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Interactive comment on "Chemical composition, microstructure, and hygroscopic properties of aerosol particles at the Zotino Tall Tower Observatory (ZOTTO), Siberia, during a summer campaign" *by* E. F. Mikhailov et al.

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We would like to thank Referee #1 for the constructive criticism and suggestions for improvement that were taken into account upon manuscript revision. Responses to individual comments are given below.

General comment

It is a bit unclear the motivation for developing the mass-based kappa interaction model

as opposed to the traditional parameterization – perhaps the authors can provide some brief motivation here.

Author Response

In p.7842, line 22 the following clarifying sentence has been added: "This model was developed to describe and parameterize the hygroscopic properties of atmospheric particles with poorly defined chemical composition. Due to the mass-based approach it can be used to characterize partly dissolved solutes that may coexist in metastable equilibrium with amorphous phases. As a consequence, the model can reproduce both the characteristics of water uptake under subsaturated conditions and predict their CCN properties (Mikhailov et al., 2013)".

Comment

Abstract, Line11: The authors should indicate what forms of sulfate actually can be detected. Specifically, does the present study have the capability to determine organic sulfates?

Author Response:

The STXM-NEXAFS analysis does not allow discriminating ammonium sulfate, letovicite, and ammonium bisulfate. Therefore the term "ammoniated sulfate" has been used here. Moreover, the presence of organic sulfate cannot be verified with the techniques used in the present study. For clarity on p.7858, line 26, the additional sentence has been added. "In the mass balance of the neutral salt compounds we first distributed the measured concentrations of Nss-SO42- and NH4+ ions (Table 2) between minor compounds: Nss-CaSO4, Nss-K2SO4 and NH4NO3. The remaining SO42-/NH4+ mass ratio was found to be 2.9 and 3.0 for accumulation and course mode, respectively. This is close to the sulfate/ammonium mass ratio in ammonium sulfate (AS), which is 2.7. The higher experimental ratio of ions as compared to the stoichiometric ratio in AS could be caused by letovicite (Mifflin et al., 2009) with a SO42-/NH4+

ratio of 3.6 or/and organosulfates (Hettiyadura et al., 2015), but these species can only account for a minor fraction because the ion balance shows that sulfate is almost fully neutralized by ammonium. Based on these calculations we assume that ammonium sulfate is the main component among other possible ammoniated sulfate salts and sulfate containing organic species".

Additional references

Mifflin, A. L., Smith, M. L. and Martin S. T.: Morphology hypothesized to influence aerosol particle deliquescence, Phys. Chem. Chem. Phys, 11, 10095–1010, 2009.

Hettiyadura, A. P. S., Stone, E. A., Kundu, S., Baker, Z., Geddes, E., Richards, K., and Humphry, T.: Determination of atmospheric organosulfates using HILIC chromatography with MS detection, Atmos. Meas. Tech., 8, 2347–2358, 2015.

Comment

Figure 2 and p. 7846, Lines 1-6: It is not clear what is being done here. How were the "initial volume distributions" measured? Judging by the discontinuity around 500 nm it is most likely a combination of APS and SMPS. The caption for figure refers to a "Boltzmann sigmoidal algorithm" but no mention is made of this in the experimental section. p. 7846: What does "series multiplying" mean?

Author Response

The total overlap range was 583-835 nm and both APS and DMPS data points were in good agreement indicating a second mode peak at ∼0.6 mcm (Fig 2b). In addition, in section 2.3.4 the following sentence has been added. "The fitting of the DMPS to the APS was done in the following way. First the DMPS mobility diameter was converted to the aerodynamic diameter using a size-correction factor with an average weighted density for the accumulation mode of 1.54 g cm-3 (Table 5) and a shape factor of 1 (Khlystov et al., 2004). Then the DMPS and APS size distributions were merged at the intersection range of 0.62-0.67 mcm."

The sentence on p.7846, lines 1-6 will be reworded as follows: "Particle size distributions at the ZOTTO site were measured continuously with an DMPS/APS system (see section 2.3.4). Figure 2b shows the initial volume distributions (black symbols) of the atmospheric aerosol particles averaged during the sampling period and those that deposited on the impactor stages I and II. The volume distributions of the deposited particles were obtained by taking the product of the input initial distribution and the collection efficiency for every stage. The output distribution of stage I was obtained by subtracting the distributions of the particles deposited on this stage from the input particle distribution, which was considered as input distribution for stage II. The obtained collection efficiency data were fitted by Boltzmann sigmoidal function (Origin 8.0 software). The distributions obtained indicate that the aerosol loading on stage I represents the CM, whereas stage II represents the AM".

