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Supermicron modes of ammonium ions related to fog in rural atmosphere

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Abstract. Fog-processed aerosols were identified and analyzed in detail from a large-sized database in which size-segregated atmospheric particles and gases were simultaneously measured at eight Canadian rural sites. In ten samples collected during or following fog events, at least one supermicron mode of particulate NH_4^+ was observed. The supermicron modes were likely associated with fog events since they were absent on non-fog days. The supermicron mode of NH_4^+ in the 5–10 µm size range probably reflected the direct contribution from fog droplets. Based on detailed analysis of the chemical compositions and the extent of neutralization, the supermicron mode of NH_4^+ in the 1–4 µm size range was believed to be caused by fog-processing of ammonium salt aerosols. These aerosol particles consisted of incompletely neutralized sulfuric acid aerosols in NH_3-poor conditions or a mixture of ammonium nitrate and ammonium sulfate aerosols in NH_3-rich conditions. Interstitial aerosols and fog droplets presented during fog events likely yielded a minor direct contribution to the measured NH_4^+. The mass median aerodynamic diameter (MMAD) of the 1–4 µm mode of NH_4^+ strongly depended on ambient temperature (T) and can be grouped into two regimes. In one regime, the MMAD was between 1.1 and 1.7 µm in four samples, when fog occurred at $T > 0\,°C$, and in two samples, at $T > -3\,°C$. The MMAD of NH_4^+ in this size range was also observed in various atmospheric environments, as discussed in the literature. In the other regime, the MMAD was between 2.8 and 3.4 µm in four samples when fog occurred at $T < -4\,°C$, a phenomenon that was first observed in this study. The MMAD was not related to chemical composition and concentration

of ammonium salts. Further investigations are needed in order to fully understand the cause of the MMAD. The larger supermicron mode of ammonium salts aerosol observed at $T < -4\,°C$ has added new knowledge on the size distributions and chemical compositions of fog-processed aerosols under various ambient conditions.

1 Introduction

Similar to clouds, fog events can modify size distributions and chemical compositions of preexisting atmospheric aerosols and thus modify their optical properties (Ondov and Wexler, 1998; Moore et al., 2004; Fahey et al., 2005; Sun et al., 2006; Aikawa et al., 2007; Herckes et al., 2007; Biswas et al., 2008; Collett Jr., et al., 2008; Dall'Osto et al., 2009; Kaul et al., 2011; Rehbein, et al., 2011; Yu et al., 2011). For example, fog droplets can efficiently scavenge atmospheric gaseous and particulate pollutants. Scavenging is followed by chemical reactions occurring in the droplets (Pandis et al., 1990; Collett Jr. et al., 1999, 2008; Fahey et al., 2005; Biswas et al., 2008). When fog dissipates, fog droplets evolve into atmospheric aerosol particles with modified physical and chemical properties and the process has been shown to take a short amount of time, from dozens of minutes to less than an hour (Ming and Russell, 2004; Fahey et al., 2005; Dall'Osto et al., 2009; Yao et al., 2011). Due to the high deposition velocity of large fog droplets (Herckes et al., 2007), a net increase of chemical species in ambient aerosols post-fog relative to pre-fog is often close to the measurement uncertainty,

Table 1. Meteorological conditions [mean (min–max)] and concentrations of gases (ppb) (BDL – below detection limit).

Site		Sample number and period	T (°C)	RH (%)	SO_2	HNO_3	NH_3	NO_2	NO_z
SPR	1	11:40, 16 November–09:50, 17 November 2004	4.8 (3.5–7.4)	83 (73–98)	1.0	0.3	0.6	8.6	1.5
	2	10:10, 17 November–09:00, 18 November 2004	7.6 (6.5–9.4)	85 (62–98)	0.3	0.2	0.4	10.8	0.9
	3	09:10, 9 December–14:20, 10 December 2004	−0.9 (−2.4–1.7)	80 (60–98)	0.1	0.1	0.2	1.7	0.5
CHA	4	09:30, 14 June–09:00, 15 June 2004	20.3 (13.6–27.0)	67 (41–97)	0.1	0.1	0.3	0.4	0.8
	5	09:15, 16 June–09:00, 20 June 2004	17.4 (5.5–29.3)	66 (38–96)	0.2	0.4	0.2	0.5	0.6
ALG	6	11:00, 19 February–10:30, 20 February 2003	−7.2 (−8.8–−5.2)	87 (49–99)	0.1	0.2	BDL	1.3	0.9
EGB	7	12:40, 6 March–18:10, 6 March 2002	0 (−0.6–0.4)	86 (84–88)	0.8	1.7	0.1	6.3	3.2
KEJ	8	17:50, 8 November–10:20, 9 November 2002	−6.4 (−8.8–−2.6)	82 (59–98)	0.3	0.04	0.1	1.1	0.8
	9	11:10, 9 November–10:20, 10 November 2002	3.7 (−1.7–7.5)	92 (68–100)	0.9	0.09	0.2	2.3	0.9
	10	10:50, 10 November–10:40, 11 November 2002	9.0 (6.5–11.3)	89 (49–100)	0.4	0.06	0.3	BDL	0.6

or even negative (Moore et al., 2004; Herckes et al., 2007). Thus, direct observation of the fog-processed aerosols is rare. Knowledge of the size distributions and chemical compositions of fog-processed aerosols is limited and the factors that determine these aerosol properties are poorly understood (Law and Stohl, 2007; Yu et al., 2011).

The 1–2 μm mode of secondary particulate species in mass size distribution was recently frequently observed in specific polluted environments (Liu et al., 2008; Guo et al., 2010; Nie et al., 2010; Li et al., 2012; Tsai et al., 2012), but the frequency of occurrence of the mode was low in less polluted environments (Zhao and Gao, 2008; Plaza et al., 2011). The 1–2 μm mode was reported to be associated with fog events in some studies (Plaza et al., 2011; Tsai et al., 2012), but it was unclear whether it was due to fog-processed aerosols post fog events or interstitial aerosols or fog droplets present during fog events. In most of these studies, the mode was observed under humid weather conditions (Liu et al., 2008; Zhao and Gao, 2008; Guo et al., 2010; Nie et al., 2010; Li et al., 2012). Secondary particulate species in the mode have also been shown to act as one of the major contributors to some particle pollution events (Guo et al., 2010; Nie et al., 2010; Tsai et al., 2012). Unlike well-documented accumulation modes of secondary particulate species in the submicron size range (Ondov and Wexler, 1998), the origins of the 1–2 μm mode need more investigations.

In addition, enhanced particle pollution in mass concentration was recently reported to be caused by fog-processing events (Sun et al., 2006; Biswas et al., 2008; Yu et al., 2011; Tsai et al., 2012). These episodes could be associated with chemical species newly-formed in fog droplets and a longer residence time of the species relative to the duration of the fog events. In general, fog droplets with smaller sizes should have longer residence times. However, the size distribution of fog droplets has been found to be highly variable in different fog events (Frank et al., 1998; Ming and Russell, 2004; Herckes et al., 2007; Quan et al., 2011), depending on supersaturation and other factors. Thus, it is highly unpredictable

whether a fog event removes aerosols from the atmosphere or additional particulate mass is created. The same difficult situation is faced when designing field experiments for observing fog-processed aerosols. A practical approach would be to search for the fog-processed aerosols from databases that have a large number of aerosol samples collected at various locations and time periods.

The purpose of the present study is to identify fog-processed aerosols from a suite of field measurements made at seven inland rural sites and one coastal rural site in Canada (Zhang et al., 2008a, b) and to investigate the size distributions, neutralization extents, and chemical compositions of these aerosols under various ambient conditions. The measurements include 192 MOUDI samples each with a duration of 6–96 h. In ten samples collected during or following fog events (Table 1), at least one supermicron mode of particulate NH_4^+ was observed. The origins of the measured NH_4^+ in the supermicron modes associated with the fog events are studied in terms of fog-processed aerosols, interstitial aerosols (inactivated into droplets) and fog droplets. The variability of the chemical composition of fog-processed aerosols is explored in terms of neutralization extents of acidic species and air mass histories. In addition, the variability of the size distributions of the measured NH_4^+ is investigated with particular attention on the impact of ambient temperature. The new findings, i.e., the 3–4 μm mode of ammonium salt aerosols and its dependence on ambient temperature, add new knowledge on size distributions of fog-processed aerosols and their probable controlling factors.

