



## Insights into Ammonium Particle-to-Gas Conversion: Non-sulfate Ammonium Coupling with Nitrate and Chloride

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### ABSTRACT

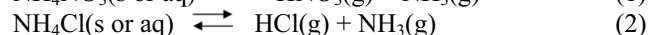
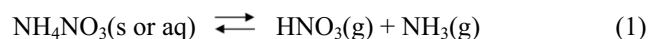
Significant amounts of ammonia, nitric acid and hydrochloric acid as ammonium particle precursors have been found in urban polluted air. In order to advance understanding the formation and dissociation of ammonium nitrate and ammonium chloride, an on-line analyzer for monitoring aerosols and gases in the ambient air was employed to measure the concentrations of sulfate, nitrate and chloride in aerosols as well as related gaseous precursors at one hour resolution. The highest levels of summed hourly-averaged sulfate, nitrate, chloride and ammonium reached up to 177.7  $\mu\text{g}/\text{m}^3$  in  $\text{PM}_{10}$  from 12 to 14 June, and 101.2  $\mu\text{g}/\text{m}^3$  in  $\text{PM}_{2.5}$  from 1 to 3 July, 2009 in Shanghai. Ammonium nitrate and ammonium chloride were popular in aerosols with a strong linear correlation between non-sulfate ammonium ( $\text{ns-NH}_4^+$ ) and nitrate (or nitrate plus chloride). Ammonium equivalent concentration was always less than the sum of sulfate, nitrate and chloride due to ammonium-poor aerosols, whereas the atmosphere was ammonia-rich in gas phase. The ratio of gaseous nitric acid to total nitrate less than that of hydrochloric acid to total chloride both in  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  indicated that ammonium nitrate was more favored to be formed than ammonium chloride.

**Keywords:** Particle-to-Gas Conversion; Chemical Coupling; pseudo-equilibrium constants; Gas/Particle Partitioning.

### INTRODUCTION

Ammonium sulfate, ammonium nitrate and ammonium chloride are common components of atmospheric aerosols. Both  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  undergo reversible exchanges between gas and particle phase (Pio *et al.*, 1987a; Allen *et al.*, 1989; Matsumoto *et al.*, 1996). The unique atmospheric process associated with the partitioning is a challenge to understand air quality, airborne acidity, visibility and climate change. Ammonia is the primary alkaline gas in the atmosphere, and thus plays a major role in the neutralization of atmospheric acid gases (McMurry *et al.*, 1983). Ammonia was believed to be neutralized first by sulfuric acid to form ammonium sulfate or ammonium bisulfate.

The excess part of  $\text{NH}_3$  could react with nitric acid to form  $\text{NH}_4\text{NO}_3$  and with hydrochloric acid to form  $\text{NH}_4\text{Cl}$  (McMurry *et al.*, 1983; Yuan *et al.*, 2003; Wang *et al.*, 2005). Alternatively,  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  are thermodynamically unstable under normal atmospheric conditions, existing in the reversible phase equilibrium with gaseous precursors as following (Pio *et al.*, 1987a):



Besides laboratory experiments that revealed the chemical equilibrium of formation and dissociation of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$ , several field measurements have tested the validity of these equilibrium assumptions (Doyle *et al.*, 1979; Harrison *et al.*, 1983; Harrison *et al.*, 1994). A qualitative agreement was found between the equilibrium constant  $K_{\text{NH}_4\text{NO}_3}$  of the reaction (1) and the product of  $[\text{HNO}_3][\text{NH}_3]$ . So was the equilibrium  $K_{\text{NH}_4\text{Cl}}$  for the reaction (2) (Stelson *et al.*, 1978). The diurnal pattern of  $K_{\text{NH}_4\text{NO}_3}$  often showed a close agreement with  $K_{\text{NH}_4\text{Cl}}$ , indicating remarkably similar behaviors of these

