Atmos. Chem. Phys. Discuss., 7, S8526–S8537, 2008
www.atmos-chem-phys-discuss.net/7/S8526/2008/

Atmospheric
Chemistry
and Physics
Discussions

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

C. Fountoukis et al.

Received and published: 19 January 2008

We thank the reviewer's thorough and thoughtful review.

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.***

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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 submicron 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]?

We do not dispute that the assumption of bulk equilibrium in general can lead to large prediction errors. We do show however that it is a good assumption for submicron Mexico City aerosol (i.e. to with 20% of measured concentrations), and suggest this happens primarily for the following reasons:

- Mexico City is unusually ammonia-rich. Most of NH_3 resides in the gas phase even after equilibration – hence particle acidity is not expected to vary substantially with size.
- Nitrate is not systematically underpredicted, which further supports that acidity

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

does not vary substantially between submicron particles.

- Aerosol at T1 is generally aged and its aerosol heterogeneity is expected to be much less, when compared to aerosol collected from downtown (T0).
- Most of the submicron aerosol mass is found in the 100-500 nm range (Salcedo et al., 2006), hence bulk equilibrium can be used for those particles.
- High-dust periods vs. low-dust periods do not exhibit substantial differences in prediction skill. If indeed the sulfate were inappropriately attributed to salts, or too much nitrate partitions to the coarse mode aerosol (which is not considered in this study) one would expect much larger deviations in water uptake and semivolatile partitioning.
- High-resolution measurements of nitrate (Hennigan et al., in review) indicates that our assessment of submicron aerosol equilibration timescale is appropriate.

These points have been added to the text.

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 PM2.5, 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 (e.g., soluble-mass weighted) diameter for the samples to support the expectation of a ˜10 min time scale?

Of course, each particle size, particle type and species has its own equilibration timescale. What we are determining (and feel is quite clear in the text) is the average timescale for the semivolatile inorganic aerosol mass, which is primarily governed by the ammonium- nitrate equilibration. We did not say that the equilibration timescale *is* 10 min, but of *order* 10 min (ranging between 6 and 20). In fact, the error metric used to assess this timescale becomes minimum somewhere between 6 and 30 minutes, so we have expanded our assessment to this range. The strongest observational support that our assessment is realistic is in the high resolution measurements of nitrate by Hennigan et al., (in review), which shows that measured nitrate lags about 30-60 minutes with respect to predictions based on bulk equilibrium. This temporal lag is in agreement with our thermodynamic calculations, as excess nitrate requires roughly the equilibration timescale to repartition onto the gas phase. Finally, AMS measurements in Mexico City (Salcedo et al., 2006) suggests that most of the submicron aerosol mass peaks at around the 0.1-0.5 μm size range, which is consistent with $\sim$ 30 min timescales.

The “impactor measurements” mentioned on p. 9208 are in fact filter-based measurements of PM2.5, so estimating the effective diameter is not possible. We apologize for this oversight.

All the above has been included in the revised version of the manuscript.

(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 PILS 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 HNO3 and PILS 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.)?

The CF=1 case refers to two 6-min averages with a 10-min interval while the 35-min averages represent an average of three 6-min samples with two 10-min intervals. This has now been made clear in the manuscript. We apologize for the confusion that this may have caused; these issues are clarified in the manuscript.

Although the CF=0/CF=1 may be influenced by factors other than the averaging time, it still remains an indication that the lower bias for the 20-min average is likely correlated with the equilibration time scale. We do chose not to compare CF=0 (with 6-min averages) and CF=0 with 20-min since in the latter, only one of the two 6-min samples would coincide with/correspond to the 5-min average of $HNO_{3(g)}$ data and possibly introduce a correlation bias.

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.

Good point. This applies to any aerosol model, as they all rely on the similar polynomials (for either predicting water uptake or constraining activity coefficient models). Fortunately, most of the datapoints in our study are for an ambient RH above 30%. Repeating the exercise neglecting datapoints for which RH < 30% yielded no discernable difference in the performance metrics.

A short comment on the above has been added to the manuscript.

(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 conditions, because the solutions could become unstable if sufficiently concentrated. For instance, Chan and Ha (1999; JGR, 104:30193-30200) estimate that a binary NH4Cl solution will become unstable at 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 (NH4)2SO4 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.

We are not in disagreement; quantifying the prediction skill for both metastable and stable paths was done to address this exact issue. With this said, the aerosol in Mexico City is far from being single-component or binary salt mixtures. It is well known that more components can drastically reduce the deliquescence point, especially when organic acids (which comprises a large fraction of Mexico City aerosol) are present (Marcolli et al., 2004). This means that the supersaturation level in metastable aerosol would be reduced and thermodynamically stable water could exist at very low RHs, certainly within the 10% of the crystallization RH (34%) mentioned in the single-component and binary salt laboratory studies. Unfortunately, we did not have in-situ measurements of particle phase state to corroborate our results; and now clearly state that the model *suggests* the semi-volatile inorganic partitioning is mostly consistent with a metastable state.

A comment about this has been added to the paper.