2 Methodology

2.1 Data

In this study, an eleven-stage MOUDI (Model 110), with 50 % cut-off points for the particle aerodynamic diameters: 18, 9.9, 6.2, 3.1, 1.8, 1.0, 0.54, 0.32, 0.18, 0.093, and 0.048 μm, was used for sampling at eight Canadian rural sites

Fig. 1. Map of sampling sites.

in eastern and central Canada (Fig. 1). A total of 192 samples were collected in both cold and warm seasons. The duration of each sample varied from 6 to 96 h. Approximately 20 % of the total samples had a 48–96-h duration and were mostly collected on weekends. Approximately 60 % of the total samples had a 16–29-h duration, while the remaining samples had a 6–10-h duration. Simultaneously, a $PM_{2.5}$ sampler, equipped with a Na_2CO_3-coated denuder and a citric-acid-coated denuder, was also used to collect SO_2, HNO_3 and NH_3 gases, and $PM_{2.5}$. Inorganic ions in particles were determined by an ion chromatograph while organics were not measured. In addition, SO_2, NO_x, NO_y and O_3 analyzers were used to measure their mixing ratios in minutes. On-site meteorological data were recorded to support data analysis. Fog events were judged by a combination of on-site observed relative humidity (RH > 95 %) and the record (weather report) obtained from the meteorological station nearest to the sampling sites (http://www.wunderground.com/history). Detailed information about the sampling sites and chemical analysis can be found in Zhang et al. (2008a, b) and Yao and Zhang (2011).

2.2 Relative acidity

The relative acidity (RA) is an important parameter for investigating chemical properties of atmospheric particles. In this study, RA was calculated using all of the observed ion species in their equivalent concentrations (Kerminen et al., 2001):

$$RA = ([NH_4^+] + [Na^+] + [Ca^{2+}] + [Mg^{2+}] + [K^+])/$$
$$([SO_4^{2-}] + [NO_3^-] + [Cl^-]) \quad (1)$$

where $[NH_4^+]$, $[Na^+]$, $[Ca^{2+}]$, $[Mg^{2+}]$, $[K^+]$, $[SO_4^{2-}]$, $[NO_3^-]$ and $[Cl^-]$ are equivalent concentrations of these water-extracted ions. Considering that analytical errors of ionic concentrations were generally about 5 %, except for some low concentration episodes, $RA \leq 0.9$ was thereby considered a threshold used to judge the presence of acidic particles in this study, while $RA \geq 1.1$ indicated that the particle was completely neutralized. When RA ranged from 0.9 to 1.1, the equivalent ratio of $[NO_3^-]/[SO_4^{2-}]$ was further used

to substantiate the judgment. For the episodes of low concentration, the extent of neutralization was judged by a combination of (1) RA, (2) RA in the neighboring size bin, and (3) the equivalent ratio of $[NO_3^-]/[SO_4^{2-}]$. The missing RA in this study was due to the concentrations of the major ion being close to the detection limit when the relative analytical error was large.

3 Results and discussion

3.1 Overview of ten samples collected during and/or post fog events

Among the total of the 192 MOUDI samples, ten samples (or about 5 % of the total) had one or two supermicron particle modes of ammonium salts (6-h duration for one sample, 17–29-h duration for eight samples, and 48-h duration for one sample, solid lines in Fig. 2). For the one sample with the 6-h duration, fog did not appear during the sampling period but appeared four hours prior to the sampling. For the other nine samples, fog appeared during part of the sampling periods and also appeared some hours prior to the sampling due to the long sampling durations of these samples. Supermicron modes of ammonium salts were absent in 158 non-fog samples (dashed lines in Fig. 2) where ammonium salt aerosols were dominantly distributed in the submicron particle size. Submicron modes of ammonium salt aerosols in the atmosphere have been well characterized in the literature, i.e., the $0.2 \pm 0.1 \, \mu m$ mode due to gas-particle condensation, the $0.4 \pm 0.1 \, \mu m$ mode due to either primary emissions or hygroscopic growth of $0.2 \, \mu m$ mode particles together with chemical reactions, and the $0.7 \pm 0.2 \, \mu m$ mode due to in-cloud processing of aerosols (Ondov and Wexler, 1998). The supermicron mode of ammonium salts coexisted with the $0.7 \pm 0.2 \, \mu m$ mode of ammonium salts in four of the ten samples and coexisted with the $0.4 \pm 0.1 \, \mu m$ mode in the rest of the samples. The measured concentrations of NH_4^+ in the supermicron atmospheric particles in the ten samples were statistically higher than those in the non-fog samples at a 95 % level of confidence. Thus, the observed supermicron modes of NH_4^+ were probably associated with fog events, e.g., fog-processed aerosols post fog events or interstitial aerosols and fog droplets during fog events. Fog processing of ammonium salt aerosols involves both physical and chemical processes. For example, gases and aerosols can be scavenged by fog droplets; additional sulfuric acid and nitric acid can be formed inside the droplets enabling the droplets to absorb more NH_3 in order to neutralize the acids. Thus, additional NH_4^+ mass was gained during the fog events and the ambient aerosols evolved from the fog droplets had larger sizes than the preexisting aerosols prior to the fog events. As presented later, the NH_4^+ in the supermicron atmospheric particles was overwhelmingly presented as ammoniated sulfuric acid and/or ammonium nitrate salts in different extents of neutralization.
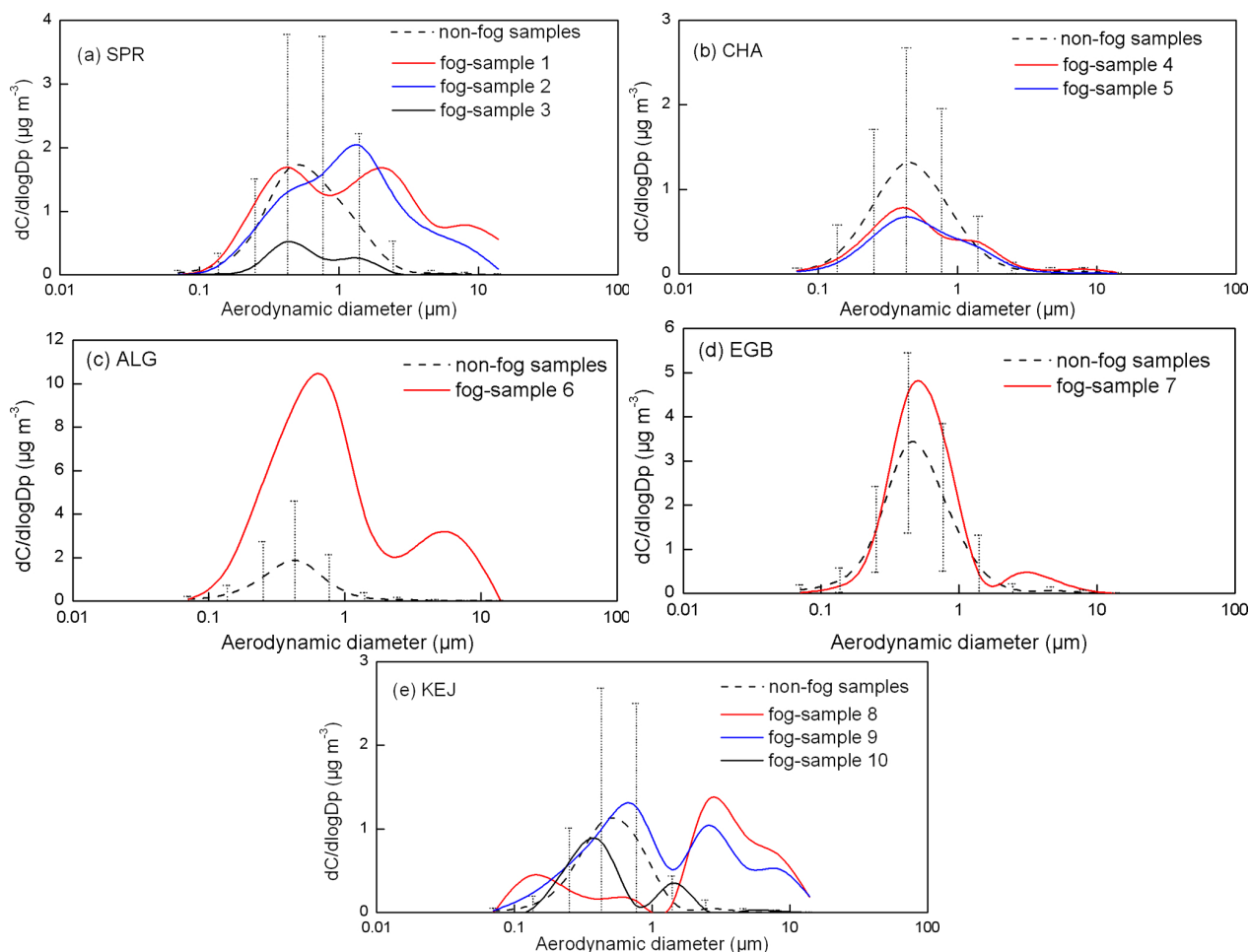
Fig. 2. Mass size distributions of NH_4^+ in fog and non-fog samples: dashed line and error bar represent the average and standard deviation of all non-fog samples in each campaign and each colored line represents one fog-sample defined in Table 1.