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components. Due to solid ammonium chloride more volatile, the equilibrium concentrations of HCl were 1.5–2 times higher than HNO<sub>3</sub> levels at the same ammonia concentration in the atmosphere (Pio *et al.*, 1987a). Cadle *et al.* (1982) has shown the theoretical products of [HNO<sub>3</sub>] [NH<sub>3</sub>] both in urban and rural sites were above or below the NH<sub>4</sub>NO<sub>3</sub> equilibrium constants. In addition, previous studies had proved the equilibrium constants of these two reversible reactions increased with temperature but decreased with relative humidity (Stelson *et al.*, 1982a; Harrison *et al.*, 1990). Therefore, particle-to-gas conversion of NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl was favored under high temperature and low relative humidity.

Recent work considered phase transitions of both NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>Cl occurred through various physical and chemical interactions and transformations (Monks *et al.*, 2009). Mehlmann *et al.* (1995) had reported that ammonium nitrate was largely absent because the product of the concentrations of nitric acid and ammonia was below the minimum required for equilibrium concentrations of particulate NH<sub>4</sub>NO<sub>3</sub> to be formed. Parmar *et al.* (2001) discussed both seasonal and diurnal pattern of ammonia, nitric acid and their equilibrium relationship, and found that measured concentration products ([HNO<sub>3</sub>] [NH<sub>3</sub>]) were qualitatively below the predicted equilibrium values for monsoon data while those lied consistently above the predicted equilibrium values in winter. Therefore, there is a need for an improved understanding of ammonium particle-to-gas conversion under present polluted environment.

Here we presented major water-soluble inorganic ions in aerosols and gaseous precursors measured by an instrument of Monitoring AeRosols and Gases (MARGA) in Shanghai with one hour resolution (Li *et al.*, 2010). This instrument can afford sample concentration with higher temporal resolution continuously than that previous studies used. This study was aimed to the ammonium particle-to-gas conversion based on chemical coupling between non-sulfate ammonium and nitrate (or nitrate plus chloride).

## EXPERIMENTAL SECTION

The observation site (31.3°N, 121.5°E) was located on the roof of No.4 Teaching Building about 20 m height above the ground in the campus of Fudan University in Shanghai. This site was under the influence of residential, traffic, and construction emissions and could be the representative of urban Shanghai.

A model ADI 2080 online analyzer for Monitoring of AeRosols and Gases (MARGA, Applikon Analytical B.V. Corp., the Netherlands) with a particulate matter sampler (PM<sub>2.5</sub> or PM<sub>10</sub>) was used to conduct intensive measurements from June to July 2009. MARGA consists of a sampling box and an analytical box. After ambient air is absorbed into the sampling box with a flow rate of 1 m<sup>3</sup>/h through inlet, gaseous components are dissolved into the liquid film (0.0035% H<sub>2</sub>O<sub>2</sub>) formed by one Wet Rotating Denuder (WRD), and then particles in remaining airflow pass through one supersaturated steam (0.0035%

