**Atmospheric Chemistry and Physics Discussions**

## *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

**C. Fountoukis and A. Nenes**

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Reply to reviewer #3

We thank the reviewer's thorough and thoughtful reviews.

General Comments: This paper presents an enhanced version of the equilibrium inorganic aerosol model ISORROPIA that explicitly includes the crustal cations K+, Ca2+ and Mg2+. The model is compared to SCAPE2 over a range of atmospherically relevant conditions. The paper describes an important advance in the modeling of atmospheric aerosols. I recommend the paper be published with minor revisions, addressed

below.

Specific Comments: The goal of this paper is to demonstrate the incorporation of atmospherically relevant crustal species (K+, Ca2+, Mg2+) into ISORROPIA. This is important for the reasons discussed in the paper. While the paper Ě not only against SCAPE2 but also against the 'old' version of ISORROPIA, where the crustal species are treated as equivalent sodium. This will answer the question of how much difference it makes to treat the crustal species explicitly versus as equivalent sodium.

Reply: This is a very important point. We have added the following comment to the manuscript to address this concern: "The consideration of crustal material in predicting the partitioning of nitrate and ammonium, especially in areas where dust comprises a significant portion of total PM, is of great importance and can considerably improve model predictions (Ansari and Pandis, 1999; Moya et al., 2002). It has been shown (Moya et al. 2002, San Martini et al. 2005) that treating crustal species as "equivalent" sodium may affect the predicted response of inorganic PM to changes in precursor concentrations." Assessing the importance of treating crustal species as equivalent sodium into the present manuscript would likely make it too lengthy. However, two manuscripts are in preparation which assess this assumption, one using measurements from the MILAGRO 2006 campaign in Mexico City, and another using CMAQ for simulating an air pollution episode in Atlanta GA.

I suggest that the authors acknowledge that double salt and hydrate species have not been incorporated into ISORROPIA-II. However, neglecting these species is not a major model weakness. Double salt and hydrate species Ě content, it is likely that for many atmospherically relevant conditions the effect of these species on model predictions will be small (San Martini, 2004; Wexler and Clegg, 2002).

Reply: A comment have been added in section 3.3 (assumptions) regarding double salts and hydrates. We thank the reviewer for pointing to the above references and we have included them in the manuscript.

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I particularly applaud the authors' focus on computational speed, a key requirement to integrating an equilibrium aerosol code into an air shed model. The authors have not mentioned an additional characteristic of ISORROPIA that makes its use particularly appealing: it is freely available via anonymous ftp. For a variety of reasons, other models are not as freely available. Making ISORROPIA so easily available is commendable.

Reply: We thank the reviewer for pointing this out.

1910/19-21: The authors may wish to consider not using the normalized mean error (NME) for their evaluation, as the use of NME may artificially weight overpredictions. Seigneur et al. (2000) recommend using average fractional bias and average fractional gross error.

Reply: Indeed, the average bias and/or gross error are a nice way of demonstrating over/under predictions. However, since we are not showing comparison with measurements, NME is considered sufficient in the sense of giving a qualitative idea of the discrepancy between the two models.

It would be useful if the authors provided information on the ionic strength of the aqueous aerosol, especially for low RH regimes. This may help provide context for the discrepancies the authors found between the models at low RH regimes (1911/11-12). The discussion of stable vs. metastable solutions (Section 4.3) would also benefit from including information on the predicted ionic strength.

Reply: Good point. A discussion about the ionic strength has been added in the revised version of the manuscript both in p.1911 and in section 4.3.

Technical Corrections: 1895/25-27: I suggest clarifying the sentence: The non-linearity is stronger under conditions of low relative humidity, where aqueous aerosol solutions are strongly non-ideal and require the use of Ě these conditions the solutions may behave non-ideally. This non-ideality is modeled with activity coefficients.

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Reply: We have changed that sentence based on the reviewer's comment for clarification.

1896/14 omit the word 'have'

Reply: Done

1897/12-17. Specify the outputs of the reverse problem.

Reply: Done The output of the reverse problem is (as in the forward problem) the concentration of species in solid, liquid and gas phase.

1897/27-29: The authors may want to consider additional references that have examined using equivalent sodium. For example, this reviewer knows of another study that found that including crustal species as sodium equivalents reduces the bias and error for nitrate but does not improve overall model performance (and may sometimes affect the predicted response of inorganic aerosol to changes in precursor concentrations).

Reply: We apologize for this oversight. Done.

1899/13 As written, gamma_i is actually the mean activity coefficient of species i. In order to be consistent with the notation in Section 2.3, I suggest you refer to electrolyte species as ij and hence activity is a_ij = ((m_i*gamma_i)Ĺnu_i)*((m_j*gamma_j)Ĺnu_j)

Reply: Corrected

1907/13: Is $CaSO_4$ assumed to be insoluble because it forms $CaSO_4.2H_2O$?

Reply: Yes, the solubility of which is very low (0.24g/100ml, 20žC).

1912/18-20: I do not understand your logic here. If SCAPE2 tries to solve for the aqueous case, hence deviating from the stable solution, should not the MNE be smaller when ISORROPIA II is run in the metastable branch?

Reply: Excellent point. There was a typo in the text created this misunderstanding, and we apologize for this. SCAPE2 tries to solve for the aqueous phase, however this

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is only at low RH ($<~40\%$). Above that, SCAPE2 follows the deliquescence branch behavior which is why the overall NME is smaller when ISORROPIA-II is run in the stable state. We have corrected that to avoid any misunderstanding.

1915/2: Should read whether.

Reply: Corrected

Figure 3 and 4. Either add units to ordinate and abscissa of all plots or specify in the figure caption that all concentrations are ug/m3.

Reply: Corrected

Figure 3f. and 4f: What does a plot comparing the pH predicted by SCAPE2 and ISORROPIA-II look like?

Reply: A plot with a pH comparison looks similar to fig. 3f and 4f. The discrepancy occurs at low RH as it scales with water content (and H+).

Figure 8: The figure makes it appear that the concentration of water and potassium goes briefly below zero just below 40% RH. This is just a function of the graphics program, but it would be nice to fix.

Reply: Corrected

Final Random Question: 1896/16-17. Is the following statement correct? "Even though direct minimization usually gives the most accurate results, it comes at a large computational cost (Ansari and Pandis, 1999b)." Thermodynamic equilibrium can be ... efficient (it walks through the entire solution space to find the minimum). AIM2 also uses a direct Gibbs free energy minimization. How does the computational efficiency of AIM2 compare with that of, for example, SCAPE2?

Reply: The reviewer is absolutely correct. One approach is mathematically equivalent to the other, and differences in computational time and accuracy are just from the numerical implementation of each. We have deleted our statement in p.1896/16-17 to

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avoid any misunderstanding.

References

Ansari, A.S., and Pandis, S.N.: Prediction of multicomponent inorganic atmospheric aerosol behavior, Atmos. Environ., 33, 745-757, 1999.

Moya, M., Pandis, S.N., and Jacobson, M.J.: Is the size distribution of urban aerosols determined by thermodynamic equilibrium? An application to Southern California, Atmos. Environ., 36, 2349-2365, 2002.

San Martini F.M., West J.J., de Foy B., Molina L.T., Molina M.J., Sosa G., McRae G.J.: Modeling inorganic aerosols and their response to changes in precursor concentration in Mexico City, Journal of the air & waste management association, 55 (6), 803-815, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 1893, 2007.

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