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Atmospheric Chemistry and Physics Discussions

Interactive comment on "

Formation of semivolatile inorganic aerosols in the mexico city metropolitan area during the milagro campaign" *by* V. A. Karydis et al.

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(1) *This paper discusses the performance of a model in simulating inorganic aerosols when compared to observations made during the 2006 MILAGRO campaign. The authors correctly point out that most aerosol modeling studies for that campaign have not focused on inorganic aerosols, but rather organics; therefore, this study provides useful information and makes a contribution to the literature. However, the motivation regarding the remaining challenges in modeling inorganic aerosols needs improvement*

and the authors do not take advantage of a large fraction of data from the campaign that could be used to further evaluate the model. There are also numerous specific comments that need to be addressed and clarified.

We have improved the discussion of the motivation for the improvement of our ability to simulate the inorganic aerosol components (see also our response to comment 2 below). We have done our best to use all the available data from the campaign that are relevant for the scientific objectives of this paper (see also our response to comment 3 below).

Major Comments:

(2) Motivation: *In the introduction, the authors discuss past research on thermodynamic modules and how they have been used to simulate inorganic aerosols. On the one hand I agree that simulating nitrate can be challenging (sulfate should be more well known), but some of the examples they give suggest that performance may not be that bad. So I found that a clear articulation of the need of further research on modeling inorganic aerosols lacking. A confusing factor is that they list the many thermodynamic modules that are available, and it is not clear from this study how they are fundamentally different, especially when some studies show a general agreement among them (line 20, page 21999). Perhaps going into that detail is appropriate for a review paper and not this study, but setting the proper context of the research is needed. For example, how do the treatments from CAMx differ from the other models?*

This is a valid concern and this section has been improved in the revised manuscript. We are now stressing the issues related to the thermodynamics of crustal elements, the condensation-evaporation dynamics and corresponding competition between the fine and coarse PM and finally the various computational and application issues. More details about the thermodynamic models used in previous studies and their results are now included in the revised manuscript. In the current study, we incorporate in our three dimensional chemical transport model (PMCAMx) the new thermodynamic model

ISORROPIA-II, in which the thermodynamics of the crustal elements of calcium, potassium and magnesium have been added to the preexisting suite of components of the ISORROPIA model. The new model combines the computational advantages of ISORROPIA with the explicit treatment of thermodynamics of crustal species. Size-resolved composition of particles is simulated using the hybrid method for aerosol dynamics, in which the mass transfer to the fine aerosol sections (up to 1 micrometer) is simulated using the bulk equilibrium assumption and to the remaining aerosol sections using the dynamic approach and MADM. During this study, we have proved that the use of this new inorganic modeling framework is essential in order to accurately simulate the effects of mineral dust to the composition and the size distribution of the predicted inorganic aerosols.

(3) Evaluation: *I did not find the plots that show horizontal variations in average concentrations of various aerosol species very insightful. The authors should elaborate as to what purpose they serve. The time-series comparisons with data were more useful than the averaged results. I am not sure why the authors have limited their analysis to only surface data. Extensive measurements of aerosol composition from several research aircraft are available from MILAGRO and I strongly suggest comparing the simulated results with those measurements as well. This will provide additional information on the processing of aerosols as aerosols and their precursors are transported away from Mexico City. An evaluation of simulated trace gases that affect inorganic aerosols also seems in order to establish whether the inorganic aerosol predictions are reasonable for the right reasons. All that is shown is the end result (inorganic aerosols), not the other components (meteorological, trace gases) that affect their evolution.*

The plots show the predicted average spatial variation of the concentrations of the major PM components inside and around Mexico City trying to put the rest of the results (focusing on specific locations) in perspective. We think that without these two figures, the comparisons in the specific measurement sites could be misleading for some of the readers. We do agree with the referee that additional discussion of these figures

would be helpful and we have added it in the revised manuscript.

The major objective of this modeling application was the testing of the model inside and near Mexico City and close to the ground. Most of the available flight data (e.g., the NSF/NCAR C130 measurements) are either outside or near the edges of our modeling domain. These airborne measurements are a good dataset for the evaluation of CTMs at scales of hundreds or thousands of kilometers focusing on regional pollution. However, this is outside the scope of the present study.