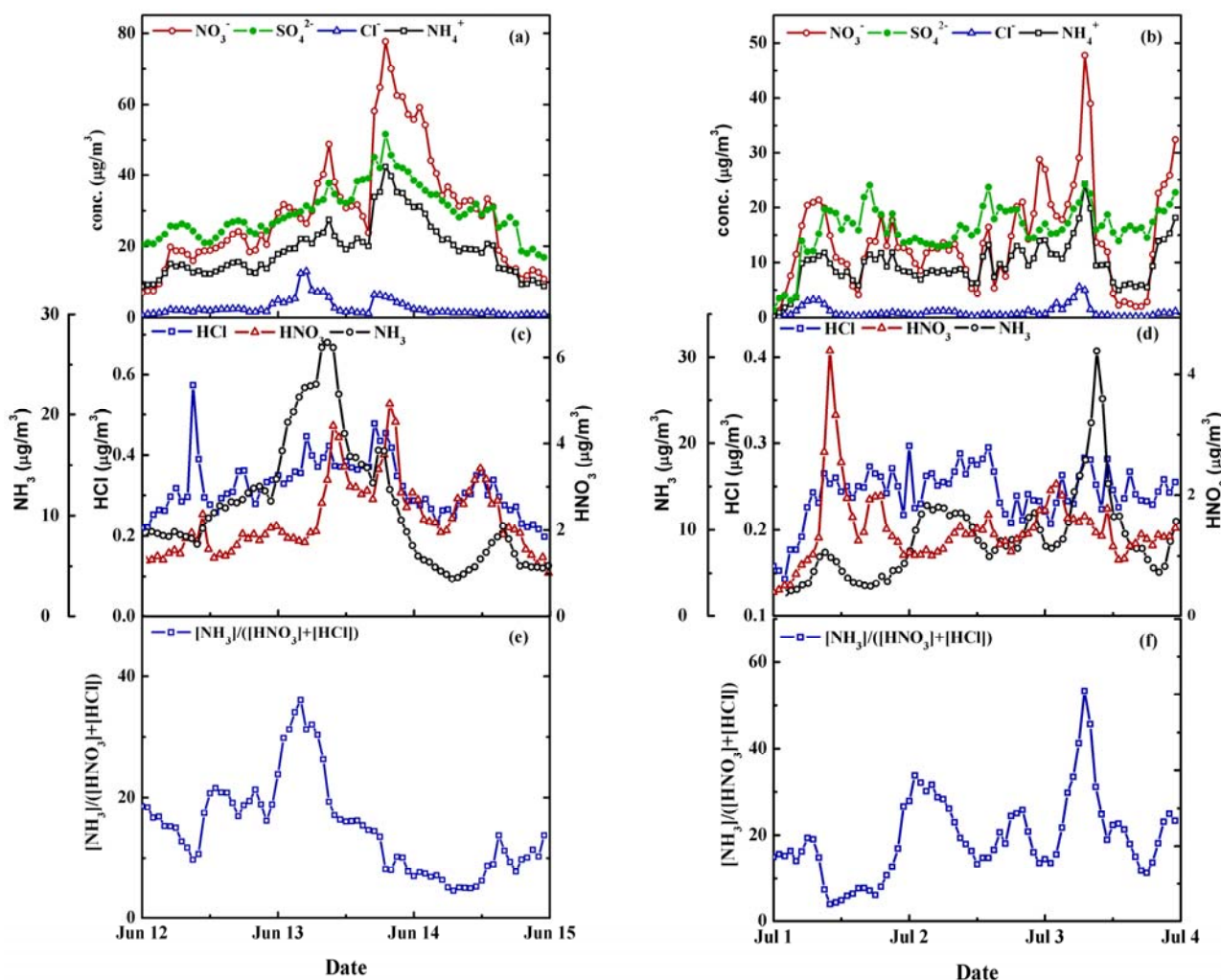
H<sub>2</sub>O<sub>2</sub>, 120–140°C) erupted out from the Steam Jet Aerosol collector (SJAC) and be pooled into its collector. Then the two liquid samples flow through filters, and are stored in syringe pumps of the analytical box and ready for ion chromatographic analysis (IC, conductivity detector, C4 100 × 4 mm column and 3.20 mM HNO<sub>3</sub> eluent for cation, A Supp 10–75 column and 7.00 mM Na<sub>2</sub>CO<sub>3</sub> + 8.00 mM NaHCO<sub>3</sub> eluent for anion), respectively. MARGA has the capability of measuring mass concentrations of major water-soluble (WS) inorganic ions in aerosols (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>) and trace gases (HCl, HNO<sub>2</sub>, SO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>) at one hour resolution. Before and after the field campaign, MARGA was calibrated by injection of standard solutions. Hourly meteorological data including temperature and relative humidity were from the China Meteorological Data Sharing Service System (<http://cdc.cma.gov.cn/>).

