg m\(^{-3}\) and 9.62 ± 2.37 µg m\(^{-3}\) during winter and summer periods, respectively, and reached the maximum peak of 44.96 µg m\(^{-3}\) on 6 August 2007. Similar variation of NO\(_3\)^{−} concentrations has been reported by other studies (Erduran and Tuncel, 2001; Gupta et al., 2003). Particulate NO\(_3\)^{−} is mostly formed through gas to particle conversion and, therefore, through the oxidation of precursor gases, such as NO\(_x\), to nitrate. In winter, local 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 NO\(_3\)^{−} because NO\(_3\)^{−} and NO\(_2\) correlated significantly \((R^2 = 0.58, p < 0.001, \) at the 99.9 % confidence level). Thus, NO\(_2\) was converted to 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). However, the nitrate formation might be also ascribed to heterogeneous processes such as the condensation or absorption of NO\(_2\) in moist aerosols in addition to N\(_2\)O\(_5\) oxidation and 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 NO$_3^-$ and NO$_2$ did not occur, while significant correlation between fine particulate 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). 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 NO$_3^-$ and PM$_{2.5}$ in summer period showing the possible heterogeneous formation of particulate nitrate at Beijing. However, the presence of large amounts of fine particulate NO$_3^-$ even in summer is surprising since NH$_4$NO$_3$ is volatile and tends to dissociate and remain in gas phase under high temperatures. The mean concentration of NH$_3$ was $31.84 \pm 16.70 \mu g m^{-3}$ in summer period at Beijing, which was 6 times higher than in winter period of $5.22 \pm 3.75 \mu g m^{-3}$ (Ianniello et al., 2010). In addition, the temperatures ranged between 1 and 14 °C and 22 and 35 °C in winter and summer periods, respectively. Thus, the high concentrations of fine particulate NO$_3^-$ in summer period might be due to higher concentrations of NH$_3$ in the atmosphere available to neutralize H$_2$SO$_4$ and 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 HNO$_3$ and NH$_3$ in humid particles, therefore enhancing fine particulate NO$_3^-$ and 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 1, the mean concentrations of fine particulate Cl$^-$ were higher during the winter period (2.94 ± 0.79 µg m$^{-3}$) than during the summer period (0.79 ± 0.10 µg m$^{-3}$) and reached the maximum peak of 10.69 µg m$^{-3}$ on 4 February 2007. The major sources of particulate Cl$^-$ in Beijing might be associated to coal burning activities, which could explain the higher 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 NH$_4$Cl.
Mean concentrations of fine particulate NH$_4^+$ and SO$_4^{2-}$ were higher during summer (12.30 ± 2.48 µg m$^{-3}$ and 18.24 ± 2.01 µg m$^{-3}$, respectively) than during winter (6.51 ± 2.51 µg m$^{-3}$ and 7.50 ± 2.34 µg m$^{-3}$, respectively). Similarly to NH$_3$ (Ianniello et al., 2010), particulate NH$_4^+$ concentrations showed higher values during warm months (Sickles, 1999b; Walker et al., 2000, 2004; Whitall and Paerl, 2001; Robarge et al., 2002; Street et al., 2007; Ianniello et al., 2010), as shown in Table 1 and in Fig. 1. The temporal variations of fine particulate NH$_4^+$ basically coincided with those of fine particulate SO$_4^{2-}$, NO$_3^-$ and Cl$^-$, indicating that 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 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 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$_2$SO$_4$). 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$_2$SO$_4$, KNO$_3$ and KCl), and they were internally mixed.

