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Size distribution of inorganic ions

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Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites

L. Zhang, R. Vet, A. Wiebe, C. Mihele, B. Sukloff, E. Chan, M. D. Moran, and S. Iqbal

Air Quality Research Division, Science and Technology Branch, Environment Canada 4905 Dufferin Street, Toronto, Ontario, M3H 5T4, Canada

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Correspondence to: L. Zhang (leiming.zhang@ec.gc.ca)

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Abstract

Size-segregated water-soluble inorganic ions, including particulate sulphate (SO $_{4}^{2-}$), nitrate (NO₃⁻), ammonium (NH₄⁺), chloride (Cl⁻) and base cations (K⁺, Na⁺, Mg²⁺, Ca²⁺), were measured using a Micro-Orifice Uniform Deposit Impactor (MOUDI) during fourteen short-term field campaigns at eight locations in both polluted and remote regions 5 of eastern and central Canada. The size distributions of SO_4^{2-} and NH_4^+ were unimodal, peaking at 0.3–0.6 μ m in diameter, during most of the campaigns, although a bimodal distribution was found during one campaign and a trimodal distribution during another campaign made at a coastal site. The size distributions of NO₃⁻ were unimodal, peaking at 4.0–7.0 μ m, during the warm-season campaigns and bimodal, with one peak at 0.3–0.6 μ m and another at 4–7 μ m, during the cold-season campaigns. A unimodal size distribution, peaking at 4–6 μ m, was found for Cl⁻, Na⁺, Mg²⁺ and Ca²⁺ during approximately half of the campaigns and a bimodal distribution, with one peak at $2 \mu m$ and the other at $6 \mu m$, was found during the rest of the campaigns. For K⁺, a bimodal distribution, with one peak at $0.3 \,\mu$ m and the other at $4 \,\mu$ m, was observed during most 15 of the campaigns. The measured ion concentrations varied by one order of magnitude across the various sites. The air-mass origins and meteorological conditions both played important roles in formulating the observed geographical and seasonal patterns of these ion species concentration levels, size distributions and fine particle acidity.

20 1 Introduction

In order to address the impacts of atmospheric aerosols on air-quality, ecosystem heath, and climate change, it is essential to gain a thorough knowledge of their chemical composition and size distributions at high temporal resolution and at local, regional, and global scales (Andreae and Crutzen, 1997; McMurry, 2000; Kaufman et al., 2002;

²⁵ IPCC, 2007). Acid deposition is one of the many atmospheric problems involving atmospheric aerosols. Acid deposition that exceeds the critical load of an ecological



system will cause long-term harmful effects. Different ecosystems have different critical loads due to their different buffering capacities or sensitivities to acid deposition. Sulphur and nitrogen species contribute to acid deposition (Whepdale et al., 1997) while the deposition of base cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) increases the alkalinity

of the surface and thus the ecosystems' buffering capacity (Watmough et al., 2005; Skeffington, 2006; McNaulty et al., 2007). To assess the effects of acid deposition on sensitive ecosystems, the atmospheric deposition of both acidic species and base cations needs to be estimated with sufficient accuracy (Environment Canada, 2005). This requires knowledge of the size distributions of the relevant particle species due to
 the strong dependence of particle deposition on particle size (Pryor et al., 2008).

Substantial knowledge has been gained on the size distributions of the major watersoluble inorganic ions during the past four decades. Non-sea salt sulphate (SO₄²⁻) and ammonium (NH_{4}^{+}) were found to be predominantly in the fine particle mode while sea spray SO_4^{2-} , CI^- , Na^+ , Mg^{2+} and Ca^{2+} were more abundant in the coarse fraction (Milford and Davidson, 1987; Hillamo et al., 1998; Heintzenberg et al., 2000; Parmar et 15 al., 2001; Lestari et al., 2003; Park and Kim, 2004; Xiu et al., 2004; Tsai et al., 2005). Nitrate (NO_3^-) was found to be predominantly in the fine particle mode in some cases and in the coarse particle mode in many other cases. The fine/coarse NO₃⁻ fractions are determined by the processes through which they are formed, i.e., by the reaction of gaseous HNO₃ with ammonia (fine) or with alkaline species in large particles (coarse) 20 (Kadawaki, 1977; Wolff, 1984; Wall et al., 1988; Zhuang et al., 1999; Parmar et al., 2001; Lee et al., 2008). Many studies have found K⁺ to be mostly in fine particles (Park and Kim, 2004; Park et al., 2004; Chen et al., 2005), although at some locations coarse K⁺ can be substantial (Krivaicsy and Molnair, 1998). In some cases, a bimodal

or trimodal distribution is needed to describe the size distribution of inorganic ions (Milford and Davidson, 1987; Zhuang et al., 1999; Lestari et al., 2003). Apparently, the particle size distributions vary greatly with season, location, and air mass origin (Birmili et al., 2001; Hazi et al., 2003; Tunved et al., 2003; Park et al., 2004; Trebs et al., 2004; Van Dingenen et al., 2005; Abdalmogith and Harrison, 2006; Fisseha et al., 2006).

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Despite some field studies conducted at various locations in eastern North America measuring the chemical composition of size-resolved particles (e.g., Hazi et al., 2003; Rupakheti et al., 2005; Lee et al., 2008), there is still a lack of understanding of the concentration levels and size distributions of many particle species in these regions, 5 especially at remote locations in northern Canada where there are no major nearby emission sources. During 2001–2005, fourteen short-term field campaigns were conducted by Environment Canada to measure the size-segregated water-soluble inorganic ions at eight rural and remote sites, which are thought to represent the regional background air in their respective locations. The study covered both the cold and the warm seasons, and was conducted at sites located in both populated and remote re-10 gions. The primary goal of this paper is to characterize the size distributions of the background inorganic ions over eastern Canada so that the information can be used to improve future acid deposition, air-quality, and climate modelling studies. Back trajectory analysis has been conducted to identify the effects of air-mass origins on the seasonal and geographical patterns of the measured ion mass concentrations and 15 size-distribution profiles. A brief discussion on the acidity of fine particles based on the molar ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- is also given here.

2 Experimental design and method

- 2.1 Emission sources and measurement sites
- The ion species measured in the 14 campaigns included SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻, K⁺, Na⁺, Mg²⁺ and Ca²⁺. The majority of SO₄²⁻, NO₃⁻ and NH₄⁺ in this region exists in secondary particles, i.e., formed from their gaseous precursors (SO₂, NO_x and NH₃, respectively) through various chemical reactions (Vet et al., 2001). Mg²⁺ and Ca²⁺ are mainly from soil dust emissions, Cl⁻ and Na⁺ from sea salt and road salt emissions, and K⁺ from soil dust emissions and from biomass burning and vegetation. In order





distributions of the precursors have to be known. Emissions of SO₂, NO_x, NH₃ and PM₁₀ (particles with aerodynamic diameter smaller than 10 μ m) combining year 2000 Canadian sources and year 2001 USA sources have been aggregated into the Canadian air-quality model grids (~42 km by 42 km) and are shown in Fig. 1. In Canada,

- ⁵ southern Ontario and southern Quebec have high emissions of SO₂, NO_x, NH₃ and PM₁₀ since these areas have a high population density, many industries, and intense agricultural activities. The southern Prairies of western Canada also have quite high emissions of SO₂, NO_x, NH₃ and PM₁₀ due to downstream oil and gas production and agricultural activities. In the USA, most parts of the eastern half of the USA have high emissions of SO₂ NO_x.
- ¹⁰ emissions of SO₂, NO_x, NH₃ and PM₁₀; however, the highest emissions of SO₂ and NO_x are located in the eastern half of the US Midwest and the Mid-Atlantic, the highest NH₃ emissions are located in the central area of the US Midwest (the Great Plains) and the highest PM₁₀ emissions are located in most parts of the US Midwest. Seasonal variations of emissions cannot be shown in Fig. 1 and they are briefly discussed wherever needed in Sect. 3.
- Eight sites were selected to conduct the field studies, seven of which were located in eastern Canada and one in central Canada (see the top-left map in Fig. 2). All these sites are ground level Canadian Air and Precipitation Monitoring Network sites (CAPMoN). The selected sites covered a large area of eastern Canada, including both polluted and relatively remote regions. Comparing Fig. 2 with Fig. 1, three sites (EGB, FRS and BRL) can be defined as located in polluted regions, three (ALG, CHA and SPR) in less polluted regions, and two (KEJ and LED) in relatively clean regions. However, long-range transport is known to transport pollutants from polluted regions to the remote locations, as will be discussed in Sect. 3.
- 25 2.2 Measurement periods

Table 1 lists the time periods when the field campaigns were conducted. Since different sites are located at different latitudes and some sites are affected by ocean air masses, the traditionally-defined seasons (based on the month of the year) might not be consis-



tent from site to site. Thus, the average daytime (09:00–17:00 local time) air temperature (see Table 1) was used to define the cold-, warm- and hot-season campaigns. Seven campaigns (FRS1, EGB1, ALG1, LED2, CHA2, SPR2, BRL1) were defined as cold-season campaigns, two campaigns (FRS2, KEJ2) were defined as warm-season campaigns, and five campaigns (KEJ1, ALG2, LED1, CHA2, SPR1) were defined as hot-season campaigns. Note that at the three polluted sites, three campaigns were carried out during the cold season (FRS1, EGB1, BRL1) and one during the warm season (FRS2); at the three less polluted sites, three campaigns were carried out during the cold season (ALG1, CHA1, SPR2) and three during the hot season (ALG2, CHA2, SPR1); and at the two clean sites, one campaign was carried out during the cold season (LED2), one during the warm season (KEJ2), and two during the hot seasons (LED1, KEJ1).