## RESULTS AND DISCUSSION

### *Chemical Compositions in Aerosols*

Fig. 1 presents hourly-averaged concentrations of major WS ions in PM<sub>10</sub> in-situ collected from 12 to 14 June (denoted period I) and in PM<sub>2.5</sub> from 1 to 3 July (denoted period II). The concentrations of all WS ions in particulate matters and gases showed remarkable change but less orderliness during day-night time (Monks *et al.*, 2009). For example, the hourly-averaged concentration of summed sulfate, nitrate, chloride and ammonium was in the range of 36.8–177.7 μg/m<sup>3</sup> in PM<sub>10</sub> in the period I and 2.6–101.2 μg/m<sup>3</sup> in PM<sub>2.5</sub> in the period II. That of sulfate was in the range of 16.9–51.6 μg/m<sup>3</sup> in PM<sub>10</sub> and 1.4–24.2 μg/m<sup>3</sup> in PM<sub>2.5</sub>. Both in PM<sub>10</sub> and PM<sub>2.5</sub> the sulfate had no obvious change day to day. In the period I (II), the concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> increased since 16:00 LT (03:00 LT), and reached peaks at 19:00 LT (07:00 LT) on 13 June (3 July), which were nearly 2–3 times higher than their respective averaged concentrations. Additionally, the fluctuating of NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> in particulate matters was accompanied with corresponding variety of their precursors HNO<sub>3</sub>, HCl and NH<sub>3</sub>. The hourly-averaged observations exhibited clearly the formation and dissociation of ammonium nitrate and ammonium chloride.

The averaged concentrations of SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, HCl, HNO<sub>3</sub> and NH<sub>3</sub> were 19.1 ± 7.8, 29.7 ± 16.2, 2.8 ± 2.4, 29.5 ± 7.3, 0.3 ± 0.07, 2.3 ± 0.8 and 11.1 ± 6.2 μg/m<sup>3</sup> during the period I, and 9.6 ± 4.1, 14.1 ± 8.9, 1.0 ± 1.1, 16.1 ± 4.6, 0.2 ± 0.03, 1.4 ± 0.6 and 9.1 ± 5.0 μg/m<sup>3</sup> during the period II, respectively. Notably, the mean summed concentration of these ionic species including Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> was 86.5 ± 32.7 μg/m<sup>3</sup> in PM<sub>10</sub> and 42.0 ± 16.8 μg/m<sup>3</sup> in PM<sub>2.5</sub> (data not showed), respectively. It was comparable to heavy haze episodes with observations in Shanghai, Suzhou and Nanjing (Fu *et al.*, 2008). Moreover, sulfate, nitrate and ammonium were predominant in the amount of total WS ions. The average fractions of sulfate, nitrate and ammonium to the total WS ions were 35.9 ± 5.8%, 32.4 ± 6.2%, 21.9 ± 1.0% in PM<sub>10</sub> and 40.8 ± 11.2%, 31.3 ± 10.6%, 22.4 ± 2.3% in PM<sub>2.5</sub>,



**Fig. 1.** Temporal variations of hourly-averaged mass concentrations of major water-soluble inorganic ions, trace gases and the ratio of  $[NH_3]$  to  $[HNO_3] + [HCl]$  during the periods of I (a) (c) (e) and II (b) (d) (f).

respectively. It was consistent with that sulfate, nitrate and ammonium together accounted for more than 80% of the total inorganic WS species mass in  $PM_{2.5}$  in Shanghai (Pathak et al., 2009; Shen et al., 2009).