It should be noted that, in 10 % of the 192 samples which might have gone through foggy days, the supermicron modes of NH_4^+ were not apparent. One explanation could be the high efficiency of the fog in removing large particles from the ambient air during the sampling periods. This could happen if the sampling duration was much longer than the fog event. Another possibility could be the low efficiency of MOUDI in collecting fog droplets larger than 10 μm and the fog-processed aerosols exceeded that size.

In the sections below, the origins of the measured NH_4^+ in supermicron atmospheric particles were analyzed in detail for each of the ten samples identified. The analysis was organized as warm fog with ambient temperature (T) > 0 °C (Sect. 3.2) and cold fog under T < 0 °C (Sect. 3.3) since the size distribution of NH_4^+ in the supermicron atmospheric particles was closely related to T. One sample collected at Kejimkujik (KEJ), two at Chalk River (CHA), and two at Sprucedale (SPR) were discussed in Sect. 3.2. One sample collected at Egbert (EGB), one at Algoma (ALG), two at KEJ, and one at SPR were discussed in Sect. 3.3. The vari-

ability of the mass median aerodynamic diameter (MMAD) of NH_4^+ in the 1–4 μm particles was further explored in Sect. 3.4 in terms of T effects and other factors.

3.2 Warm fog (T > 0 °C)

3.2.1 Supermicron mode of incompletely neutralized ammonium salt aerosols

Size distributions of ionic species and RA in the sample collected at KEJ during 10–11 November 2002 are shown in Fig. 3. Two fog events possibly affected the sample, i.e., fog occurred from 05:00 p.m. on 9 November to 11:00 a.m. on 10 November (prior to the sampling) and fog occurred from 08:00 p.m. on 10 November to 12:00 a.m. on 11 November (during the sampling), judging by the measured RH > 95 % and the weather record at the nearest meteorological station (http://www.wunderground.com/history). When log-normal functions were used to fit the size distribution of NH_4^+ (Lan et al., 2011), two modes of NH_4^+ were observed with the
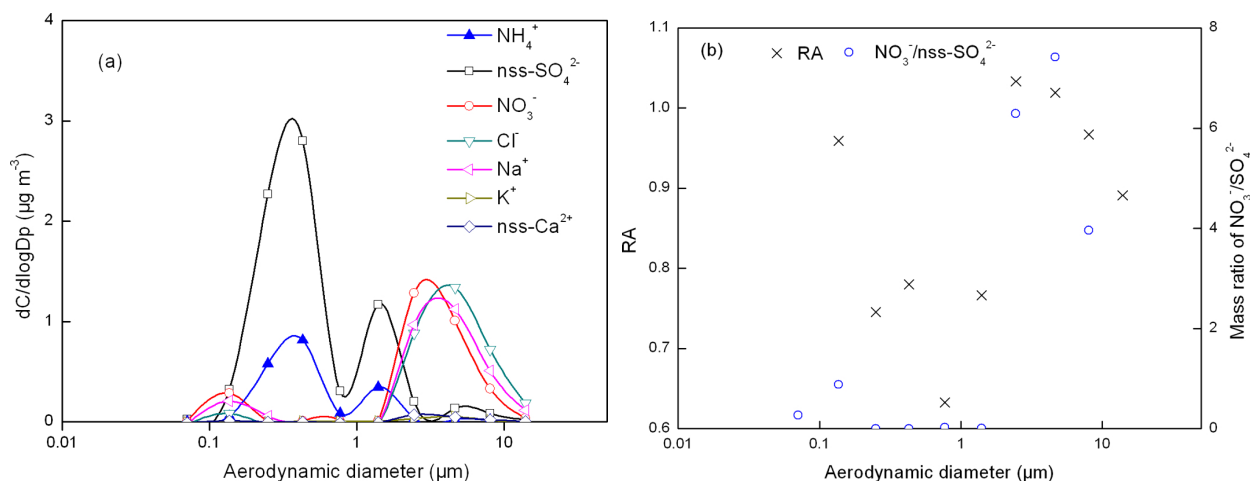
Fig. 3. Mass size distributions of ions, relative acidity (cross symbol) and mass ratio of NO_3^-/SO_4^{2-} (circle symbol) for fog-sample 10 listed in Table 1.

median mass aerodynamic diameters (MMAD) at 0.3 and 1.4 μm, respectively (Fig. S1a). In the 1–1.8 μm size bin, NH_4^+ and non-sea-salt-SO_4^{2-} (nss-SO_4^{2-}) were two dominant inorganic species while Ca^{2+} and K^+ were negligible. The latter suggested that the contributions of soil and biomass burning sources to the NH_4^+ at the 1.4 μm mode were probably negligible, although soil particles and biomass burning aerosols can have a supermicron mode (Eck et al., 2003; Yao et al., 2003). The calculated air mass back trajectory showed that the air was from clear southwestern marine environments (Fig. S2a, b), supporting a high contribution of sea-salt aerosols at 2–10 μm (Fig. 3a) and negligible contributions from soil particles and biomass burning aerosols. Thus, there were three potential sources for the measured NH_4^+ at the 1.4 μm mode, i.e., fog-processed aerosols collected after the first fog event (from 05:00 p.m. on 9 November to 11:00 a.m. on 10 November) or interstitial aerosols or fog droplets collected during the second fog event (from 08:00 p.m. on 10 November to 12:00 a.m. on 11 November). These three potential sources are explored in detail below.

The RA value of the 1–1.8 μm size bin was 0.77, indicating that the measured particles were acidic and that the sulfuric acid was not completely neutralized by the NH_4^+ (note that the relative error of RA at the 0.093–0.18 μm, 0.54–1.0 μm and 10–18 μm bins could be larger than 10 % since the measured concentrations of the major ions were just above five times the detection limits, but errors for the other size ranges were expected to be smaller). When the acidic fog droplets evaporated, the formed aerosols could have been acidic and could have contained a much smaller amount of nitrate through the evaporation of HNO_3 gas (Yao et al., 2011). This was exactly what was observed for the 1–1.8 μm size bin, where the concentration of NO_3^- was negligible. Thus, the 1.4 μm mode of NH_4^+ observed in this sample was likely from the fog-processed ammonium salt aerosols.

