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Atmospheric Chemistry and Physics Discussions

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' Comment

RC: In my opinion, the fundamental problem with this work is that the authors discuss their results of sampling with a MOUDI under fog conditions as being "fog-processed", and the discussion and analysis of the physics and chemistry of the particles appears

to be based on that assumption. Based on the results presented in the figures, I believe that the authors sampled fog droplets directly in the 10 cases they describe, and that the concept of 'fog-processed' is misleading as it implies that most of the water was removed from the droplets prior to sampling with the MOUDI. The differences are not subtle, and the resulting interpretations can be very different. The authors need to carefully consider what the samples represent, discuss the sampling in a clear and concise manner, and then re-evaluate their results taking into account how fog droplets are sampled with a MOUDI; they are likely not significantly dried in the MOUDI. At this time, the paper is not suitable for publication in ACP.

AC: This comment provided us an important point that we missed in the first version of the paper; that is, the second supermicron mode of ammonium observed in some samples was likely the direct collection of fog droplets with a MOUDI. We agree with this reviewer that the 5-10 μm modes of ammonium salts probably reflected the direct contribution from fog droplets. This was supported by existing studies. For example, Hoag et al. (1999) reported an evident increase of ammonium (neutralized sulphate) mass concentrations at the 5-10 μm size range relative to those at 1-5 μm in the mass size distribution of fog droplets. Fahey et al. (2005) also found that ammonium (neutralized sulphate) mass concentrations peaking at 7–13 μm fog droplets were from the formation of ammonium sulfate.

Based on this comment and many other comments from all the reviewers, we reanalyzed our data and revised our interpretations. We also identified more important findings from the data analysis. In the revised paper, we focused on the measured ammonium and anions associated in the supermicron atmospheric particles of the ten samples. We presented novel analyses of chemical composition and neutralization extent for the particles < 4 μm. Building on these analyses, we concluded that the 1-4 μm mode of the measured ammonium was mainly ascribed to fog-processing of ammonium salt aerosols while interstitial aerosols during fog events likely yielded a minor contribution to the measured ammonium. The analysis for the 5-10 μm mode of

ammonium salts has also been added in the revised paper.

RC: Some specific comments:

Abstract - There are only 10 of 192 samples defined as fog processed, and you separate those 10 among coastal and inland as well as between temperatures above and below 0oC. The abstract needs to indicate the durations of the 192 samples (1 day, 1 week, ...?) and how many of the 10 fog-processed samples collected at <0oC.

AC: The abstract was completely rewritten to reflect the new analysis results. In the revised paper, the samples were only separated into above and below freezing temperature conditions and sample durations were given in the Abstract, the Introduction, and the Data description section. The numbers of the samples below and above freezing point were shown in the Abstract, so were the number of the samples below and above -4 C temperature condition because this is the temperature point below which much larger supermicron modes of ammonium were observed.

RC: P 5521, lines 5-7 - Deposition will remove particles, but what are left are as easily characterized as any others, are they not?

AC: This has been revised to: “Due to the high deposition velocity of large fog droplets (Herckes et al., 2007), a net increase of chemical species in ambient aerosol post fog relative to pre-fog (fog-processed aerosol) was often close to measurement uncertainty, or even negative (Moore et al., 2004; Herckes et al., 2007). Thus, direct observation of the fog-processed aerosols was rare.”

RC: P 5521, line 10 - by "enhanced particle pollution", do you mean increased mass or number? P 5521, lines 10-21 – I do not get a clear picture from this paragraph as to how the result of fog processing is viewed. Are you saying that fog processing increases the number concentrations of particles or just makes particles larger? Are you saying that how fog processes aerosol particles depends on the initial number concentration of particles?

AC: We agree that the description in the origin manuscript was not clear. We revised the paragraph as follows: “Enhanced particle pollution in mass concentration was recently reported due to fog-processing events (Sun et al., 2006; Biswas et al., 2008; Yu et al., 2011). 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 fog events. In general, fog droplets with smaller sizes should have longer residence time. However, size distribution of fog droplets was found to be highly variable in different fog events (Frank et al., 1998; Ming and Russell, 2005; Herckes et al., 2007; Quan et al., 2011), depending on supersatuation and other factors. Thus, it is highly unpredictable whether a fog event removes aerosols from the atmosphere or generates more new aerosols. The same difficult situation is faced in designing field experiments observing fog-processed aerosols. A practical approach would be to search for the fog-processed aerosols from databases with large number of aerosol samples collected at various locations and time periods.”

RC: P 5522, lines 5-10 -what was the duration and frequency of sample collection?

AC: The information has been added in the revised paper in several places.

RC: P 5522, line 22 - The lines in Figure 2 are difficult to see.

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: P 5522, lines 22-23 - statistically different in what sense?

AC: This has been revised as “The measured concentration of NH4+ in supermicron atmospheric particles in the 10 samples was statistically higher than that in non-fog samples at 95% confidence level.”

RC: P 5522, line 19 - p 5523, line 8 - You start by inferring that the supermicron mode in 10 samples was due to cloud processing, and then you identify that as your hypothesis.

But then you apparently dismiss that hypothesis for the reasons identified as 1 and 2?

AC: We removed this discussion in the revised paper. Instead, we presented a new analysis of the supemicron modes.

RC: P 5524, lines 11-25 - While instances of "frozen fog" may occur at temperatures above -12oC, it is not uncommon for clouds and, by extension, fog to supercool. But if ice fog existed rather than liquid fog droplets, the cloud particle distribution will be much different. Thus, the temperature effect you imply will be partly due to changes in chemical rate constants and partitioning and partly due to the fact that your cloud particle distribution is completely different.

AC: This comment provided us another important idea in explaining the observed phenomena. In the revised paper, we conducted a correlation analysis between the mode sizes (the first supermicron mode of ammonium in the size range of 1-4 μm) and the ambient temperature. We found that the mode sizes at T>-3 C and T<-4 C differed significantly, suggesting the possibility of the occurrences of heterogeneous ice nucleation under T< 4 C. Note that in the literature heterogeneous ice nucleation was mostly observed at T<-12°C. The present data set provided some indirect evidences of the occurrence of the heterogeneous ice nucleation at warm temperatures (-12 to -4 C). It is worth to point out that our analysis excluded the possibility that the sizes of the supermicron mode of ammonium were 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. Details can be found in Section 3.4 of the revised paper.

RC: P 5527, lines 26-28 - I don't see 30 um in Figure 3.

AC: To avoid confusion, this part has been deleted in the revised paper.

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