

Interactive comment on “Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006” by C. Fountoukis et al.

Anonymous Referee #3

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General comments

Fountoukis et al. compare predictions of the ISORROPIA-II equilibrium aerosol model with measurements from the MILAGRO 2006 campaign. The goals of the study are to test the assumption of aerosol-gas equilibrium, gain insight on deliquescence versus efflorescence behavior, and assess the importance of crustal elements in the aerosol formulation. These topics would be of interest to those involved in the MILAGRO campaign as well as ISORROPIA users and general readers. However, I am not fully convinced of the study's conclusions on aerosol-gas equilibrium or deliquescence/efflorescence. If the comments below are addressed, I would recommend publication.

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Specific comments

I. Comment on Bulk Equilibrium Approach:

A limitation of the study that is not discussed is the use of a bulk equilibrium approach, which assumes that all particles have the same composition. This approach may not adequately reflect the atmosphere, where particles of similar size often have distinct compositions. Also, smaller particles tend to be more acidic than larger ones, and grouping the components of all particles into a bulk mixture could introduce error into partitioning calculations. For instance, sulfate may exist in a highly soluble form in sub-micron particles, but could exist in a nearly insoluble form if mixed with calcium present in larger particles. Lumping sub- and super-micron particles into a single mixture could therefore compromise particle water content and vapor pressure calculations. Such limitations have been recognized previously: e.g., Ansari and Pandis (2000; *Atm. Environ.*, 34:157-168) attributed the major cause of nitrate underprediction to the bulk equilibrium approach. Can the authors estimate the error in overall partitioning associated with the bulk equilibrium assumption [e.g., by comparing bulk and size-resolved approaches using data from the impactor measurements mentioned on p. 9208]?

II. Comments on Evaluating if Gas and Aerosol are in Equilibrium:

(1) Time Scale. To support the case for gas-aerosol equilibrium, the authors state on p. 9213 that the time scale for equilibration should be about 10 min. However, previous work shows wide variations in time scales depending on particle size and accommodation coefficient, and the current study does not provide adequate support for a ~10-min time scale. Since the PILS was configured to measure $PM_{2.5}$, ions from largest (~2.5 micron) particles may dominate contributions from smaller particles. In this case, an effective diameter of the sample could be > 1 micron, and the time scale for equilibration could be much longer than 10 min. Conversely, an effective diameter for the sample could be < 1 micron and time scales short if the soluble components were primarily in the submicron size range (since PILS only measures soluble components). Using the impactor measurements mentioned on p. 9208, can the authors estimate an effective

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(e.g., soluble-mass weighted) diameter for the samples to support the expectation of a ~ 10 min time scale?

(2) Bias $CF=0/CF=1$. Central to the argument for gas-aerosol equilibrium is the lower prediction bias for the 20-min ($CF=1$) average PLS measurements than the 6-min ($CF=0$) average. I am a bit confused on the details in this area of the discussion. Does the $CF=1$ case refer to two 6-min averages with a 10-min interlude or to a 20-min average [this should be made clear on p. 9211 and in Table 2]? Also, how many 6-min samples and what intermission are associated with the 35-min ($CF=0$) average? I am not fully convinced that the lower bias for the 20-min average necessarily means that gas-particle equilibration occurs at this time scale. The 35-min ($CF=0$) average has similar bias to the 6-min ($CF=0$) average and could suggest that the differences between the 6-min and 20-min average bias result from differences inherent in the $CF=0$ and $CF=1$ cases, rather than differences in averaging time. For instance, details on p. 9208 suggest that there is a different degree of coincidence between HNO_3 and PLS data for $CF=0$ and $CF=1$ cases. Did the $CF=0/CF=1$ cases correspond to similar atmospheric conditions (e.g., time of day, RH, etc.)?

III. Comments on Deliquescence/Efflorescence:

(1) Water Activity. The authors state that the wide range of RH (19–94%) makes it possible to assess the preferred phase transition path (deliquescence or efflorescence) for the Mexico City aerosol. Actually, the low RH reached during the study complicates an evaluation of the phase transition path. A number of the water activity-molality polynomials used in ISORROPIA-II were developed by fitting electro-dynamic balance measurements at > 30 %RH and are not valid for the lower RHs of this study. Inaccuracies in water content associated with water-activity extrapolation could compromise predictions along the supersaturated pathway. Such errors would bias the deliquescence vs. supersaturation comparison in favor of deliquescence for the low-RH samples.

