

Interactive comment on “Mass-based hygroscopicity parameter interaction model and measurement of atmospheric aerosol water uptake” by E. Mikhailov et al.

We would like to thank Referee #2 for the remarks and constructive comments, which will be taken into account upon manuscript revision. Responses to individual comments are given below.

General comments: Measurements

Comment

How long are the samples given to equilibrate at each relative humidity? In HTDMA studies the “residence time” (nominally the time for which the humidified size sample is exposed at a given relative humidity prior to reclassification) can be an important variable in interpreting the results. HTDMA residence times of less than the order of 10’s seconds have been shown to produce growth factors in a transient regime for particles composed of secondary organics (Duplissy et. al., 2009, Sjogren et. al, 2007), although artefacts attributable to evaporation have been observed at residence times of around 60 seconds (Gysel et. al., 2007). In EDB studies where it is possible to hold a particle at a given relative humidity for much longer e.g. for hours / days it has been observed that equilibrium is only achieved after much longer time (of the order of minutes and longer) for certain compounds e.g. Chan et. al., 2006. Given these previous findings it is clearly important that the residence time is well defined. Has the rate of water uptake been recorded and if so what does this tell us about the nature of the sample?

Response

The paper with detailed description of the Filter-based Differential Hygroscopicity Analyzer (FDHA) has been recently published in *Izvestiya, Atmospheric and Oceanic Physics*, 2011, Vol. 47, No. 6, pp. 747–759. The English version can be ordered under the following link <http://www.springerlink.com/content/m63203237157248g/>.

The FDHA technique rules out potential errors caused by kinetic effects in the aerosol-water vapor system. The diagram of water uptake looks like a gas chromatographic curve (peak) with zero signals at start and end points. Thus the water uptake (release) experiment was stopped when the initial zero level was reached.

Hydration/dehydration mass growth factor measurements took on average 10-60 min at 10-70% RH, while above 98% RH it took 1-2 days to reach thermodynamic equilibrium.

The experimental data were obtained with 2-3 drying and humidifying cycles on each sample. This information has been added to the revised manuscript.

Comment

The volatility of the sampled particles could be an issue. As the sample is heated and the helium is continuously purging the chamber there is the potential to remove particulate material from the filter. The key question here is if this is a significant process for the experiments in the manuscript. For the sodium chloride it will not be an issue, for the field samples the authors should justify why they believe evaporation will have a negligible effect. (N.B. as an aside: this type of apparatus might be useful for experiments designed to look at hygroscopicity and volatility).

Response

The dry particle mass was measured before and after water uptake measurements. We do not exclude particle evaporation due to volatile species, for example, upon shipping the Amazon sample to Russia. However, we can claim that during the hygroscopicity experiment the particle

evaporation was insignificant because the total particle mass change was small and the hygroscopic curves obtained at the drying and humidifying cycles were identical. The potential particle evaporation can be reduced since the FDHA system allows to conduct the hygroscopic measurement at low temperatures as small as -10 °C.

Comment

These two previous points lead on to a question on the dry sample treatment. At what RH is the sample deemed dry (I assume <1).

Response

Yes, we can keep the samples at RH <1%, but to minimize the particle evaporation we usually kept the samples at RH=5-7% (starting point). Additionally, the bypass was used upon warm-up setup (not shown in Fig.1).

Comment

The authors justify the applicability of their bulk sampling method by noting that the mode of the mass size distributions sampled tend to be above 250 nm (for the AMAZE sample) and hence the Kelvin effect can be ignored. The discussion on the applicability of the bulk sampling method should be expanded to address other factors that may limit the method:

The characteristics of the boreal mass size distributions should be mentioned briefly.

Response

The following extended text regarding the particle size distribution has been added to the paper. “The size distributions of the investigated aerosols were measured with a mobility particle sizer. The mean diameters (and geometric standard deviations) of the number size distribution distributions were: 139 nm (2.38) for AMAZE; 109.7 nm (1.77) for SPB; 81.6 nm (1.71) for AS; and 59.4nm (1.47) for NaCl.”

