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

C. Fountoukis et al.

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We thank the reviewer for raising important issues; they have now been addressed in the revised manuscript.

Reviewer's comments

The authors have applied the bulk equilibrium model ISORROPIA II to Mexico City aerosols sampled at the T1 site to examine the gas-particle partitioning of semi-volatile inorganic species, deliquescence behavior, and the particle phase state. They conclude that the bulk equilibrium assumption is appropriate for the complex Mexico City aerosols, with the equilibration time scales ranging between 6 and 20 min. They also infer from their model analysis that Mexico City aerosols prefer the stable state when particulate SO4/NO3 < 1 and the metastable

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state when SO4/NO3 > 1. Another major conclusion they draw from their analysis is that crustal species (Ca, Mg, K) must be explicitly treated in models for accurately predicting gas-aerosol partitioning and phase state. While some of these conclusions may or may not be correct, I question the entire approach used to arrive at them. I recommend that this manuscript be rejected due to specific issues listed below.

Specific comments

First of all, I would like to echo all the specific comments and concerns raised by Referee #3. I completely agree with each and every one of them.

All the comments raised by referee #3 have been addressed.

My specific concerns are as follows:

1. Line 10, page 9205, the authors state "An important question regarding the partitioning of semi-volatile inorganic aerosol phase is whether the assumption of thermodynamic equilibrium is adequate to predict chemical composition."

In my opinion the assumption of [bulk] thermodynamic equilibrium is not adequate to predict chemical composition. The approach adopted in this study (and several other similar studies in the past) is at odds with the conclusions from a number of studies that have used dynamic models to simulate partitioning of semi-volatile inorganic gases to size- and composition-resolved aerosols. While the authors cite some of these studies here, they simply proceed further to test the bulk equilibrium assumption anyway. It is now pretty clear that a dynamic mass transfer treatment is needed for simulating size-resolved aerosol composition, especially when significant compositional differences exist between different sized particles. Therefore any attempt to test the bulk equilibrium assumption, especially for complex aerosol such as found in Mexico City, is a meaningless exercise. However, if the authors still wish to examine the equilibrium as-

sumption, then they must at least solve the “size-resolved equilibrium” problem instead of the "bulk equilibrium" problem (e.g., see Jacobson, M. Z., Studying the effects of calcium and magnesium on size-distributed nitrate and ammonium with EQUISOLV II, Atmos. Environ., 33, 3635- 3649, 1999).

The issue on whether the equilibrium assumption can be used in this study was already raised by reviewer #3, and we refer to those responses. Furthermore, we add that:

- The substantial and important work on the usage of bulk equilibrium are far from being “meaningless excercises”. For example, Ansari and Pandis (1999, 2000), Moya et al. (2001), Zhang et al. (2003), Takahama et al. (2004), San Martini et al. (2005), Yu et al. (2005), and Nowak et al., (2006) (and these are only a few of the studies available) used bulk thermodynamic equilibrium models to predict chemical composition and phase state of aerosols quite successfully (note that Mexico City aerosol is examined in a few of the references, while Atlanta aerosol is examined by Nowak et al.).

- The aerosol in our study focuses on aged submicron aerosol composition in an ammonia-rich environment; more than 70% of the time, the aerosol is regional (i.e. well aged), and when it does come from Mexico City, it’s been aged for roughly one day. This is far from being the highly externally-mixed aerosol characteristic of downtown Mexico City (the so-called T0) site. Bulk equilibrium can be a simple and quite effective approach towards understanding the semi-volatile partitioning. The rather good agreement between model predictions and observations is a testament to that.

- Given that there are no size-resolved data available with a temporal resolution of minutes, applying a size-resolved analysis would require numerous assumptions that would introduce rather important uncertainties.

- There are many approaches for interpreting data, and simple ones (like done in this study) often give very useful information.