It is worth to point out that [NH$_3$] in units of µmol m$^{-3}$ was always in same time scale above that of [HNO$_3$] + [HCl] in gas phase. Indeed, the ratio of [NH$_3$] to [HNO$_3$] + [HCl] was 27.90 ± 12.70 in the winter period and 54.06 ± 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. Thus, the evaluation of the chemical composition of fine particulate species collected on annular denuder/filter pack system can be used to calculate the \( \text{NH}_4^+ \) neutralization factor, defined as the molar ratio of \( \text{NH}_4^+ \) to the theoretical one, assuming complete conversion to \((\text{NH}_4)_2\text{SO}_4\), \(\text{NH}_4\text{NO}_3\) and \(\text{NH}_4\text{Cl}\). Thus, the ionic composition of PM\(_{2.5}\) has been evaluated with regard to the balance between the major anions (\(\text{NO}_3^-\), \(\text{Cl}^-\), \(\text{SO}_4^{2-}\)) 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 \(\text{NH}_4^+\) and \(\mu\text{mol m}^{-3}\) concentrations of fine particulate \(\text{SO}_4^{2-}\) \((R^2 = 0.85, p = 0.001)\) collected on the Teflon filters and a slope of this regression line of 3.82, higher than 2, suggested the complete neutralization of \(\text{H}_2\text{SO}_4\) by \(\text{NH}_3\) and a predominance of particulate \((\text{NH}_4)_2\text{SO}_4\) during the winter period (Possanzini et al., 1999; Walker et al., 2004). Thus, the excess of \(\text{NH}_4^+\) was inferred to be associated with fine particulate \(\text{Cl}^-\) and \(\text{NO}_3^-\). In addition, the ionic composition of PM\(_{2.5}\) has been also evaluated with regard to the balance between the major anions (\(\text{NO}_3^-\), \(\text{SO}_4^{2-}\), \(\text{Cl}^-\)) and ammonium. Indeed, 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 \(\text{NH}_3\) was present to completely neutralize all 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 \(\text{NH}_4\text{Cl}\). 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., \(\text{NaNO}_3\), \(\text{KNO}_3\), \(\text{NaCl}\), \(\text{KCl}\)). 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). Indeed, 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 \((R^2 = 0.90, \ p < 0.001)\). The slope of this regression line was 1.65, indicating an excellent ion balance and, thus, the presence on Nylon filters of \(\text{NH}_4\text{NO}_3\) and \(\text{NH}_4\text{Cl}\) 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 \(\text{NH}_3\), which represents the quantity of \(\text{NH}_3\) that would remain after complete neutralization of available aerosol and acid gases, is defined as:

\[
\text{Excess ammonia} = [\text{NH}_3] + [\text{NH}_4^+] - 2[\text{SO}_4^{2-}] - [\text{NO}_3^-] - [\text{HNO}_3] - [\text{HCl}] - [\text{Cl}^-]
\]

(7)

where all concentrations are in units of \(\mu\text{mol m}^{-3}\). Our results showed that excess \(\text{NH}_3\) 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 \(\text{NH}_4\text{NO}_3\) and \(\text{NH}_4\text{Cl}\). Hence, a part of the fine particulate nitrate and chloride might be bound as a relatively non-volatile salts of \(\text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^+\) or \(\text{Na}^+\). 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:

Free nitrate = \([\text{NO}_3^-] - \{2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+] - [\text{Cl}^-]\}\)

(8)

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

(9)