Moore et al. (2004) and Liu et al. (2008) have also reported the mode of NH_4^+ at 1–2 μm after fog events. The water mole fraction of the 1–2 μm aerosols in this sample was calculated to be 0.85 using an Aerosol Inorganic Model (AIM-II, Clegg, et al., 1998; http://www.aim.env.uea.ac.uk/aim/aim.php). In modeling, the chemical composition of inorganic species in the 1–2 μm size range, as well as the averaged temperature and relative humidity during the sampling period, were used as input and the gas-aerosol equilibrium was disabled since the equilibrium was unable to be achieved for incompletely neutralized aerosols (Yao et al., 2006, 2007). The calculated water mole fraction was lower, compared to that in fog droplets, where the water mole fraction has been shown to reach over 0.999 (Moore et al., 2004). The estimated in-situ pH of the 1–2 μm aerosols reached as low as 0.6 units, which does not allow the existence of NH_4NO_3 in the particle phase.

Below, we have further excluded the possibility that the supermicron mode of ammonium salts was the result of the direct collection of interstitial aerosols or fog droplets. Interstitial aerosol particles during fog events have been shown to contain significant amounts of NO_3^- co-existing with NH_4^+ and SO_4^{2-} (Klemm et al., 1994; Hoag et al., 1999; Fahey et al., 2005; Ming and Russell, 2004, Yao et al., 2011) because of the large quantity of liquid water at supersaturation conditions. However, the concentration of NO_3^- was negligible in this sample. In addition, approximately 23 % of the sulfuric acid in the 1–1.8 μm size bin was not neutralized. Formation of sulfate in inactivated supermicron particles strongly relied on the alkalinity of aerosols, leading to the formed sulfate associated with either crustal species or sea-salt sodium (Keene et al., 1998; Zhuang et al., 1999). When the alkalinity of the aerosol was completely consumed, the in-situ pH of the aerosol rapidly lowered and formation of sulfate acid was substantially suppressed in a matter of a few seconds (Keene
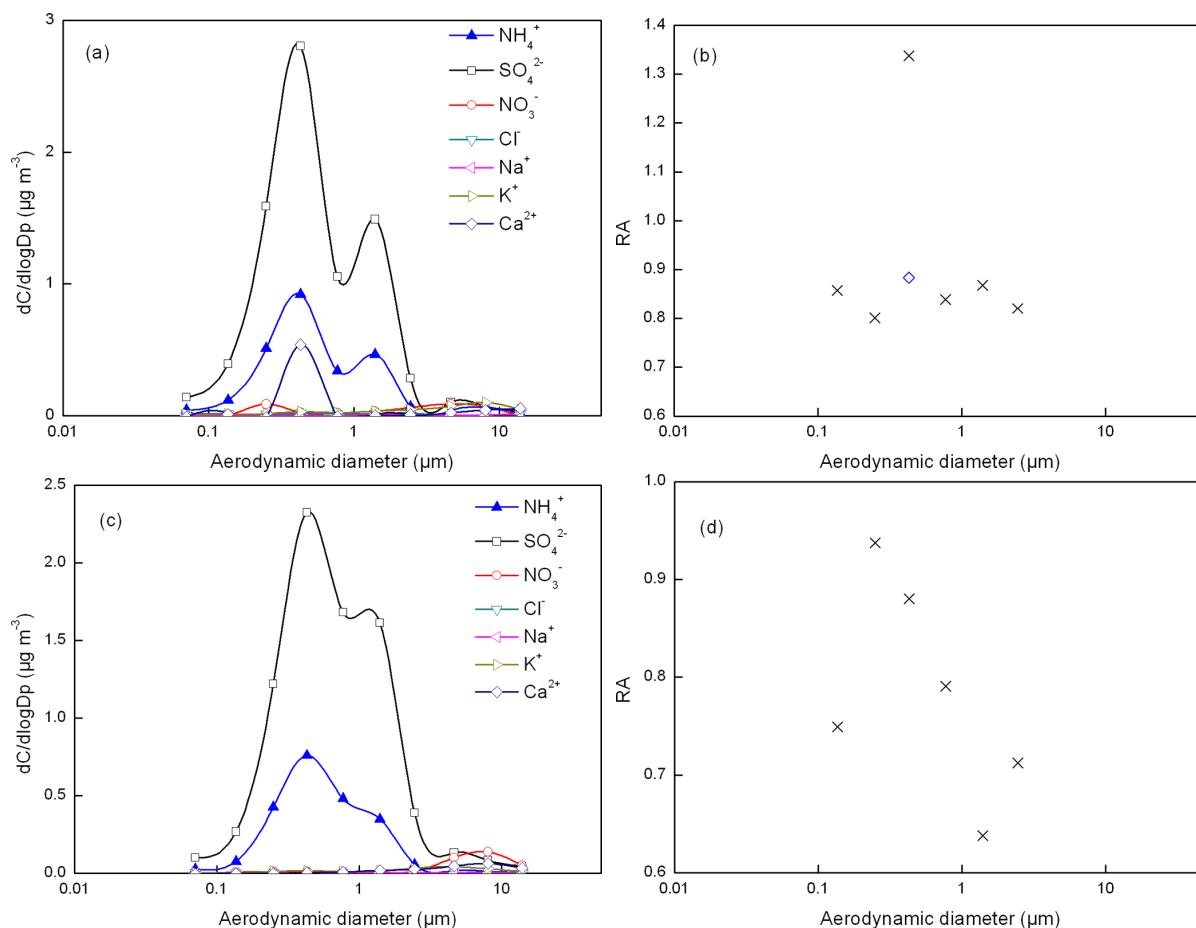
Fig. 4. Mass size distributions of ions and RA for fog-sample 4 (**a** and **b**) and fog-sample 5 (**c** and **d**). The diamond symbol in (**b**) represents RA in which Ca^{2+} was excluded from the estimation.

et al., 1998, 2004). Thus, it was almost impossible to form this high of a percentage of incompletely neutralized sulfuric acid on inactivated 1–1.8 µm aerosols. Alternatively, the high percentage of the incompletely neutralized sulfate acid can be formed in fog droplets (Hoag et al., 1999). Moreover, fog droplets have also been reported to contain a large amount of NH_4^+, SO_4^{2-} and NO_3^- (Klemm et al., 1994; Collett Jr. et al., 1999; Moore et al., 2004; Ming and Russell, 2004; Biswas et al., 2008; Sträter et al., 2010; Watanabe et al., 2010). The negligible concentration of nitrate in the 1–2 µm mode suggested that the measured concentration of NH_4^+ in this sample was unlikely from the direct collection of fog droplets. A significantly high concentration of ammonium nitrate salt was indeed observed at the 5–10 µm mode in some samples in this study, in which the ammonium nitrate was probably from the direct collection of fog droplets, as discussed later.

It can be argued that several factors might also cause the 1–2 µm mode of ammonium salt aerosols, e.g., variability in the relative length of time when fog was sampled, differing degrees of drying, and potential splashing of droplets in the impactor. If the 1–2 µm mode was indeed caused by these proposed factors, any one of them would also lead to one broad mode or multiple modes of NH_4^+ at 2–10 µm. However, no mode of NH_4^+ was observed in the size range from 2 to 10 µm in this sample. Thus, the 1–2 µm mode was unlikely caused by these factors. Overall, we inferred that the 1.4 µm mode of NH_4^+ was probably from the evaporation of droplets.