2.3 Sample and analysis

Air samples were collected using a Micro-Orifice Uniform Deposit Impactor sampler (MOUDI Model 110, MSN Minneapolis, MN, USA) at a mass flow rate of 30 L/min at 0°C and 1 atm. The sampler was run with 11 fractionation stages with the following 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 μ m, followed by a backup filter. The MOUDI sampler was located 5 m above ground level under a rain shelter that allowed for free ventilation.

Teflon® filters of 47 mm diameter and 0.1 mm thickness (PTFE, Savillex Corporation, Minnetonka, Minnesota) were used in all stages. After sampling, the filters were stored in pre-washed 10 mL plastic vials at 5–10°C.

Blank values were determined from filters that were loaded into a MOUDI sampler and then unloaded after 24 h of inactive sampling near the same location as the active

²⁵ sampling. This duplicated all handling procedures for both the active and blank filters. Standard ion chromatography (Dionex Corporation, Sunnyvale, California) was used for analyses of all filters after extraction in deionized water. Average field blank values were calculated by replacing all negative and "no response" values from the laboratory



with 2/3 of their reported analytical detection limit (BDL). The BDL was described as 3 standard deviations of repeated measurements of a quality control solution at about 40 parts per trillion (ppt). Air concentrations for each aerosol species were then calculated as: $C_i = (M_i - BV_i)/(MFR^*Et)$, where C_i , M_i and BV_i are concentration, collected mass s and blank value, respectively, of species i during one sample period (Et) and MFR is the mass flow rate (so MFR*Et represents sampled air volume). The sampling duration (Et) ranged from 6 to 152 h (Table 1) depending on the perceived concentration levels at the time of sampling. The number of samples during each campaign is listed in Table 1.

Quality of MOUDI data 2.4 10

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All samples were plotted for data quality control purposes (see Fig. 3 for two examples). It was not uncommon that concentrations were lower than the 3-times standard deviation of all blanks divided by the mean air volume sampled (3SDB) (e.g., Fig. 3b). Under such circumstances, the data were not quantitative due to a large noise-to-signal problem. For each ion species and for every campaign, the percentage of samples hav-

- ing a concentration lower than blank values (3SDB) was calculated. When calculating these percentages, only samples from stages 3–10 (mid-point size 6.2 to 0.093 μ m) were used for SO_{4}^{2-} , NO_{3}^{-} , NH_{3} and K^{+} because the other stages, i.e., the first two and the last two, had very low concentrations of these species; similarly only samples from
- stages 1–8 (sizes larger than 0.32 μ m) were used for the other four species. The data 20 were grouped into four data-quality categories based on these percentage numbers and based on scrutiny of the size-distribution plots as shown in Fig. 3. This is because, under certain circumstances, a clear peak in the size distribution was evident from all samples, yet the percentage of samples having concentrations higher than blank val-
- ues (3SDB) was very low due to the extremely low concentrations in the stages not 25 corresponding to the peak sizes (e.g., Fig. 3b). Under this scenario, the data were believed to represent the real size distribution profiles. The percentage numbers (using samples from MOUDI stages 3–10 for SO_4^{2-} , NO_3^{-} , NH_3 and K^+ and stages 1–8 for the



other four species) and the defined data quality category are all shown in Table 2. For SO_4^{2-} , NO_3^{-} and NH_4^{+} , 90–100%, 80–90% and <80% of data from categories 1, 2 and 3, respectively, had concentrations higher than their respective blank values (3SDB). No category 4 data were identified for these three ion species. For the other five species, 85–100% and 50–85% of categories 1 and 2 data, respectively, had 5 concentrations higher than their respective blank values (3SDB) values; the rest of the data were identified as categories 3 and 4, based mainly on the plotted size-distribution profiles. Data belonging to categories 1 and 2 were thought to be reliable while data belonging to categories 3 and 4 were less reliable. Note that errors caused by chemical transformation (e.g., NH₄NO₃ volatility) during sampling process were not considered 10 in this approach. As a short summary, data for SO_4^{2-} and NH_4^+ during all fourteen campaigns and data for NO₃⁻ during most of the campaigns were of good quality in categories 1 and 2. For the rest of the species, the data guality ranged from relatively good (category 2) to very poor (category 4) depending on the nature of the site and the time of the year. 15

2.5 Back trajectory cluster analysis

In order to identify the source regions of the sampled aerosols and to better explain the geographical and seasonal patterns of the observed concentrations and size distributions, back trajectory cluster analyses, similar to the approach used in many previous studies (Abdalmogith and Harrison, 2005 and references therein), were conducted. Cluster analysis can account for variations in transport speed and direction simultaneously, yielding clusters of trajectories having similar length and curvature. Three-day back trajectories (every six hour) created by the Canadian Meteorological Centre for the period of 2001–2005 were run through a K-means clustering technique for each

site. They were organized into six common clusters based on the commonality of Euclidian distance from trajectory to trajectory (Dorling, 1982). Figure 2 shows the six clusters at the eight sites where the 14 campaigns were conducted.



The correlations between the ion concentrations and the pre-defined trajectoryclusters can be explored by comparing the distributions of ion concentrations associated with different trajectory clusters. Since the samples collected in this study had variable durations and some samples had a very long duration (up to 6 days, see Table 1),

- and the campaigns covered only short periods of several weeks, it is difficult to assign the measured concentrations of individual samples to different trajectory clusters. Thus, we used 5 years of CAPMoN 24-hour bulk (not size-resolved) concentrations to identify the dependence of the ion concentrations on the defined trajectory-clusters. Note that there were 4 trajectories every day and CAPMoN monitored concentrations
 daily. Thus, each and every daily concentration was assigned to whatever clusters
- were associated with the 4 daily trajectories. The mean and median concentrations of the eight ion species for each trajectory cluster were generated from the 2001–2005 CAPMoN data (Table 3).
- It can be seen from Table 3 that the highest concentrations of SO₄²⁻, NO₃⁻ and NH₄⁺
 ¹⁵ were associated with clusters SSW at Algoma, SSE and WNW₋L at Bratt's Lake, WSW at Chalk River, SSE and WSW at Egbert, WSW at Frelighsburg, WNW at Kejimkujik, WSW at Lac Edouard and WSW Sprucedale. Air masses associated with NNE and NNW had lowest concentrations of SO₄²⁻, NO₃⁻ and NH₄⁺ at Algoma, Chalk River, Egbert, Kejimkujik, Lac Edouard and Sprucedale. At many locations (e.g., ALG, BRL, CHA, KEJ, LED and SPR), the clusters associated with highest concentrations of SO₄²⁻,

 NO_3^- and NH_4^+ also associated with highest concentrations of K⁺, Mg^{2+} and Ca^{2+} due to the similar geographical patterns of the emissions of SO₂, NO_x , NH_3 and PM_{10} at these locations.

The 5-year average concentrations showed clear geographical patterns for most species. For example, EGB, FRS, SPR and ALG had higher SO₄²⁻ concentrations compared to the rest of the sites, while EGB, FRS and BRL had higher concentrations of NO₃⁻, NH₄⁺ and Ca²⁺, and KEJ and FRS had higher concentrations of Cl⁻ and Na⁺. Geographical patterns of K⁺ and Mg²⁺ were not apparent due to the very low concentrations of these two species, although BRL showed highest concentrations.

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It is known that the slowest (i.e., shortest) trajectory clusters passing over high emission areas will have the highest pollutant concentrations and the fastest clusters from clean areas will have the lowest concentrations (Hazi et al., 2003). Results shown in Table 3 support this theory when comparing the defined trajectory clusters shown in Fig. 3 with the emission distributions shown in Fig. 2. The information provided above will be used to support the discussions presented in Sect. 3.

3 Results

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Short and long range transport of emissions, meteorological conditions (temperature, precipitation, solar radiation/cloudiness, mixing layer height, etc.), and physical and chemical mechanisms from which aerosols are produced are important factors relating to aerosol concentration levels and size distributions. In this section, we discuss in detail the seasonal and geographical patterns of the observed aerosol concentrations and size distributions and the possible causes of these patterns. For every ion species (Sects. 3.1–3.5), the following discussions are presented in sequence: (1) the produc-

- tion mechanism for each ion, (2) the seasonal contrast and associated causes of the campaign-average concentrations (each sample was weighted by its duration) at the six sites that each had two campaigns, (3) the geographical patterns of the campaign-average concentrations, (4) the fine and coarse fractions of the ion mass concentrations, and (5) the characterization of size distributions including the size-distribution
- ²⁰ profiles and related parameters. Two campaigns made at Algoma are discussed in more detail in Section 3.6 considering the strong effects of local sources (road salt) and the unusual seasonal pattern of several observed species (e.g., SO_4^{2-} , NH_4^+). Fine particle acidities are explored in Section 3.7 based on the molar ratio of NH_4^+ to the sum of SO_4^{2-} and NO_3^- .
- Fine particles were defined as the particles having an aerodynamic diameter smaller than 2.5 μ m (PM_{2.5}); however, MOUDI stages do not have a size cut at 2.5 μ m. Thus, the measured MOUDI sizes were inverted to give continuous size-distribution profiles



using a modified Twomey inversion technique (Winklmyr et al., 1990) and kernel functions from Marple et al. (1991), as was done in previous studies (e.g., Li et al., 1998). Fine fractions of the total mass were then obtained by integrating the profiles from 0-2.5 μ m. Also, for future applications of the particle size distributions, the mass mean diameter (MMD) and associated geometric standard deviation (GSD) were calculated for the total mass and for the fine and coarse fractions of the total mass. The discussions presented in this section are based on results shown in Tables 4 and 5 and in Figs. 4–8. Information presented in Table 1, Figs. 1 and 2, and Sect. 2.5 is needed to explain the observed phenomena.

