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Atmospheric
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Discussions

Interactive comment on "Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites" *by* L. Zhang et al.

L. Zhang et al.

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We appreciate this reviewer’s constructive comments, which have improved the revised paper. We have addressed all of the comments carefully and our answers to this reviewer’s general and specific comments are listed below. The paper has been revised by incorporating all three reviewers’ suggestions.

Answers to the general comments:

We agree with this reviewer that there are many previous studies on this topic at different locations around the world. Many phenomena have been identified and explained in previous studies. However, data over eastern North America is still limited and few studies have covered multiple sites in this region. The present study is unique in that it covers a large region, which includes both polluted and remote areas and was con-

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ducted during different seasons. The data will be very useful in future air-quality and climate modelling studies. It is also useful for improving acid deposition/critical load studies considering the strong dependence of particle deposition on particle size. For example, size-resolved atmospheric aerosol concentrations are needed as model input in the recently developed size-resolved air-quality and climate models (sectional or moment approach). Results shown in original Figures 4 and 5 can be used directly for sectional-approach aerosol models. For moment-approach aerosol models, a sum of two or three lognormal distributions is commonly used. In the present study, fine and coarse particles are separately fitted into lognormal distributions for these types of applications. The results will not only be useful locally, but also for other parts of the world. For example, the US CASNeT calculates nitrate dry deposition by assuming all monitored nitrate concentrations are fine particles. Results in this study suggest that this approach underestimates nitrate dry deposition substantially because coarse nitrates dominate during warm seasons and the deposition velocities of coarse nitrates are 5-10 times higher than the fine nitrates.

We have added a discussion on the sea salt contributions to potassium and magnesium contributions in the revised paper based on this reviewer’s comments and discussed size-dependent particle acidity according to this reviewer and the other two reviewers’ suggestions. These results provide new knowledge on size-resolved aerosols, especially for the region of eastern North America.

Answers to the specific comments:

(1) The reviewer is right that the total cations and anions should be equivalent for those samples having a balance between ammonium and sulfate plus nitrate. Such a phenomenon can be seen from the new Figure 6 in the revised paper, which shows the cation/anion ratio being close to one for particle sizes 0.1-1 m during several campaigns, which were shown in the original Figures 8b and 8c. Section 3.7 has been rewritten based on all three reviewers’ comments related to cation-anion balance.

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2) As mentioned above, fine and coarse particles are separately fitted into lognormal distributions for potential future applications in moment-approach aerosol models. A brief explanation on this practice has been added in the revised paper (second paragraph in Section 3). The two parameters describing the lognormal distribution, mass median diameter (MMD), and the associated geometric standard deviation (GSD), were generated and presented in Table 5. The caption of Table 5 correctly states what MMD represents. Unfortunately, it was mistakenly defined as mass mean diameter at its first appearance in Section 3. This has been corrected in the revised text. We have also changed MMD to MMAD (mass median aerodynamic diameter) based on this reviewer’s comment.

(3) We agree with the reviewer that the short period of several weeks during each campaign might not represent the entire season, especially for the bulk concentration of each ion due to their strong dependence on air-mass origin. That is why we have based it on five years of data to generate the mean trajectory clusters (Figure 2) and the median and mean concentrations of all the ions associated with each cluster (Table 3). The discussion of the seasonal variations is mostly for the shape of the size distributions and the associated parameters (i.e., MMAD and GSD), which are mainly controlled by thermodynamics (temperature differences); thus, the seasonal variations shown from the several-week data are good enough to represent the seasonal patterns of the size distributions.

(4) The reviewer is right that the relative humidity is the most important factor. We have compared our seasonally monitored wet deposition and the hourly-averaged relative humidity. Despite the fact that the winter season generally has the lowest wet deposition compared to the rest of the seasons at the majority of the locations, the seasonal differences can be mostly explained by the seasonal differences in the air concentration of sulphate. On the other hand, the seasonal differences in relative humidity correlated very well with the size differences shown in the original Figure 4 and Table 5. Thus, we have added the campaign-averaged hourly RH in Table 1 and revised the discussion

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accordingly in the revised paper.

(5) ‘reaction kinetics’ has been changed to ‘thermodynamics’ in the revised text.

