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Atmospheric Chemistry and Physics
Discussions

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 #2 for the constructive criticism and suggestions for improvement that were taken into account upon manuscript revision. Responses to individual comments are given below. Major comments: Total Comment

One of the key point the paper is the disagreement between composition derived kappa and filter-based measurement derived kappa up to 99.6% RH. This discrepancy is noted to be outside the experimenter and PM chemical analysis uncertainties (pg.

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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 volatilzation of other compounds. Composition assignment of CaSO4 or organic sulfates may give very different kappa than assumed (NH4)2SO4. 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.

Response

We will respond to this comment step by step.

Comment

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 volatilzation of other compounds. The assigned reconstructed composition may not represent the actual composition in the particles with respect to the actual chemical state.

Response

As noted (p.7844, line 25), before being analyzed the samples were placed in Ziploc bags and stored at 4C instead of room temperature. The chemical analysis and water uptake measurements were performed on filters with the same travel and storing history, therefore we suggest that the hygroscopic growth results reflect the actual composition measured in the lab. Moreover, as stated in p. 7847 (line 14), the ion chromatography analysis was conducted on the same filters after the water uptake measurements. We do not exclude potential evaporation of volatile species, for example, while shipping the Siberian samples to Saint-Petersburg lab during ∼48 hours. However, we can claim that during the hygroscopicity experiment the particle evaporation was insignificant. The potential particle mass lost due to evaporation was monitored by weighing the loaded filters before and after water uptake measurements. These measurements as well as subsequent hygroscopic data obtained in repetitive drying/humidifying cycles showed that the effect of particle evaporation was negligibly small (see p. 7849, line 27). In Fig.8 varied symbols in panels (a) and (c) represent different experimental runs on the same sample and these data are in a good agreement.

Comment

Composition assignment of CaSO4 or organic sulfates may give very different kappa than assumed (NH4)2SO4.

Response

In p.7858, line 26 the following clarification has been added: “In the mass balance of the neutral salt compounds we first distributed the measured concentrations of

Nss-(SO4)2- and NH4+ ions (Table 2) between minor compounds: Nss-CaSO4, Nss-K2SO4 and NH4NO3. The remaining (SO4)2-/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 (SO4)2-/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.

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Comment

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.

Response

We purposely compared experimental (kappa) kv,ws with predicted kv,p using simplified ZSR equations (15) and (16) . These equations should provide lower-limit values of kv,p (p. 7861, line 5). For the water soluble fraction the key components are ammonium sulfate and WSOM. Uncertainties for AS and WSOM concentrations are $\sim$ 10 and $\sim$ 30 %, respectively. Due to the high hygroscopicity of ammonium sulfate, the uncertainty associated with the AS concentration provides the greatest contribution to the total error of kv,p . The volume ratios, eAS, independently retrieved from the measured sulfate and ammonium ions were 0.30; 0.34 and 0.72; 0.76 for accumulation and coarse mode, respectively. The minimum values of eAS (Table 4) we used for the calculations. Nevertheless, the predicted kv,p values still significantly exceed the FDHA-derived kv,ws . Based on the argumentation presented above we suggest that the reconstructed filter composition was representative enough and the obtained positive difference between predicted kv,p and measured kv,ws values is beyond the chemical analysis uncertainties.

Comment

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”. 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.

Response

Please note that the FDHA method operates with an assembly of isolated particles and not with bulk samples. Therefore, the time scale to equilibration for submicron particles can be comparable to that for HTDMA and CCNc instruments. Moreover by definition (Eq. 17) the diffusion coefficient is not a size dependent parameter. As a first approximation it can be used to estimate kinetic limitations even for submicron particles. In p.7864, line 24 the following clarification will be added: “From the FDHA-derived upper value of Dw $\sim$ 10(-12) cm2 s-1 and the typical particle size range of 20 - 200 nm used in HTDMA and CCNc instruments it follows that the characteristic time scale for water diffusion into aerosol particles is 3 – 300 s (Eq.17). These estimates are consistent with several HTDMA and CCNC studies where kinetic limitations have been observed due to organic coatings and the multi-second residence time used in these instruments (CNN: Abbat et al.,2005; Henning et al., 2005; VanReken et al.,2005; Shants et al., 2010; Engelhart at al., 2008; Ruehl et al., 2009; HTDMA: Xiong et al., 1998; Chuang, 2003 Mikhailov et al., 2004; Sjogren et al., 2007)”.

Additional references

Abbatt, J. P. D., Broekhuizen, K., and Kumar, P. P.: Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles, Atmos. Environ., 39, 4767–4778, 2005.