Comment

Ignoring the Kelvin effect will bias the derived hygroscopicity to a lower value. Could the authors calculate how big an effect this is for the typically observed number size distributions e.g. from the difference in the theoretical size resolved vs. bulk water content or some other metric? It might also be useful for future reference if the limits of the applicability of the assumption are tested (theoretically).

Response

We have estimated the potential errors in κ_m caused by ignoring the Kelvin effect based on the particle size distribution of the polydisperse samples. Thus, the obtained results for the AMAZE sample are as follows: at RH < 85% the relative error, $\delta\kappa_m/\kappa_m$ (%), is ~4%; from 85% to 99.4% RH the error gradually increases from 4% to 23%.

The calculation procedure is described in the Appendix C of the revised manuscript. Using this algorithm we re-counted κ_m for atmospheric samples and for reference AS and NaCl particles. These revised κ_m values were used to compare experimental data with KIM calculations (Fig.2, Fig.5 and Fig. 6).

Comment

To be more complete the authors could consider the impact of size dependent composition on the hygroscopicity in more detail (an issue that is mentioned in the manuscript) and the hygroscopic mixing state (is there any information on this available for the ambient samples? Is there an

implication for the FDHA technique? Is the FDHA technique sensitive to mixing state and how might an externally mixed particle population manifesting itself in the KIM analysis?).

Response

In the presented paper the filter based measurements were conducted for submicron aerosols and they do not allow resolving any size dependence of the hygroscopicity.

A tandem of FDHA with size selection instruments like a MOUDI impactor or electrospray generators can be used to analyze in detail the size dependent water uptake.

Comment

The filter sampling duration should be stated in the paper. Values for the mass collected, dry mass and wetted mass of the samples could be given. Any temporal variability in the particle's hygroscopicity cannot be captured using this method. If online hygroscopicity measurements are available these should be discussed in the context of the FDHA measurements i.e. any smearing of the hygroscopicity. Composition measurements could also be used to infer temporal variation in the hygroscopicity to some extent if a more direct measure is not available.

Response

The mass of the atmospheric particles used for the FDHA analysis and the sampling time are shown in Table 2, and the deposited mass of the reference NaCl and AS particles is indicated in the text (section 3.2). The obtained results are temporally averaged and more suited for solving climate problems, where detailed temporal variations of the particle chemical composition is not required. Accordingly, the KIM was structured so that it was possible to describe the hygroscopic properties of multi-component particles with poorly defined chemical composition.

Comment

A final point on the measurement technique is how well the integrity of the individual particles is conserved on the filter as it is put through drying and humidifying cycles? If the sample is put through a number of cycles are the results the same? Perhaps microscopy could be used to look at this point.

Response

To avoid or minimize potential particle coagulation in the course of humidification and drying cycles we used relatively low filter loadings ($\sim 0.1 \text{ mg cm}^{-2}$). SEM analyses showed that under these conditions the average distance between particles was larger than the expected diameter growth factors ($G_D = 2-10$ for NaCl at RH= 80-99%; Mikhailov et al., 2011). Moreover, the hydration and dehydration experiments were performed in multiple cycles that went up to different maximum RH values (60%, 80%, 99%) and yielded consistent results, indicating that potential coagulation at high RH had no significant effect.

General comments: Parameterization

Comment

My main query here is on the purpose of the KIM parameterisation. Is it just a method to provide a fit to the measurement data? The authors state it performs well compared to a rigorous thermodynamic approach (for the sodium chloride sample), but is this not simply due to the measurements being consistent with the rigorous thermodynamic model rather than any predictive skill of the model. You would always expect the KIM to perform well provided the measurements agree with the rigorous thermodynamic approach if there are enough inflection points.

Response

The so called “rigorous thermodynamic models” like the Aerosol Inorganic Model (AIM; Clegg et al. 1998) contain unknown interaction parameters. Their values generally result from the fit of either bulk water activity measurements or electrodynamic balance data. The difference between KIM and these thermodynamic models is that there is a much less number of unknown parameters in KIM. In addition, like the regular κ - model, the KIM can be applied to arbitrary mixtures of unknown particle composition. For a detailed answer to this comment we refer to the authors’ general comments in the public discussion of ACP. See also Appendix A of the updated paper.