**Chemical Coupling of ns- $NH_4^+$  with  $[NO_3^-]$  (or  $[NO_3^-] + [Cl^-]$ )**

Because most of the ratios of ammonium to sulfate molar concentration was calculated as far as the value of 2, we assume all existent sulfates in particles for  $(NH_4)_2SO_4$  as Kiyoshi et al. (1996) reported. The excess part of ammonium is defined as ns- $NH_4^+$  (non-sulfate ammonium). The molar concentrations of ns- $NH_4^+$  is described by the following Eq. (3):

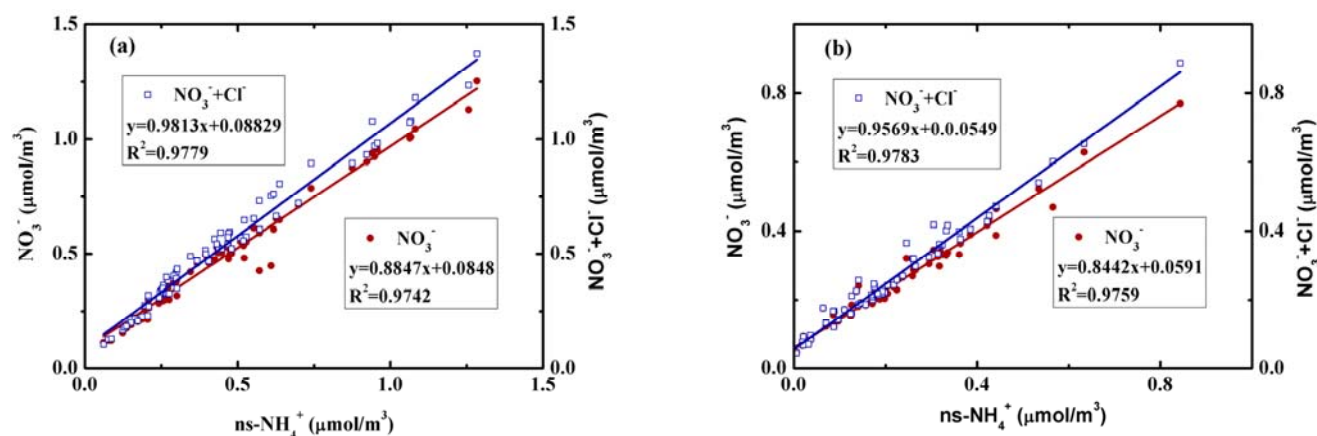
$$[ns-NH_4^+] = [NH_4^+] - 2 \times [SO_4^{2-}] \quad (3)$$

where  $[ns-NH_4^+]$ , in units of  $\mu mol/m^3$ , is non-sulfate ammonium.  $[NH_4^+]$  and  $[SO_4^{2-}]$ , in units of  $\mu mol/m^3$ , are the molar concentrations in  $PM_{2.5}$  or  $PM_{10}$ .

As shown in Fig. 2,  $[ns-NH_4^+]$  presented an extremely strong linear correlation with  $[NO_3^-]$  and  $[NO_3^-] + [Cl^-]$

both in  $PM_{10}$  and  $PM_{2.5}$  samples despite various temperatures and relative humidities. It was different from that most of ammonium and nitrate concentrations lay above the 1:1 mole ratio line in atmospheric particulate samples from a variety of locations (Stelson et al., 1978). Compared with Stelson et al. (1978), the present regression functions revealed ns- $NH_4^+$  not enough to couple  $NO_3^-$  in particles.

The slopes of the regression functions between  $[ns-NH_4^+]$  and  $[NO_3^-]$  were 0.885 in the period I and 0.844 in the period II, and those between  $[ns-NH_4^+]$  and  $[NO_3^-] + [Cl^-]$  were close to 1 with 0.981 in the period I and 0.957 in the period II. It indicated that  $HNO_3$  and  $HCl$  favor to be neutralized synchronously by ammonia. The intercepts of these regression functions were 0.088 in the period I and 0.055 in the period II, suggesting an incomplete chemical coupling of  $NO_3^-$  and  $Cl^-$  by ns- $NH_4^+$  due to ammonium-poor in the sampled aerosols (Wang et al., 2006). Our observation agrees with previous researches on the ionic-chemistry of aerosols (Wang et al., 2006; Pathak et al., 2009). Within a two-year field measurement conducted in Shanghai, Wang et al. (2006) found that  $SO_4^{2-}$  was