Chuang, P. Y.: Measurement of the timescale of hygroscopic growth for atmospheric aerosols, J. Geophys. Res., 108(D9), 4282, doi:10.1029/2002JD002757, 2003.

Engelhart, G. J., Asa-Awuku, A., Nenes, A., and Pandis, S. N.: CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol, Atmos. Chem. Phys., 8, 3937–3949, 2008. Henning, S., Rosenørn, T., Anna, B. D, Gola, A. A., Svenningsson, B., and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organic and inorganic salt, Atmos. Chem. Phys., 5, 575–582, 2005.

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Ruehl, C. R. Chuang, P. Y. and Nenes A.: Distinct CCN activation kinetics above the marine boundary layer along the California coast, Geophys. Res, Lett.. 36, L15814, doi:10.1029/2009GL038839, 2009

Shantz, N. C., Chang, R. Y.-W., Slowik, J. G., Vlasenko, A., Abbatt, J. P. D., and Leaitch, W. R.: Slower CCN growth kinetics of anthropogenic aerosol compared to biogenic aerosol observed at a rural site, Atmos. Chem. Phys., 10, 299–312, 2010.

Sjogren, S., Gysel, M.,Weingartner, E., Baltensperger, U., Cubison, M. J., Coe, H., Zardini, A. A., Marcolli, C., Krieger, U. K., and Peter, T.: Hygroscopic growth and water uptake kinetics of twophase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures, J. Aerosol Sci., 38, 157–171, 2007.

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Xiong, J. Q., Zhong, M. H., Fang, C. P., Chen, L. C., and Lippmann, M.: Influence of organic films on hygroscopicity of ultrafine sulfuric acid aerosol, Environ. Sci. Technol., 32, 3536–3541, 1998.

Comment

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.

Response

There are several limiting steps during water uptake/release by a particle: gas diffusion of water molecules to the particle's surface, gas-surface transport (reversible adsorption), surface-bulk transport and bulk diffusion. Additionally, vapor is absorbed by walls and filter surfaces both in the measuring cell and in the reference cell with the blank filter. The difference in the concentrations of water molecules passing through the measuring and comparison cells is measured. As a result we cannot directly assign the observed time scale of water uptake to aerosol particles (Fig. 10a and 10c). The mass transfer kinetic limitation was detected upon particle dehydration. Figure 10b clearly shows that several water release peaks appear between quasi equilibrium states of the system with a background signal at constant RH. The water release time of the peaks 1 and 2 (Fig.10) were used to estimate the transport characteristics of water molecules through the organic coating.

Comment

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

Response

The water purity will be added to the revised manuscript:“ ..4 mL Millipore Simplicity water (TOC <5 ppb; specific resistance > 18.2 Megohm cm) . . ..”

Comment

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

Response

The total overlap range was 583-835 nm and both APS and DMPS data points were in a good agreement indicating a second mode peak at ∼0.6 mcm (Fig 2b). The following sentence in section 2.3.4 has been added to the updated manuscript: “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..”

Comment

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

Response

In p. 7856, line 26, the following text has been added. “Limited particle statistics is an inherent difficulty of most single particle techniques. Thus, we applied two different single particle approaches in this study to broaden the statistical basis and to check the consistency of the independent data sets. The total particle number that has been probed with STXM is 150, while the total particle number for TEM analysis is 810. The TEM data allows a classification of the particle ensemble based on morphology, while the STXM data (though more limited in statistics) provide more detailed insights into the chemical composition and therefore complement the TEM data set. The visual TEM analysis of 725 AM and 85 CM aerosol particles has revealed three main morphology types: (i) homogeneous spheres, which can be attributed to terpene- and isoprene-based SOA droplets (Kourtchev et al.,2005; Pöschl et al., 2010), (ii) mixed SOA-inorganic particles with core-shell morphology, and (iii) irregularly shaped primary biological aerosol (PBA) particles, such as plant fragments. In the submicron particle range the balance between uncoated (type i) and coated (type ii) aerosol particles is 32% and 62%, respectively, which agrees with the STXM data. Approximately 5% can be attributed to PBA particles with an organic coating fraction of ∼50%. In the coarse particle mode almost all aerosol particles are internally mixed with surface organic coating (∼80%). Among them ∼20% have a high-contrast-density outer core (Fig. 7d-f) presumably formed from sparingly soluble organic species due to liquid-liquid phase separation upon particle dehydration (Song et al., 2012). Approximately 13% are PBA particles. In addition, a minor fraction (<1%) of the fractal-like soot aggregates was found on the TEM images of the AM and CM aerosol particles”.