Comment

Regarding the three defined KIM regimes. I find the generality of these definitions questionable and find the question of their relevance unanswered. Whilst pure substances undergo abrupt phase changes others (multi-component) may be more gradual and the relative humidities at which the phase changes / dissolution etc take place may cover a wide range and be highly variable from mixture to mixture.

Response

The three defined KIM regimes emerge from modeling the evolution of multicomponent particles upon interaction with water vapor. In spite of the mixed composition their water soluble fraction passes through the three modes: formation of the eutonic (or quasi-eutonic) solution, gradual dissolution of components and dilution of the concentrated solution. The KIM model just helps to identify these modes. The KIM is also a universal model which can describe abrupt and gradual phase transitions including metastable states of the aqueous solutions.

Specific comments:**Comment**

P 30879 – line 6 – definition of critical diameter – I don’t think it is the measured critical diameter that is, rather it is the smallest dry diameter at which particles activate at a given super-saturation measured (sometimes called the activation diameter). The authors make this clearer later in the manuscript e.g. using the term critical dry diameter in the caption of figure 4. The difference between the conventional definition of critical diameter should be made clear throughout the paper to avoid confusion.

Response

1. P 30879 – line 6. The phrase “... we obtained good agreement between the predicted and measured critical diameters of CCN activation.” has been replaced by the following: “... we obtained good agreement between the KIM predicted critical dry diameters and directly measured dry particle activation diameters.”

Comment

P 30882 – line 18 – ideality – this is an example of where the authors need to be more precise when talking about ideality. I don’t believe that anyone is seriously assuming constant activity coefficients of unity. Rather it is the change in non-ideality that is not dealt with rigorously when simply adding up volumes (e.g. when using ZSR type approaches to interpret HTDMA data). With this in mind the statement on line 18 (p 30882) is probably not the most informative way of illustrating the advantage gained from a mass based hygroscopicity metric.

Response

As described in the referenced studies, the mobility equivalent diameters of porous and irregularly shaped particles can be by up to a factor of 2 larger than the volume or mass equivalent diameters implying deviations up to a factor of eight in effective particle density (Krämer et al., 2000). To avoid confusion about the meaning of ideality in this context (sphericity, compactness/density), we removed the above sentence from the revised manuscript.

Comment

Perhaps, calculating the change in kappa derived from a volume additive approach vs. a mass based approach for some relevant binary and ternary systems would be more informative (e.g. sodium chloride + water and sodium chloride + water + X).

Response

We are currently working on this issue and the comparison of FDHA and HTDMA results for relevant binary and ternary systems will be presented soon. The first results have shown that the κ -volume interaction model KIM_V can be applied for volume based measurements, although at low RH it does not match the experimental results very well. Probably, the additional parameters which compensate volume non-additivity caused by particle shape and restructuring have to be used.

Minor points:

There is some mixing of US and UK English in the manuscript.

P 30879 – line 15 – the use of “etc” here makes the sentence somewhat colloquial. I would suggest making this a full sentence explaining precisely what is meant.

P 30889 – line 13 – Spelling of Setschenow – references I have seen to this author spell it “Setschenov”.

P 30901 – lines 6 to 7 - this should be one paragraph

P 30901 – line 14 – “along these lines” sounds this sounds somewhat colloquial. As the final statement in the paper this sentence should be reworded to be neater and more precise.

Response

All the reviewer’s minor comments have been accounted for in the revised text.

References

Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: A thermodynamic model of the system $H^+ - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O$ at 298.15 K, *J. Phys. Chem. A.*, 102, 2155–2171, 1998.

Krämer, L., Pöschl, U., and Niessner, R.: Microstructural rearrangement of sodium chloride condensation aerosol particles on interaction with water vapor, *J. Aerosol. Sci.*, 31, 6, 673-685, doi:10.1016/S0021-8502(99)00551-0, 2000.

Mikhailov, E. F., Merkulov, V. V., Vlasenko, S. S., and Pöschl, U.: Filter-based differential hygroscopicity analyzer, *Izvestiya atmospheric and oceanic Physics*, 47(6), 747-759, 2011.