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Gas-to-particle conversion of atmospheric ammonia and sampling artifacts of ammonium in spring of Beijing

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$PM_{2.5}$ and gaseous pollutants (SO_2, HNO_2, HNO_3, HCl, and NH_3) were simultaneously collected by Partisol® Model 2300 Sequential Speciation Sampler with denuder-filter pack system in the spring of 2013 in Beijing. Water-soluble inorganic ions and gaseous pollutants were measured by Ion Chromatography. Results showed that the concentrations of NH_3, NH_4^+ and $PM_{2.5}$ had similar diurnal variation trends and their concentrations were higher at night than in daytime. The results of gas-to-particle conversion revealed that $[NH_3]:[NH_4^+]$ ratio was usually higher than 1; however, it was less than 1 and the concentration of NH_4^+ increased significantly during the haze episode, indicating that NH_3 played an important role in the formation of fine particle. Research on the sampling artifacts suggested that the volatilization loss of NH_4^+ was prevalent in the traditional single filter-based sampling. The excess loss of HNO_3 and HCl resulted from ammonium-poor aerosols and semivolatile inorganic species had severe losses in the clean day, whereas the mass of NH_4^+ was usually overestimated during the single filter-based sampling due to the positive artifacts. Correlation analysis was used to evaluate the influence of meteorological conditions on the volatilization loss of NH_4^+. It was found that the average relative humidity and temperature had great effects on the loss of NH_4^+. The loss of NH_4^+ was significantly under high temperature and low humidity, and tended to increase with the increasing of absorption of gaseous pollutants by denuder. The total mass of volatile loss of NH_4^+, NO_3^- and Cl^- could not be ignored and its maximum value was 12.17 μg m^{-3}. Therefore it is important to compensate sampling artifacts for semivolatile inorganic species.

ammonia, gas-to-particle conversion, $PM_{2.5}$, ammonium, sampling artifacts, diurnal variation

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Sulfate, nitrate, and ammonium (SNA) are important inorganic constituents of urban aerosol particle and account for 30%–70% of $PM_{2.5}$. SNA are formed mainly from the gas-to-particle transformation in the atmosphere, usually identified as secondary aerosol components, and influenced by the sources, energy structures, climatic conditions, and sampling locations (He et al., 2001; Yang et al., 2011; Deng et al., 2011; Tao et al., 2013). Ammonia (NH_3) are the prin-

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*Corresponding author (email: tanjh@ucas.ac.cn) cipal gaseous alkaline species in the atmosphere and primary precursors of NH_4^+ due to their neutralization with sulfuric acid, nitric acid, and hydrogen chloride to form NH_4NO_3, $(NH_4)_2SO_4$ and NH_4Cl (Seinfeld et al., 2012). So ammonia play an important role in the formation of SNA, especially the formation of haze (Sharma et al., 2007; Wang et al., 2011; Ye et al., 2011; Liu et al., 2005). Atmospheric ammonia are affected by the reaction with other gases and fine particles, and these interactions affect the gas-to-particle conversion, which is the key to understanding the formation of fine particle and haze (Baek et al., 2004b; Sharma et al., 2007; Tan et al., 2009a,b ; Ye et al., 2011).

Usually both NH_4NO_3 and NH_4Cl existed between gas and particulate phase. Negative sampling artifacts will occur due to the volatilization of nitric acid, hydrogen chloride and ammonia (eq. (1)) with the utilization of single filter-based sampling (Pathak et al., 2009; Wang et al., 2013; Ye et al., 2011). Moreover, ammonium nitrate may react with gaseous acids and release gaseous HNO_3 and NH_3 (eq. (2)), and then result in negative sampling artifact (Cheng et al., 1997; Pathak et al., 2009; Zhang et al., 1992). On the other hand, upstream denuders have not been commonly used to absorb acid-base gas (SO_2, HNO_2, HNO_3, HCl, and NH_3) in the domestic filter-based sampling system; therefore positive artifact will result from the uptake of gaseous pollutants by the filter and reaction between gaseous pollutants and particle collected on the filter bed.

$$NH_4NO_3\ (NH_4Cl)\ (p) \Leftrightarrow NH_3\ (g) + HNO_3\ (HCl)\ (g) \quad (1)$$

$$NH_4NO_3\ (p) + H_2SO_4,\ NH_4HSO_4,\ (NH_4)_3H(SO_4)_2 \rightarrow (NH_4)_2SO_4 + HNO_3\ (g) \quad (2)$$

Single filter-based sampling and filter pack systems without any denuders or without backup filters are still widely used and the extent of the sampling artifacts of volatile species in these sampling systems is not well understood (Cheng et al., 2010). But researches on semivolatile inorganic constituents sampling method have been carried out abroad since the 1980s and a systemic denuder-filter-post filter sampling method has been utilized in many chemical speciation monitoring networks. It is acknowledged that denuder-filter pack systems can reduce sampling artifacts by absorbing the interfering gases prior to particle collection and compensation with backup filters (Pathak et al., 2005). Despite the importance of sampling artifacts, there has been little domestic research on ammonium sampling artifacts. In reference to the USEPA aerosol speciation monitoring method and previous denuder-filter systems, this study tries to determine the extent of sampling artifacts in atmospheric ammonium measurement and its effect on $PM_{2.5}$. The results will be very helpful to providing higher accuracy and precision in the chemical composition monitor and mass closure of particulate matter, source apportionment, atmospheric environment modeling, and climate change assessment.

1 Experiment and methods

1.1 Site description

The sampling site was located on the roof (fifth floor) of a research building of University of Chinese Academy of Sciences (UCAS, 39.91°N, 116.24°E), in Shijingshan District, Beijing (Figure 1), which is surrounded by traffic roads, residential buildings, and business offices. There are no obvious industrial and local sources in the vicinity. A total of 180 samples were collected in the daytime (08:00 a.m.–07:00 p.m.) and at the nighttime (08:00 p.m.–07:00 a.m.) from April 9 to 27, 2013. The average temperature (*T*) and relative humidity (*RH*) were 12.9°C and 41.5% during the sampling period and wind directions were mainly from south, southeast or north.

1.2 Sampling method

Partisol® Model 2300 Sequential Speciation Sampler (Thermo Fisher Scientific Inc., USA) was used to collect $PM_{2.5}$ and gaseous SO_2, HNO_2, HNO_3, HCl, and NH_3. The schematic diagram of denuder-filter pack systems is shown in Figure 2. Channel A was set at a flow rate of 16.7 L/min with a single Teflon filter. Channel B consisted of two honeycomb glass denuders and a filter pack containing Teflon, Nylon, and Quartz fiber filter impregnated with citric acid, with a flow rate of 10.0 L/min. The Teflon filters were utilized for the collection of aerosol, the Nylon filters for the collection of HNO_3 and HCl released from particulate matter, and the Quartz fiber filters for the collection of NH_3 released from the evaporation of particle ammonium.