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Additional references

Song, M., Marcolli, C., Krieger, U. K., Zuend A., and Peter T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, Atmos. Chem. Phys., 12, 2691–2712, 2012; www.atmos-chem-phys.net/12/2691/2012/.

Kourtchev, I., Ruuskanen, T., Maenhaut, W., Kulmala, M., and Claeys, M.: Observation of 2-methyltetrols and related photo-oxidation products of isoprene in boreal forest aerosols from Hyytiala, Finland, Atmos. Chem. Phys., 5, 2761–2770, 2005.

Comment

“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 k6(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 k5 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.

Response

This text will be updated as follows. “In the dilution regime (III) (Eq. 8), the fit parameter k6=km(0) obtained for submicron aerosol particles is 0.061±0.002 (Table 3). This value can be compared to the dilute hygroscopicity obtained for PM1 samples during the Amazonian Aerosol Characterization Experiment (AMAZE-08) in the wet season (Mikhailov et al., 2013), where km(0) = 0.104±0.002. The observed ∼40% discrepancy in km(0) between Amazon and Siberian samples may be caused by differences

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in their chemical composition. Hygroscopic ammoniated sulfate is a good candidate for the observed difference. However, for the AMAZE-08 campaign the average sulfate loading measured by ion chromatography was only 0.21 mcg m-3 (Chen et al.,2009). This concentration is less than half that determined in the Siberian sample (0.44 mcg m-3, Table 2). One possible explanation is that the ammoniated sulfate in the Siberian aerosol sample was partly isolated by sparingly soluble organic species and therefore was not completely involved in hygroscopic growth. This potential mass transfer limitation effect will be considered below. Another possible reason for the increased hygroscopicity of the Amazon sample is that the biogenic SOA produced by tropical rainforests contains more hygroscopic species than that produced in the Siberian boreal zone. It was found that the formation of WSOC is closely linked to photosynthetic activity by the forest ecosystem, which depends on both temperature and solar radiation (Zhang et al., 2010; Miyazaki et al., 2012). Among these compounds are the highly water soluble and hygroscopic isoprene-derived 2-methyltetrols (Claeys et al., 2004; Ekström at al., 2009; Engelhart et al., 2011). Because solar radiation and the production of OH radicals are at a maximum in the tropics, the concentration of 2-methyltetrols in the Amazon Basin is higher than in boreal forests. The average concentration of 2- methyltetrols in Amazonian PM1 particles in the wet season is 45 ng m-3 (Decesari et al., 2006) while for the boreal ecosystem in the summertime it is only $\sim$ 26 ng m-3 (Kourtchev et al. 2005). Given that the WSOC\OC ratio for AMAZE and ZOTTO samples is comparable (63±4 %) it seems possible, therefore, that the water uptake associated with WSOM in the AMAZE sample was higher than that in the ZOTTO sample”.

Additional references

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Decesari, S., Fuzzi, S., Facchini, M. C., Maenhaut, W., Chi, X., Schkolnik, G., Falkovich, A., Rudich, Y., Claeys, M., Pashynska, V., Vas, G., Kourtchev, I., Vermeylen, R., Hoffer, A., Andreae, M. O., Tagliavini, E., Moretti, F., and Artaxo, P.: Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds, Atmos. Chem. Phys., 6, 375–402, 2006, http://www.atmos-chem-phys.net/6/375/2006/.

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Phys., 10, 7859–7873, 2010, doi:10.5194/acp-10-7859-2010.

Comment

“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, k6=km(0) (Table 3) and a reduction of the km 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 km”.

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. - 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.

Response

We restate this section as follows: “Overall, the observed hygroscopicity behavior of the sub- and supermicron samples can be attributed to differences in their chemical composition. A twofold decrease in the dilute hygroscopicity parameter, k6=km(0) (Table 3), and a reduction of the km top value from ∼0.22 (Fig. 8d) to ∼0.12 (Fig. 8b) is consistent with a high fraction of organic carbon in the accumulation mode compared to the coarse mode. Likewise, the observed decrease of the quasi-eutonic efflorescence transition in the dehydration mode by 15% RH (i.e., the quasi-eutonic efflorescence

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transition is ∼50% RH in the coarse mode (Fig. 8c) versus ∼35% in the accumulation mode (Fig. 8a)) can also be associated with a high fraction of organic species in the accumulation mode".

Comment

Refers to Fig. 8, I presume?

Response

This misprint has been accounted for in the revised text.

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