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***Interactive comment on “Modes in the size distributions and neutralization extent of fog-processed ammonium salt aerosols observed at Canadian rural locations” by X. H. Yao and L. Zhang***

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We greatly appreciate all of the comments, which have substantially improved the paper. Our responses are detailed below.

RC- Reviewer's Comments; AC – Authors' Comments

RC: This paper reports the size-resolved inorganic chemical composition of particulates in air samples from a number of Canadian sites, collected with a MOUDI. The focus of the paper is upon the identification of fog-processed air from specific super-

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micron modes in the size distributions. There would be merit to a large collection of air particulate samples that had experienced fog processing, to learn how this mechanism may affect the size-resolved chemical distributions. Indeed, to have such distributions before, during and after a fog event would be of considerable value. Unfortunately, this study is limited by a very small number of fog samples (ten) and so major conclusions are hard to make. Also, the paper is extremely poorly written, to the point that once one starts to read the Results and Discussion section, it is frequently not possible (for me) to determine what the authors are discussing. As an example, the Abstract starts with a statement that “192 samples” were collected but it does not state what the samples are of (line 2). Are these particulates collected during fogs, in clouds, or in clear air? In what way do the large supermicron particle modes indicate fog processing (line 5)? I cannot understand the sentence between line 8 and line 12. For example, what is meant by “ammonium sulfate incompletely neutralized”? If ammonium sulfate is present, then it is completely neutralized. However, the Abstract is much easier to read than the Results and Discussion section which is almost incomprehensible. For example, on page 5525, line 6 what is the SPR site? The logic in the sentence starting at line 3, page 5526 is not obvious. I do not know what is meant by the sentence on line 15-17 on page 5526, nor that at line 20-22 on page 5526. And so on, throughout the paper. For this reason alone I recommend that this paper be rejected. The issue is not only one of facility in English but clarity of thought.

AC: Although we discussed in detail only ten fog-processed samples, the total number of the samples in this dataset was 192 which were collected in more than one year time. Comparing to studies on fog events in literature, the size of the dataset used in this study was definitely not small. Fog events could have occurred up to 15% of the samples, but only 5% of the data samples were clearly identified to have fingerprints of fog-processed aerosols. From the detailed analysis of these ten samples, we identified substantial new findings and obtained some solid conclusions.

We agree that the first version of the paper needed a better focus and clearer interpre-

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tation. With the help of the three reviewers' comments, we reanalyzed our data and chose to focus only on the supermicron modes of ammonium aerosols. We generated logical explanations behind the observed phenomena. The main findings of this study include: (i) one or two supermicron modes were found in fog-processed ammonium aerosols, (ii) the first supermicron mode was in the size range of 1.1-1.7  $\mu\text{m}$  if  $T > -3$  C and in the size range of 2.8-3.4  $\mu\text{m}$  if  $T < -4$  C, (iii) the second supermicron mode appeared in the size ranges of 5-10  $\mu\text{m}$ , but not necessarily appeared in every fog event, (iv) the first mode was mainly caused by fog-processed ammonium aerosols and the second mode was likely the direct collection of fog droplets, (v) heterogeneous ice nucleation likely played a role in the larger size mode under  $T < -4$  C. We think these findings are important in the understanding of fog-processed aerosols. Based on these main findings, we reconstructed our presentation of the results and discussions. The abstract was completely rewritten to reflect the major analysis and findings as summarized above; the introduction was revised to include additional materials related to heterogeneous ice nucleation and to remove materials that were not directly relevant to the analysis; Section 3.1 was rewritten to give a better description of the available data; Sections 3.2 and 3.3 were designed to present data analysis results under different temperature conditions; and Section 3.4 further demonstrated how the supermicron mode of ammonium (in the size range of 1-4  $\mu\text{m}$ ) varied with temperature. The presentations in the revised paper are easy to follow.

RC: Other points: 1. The figures are in such a poor form that it is extremely difficult to read the plots

AC: The quality of the original Figures in the Word file was good, but this was not the case in the published pdf file. We redrew and rearranged the subset figures in the revised paper to make it clearer.

RC: 2. I am sceptical that any firm conclusions can be made with respect to different fog compositions collected under freezing conditions ( $T < 273\text{K}$ ) and non-freezing conditions. Only 10 samples were collected in total of which only 3 were in the freezing

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domain, so the statistics are poor. Also, the temperatures are only just below 273, and so it is unlikely the fog droplets will have frozen. Finally, how can different meteorological conditions be ruled out as the cause of different size-resolved compositions, if they are indeed observed?

AC: As mentioned in our responses above, we found that significant new findings can be identified from these data samples. We first separately discussed samples under temperatures above and below freezing point (Sections 3.2 and 3.3). We further looked in detail in Section 3.4 the dependence of the supermicron mode (in the size range of 1-4  $\mu\text{m}$ ) of ammonium on the temperature. Also in Section 3.4, our analysis indicated that the sizes of the supermicron mode of ammonium were not likely determined by the chemical compositions and concentrations of ammonium salts, the size distributions of fog droplets, or the chemical rate constants and partitioning of secondary species. Instead, the mode sizes were found to be strongly affected by the ambient temperature at the time of fog occurrence. We argued that heterogeneous ice nucleation likely took place and led to the larger size mode at  $T < -4^\circ\text{C}$ . In literature, biological ice nucleators have been found to freeze water at temperature as warm as  $-2^\circ\text{C}$ . All these results are documented in detail in Section 3.4 in the revised paper.

RC: 3. On that topic, no meteorological analyses were presented for the different samples. Where was the air coming from for each sample? How may its provenance affect the sample?

AC: Temperature and relative humidity were used in the analysis. Other meteorological variables were not directly useful to the focus of the analysis. For example, we analyzed the air mass origins of each sample and reported in Zhang et al. (2008, Atmos. Chem. Phys., 7133-7151). However, the air mass origins were not relevant to the interpretation and discussion of fog events.

RC: 4. What is the experimental uncertainty in the relative acidity value? For example, how significant are the data if that ratio is just above or just below unity?

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AC: Additional explanation was added in the revised paper: “Considering that analytical errors of ionic concentrations were about 5%,  $RA \leq 0.9$  was thereby considered a threshold to judge the presence of acidic aerosols in this study while  $RA \geq 1.1$  indicated that the aerosol 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.”

RC: 5. Should there be a factor of two in front of the sulfate quantity in the equation on page 5524. This is another example of technical issues. I.e. there should be an equation number associated with this equation. Also, the equation should use symbols to express that these are concentrations, not simply have the quantities written as  $NO_3^-$ ,  $Cl^-$ , etc. )

AC: The equivalent concentration is used so the factor of 2 is implicitly included in the calculation (see Kerminen et al., 2001). The equation is revised according to this comment.

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 5519, 2012.

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