10 3.1 Sulphate

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Fine particle SO_4^{2-} is commonly generated by the oxidation of SO_2 through a slow gasphase (homogeneous) oxidation and/or gas/particle phase (heterogeneous) oxidation. The rate of SO_4^{2-} production is expected to be higher in the warm and hot seasons when compared to the cold seasons (see some detailed discussions in Hazi et al., 2003 and references therein). Coarse SO_4^{2-} is produced by reactions of SO_2 or sulfuric acid on the wet surface of sea salt or soil particles (Wall et al., 1988).

At Frelighsburg, the average SO₄²⁻ concentration during FRS1 was slightly higher than during FRS2 (Table 4). By looking at the back trajectories shown in Fig. 2, it can be seen that 59% of the air masses during FRS1 (clusters SSW and WSW) were from the high SO₂ emission regions of eastern USA and the industrial areas of southern Ontario and southern Quebec, while only 25% of the air masses during FRS2 were from these same regions. Thus, despite the slightly colder weather during FRS1, the

 SO_4^{2-} concentrations were higher because of the more polluted air masses.

At Chalk River, Sprucedale, and Lac Edouard, the hot-season campaigns generally had a higher percentage of polluted air masses (e.g., clusters WSW and ESE clusters were the most polluted and clusters NNW and NNE were the least polluted at all three locations). The campaign-average SO_4^{2-} concentrations were higher during the hot-season campaigns at all three locations due to a combination of the effects of tem-

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perature differences and air-mass origins. The campaign-average SO_4^{2-} concentration was 50% higher in the hot season compared to the cold season at Chalk River, >100% higher at Lac Edouard and ~400% higher at Sprucedale.

At Kejimkujik, the campaign-average SO₄²⁻ concentration was three times higher during the hot-season campaign (KEJ1) compared to the warm-season campaign (KEJ2). This was likely due to a combination of the effects of temperature differences and different air-mass origins. During KEJ1, 28% of the air masses were from the high emission region (cluster WNW) and 13% were from the Atlantic Ocean (clusters SSW and ESE) while during KEJ2, these numbers were about the reverse, i.e., 14% and 25%, respectively. Because of the differences in the air-mass origins during these two campaigns, the concentrations of coarse SO₄²⁻ during KEJ1 were slightly lower than during KEJ2

(0.15 vs. 0.23 μ g m⁻³) while concentrations of fine SO₄²⁻ during KEJ1 were much higher than during KEJ2 (3.3 vs. 0.9 μ g m⁻³).

- At Algoma, the campaign-average SO₄²⁻ concentration was higher during ALG1 than ¹⁵ during ALG2. The air-mass origins shown in Figure 2 cannot explain this phenomena since ALG1 had a lower percentage of air masses from clusters SSW and ESE (passing over high emission regions) and a higher percentage of air masses from NNW and NNE (passing over clean regions) when compared to ALG2. The phenomena is also in contradiction to the theory that SO₄²⁻ production was higher during the hot seasons ²⁰ since ALG1 was a cold-season campaign and ALG2 was a hot-season campaign. The causes of higher campaign-average concentration during the cold-season campaign at
- causes of higher campaign-average concentration during the cold-season campaign at this location will be discussed in Sect. 3.6. In comparing campaign-average concentrations conducted during the same season,

higher SO_4^{2-} concentrations were observed at locations close to high SO_2 emission areas and/or with air masses from high emission sources. For example, SO_4^{2-} concentrations were higher at locations close to the industrial areas of southern Ontario and southern Quebec (e.g., Sprucedale, Egbert and Frelighsberg) compared to remote locations (e.g., Lac Edouard). The average SO_4^{2-} concentrations varied by >5 times

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from site to site during any season.

The fine fraction of SO_4^{2-} mass concentrations made up ≥95% of the total SO_4^{2-} mass in ten campaigns (FRS1, FRS2, EGB1, KEJ1, ALG2, LED1, LED2, CHA1, CHA2, SPR1), around 90% in three campaigns (ALG1, SPR2, BRL1) and 79% in one campaign at a coastal site (KEJ2) in late fall. Note that another campaign at the same coastal site (KEJ1) showed different concentrations (>3 times higher) and fine/total fractions (96%) from those of KEJ2. The differences were caused by different air-mass origins as shown in Fig. 2. Since fine SO_4^{2-} particles dominated the total SO_4^{2-} mass concentrations, their geographical distributions and seasonal variations were similar to the total SO_4^{2-} mass concentrations (Table 4). Coarse SO_4^{2-} particle concentrations (total minus fine particles) were generally very low, ranging from 0.03–0.32 µg m⁻³ during the fourteen campaigns.

Because of the very small fraction of coarse SO_4^{2-} during most campaigns, SO_4^{2-} size distribution was dominated by a single mode peaking at 0.3–0.6 μ m (Fig. 4). A campaign-average trimodal size distribution was apparent at KEJ2 due to the non-negligible coarse SO_4^{2-} fraction. A very small second peak in the coarse particle size range of 2–5 μ m was also observed in several campaigns (e.g., ALG1, SPR2). In general, the SO_4^{2-} size distribution profiles were similar at different locations and during different seasons; however, there was a tendency for SO_4^{2-} concentrations to peak at a lightly larger size in the coal decrease (0.5

²⁰ slightly larger sizes in the cold season (0.5–0.6 μ m) compared to the hot season (0.3– 0.4 μ m). As mentioned above, the rate of SO^{2–}₄ production is probably higher in the warm and hot seasons and the removal rate through dry deposition process is also expected to be higher; thus, SO^{2–}₄ in the cold season probably had a longer life time and was able to grow to larger sizes.

²⁵ The MMD for SO_4^{2-} over all campaigns except KEJ2 ranged from 0.28 to 0.56 μ m with GSDs around 2.3 to 2.8 (Table 5). The KEJ2 campaign exhibited a higher MMD and GSD due to the contribution of sea salt sulphate particles. By fitting fine and coarse SO_4^{2-} particles separately into lognormal distributions, the MMD ranged from 0.26 to 0.49 μ m for fine particles and 4.0 to 4.6 μ m for coarse particles, with the GSD

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ranging from 2.1 to 2.4 for fine particles and from 1.4 to 1.5 for coarse particles. Most previous studies showed the MMD values ranged from $0.3-0.5 \,\mu$ m (Milford and Davidson, 1987). Results shown above confirm that the variations in the MMD and GSD values of SO₄²⁻ were caused by different air mass origins (which control the emissions of the gaseous precursor) and by meteorological conditions (which control physical and chemical processes that produce SO₄²⁻ and remove it from the atmosphere).

3.2 Nitrate

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Fine NO_3^- is produced by the gas-phase reaction of HNO_3 with NH_3 while coarse NO_3^- is formed by the heterogeneous reaction of HNO_3 gas with sea salt or soil dust particles (Yoshizumi and Hoshi, 1985). The chemistry favors the production of NH_4NO_3 at high humidity and low temperature (Allen et al., 1989).

Unlike SO₄²⁻, whose concentrations are usually higher in the hot season, NO₃⁻ concentrations are much higher during the cold season due to its favoured low temperature reaction thermodynamics and its volatility in hot weather. This was found to be the case for the campaign-average NO₃⁻ concentrations at Frelighsberg, Algoma, Chalk River, and Lac Edouard. It is noted that the NO₃⁻ concentrations during FRS1 (November, 2001) were more than ten times higher than during FRS2 (may, 2002) despite the fact that the temperature difference during these two campaigns was small (a few degrees). The very large difference in the campaign-average NO₃⁻ concentrations was caused

- ²⁰ by a combination of the different air-mass origins and different temperatures since a larger percentage of air mass trajectories were from the high emission regions and the temperature was lower during FRS1 compared to FRS2. At Sprucedale, no apparent seasonal difference was found, suggesting that the effects of different air-mass origins and the effects of different temperatures during the two campaigns cancelled each
- $_{25}$ other out. At Kejimkujik, the hot season campaign had a slightly higher average $\rm NO_3^-$ concentration than the warm season campaign, but the hot season was determined by coarse particle $\rm NO_3^-$, consistent with considerably higher $\rm Ca^{2+}$ concentrations and more frequent trajectories over the high $\rm NO_x$ emission areas of eastern North America.

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Similar to SO_4^{2-} , higher NO_3^{-} concentrations were found in general at locations close to the high NO_x and NH_3 emission areas and/or with higher frequencies of air masses over the high emission areas. The campaign-average mass concentrations of NO_3^{-} ranged from 0.1–3.6 μ g m⁻³ depending on location and season (Table 4).

- ⁵ The fraction NO₃⁻ mass concentrations in the fine mode were 78–90% during the seven cold-season campaigns (FRS1, EGB1, ALG1, LED2, CHA1, SPR2 and BRL1) and 23–36% during the seven warm-season campaigns (FRS2, KEJ1, KEJ2, ALG2, LED1, CHA2 and SPR1). Thus, as expected from reaction kinetics, coarse particle NO₃⁻ dominated in the warm seasons while fine particle NO₃⁻ dominated in the cold access (average of the seven to the seven seasons while fine particle NO₃⁻ dominated in the cold access (average of the seven seasons). This also average to the much bighter
- ¹⁰ seasons (except at Kejimkujik and Sprucedale). This also explains the much higher NO_3^- concentrations during the cold seasons compared to the warm seasons. These results agree with previous studies at different locations (e.g., Kadowaki, 1976; Fisseha et al., 2006). Note that the fine fraction of the total NO_3^- mass concentrations also depends on the amount of available NH_3 as discussed below in Sect. 3.7. The coarse
- ¹⁵ nitrate fractions in the hot seasons discussed above should be treated as an upperend estimation due to the possibility of the loss of fine particle NH₄NO₃ collected by MOUDI which could have exaggerated the relative importance of coarse versus fine mode nitrate (Lee et al., 2008).

During the seven cold-season campaigns, the campaign-average NO₃⁻ size distributions showed a bimodal distribution with one peak located in the 0.3–0.6 μ m range and another in the 4.0–7.0 μ m range (Fig. 4). During the seven warm or hot-season campaigns, NO₃⁻ showed only one coarse mode peak at 4.0–7.0 μ m. The size distribution profiles varied significantly with location and season.

