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 #4 for the remarks and constructive comments, which will be taken into account upon manuscript revision. Responses to individual comments are given below.

Major comments:

Comment

The main criticism is that I am not sure if the manuscript is meant to describe the new model and somehow evaluate its performance, or is it just used as a tool to analyze RH dependent hygroscopicity parameter and a method to estimate CCN properties. At the moment it is somehow failing in both. For model evaluation I would have liked to see more comparison on the full thermodynamical models like AIM so that the model would be tested against the mixtures of several inorganic species and then for some well known organics. At the moment in the manuscript only two extreme examples are presented, one with well known substance and the second with atmospheric mixtures without knowledge of exact composition. I would like to see how the model works with few compounds and is it actually bridging the "gap between the results of simplified single parameter models widely used in atmospheric or climate science and the results of complex multi-parameter ion- and molecule interaction models frequently used in physical chemistry and thermodynamics" like authors claim.

Response

The KIM was built to describe the hygroscopic properties of complex particles with poorly defined chemical composition (see the authors' general comments). This was demonstrated by example measurements of ambient AMAZE and SPB aerosols showing that both sub- and super-saturated ambient conditions were captured by KIM. In the revised manuscript we have confirmed the model efficiency by including new substances and comparing the modeling results with E-AIM. The added compounds are: ammonium sulfate (AS), levoglucosan, malonic acid (MA), and AS-MA with 1:1 mole. In addition CCN predicted dry activation diameters for AS particles are also presented. Testing results have shown that the KIM provides good agreement for all listed species and that the obtained quantities of the fit parameters have reasonable physical interpretation. For a detailed response please see the authors' general comment.

Comment

If the main message of the manuscript is a new method to estimate CCN-properties of aerosol, then authors should concentrate more on that part and somehow show this method is better than the others used. More data would be needed also for that and also information how many data points at different RH is needed and how much better results can be achieved compared to estimating CCN-properties from one single RH. The measurement data for NaCl is fine, but comparison to field data is not so well justified, especially from Saint-Petersburg. There are only measurements showing the water uptake of aerosol without any other information about composition. It only shows that aerosol in the area is different to aerosol in Amazonian area, but as there is no idea how much different, then the presentation of different fit parameters is meaningless.

Response

The main goal of the manuscript is to present a new method that describes the hygroscopicity of complex ambient particles with poorly defined composition by a simple parameterization, much simpler than that of other complex multi-parameter ion- and molecule interaction models (e.g., AIM or UNIFAC). For more details we refer to the authors' general comments in the public discussion of ACP.

Comment

I have also some concerns about using bulk aerosol samples, like done with FDHA method, to estimate aerosol hycroscopicity, which is quite often size dependent and aerosol is even externally mixed. However, that method is not evaluated in this manuscript.

Response

The Filter-based Differential Hygroscopicity Analyzer (FDHA) (Izvestiya, Atmospheric and Oceanic Physics, 2011, Vol. 47, No. 6, pp. 747–759 (http://www.springerlink.com/content/m63203237157248g/) , which we used for the measurement of mass water uptake at different RH consists of two cells. A filter (*D*=13mm) with aerosol particles is placed inside the measuring cell, and a pure filter is placed in the comparison cell. Vapor is absorbed by walls and filter surfaces in both cells; it is additionally absorbed by aerosol particles in the measuring cell. The difference in the concentrations of water molecules in the flows passing through the measuring and comparison cell is detected with a differential sensor. Thus, the potential capillary condensation on the fibers is subtracted. A good agreement between FDHA-measured water uptake with AIM confirms that capillary condensation between the fibers and aerosols is beyond the sensitivity of this method even at 99% RH. Moreover we have tested tissuquartz and fiber glass Teflon coated filters to estimate capillary effects and did not find any difference.

We also conducted additional FDHA measurements with size selected ammonium sulfate and sodium chloride particles. These data demonstrate stepwise deliquescence and efflorescence transitions. Moreover the water uptake FDHA results are identical to these obtained by a single particle levitation method and are in excellent agreement with thermodynamic AIM (see updated Fig. 2a and Fig. 2b).

Minor comments:

Comment

Equation 16: Where do you take the definition for $y_{m,i}$*?*

Response

The mass-based relation for $y_{m,i}$ is equal to the volume based relation taken from Petters and Kreidenweis (2007) and Raymond and Pandis (2003). In this paper $y_{m,i}$ is the dissolved mass fraction of solute *i* :

$$y_{m,i} = \frac{m_i^0}{m_w^0}\frac{m_w}{m_i} = C_i\frac{m_w}{m_i} = C_i\frac{m_w}{f_i\sum_i m_i} = C_i\left(G_m - 1\right)/f_i \ ,$$

where $m_i^0/m_w^0 = C_i$ is the solubility (g g^{-1}) of the solute *i*, m_i and f_i are the mass and the mass fraction of solute *i* in the dry particle, $G_m = \left(m_w + m_s\right)/m_s$ is the mass growth factor.

Comment

Page 30881, equation 2: Equation is approximation, so maybe "=" should be "≈"

Response
In Eq.(2) we replaced the symbol *“=”* by *“≈”*.

Comment
page 30893, line 15-17: How sure you are that it is the particle size causing the difference in the efflorescence RH? I guess particles do coagulate on the filter at high RH making them much larger during evaporation than they were during wetting. Could the filter surface then maybe trigger the efflorescence?

Response
As noted before we have conducted additional FDHA measurements with size selected ammonium sulfate and sodium chloride particles. These data demonstrate sharp deliquescence and efflorescence transitions. Moreover the water uptake FDHA results are identical to the ones that were obtained by single particle levitation method and are in excellent agreement with thermodynamic AIM (see updated text and Fig.2).

To avoid or minimize potential particle coagulation in the course of humidification and drying cycles we used relatively low filter loadings (~0. 1 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.

We do not exclude that the filter surface may trigger the particles’ efflorescence due to surface impurities. Additional experiments are needed that would give an unambiguous answer to this question.

References

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

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, doi:10.5194/acp-7-1961-2007, 2007.

Raymond, T. M. and Pandis, S. N.: Formation of cloud droplets by multicomponent organic particles, J. Geophys. Res., 108, D15, 4469, doi:10.1029/2003JD003503, 2003.