Denuders were cleaned and coated each time before sampling. The first denuder was coated with 10 mL of 1% (w/v) sodium carbonate and 1% (w/v) glycerin in the mixture of methanol/water (1∶1) to absorb HNO_3, HCl, HNO_2, and sulfur dioxide (SO_2). The second denuder was coated with 10 mL of 1% (w/v) citric acid in methanol solution for the absorption of gaseous NH_3. After coating, denuders were dried under N_2 in a positive-pressure glove box. Both ends of the denuder were capped with a polyethylene cap before use. More information about denuder coating and extraction is referred to Partisol® Model 2300 Sequential Speciation Sampler operating manual and USEPA standard operating procedure (USEPA, 1999).

1.3 Analysis

(1) Gravimetric measurements. Teflon filters were equilibrated in an *RH* (40±5%) and temperature (20±1°C) constant environment for at least 48 h before gravimetric analysis. Teflon filters were weighed at Peking University's clean room and exposed to a low-level radioactive source to remove the static charge at first and then weighed using Mettler micro-balance (Mettler-Toledo, AX105DR, Switzerland)

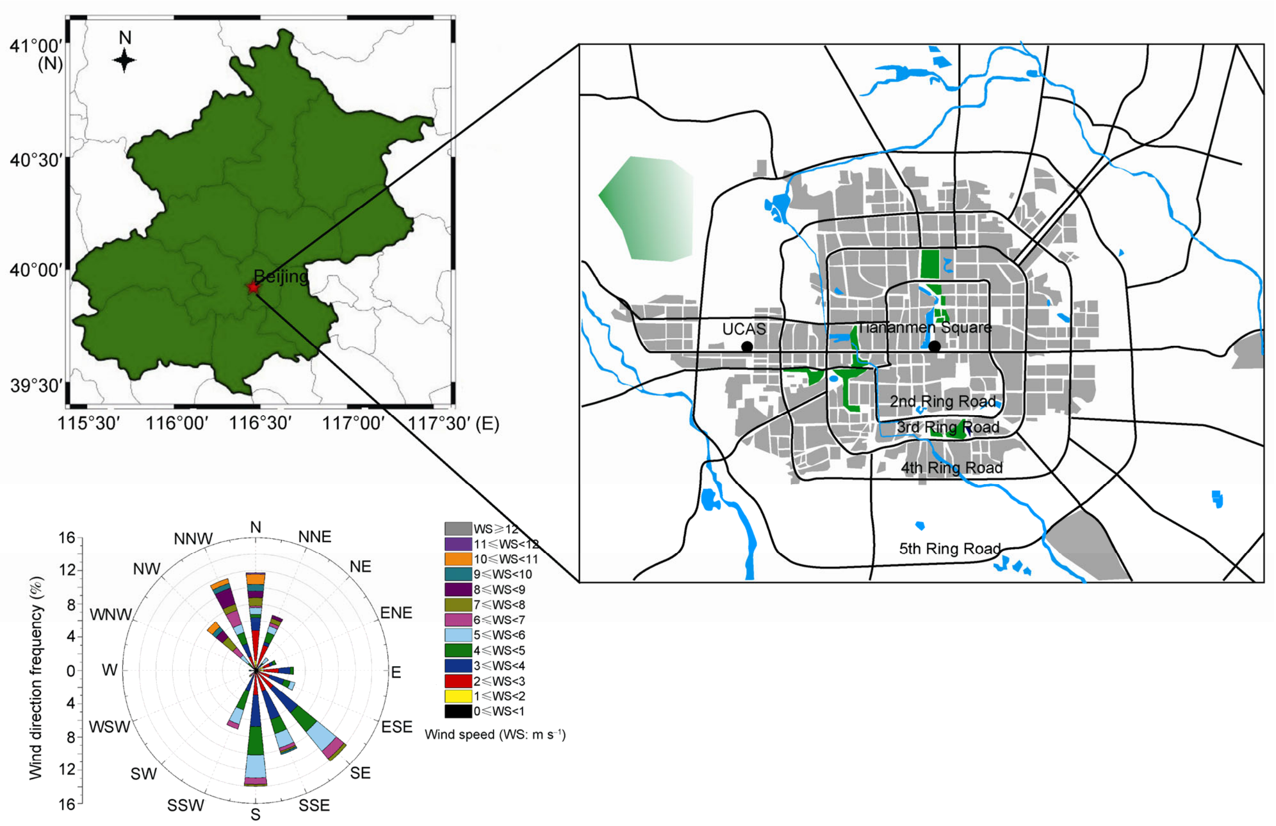

Figure 1 Location of sampling site and wind rose plot in April 2013.

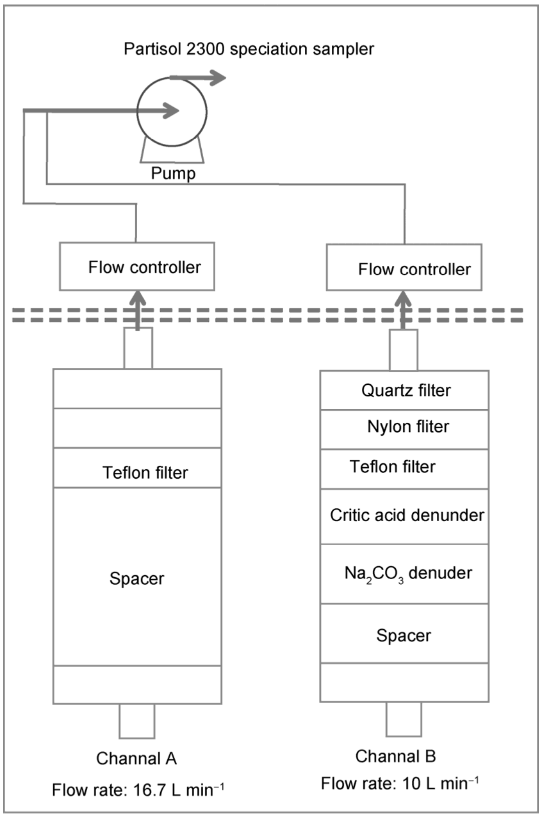

Figure 2 Schematics of sampling configuration.

with a sensitivity of ±1 μg. Each filter was measured three times before and after sampling and the average value was used. After being weighed, the exposed filters were stored at 4°C for chemical analysis.

(2) Filter extraction. Nylon and Quartz filters were extracted first with 10 mL ultrapure water and then with sonicate for 30 min. Since Teflon filter is hydrophobic, 100 μL ACS grade anhydrous ethanol (Sigma-Aldrich, USA) was added to the filter surface before water extraction. All extracts were refrigerated until analysis.