The MMD for fine NO₃⁻ ranged from 0.38 to 0.66 μ m at non-coastal sites, with GSD ranging from 2.0 to 2.3 (Table 5). At the coastal site (KEJ1, KEJ2), the MMD and GSD were around 1.0 μ m and 3.0, respectively, larger than at other rural sites. The MMD and GSD for coarse NO₃⁻ were 4.4–5.4 μ m and 1.4–1.47, respectively. The MMD and GSD values for both fine and coarse NO₃⁻ are quite close to previous measurements at different locations (e.g., Ruijgrok et al., 1997).

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3.3 Ammonium

NH₄⁺ is formed from its gaseous precursor NH₃ through gas-phase and aqueous-phase reactions with acidic species (e.g., H₂SO₄, HNO₃ and HCI). Among the reaction products, (NH₄)₂SO₄ is preferentially formed and the least volatile; NH₄NO₃ is relatively
 volatile and NH₄CI is the most volatile. Volatility increases with increasing air temper-

ature and decreasing humidity (Pio et al., 1987; Mozurkewich, 1993). Note that NH₃ emissions are considerably higher during the warm/hot seasons than during the cold seasons due to increased agricultural activity and temperature-related emissions.

It was noted above that SO_4^{2-} production is higher in the warm/hot seasons. NH_4^+ production is also expected to be higher in the warm/hot seasons due to higher NH_3 emissions and the preference of the formation of $(NH_4)_2SO_4$. Thus, the seasonal cycles of NH_4^+ concentrations should be similar to SO_4^{2-} at the same locations. This is consistent with the campaign-average SO_4^{2-} and NH_4^+ concentrations shown in Table 4. Higher NH_4^+ concentrations were found at locations close to high NH_3 emission ar-

eas and/or with a higher frequency of air masses that traveled over high NH₃ emission areas. For example, very high concentrations of NH₄⁺ were observed at Egbert and Bratt's Lake in the cold season. At Egbert, only 6% of the air masses were from the low NH₃ emissions clusters (NNW and NNE). At Bratt's Lake, Clusters SSE, WNW₋L, WNW, NNW all passed over high NH₃ areas. Thus, these two campaigns had the highest NH₄⁺ concentrations. Both local sources and long range transport played important roles in the observed high NH₄⁺ concentrations. The campaign-average mass concentrations of NH₄⁺ ranged from 0.2–2.0 µg m⁻³ across the region.

The fine fraction of NH_4^+ mass concentrations constituted 92–99% of the total NH_4^+ during thirteen of the fourteen campaigns. The only exception was during KEJ2 when the fine fraction was 80% of the total. The dominance of the fine NH_4^+ fractions shown in Table 4 and in Fig. 4 suggests that most NH_4^+ was created by homogeneous reactions with a unimodal size distribution peaking at 0.3–0.6 μ m over most campaigns. A small second mode, with a peak at 6 μ m, was found during ALG1 and a trimodal distri-

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bution was found during KEJ2 at a coastal site. Such trimodal distributions have been observed at other coastal locations and are likely caused by a combination of different physical and chemical processes (e.g., aqueous phase chemistry, condensational growth, droplet evaporation, see discussions in Zhuang et al., 1999). The MMD and ${}_{5}$ GSD for fine NH₄⁺ were in the range of 0.25–0.48 μ m and 2.0–2.5, respectively, and for coarse NH₄⁺, in the range of 3.6–4.6 μ m and 1.3–1.5, respectively. Not surprisingly, these values are very close to those of SO₄²⁻. These two species also had very similar geographical distributions and size distributions.

3.4 Chloride and sodium

- Most Cl⁻ and Na⁺ measured during the campaigns are thought to be due to sea salt (KEJ1 and KEJ2) and road salt (other campaigns). Note that salt is spread on roads in the wintertime in many areas of Canada to melt ice and snow. The campaign-average concentrations for both Cl⁻ and Na⁺ were very low during most campaigns, but as expected, relatively high during KEJ1 and KEJ2 (coastal site). The KEJ2 campaign had
 ¹⁵ much higher concentrations of Cl⁻ and Na⁺ compared to KEJ1 (0.42 vs. 0.16 µg m⁻³ for Cl⁻ and 0.34 vs. 0.24 µg m⁻³ for Na⁺). On the other hand, KEJ2 had much lower concentrations of the rest of the species, e.g., the concentrations of Ca²⁺ and K⁺ during KEJ2 were only ~15% of those during KEJ1. The different air mass origins shown in Fig. 2 certainly played the major role in the concentration differences of all ion species.
- ²⁰ By comparing wind speed observed during these two campaigns and the length of 1day back trajectories (figure not provided), it was found that the trajectory speeds from the Atlantic Ocean were stronger during KEJ2 than during KEJ1. This also caused higher sea salt emissions during KEJ1. During a cold-season campaign at Algoma, very high concentrations of Cl⁻ and Na⁺ were observed, which was identified to be ²⁵ caused by a local source of road salt as will be discussed in Sect. 3.6.

At the coastal site (KEJ1, KEJ2), only around 10% of the Cl⁻ mass and 15–30% of the Na⁺ mass were found in the fine fraction. At other locations, the fine fraction of Cl⁻ and Na⁺ mass ranged from 35–70%. This is because of limited sea salt penetration



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Size distributions of Cl⁻ and Na⁺ were very similar during most campaigns, except for KEJ1, which exhibited different modes for Na⁺ and Cl⁻ (Fig. 5). For the campaigns with very low concentrations, the size distributions shown in Fig. 5 will be highly uncertain 5 due to large measurement uncertainties. For those campaigns with relatively high concentrations, the size distributions were either unimodal at $\sim 6 \,\mu m$ for both Cl⁻ and Na⁺ during EGB1 and KEJ2 or bimodal, with one mode at 2 μ m and the other at 6 μ m, during ALG1 and CHA1. The size distributions of Cl⁻ and Na⁺ were also unimodal during KEJ1, although at a different mode size. Note that during ALG1, the first mode $(\sim 2 \,\mu \text{m})$ had higher concentrations than the second mode $(\sim 6 \,\mu \text{m})$ while during CHA1,

the first mode had lower concentrations compared to the second mode.

The MMD for Cl⁻ and Na⁺ are only presented in Table 5 for those campaigns in which the concentrations were not too low and the data was of relatively good quality. MMD for both Cl⁻ and Na⁺ were around 4–5 μ m for the coarse fractions and 0.4–0.7 μ m for

- the fine fractions. GSD for the coarse and fine fractions were around 1.5 and 3.5-6. 15 respectively.
 - Potassium, magnesium and calcium 3.5

 K^{+} has additional sources than the other cations, which are mainly soil-derived, that is, biomass burning and vegetation. Mg²⁺ and Ca²⁺ are generally from soil particles with a small component from sea salt. Very low concentrations were observed for K⁺ and Mg²⁺ at all rural sites. Ca²⁺ had the highest concentrations among all cations during most campaigns at non-coastal sites.

Fine particle K^+ concentrations and coarse particle Mg^{2+} and Ca^{2+} concentrations dominated their respective total mass concentrations during most campaigns. The almost equal amounts of K^+ in the fine and coarse fractions during KEJ1 and a few other 25 campaigns suggest that emissions from soil dust and emissions from biomass burning and vegetation were equally important. Enhanced K⁺ concentrations in submicron particles were also found in previous studies (Andreae, 1983; Gaudichet et al., 1995;

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Jaffrezo et al., 1998). The size distribution of K⁺ was bimodal, with one mode peaking at 0.3–0.5 μ m and the other at 4–6 μ m. Mg²⁺ and Ca²⁺ also had bimodal distributions (one at 2.5 μ m and the other at 6 μ m) during several campaigns. In a few campaigns, an extra fine mode was also observed (e.g., Ca²⁺ in CHA1 and CHA2); however, the concentrations were extremely low and thus, the size distributions shown in Fig. 5 might not represent the real situation. The size distribution of Mg²⁺ shown for ALG1 seems to be real since it also had two modes similar to other cation species. The MMD for fine and coarse K⁺ were 0.4–1.4 μ m and 5 μ m, respectively. The MMD for Mg²⁺ were 0.8– 1.4 μ m for fine fractions and around 5 μ m for coarse fractions, and the corresponding GSD were 2–3 and 5, respectively. MMD and GSD for coarse Ca²⁺ were around 5 μ m and 1.5, respectively.

3.6 Comparison of campaigns ALG1 and ALG2

ALG1 (cold season) had higher campaign-average concentrations than ALG2 (hot season) for all the species (Table 4). Individual samples collected during ALG1 and ALG2 and associated trajectory clusters and local meteorology were studied in detail. It was found that the majority of samples from ALG1 had much higher Cl⁻ and Na⁺ concentrations than in ALG2, in particular three samples in ALG1. The Trans-Canada Highway, a major transport route, is located 12 km southwest of this site at its closest. During the winter season, road salt was heavily used to help melt the ice and snow on this highway. Winds coming from any direction between the south and northwest (150– 315°) would have brought the air to this site that passed over the highway. Thus, the much higher Cl⁻ and Na⁺ concentrations in ALG1 (>0.4 µg m⁻³) compared to ALG2 (<0.02 µg m⁻³) was thought to be caused by the local source of the road salt. The five year (2001–2005) CAPMoN daily concentration also showed that the average concen-

²⁵ trations of Cl⁻ and Na⁺in winter (December, January, February) were ~5 times higher than the rest of the seasons.