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 KNO_3 and NaNO_3 salts along with NH_4NO_3. Cl^- had also good correlations with cations K^+ (R^2 = 0.75, p < 0.001), suggesting the possible formation of KCl along with NH_4Cl. The presence of 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 K^+ concentrations were low (mean values of 1.07 µg 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 NH_4^+ with SO_4^{2-} collected on Teflon filters was also very strong (R^2 = 0.85, p < 0.001). The mean value of NH_4^+/SO_4^{2-} molar ratio was 2.10, indicating the complete neutralization of H_2SO_4 by NH_3 and a predominance of (NH_4)_2SO_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 NH_3 was present to neutralize the acidic components (H_2SO_4, HNO_3 and HCl) to form (NH_4)_2SO_4, NH_4NO_3 and NH_4Cl. Indeed, our results show also that excess NH_3 exists with a mean value of 1.60 µmol m^{-3} (27.20 µg 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). Indeed, a comparison between µmol m^{-3} amount of NH_4^+ with sum of µmol 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 = 0.70, p = 0.001) indicating the presence of NH_4NO_3 and NH_4Cl as constituent of the total fine particles.
Furthermore, free nitrate and chloride concentrations were also present with mean values of 0.10 µmol m\(^{-3}\) (6.20 µg m\(^{-3}\)) and 0.06 µmol m\(^{-3}\) (2.13 µg m\(^{-3}\)), respectively. Besides, NO\(^-\) showed significant correlation with cationic species such as K\(^+\) \((R^2 = 0.24, p < 0.001)\), indicating possible presence of non-volatile KNO\(_3\) salt along with NH\(_4\)NO\(_3\). However, the observed K\(^+\) concentrations were also low (mean values of 1.74 µg m\(^{-3}\)) and might not play a significant role in the formation of these particles in Beijing during summer period.

These results indicate that NH\(_4\)NO\(_3\), NH\(_4\)Cl, (NH\(_4\))\(_2\)SO\(_4\), K\(_2\)SO\(_4\) and 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 NH\(_3\)/HNO\(_3\)/NH\(_4\)NO\(_3\) (HNO\(_3\)(g) + NH\(_3\)(g) ↔ NH\(_4\)NO\(_3\)(s or aq)) and NH\(_3\)/HCl/NH\(_4\)Cl (HCl(g) + NH\(_3\)(g) ↔ NH\(_4\)Cl(s or aq)) systems under the meteorological conditions in Beijing during the winter and summer periods. The theoretical equilibrium dissociation constants for solid NH\(_4\)NO\(_3\) \((K_n)\) and for solid NH\(_4\)Cl \((K_c)\) were calculated and compared to the measured concentration products of NH\(_3\) and HNO\(_3\) \((K_{mn} = [HNO_3][NH_3])\) and of NH\(_3\) and HCl \((K_{mc} = [HCl][NH_3])\). The measured concentration product \(K_{mn}\) in units of ppb\(^2\) was determined using the measured data for 24-h sampling time while the theoretical equilibrium constant \(K_n\) in units of 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):

\[
\ln K_n = 84.6 - 24.220/T - 6.1 \ln(T/298) \quad (10)
\]

\[
\ln(RHD) = 723.7/T + 1.7037 \quad (11)
\]

The deliquescence relative humidity (DRH) (62 % RH for pure NH\(_4\)NO\(_3\), 298 K) 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 NH\(_4\)NO\(_3\) is modeled as a solid. At relative humidity
above that of deliquescence, NH$_4$NO$_3$ is modeled in the aqueous state. During the winter the ambient RH was always lower than RHD (Fig. 3), thus, NH$_4$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, NH$_4$NO$_3$ will be also in equilibrium with the aqueous phase and deliquescent particles. 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 NH$_4$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 K$^{-1}$ and from 3.3 to 3.4 K$^{-1}$ in the winter and summer, respectively, during the 24-h sampling periods in both seasons. In order for solid NH$_4$NO$_3$ to be formed in the atmosphere, the concentration products of HNO$_3$ and 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 2) 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 NH$_4$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 NH$_3$ even during the winter.

During the summer period, the results of thermodynamic calculations (Fig. 5) showed that almost on all days NH$_4$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 2), despite the fact that our measurements showed that the fine particulate ammonium nitrate was present at Bei-
jing 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 HNO$_3$ can easily be absorbed into the droplets. This coexistence of sulphate considerably reduces the thermodynamic dissociation constant $K_n$ for NH$_4$NO$_3$. Thus, the fine particulate nitrate can be formed from HNO$_3$ and NH$_3$ through heterogeneous reactions on fully neutralized fine particulate sulphate, which is abundantly present in an urban area. Indeed, 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%). Indeed, good and 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 NH$_3$ and 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 SO$_4^{2-}$, the NH$_4$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 NH$_4^+$, NO$_3^-$ and 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 NH$_4$NO$_3$ at Beijing site in summer period.