(3) Denuder extraction. Each denuder was extracted using 10 mL ultrapure water after sampling. 0.1 mL 3% hydrogen peroxide was added to the HNO_3 denuder to ensure the complete conversion of SO_3^{2-} to sulfate anion (SO_4^{2-}).

(4) Ion Chromatography (IC) analysis. The extraction from the denuder and filter was determined at Analysis and Testing Center of Beijing Normal University. Dionex DX-600 and ICS-2100 were used to analyze the major inorganic cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (F^-, Cl^-, NO_2^-, SO_4^{2-}, and NO_3^-), respectively.

1.4 Meteorological data

Meteorological data (temperature, pressure, dew point, relative humidity, wind speed, and precipitation activities, etc.) for Beijing Houhai Station in the vicinity of the UCAS sampling site were downloaded from wunderground website (http: //www.wunderground.com/).

2 Results and discussion

2.1 Diurnal variation of NH_3, NH_4^+ and $PM_{2.5}$

Gaseous pollutants and water soluble ionic species in fine particles were affected by meteorological conditions, emission sources, chemical reactions, etc. Figure 3 shows the time series variation of NH_3, NH_4^+, $PM_{2.5}$, and meteorological parameters (*T*, *RH*, wind direction and speed) during the sampling period. The concentrations of NH_3 and NH_4^+ both had similar diurnal variation trends with $PM_{2.5}$. The average concentration of NH_3, NH_4^+, $PM_{2.5}$ and meteorological parameters between day and night during non-haze and haze days are listed in Table 1. Under the constant wind direction, the concentration of pollutants showed a significant difference between daytime and nighttime and the concentrations at night were much higher than those in daytime. The mean ratios of NH_3, NH_4^+ and $PM_{2.5}$ between the night and daytime were 1.5, 1.2 and 1.3, respectively. Little increase of atmospheric pollutants at night resulted from the formation of inversion layer, low mixing height and low wind speed, and more pollutants that were accumulated near the ground (Wang et al., 2014).

In general, NH_4^+ constituted 10.8% of $PM_{2.5}$ mass on average, ranging from 3.5% to 20.5% and was the major cation in $PM_{2.5}$ during sampling period. A heavy haze episode was observed during April 21–23, and stagnation condition dominated under the alternation of northern winds and southern winds. Surface winds from north were dry with lower temperature and *RH*, which indicates the north continental air; surface winds from south with higher temperature and *RH*, indicative of south wind. The concentration of NH_3, NH_4^+ and $PM_{2.5}$ increased significantly from April 21 and reached the maximum concentration of 20.7, 34.3 and 209.2 μg m^{-3}, respectively, at night on April 23. When the wind came from northern China on April 24, the relatively clean air blew off the pollutants and it was not favorable for the formation of secondary aerosol. The concentrations of NH_3, NH_4^+ and $PM_{2.5}$ were 14.1, 24.1 and 150.1 μg m^{-3}, respectively, during haze episode, with an increase by the factors of 1.2, 5.5 and 3.2 from non-haze days. NH_4^+ showed a more remarkable increase than others and its contribution (15.9%) to $PM_{2.5}$ also showed an increase during haze episode. It was implied that NH_4^+ was the prime component of fine particles and NH_3 played an important role in the formation of inorganic secondary particles during the fog and haze episode (Tao et al., 2014).

2.2 Ammonia gas-to-particle conversion

SO_2 and NO*x* are subsequently oxidized to sulfuric acid and nitric acid by ozone or free radicals in the atmosphere, then form inorganic secondary particles, such as NH_4NO_3, $(NH_4)_2SO_4$ and NH_4HSO_4, via reaction with gaseous NH_3. However, the equilibrium of NH_4NO_3 and NH_4Cl between gas and particulate phase depends on temperature and relative humidity; meanwhile NH_4NO_3 and NH_4Cl are easily volatile under condition of high temperature and low relative humidity because of their low vapor pressure. Therefore the conversion between NH_3 and NH_4^+ is one of the important paths for their migration and transformation in the atmosphere.

As could be seen from Figure 4 and Table 1, the molar volume concentration ratios of NH_3 and NH_4^+ ($[NH_3]$:$[NH_4^+]$) were usually higher than 1, and they reached the maximum of 4.5 at night on April 13, while the concentrations of NH_3 and NH_4^+ were the lowest. It was reported that the gas-to-particle conversion of NH_3 and NH_4^+ was strongly affected by temperature, relative humidity, radiation conditions and the concentration of primary acid gas, and other factors. Low temperature, high relative humidity, and high levels of gaseous pollutants favor the formation of ammonium. So the conversion rate of NH_3 was low and the atmosphere was ammonia rich in the clear clean day. The ratio of $[NH_3]$:$[NH_4^+]$ showed statistically significant diurnal variation with high value at night compared to daytime. In spite of the accumulation of pollutants near the ground at

Table 1 NH_3, NH_4^+ and $PM_{2.5}$ concentration (μg m^{-3}) and meteorological parameters between day and night and during non-haze and haze days

	NH_3	NH_4^+	$PM_{2.5}$	$NH_4^+/PM_{2.5}$ (%)	$[NH_3]$:$[NH_4^+]$	*RH* (%)	*T* (°C)
Day	7.0[a)] (1.3–12.7)	8.6 (0.8–29.7)	61.3 (9.7–170.4)	10.5 (3.5–15.0)	1.5 (0.5–2.6)	30.8 (11.8–68.4)	17.1 (11.3–22.2)
Night	9.1 (1.2–20.7)	8.2 (0.7–34.3)	62.7 (4.1–209.2)	10.5 (5.4–17.8)	2.0 (0.6–4.5)	50.5 (16.5–90.8)	11.5 (5.6–14.8)
Night/day	1.5 (0.3–5.1)	1.2 (0.1–2.7)	1.3 (0.1–3.4)	1.1 (0.28–1.29)	1.5 (0.6–2.5)	–	–
Non-haze day	6.3 (1.2–14.3)	3.7 (0.7–7.1)	35.6 (4.1–80.4)	11.2 (5.7–25.8)	1.1 (2.1–4.5)	32.6 (11.8–57.4)	14.8 (5.6–22.2)
Haze day	14.1 (9.0–20.7)	24.1 (16.7–34.3)	150.1 (103.6–209.2)	15.9 (13.1–17.7)	0.7 (0.4–0.9)	67.7 (43.7–90.8)	12.8 (10.5–15.6)

a) The numerical representation of average (minimum–maximum).