As mentioned in Sect. 3.1, ALG1 had a lower percentage of air masses from clusters SSW and ESE (passing over high emission regions) and a higher percentage



of air masses from NNW and NNE (passing over clean regions) when compared to ALG2. The SO_4^{2-} production rate was also expected to be higher during ALG2 (the hot season campaign). By looking at the median and mean SO_4^{2-} concentrations associated with the different trajectory clusters from the five year (2001-2005) CAPMoN daily data, it was found that clusters associated with high emission areas had higher SO_4^{2-} concentrations in summer than in winter while clusters associated with clean areas had lower SO_4^{2-} concentrations in summer than in winter (Fig. 6a, only median values were shown here, mean values have similar seasonal patterns). For example, clusters SSW, ESE and WNW₋L had higher SO_4^{2-} concentration in summer while clusters NNE, NNW and WNW had lower SO_4^{2-} concentrations in summer compared to winter. 10 The higher SO_4^{2-} concentrations in summer from polluted-clusters were caused by the higher SO_4^{2-} production rate. One cause of the lower SO_4^{2-} concentration in summer compared to winter from clean-clusters was probably due to the fast removal rate (e.g., by dry deposition). However, further studies are needed to identify all possible causes. It is noted that many samples in ALG1 associated with clean-clusters had a concentration of ~2 μ g m⁻³ while many samples in ALG2 had a concentration of $\leq 0.5 \mu$ g m⁻³

tration of ~2 μ g m⁻³ while many samples in ALG2 had a concentration of $\leq 0.5 \mu$ g m⁻³ (Fig. 6b and c). This partially explains the higher SO₄²⁻ concentration in ALG1 than in ALG2.

Another reason for the higher $SO_4^{2^-}$ mass concentration in ALG1 is that there was one 24-h sample (starting at 11:30 of 19 February) that had very a very high concentration (~20 μ g m⁻³). The sample was associated with clusters SSW and WNW_L and the wind speed during the period of 19 February was extremely low. As noted in Sect. 2.5, the slow-moving air-mass passing over high emission areas causes high pollutant concentrations, which likely explains the very high concentration of the sample collected

on 19 February. It is worth mentioning that the very low mixing heights in the winter will likely have also played a role in the high pollutant concentrations associated with polluted air masses. As a comparison, ALG2 had seven samples during the three-day period (23–25 June) associated with cluster SSW. The concentrations of these seven

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samples were much higher than the rest of the samples (e.g., $6-12 \mu g m^{-3}$ versus 0.5– $3 \mu g m^{-3}$), but substantially lower than the extreme sample collected on 19 February in ALG1. Thus, despite the higher percentage of air-masses associated with polluted trajectory clusters in ALG2, the campaign-average concentration was 30% lower compared to ALG1. Several other species (NO₃⁻, NH₄⁺, K⁺ and Ca²⁺) had similar day to day variations as SO₄²⁻ shown in Fig. 6b and c. Thus, these species also had higher campaign-average concentrations in ALG1 than in ALG2, although the magnitudes of the differences between the two campaigns were different for different species due to their different chemical mechanisms and emission sources.

10 3.7 Acidity of fine particles

Fine particles are known to be responsible for many adverse health effects for which aerosol acidity seems to play a role (see discussions and references in Haze et al., 2003 and Moya et al., 2003). NH⁺₄, SO²⁻₄ and NO⁻₃ frequently dominate the mass concentrations of total fine particles. These ions, and to some extent Cl⁻, are formed by gas-to-particle conversion processes through reactions among the gases NH₃, H₂SO₄, HNO₃ and HCl. In this chemical system, the formation of nonvolatile (NH₄)₂SO₄ is preferred and the formation of semivolatile compounds (NH₄NO₃ and NH₄Cl) only occurs when NH₃ is in excess of H₂SO₄ and when favorable meteorological conditions prevail (e.g., low temperature and high humidity). Since NH₃ is the major neutralizer of fine particles (considering the fine particle concentrations of other cation species are very low, as can be seen in Table 4), the equivalent ratio of NH⁺₄ to the sum of SO²⁻₄ and NO⁻₃ can be a measure of the acidity of fine particles.

Figure 7 shows the ratio of the campaign-average mole-equivalent concentrations of NH⁺₄ to (2*SO²⁻₄) and NH⁺₄ to (2*SO²⁻₄+NO⁻₃) using the fine fractions of their respective total mass concentrations. Values of the latter less than unity strongly suggest that the particles are acidic. In general, NH⁺₄ appears to be in excess of SO²⁻₄ during most of the cold-season campaigns (except SPR2) and barely neutralizes SO²⁻₄ during most of the

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hot-season campaigns. This was caused by higher production of SO₄²⁻ in the warm/hot seasons compared to the cold seasons (as discussed in section 3.1), despite the fact that the NH₃ emissions were also higher in the hot/warm seasons. The lowest ratio of NH₄⁺ to (2*SO₄²⁻) appeared in the KEJ2, likely due to the low NH₃ emission in the area as well as the low frequency of trajectories that traveled over the high ammonia emission areas of the US Midwest, Southern Ontario and Southern Quebec. This is consistent with previous reported high incidences of acidic particles in Atlantic Canada (Brook et al., 1997). Locations close to high NH₃ emissions (e.g., Bratt's Lake, Egbert and Frelighsberg) had the highest ratios of NH₄⁺ to (2*SO₄²⁻). The mole-concentration ratio of NH₄⁺ to (2*SO₄²⁻ +NO₃⁻) was around 1.0 during five campaigns (BRL1, EGB1, FRS1, FRS2 and ALG2), between 0.8-0.9 during five campaigns. The ratio was much

higher at locations close to high NH₃ emissions than at other locations and slightly higher during the warm/hot seasons than during the cold seasons due a combination of higher NH₃ emissions and the very low concentrations of fine NO₃⁻ particles.

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To further investigate the details of NH_4^+ - SO_4^{2-} and NH_4^+ - NO_3^- association, the moleequivalent concentration of NH_4^+ versus SO_4^{2-} and NH_4^+ versus (2* SO_4^{2-} + NO_3^-) were plotted using collected samples from all of the fine particle stages. Based on the scatter plots, the 14 campaigns were grouped into four categories of fine-particle-acidity (Fig. 8a, b c and d, respectively) and are discussed in details below.

In category 1 (see campaigns KEJ1, KEJ2, LED1 SPR1 shown in Fig. 8a), the ratio of $NH_4^+/SO_4^{2^-}$ is consistently smaller than 2 (Fig. 8a), but mostly larger than 1. This suggests that NH_4^+ was insufficient in neutralizing $SO_4^{2^-}$ to $(NH_4)_2SO_4$. Thus, NH_4^+ existed as a mix of $(NH_4)_2SO_4$ and NH_4HSO_4 (or H_2SO_4 if too little NH_4^+ is available). At the coastal site (KEJ1, KEJ2), there were also cases having the mole ratio of $NH_4^+/SO_4^{2^-}$ smaller than 1. This suggests that there was an excess of fine $SO_4^{2^-}$, which was likely in the form of H_2SO_4 or associated with base cations. Since no excess NH_4^+ was left to associate with fine NO_3^- , the fine NO_3^- concentrations during these four campaigns

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(KEJ1, KEJ2 LED1 and SPR1) were much lower compared to SO_4^{2-} or NH_4^+ , as was confirmed by the values shown in Table 4.

In category 2 (FRS2, ALG2 and CHA2 in Fig. 8b), the mole ratio of NH_4^+/SO_4^{2-} essentially lies on the line of 2:1 (Fig. 8b). This implies that all fine NH_4^+ and fine SO_4^{2-} existed as $(NH_4)_2SO_4$ and the fine NO_3^- concentrations were low since no NH_4^+ was left. This is confirmed in Table 4 where one can see that the fine NO_3^- concentrations during these three campaigns were 1–2 orders of magnitude lower than SO_4^{2-} or NH_4^+ . Note that there were a few samples from ALG2 and CHA2 belonging to category 1, although most samples from these two campaigns belonged to category 2.

¹⁰ In category 3 (FRS1, EGB1 and BRL1 in Fig. 8c), the mole ratio of NH_4^+/SO_4^{2-} is larger than 2 (Fig. 8c, upper row), but the mole ratio of $NH_4^+/(2*SO_4^{2-}+NO_3^-)$ lies on the line of 1:1 (Fig. 8c, lower row). The average mole ratio of $NH_4^+/(2*SO_4^{2-}+NO_3^-)$ were 0.96, 0.96 and 0.94, respectively, during FRS1, EGB1 and BRL1 (Fig. 7). This implies that fine NH_4^+ basically existed as $(NH_4)_2SO_4$ and NH_4NO_3 . Table 4 shows that fine NO_3^- concentrations were on the same order of magnitude as SO_4^{2-} and NH_4^+ . Note that these three studies took place in cold months of the year in areas near high agricultural emissions sources of NH_3 .

In category 4 (ALG1, LED2, CHA1 and SPR2 in Fig. 8d), the mole ratio of NH_4^+/SO_4^{2-} lies on both sides of the 2:1 line (Fig. 8d, upper row), but the mole ra-

- ²⁰ tios of NH₄⁺/(2*SO₄²⁻+NO₃⁻) were equal to or smaller than 1:1 (Fig. 8d, lower row). This category is actually a mix of the cases of the above three categories plus the situation when the mole ratios of NH₄⁺/(2*SO₄²⁻+NO₃⁻) were smaller than 1:1. Under these ammonia-limited situations, there was not enough NH₄⁺ to neutralize both SO₄²⁻+NO₃⁻ and sometimes not enough just to neutralize SO₄²⁻.
- It is noted that campaigns belonging to the SO_4^{2-} -only categories 1 and 2 were made during the warm/hot seasons while $SO_4^{2-}+NO_3^-$ categories 3 and 4 were during the cold seasons. Figures 7 and 8 indicate that the acidity of fine particles depends on





location and season. The air-mass origins certainly also play an important role as can be seen from the differences between KEJ1 and KEJ2 shown in Fig. 7. A recent study at several USA locations also suggested that the relationship between NH_4^+ and $SO_4^{2-}+NO_3^-$ strong depend on location (different emission sources) and season (different meteorological conditions) (Lee et al., 2008).