**Fig. 2.** Linear relationships and corresponding correlation coefficients between  $[ns-NH_4^+]$  and  $[NO_3^-]$ ,  $[NO_3^-+Cl^-]$  during the periods of I (a) and II (b).

incompletely neutralized by  $NH_4^+$  in aerosols and both  $NH_4HSO_4$  and  $(NH_4)_2SO_4$  were formed but  $SO_4^{2-}$  mainly existed as  $(NH_4)_2SO_4$  in Shanghai. Pathak *et al.* (2009) also found ammonium-poor aerosols in Shanghai and Beijing.

It is worth to point out that  $[NH_3]$  in units of  $nmol/m^3$  was always in same time scale above that of  $[HNO_3] + [HCl]$  in gas phase as showed in Fig. 1(c) and (d). The ratio of  $[NH_3]$  to  $[HNO_3] + [HCl]$  was  $15.1 \pm 7.7$  in the period I and  $19.3 \pm 9.6$  in the period II (Fig. 1(e) and (f)), respectively. It implied that the atmosphere was ammonia-rich in gas phase although it was ammonium-poor aerosols as described above. It was disagree with our former observation based on the single particle ATOFMS analysis. It had been found no abundant  $NH_4NO_3$  expected in fine particles during Aug 1–5 2008 because of insufficient  $NH_3$  (Wang *et al.*, 2009). The likely reason was  $NH_3$  surface-adsorbed control process in aerosols, or  $HNO_3/HCl$  consumed away by other atmospheric chemical processes (Pöschl *et al.*, 2007). Although the above findings are of short duration, it was also indicated that the ammonia-to-ammonium conversion might undergo more complicated processes, which may need to be studied in the future.

#### Gas/Particle Partitioning

Phase changes of  $NH_4NO_3/HNO_3$  depended on temperature. In the high-temperature range,  $NH_4NO_3$  were easily volatilized and its gaseous precursor  $HNO_3$  was released. Conversely, in the low-temperature range,  $NH_4NO_3$  formed in the fine mode aerosols, and the gaseous  $HNO_3$  decreased. The above results can be applied to the case of  $NH_4Cl$  (Matsumoto *et al.*, 1996). Fig. 3 shows the temporal variation of pseudo-equilibrium constants  $K_{NH_4NO_3}$  and  $K_{NH_4Cl}$  as well as temperatures and relative humidities. The strong positive correlation between  $[HNO_3]/([HNO_3] + [NO_3^-])$  (or  $[HCl]/([HCl] + [Cl^-])$ ) and temperature and negative correlation between  $K_{NH_4NO_3}$  (or  $K_{NH_4Cl}$ ) and temperature are observed.