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

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

As far as the formation of solid NH$_4$Cl is concerned, the same procedure was applied. It is well known that the thermodynamic equilibrium conditions for the formation of NH$_4$NO$_3$ and NH$_4$Cl aerosols are similar and depend on humidity and temperature, with NH$_4$Cl showing a volatility 2–3 times higher than that of NH$_4$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 NH$_4$Cl exists in the solid phase in equilibrium with the gaseous products. The theoretical equilibrium constant $K_c$ in units of pbb$^2$ for solid NH$_4$Cl was calculated by Pio and Harrison (1987), when the ambient relative humidity is below the respective deliquescence relative humidity (DRH):

$$\ln K_c = 2.23581 \ln T - 2.13204 \times 10^4 T^{-1} + 65.4375 - 8.167 \times 10^{-3} T + 4.644 \times 10^{-7} T^2$$
$$- 1.105 \times 10^{-10} T^3$$ (12)

Thus, 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. Since HCl is more volatile than HNO$_3$, $K_c$ for NH$_4$Cl was higher than the theoretical value for NH$_4$NO$_3$ (Table 2), as seen in previous papers (Allen et al., 1989).
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. 11 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. Instead, 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 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 volatized 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). Indeed, 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%). Indeed, a good and 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 NH3 through heterogeneous reactions on neutralized sulphate particles.
These results indicate that NH₄Cl 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 Cl⁻, NO₃⁻, SO₄²⁻, and gaseous HNO₃, HCl and NH₃ along with meteorological 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°C and increased at 08:00 reaching maxima values of about 13.98°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 m s⁻¹ (0.02–8.85 m s⁻¹) and blew mainly from northwest, southwest and southeast.

The mean concentrations of fine particulate Cl⁻, NO₃⁻, SO₄²⁻, and NH₄⁺ for the entire data (N = 23) were 1.14±0.82 µg m⁻³, 2.01±1.09 µg m⁻³, 3.26±1.50 µg m⁻³ and 3.42±1.47 µg m⁻³, respectively. Besides, the concentration ranges were 0.28–3.22 µg m⁻³, 0.55–7.28 µg m⁻³, 1.35–7.25 µg m⁻³ and 1.53–8.98 µg m⁻³ for fine particulate Cl⁻, NO₃⁻, SO₄²⁻, and NH₄⁺, respectively.

The diurnal variations are evaluated applying the paired t test (p ≤ 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 Cl⁻, NO₃⁻, SO₄²⁻ and NH₄⁺ 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 Cl⁻ showed broad peaks in the morning (between 08:00 and 10:00) and in the evening (between 20:00 and 22:00). Indeed, the
mean chloride concentrations ranged from 0.28 to 3.51 $\mu$g m$^{-3}$ during the day and from 0.50 to 2.85 $\mu$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 NH$_4$Cl, NH$_4$NO$_3$, and ammonium sulphate salts. In addition, the similar diurnal variations of these measured species are consistent with the strong correlations between NH$_4^+$ and Cl$^-$, NO$_3^-$ and SO$_4^{2-}$. Indeed, the correlation coefficients were 0.86 ($p < 0.001$) for NH$_4^+$.Cl$^-$, 0.90 ($p < 0.001$) for NH$_4^+$.NO$_3^-$, and 0.96 ($p < 0.001$) for NH$_4^+$.SO$_4^{2-}$.