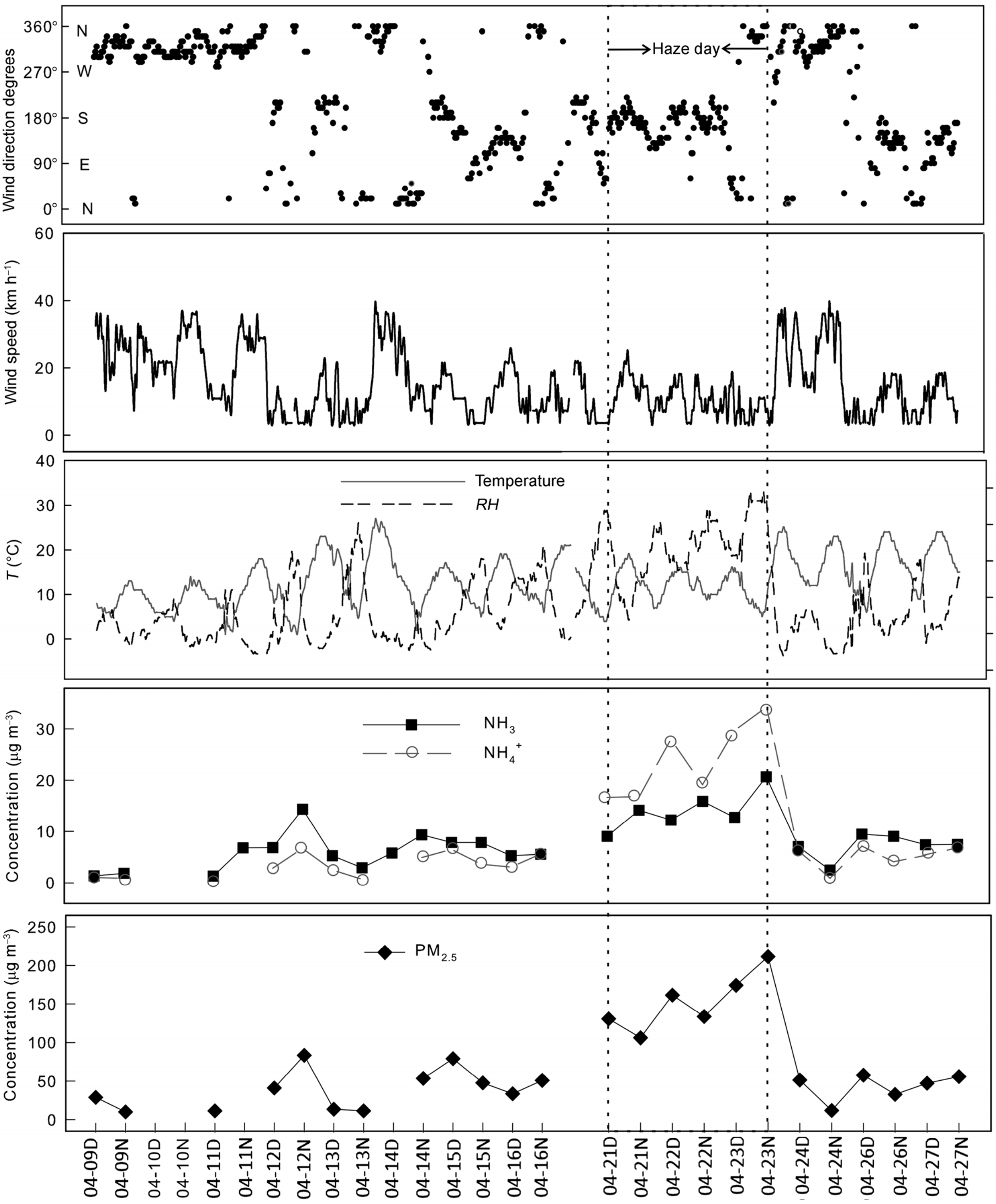

Figure 3 Time series variation of NH_3, NH_4^+, $PM_{2.5}$, and meteorological parameters. D, Day; N, night.

night, the conversion rate of NH_3 to NH_4^+ played a prominent role and was higher than that in the daytime in spring.

Unlike non-haze days, the ratio of $[NH_3]:[NH_4^+]$ was less than 1 during the haze period. Based on the analysis of acid gases (SO_2, HNO_2, HNO_3 and HCl) and meteorological parameters, it was found that the concentrations of acid gases and average *RH* (67.7%) had a significant increase from non-haze day to haze episode. The increased reaction rate of NH_3 and acidic gas would promote the transformation of NH_3 to NH_4^+. Previous studies had shown that NH_3 could easily react with H_2SO_4, HNO_3, HCl or other gaseous pollutants to form inorganic secondary particulate matter, resulting in the increase of fine particles (Baek et al, 2004a; Turšič et al, 2004). Under the condition of high *RH* and sufficient atmospheric NH_3, the production of sulfate increased significantly (Turšič et al., 2004). Hence, heterogeneous reactions would significantly enhance the conversion rate of gaseous precursors and formation rate of sec-

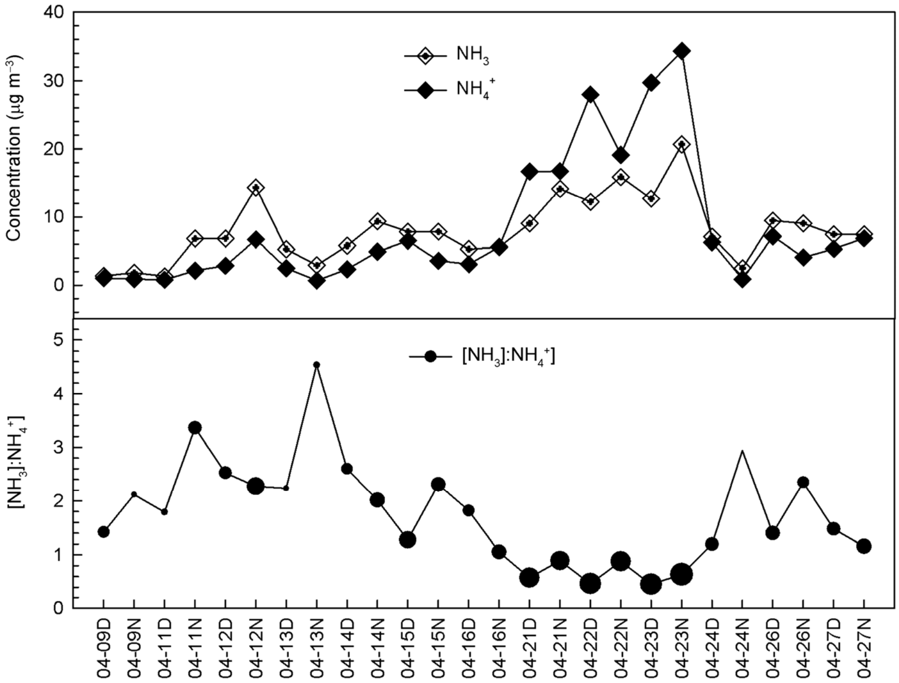

Figure 4 Diurnal variation of NH_3, NH_4^+ and $[NH_3]:[NH_4^+]$. The circle size represents $PM_{2.5}$ mass concentration.

ondary inorganic components, causing a substantial increase of particulate constituent such as NH_4^+ and SO_4^{2-} and resulting in the decrease of $[NH_3]:[NH_4^+]$ ratio. It could be concluded that NH_3 played a vital role in the neutralization of atmospheric acids and the formation of SNA. As a consequence, it would be effective to reduce the concentration of secondary inorganic particles and $PM_{2.5}$ by controlling the emission of NH_3.