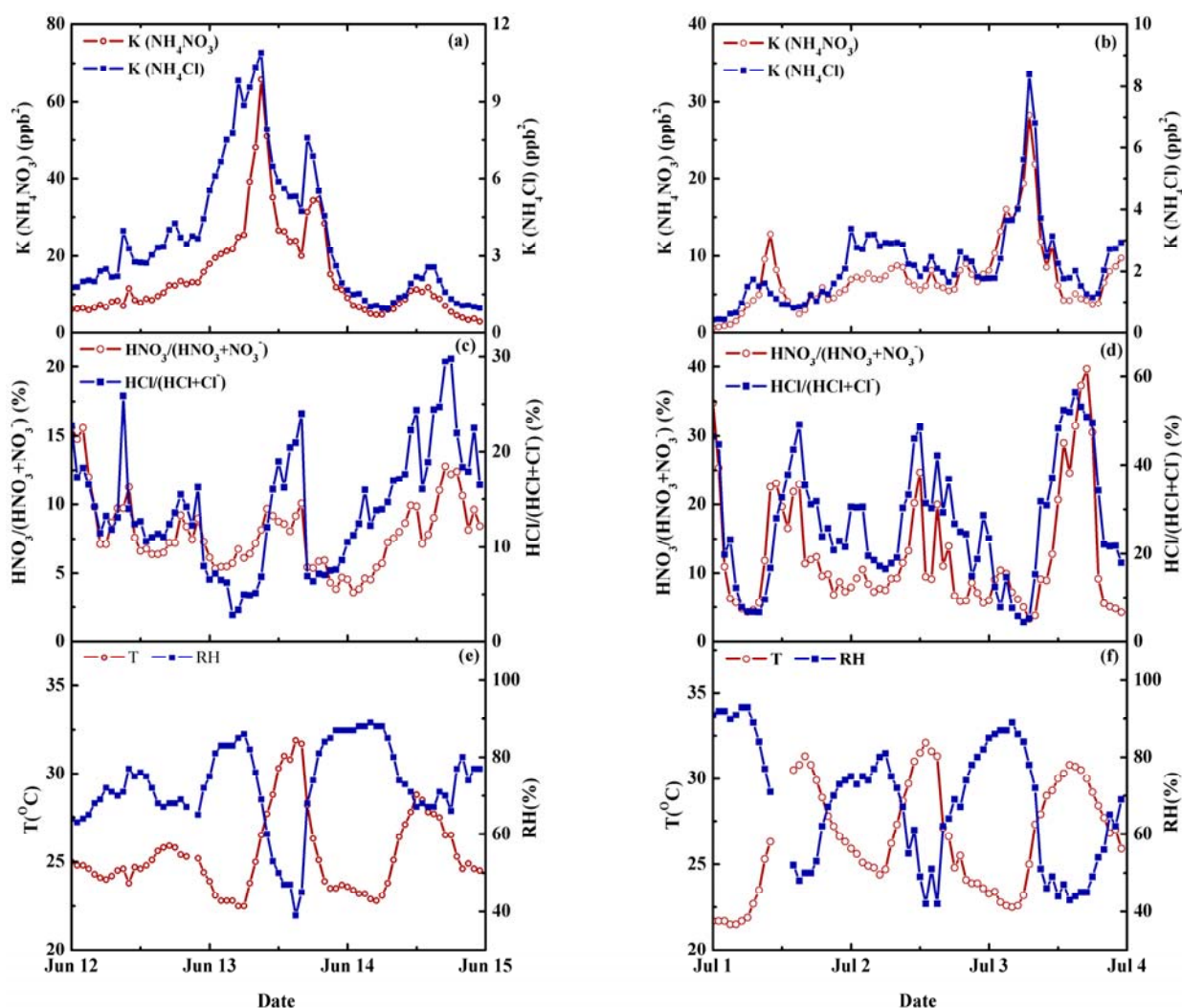
It was also found that the diurnal pattern of solid ammonium chloride was remarkably similar to that of solid ammonium nitrate during the two periods, with a high correlation coefficient between  $K_{NH_4NO_3}$  and  $K_{NH_4Cl}$ , which

was in agreement with previous studies (McMurry *et al.*, 1983; Pio *et al.*, 1987a; Allen *et al.*, 1989; Matsumoto *et al.*, 1996). However,  $K_{NH_4NO_3}$  was 4–5 times higher than  $K_{NH_4Cl}$ . It was quite different to the conclusion that the equilibrium concentrations of  $HCl$  were 1.5–2 times higher than  $HNO_3$  levels at the same ammonia concentration in the atmosphere as solid ammonium chloride more volatile (Pio *et al.*, 1987a). Moreover,  $K_{NH_4Cl}$  approached to the highest value of 10  $ppb^2$  in this study ( $26^\circ C$ ,  $RH = 61\%$  at 09:00LT on 13 June 2009), far below approximately 70  $ppb^2$  at  $25^\circ C$  reported by Pio *et al.* (1987a). The probable reason was ammonium-poor in Shanghai as described above. Whether or no,  $K_{NH_4NO_3}$  was found close to that reported by Pio *et al.* (1987a). It was in consistent with heavy traffic time while  $K_{NH_4NO_3}$  reached a peak at about 08:00LT, indicating nitric acid precursors  $NO_x$  emitted by automobile made great contribution to the formation of nitric acid.