2. The second issue with this study is the use of an approximate thermodynamic model to examine the phase state of complex aerosols. While ISORROPIA has been widely applied and used in a number of 3-D models, the fact still remains that it is an approximate model which cannot accurately simulate multicomponent deliquescence and phase transitions in complex aerosol particles. This is because, ISORROPIA does not explicitly solve the solid-liquid phase equilibria, but rather simply tries to approximate it using an ad-hoc approach. This can introduce significant errors in the equilibrium phase-state, water content, and composition of aerosol particles.

Any thermodynamic model is approximate, as it cannot account for all the complexities found in ambient aerosol. Even a perfect solver for the inorganic thermodynamic problem still does not account for the (unresolved) effects of organics species (which we all know how important they can be!). That is why it is so important to evaluate thermodynamic modules against ambient data whenever they possible. In that sense, ISORROPIA and ISORROPIA-II (despite their well documented approximations) performs quite well when tested against ambient observations. The good agreement between model predictions and observations in this study is one characteristic example but not the only one (e.g., Nowak et al., 2007). Over the years, the code has been thoroughly tested against more comprehensive models. For example, Yu et al. (2006) used a large ambient dataset to assess the prediction skill of ISORROPIA against AIM and both were comparable.

To illustrate this point, I show below a comparison of aqueous-phase concentrations of various ions predicted by ISORROPIA and AIM2 as a function of RH for a relatively simple aerosol particle composed of: SO4 = 1 μmole/m3, NO3 = 1 μmole/m3, Cl = 0.2 μmole/m3, and NH4 = 3.2 μmole/m3. AIM2 serves as the "truth" model because it uses a highly accurate activity coefficient model

and employs a direct Gibbs free energy minimization approach for solving multicomponent phase equilibria. ISORROPIA was run in the "reverse" mode while gas-particle partitioning in AIM2 as turned off so that the results from both the models can be directly compared. Also, formation of double salts in AIM2 was turned off to maintain consistency between the two models. Temperature was 298 K. The above results show that the mutual deliquescence RH (MDRH) predicted by ISORROPIA is 48% instead of the correct value of 54% as predicted by AIM2. But more importantly, the composition of the liquid-phase predicted by ISORROPIA is completely wrong between 42 and 72% RH. For instance, according to AIM2, NH4NO3 and NH4Cl are completely deliquesced at 54% RH while (NH4)2SO4 is partially deliquesced. More (NH4)2SO4 dissolves as RH increases, and it is completely dissolved at 74% RH. On the other hand, ISORROPIA gradually dissolves all three salts starting at 48% RH until they are all completely dissolved at 62% RH. This is thermodynamically incorrect. Large errors can also be seen in the water content predicted by ISORROPIA. Clearly, there is no resemblance between the approximate aerosol phase state, water content, and composition predicted by ISORROPIA and the true thermodynamic equilibrium composition predicted by AIM2 for this aerosol case. According to the species concentrations listed in Table 1 of this manuscript, Mexico City aerosols should have similar or more complex compositions.

First of all, using one set of conditions is far from being a thorough evaluation of the model. Many studies in the literature (some cited in this review) have done a much more thorough and careful job of evaluating ISORROPIA, and the reviewer is referred to them. Nevertheless, we thank the reviewer for providing the detailed table because it allows us to stress the following:

- Our assessment of the aerosol phase state (i.e., metastable or stable) was done for data which RH < 55%. This was deliberately chosen, as the “stable” aerosol state in this part of the phase diagram is *mostly solid*. Thus, the issue raised by

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the reviewer is most of the time irrelevant.