The size distributions of ionic species in two samples collected at CHA on 14–15 June 2004 and 16–20 June 2004 are shown in Fig. 4. Fog occurred from 04:00 to 06:00 a.m. on 14 June from 10:00 p.m. on 14 June to 05:00 a.m. on 15 June from 09:00 to 11:00 a.m. on 16 June and from 01:00 to 04:00 a.m. on 19 June judging by the on-site observed RH. For the sample collected during 16–20 June 2004, two modes of NH_4^+ had MMADs at 0.4 and 1.1 µm, respectively (Fig. S1b). NH_4^+ and SO_4^{2-} were two dominant inorganic ions in the 1.0–1.8 µm particles where Ca^{2+} and K^+ were negligible. NO_3^- in the 1.0–1.8 µm particles was also negligible and the RA was 0.64 (note that the relative error of RA at 0.093–0.18 µm and 1.0–1.8 µm on 14–15 June could be larger than 10 % due to the low concentrations). Following the same analysis presented above, the 1.1 µm mode of
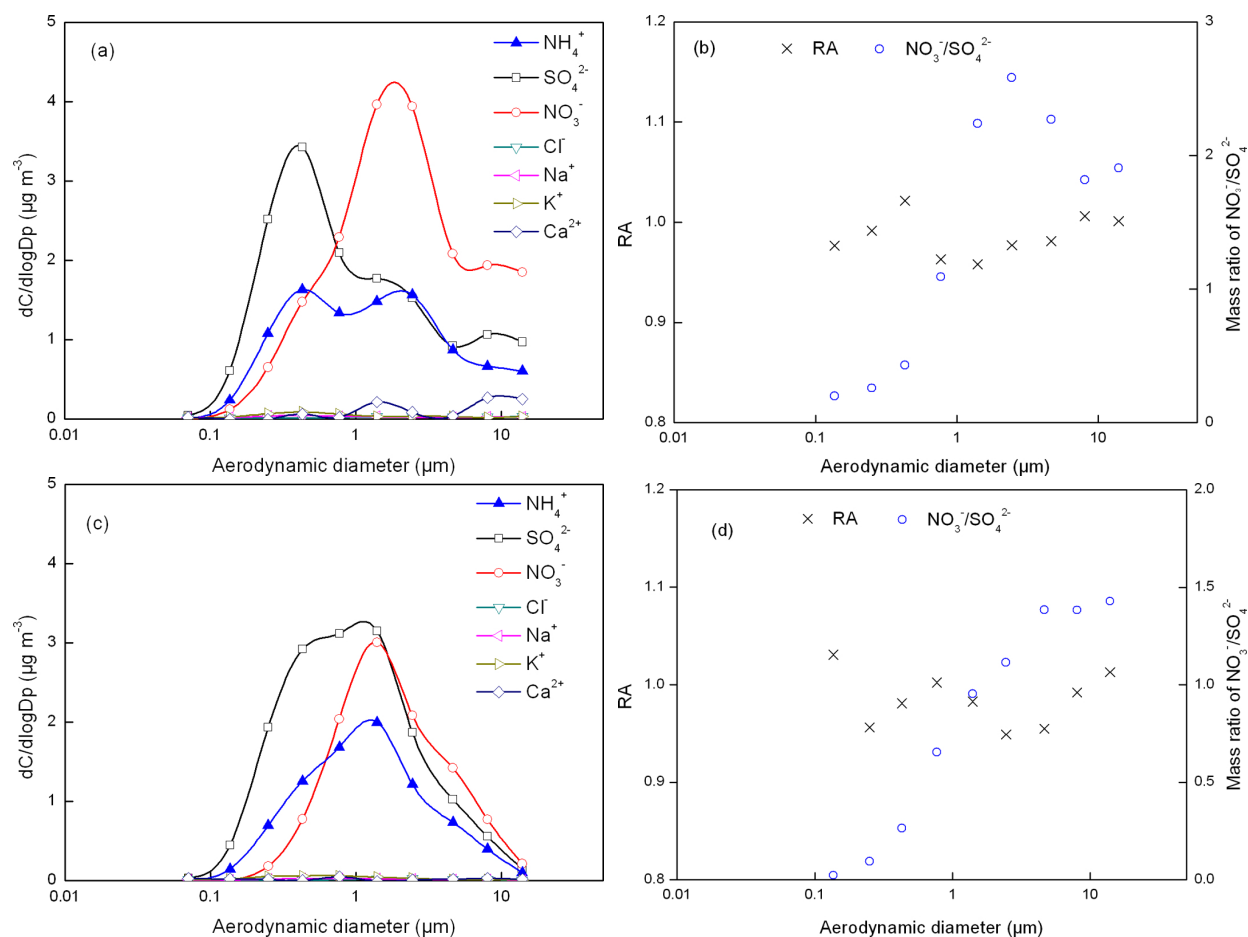
Fig. 5. Same as in Fig. 3 except for fog-sample 1 (**a** and **b**) and fog-sample 2 (**c** and **d**).

the measured NH_4^+ was also ascribed to fog-processed ammonium salt aerosols (incompletely neutralized). In addition, the 1.3 μm mode of the measured NH_4^+ on 14–15 June 2004 can also be the result of fog-processing of ammonium salt aerosols (Fig. S1c) and the NH_4^+ was also overwhelmingly associated with SO_4^{2-}.

3.2.2 Supermicron modes of completely neutralized ammonium salt aerosols

The two samples collected at SPR on 16–17 November and on 17–18 November 2004 contained significant amounts of NH_4^+ in supermicron particles (Fig. 5a, c) when T was higher than 0 °C. Fog occurred from 08:00 to 10:00 a.m. on 16 November (T varied from −1.9 to 0 °C) prior to the sampling, from 09:00 p.m. on 16 November to 10:00 a.m. on 17 November and from 05:00 p.m. on 17 November to 09:00 a.m. on 18 November judging by the observed RH and weather records at stations over a radius of 100 km during the two days. The RAs (0.95–1.03) narrowly oscillated around unity in the different size bins of the two samples (Fig. 5b, d), suggesting that the measured particles were neutral. In

the 1–3 μm particles, about 90 % of the SO_4^{2-} and NO_3^- were probably associated with NH_4^+. In the particles > 3 μm, there was still about 70 % of the SO_4^{2-} and NO_3^- associated with NH_4^+ and the remaining less than 30 % of the SO_4^{2-} and NO_3^- appeared to be associated with metal ions. The elevated concentrations of NH_3 gas (Table 1) apparently led to the neutral particles and the elevated concentrations of NO_2 and NO_z, as well as NH_3 (Table 1), also favored the formation of ammonium nitrate. The calculated air mass back trajectories also showed that the air came from industrial areas in the southwest (Fig. S2c, d, e).

When the log-normal functions were used to fit the NH_4^+ size distributions on the sample collected during 16–17 November 2004, the NH_4^+ in the supermicron size range exhibited a bi-modal size distribution, i.e., 1.6 and 7.9 μm (Fig. S1d). In the supermicron particles, the sum of $[Ca^{2+}]$ and $[K^+]$ in equivalent concentrations was only 15–30 % of the $[NH_4^+]$. Again, the two supermicron modes of NH_4^+ were not observed in dozens of non-fog samples collected at SPR. Thus, the two supermicron modes of NH_4^+ were probably associated with fog events.
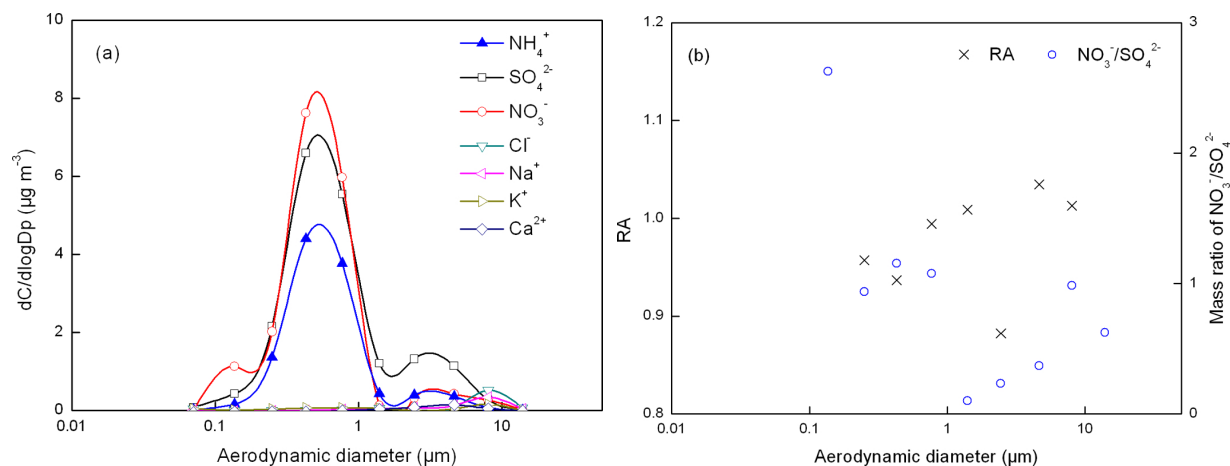
Fig. 6. Same as in Fig. 3 except for fog-sample 7.