Comment

p. 7847: How was the range of the STXM measurement determined?

Author Response

The aerosol particle size range was determined according to the procedure in Pöhlker et al. 2012. Based on size resolved x-ray absorption, the mass of C, N, and O in individual particles can be determined, which allows a retrieval of the volume equivalent diameter. The reference "(Pöhlker et al., 2012)" has been added to the sentence: "We applied scanning transmission x-ray microscopy with near-edge x-ray absorption fine structure analysis (STXM-NEXAFS) to determine the microstructure and chemical composition of aerosol particles with a volume equivalent diameter in the range of 0.3–3 μm (Pöhlker et al., 2012)." on p. 7847, line 21-24. A figure of the retrieved size distribution has been added to the supplementary material.

Comment

p. 7848: In the experimental section, no mention is made of where the Al and Fe data was obtained. The authors should note this.

Author Response:

The sentence: “Spectroscopic information is obtained by scanning the energy of the incident photons across the x-ray absorption edges of several elements of interest.” has been changed to: “Spectroscopic information is obtained by scanning the energy of the incident photons across the x-ray absorption edges of several elements of interest (i.e., C, N, O, K, Ca, Fe, Al, and Na).” to specify the elements analyzed by STXM-NEXAFS at both synchrotron facilities mentioned in Section 2.3.3.

Comment

p. 7848:There is a reference to a commercial brochure. This is not an appropriate reference. The company name and model of the microscope will suffice. Reference to any peer reviewed literature documenting this microscope would also be pertinent.

Author Response:

The reference was deleted from text.

Comment

p. 7856, line 6: a distribution of analyzed particles would better illustrate the sizes of particles subjected to STXM measurement.

Author response:

The size distribution of all particles analyzed by STXM-NEXAFS has been added to the supplementary material.

Comment

p. 7856: The authors have /OMËĘ(-1). This appears to be denoting normalization by total OM. The addition of a / symbol makes it seem as if you are divining by the inverse – was this really intended?

Author Response:

We thank the referee for indicating this typing error. In p.7856 l. 25, the sentence: “The difference in OM content can also be seen in Fig. 6. All internally mixed (NH4)2-xHx(SO4)/OM-1 particles reveal a clear separation of the inorganic and organic phases.” has been changed to: “The difference in OM content can also be seen in Fig. 6. All internally mixed (NH4)2-xHx(SO4)/OM particles reveal a clear separation of the inorganic and organic phases.”

Comment

Figure 1: The fires (red dots) need to be indicated somewhere in the figure or the caption.

Author response:

The caption of Fig.1 has been revised as following. “Figure 1. (a) 120 h HYSPLIT air-mass backward trajectories during the sampling period at ZOTTO, originating at 300m from 16 to 21 June 2013 and (b) their height above ground level (a.g.l.). Red dots indicate the fire locations within the sampling period (http://rapidfire.sci.gsfc.nasa.gov)”.

Comment

Figure 3: What are the limits of the A-B axis? How can mixed phase II exist if 100% A is present? Can the authors perhaps use an actual system here using actual data? Also, (a, b) should be capitalized (A, B) in the figure caption. Author response The left limit of the A-B axis (point A) corresponds to 100% of component A and 0% of component B. The right limit (point B) corresponds to 100% of component B and 0% of component A. Units have been added to Fig. 3a. The region II in Fig.3a (at CA,B<Ceu) represents the states where the particle exists as a mixture of solid component A in equilibrium with a solution of both components A and B (B – fully dissolved). As the RH increases (moving along the vertical line) more solid A dissolves in the solution. When there is only A component in the particle (B=0) the deliquescence relative humidity of the

particle is DRHA. If RH<DRHA the particle is solid. This diagram just demonstrates behavior of the mixed particles and the respective KIM response on the phase state changes. The actual phase diagrams can be found elsewhere, for example in Seinfeld and Pandis, Atmos. Chem. and Phys., 1998, Fig. 9.8, Fig. 9.9. Figure 3a has been revised. In the figure caption the designations (a,b) are replaced by (A,B). In addition, in the composition axis the left and the right limits are designated as 100% A and 100% B, respectively.

Comment

Figure 5: The size scale needs units.

Author Response:

Units have been added to the size scales in Figs. 5 and 6.

Comment

Figure 8: While the logarithmic axis may be necessary to capture the true range in G, the goodness of fit near the deliquescence RH is difficult to evaluate.

Author Response

To evaluate the goodness of fit near the deliquescence RH, an insert has been added in Fig.8c.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 7837, 2015.