The ability of PMCAMx and WRF-Chem to reproduce the observed concentrations of trace gases during MILAGRO has been discussed in previous publications (Lei et al., 2007; Song et al., 2009; Tsimpidi et al., 2011; Li et al., 2010, 2011) by our team. These studies have used the same emissions and meteorological fields as the present study. A brief summary of the main results of these publications and the corresponding references have been added.

Specific Comments:

(4) *Title: "mexico city" should be "Mexico City" and "milagro" should be "MILAGRO".*

Corrected.

(5) *Abstract: The performance of the model is defined in terms of average concentrations compared to observations, which is one of many metrics that could have been used. It is certainly important to report this information, but the abstract does not convey the importance of these numbers for regions other than Mexico City to make this paper more relevant. The focus of the paper is on inorganic aerosols, but some mention of organic aerosol needs to be made since it is often the largest component of aerosol mass in Mexico City. So in terms of human health issues and regulations, errors in predicted inorganic material may not be as significant as errors in predicted organic matter (except during dust events). I do not see this sort of context on inorganic*

aerosols described in the paper.

The performance of the model was also evaluated against measurements taken form a suburban background site (T1) located north of Mexico City. The average predicted $PM_{2.5}$ sulfate, nitrate, ammonium, chloride, sodium, calcium, and magnesium are 3.3, 3.3, 1.3, 0.3, 0.4, 1.0, and 0.15 μg m^{-3} respectively. The corresponding measured concentrations are 4.4, 3.2, 1.1, 0.4, 0.3, 0.7, and 0.15 μg m^{-3}. This information has also been added to the Abstract.

The formation of the organic aerosol components (OA) over Mexico City has been thoroughly examined in our recently published work (Tsimpidi et al., 2011). The average PM1 OA has been predicted to be equal to 18 μg m^{-3} (versus 17.2 μg m^{-3} measured) and 11.6 μg m^{-3} (versus 11 μg m^{-3} measured) at T0 and T1 respectively. The current study focuses on inorganic aerosols and therefore we believe that it would be more appropriate to include this information in the Introduction section than in the Abstract. A brief discussion of the organic aerosol predictions of the model has been added.

(6) *Page 21997, lines: 6 – 24: The paragraph starts by discussing anthropogenic emissions and then mentions dust, which could be considered either a natural source or man-made one (if human activity alters the landscape). So why is biomass burning not mentioned in this discussion? This seems to imply that biomass burning is not important in terms of aerosol loading. Other works suggest that modern carbon is a large fraction of total aerosol carbon.*

We now clarify early on in the paper that the organic aerosol sources, concentrations and processes have been discussed in our recent paper (Tsimpidi et al., 2011) and this study will focus exclusively on the inorganic PM components. Biomass burning is indeed one of the major sources of primary fine carbonaceous particles in Mexico City. However, this paragraph focuses on the presence and composition of inorganic aerosols in the atmosphere of MCMA. In order to provide additional details, we have added some text about the important sources of inorganic aerosol and their precursors

in and around Mexico City such as the Miguel Hidalgo Refinery and the Francisco Perez Rios Power Plant in Tula (major source of SO_2 emissions), the CEMEX cement plant in Tolteca (major source of Ca emissions), and mobile emissions from Mexico City (major source of NOx emissions).

(7) *Page 21998, lines 7-29: The paragraph is a summary and review of equilibrium thermodynamic models. Did the authors mean to omit dynamic (e.g. MOSAIC, Zaveri et al., 2008) approaches when simulating inorganic aerosols?*

Dynamic models such as MOSAIC (Zaveri et al. 2008), MADM (Pilinis et al., 2000), and UCD (Zhang and Wexler, 2008) have also been included in this brief review in the revised manuscript. The hybrid approach used in this paper is also dynamic (at least for the coarse particles).

(8) *Page 2200: Since the authors mention some studies that employ WRF-Chem, there are at least two others that have not been described (Shrivastava et al. 2011; Fast et al., 2009).*

We have included a short description of these modeling studies in the revised manuscript.

(9) *Page 22001, line 9: "model domain is expanded : : :". Expanded compared to what? Compared to a previous application of CAMx I assume, but the authors need to be specific.*

The model domain is expanded compared to Karydis et al. (2010) study focusing on the MCMA-2003 campaign in the same area. This is now clarified in the text.