Hoag et al. (1999) reported an evident increase of NH_4^+ (neutralized sulfate) mass concentration in the 5–10 μm size range during fog events. Fahey et al. (2005) also found that the mass concentration of NH_4^+ (neutralized sulfate) peaked in 7–13 μm fog droplets due to a rapid formation of ammonium sulfate. The NH_4^+ at the 7.9 μm mode from the SPR 16–17 November sample was most likely caused by the direct collection of fog droplets. Also in the same studies by Hoag et al. (1999) and Fahey et al. (2005), the simulated concentration of NH_4^+ in the 1–3 μm interstitial aerosols and droplets was several times less than that in the 5–10 μm fog droplets. However, the measured concentration of NH_4^+ in the 1–3 μm particles in this SPR sample was over two times that in the 5–10 μm particles. Thus, the direct collection of interstitial aerosols and fog droplets probably yielded a minor contribution to the NH_4^+ at the 1.6 μm mode in this sample. Like the 1–2 μm mode of incompletely neutralized ammonium salt aerosols, the 1.6 μm mode of NH_4^+ was also mainly from fog-processed aerosols.

Two supermicron modes (at 1.2 and 5.0 μm) of NH_4^+ were also identified for the second SPR sample collected on 17–18 November 2004 (Fig. S1e). Following the same analysis approach as for the first SPR sample, the 1.2 μm mode of NH_4^+ was mainly due to fog-processing of a mixture of ammonium nitrate and ammonium sulfate aerosols with an equivalent ratio of $[NO_3^-]/[SO_4^{2-}]$ at 0.74, while the 5.0 μm mode of NH_4^+ was probably due to the direct collection of fog droplets.

It is interesting that the mass concentrations of NH_4^+ in the 1.2 μm mode aerosols were higher than those in the 0.3 μm mode aerosols on 17–18 November 2004 at SPR, indicating that fog probably increased the concentration of ammonium salt in the atmosphere in this sample. Moreover, mass size distributions of fog droplets have been shown to strongly rely on supersaturation and the chemical and physical properties of the preexisting aerosols before fog events (Frank et al., 1998; Ming and Russell, 2004). Thus, it is not surprising that

the 5.0–10 μm mode of NH_4^+ was sometimes observed, but at other times was not detected.

3.3 Cold fog ($T < 0\,°C$)

No fog occurred during the sampling period between 12:40 to 18:10 on 6 March 2002 at Egbert (EGB); however, fog lasted for four hours prior to sampling when T was at -4 to $-5\,°C$, and dissipated after 10:00 (less than three hours prior to sampling). The calculated air mass trajectory during the fog event showed that the air came from industrial areas in the west (Fig. S2f, g). A supermicron mode of NH_4^+ had the MMAD at 3.2 μm in this sample (Figs. 6a, b and S1f) and NH_4^+ was overwhelmingly associated with SO_4^{2-}. The sum of $[Ca^{2+}]$ and $[K^+]$ was only 25 % of the $[NH_4^+]$ at this mode, suggesting a minor contribution from soil and biomass burning sources. The 3.2 μm mode of NH_4^+ was probably due to fog-processing of ammonium salt aerosols before sampling since the half lifetimes of particles in this size range were more than five hours based on their typical dry deposition velocity (e.g., on the order of $1\,cm\,s^{-1}$).

In addition, a very high concentration of HNO_3 gas (1.7 ppb, Table 1) was observed during the sampling period. The value was even higher than the maximum daily-averaged concentration of HNO_3 gas observed in the winter in urban areas of North American cities, e.g., Toronto (Godri et al., 2009) and New York (Ren et al., 2006), even under high NO_2 concentration conditions. Photochemical formation of HNO_3 in the gas-phase under such cold conditions and low NO_2 concentrations at EGB should not be able to produce the observed high concentration of HNO_3 gas. Besides, the mass ratio of NO_3^- to SO_4^{2-} at the 3.2 μm mode was substantially lower than the ratio in the submicron sizes (Fig. 6b). All of this evidence points to the possibility that a large quantity of HNO_3 was released into the gas phase when the fog droplets evolved into aerosols. On this occasion, the fog droplets were probably acidic. This hypothesis was also supported by the
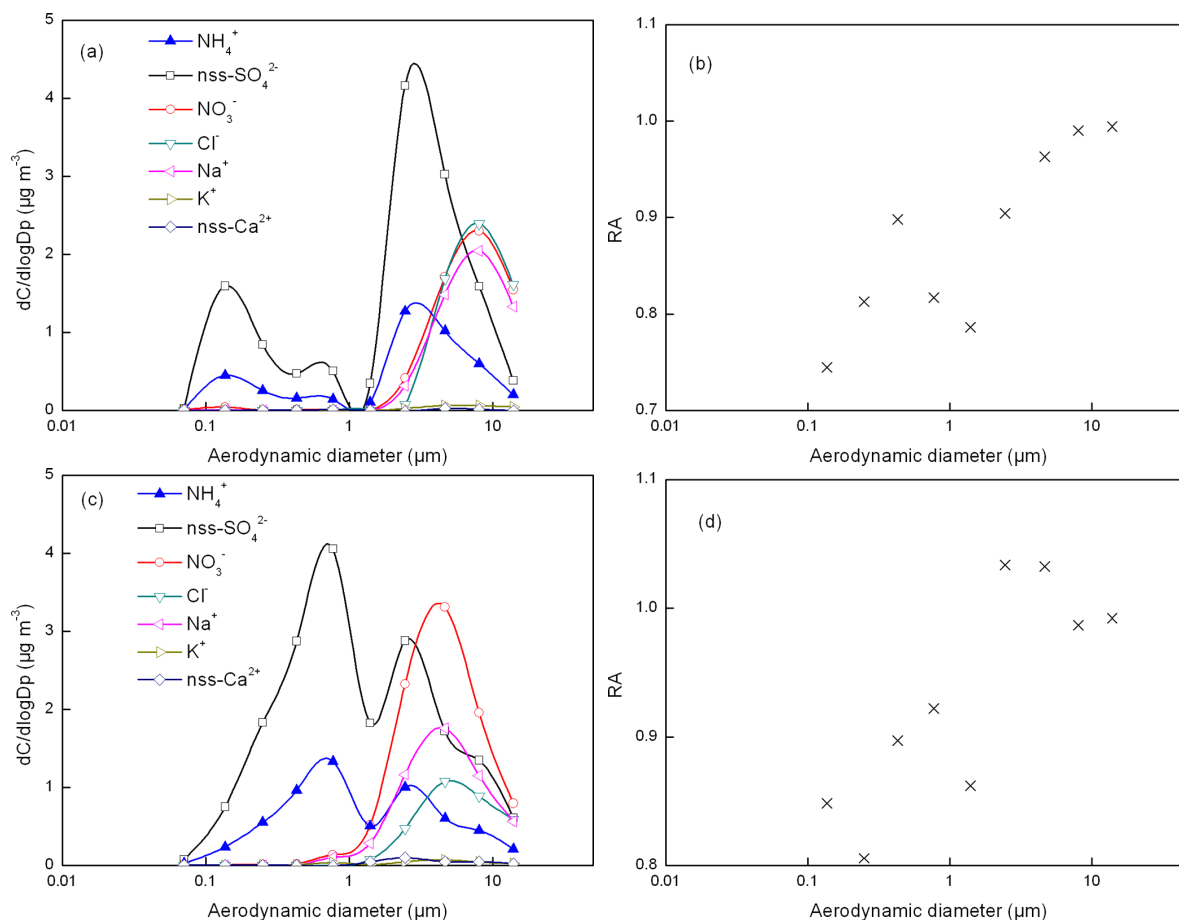
Fig. 7. Same as in Fig. 3 except for fog-sample 8 (**a** and **b**) and fog-sample 9 (**c** and **d**).