The ratios of gaseous nitric acid to total nitrate ( $[HNO_3]/([HNO_3] + [NO_3^-])$ ) and gaseous hydrochloric acid to total chloride ( $[HCl]/([HCl] + [Cl^-])$ ) had been evaluated to understand gas/particle partitioning (Mehlmann *et al.*, 1995; Pöschl *et al.*, 2007). Fig. 3(e) and (f) shows that  $[HNO_3]/([HNO_3] + [NO_3^-])$  correlated closely to  $[HCl]/([HCl]+[Cl^-])$ , and both of them anti-correlated to relative humidities. It indicated that high relative humidity is of benefit to the gas-to-particle conversion. Both  $[HNO_3]/([HNO_3] + [NO_3^-])$  and  $[HCl]/([HCl] + [Cl^-])$  were far smaller than 50%, but  $[HNO_3]/([HNO_3] + [NO_3^-])$  was smaller than  $[HCl]/([HCl] + [Cl^-])$  both in the period I and II. It suggested that nitrate and chloride were mainly existed in particle phase, and solid  $NH_4NO_3$  was more favored to be formed than  $NH_4Cl$ .

#### CONCLUSIONS

The formation and dissociation of ammonium nitrate and ammonium chloride were investigated using an on-line MARGA. It is efficient to reveal more details about  $NH_4NO_3$  and  $NH_4Cl$  particle-to-gas conversion to their gaseous precursors at 1h resolution of mass concentrations.



**Fig. 3.** Series of equilibrium constants of  $K(\text{NH}_4\text{NO}_3)$ ,  $K(\text{NH}_4\text{Cl})$ , diurnal pattern of the ratio of nitric acid (hydrochloric acid) over total nitrate (chloride), temporal profiles for temperature, relative humidity during the periods of I (a) (c) (e) and II (b) (d) (f).

We observed the highest levels of summed hourly-averaged sulfate, nitrate, chloride and ammonium from 12 to 14 June, and 1 to 3 July, 2009 in Shanghai. It was found ammonium-poor aerosols existed with the agreement of previous observations whereas the atmosphere was ammonia-rich in gas phase.

In this work, an extremely strong linear correlation between non-sulfate ammonium and nitrate and chloride was presented despite the variation of temperatures and relative humidities. Moreover, both the ratios of gaseous nitric acid over total nitrate and gaseous hydrochloric acid over total chloride were smaller than 50%, suggesting that nitrate and chloride were mainly existed in particle phase. The temporal variation of pseudo-equilibrium constants  $K_{\text{NH}_4\text{NO}_3}$  was 4–5 times higher than that of  $K_{\text{NH}_4\text{Cl}}$ . It was quite different from the conclusion of solid ammonium chloride more volatile as the equilibrium concentrations of HCl were 1.5–2 times higher than  $\text{HNO}_3$  levels at the same ammonia concentration in the atmosphere. In addition, the ratio of  $[\text{NH}_3]$  to  $[\text{HNO}_3] + [\text{HCl}]$  in units of  $\text{nmol}/\text{m}^3$  was

far more than the value of 1, implying  $\text{HNO}_3/\text{HCl}$  could be consumed away by other atmospheric chemical process. It was further indicated that the ammonia-to-ammonium conversion might undergo more complicated process, which may need to be further studied.

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