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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.***

## **Anonymous Referee #2**

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Mikhailov et al. present five days of aerosol data obtained from the ZOTTO site in Siberia in June 2013. The focus of the paper are the measurement and interpretation of filter based water uptake measurements. Interpretation is done in the relatively new mass-based hygroscopicity framework. Chemical composition from filter samples and single particle analysis using TEM and STXM/NEXAFS are used to aid the interpretation. The paper motivates the need for the measurements well. It provides substantial new data on an important and undersampled region. The application of the filter based methods are appropriate and the data are generally well analyzed. I do have some

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reservations regarding several claims made the authors that will require clarification and revision. I would expect that a suitably revised paper will meet the standard for publication in ACP.

Major comments:

One of the key point the paper is the disagreement between composition derived kappa and filter-based measurement derived kappa up o 99.6% RH. This discrepancy is noted to be outside the experimenter and PM chemical analysis uncertainties (pg. 7861). This discrepancy is attributed to mixture of phenomena: presence of sparingly soluble organics resulting in a discrepancy between kgf and kccn (presumably modeled by the chemical composition), presence of undissolved inorganic compounds due to kinetic limitations by sparingly soluble organic coatings. From this the authors state in the abstract and conclusions that the observed “kinetic limitations can strongly influence the outcome performed on multi-second time scales such as the commonly used HTDMA and CCNc instruments”.

The observed discrepancy, the inference about diffusion limitations and conclusion as drawn by authors are too strong given the data set. Significant qualification is needed.

First, analysis of kinetic rates is predicated on knowledge of the correct thermodynamic state. Here the presumed thermodynamic endpoint is the derived kappa from the reconstructed filter composition. That is as much, if not more uncertain than the filter uptake measurements. The fact that the observations do not match the estimated kappa from filter is at best weak indication for a discrepancy, much less justification for the detailed attributions made in the paper. For example, it is stated that the discrepancy is outside the uncertainties. However, potential biases are not discussed. Storage of samples may potentially alter the chemical composition via heterogeneous oxidation (the samples were stored at room temperature), polymerization reactions of the organics, and volatilization of other compounds. The assigned reconstructed composition may not represent the actual composition in the particles with respect to the

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actual chemical state. Composition assignment of  $\text{CaSO}_4$  or organic sulfates may give very different kappa than assumed  $\text{NH}_4\text{SO}_4$ . Overall, the filter estimated kappa is an important data point that is not strong enough to be suitable as the thermodynamic reference against which kinetic limitation can be evaluated.

Second, Fig. 10 suggests that the filter equilibration was done for several hours in some cases. It appears that there is little change after several minutes. If kinetics are limiting water uptake, then the sample should gradually converge to the equilibrium point. Since the observations seem to be flat, the data itself should be considered thermodynamically stable. In fact, if they weren't there would be little point in the preceding analysis in Figure as it is meant to represent equilibrium states.

Third, even if kinetic limitations are observed with the filter-based methods it does not follow that HTDMA and CCNc would be affected. Time scales to equilibration are typically much longer for bulk samples and only studies that vary residence time in those instruments can conclude whether or not it is an issue.

Combined, that means that the matter of fact stated conclusion drawn by the authors is not warranted.

Other comments:

7846: Simplicity water → rather than stating the company, please state the purity (resistivity or organic content).

Figure 2b – Input size distribution is merged APS/DMPS? Where is hand-off? How was mobility diameter converted to Aerodynamic diameter?

7852: “regarded as the dilute hygroscopicity parameter of the investigated sample of particulate matter (Fig. 2b)” → Fig. 2b seems to refer to Fig. 3b. However, Figure 3 is only discussed in the next paragraph. The text needs to be rearranged.

The STXM and TEM analysis could be improved? Presumably these representative? Can the data be somehow reduced and quantified in addition to showing images (e.g.

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a Table with number of particles analyzed and composition data?)

“This is by a factor of 5 more than the value obtained for an Amazon sample ( $k_5$  (III) = 0.09) in our previous study (Mikhailov et al., 2013). The observed difference in the values can be explained by the high content of water soluble species in the ZOTTO samples (Table 2) and the strong interaction between inorganic ions and organic molecules as a consequence.”

→ To me it would have seemed to be more logical to compare  $k_6$ (III) first, as it gives the limiting value. Is ZOTTO aerosol more or less hygroscopic than that in the Amazon?

→ The idea that an increase in  $k_5$  describes the strength of inorganic/organic interactions may be valid. However, it is not self-evident from the equation (it's a fit parameter) or from the text in the method or the paragraph. Clarification and justification is needed.

“The high fraction of organic carbon in the accumulation mode compared to the coarse mode results in a twofold decrease in the dilute hygroscopicity parameter,  $k_6 = \kappa_m$  (Table 3) and a reduction of the  $\kappa_m$  top value from 0.22 (Fig. 8d) to 0.12 (Fig. 8b).”

→ The assertion “results” is too strong since this study has no direct information about the hygroscopicity of the individual species. A more circumspect description would be that “the high organic fraction is consistent with the observed decreased in  $\kappa_m$ ”.

→ The behavior of the top value vis-a-vis organic content may well be controlled by a number of phenomena outside the range of study here (e.g. presence or absence of a strongly non-ideal inorganic or differences in organic speciation). Again the assertion “results” is too strong.

“Moreover, the quasi-eutonic efflorescence transition in the dehydration mode is decreased by the organic species at 15 % RH, i.e., 35 % RH for AM vs. 50 % RH for CM (Fig. 5a and c).”

→ Refers to Fig. 8, I presume?

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→ should be reworded more clearly to remove the ambiguity in the sentence e.g. “ the quasi-eutonic efflorescence transition is 50% in the coarse mode (Fig. 8c) and 35% in the accumulation mode (Fig. 8a)”

→ The assertion that this is caused by the organic species is speculative. Yes, organic coatings may decrease DRH but so will the displacement of sulfate with nitrates. Not all organics are non-deliquescent. There is no evidence in this paper to directly attribute the observed changes in Gm curves to chemical composition. Again, “consistent with” is the best this work should claim.

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