RA (0.88) of the 1.8–3.2 µm size bin. The estimated in-situ pH of aerosols at this size bin was as low as 0.04, while the water mole fraction was estimated to be 0.83. In such an acidic and concentrated aerosol solution, NO_3^- would be released as HNO_3 into the gas phase. RAs of all the supermicron size bins (except 1.8–3.2 µm) in this sample were in the range of 1.0 and 1.03, which could be explained by the release of HNO_3 that decreased the particle acidity. Thus, the post process of fog-processing during this sampling period may have been a source of HNO_3 gas.

Two samples collected at KEJ encountered fog under $T < 0\,^\circ\text{C}$ conditions. One sample was collected during 8–9 November 2002 (Fig. 7a, b) and another one was during 9–10 November 2002 (Fig. 7c, d). The ambient temperature ranged from -2.6 to $-8.8\,^\circ\text{C}$ during the first sampling period (Table 1) and fog occurred from 05:00 to 08:00 a.m. on 8 November, judging by the measured RH. In this sample, NH_4^+ and $nss\text{-}SO_4^{2-}$ were two dominant ionic species in the particles that were < 3 µm where the RA varied from 0.7 to 0.9, suggesting that the ammonium salt was incompletely neutralized. Two supermicron modes of NH_4^+ had MMADs at 2.8 and 7.5 µm, respectively, in this sample (Fig. S1h).

The mass ratio of $NO_3^-/nss\text{-}SO_4^{2-}$ was generally less than 0.1 in the 2.8 µm mode particles while it was over 1 in the 7.5 µm mode particles. The incompletely neutralized ammonium salt aerosols at the 2.8 µm mode contained a much smaller amount of nitrate, suggesting that the NH_4^+ was mainly due to fog-processed aerosols. However, the ammonium salt aerosols at the 7.5 µm mode were likely completely neutralized and contained a significant amount of nitrate and sea-salts. This suggested that the 7.5 µm mode NH_4^+ was probably from the direct collection of fog droplets. The calculated air mass back trajectory showed that the air came from the coastal areas in the southwest and the high concentration of sea-salt aerosols was thereby observed in fog droplets (Figs. 7a, b, S2j). The absence of nitrate and sea-salts at the 2.8 µm mode and the abundance of nitrate and sea-salts at the 7.5 µm mode (fog droplets) suggest that potential splashing of 5–10 µm droplets in the impactor played a negligible role in the formation of the 2.8 µm mode. The calculated RA in this sample showed that the incompletely neutralized acids, as was observed for the 2.8 µm mode, was absent for particles > 4 µm. This excluded the possibility that the variability in the relative length of time fog was sampled,

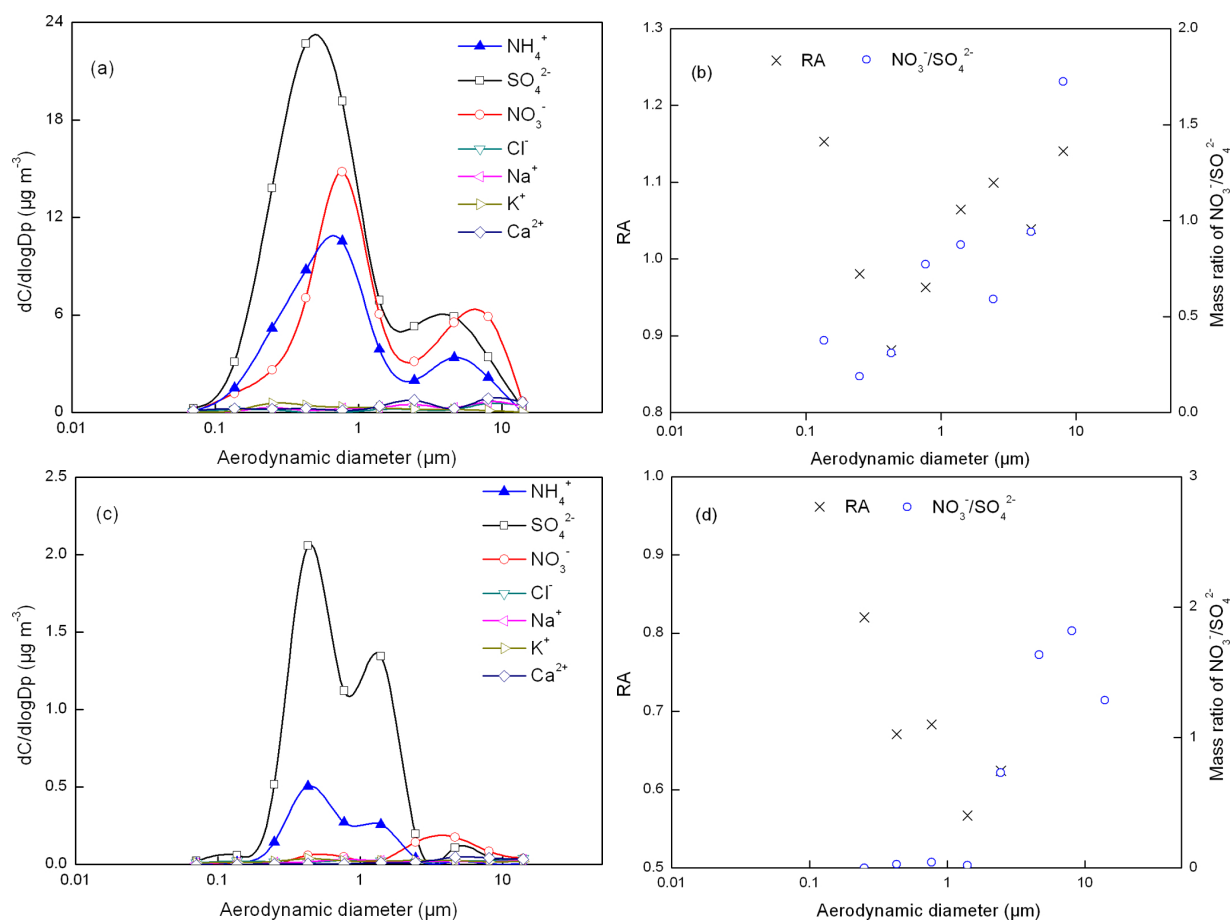**Fig. 8.** Same as in Fig. 3 except for fog-sample 6 (**a** and **b**) and fog-sample 3 (**c** and **d**).

and/or the differing degrees of drying, played any significant role on the formation of the 2.8 μm mode (otherwise, the incompletely neutralized acids would be consistent for particles of the 2.8 μm mode and larger particles).

The second sample on 9–10 November at KEJ was the sample collected immediately after the first sample on 8–9 November. Similar to the findings in sample 1, the NH_4^+ in supermicron particles also had two modes at 2.8 and 7.5 μm, respectively (Figs. 7c, d, S1i). The 2.8 μm mode of NH_4^+ observed on 9–10 November was likely associated with the fog event at $T < -4\,°C$ before sampling. The NH_4^+ was apparently associated with SO_4^{2-} and the ammoniated sulfuric acid salt aerosols were incompletely neutralized (Yao and Zhang, 2012). Fog occurred from 05:00 p.m. on 9 November to 11:00 a.m. on 10 November when $T > 0\,°C$. The 7.5 μm mode of NH_4^+ was likely due to the direct collection of fog droplets.