(10) *Page 22002, lines 23-25: I presume the boundary conditions are invariant with height? This could be a bad assumption since aerosol concentrations are often higher*

in the boundary layer than in the free atmosphere. This would mean that the model could be entraining the wrong amount of aerosols from the free atmosphere into the boundary layer every day as the convective boundary layer grows during the day. The constant values along each boundary will introduce discontinuities into the results near the corners. I would also expect that large-scale aerosol concentrations over a month long-period will change significantly. Please discuss the impact of these affects on the present model set up.

The boundary conditions (BCs) are indeed invariant with height and along each boundary however they are quite far from the area of interest (Mexico City). In order to estimate the effect the BCs have on the predicted inorganic aerosol concentrations, we have conducted a sensitivity simulation where the only source of aerosols is the BCs (zero emissions). Based on the results of the base case and the BC-sensitivity case simulation, at T0, the percentage of the predicted PM10 sulfate, total (gas and aerosol) nitrate, total ammonium, total chloride, sodium, calcium, potassium, and magnesium that is coming from the BCs is 37, 12, 3, 38, 45, 6, 27, and 26 percent respectively. This fraction is of course high close to the boundaries and very small close to sources such as Tula vicinity for sulfate (4 percent) and ammonium (11 percent), Mexico City center for nitrate (9 percent) and ammonium (3 percent), Tolteca vicinity for nitrate (9 percent) and calcium (1 percent), and Texcoco Lake for chloride (25 percent), sodium (28 percent), potassium (6 percent), and magnesium (5 percent). Based on these results, while we recognize that BCs are important in relatively small domains, they seem to have small impact close to sources and thus they do not affect the conclusions of this study. Sodium and chloride are considered an exception as they are significantly influenced from the imposed south BC. Please note that these are the upper limits of the effects of the BCs in the upper layers of the model, because they include the effects of all the layers. A short discussion of this issue has been added to the revised manuscript.

(11) *Page 22002, line 26: Is the 6 km above ground level or sea level? This makes a*

big difference for the Mexico City plateau which is 2 km MSL. Boundary layer heights during MILAGRO were often between 3-4 km AGL which would mean that the boundary layer could grow above the top of the model domain (if the model domain top is at 6 km MSL).

The model domain extends to 6 km above ground level. This is now clarified in the text in order to avoid such potential misunderstandings.

(12) *Page 22003, lines 1-2: Much more information on WRF is needed to assess the simulated inorganic aerosols in this study. Was WRF run at the same resolution as CAMx? What frequency was the meteorology used to drive CAMx? How did WRF perform and is this described in a previous paper? As stated in a few instance later, meteorological uncertainties can impact predictions of inorganic aerosols but the reader is given no information as to the performance of WRF in this study.*

We have added the following text to the revised paper at this point: “PMCAMx was driven by hourly meteorological output fields from the Advanced Research WRF model (WRF v2.2.1; Skamarock et al., 2005), including horizontal wind components, temperature, pressure, water vapor, vertical diffusivity, clouds, and rainfall. The WRF simulation used three one-way nested grids with horizontal resolutions of 36, 12, and 3 km and 35 sigma levels in the vertical direction. The PMCAMx model subdomain was similar to the WRF D3 domain (same map projection, same domain center and same horizontal grid resolution). To improve the accuracy of the simulated fields, a continuous four-dimensional data assimilation scheme was employed in the domain with a horizontal resolution of 3 km. Multi-level upper-air observations were assimilated, including radar wind profilers, tethered balloon measurements, controlled meteorological balloon observations, aircraft observations, additional soundings inside the Mexico City basin operated during the MILAGRO campaign, and routine soundings observations. Details of the WRF setup are described by Song et al. (2010).”

(13) *Page 22003, line 3: It would be useful to include in a table the emission totals used in this study from the inventory. Does the emission inventory extend over the entire modeling domain? The MCMA is a definition that applies only to the immediate vicinity of Mexico City.*

A table that includes the total emissions of the inorganic aerosol precursors has been added to the paper. The emission inventory is based on MCMA 2006 emission inventory and has been expanded to the modeling domain of this study in order to include major emission sources outside of the MCMA such as the refineries and the power plants located in the Tula vicinity.