Furthermore, the nitrate, sulphate and ammonium concentrations reached maxima values of 7.30 $\mu$g m$^{-3}$, 7.25 $\mu$g m$^{-3}$ and 8.98 $\mu$g m$^{-3}$, respectively, at daytime and of 2.76 $\mu$g m$^{-3}$, 4.94 $\mu$g m$^{-3}$ and 4.04 $\mu$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). Indeed, lower wind speeds between 00:00 and 12:00 (0.02–1.53 m s$^{-1}$) and southeasterly and southwesterly wind directions (60 %) on 9 February, in combination with higher NO$_x$ concentrations and relative 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, NH$_4^+$ was strongly influenced by its gas phase precursor, such as NH$_3$, peaking between 08:00 and 10:00 in the morning and revealing much higher concentrations than the anionic species. Possible evaporation of 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 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 2). The mean values of $K_{mn}$ and $K_n$ for NH$_4$NO$_3$ were 1.49 ppb$^2$ and
0.35 ppb$^2$, respectively, and the mean values of $K_{mc}$ and $K_c$ for NH$_4$Cl were 0.78 ppb$^2$ and 0.60 ppb$^2$, respectively, during the intensive winter measurements. As discussed above, the atmosphere is ammonia rich in Beijing during winter period and, thus, ammonium nitrate and chloride formations were permitted.

To gain an insight into the impact of regional transport on 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 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 m s$^{-1}$), especially on 9 February between 00:00 and 12:00 (0.02–1.29 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 NO$_x$ concentrations in rush hours.

### 3.2.2 Summer

The diurnal variations of fine particulate species Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$, and gaseous HNO$_3$, HCl and NH$_3$, along with meteorological parameters (temperature, $T$, relative humidity, 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 ranged between 23.86°C and 33.22°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 m s\(^{-1}\) at 18:00 and blew mainly from south, northwest and southwest.

The mean concentrations of fine particulate Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), and NH\(_4^+\) for the entire data (\(N = 47\)) were 1.87 ± 1.05 µg m\(^{-3}\), 17.92 ± 8.38 µg m\(^{-3}\), 37.40 ± 10.80 µg m\(^{-3}\) and 23.81 ± 6.95 µg m\(^{-3}\), respectively. Besides, the concentration ranges were 0.07–5.52 µg m\(^{-3}\), 0.45–44.65 µg m\(^{-3}\), 14.56–83.71 µg m\(^{-3}\) and 7.80–39.23 µg m\(^{-3}\) for fine particulate Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), and NH\(_4^+\), respectively. The presence of substantial amounts of fine particulate matter such as fine particulate NO\(_3^-\) in summer period is interesting since fine particulate ammonium salts (NH\(_4^+\)NO\(_3^-\) and NH\(_4^+\)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 NO\(_3^-\) in August is that there was abundant NH\(_3\) to neutralize H\(_2\)SO\(_4\) and HNO\(_3\) and HCl, which is consistent with the results obtained from our measurements on the predominance of overall neutralized particles, such as (NH\(_4^+)\_2\)SO\(_4\) (see Sect. 3.1). In addition, the particulate matter in Beijing was likely humid due to high RH conditions, which might favor the absorption of NH\(_3\) and 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 Cl\(^-\), NO\(_3^-\) and 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 NH\(_4^+\) and Cl\(^-\), NO\(_3^-\) and SO\(_4^{2-}\). Indeed, the correlation coefficients were 0.80 (\(p = 0.001\)) for NH\(_4^+\)-Cl\(^-\), 0.85 (\(p < 0.001\)) for NH\(_4^+\)-NO\(_3^-\), and 0.90 (\(p < 0.001\)) for NH\(_4^+\)-SO\(_4^{2-}\). The variation of NH\(_4^+\) coincided with those of SO\(_4^{2-}\), NO\(_3^-\) and Cl\(^-\), indicating that NH\(_4^+\) largely originated from the neutralization between ammonia and acidic species. 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 NH\(_3\) dissolved in humid particles under high
RH conditions which increases $\text{NH}_4^+$ formation (Stelson and Seinfeld, 1982b,c; 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 be explained by a more regional formation originating from distant sources. Indeed, 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 good correlations between $\text{SO}_4^{2-}$ and RH, $\text{NO}_x$ and $\text{PM}_{2.5}$. Indeed, 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 2). The mean values of $K_{mn}$ and $K_n$ for $\text{NH}_4\text{NO}_3$ were 51.35 ppb$^2$ and 116.26 ppb$^2$ for $K_{mn}$ and $K_n$, respectively,
and the mean values of \( K_{mc} \) and \( K_c \) for NH\(_4\)Cl were 18.72 ppb\(^2\) and 267.01 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 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 NH\(_4^+\), NO\(_3^-\) and 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 NH\(_3\), SO\(_2\) and 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. Indeed, the local wind speeds, coming mainly from south and northwest of Beijing, arrived also slowly (0.02–3.83 m s\(^{-1}\)), especially between 06:00 and 10:00 (0.02–1.30 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 NO\(_x\) and PM\(_{2.5}\) between 06:00 and 10:00 (morning rush hour) for all days. Indeed, in Beijing 74\% of ground NO\(_x\) originates from vehicular emissions (Hao et al., 2005; Xu et al., 2011), while PM\(_{2.5}\) accounted for 90\% of total PM emissions from vehicle exhaust emissions (Zheng et al., 2005). The observed morning peaks of NO\(_x\) and 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 NH₃ and NOₓ, could be an effective method for alleviating secondary inorganic PM_{2.5} pollution in the urban atmospheres as in Beijing.