4 Conclusions

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Fourteen short-term field campaigns were conducted at eight selected Canadian rural sites to measure size distributions of SO_4^{2-} , NO_3^- , NH_4^+ , CI^- , K^+ , Na^+ , Mg^{2+} and Ca^{2+} using a micro-orifice uniform deposit impactor. Measurement data show that SO_4^{2-} and NH_4^+ were predominately in the fine particle mode at most sites. Fine mode NO_3^- dominated its concentrations during the cold seasons while coarse mode dominated during the warm/hot seasons. Fine mode K⁺ and coarse mode Mg^{2+} and Ca^{2+} dominated their respective mass concentrations. Coarse particles of CI^- and Na^+ dominated their total concentrations at a coastal site, although substantial amounts of fine particles were also observed at locations far from the seashore.

A bimodal distribution of SO_4^{2-} and NH_4^+ was found during one campaign, a trimodal distribution during another campaign made at a coastal site, and a unimodal distribution during the rest of the campaigns. A bimodal distribution, one fine mode and one coarse mode, of NO_3^- was found during the cold-season campaigns and a unimodal distribution in the coarse mode during the rest of the campaigns. A unimodal size dis-

- ²⁰ distribution in the coarse mode during the rest of the campaigns. A unimodal size distribution in the coarse mode was found for Cl⁻, Na⁺, Mg²⁺ and Ca²⁺ during half of the campaigns and a bimodal distribution, both in the coarse mode, was found during the rest of the campaigns. A bimodal distribution, one in the fine mode and one in the coarse mode, of K⁺ was observed during most campaigns.
- ²⁵ Campaign-average air concentrations of all ion species varied by one order of magnitude with the highest concentrations observed at locations with polluted regions and

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the lowest concentrations at remote locations. The geographical and seasonal patterns of the concentration levels, size distributions and the acidity of fine particles clearly depend on location, season, air-mass origin, and sometimes, local sources. Information presented in this study will be useful to improve future acid deposition, air-quality and climate modelling studies.

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Table 1. List of 14 field campaigns.

Campaign	Site	Lat N, long W	Campaign period	Mean daytime temperature (°C)	No. of Samples	Sample duration (hour)
FRS1		45.05.30.00	15-28 Nov 2001	7	17	6–25
FRS2	Frelighsberg, Quebec	45.05, 73.06	4–16 May 2002	12	7	11–48
EGB1	Egbert, Ontario	44.23, 79.78	6–13 Mar. 2002	2	8	6–16
KEJ1			29 Jun.–15 Jul. 2002	23	17	8–47
KEJ2	Kejimkujik, Nova Scotia	44.43, 65.21	25 Oct15 Nov. 2002	6	20	13–25
ALG1			8–27 Feb. 2003	-13	13	19–71
ALG2	Algoma, Ontario	47.04, 84.38	5–26 Jun. 2003	22	24	10–50
LED1			11–27 Aug. 2003	19	12	24–48
LED2	Lac Edouard, Quebec	47.68, 72.44	17 Oct3 Nov. 2003	2	9	21–72
CHA1			22 Jan.–21 Feb. 2004	-10	14	8–127
CHA2	Chalk River, Ontario	46.06, 77.40	4–26 Jun. 2004	19	11	24–119
SPR1			17 Aug18 Sep. 2004	19	17	24–96
SPR2	Sprucedale, Ontario	45.42, 79.49	16 Nov12 Dec. 2004	0	12	13–152
BRL1	Bratt's Lake, Saskatchewan	50.20, 104.20	11 Feb4 Mar. 2005	8	11	21-106

Table 2. Percentage of data from selected size stages (3–10 stages for SO_4^{2-} , NH_4^+ , NO_3^- and K^+ and 1–8 stages for CI^- , Na^+ , Mg^{2+} and Ca^{2+}) having concentrations higher than their respective 3SDB (3 times standard deviation of all blanks divided by the mean sample volume) and defined data -quality categories for all particle species during 14 campaigns (1 represents most reliable and 4 represents least reliable).

	FRS1	FRS2	EGB1	KEJ1	KEJ2	ALG1	ALG2	LED1	LED2	CHA1	CHA2	SPR1	SPR2	BRL1
				Pe	rcent da	ta compl	eteness	in Releva	ant Size	Bins				
SO ₄ ²⁻	99	96	98	100	98	100	90	82	96	100	98	100	100	99
NH₄	93	93	94	88	85	94	92	53	90	99	94	81	92	90
NO ¹	87	34	88	78	94	75	100	27	47	93	64	82	89	100
Cl⁻ຶ	7	0	31	10	46	60	6	16	28	68	20	1	19	80
Na ⁺	20	4	31	20	49	83	15	21	43	93	17	16	49	88
K^+	35	27	30	21	3	43	26	43	26	57	43	40	41	78
Mg ²⁺	1	2	31	69	64	85	49	9	24	63	77	41	32	86
Ca ²⁺	19	48	52	42	8	51	45	36	31	43	65	95	76	70
						Data-0	Quality C	ategory						
SO42-	1	1	1	1	1	1	1	2	1	1	1	1	1	1
NH_4^{\mp}	1	1	1	2	2	1	1	3	1	1	1	2	1	1
NO_3^-	2	3	2	2	1	2	1	3	3	1	3	2	2	1
Cl⁻ັ	4	4	3	3	2	2	4	3	3	2	4	4	3	2
Na ⁺	4	4	3	3	2	2	3	3	3	1	4	3	2	2
K^+	3	3	3	3	4	3	3	3	3	3	3	3	3	2
Mg ²⁺	4	4	4	2	2	1	2	4	4	2	2	3	3	1
Ca ²⁺	3	3	3	3	4	2	3	3	3	3	2	1	3	2

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Table 3. Mean and median (left and right column separated by ",") atmospheric concentrations (μ g m⁻³) of SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻, Na⁺, K⁺, Mg²⁺ and Ca²⁺ generated from CAPMoN monitored data during the period of 2001–2005.