2.3 Atmospheric particulate matter sampling artifacts

2.3.1 Particles ammonium negative sampling artifacts

SO_4^{2-}, NO_3^-, and NH_4^+ usually tend to exist as NH_4NO_3, $(NH_4)_2SO_4$, and NH_4Cl in particulate matter (Seinfeld et al., 2012). However, ammonium nitrate or ammonium chloride collected on the Telfon filter is easily to dissociate with changes in pressure drop, the concentration of ammonia and nitric acid, temperature or relative humidity during the conventional single filter-based sampling system, resulting in ammonium loss (Cheng et al., 1997).

This study reduced the positive sampling artifacts through the utilization of upstream denuders. The volatilization loss from the Teflon filter (Negative sampling artifacts) was collected on Nylon filter and Quartz filter coated with citric acid. NH_4^+ was detected on Quartz filter through all the experiments, indicating that the loss of ammonium was ubiquitous in our experiment. The ammonium loss was modest, with an average concentration of 0.7 µg m^{-3}, ranging from 0.1 to 1.9 µg/m^3. However, the loss percentage of NH_4^+ (the mass ratio of ammonium collected by Quartz filter to the total concentration of NH_4^+, which was defined as the sum of NH_4^+ from Teflon and Quartz filter) showed significant variations, ranging from 1.6% to 68.4%, with the average loss percentage of 16.1% (Figure 5). A negative correlation ($R = -0.50$, $P<0.01$, $N=26$) between the loss percentage of NH_4^+ and the total concentration of NH_4^+ indicates that the loss percentage of NH_4^+ decreased as the total concentration of NH_4^+ increased, and reached the minimum during haze episode, but the loss of NH_4^+ was still up to 1.9 µg m^{-3}. Meanwhile, under the condition of high temperature and low *RH* in the daytime, the equilibrium shifted from NH_4NO_3 and NH_4Cl to NH_3, HNO_3 and HCl, resulting in the higher loss percentage of NH_4^+ (Stelson et al., 1982). Thus the ammonium loss had little impact on NH_4^+ and $PM_{2.5}$ mass during the heavy pollution episode and there would be serious underestimations of NH_4^+ and $PM_{2.5}$ mass in clean days.

2.3.2 Sampling artifacts assessment

Compared to the determination of negative sampling artifacts of NH_4^+, it was difficult to determine its positive sampling artifacts. In this study, positive sampling artifacts were determined indirectly through the difference between two parallel channels. Since the total sampling artifacts of single filter-based sampling methods consist of positive and negative artifacts. Figure 6 shows the concentration of $PM_{2.5}$ and NH_4^+ for channel A and channel B. The concentrations of $PM_{2.5}$ and NH_4^+ for channel B were used to correct negative artifacts, i.e., $PM_{2.5\text{-B}}=PM_{2.5\text{-Teflon}}+NH_4^+{}_{\text{-Quartz}}+NO_3^-{}_{\text{-Nylon}}+Cl^-{}_{\text{-Nylon}}$; $NH_4^+{}_{\text{-B}}=NH_4^+{}_{\text{-Teflon}}+NH_4^+{}_{\text{-Quartz}}$. No significant

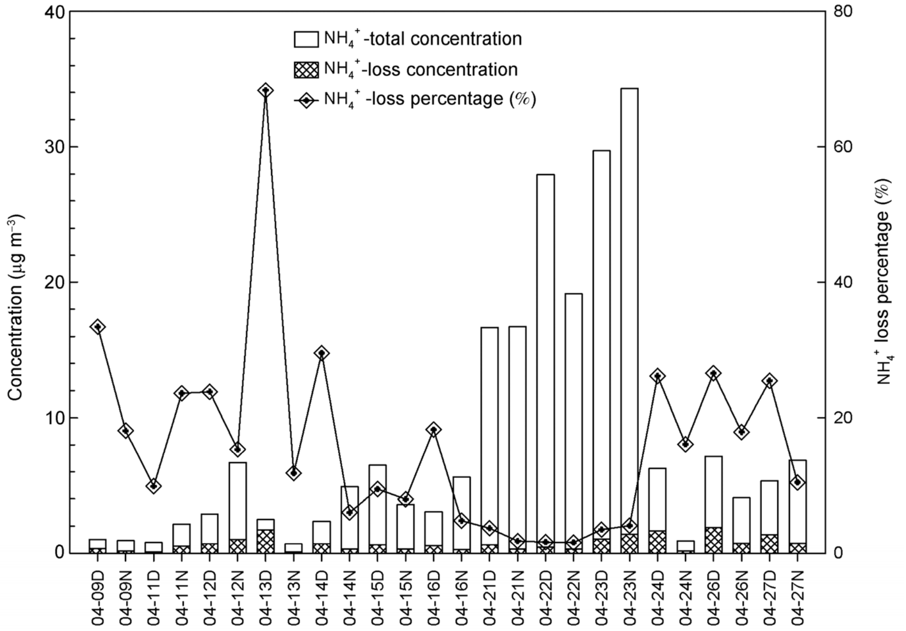

Figure 5 Diurnal variations of total NH_4^+, loss concentration and its loss percentage.