As a side note, acidic solutions can contain water at extremely low RH's, so the comment refers to the neutral aerosol typically found in Mexico City.

(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 CaSO4 is predicted by ISORROPIA-II, the existence of CaSO4 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.

The existence of metastable aerosol for low RH may seem at first surprising. If substantial amounts of predicted solid CaSO4 is used as a proxy for crustal influence (excellent suggestion, thank you!), only 25% of the points for which $SO_4/NO_3 > 1$ are influenced; 48% of the data are influenced when $SO_4/NO_3<1$. This suggests that crustals may indeed influence the phase state of aerosol, although organic compounds (not considered by ISORROPIA-II) can form eutectic mixtures that contain thermodynamically stable water down to very low relative RH, thus giving the “appearance” of a metastable state (Marcolli et al., 2004). Unfortunately, there were no in-situ measurements of particle phase state or size-resolved compositional data available with the time resolution required to further support our results, although the model suggests the semi-volatile inorganic partitioning is mostly consistent with a metastable state whenever dust is not present in significant amounts.

This has been added to the text.

(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.”

The term “efflorescence” has been changed by the term “metastable” throughout the manuscript and define in the beginning the term. We feel that using a more descriptive term “potentially metastable” or “non-equilibrium” is cumbersome.

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., NH3/TA) on the vertical. The vertical axis ranges from 0-1 in this approach and symbols are used for observations and predictions. The 0-1 vertical scale may better illustrate the fraction of mass that resides in the gas and aerosol phases.

Although what the reviewer suggests is in general an excellent way of illustrating predictions versus observations, all the data would aggregate around a point (as most of the ammonia resides in the gas phase) which makes such a figure less informative. The same applies for nitrate which resides in large fraction in the aerosol phase.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

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.

We clearly describe throughout the text what is known and the analysis followed, so we feel that misinterpretation by a casual (but careful) reader is unlikely.

Technical Corrections

–Abstract: Please change "are" to "is" on line 14

Done

–p. 9205, line 1. NH3, HNO3, etc. would volatilize, not the ions

Corrected

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

Corrected

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

Changed to "metastable".

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

Done

–p. 9207, line 1. "effluorescent" is misspelled

Corrected

–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.

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

What is meant by this statement is that Mexico City is considered a dust-rich environment.

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

Gas-phase HCl measurements were not available.

–p. 9208, line 25. "were" should be "was"

Corrected.

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

Done.

–p. 9212, line 10 p. 9213 line 24. Do you mean "> PM2.5" rather than "PM10-PM2.5"?

Yes. Manuscript now corrected.

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

Changed to: ". . . . for RH <60%, where crystallization may occur."

–p. 9214, lines 10-14. The parenthetical statement is confusing. Even if the MDRH is < 50%, solid phase NH4NO3 may still exist in equilibrium with the solution at RHs somewhat above 50%, and the reaction on line 14 will hold until all NH4NO3 has dissolved.

Agreed. Statement delete.

–p. 9215-6. Use of the term "aerosol precursor" seems non-standard. For example, aren't crustal elements usually considered as primary aerosol components

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

rather than precursors?

This is a matter of semantics. We feel the text is quite understandable as is; no changes made.

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

Corrected.

–p. 9217, line 20. Why is nitrate considered non-volatile in these salts? Wouldn't a reaction such as H2SO4(g) + Ca(NO3)2 ! CaSO4 + 2HNO3(g) be preferred for some conditions?

Yes, and that is why ISORROPIA-II first neutralizes $CaCO_3$ with H_2SO_4 before any reacts with HNO_3.

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

Done.

–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 PM2.5.

Changed to: Our simulations suggest that the equilibration timescale ranges between 6 and 30 min.

–p. 9219, conclusion 3. Do you mean > PM2.5, rather than between PM2.5 and PM10? Do the impactor measurements confirm the estimate of 30% of nitrate in coarse particles?

Indeed. Text is now corrected. Unfortunately, compositional data for sizes larger than PM2.5 were not available to confirm the estimated partitioning.

References

Marcolli, C., Luo, B., and Peter, T., Mixing of the Organic Aerosol Fractions: Liquids as

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

the Thermodynamically Stable Phases, J. Phys. Chem. A, 108, 2216-2224, 2004.

Hennigan, C., Sullivan, A.P., Fountoukis, C.I., Nenes, A., Hecobian, A., Vargas, O., Case Hanks, A.T., Huey, L.G., Lefer, B.L., Russell, A.G., 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. Discuss., ACPD-2008-0036.

Salcedo, D., Onasch, T.B., Dzepina, K., Canagaratna, M.R., Zhang, Q., Huffman, J.A., DeCarlo, P.F., Jayne, J.T., Mortimer, P., Worsnop, D.R., Kolb, C.E., Johnson, K.S., Zuberi, B., Marr, L.C., Volkamer, R., Molina, L.T., Molina, M.J., Cardenas, B., Bernabe, R.M., Marquez, C., Gaffney, J.S., Marley, N.A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Lesher, R., Shirley, T., and Jimenez, J.L., Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, Atmos. Chem. Phys., 6, 925–946, 2006.

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