(2) Unstable Solutions/Pure-Solution Efflorescence. The low RHs of the study period could make the treatment of particles as metastable solutions unrealistic for some con-

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ditions, because the solutions could become unstable if sufficiently concentrated. For instance, Chan and Ha (1999; JGR, 104:30193-30200) estimate that a binary NH_4Cl solution will become unstable at $\text{RH}=34\%$. Also, efflorescence of some pure solutions has been observed at RHs significantly above the lower limit of this study [e.g., Martin et al. (2001) reported that efflorescence is rapid at 35 %RH for aqueous $(\text{NH}_4)_2\text{SO}_4$ solutions]. Therefore modeling the Mexico City particles as supersaturated solutions may be unrealistic for the low-RH samples and could bias the deliquescence vs. supersaturation comparison in favor of deliquescence.

(3) Heterogeneous Nucleation. Laboratory measurements [e.g., Martin et al. 2001, GRL 28 (13): 2601-2604] indicate that trace mineral components in particles can induce efflorescence at RHs between those of deliquescence and homogeneous nucleation. Therefore solid phases in the Mexico City aerosol may have enabled efflorescence at RHs significantly greater than 19%. Since solid-phase CaSO_4 is predicted by ISORROPIA-II, the existence of CaSO_4 could be used in estimating such efflorescence values. The existence of other possible insoluble nuclei could also be roughly verified from the MOUDI or single-particle measurements. Even if the authors do not attempt to predict efflorescence, evidence of insoluble mineral components would suggest that treating particles as solutions on the supersaturation pathway is unrealistic for the low-RH samples and could bias the deliquescence vs. supersaturation comparison in favor of deliquescence.

(4) Given that ISORROPIA-II does not calculate efflorescence and the solutions could be unstable, the terms “efflorescence” and “metastable” should be changed to something like “non-equilibrium solution.”

IV. Comment on Figure 2:

A possibly clearer way to organize Figure 2 is to show observed total concentrations (e.g., Total Ammonia/Ammonium; TA) on the horizontal axis and normalized predicted and observed species concentrations (e.g., NH_3/TA) on the vertical. The vertical axis ranges from 0-1 in this approach and symbols are used for observations and predic-

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tions. The 0-1 vertical scale may better illustrate the fraction of mass that resides in the gas and aerosol phases. Also, this approach highlights that the study attempts to partition known total quantities between the gas and aerosol. In their current form, the figures may mislead a casual reader into thinking that species' predictions were made as in air quality models, where both total concentration and partitioning must be predicted.

Technical Corrections

–Abstract: Please change “are” to “is” on line 14

–p. 9205, line 1. NH_3 , HNO_3 , etc. would volatilize, not the ions

–p. 9206, line 19. The Nowak reference does not appear in the reference list.

–p. 9206, line 25-26. The definition of the efflorescence branch is incorrect, since efflorescence refers to crystallization.

–p. 9206, line 28. Please insert “a” before “particle”

–p. 9207, line 1. “effluorescent” is misspelled

–p. 9207, line 23. Are all inorganic species in significant concentrations? On p. 9209, concentrations of crustal elements are given as within 1 standard error of zero.

–p. 9208, line 7. If HCl was measured, then why is it assumed to have zero concentration in the model?

–p. 9208, line 25. “were” should be “was”

–p. 9210, line 15. Ionic charges are indicated with superscripts in some places in the manuscript, but not in others. Please be consistent throughout.

–p. 9212, line 10 p. 9213 line 24. Do you mean “> $\text{PM}_{2.5}$ ” rather than “ PM_{10} - $\text{PM}_{2.5}$ ”?

–p. 9214, line 3. The writing here appears to state that salts do not precipitate in particles when $\text{RH} > 60\%$ and that an RH of 60% is somehow special in general. Please clarify.

–p. 9214, lines 10-14. The parenthetical statement is confusing. Even if the MDRH is $< 50\%$, solid phase NH_4NO_3 may still exist in equilibrium with the solution at RH s somewhat above 50% , and the reaction on line 14 will hold until all NH_4NO_3 has dis-

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solved.

–p. 9215-6. Use of the term “aerosol precursor” seems non-standard. For example, aren’t crustal elements usually considered as primary aerosol components rather than precursors?

–p. 9216, line 20. Should this be “Fig. 4” rather than “Fig. 3”?

–p. 9217, line 20. Why is nitrate considered non-volatile in these salts? Wouldn’t a reaction such as $\text{H}_2\text{SO}_4(\text{g}) + \text{Ca}(\text{NO}_3)_2 \rightarrow \text{CaSO}_4 + 2\text{HNO}_3(\text{g})$ be preferred for some conditions?

–p. 9218, conclusion 1. Please indicate that this conclusion refers to fine particles.

–p. 9218, conclusion 2. I am not convinced that this conclusion can be drawn so definitively. Also, please mention that the time scale refers to $\text{PM}_{2.5}$.

–p. 9219, conclusion 3. Do you mean $> \text{PM}_{2.5}$, rather than between $\text{PM}_{2.5}$ and PM_{10} ? Do the impactor measurements confirm the estimate of 30% of nitrate in coarse particles?

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9203, 2007.

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