(6) We have mentioned sea salt as a source of magnesium in the text, but not as a source of potassium. Based on this reviewer’s comment, we have generated the ratio of inorganic ions to sodium for total, fine, and coarse particle masses, and compared with the seawater ratios. We have completely rewritten Section 3.5 to address this comment. The major conclusion is that sea salt is the major contributor in terms of percentage contribution for potassium, magnesium, and calcium only at the coastal site. At the rest of the locations, sea salt contribution to these ions is smaller than a few percent.

The multi-modal distributions of magnesium and calcium have also been observed in many other locations. For example, Lin et al. (2007) showed that magnesium and calcium have a bi-modal distribution at a rural site and a multi-modal distribution at a roadside site. The size distributions are influenced by different emissions sources, distances from sources, and meteorological conditions, e.g., particle size increase under high humidity conditions, dry and wet removal rates are different under different meteorological conditions. A combination of the following two factors would have produced a bi-modal distribution as seen in the present study: (1) the emission of these two species (mainly from soil dust) has a peak at sizes larger than 6 m, and (2) the removal of particles by dry deposition and by precipitation scavenging is least efficient for particles around the size of 1 m in diameter. Thus a mix of different-aged air masses will cause a bi-modal distribution as observed here. A brief discussion on this point has been added in the revised text in Section 3.5.

The large fractions of fine potassium suggest that the biomass burning is as important as, or more important than soil dust emissions for potassium in this region. This suggests that biomass burning could also be an important source for those particle species

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that originated from biomass burning (e.g., organic carbon). On the other hand, the potassium concentrations at the majority locations were quite low. Without knowing the concentration ratio of potassium to other emitted species from biomass burning in this region, it is impossible to estimate the importance of its contributions to the total aerosol loading. Detailed discussion on this topic is out of the scope of the present study. It is worth noting that the relative amounts of emitted aerosol species are different in different regions (see discussions in Ryu et al., 2007; Atmospheric Research 84, 362–373).

(7) During the winter, road salt was heavily used to help melt the ice and snow on this highway. Local concentrations adjacent to the road were surely much higher than observed at the site 12 km away. Despite the fact that the source was at ground level, wind and local traffic would have certainly brought the melted salt, especially the smaller sizes, to higher levels and further transported it to downwind directions. For example, Asian soil dust can be transported as far as North America. The five year (2001-2005) CAPMoN daily concentrations also showed that the average concentrations of Cl and Na+ in the winter (Dec, Jan, Feb) were ˜5 times higher than during the rest of the seasons. Road salt was the only extra source that existed in the winter but not during the other seasons. At other locations (e.g., EGB), road salt was also seen to play an important role on the observed concentrations of sodium and chloride.

To further investigate this issue, we contacted the Ontario Ministry of Transportation for detailed information on the practice of road salt spray in winter. Here is the information we obtained: (a) During storms, they normally pre-wet the pavement with a wet solution of low concentration magnesium chloride. This provides a stickier surface for sand and salt. After this, they normally spread sand on the road for traction using local sand mixed with 3% by volume salt (to prevent the sand piles from freezing). No exact information on the chemical composition of the sand is known but it likely contains Ca and Mg. They only spread salt after the storm ends. (b) After the storms, if the

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temperature is above -15 degrees C, they pre-wet the road with MgCl2 and spread road salt (pure NaCl). If the temperature is below -15, they spread sand only (for traction).

Based on the above information, we have the following hypothesis: (a) The signal of road salt at the site will vary depending on when the air sampling occurred with respect to the time of the storm and its end, the temperature during the storm and its end, and the wind speed and direction during the storm. One might also say that it depends somewhat on the intensity of the traffic; (b) As a result, it isn’t surprising that when Na and Cl are high, there one sometimes sees enhanced Cl, Mg and Ca; (c) Since road sand is very coarse, the sand would need to be ground into fine particles in order to be transported to the Algoma site; (d) On the other hand, the NaCl and MgCl2 is likely generated in aqueous droplets from tire spray. These droplets could be large and small, perhaps evaporating into fine aqueous or solid aerosols that could be transported over large distances.

This might explain why we sometimes see samples with (i) high Ca and Mg but low Na and Cl (sand only), (ii) high Na and Cl but low Ca and Mg (salt only) and (iii) high Na, Cl, Mg and Ca (sand and salt). Although it is very difficult to characterize the chemical signature of road salt and sand at the Algoma site from our data, we know for sure that there are no other sources of salt in the area except operator contamination (which is minimized through our careful operating procedures, e.g., wearing gloves, covering the sample).

(8) No action is required.

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