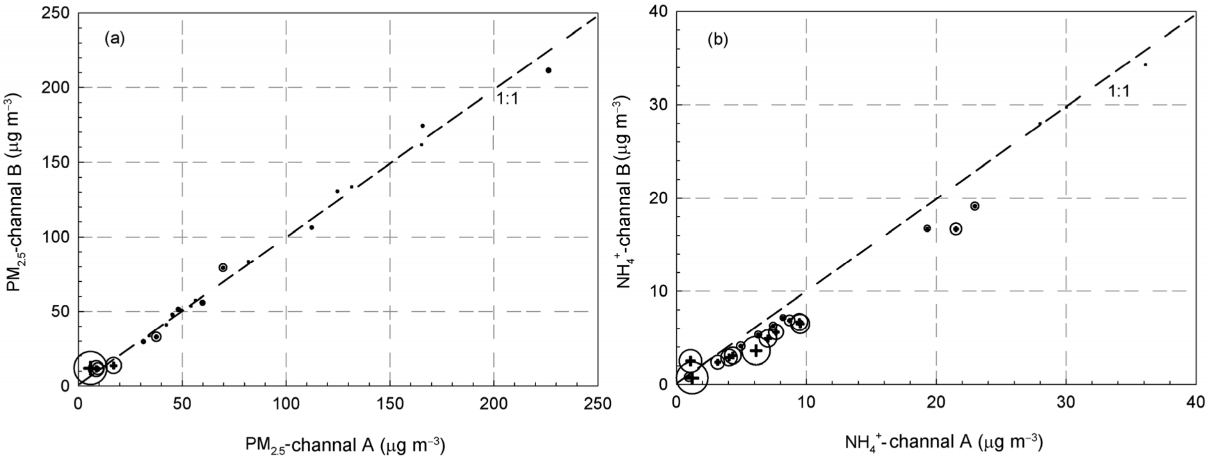

Figure 6 Comparison of $PM_{2.5}$ and NH_4^+ between channel A and channel B. Channel A is a single Teflon filter sampling method; channel B is denuder-filter pack systems. Circle size represents the extent of their sampling deviation ratio, defined as sampling deviation ratio of $PM_{2.5}=|(PM_{2.5\text{-}B})-(PM_{2.5\text{-}A})|/(PM_{2.5\text{-}B})$.

difference was found ($t=-0.27$, $P=0.79$, $N=26$) between two channels for $PM_{2.5}$ mass, whereas NH_4^+ was significantly different between two channels ($t=4.36$, $P<0.05$, $N=26$) through *t*-test analysis. It was concluded that the traditional single filter-based sampling method overestimated NH_4^+ mass in this study and the mean sample absolute deviation rate was 29.8%. Therefore, sampling positive artifacts of NH_4^+ were higher than the negative artifacts in spring. In addition, there was an inaccurate assessment of particulate matter and NH_4^+ in clear day because of their obvious sampling artifacts, which were influenced by many factors, including sampling seasons, locations, and pollution levels. So the key to reducing sampling artifacts of particulate matter and inorganic constituents is to improve filter sampling methods.

2.4 Influence factors of ammonium negative samples artifacts

2.4.1 *Relative humidity and temperature*

Previous studies indicated that the equilibrium of NH_4NO_3 and NH_4Cl could be affected by many factors, such as temperature, relative humidity, gaseous precursors (NH_3, HNO_3, etc.) as well as pressure drop during sampling process (Baek et al., 2004b). This study would investigate the effects of temperature difference (ΔT), average temperature (T_{ave}), relative humidity (RH_{ave}) and relative humidity difference (ΔRH) on ammonium loss. We defined the temperature difference (ΔT) as the difference between maximum and minimum temperature during the sampling period and the same as the definition of relative humidity difference (ΔRH).

Figure 7 shows the relationship of the loss percentage of ammonium with T_{ave}, ΔT, RH_{ave} and ΔRH. T and RH had different impacts on the volatilization loss of NH_4^+. The results of Curve Estimation Analysis in SPSS between influence factors and the volatilization loss of NH_4^+ indicated that there were weak positive correlations between T_{ave}, ΔT and loss percentage of ammonium, and the correlation coefficients (R) between T_{ave} and loss percentage of ammonium were 0.36 ($P<0.1$, $N=26$) and between ΔT and loss percentage were 0.39 ($P<0.1$, $N=26$). RH_{ave} had an obvious negative correlation with loss percentage of NH_4^+ ($R=-0.73$, $P<0.001$, $N=26$), whereas there was no significant correlation between ΔRH and loss percentage of NH_4^+. There were no obvious linear correlations between T, RH and volatilization loss of NH_4^+, probably due to the limited number of samples and the effects of temperature and RH on the equilibrium constant. Because gas-to-particle transformation of ammonium nitrate or ammonium chloride was not isolated, they did not exhibit a simple linear relationship (Yu et al., 2006). Hence, it was hard to determine the function between the sole factor and ammonium loss.

The loss rate of NH_4^+ tended to increase to some extent as ΔT increased, since the variation of temperature would influence the equilibrium of NH_4NO_3. Especially high temperature favored the volatilization of NH_4NO_3 to release gaseous NH_3 and HNO_3. When ΔT reached 18°C, average daily temperature came to a maximum and the loss was highest. Since the deliquescence and crystallization processes of NH_4NO_3 are irreversible, and the crystallization point is lower than deliquescence point, there will be a certain lag for the influence of temperature on NH_4^+ volatilization loss when T ranged from 18 to 23°C, resulting in little change of loss rate. Though the equilibrium constant of NH_4NO_3 was not sensitive to temperature changes under this condition, there was still a considerable amount of volatilization loss (Seinfeld et al., 2012).

