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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The effect of meteorological and chemical factors on the agreement between observations and predictions of fine aerosol composition in Southwestern Ontario during BAQS-Met" *by* M. Z. Markovic et al.

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Anonymous Referee 2 Received and published: 30 November 2010 This paper presents a thorough analysis of the ability of a model to predict fine particulate nitrate and the potential sources of errors in the agreement with high time resolution measurements both from ground and aloft. The use of high time resolution measurements is essential for a study like that. The authors should be complimented for including

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airborne data in their analysis in addition to ground data. It is well known that nitrate is the hardest to predict for a number of reasons and thus this work should also be complimented for looking at this issue in such a comprehensive way. The paper deserves publication, after the following points are addressed by the authors.

1) The literature review on thermodynamic equilibrium modeling is poor. Since all the discussion and conclusions are partly dependent on the thermo model used, a more thorough literature review on this part is necessary. P24785, lines11-28. The papers cited here are referred to rather older models than recent ones (as stated in line 13). In addition to what you have referenced, please give references for more recent developments (e.g. SCAPE2, AIM2, ISORROPIA2, EQUISOLV2, and others (e.g. GFEMN, UHAERO, MESA etc.). Also, although you spend some lines to explain why ISORROPIA is your model of choice for this study, you should also add some lines referring to the previous successful applications of this model, its evaluation compared to other models/measurements and its use in similar studies. E.g. I suggest you consider referring to studies such as:

Karydis, V. A., Tsimpidi, A. P., Fountoukis, C., Nenes A., Zavala, M., Lei, W., Molina, L. T., and Pandis, S. N.: Simulating the fine and coarse inorganic particulate matter concentrations in a polluted megacity, Atmos. Environ., 44, 608-620, 2010.

Fountoukis, C., Nenes, A., Sullivan, A.,Weber, R., VanReken, T., Fischer, M., Matias, E., Moya, M., Farmer, D., Cohen, R., 2009. Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006. Atmospheric Chemistry and Physics 9, 2141-2156.

Hennigan, C. J., Sullivan, A. P., Fountoukis, C. I., Nenes, A., Hecobian, A., Vargas, O.,Case, A. T., Hanks, L., Huey, G., Lefer, B. L., and Weber, R. J.: On the Volatility and Production Mechanisms of Newly Formed Nitrate and Water Soluble Organic Aerosol in Mexico City, Atmos. Chem. Phys., 8, 3761–3768, 2008.

Nowak, J. B., Huey, L. G., Russell, A. G., Tian, D., Neuman, J. A., Orsini, D., Sjostedt, S.

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J., Sullivan, A. P., Tanner, D. J., Weber, R. J., Nenes, A., Edgerton, E., and Fehsenfeld, F. C.: Analysis of urban gas phase ammonia measurements from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE), J. Geophys. Res., 111, D17308, doi:10.1029/2006JD007113, 2006.

San Martini, F. M., Dunlea, E. J., Volkamer, R., Onasch, T. B., Jayne, J. T., Canagaratna, M. R., Worsnop, D. R., Kolb, C. E., Shorter, J. H., Herndon, S. C., Zahniser, M. S., Salcedo, D., Dzepina, K., Jimenez, J. L., Ortega, J. M., Johnson, K. S., McRae, G. J., Molina, L. T., and Molina M. J.: Implementation of a Markov Chain Monte Carlo method to inorganic aerosol modeling of observations from the MCMA-2003 campaign – Part II: Model application to the CENICA, Pedregal and Santa Ana sites, Atmos. Chem. Phys., 6, 4889–4904, 2006.

Yu, S., Dennis, R., Roselle, S., Nenes, A., Walker, J., Eder, B., Schere, K., Swall, J., and Robarge, W.: An assessment of the ability of three-dimensional air quality models with current thermodynamic equilibrium models to predict aerosol NO−3 , J. Geophys. Res., 110, D07S13, doi:10.1029/2004JD004718, 2005.

Zhang, J., Chameides, W. L., Weber, R., Cass, G., Orsini, D., Edgerton, E. S., Jongejan, P., and Slanina, J.: An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during the 1999 Atlanta Supersite Experiment, J. Geophys. Res., 107, 8414, doi:10.1029/2001JD001592, 2003.