(14) *Page 22003, line 12: It would be useful to include a plot that shows the distribution of a) anthropogenic sources and b) dust emission sources. This would help the reader understand the spatial distribution plots of aerosols shown later. A discussion of how dust emission sources were determined would be useful.*

Four maps that depict the spatial distribution of NOx, NH_3, SO_2, and mineral dust emissions have been added to the revised manuscript. Dust emissions are calculated based on the algorithm of Draxler et al. (2001) which uses the concept of a threshold friction velocity which is dependent on surface roughness. The fugitive dust chemical composition is determined based on the geological materials that exist in the different regions of the model domain according to the findings of Vega et al. (2001). Fugitive dust emitters in and around MCMA are considered to be unpaved and paved roads, agricultural soil, dried Lake, asphalt, cement plants, landfill, gravel, and tezontle soil.

(15) *Page 22003, section 3: Are biomass-burning emissions included in the simulation? Presumably they are composed mostly of carbonaceous aerosols anyway, but trace gas emissions could affect inorganic aerosol evolution. What about volcanic emissions of sulfur dioxide that affects sulfate production? Are those included or not?*

Biomass-burning emissions are not included in the inventory used in this study. These

are introduced in the model through the boundary conditions based on the measurements and analysis of Crounse et al. (2009) for the MILAGRO period. Volcanic emissions on the other hand, are explicitly included in the emission inventory. This information has been added to the revised manuscript.

(16) *Page 22004, line 2: Texcoco Lake is not indicated on any figure. How are readers supposed to know where this is located? In many places in the manuscript, the authors seem to expect the reader to follow Mexico City literature.*

The location of the Texcoco Lake is now depicted in Figure 1.

(17) *Page 22005, line 12: Meteorological errors are mentioned. The authors should be more specific on this point given the lack of context of the WRF predictions in this paper. Are the errors reported elsewhere? A few lines later (line 18-19) suggest a transport error, but not evidence is given to support the statement regarding errors in simulated peaks of sulfate.*

Sulfate peaks at T1 and T0 sites are the result of transport of the high concentrations of sulfate produced near Tula vicinity. When the winds at T1 and T0 are northerly, high sulfate concentrations are observed (or predicted) in these sites, while in periods where southerly winds are dominant, the concentrations of sulfate are low. The measured sulfate peak on March 18 is a good example. WRF predicts a shift in wind direction from northerly to southerly several hours earlier than it should. As a result the model misses the observed sulfate concentration peak on that day.

(18) *Section 4: The authors should include somewhere (perhaps a table) a list of instruments in which the measurements were used in this study. Also including the principal investigator of each instrument is needed, along with an estimate of the uncertainties in the measurements and citations to papers that describe the measurements (if possible). It is a bit disappointing to not acknowledge the hard work of many scientists on*

which this study benefits.

Most of the corresponding references existed in the original paper but at different parts of the manuscript. We have created a new subsection in the revised named Ground Observations where we describe with more detail all the measurements that were used to evaluate the PMCAMx performance. We have also added a reference here to the MILAGRO overview paper that has a complete table with all the groups that contributed to the measurements in the program.

(19) *Page 22007, lines 9-10: I cannot verify this statement from the plot. Perhaps that is due to the poor choice of scaling in the plot.*

We have revised the scale used on the vertical axes of all hourly and diurnal plots.

(20) *Page 22007, line 14: AMS is not defined.*

The definition of AMS (Aerosol Mass Spectrometer) has now been added to the text.

(21) *Page 22007, lines 21-29: In the discussion of the emissions in Section 3, the authors should describe how emissions of various dust species are determined.*

Total dust emissions were calculated based on the algorithm of Draxler et al. (2001). Emissions of individual dust species (sodium, potassium, calcium, magnesium) are considered to be a fraction of total dust emissions. This fraction is determined based on the geological materials that produce fugitive dust emissions (Vega et al., 2001). Fugitive dust emitters in and around MCMA are considered to be unpaved and paved roads, agricultural soil, dried Lake, asphalt, cement plants, landfill, gravel, and tezontle soil. The original discussion in Section 3 has been re-written in the revised manuscript providing additional details.

(22) *Page 22008, section 6: The authors present one figure on the differences in ni-*

trate between simulations that employ either the hybrid or equilibrium approach. They should also include the relative effect when compared to observations. Presumably the hybrid (or even a dynamic) approach would be better. Is this true?