It was reported that the volatilization loss of ammonium

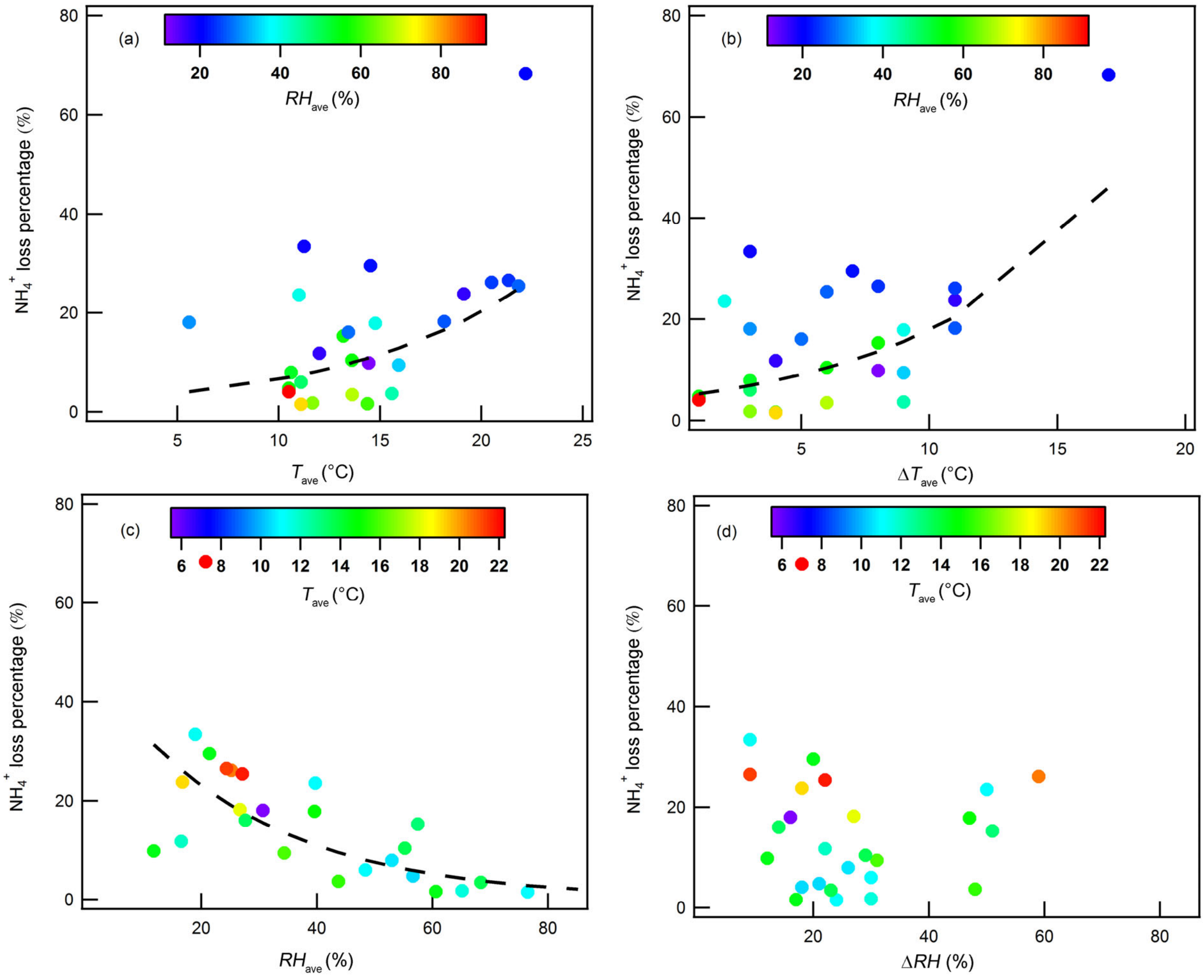

Figure 7 Relationships among NH_4^+ volatilization loss, temperature, and relative humidity. The dotted line is a fitting curve for all data points, indicating trends of influence factors on loss.

nitrate was significant when relative humidity was below its deliquescence point (*RH*=60% at 25°C); however, it could be negligible when *RH* was near ~100% (Forrest et al., 1980. Tang, 1980). This study also showed an obvious ammonium loss when *RH* was below 60% and there was an increasing trend of evaporation loss as *RH* decreased, whereas the loss percentage of NH_4^+ could be negligible when *RH* was higher than 60%. Compared to the prediction of theory model, the measured sharp transition point for the relationship between *RH* and loss rate would shift toward lower *RH* direction in this study, resulting in lower deliquescence point of NH_4NO_3 because of mixed impurities in particulate matter, such as $NaNO_3$. For the most part, *RH* and temperature both had great influences on ammonium volatilization, the dissociation of semivolatile ammonium species would be easily promoted, and gaseous NH_3 would be released under the condition of high temperature and low relative humidity (Du et al., 2010).

2.4.2 *Gaseous pollutions*

Figure 8 shows the dependence of NH_4^+ loss rate on $[NH_3]$: $[N(-III)]$ and $[HNO_3][NH_3]$. An exponential growth relationship between the NH_4^+ loss rate and $[NH_3]$: $[N(-III)]$ ($[N(-III)]$= particulate NH_4^+ +gaseous NH_3 was found in this study, and they were significantly correlated (*R*=0.49, *P*<0.001, *N*=26). When the proportion of gaseous NH_3 in the total ammonia increased, the NH_4^+ loss rate increased at the same time. Meanwhile there appeared to be a significant growth of loss rate as the ratio of $[NH_3]$: $[N(-III)]$ exceeded a value about 0.5, which was consistent with Zhang and McCurry's theoretical predictions (Zhang et al., 1992).

In addition, the concentrations of primary gaseous precursors, such as HNO_3, HCl and NH_3, also simultaneously affect the equilibrium of NH_4NO_3 and NH_4Cl. As could be seen from the relationship between $[HNO_3][NH_3]$ and $[NH_4^+]$ molar yield loss, they were in a quadratic growth correlation (*R*=0.50, *P*<0.05, *N*=26). But there was no significant relationship between $[HCl][NH_3]$ and $[NH_4^+]$ molar yield loss, probably due to the lower concentration of particulate NH_4Cl. The absorption of gaseous pollutants by the two upstream denuders broke the balance of NH_4NO_3 or NH_4Cl, resulting in higher volatilization loss to gaseous NH_3 and HNO_3. Therefore it is important to take compensation for negative sampling artifacts with backup filters.

2.5 Sampling artifacts compensation for semivolatile inorganic components

Loss of $[NH_4^+]$ (unit in molar concentration) against the sum of $[NO_3^-]$ and $[Cl^-]$ is shown in Figure 9. The loss of NH_4NO_3 and NH_4Cl ranged from 0.08 to 10.53 μg/m^3, with an average of 2.99 μg m^{-3}. Assuming the loss was caused mainly by the evaporation of NH_4NO_3 and NH_4Cl, the ratio of $([NO_3^-] + [Cl^-]):[NH_4^+]$ should be about 1. But the results indicated that the loss of $([NO_3^-] + [Cl^-])$ were higher than $[NH_4^+]$ and $([NO_3^-] + [Cl^-]):[NH_4^+]$ ratio could reach the maximum value of 3.03, with an average ratio of 1.49 (Figure 9), implying that there were excess losses of HNO_3 and HCl during sampling period in spring. When atmosphere was ammonium poor and the molar ratio of $[NH_4^+]$ and $[SO_4^{2-}]$ was less than or equal to 1.5, this phenomenon was particularly obvious (Pathak et al, 2004.). Matsumoto and Okita (1998), however, suggested that the dissociation of NH_4NO_3 and NH_4Cl from the filter was the principal loss of aerosol in Japan and the ratio $([NO_3^-] + [Cl^-]):[NH_4^+]$ was about 1, which was very different from our study. Hence further research on sampling loss should be carried out.

