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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.

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Reply to Reviewer #1

We thank the reviewer for the positive feedback and the thoughtful comments.

Major Comments

A substantial amount of work has been conducted to characterize Mexico City aerosol. This broad body of work has furthered our understanding of aerosols in Mexico City, including of inorganic aerosols and their precursors. The authors do not adequately compare their measurements and model predictions with previous work. This inadequacy makes it difficult to understand the context of this

work as well as its original contributions. This weakness is exacerbated by the long time-resolution of the measurements (4-hour averages) relative to previous measurements. For example, when discussing work that has been conducted since IMADA-AVER to chemically characterize the fine fraction of aerosols along with the gas-phase precursors since IMADA-AVER, the authors only cite their work (line 5, page 11260).

We apologize for this oversight. We have now added more references and discussion in the text.

How do the measurements compare with those of Fountoukis, Nenes et al. (2007)? This comparison is all the more important given the long averaging time of the measurements (4-hour averages, almost two orders of magnitude longer than those of Fountoukis, Nenes et al. (2007) and observations taken during MCMA-2003). In addition to (Fountoukis, Nenes et al., 2007), the authors should compare their observations and predictions with other work. Molina, Kolb et al. (2007) provide an excellent overview of aerosol studies based on data taken during MCMA-2003. Salcedo, Onasch et al.(2006) provide hightime resolution aerosol measurements (including of inorganic aerosol species) taken at CENICA during MCMA-2003 with an Aerodyne aerosol mass spectrometer, and compare their measurements with data from other instruments as well as with observations from IMADA-AVER. Observations of Na, K, Ca and Cl are given by Johnson, De Foy et al. (2006). San Martini, Dunlea et al.(2006a) and San Martini, Dunlea et al. (2006b) analyze the chemical characteristics of the fine fraction of aerosols and gas-phase precursors based on high-time resolution observations. How do these measurements compare with those in this work?

Good point. We have now added more references as well as text in the revised manuscript to address these questions.

Similarly, when the authors discuss the effect of including crustal species on the

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partitioning of semi-volatile inorganics in Mexico City the authors again only cite their own work (line 11-12, page 11260). This issue was also examined by San Martini, West et al. (2005).

We apologize for this oversight. It has now been added to the revised manuscript.

On page 11263 the authors discuss gas-phase measurements of ammonia. Again, they only cite their work (line 18). How do these measurements compare with measurements taken during other campaigns? Ammonia observations were available during IMADA-AVER at La Merced. San Martini, Dunlea et al. (2006a) describe two sets of ammonia measurements at La Merced taken during MCMA-2003. San Martini, Dunlea et al. (2006b) describe ammonia measurements at other sites (CENICA, Pedregal, Santa Ana) taken during MCMA-2003. Shorter, Herndon et al. (2004) describe ambient concentrations and mobile sources of ammonia in Mexico City.

We have now added the suggested references as well as a text relative to this comment.

On page 11263, line 25 through page 11264, line 1 the authors compare measurements of nitric acid taken during this work with those taken during the 1997 IMADAAVER campaign. It is encouraging that the authors compare this measurement with measurements taken during another campaign. As indicated above, the authors need to do a similar exercise for other species (and not only with IMADA-AVER but also, for example, MCMA-2003).

This has now been corrected. See section 2.4.

Furthermore, the authors conclude that the FITR HNO3 observations are less reliable than those taken with the denuder system. It would be useful if the authors provided both sets of data so that the reader can better understand the basis for this claim.

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We have clarified this part of the manuscript as follows: "A comparison of the FTIR-HNO_3 observations recorded during a previous campaign (Moya *et al*., 2004) at the MER site versus the FTIR-HNO_3 observations reported at the present work showed a higher uncertainty ($>$ 50%). This was due not only to the small HNO_3 infrared fingerprint but because an unexpected variability in atmospheric conditions (RH) during the sampling period provided a very strong water interference in the spectral window for the determination of HNO_3. However, even if the uncertainty of the HNO_3 measurement is larger in 2005, the diurnal pattern observed at the MER site is similar to that reported in previous field campaigns (MCMA-2003, San Martini et al., 2006a). The DDM HNO_3 observations are subject to less uncertainty ($\sim$30%, Shaw *et al*. 1982; Chow *et al*., 1993) and those reported in the present work compare well (in diurnal pattern; in concentration range) with previous field campaigns (IMADA-AVER 1997) and with average predicted values reported by San Martini *et al*. (2006a)."

