

Interactive comment on “ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosols” by C. Fountoukis and A. Nenes

Anonymous Referee #1

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General Comment

The authors present a new version of the thermodynamic equilibrium model ISORROPIA (II) that adds K^+ - Ca^{2+} - Mg^{2+} to the NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosol system, by which ISORROPIA II is evaluated against the thermodynamic module SCAPE2.

The inclusion of the mineral cations K^+ - Ca^{2+} - Mg^{2+} (and their salt compounds) in ISORROPIA II is commendable, but the following aspects of the manuscript needs to

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be improved or clarified, before I can recommend publication:

(1) Considering mineral cations K^+ - Ca^{2+} - Mg^{2+} in aerosol thermodynamics is important, as these cations (a) can strongly influence the ion balance. Their presence is in particular important for cations that form (semi-) volatile compounds, such as NH_4^+ . Ammonium, now being the weakest base of the above cations, can only be present in the liquid or solid aerosol phase, in case of excess anions (with respect to Na^+ - K^+ - Ca^{2+} - Mg^{2+}). In the other case ammonium salts cannot form, as ammonium is driven out of the aerosol phase as ammonia (NH_3).

In this respect, it is of crucial importance to include at least the major mineral cations K^+ - Ca^{2+} - Mg^{2+} in aerosol thermodynamics modeling. But also, because (b) the deliquescence relative humidities (RHD) of these additional mineral salt compounds differ considerably from those of the ammonium salts, being usually higher for strong anions such as sulfate, SO_4^{2-} (and except Ca^{2+} and some hydrates also for nitrate, NO_3^-). The corresponding ammonium salts are more soluble and hence have lower RHDs; less soluble salts drop out earlier of the solution in case the water activity decrease, e.g. as the relative humidity (RH) decreases.

These differences, both (a) in the cation-anion balance, and (b) in RHDs (of binary or multicomponent solutions) are of crucial importance for the water uptake, as the water uptake subsequently determines not only the gas/liquid/solid partitioning but also the ambient aerosol size-distribution, aerosol optical properties and aerosol-cloud interactions.

However, for the same reason the inclusion of organic acids is of crucial importance. For instance, Trebs et al. (2005) and Metzger et al. (2006) have shown that the consideration of mineral cations K^+ - Ca^{2+} - Mg^{2+} with SCAPE2 causes a larger discrepancy to the observed ammonium concentrations compared to ISORROPIA, if these compounds were neglected. The reason was that especially the additional cation potassium (K^+), which is being emitted during biomass burning events can substantially

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contribute to the total cations observed in the fine aerosol mass fraction, inhibited the partitioning of ammonia into the aerosol phase. Therefore, all modeling exercises that have accounted for these additional mineral cations but not for the observed (associated) organic acids obtained poorer agreement for the ion-balance and in particular for ammonium, whereas the omission of both (K^+ - Ca^{2+} - Mg^{2+} and organic acids) with ISORROPIA yielded reasonable agreement (for the wrong reason). Interestingly, this could be seen at two quite distinct locations and campaigns, i.e. during the framework of LBA-SMOCC (Large-Scale Biosphere Atmosphere Experiment in Amazonia - Smoke Aerosols, Clouds, Rainfall, and Climate: Aerosols From Biomass Burning Perturb Global and Regional Climate) which took place during the dry season of 2002, and MINOS (Mediterranean INTensive Oxidant Study), which took place during July and August 2001.

Thus, the results of Trebs et al. (2005) and Metzger et al. (2006) indicate that it is of crucial importance for the modeling of aerosol thermodynamics that at least major mineral cations and organic acids are consistently included. However, the new problem with ISORROPIA II is that the user has to be aware that the results may sometimes agree less well with observations even though the model has improved with respect to ISORROPIA. I therefore recommend to make this point as clear as possible, not only in the manuscript but also in the user manual that might be distributed with ISORROPIA II. Furthermore, I encourage the ISORROPIA II developers to further include at least major organic acids.

(2) The manuscript is mostly a technical description, as no new scientific results are presented. Therefore, I suggest to either present this work accordingly, i.e. by changing the title and introduction to include "Technical Note", or to add new scientific results, which would however require another iteration step in the review process.

(3) Furthermore, like most of the literature in this field, the manuscript is uncritical in applying laboratory measurements of activity coefficients - central in aerosol equilibrium thermodynamics - to atmospheric conditions. The implicit assumption is that the activ-

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ity coefficients, measured at a fixed water mass, are valid for conditions in which the water mass is variable, being a strong function of RH in the atmosphere (see Metzger and Lelieveld, 2007).

Considering the two main assumptions on which ISORROPIA (and ISORROPIA II) builds, i.e. (1) equilibrium and (2) that the water activity (a_w) equals the fractional relative humidity ($a_w = RH$; Eq. 15) - both assumptions already imply Eq. (16) - it is assumed that the equilibrium relative humidity (ERH) determines the saturation molality. This is well known and has been shown to be a sufficient approximation for many atmospheric conditions by various research groups. However, it is usually overlooked that these assumptions also determine both solvent and solute activities, thus including activity coefficients. Therefore, in the atmosphere aerosol activity coefficients are a function of ERH. I recommend adding a remark in the manuscript that this is a model limitation that should be addressed in future (also with respect to the computational performance).

Specific Comments

Abstract: please delete last sentence (the computational performance is not really satisfactory for large scale air quality and atmospheric transport model)

p1896, line 24-25: change sentence to: "EQSAM2 considers activity coefficients for (semi-) volatile compounds according to Metzger et al. (2002a) to solve the $NH_4^+/Na^+/NO_3^-/SO_4^{2-}/Cl^-/Ca^{2+}/Mg^{2+}/K^+/RCOO^-$ system; earlier versions were based on a simplified parameterization of the non-ideal solution properties that employed a relationship between activity coefficients and relative humidity (Metzger et al., 1999) and excluded mineral cations and organic acids".

p1896, p1896, line 25+: please add: "In comparison, EQSAM3 applies the thermodynamic principles as described in Metzger and Lelieveld (2007)."

Section 2: please clarify throughout all subsections that you follow the "classical" ap-

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proach.

Section 2.3: please mention alternative concepts (mentioned above) and clarify the restriction/problems with the "classical" methods.

References

Metzger, S. and J. Lelieveld, Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into haze and clouds, *Atmos. Chem. Phys., Discuss.*, <http://www.copernicus.org/EGU/acp/acpd/7/849/acpd-7-849.htm>, Vol.7, pp. 849-910, 2007.

Trebs, I., S. Metzger, F. X. Meixner, G. Helas, A. Hoffer, M. O. Andreae, M. A.L. Moura, R. S. da Silva (Jr.), J. Slanina, Y. Rudich, A. Falkovich, P. Artaxo, The NH_4^+ - NO_3 - Cl - SO_4^{2-} - H_2O system and its gas phase precursors at a rural site in the Amazon Basin: How relevant are crustal species and soluble organic compounds?, *J Geophys. Res.-Atmos.*, 110 (D07303), doi:10.1029/2004JD005478, <http://www.agu.org/journals/jd/jd0507/2004JD005478/>, 2005.

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