4 Conclusions

The atmospheric concentrations of gaseous HNO₃, HCl and NH₃ and their chemically related fine particulate species NH₄⁺, NO₃⁻, Cl⁻ and SO₄²⁻ 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 NH₃ and the particulate components (NH₄NO₃ and NH₄Cl). 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 Cl⁻, NH₄⁺ and SO₄²⁻ exhibited distinct temporal variations, while fine particulate NO₃⁻ did not show much variation with respect to season.

2. 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.

3. The atmosphere of Beijing was ammonia-rich in gas phase during the winter and summer periods. Thus, abundant NH₃ was present to neutralized the acid components, such as H₂SO₄, HNO₃ and 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.

4. 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.

5. 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 an influence by traffic emissions at Beijing.

6. Emissions from regional sources contributed also to the atmospheric levels of fine particulate species in winter and summer seasons at Beijing.

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| Species     | N | Min  | Max  | Median | Mean  | SD   |
|-------------|---|------|------|--------|-------|------|
|             |   | Winter |      |        |       |      |
| HNO$_3$     | 23 | 0.10 | 0.60 | 0.40   | 0.35  | 0.14 |
| HCl         | 23 | 0.07 | 0.77 | 0.17   | 0.22  | 0.10 |
| Cl$^-$      | 23 | 0.23 | 10.69| 1.96   | 2.94  | 0.79 |
| NO$_3^-$    | 23 | 0.25 | 31.80| 5.06   | 8.38  | 3.00 |
| SO$_4^{2-}$ | 23 | 0.40 | 22.37| 5.38   | 7.50  | 2.34 |
| NH$_4^+$    | 23 | 0.32 | 20.38| 4.50   | 6.51  | 2.51 |
| Na$^+$      | 23 | 0.04 | 3.60 | 0.41   | 0.59  | 0.73 |
| K$^+$       | 23 | 0.03 | 4.13 | 0.61   | 1.07  | 0.95 |
| Mg$^{2+}$   | 23 | 0.01 | 0.46 | 0.09   | 0.14  | 0.13 |
| Ca$^{2+}$   | 23 | 0.05 | 0.99 | 0.40   | 0.44  | 0.28 |
|             |   | Summer |      |        |       |      |
| HNO$_3$     | 30 | 0.26 | 3.94 | 2.08   | 1.92  | 0.91 |
| HCl         | 30 | 0.40 | 1.06 | 0.38   | 0.45  | 0.27 |
| Cl$^-$      | 30 | 0.06 | 3.02 | 0.57   | 0.79  | 0.10 |
| NO$_3^-$    | 30 | 1.09 | 44.96| 4.28   | 9.62  | 2.37 |
| SO$_4^{2-}$ | 30 | 2.70 | 57.13| 11.15  | 18.24 | 2.01 |
| NH$_4^+$    | 30 | 2.11 | 28.46| 8.78   | 12.30 | 2.48 |
| Na$^+$      | 30 | 0.14 | 1.89 | 0.47   | 0.57  | 0.42 |
| K$^+$       | 30 | 0.13 | 6.52 | 1.23   | 1.74  | 1.36 |
| Mg$^{2+}$   | 30 | 0.02 | 1.00 | 0.09   | 0.15  | 0.10 |
| Ca$^{2+}$   | 30 | 0.11 | 2.47 | 0.44   | 0.58  | 0.49 |
Table 2. Mean values ± standard deviation of some components, such as theoretical equilibrium constant ($K_n$) and measured concentration product ($K_{mn}$) of $NH_4NO_3$ formation and theoretical equilibrium constant ($K_c$) and measured concentration product ($K_{mc}$) of $NH_4Cl$ formation in the winter and summer periods at Beijing.