Furthermore, recent measurements of nitric acid at the same site are available in San Martini, Dunlea et al.(2006a). How do the measurements in this work compare with those in San Martini, Dunlea et al.(2006a)? How do they compare with the nitric acid concentrations predicted by San Martini, Dunlea et al. (2006a)?

We have added a text in paragraph 2.4 to address this question.

On page 11267, lines 2-4 the authors write: "Based on this, Moya et al. (2001) postulated that assuming a metastable aerosol for winter-dry ambient conditions would improve Mexico City PM2.5 nitrate predictions; the validity of this postulation is assessed." The validity of this hypothesis was also assessed by others.

True indeed. Corrected now.

When discussing the importance of including crustal species (pages 11267–11267), it would be useful if the authors compared and contrasted both their observations and model performance with previous work. Specifically:

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- ***How do the observations of crustal species compare with those given in Johnson et al. (2006)?***
- ***Research indicates that including both crustal species and organic acids can be important to accurately modeling aerosol thermodynamics (Trebs, Metzger et al., 2005; Metzger, Mihalopoulos et al., 2006). The authors should acknowledge this issue.***
- ***The authors should include a brief synopsis of the findings from Fountoukis, Nenes et al.(2007), who examined the importance of including crustal species in modeling inorganic aerosol in Mexico City.***
- ***Based on data from the 1997 IMADA-AVER campaign in Mexico City, San Martini et al. (2005) found that including crustal species reduces the bias and error for nitrate but does not improve overall model performance.***

We have added a text in paragraph 4.3 discussing all the above comments.

In discussing errors associated with a bulk aerosol approach the authors indicate that "[t]he extent of "bulk" vs. "size-resolved" partitioning on prediction error cannot be fully assessed, as our measurement contains no information regarding the change in alkalinity/acidity of particles with size." The authors then suggest that the error due to the bulk approach is approximately 10%. I do not understand where this number came from. Can the authors provide the reader some rationale for this?

We have replaced this sentence with a more extensive discussion on the bulk error approach.

On page 11268 the authors discuss the issue of long sampling times. The authors point out that the 4-hour averaged measurements are an improvement over the 6-hour averaged measurements from the 1997 IMADA-AVER campaign. This

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is correct. However, other observations taken after the 1997 IMADA-AVER were taken with a substantially shorter sampling period than those in this study. In Mexico City alone, Fountoukis et al (2007) provide 6-minute averaged observations and Salcedo et al (2006) provides 5-minute averaged observations. I do not think the authors can reasonably conclude, based only on a comparison with their measurements and those taken during IMADAAVER, that "under periods of high variability of T and RH (Fig. 1), a faster time resolution in measurements is required for thermodynamic analysis." This is well known. The issue of nitrate loss due to volatilization discussed on page 11269 is indeed well known. It is for this reason that it would be useful if the authors compared their observations with observations taken during other field campaigns.

This phrase has been changed to: "In spite of the reduction of PM sampling periods (4 hours) in the MER 2005 study versus previous ones (e.g. 6 h, IMADA-AVER field study; Edgerton et al., 1999), a faster time resolution in measurements is likely required for higher accuracy in thermodynamic predictions (Fountoukis et al., 2007; San Martini et al., 2006a,b; Salcedo et al., 2006)."

The authors find that at low RH ($<$30%) characteristic of afternoon sampling periods (14:00-18:00 h), the metastable branch of the equilibrium assumption improves significantly (by 50% of 20 MNE, ISORROPIA II simulations) predicted PM2.5 nitrate. What is the ionic strength of the metastable solution during these periods? This information is needed for the reader to understand whether the predictions of ISORROPIA-II are reasonable or are extrapolating beyond the data used to model the activity coefficients.

For such highly concentrated solutions the ionic strength is around 50-70 mol kg^{-1}, which is outside of the range of data used to constrain activity coefficient models. Therefore, this improvement may be fortuitous; it is less likely however given that the improvment is seen over a large range of precursor concentrations. Text has been added stating this and its implications for model predictions.

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On page 11269 the authors state: "This study suggests that knowledge of the real state of the aerosol is of relevance for adequately modeling partitioning of semivolatile species between the gas and particulate phases, under Mexico City conditions." This is already well known and has been examined in previous work.

This phrase has been changed to: "This study corroborates previous findings (San Martini et al., 2005; Fountoukis et al., 2007), that, knowledge of the aerosol phase state is important for adequately predicting the partitioning of semivolatile species."

Technical Corrections

11261/6: Strike "attempt to"

Done

11262/8-9: Strike "as follows"

Done

11262/22-26: Confusing sentence! Please re-write this sentence to clarify what you are trying to say.

Done.

11268/21: Strike "is"

Done

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11257, 2007.