The highest concentration of NH_4^+ in supermicron particles was observed on 19–20 February 2003 at ALG (Fig. 8a, b) when T ranged from −5.2 to −8.8 °C. Fog occurred from 07:00 to 10:00 a.m. on 19 February with $-8.0 < T < -7.0$, and from 08:00 p.m. on 19 February to 11:00 a.m. on

20 February with $-8.8 < T < -5.2\,°C$. Two supermicron modes of NH_4^+ had MMADs at 3.4 and 7.5 μm (Fig. S1g). Following the analysis of bi-modal supermicron modes of NH_4^+ presented above, the NH_4^+ in the 3.4 μm mode was mainly ascribed to fog-processed ammonium salt aerosols prior to the sampling (air mass came from the northeast, Fig. S2h) while the NH_4^+ in the 7.5 μm mode was probably from the direct contribution of fog droplets in the sampling (air mass came from the southeast, Fig. S2i).

One sample collected on 9–10 December 2004 at SPR, with T in the range of −2.4 to 1.7 °C, had a similar size distribution and composition of fog-processed ammonium salts (Figs. 8c, d and S1j) to some of the samples collected under $T > 0\,°C$ and acidic conditions. Fog occurred from 06:00 p.m. on 8 December to 11:00 a.m. on 9 December with $-2.6 < T < -1.0\,°C$ prior to the sampling and from 05:00 p.m. on 9 December to 08:00 a.m. on 10 December with $-2.2\,°C < T < -1.2\,°C$. The 1–2 μm mode observed was likely associated with the former fog event.
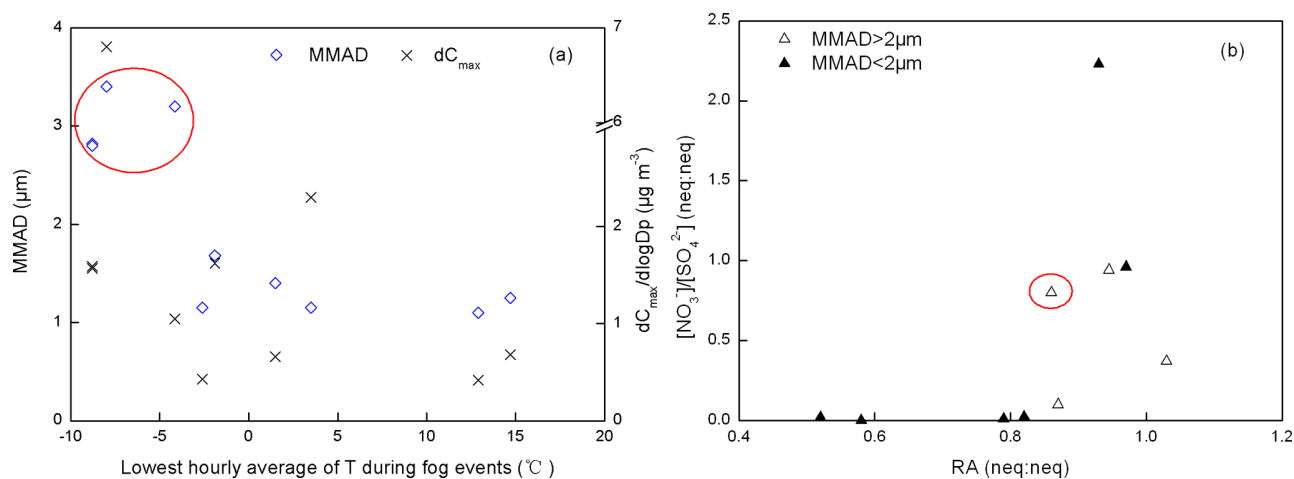
Fig. 9. Variations of MMAD and dC_{max} of fog-processed NH_4^+ aerosol versus lowest hourly average of T in the fog event associated with the aerosols, and $[NO_3^-]/[SO_4^{2-}]$ versus RA in fog-processed aerosol ($dC_{max}/dlogD_p$ was obtained when log-normal functions were fitting the size distribution of NH_4^+), high $[NO_3^-]/[SO_4^{2-}]$ in (b, the circled point) is because ammonium salt externally coexisted with nitrate (Yao and Zhang, 2012).

3.4 Variability of MMAD of fog-processed ammonium salt aerosols

When the MMAD of fog-processed ammonium salt aerosols ($< 4\,\mu m$) was plotted against the lowest hourly average of T during the fog event associated with the aerosols, it was found that the MMAD could be grouped into two regimes (Fig. 9a). In Regime 1, the MMAD was between 2.8 and $3.4\,\mu m$, when the lowest hourly average of T during the fog events was less than $-4\,°C$. In Regime 2, the MAAD was between 1.1 and $1.7\,\mu m$, when the lowest hourly average of T was over $-3\,°C$ and most of the T was over $0\,°C$. The concentrations of the measured NH_4^+ in Regime 1 were sometimes higher and other times lower than those in Regime 2 (Fig. 9a). Thus, the differences of MMADs between the two regimes were not likely determined by the concentrations of NH_4^+. Neither were the differences likely determined by the chemical compositions and neutralization extents of ammonium salts, as shown in Fig. 9b.

Theoretically, the MMAD of fog-processed aerosols should be determined by four factors, i.e., chemical composition, the absolute amount of different chemical species, ambient temperature, and relative humidity. The relative humidity can affect the mole fractions of water and change the MMAD. The calculated mole fractions of water were similar between the two regimes. For example, the fraction was 0.85 for the $1.4\,\mu m$ mode aerosol collected at KEJ during 10–11 November 2002; 0.83 for the $3.2\,\mu m$ mode aerosol collected at EGB on 6 March 2002; and 0.84 for the $2.8\,\mu m$ mode aerosol collected at ALG on 19–20 February 2003. The liquid water content was thus unlikely to explain the mode size differences between the two regimes (note that only inorganic species are included in the AIM model). The mass

transfer of water could not be the cause for the mode size differences because the time scale to attain an equilibrium between water vapor and liquid water is within a few minutes (Kerminen, 1997; Chan and Chan, 2005; DeMott et al., 2009).

It should be noted that our analysis was based on the measured inorganic species. Yao et al. (2011) reported that ammonium salts were usually internally mixed with organics in atmospheric particles in eastern Canada. Organics can play an important role in fog events (Ming and Russell, 2004; Russell et al., 2009; Moore et al., 2011; Asa-Awuku et al., 2011; Gierlus et al., 2012). Rehbein et al. (2011) recently reported that more semi-volatile species can partition in the particulate phase in those low T fog events. The impact of organics on the two regimes should be investigated further in the future.

4 Conclusions

Fog-processed aerosols observed at Canadian inland and coastal rural sites were identified and factors determining their size distributions and chemical compositions were investigated. It is well known that the mass concentration of supermicron NH_4^+ is much lower than that of submicron NH_4^+. This was the case for all of the non-fog samples and was also the case for seven of the fog samples. However, in three of the fog samples, the concentrations of NH_4^+ at 1–$4\,\mu m$ modes were found to be higher than those at submicron modes, suggesting that fog events significantly increased the concentrations of supermicron ammonium at certain ambient conditions. In addition, for particles less than $4\,\mu m$, the concentrations of NH_4^+ of the three fog samples almost doubled

when compared to the average value of non-fog samples at the same site. The 1–4 µm mode of NH_4^+ was absent in non-fog samples which indirectly supported that the mode was associated with fog-processing of aerosols. Fog- processed aerosols at 1–4 µm can be acidic or neutral, depending on the abundance of NH_3 gas. When the fog-processed aerosols were acidic, ammoniated sulfuric acid salts were observed. When the fog-processed aerosols were neutral, ammonium sulfate and ammonium nitrate co-existed.

Consistent with previous studies, it was found that fog events can lead ammonium salt aerosols to a mode of 1–2 µm. The present study further identified that fog events could also lead ammonium salt aerosols to a mode of 3–4 µm when $T < -4\,°C$. The MMADs were found to be closely related to T, but not to the chemical compositions and concentrations of ammonium salts.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys.net/12/11165/2012/acp-12-11165-2012-supplement.pdf.

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