At T0 the average measured concentration of PM1 nitrate is 3.5 μg m^{-3}. Using the hybrid approach for aerosol dynamics, the model underpredicts the average PM1 nitrate concentration by 0.9 μg m^{-3}. Nevertheless, as we discuss in the manuscript, we believe that this discrepancy is not caused by errors in size distribution or in the partition between the aerosol and the gas phase but in the lack of HONO emissions. On the other hand, assuming bulk equilibrium between the gas and the aerosol phase, the model overpredicts the PM1 nitrate concentration by 1.2 μg m^{-3}. This overprediction can be even larger if the model uses more accurate HONO emissions. At T1, where the impact of HONO emissions is not as important as at T0 (which is an urban site) and the dust concentration is higher than the urban center (which results in more nitrate in the coarse mode), the model, using the hybrid approach, agrees well with the observations for $PM_{2.5}$ nitrate (the mean bias is 0.1 μg m^{-3}). Using the bulk equilibrium approach though, results in an average overprediction of PM2.5 nitrate by 1.2 μg m^{-3}. This discussion has been added to Section 6.

(23) *Page 22009, section 7: The authors give net changes in PM species based on changes of emissions. It would be useful to include the relative change in total PM, since that is the real metric in terms of human health.*

Total PM_1 decreases by 1.3 percent in Mexico City center and 1.1 percent in Tula after a 50% reduction of SO2 emissions. The predicted decrease of total PM_1 concentration after a 50% reduction of NH3 emissions is 4.4 percent and 2 percent in Mexico City center and Tula respectively. Finally, when NOx emissions are reduced in half, total PM_1 concentration decreases by 3.5 percent and 0.1 percent in Mexico City and Tula respectively. This information has been added to the text.

(24) *Page 22011: line 5: The "conclusions" read more like a summary to me.*

After the recommendation of both reviewers, we have replaced the list in the Conclusions section with a comprehensive discussion of the main findings of this study.

(25) *Page 22012: lines 1-2: This statement is an obvious one, but unproven by this study. They authors have not shown this result at all.*

We agree that the appropriate proof of this statement would require development of a day-specific inventory and demonstration of the improvement of the model performance. This is outside the scope of the paper and this rather secondary statement has been deleted.

(26) *Conclusion: This study is evaluating one model for one case, and it is not clear what that means in terms of applicability beyond MILAGRO. It would be useful to include some discussion along these lines in the conclusion.*

This study is part of a continuous effort to build a chemical transport model (PMCAMx) that can accurately describe the formation of both organic (Gaydos et al., 2007; Karydis et al., 2007; Lane et al., 2008; Shrivastava et al., 2008; Murphy et al., 2009; Tsimpidi et al., 2010; 2011) and inorganic (Gaydos et al., 2007; Karydis et al., 2007; Karydis et al., 2010) aerosols in urban (Tsimpidi et al., 2010; 2011; Karydis et al., 2010) and regional (Gaydos et al., 2007; Karydis et al., 2007; Lane et al., 2008; Shrivastava et al., 2008; Murphy et al., 2009) scale. It has been tested successfully in different scales and environments (Murphy et al., 2009; Tsimpidi et al., 2011; Fountoukis et al., 2011; current study). A brief discussion has been added to the Conclusions.

(27) *Figure 2 (and other similar figures): Most readers unfamiliar with Mexico City will not understand the spatial scales in these plots. Please include a scale to indicate distance in kilometers. There are a number of other sites listed but it is not clear what*

there relevance is. This should be included in the figure caption. Including topography and/or a Mexico City boundary would also be very useful. The black text is often virtually impossible to read on top of the colors (especially dark read and blue).

All figures have been revised in order to be more clear and informative.

(28) *Figures 4 and 5: There is a misspelling "preridcted". I have not look specifically for errors in spelling, but this suggests the authors should check the manuscript again. Vertical axes on time series plots: There seems to be poor choice of the scales used on the vertical axes. In many cases most of the model results appear in a narrow range at the bottom of the plot; therefore, a reader cannot tell the differences between the observed and simulated values.*

We have corrected the typo and revised the scale used on the vertical axes of all hourly and diurnal plots.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 21995, 2011.