| Time | $N$ | $HNO_3$ (ppb) | HCl (ppb) | NH$_3$ (ppb) | $K_n$ (ppb$^2$) | $K_{mn}$ (ppb$^2$) | $K_c$ (ppb$^2$) | $K_{mc}$ (ppb$^2$) | $1000/T$ (K$^{-1}$) |
|------|-----|---------------|-----------|--------------|----------------|------------------|----------------|------------------|------------------|
| 2 h  | 24  | 0.18±0.11     | 0.10±0.12 | 7.21±1.50    | 0.35±0.19      | 1.49±0.40        | 0.60±0.40      | 0.78±0.25        | 3.58±0.04        |
| 24 h | 23  | 0.14±0.05     | 0.14±0.11 | 7.88±1.40    | 0.11±0.08      | 1.25±1.13        | 0.36±0.27      | 1.41±1.00        | 3.62±0.04        |
| 2 h  | 47  | 1.15±1.12     | 0.43±0.23 | 45.89±13.87  | 116.26±85.97   | 51.35±23.49      | 267.01±86.45   | 18.72±10.25      | 3.30±0.03        |
| 24 h | 30  | 0.75±0.35     | 0.30±0.17 | 36.59±9.96   | 73.51±20.23    | 27.79±17.33      | 172.65±40.07   | 11.75±9.28       | 3.32±0.02        |
Fig. 1. Temporal trends of fine particulate Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$, and gaseous HNO$_3$, HCl and NH$_3$, and temperature ($T$) during the winter and summer measurements at Beijing.
Fig. 2. Relationship between molar concentrations of fine particulate ammonium ($\text{NH}_4^+$) and the sum of the molar concentrations of fine particulate sulphate ($\text{SO}_4^{2-}$), nitrate ($\text{NO}_3^-$) and chloride ($\text{Cl}^-$) on the Teflon filters during the winter and summer measurements at Beijing.
Fig. 3. Temporal trends of temperature (T), relative humidity (RH), deliquescent relative humidity (RHD), and evolved and unevolved fine particulate ammonium (NH$_4^+$), sulphate (SO$_4^{2-}$), nitrate (NO$_3^-$) and chloride (Cl$^-$) during the winter measurements 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 at Beijing.
Fig. 5. Thermodynamically predicted equilibrium dissociation constant $K_n$ (black solid line) for pure NH$_4$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.
Fig. 6. Thermodynamically predicted equilibrium dissociation constant $K_n$ (black solid line) for pure NH$_4$NO$_3$, $K_n^*$ (grey solid line) for NH$_4^+$/NO$_3^-$/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.
Fig. 7. Thermodynamically predicted equilibrium dissociation constant $K_c$ (black solid line) for pure NH$_4$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.
Fig. 8. Diurnal trends of fine particulate Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$, and gaseous HNO$_3$, HCl and NH$_3$, and temperature ($T$), relative humidity (RH), wind speed and direction during the intensive winter measurements at Beijing.
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 at Beijing.