Atmos. Chem. Phys. Discuss., 7, S9993–S9997, 2009
www.atmos-chem-phys-discuss.net/7/S9993/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Predicting diurnal variability of fine inorganic aerosols and their gas-phase precursors near downtown Mexico City" *by* M. Moya et al.

M. Moya et al.

Received and published: 4 February 2009

Reply to Reviewer #2

We thank the reviewer's comments on the manuscript.

General comments

The authors have predicted the diurnal variability of fine inorganic particulate matter and gas-phase species near downtown Mexico City using two equilibrium models SCAPE2 and ISORROPIA II. They report no significant overall difference between the predictions of the two models. Although they do not explicitly state that the bulk equilibrium assumption is adequate for the Mexico City aerosols,

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this seems to be the basis of the analysis, despite large differences between the predicted and observed concentrations of semi-volatile species in the gas and particulate phases. The conclusions are therefore rather weak and very similar to the ones reported in the study of Fountoukis et al (2007) who have applied the same models to aerosols observed at the T1 site. I would recommend publication only if the authors can clearly address the specific concerns listed below:

Regarding similarities and differences between the current work and that of Fountoukis et al. (2007), we would like to clarify the following: i) The focus of the current work is to analyze the diurnal variability of the partitioning between the gas and aerosol phase for both PM2.5 and PM1 measurements while in Fountoukis et al. (2007) the focus was largely on the timescale for equilibrium and its dependence on changes in RH, T and aerosol precursor concentrations. ii) The sampling sites for the two studies are different, with substantially different mixing states; the time period is quite different as well (winter in this study vs. Spring in Fountoukis et al.). iii) In the current work we utilize two thermodynamic models (ISORROPIA-II and SCAPE2) while in Fountoukis et al. (2007) the focus is on the predictions of ISORROPIA-II only. iv) Similar conclusions were drawn for the treatment of crustal species and the deliquescence vs. efflorescence predictions of the models.

Specific comments

1. According to the statistics given in Tables 3 through 10, there are rather large differences between the model predictions and observations for gas and particulate phase nitrate and ammonium. Why then are the aerosols still assumed to be in equilibrium with the gas phase? Based on these results, one would conclude that the aerosols are not in equilibrium.

As analyzed in paragraph 4.2 and can be seen from Tables 3-10, for the first and second sampling periods, particulate PM1 and PM2.5 ammonium as well as PM2.5 nitrate

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are predicted within 20-40% of error, which is of the order of the experimental uncertainty. Furthermore, gas phase ammonia is predicted within <15% of error. These results are definitely not discouraging and very similar to previous similar studies in Mexico City (San Martini et al., 2006a,b; Moya et al., 2001). Larger differences have identified in subsets of the data and triggered a discussion about the possible errors (paragraphs 4.2, 4.3, 4.4). In addition to that, we have added more references to previous similar studies and more discussion about the discrepancies between the model and observations in the revised version of the manuscript.

2. Are these large differences in the predicted and observed concentrations due to the use of 4-hour average data? How much variation might be expected over this period, given that the measurement site is located in a highly dynamic source region?

According to the reviewer suggestion, text has been added (paragraph 4.2) on the possible errors from the highly variable environment of downtown Mexico City combined with the 4-hour averaging of data.

3. Is the bulk equilibrium assumption for PM1 and PM2.5 particles even valid, since large differences are expected in the composition of the particles of different sizes? For instance, particles smaller than 0.1 um may reach equilibrium in a few minutes, but larger particles, especially greater than 1 um may take several hours to reach equilibrium.

This is one of the questions we are trying to answer with this study. By carefully looking at the results of this analysis, it seems that during the first sampling period (when RH varied a lot, 39-72%) and the third one when RH < 30% the errors tend to increase significantly prohibiting an accurate prediction of the partitioning between the gas and aerosol phase. This is now more explicitly clarified in the revised manuscript.

4. Can ISORROPIA II and/or SCAPE2 reliably simulate the deliquescence and growth of complex aerosols at low and moderate RH? It is well known that these

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models have significant errors in the equilibrium phase-state, water content, and composition of aerosol particles in the mixed-phase region that is often encountered at moderate relative humidities.

We thank the reviewer for raising such an important issue, which is further discussed now in Section 4:

"The two branches express the upper and lower limit of water uptake for all RH. In reality, the aerosol will lie somewhere between these two states, henceforth it is useful to examine the errors associated with their application.

As stated in paragraph 4.2, the use of the efflorescence branch in the modeling framework improves predictions by 20-50%. Although this is encouraging, even the efflorescence branch implies errors when RH is extremely low. These errors are probably the result of different issues such as the presence of WSOC influencing the partitioning of inorganics (not considered in the thermodynamic calculations) or high uncertainty related to long integration time of our measurements (4 h) which might influence the equilibration state and aerosol composition calculations. A further discussion has been added in the revised manuscript."

The issue on application of a thermodynamic model with a simplified phase diagram has been already discussed (following reviewers suggestions) by Fountoukis et al., Atmos. Chem. Phys. 7, 9203-9233, 2007 and we refer to those responses included in the final revised manuscript.

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