If atmospheric particle sampling artifacts were only corrected with the loss of NH_4^+, Cl^- or NO_3^-, the mass of atmospheric particle would also be underestimated. Previous study confirmed that, except for semivolatile inorganic components, such as NH_4NO_3 and NH_4Cl, ammoniated organic salts were also observed as important contributors to ammonium loss at the Great Smoky Mountains National

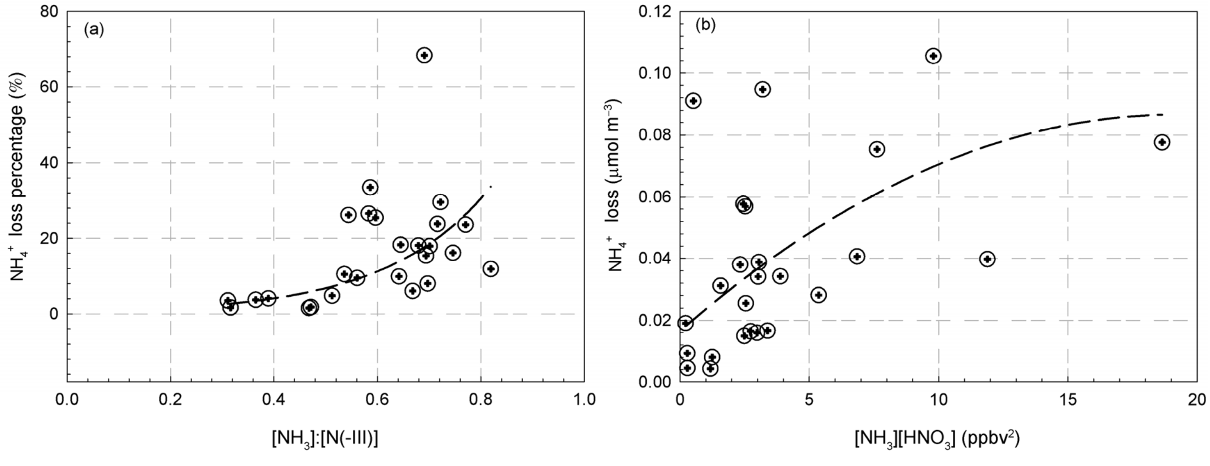

Figure 8 The relationship between NH_4^+ loss and $[NH_3]:[N(-III)]$, $[NH_3][HNO_3]$. The dotted line is a fitting curve for all data points.

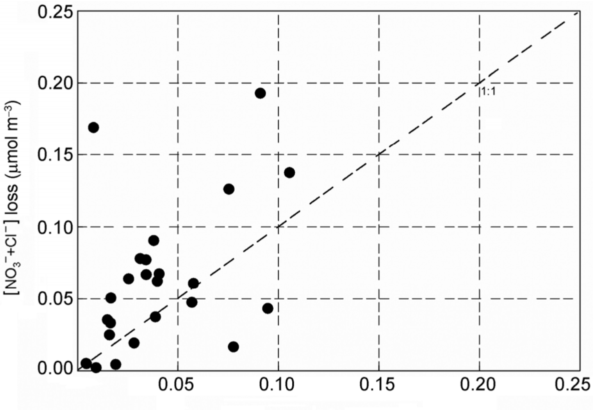

Figure 9 Relationship between $[NH_4^+]$ loss and ($[NO_3^-]$ + $[Cl^-]$) loss.

Park in America, which resulted in more $[NH_4^+]$ loss than the measured total $[NO_3^-]$ (Yu et al., 2006). Figyre 10 compares the measured inorganic species loss and the calculated NH_4NO_3 loss. The measured volatilization loss of NH_4^+, NO_3^- and Cl^- could not be ignored, with the average concentration of 3.68 μg m^{-3} and the maximum of 12.17 μg m^{-3}. The proportion of total concentration of loss to $PM_{2.5}$ mass ranged from 1.85% to 41.44%, and was mostly about 10%. Therefore, the single Teflon filter-based sampling method without any compensation for semivolatile constituents sample loss will overestimate or underestimate the concentration of secondary inorganic particles, and thereby lead to an inaccurate assessment of aerosol acidity, formation mechanism of secondary inorganic aerosols, source apportionment, and pollution control measurement.

3 Conclusions

The ratio of $[NH_3]:[NH_4^+]$ was generally higher than 1, but less than 1 due to the enhancement of the reaction rate of NH_3 with acid gas and the formation rate of NH_4^+ during haze episode. Ammonium volatilization loss occurred through the experiments and its proportion to $PM_{2.5}$ mass ranged from 1.56% to 68.35%, and the proportion reached the lowest with the concentration of loss of 1.90 μg/m^3 in haze days. Meteorological parameters, especially for relative humidity, had a great impact on ammonium loss, which increased with the increase of absorption of gaseous pollution by upstream denuders. However, the concentration of NH_4^+ was overestimated because of positive sampling artifacts using single traditional filter-based sampling methods. The loss of semivolatile inorganic components could not be ignored during atmospheric particle sampling process. The loss of NH_4^+, NO_3^-, and Cl^- accounting for particulate matter ranged from 1.85% to 41.44%, and there were excessive losses of HNO_3 and HCl. Thus more researches on the sampling artifacts of particulate matter and its chemical composition will be helpful to accurately determining aerosol acidity, formation mechanism of secondary inorganic aerosol, source apportionment, and pollution control.

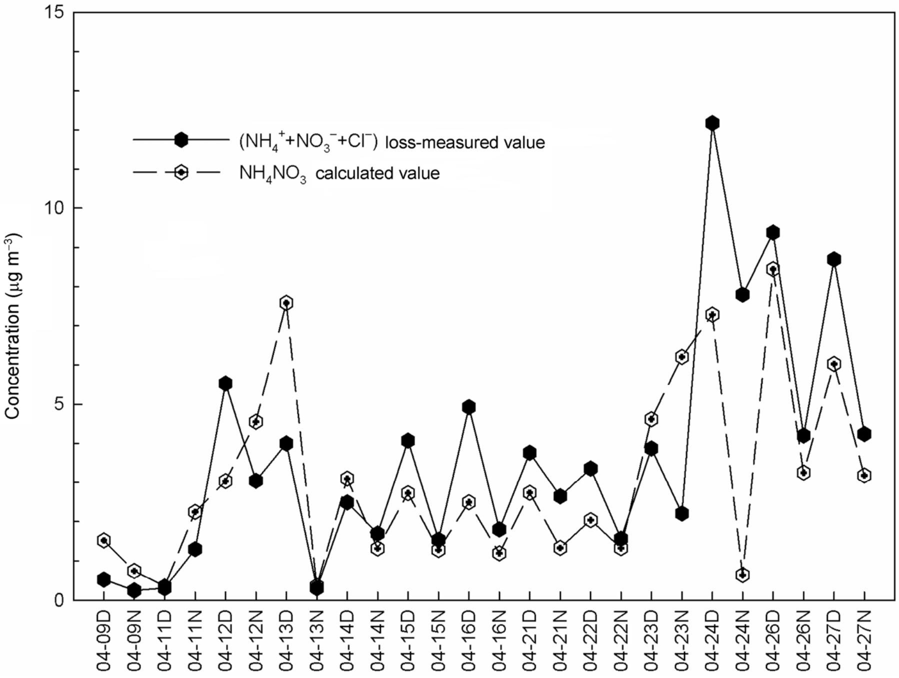

Figure 10 Relationship between the measured and calculated loss of NH_4NO_3.

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