- Showing that ISORROPIA is in disagreement with AIM is not useful, as the discrepancies may not be important. For example, carefully examining the predictions of the two models in the provided table, one can observe that rather small differences are seen in the predicted partitioning of aerosol sulfate, nitrate and ammonium. If ISORROPIA tends to slightly overpredict aerosol water, this is not as important as implied because: i) for intermediate RH data, both "metastable" and "stable" solutions tend to provide the same prediction skill even though the compositions are different, and, *ii*) for RH < 55%, the "metastable" state is strongly preferred for most data points. Using AIM (if possible) would not change our conclusions, as the "stable" solution would be even *dryer*, hence in *larger disagreement with observations*. As stated in our response to reviewer #3, the preference for a metastable state is not surprising, given the multicomponent nature of Mexico City aerosol.

- The "reverse mode" of ISORROPIA is an open-system calculation; lack of a total mass constraint tends to maximize differences in predicted aerosol concentrations/speciation. If one ran AIM and ISORROPIA in the "forward mode", one would find that the *partitioning* of semivolatiles (which is the objective of this study) does not deviate as much. By the way, we refer to the study of Yu et al (2006) for an intercomparison between AIM and ISORROPIA.

Ansari and Pandis (Aerosol Sci. and Technol., 31, 129-153, 1999) also showed that ISORROPIA has difficulty in reproducing the complex multistage deliquescence behavior in multicomponent aerosols. How can then one expect ISORROPIA to give reliable answers when applied to examine equilibrium assumption and the deliquescence behavior and phase state of real atmospheric aerosols as complex as the ones found in Mexico City? Thus, if the authors still wish to examine the bulk equilibrium assumption and the deliquescence behavior and phase state of the complex Mexico City

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aerosols, then they must at least use a true thermodynamic aerosol model such as EQUISOLV II, which includes the crustal species that the even more accurate thermodynamic models such as AIM2 and GFEMN currently lack.

For the reasons given above, we feel that ISORROPIA-II can be used to assess the thermodynamic state in Mexico City aerosol. By the way, the main conclusion of the Ansari and Pandis (1999) paper is that "based on its overall agreement with GFEMN and its computational efficiency, ISORROPIA appears to be the model of choice for use in large-scale aerosol transport models" (see last sentence of the abstract of Ansari and Pandis, 1999). Using EQUISOLV II would be interesting, but is left for a future study.

3. Plots of "predicted" - "observed" in Figure 3 show many points with large positive values for both for NH4(p) and NO3(p) for RH > 50%. Doesn't this automatically mean that the bulk equilibrium assumption is invalid for those points?

For 55% < RH < 90%, the discrepancy in predicted nitrate is no more than 4 μg m^{-3}, and 2.5 μg m^{-3} for ammonium. This is a notable, but not large fraction of the total particulate mass (see Table 3). Above 90% RH there is a larger overprediction, which could indeed be from non-equilibrium effects, but also from uncertainties of the RH measurement itself (which could be quite large). Given that there are only a few points in the dataset (about 7) where this occurs, it is safe to say that, neglecting measurement uncertainty, the bulk equilibrium assumption gives to within 35% (25%) the correct answer for nitrate (ammonium) for more than 90% of the data collected.

4. What is the physical basis for the SO4/NO3 ratio in determining the phase state preference of aerosol particles (i.e., stable vs. metastable branch)?

The existence of metastable aerosol for low RH may seem at first surprising, particularly since crustal species, which tend to promote efflorescence under supersaturated conditions, are present (e.g., Martin et al. (2001) reported that efflorescence is rapid at for deliquesced $(NH_4)_2SO_4$ aerosol at 35% RH). If substantial amounts of predicted solid $CaSO_4$ is used as a proxy for crustal influence, 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.

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

In any case, the statement in Conclusion 4 (line 10, page 9219) that “This can serve as an important constraint for three-dimensional air quality models that simulate ambient particle concentrations under conditions characteristic of Mexico City” is a stretch in the light of above arguments.

This statement summarizes what was found in the analysis; we state that it *could* serve as an important simplification when solving for the partitioning of semivolatiles on multicomponent aerosol *under conditions characteristic of Mexico City* (i.e., with a large amount of soluble organics). The robustness of this finding (and its relation to the amount of organics present) is left for future studies.

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