Site	Cluster	SO42-	NO_3^-	NH_4^+	Cl⁻	Na ⁺	K^+	Mg ²⁺	Ca ²⁺
ALG	ESE	2.29, 1.19	0.33, 0.11	0.70, 0.34	0.01, 0.00	0.04, 0.02	0.04, 0.03	0.03, 0.01	0.12, 0.04
	NNE	0.72, 0.58	0.22, 0.10	0.22, 0.14	0.02, 0.01	0.05, 0.03	0.02, 0.02	0.02, 0.01	0.06, 0.03
	NNW	0.76, 0.66	0.30, 0.11	0.23, 0.13	0.04, 0.01	0.07, 0.04	0.02, 0.02	0.03, 0.01	0.08, 0.03
	SSW	4.04, 2.60	1.32, 0.41	1.54, 1.12	0.02, 0.01	0.05, 0.02	0.07, 0.06	0.05, 0.02	0.25, 0.11
	WNW	1.10, 0.91	0.70, 0.17	0.47, 0.27	0.02, 0.00	0.05, 0.02	0.03, 0.02	0.03, 0.02	0.12, 0.06
	WNW:L	1.69, 1.20	0.61, 0.16	0.61, 0.34	0.02, 0.01	0.04, 0.02	0.04, 0.03	0.03, 0.02	0.15, 0.06
	NNE	1.23, 1.05	0.83, 0.56	0.56, 0.47	0.04, 0.01	0.05, 0.03	0.07, 0.05	0.12, 0.07	0.44, 0.23
	NNW	0.85, 0.74	0.74, 0.49	0.40, 0.29	0.06, 0.02	0.06, 0.04	0.10, 0.05	0.11, 0.06	0.40, 0.21
	SSE	1.55, 1.29	1.22, 0.70	0.71, 0.50	0.03, 0.02	0.08, 0.03	0.12, 0.07	0.17, 0.10	0.67, 0.40
BRL	WNW	0.75, 0.56	0.92, 0.54	0.39, 0.26	0.05, 0.03	0.09, 0.03	0.10, 0.06	0.12, 0.06	0.45, 0.25
	WNW:L	1.31, 1.11	1.27, 0.77	0.68, 0.50	0.04, 0.02	0.07, 0.04	0.10, 0.07	0.14, 0.07	0.51, 0.26
	WSW	0.92, 0.63	1.30, 0.68	0.55, 0.29	0.05, 0.03	0.10, 0.04	0.09, 0.06	0.10, 0.06	0.41, 0.24
	ESE	2.30, 1.48	0.41, 0.13	0.72, 0.43	0.02, 0.01	0.07, 0.03	0.06, 0.05	0.02, 0.02	0.12, 0.05
	NNE	0.85, 0.63	0.25, 0.10	0.24, 0.13	0.04, 0.01	0.08, 0.05	0.03, 0.02	0.02, 0.01	0.08, 0.03
	NNW	0.87, 0.73	0.36, 0.14	0.27, 0.15	0.08, 0.01	0.11, 0.05	0.03, 0.02	0.03, 0.02	0.09, 0.04
CHA	WNW	1.50, 1.13	0.68, 0.19	0.59, 0.33	0.05, 0.01	0.08, 0.03	0.04, 0.04	0.03, 0.02	0.11, 0.06
	WNW:L	2.14, 1.34	0.46, 0.16	0.69, 0.38	0.03, 0.01	0.07, 0.03	0.05, 0.04	0.03, 0.02	0.13, 0.06
	WSW	3.70, 2.46	0.92, 0.26	1.32, 1.02	0.03, 0.01	0.06, 0.03	0.08, 0.06	0.03, 0.02	0.15, 0.07
	NNE	1.57, 1.15	1.53, 0.74	0.75, 0.47	0.14, 0.05	0.12, 0.05	0.05, 0.04	0.08, 0.06	0.99, 0.46
	NNW	1.37, 1.11	1.84, 0.90	0.77, 0.47	0.32, 0.08	0.24, 0.07	0.04, 0.04	0.09, 0.07	1.04, 0.54
	SSE	5.31, 3.42	2.74, 1.86	2.26, 1.67	0.12, 0.04	0.10, 0.05	0.08, 0.07	0.10, 0.06	1.08, 0.52
EGB		1.97, 1.49	2.66, 1.34	1.22, 0.77	0.19, 0.06	0.14, 0.05	0.05, 0.04	0.08, 0.06	0.78, 0.42
	WINW:L	3.52, 2.30	3.12, 2.00	1.76, 1.27	0.19, 0.06	0.15, 0.05	0.07, 0.06	0.10, 0.07	1.16, 0.57
		4.91, 3.60	3.45, 2.05	2.37, 1.03	0.12, 0.05	0.10, 0.05	0.09, 0.08	0.10, 0.08	0.07, 0.40
		1.40, 1.05	0.73, 0.39	0.61, 0.46	0.06, 0.02	0.10, 0.04	0.04, 0.04	0.03, 0.02	0.22, 0.13
		1.17, 0.09	0.93, 0.03	0.55, 0.59	0.24, 0.03	0.22, 0.09	0.04, 0.04	0.04, 0.04	0.41, 0.30
FDF	SSW/	3 51 2 37	1 11 0 64	1 45 1 02	0.15, 0.03	0.13, 0.00	0.05, 0.04	0.04, 0.03	0.33, 0.28
FRE		2 11 1 51	1 35 0.81	1.43, 1.02	0.03, 0.02	0.12, 0.04	0.00, 0.00	0.03, 0.03	0.27, 0.10
	W/S/W	1 12 2 01	1.84 0.00	1.02, 0.70	0.14, 0.03	0.14, 0.04	0.03, 0.03	0.04, 0.03	0.33, 0.25
	ESE	1.33 1.00	0.30 0.12	0.26 0.15	0.40 0.08	0.39 0.19	0.04, 0.03	0.05, 0.03	0.05, 0.02
	NNF	0.82 0.73	0.24 0.19	0.15, 0.11	0.42 0.26	0.40, 0.31	0.03.0.02	0.05, 0.04	0.04 0.03
	NNW	1.16. 0.82	0.36, 0.20	0.25, 0.15	0.44, 0.28	0.45, 0.34	0.04, 0.03	0.06, 0.04	0.05, 0.04
KE.I	SSW	2.68, 1.60	0.27. 0.12	0.51, 0.31	0.31, 0.04	0.40, 0.22	0.06. 0.04	0.05, 0.03	0.04. 0.03
IXE0	WNW	2.86, 1.92	0.54, 0.28	0.69, 0.47	0.32, 0.09	0.47. 0.33	0.06. 0.05	0.06. 0.04	0.08. 0.04
	WNW:L	1.98, 1.27	0.29, 0.18	0.42, 0.25	0.28, 0.07	0.36, 0.26	0.05, 0.03	0.05, 0.03	0.05, 0.03
	ESE	1.24, 0.89	0.15, 0.06	0.34, 0.21	0.02, 0.01	0.06, 0.02	0.03, 0.03	0.01, 0.01	0.05, 0.02
	NNE	0.58, 0.44	0.16, 0.09	0.15, 0.08	0.04, 0.01	0.07, 0.05	0.03, 0.02	0.01, 0.01	0.05, 0.02
	NNW	0.68, 0.50	0.22, 0.10	0.18, 0.09	0.07, 0.01	0.10, 0.05	0.02, 0.02	0.02, 0.01	0.05, 0.03
LED	WNW	1.27, 0.94	0.40, 0.14	0.44, 0.23	0.04, 0.01	0.09, 0.03	0.04, 0.03	0.02, 0.01	0.06, 0.03
	WNW:L	1.30, 0.84	0.26, 0.11	0.40, 0.21	0.04, 0.01	0.07, 0.03	0.04, 0.03	0.02, 0.01	0.07, 0.03
	WSW	3.11, 1.98	0.46, 0.14	1.01, 0.68	0.02, 0.01	0.06, 0.03	0.06, 0.05	0.02, 0.01	0.09, 0.04
SPR	ESE	3.67, 2.03	0.38, 0.15	1.12, 0.65	0.01, 0.01	0.04, 0.02	0.05, 0.04	0.02, 0.01	0.14, 0.07
	NNE	0.99, 0.71	0.24, 0.09	0.29, 0.16	0.02, 0.01	0.05, 0.02	0.03, 0.02	0.02, 0.01	0.08, 0.03
	NNW	0.80, 0.70	0.39, 0.13	0.27, 0.15	0.06, 0.01	0.08, 0.03	0.03, 0.02	0.02, 0.01	0.08, 0.04
	WNW	1.29, 0.89	0.63, 0.15	0.52, 0.25	0.03, 0.00	0.05, 0.02	0.03, 0.03	0.02, 0.01	0.11, 0.05
	WNW:L	2.24, 1.37	0.60, 0.18	0.78, 0.41	0.02, 0.01	0.05, 0.02	0.04, 0.03	0.03, 0.02	0.14, 0.06
	WSW	4.42, 2.74	0.92, 0.32	1.59, 1.06	0.02, 0.01	0.04, 0.02	0.07, 0.06	0.04, 0.02	0.19, 0.09

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Table 4. Campaign-average species mass concentrations (C, $\mu g m^{-3}$), fine fraction ($PM_{2.5}$) species concentrations (C_f , $\mu g m^{-3}$) and percentage of mass in the $PM_{2.5}$ fine fraction (P_f , %) for SO_4^{2-} , NO_3^- , NH_4^+ , CI^- , Na^+ , K^+ , Mg^{2+} and Ca^{2+} . Standard deviations are shown after the \pm . The mean value of 0 represents a value <0.005.

	FRS1	FRS2	EGB1	KEJ1	KEJ2	ALG1	ALG2	LED1	LED2	CHA1	CHA2	SPR1	SPR2	BRL1
$C(SO_4^{2-})$	2.46±2.35	2.05±1.88	3.22±1.87	3.41±4.4	1.09±1.2	3.98±5.23	2.91±4.37	1.46±3.76	0.65±0.79	1.63±1.69	2.44±1.62	4.45±5.84	0.88±0.38	1.16±0.63
$C_f(SO_4^{2-})$	2.34±2.31	2±1.84	3.07±1.74	3.26±4.19	0.86±0.74	3.64 ± 4.42	2.85±4.31	1.41±3.68	0.61 ± 0.76	1.55±1.62	2.32 ± 1.54	4.32±5.66	0.82±0.35	1.04±0.58
$P_{f}(SO_{4}^{2-})$	95	98	96	96	79	91	98	97	95	95	95	97	93	90
$C(NO_3^-)$	1.77±2.2	0.13±0.18	3.13±2.44	0.55±0.63	0.34±0.65	3.62±3.31	0.29±0.4	0.09±0.17	0.28±0.67	0.87±2.09	0.16±0.09	0.33±0.46	0.33±0.4	2.36±1.9
$C_f(NO_3^-)$	1.52±1.99	0.05±0.06	2.8±2.22	0.17±0.18	0.09±0.12	2.83±2.42	0.07±0.08	0.02±0.02	0.23±0.55	0.73±1.83	0.05±0.04	0.11±0.29	0.26±0.36	2.07±1.73
$P_f(NO_3^-)$	86	37	90	31	25	78	24	23	83	84	28	33	79	88
$C(NH_4^+)$	1.37±1.35	0.77±0.73	2±1.24	1.05±1.22	0.25±0.38	1.94±2.54	1.08±1.59	0.41±1.06	0.24±0.45	0.67±1.06	0.78±0.54	1.42±1.89	0.31 ± 0.23	1.05±0.63
$C_f(NH_4^+)$	1.32±1.32	0.76±0.73	1.96±1.2	1.03±1.19	0.2±0.24	1.8±2.1	1.06±1.57	0.41±1.04	0.23±0.43	0.65±1.04	0.76±0.53	1.39±1.84	0.29±0.22	0.99±0.59
$P_f(NH_4^+)$	97	99	98	98	80	92	98	98	95	97	97	98	95	94
C(Cl⁻)	0.06±0.06	0.01±0.01	0.23±0.11	0.16±0.24	0.42±0.44	0.48±0.39	0.01 ± 0.01	0.05±0.06	0.02±0.03	0.12±0.17	0.01±0.02	0.01±0.01	0.02±0.02	0.07±0.05
$C_f(CI^-)$	0.04±0.06	0.01±0	0.1±0.06	0.02±0.03	0.04±0.05	0.22±0.2	0.01 ± 0.01	0.02±0.03	0.01 ± 0.02	0.04 ± 0.04	0.01 ± 0.01	0±0	0.01 ± 0.01	0.04±0.03
P _f (Cl [−])	71	69	42	14	11	45	58	49	64	34	59	53	49	65
$C(Na^+)$	0.06±0.04	0.02±0.01	0.19±0.07	0.24±0.33	0.34 ± 0.44	0.43±0.29	0.02±0.02	0.05±0.04	0.02±0.02	0.15±0.16	0.02±0.02	0.03±0.02	0.04±0.01	0.04±0.02
$C_f(Na^+)$	0.03±0.02	0.01±0.01	0.07±0.03	0.07±0.09	0.05±0.07	0.22±0.16	0.01 ± 0.01	0.03±0.03	0.01 ± 0.01	0.07±0.06	0.01 ± 0.01	0.02±0.01	0.02±0.01	0.02±0.01
$P_f(Na^+)$	55	67	35	28	16	51	70	64	69	49	53	64	65	55
C(K⁺)	0.06±0.04	0.03±0.01	0.11±0.05	0.09±0.07	0.01±0.02	0.16±0.15	0.08±0.08	0.06±0.03	0.03±0.03	0.06±0.06	0.06±0.03	0.06±0.03	0.03±0.02	0.07±0.07
$C_f(K^+)$	0.05±0.03	0.03±0.01	0.08±0.03	0.07±0.07	0.01±0.01	0.12±0.13	0.06±0.07	0.03±0.02	0.02±0.02	0.05 ± 0.05	0.03±0.02	0.04±0.03	0.02±0.01	0.06±0.06
$P_f(K^{\dagger})$	82	80	78	83	36	77	72	55	68	88	50	66	77	81
$C(Mg^{2+})$	0.01 ± 0.01	0±0.01	0.02±0.01	0.05±0.05	0.04±0.05	0.12±0.07	0.07±0.22	0.01 ± 0.01	0±0	0.02±0.03	0.02±0.01	0.02±0.01	0.01±0	0.05±0.04
$C_{f}(Mg^{2+})$	0±0	0±0	0±0	0.01±0.01	0.01 ± 0.01	0.06±0.05	0.02±0.09	0±0	0±0	0.01±0.01	0.01±0	0±0	0±0	0.01±0.01
$P_{f}(Mg^{2+})$	7	12	23	30	19	45	30	33	51	52	31	21	53	18
C(Ca ²⁺)	0.14±0.2	0.14±0.14	0.23±0.14	0.12±0.12	0.02±0.02	0.41±0.26	0.2±0.26	0.05±0.07	0.02±0.04	0.09 ± 0.25	0.1±0.09	0.16±0.12	0.04±0.02	0.21±0.14
$C_f(Ca^{2+})$	0.02±0.02	0.03±0.03	0.08±0.06	0.04±0.04	0.01±0.02	0.12±0.12	0.05±0.09	0.02±0.02	0.01±0	0.03±0.07	0.03±0.06	0.03±0.03	0.02±0.01	0.03±0.02
$P_f(Ca^{2+})$	13	21	35	34	44	29	26	30	22	37	29	21	41	17