The authors expanded this section to allow for more thorough review of thermodynamic partitioning models including previous studies that compared ISORROPIA to other models and observations. The authors also included the suggested references.

P24791, line9: Since ISORROPIAv2.1 is used here, the appropriate reference is missing (Fountoukis and Nenes, 2007). Fountoukis, C., and Nenes, A.: ISORROPIA II: A computationally efficient thermodynamic equilibrium model for K+-Ca2+-Mg2+-NH+4 -Na+-SO2−4 -NO−3 -Cl−-H2O aerosols, Atmos. Chem. Phys., 7, 4639–4659, 2007.

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The authors inserted the suggested reference.

2) p24791, lines 6-7. I do not agree with this. More details about the large scale model are needed here. The reader should not be forced to go to another paper. At least some critical aspects of the model need to be described, because possible reasons for the discrepancies between predictions and measurements could include problems in the large scale model.

The authors added several sentences on emission inventories, chemical and physical mechanisms in the model framework, and size bins in the model output.

3) Statistics. The statistical analysis (Tables 1 and 2) is incomplete. In addition to the mean bias, the mean error should also be calculated. Also, you might want to consider adding the normalized mean bias and normalized mean error.

The authors updated Tables 1 and 2 to include the following statistical parameters: mean error (ME), normalized mean error (NME), and normalized mean bias (NMB)

4) p24793, lines 2-13. The conclusions drawn here are not easily seen in Figure 3. In addition to Figs.3a, b, c, I strongly suggest the addition of 3 more Figures showing the average vertical concentration distribution for 500 altitude bins, from both modeled and measured values, with a standard deviation for each average value. In this way, the reader can easily check how the model performs compared to the measurements for each species in a clearer way.

The authors added 3 more graphs showing binned (500m), averaged ($\pm$ stdev) vertical profiles for both measured and modelled sulphate, ammonium and nitrate mass loadings to the existing 3 panels in Fig. 3.

5) p24794, lines 10-22. The authors conclude here that point emissions such as plumes are not the main reason for the disagreement between model and measured values. What about the area emissions? Has the emission inventory been evaluated?

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If yes, could you give the appropriate reference(s)?

It wasn't our intention in the analysis in section 3.1.3 to suggest that the magnitude of the emissions is well represented in the model, but rather that the representation of the spatial distribution of pollutants was not responsible for large model/measurement discrepancy. The major point sources in the model domain emissions were corrected using CEMS data but the quality of the mobile and area source emissions are not well known. In fact, our paper indicates that regional NHx emissions are likely underestimated, consistent with the analysis by Ellis et al 2011.

6) p24796, Fig5b. Have the authors tried running the thermo model assuming the formation of solid and liquid instead of only aqueous phase? Does the agreement in Fig.5b get any better, at least for specific RH ranges?

The authors have tried re-partitioning modeled and observed data with the "metastable state" option off which allows ISORROPIA to predict the formation of crystalline solids in addition to aqueous particles. In general, including the formation of solids did not improve the prediction of nitrate mass loadings over the range of meteorological conditions. Because there was no improved agreement between observations and repartitioned AURAMS predictions with the option off, we did not include this analysis in the manuscript.

Minor/Technical corrections -Abstract, line 22. Shouldn't be 2 x SO4-

We believe what referee meant to say was that there should be " 2 x" in front of SO42- in Abstract. Line 22. The authors agreed with this suggestion and they corrected the sentence to include " 2 x" in front of SO42- . The authors also added (g) and p to specify the phases of the chemical species in the equation and also to keep it consistent with the notation used in the remainder of the manuscript. In conclusion " FA $\equiv$ NH3 + NH4+ – SO42- " was changed to "FA $\equiv$ NH3(g) + pNH4+ – 2 * pSO42-".

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-Please increase all fonts in Fig.7.

The authors increased all fonts in Fig. 7

-p24799, lines1-3. This sentence does not make sense.

The authors updated Fig. 6 to include the S-shaped transition curve, and also labelled the two pNO3 regimes in order to clarify the regions of the map they referred to in the text.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 24781, 2010.