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Table 5. Mass median diameter (MMD) (in μ m) and geometric standard deviation (GSD) (sep-
arated by ";") for total, fine (F) and coarse (C) particles for 8 species measured.

	FRS1	FRS2	EGB1	KEJ1	KEJ2	ALG1	ALG2	LED1	LED2	CHA1	CHA2	SPR1	SPR2	BRL1
SO42-	0.45; 2.47	0.28; 2.69	0.44; 2.4	0.38; 2.65	0.67; 3.74	0.5; 2.7	0.29; 2.61	0.44; 2.28	0.47; 2.37	0.42; 2.59	0.42; 2.7	0.46; 2.39	0.56; 2.56	0.43; 2.8
$F(SO_4^{2-})$	0.4; 2.1	0.26; 2.42	0.4; 2.13	0.35; 2.37	0.4; 2.38	0.41; 2.17	0.27; 2.44	0.42; 2.12	0.43; 2.1	0.38; 2.24	0.38; 2.37	0.44; 2.2	0.49; 2.21	0.37; 2.26
$C(SO_{4}^{2-})$	4.4; 1.45	4.45; 1.47	4.16; 1.41	4.14; 1.45	4.63; 1.47	4.39; 1.46	4.25; 1.47	4.03; 1.46	4.01; 1.45	4.28; 1.47	4.25; 1.48	4.04; 1.49	4.11; 1.45	4.38; 1.45
NO ₃	0.63; 2.91	2.03; 3.96	0.55; 2.58	3.15; 2.64	3.93; 2.99	0.73; 3.66	3.76; 4.25	3.41; 4.03	0.79; 3.22	0.63; 3.4	2.58; 5.22	2.41; 5.04	0.98; 3.08	0.48; 2.92
$F(NO_3^-)$	0.46; 2.06		0.44; 1.96	1.09; 2.66	1.01; 3.3	0.43; 2.29			0.55; 2.28	0.44; 2.45			0.66; 2.24	0.38; 2.13
$C(NO_3^-)$	4.37; 1.42	4.57; 1.41	4.38; 1.4	4.58; 1.44	4.85; 1.46	4.94; 1.46	5.43; 1.43	5.03; 1.41	4.61; 1.47	4.54; 1.45	5.29; 1.43	5.11; 1.43	4.44; 1.46	4.55; 1.46
NH ⁺	0.43; 2.25	0.26; 2.58	0.41; 2.16	0.35; 2.44	0.67; 3.69	0.46; 2.65	0.28; 2.67	0.42; 2.17	0.5; 2.3	0.39; 2.47	0.38; 2.5	0.45; 2.33	0.53; 2.52	0.39; 2.43
$F(NH_4^+)$	0.4; 2.04	0.25; 2.42	0.4; 2.05	0.34; 2.34	0.42; 2.42	0.39; 2.17	0.26; 2.48	0.4; 2.05	0.47; 2.09	0.36; 2.26	0.36; 2.3	0.43; 2.21	0.48; 2.26	0.35; 2.14
$C(NH_4^+)$	4.21; 1.43	4.62; 1.48	3.63; 1.29	4.04; 1.48	4.6; 1.48	4.51; 1.44	4.45; 1.51	4.12; 1.46	3.88; 1.44	4.29; 1.48	4.6; 1.52	3.76; 1.48	3.93; 1.43	4.18; 1.43
CI				4.38; 1.88	5.64; 2.07	1.87; 5.48		1.77; 4.48		2.11; 6.48				0.86; 5.63
F(Cl [−])						0.63; 5.06		0.74; 4.37		0.38; 6.12				0.38; 3.59
C(CI ⁻)			5.3; 1.42	4.89; 1.41	5.13; 1.43	4.59; 1.49		4.15; 1.43		5.13; 1.47				4.84; 1.49
Na ⁺				3.49; 1.81		1.75; 4.7		1.28; 4.16		1.79; 4.89				1.16; 5.01
F(Na ⁺)						0.67; 3.79		0.69; 3.61		0.61; 4.06				0.51; 3.53
<i>C</i> (Na ⁺)			4.92; 1.43	4.49; 1.43	4.99; 1.44	4.68;1.48		4.02; 1.43		4.87; 1.47				4.59; 1.48
K ⁺						0.55; 5.62		1.05; 6.22		0.42; 4.12	1.38; 6.03			0.61; 3.17
$F(K^+)$	0.28; 3.2		0.2; 4.6	0.34; 2.87		0.31; 3.77	0.26; 3.55	0.35; 4.19		0.31; 3.01	0.37; 3.91			0.45; 2.35
$C(K^+)$						4.77; 1.5		4.53; 1.44		4.77; 1.52	5.05; 1.46			4.49; 1.45
Mg ²⁺		3.4; 3.76		3.48; 2.31	4.7; 2.51	2.56; 3.26	2.27; 7.78	3.11; 3.55		2.25; 2.88	2.91; 4.99			
F(Mg ²⁺)		0.86; 3.38		1.4; 2.18	1.23; 2.97	1; 2.44		0.92; 3.13		1.07; 2.18				
$C(Mq^{2+})$		4.95; 1.47		4.61; 1.45	4.98; 1.44	4.93; 1.49	5.45; 1.45	4.81;1.47		4.65; 1.47	5.18; 1.47			
Ca ²⁺						2.79; 5.65	3.43; 4.95			2.63; 4.04	3.17; 4.66			4.98; 2.6
F(Ca ²⁺)						0.36; 5.3	0.48; 4.73			0.7; 3.52	0.53; 4.16			1.21; 2.62
C(Ca ²⁺)	5.27; 1.47	5.3; 1.46	4.96; 1.44	5; 1.48		5.43; 1.46	5.4; 1.46	5.06; 1.46	5.37; 1.46	5.1; 1.46	5.3; 1.46	5.35; 1.44		5.23; 1.45



Fig. 1. Maps of emission sources of SO₂, NO_x (in the equivalent mass of NO₂), NH₃ and PM₁₀ based on 2000 Canadian and 2001 US emission inventory (the unit is tonnes/grid/year with the grid size of ~42 km by 42 km).

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Fig. 2. Locations of the eight measurement sites and the six trajectory-clusters at these sites defined from the average of 2001–2005 three-day six-hourly back trajectories. Number in the bracket positioned at the end of each cluster represents the percentage of all trajectories associated with that cluster during the specific campaign period.

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Fig. 3. Examples of measured data, each color/symbol represents one sample at all MOUDI stages. Dashed blue line represents 3SDB (3 times standard deviation of all blank values divided by mean air volume collected during all samples).

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Fig. 4. Average size distributions of SO_4^{2-} , NH_4^+ and NO_3^- during 14 field campaigns.

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ALG2, respectively.

Fig. 6. (a) Median SO_4^{2-} concentration for 6 trajectory clusters from CAPMoN 2001–2005 daily data, (b) and (c) SO_4^{2-} concentrations from individual samples measured during ALG1 and

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Fig. 7. Average fine fraction mole-equivalent concentration ratios of NH_4^+ to SO_4^{2-} and NH_4^+ to the sum of SO_4^{2-} and NO_3^- during 14 campaigns (left to right, from the coldest season to the warmest season).





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Fig. 8a. Scatter plot of NH_4^+ vs. SO_4^{2-} using all stage samples of fine particles for 4 campaigns. Solid lines represent 2:1. See category 1 discussion in Sect. 3.7.

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Fig. 8c. Scatter plot of NH_4^+ vs. SO_4^{2-} (upper row) and NH_4^+ vs. $(2^*SO_4^{2-} + NO_3^-)$ (lower row) using all stage samples of fine particles. Solid lines represent 2:1 (upper row) or 1:1 (lower row). See category 3 discussions in Sect. 3.7.



Fig. 8d. Same as Fig. 8c except for different campaigns. See category 4 discussions in Sect. 3.7.

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