**Atmospheric
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Discussions**

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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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General comments : (1) *In this study, the authors mainly used the measurements on March 2006 during the MILAGRO campaign to evaluate three dimensional CTM PM-CAMx and then to use the model to test three different emission strategies (i.e., reducing 50 percent SO2, NH3 and NOx emissions, respectively). The subject of this study is suitable for interests of ACP. However, it seems the authors spend more paragraphs and figures to repeat evaluation of the CTM following the previous study (Karydis et al.*

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Interactive Discussion

Discussion Paper

2010) against another set of ground-level measurements during the MILAGRO campaign which is not novel while comparably fewer discussions are made on the most interesting and novel part of the current manuscript (i.e., to use the CTM to test three emission strategies is eventual goal of both MILAGRO field campaign and the chemical transport model as stated by the authors). Moreover, the difference of the model setup as well as emission inventories in the current work in contrast to the previous study (Karydis et al., 2010) is not clearly addressed, which brings a question: what's the advantage of this new version of PMCAMx? The abstract does not provides a concise and complete summary while the conclusions sound more like summary. The overall presentation of the manuscript needs to be significantly revised and following specific comments are needed to be clarified.

In contrast to our previous work (Karydis et al. 2010), where we evaluated the model against a limited dataset (five-days and one site in the center of Mexico City) in this study we evaluate the model against one of the best available datasets in a highly polluted urban area which includes one month of continuous measurements for the major inorganic aerosol components as well as filter-based measurements for the major mineral dust components (not available before) in urban and suburban sites. This evaluation provides a valuable test of the current state-of-the-art in atmospheric inorganic aerosol modeling in a polluted megacity and is clearly a necessary step before the model can be used for the investigation of the efficiency of different emission control measures. Moreover, during this study, the model domain was expanded in order to include major sources of inorganic aerosols from the surrounding areas of MCMA such as the Miguel Hidalgo Refinery and the Francisco Perez Rios Power Plant in Tula (major source of SO_2 emissions), and the CEMEX cement plant in Tolteca (major source of Ca emissions). In addition, the composition of the fugitive dust emissions is now determined based on the geological materials existing in the different regions of the model domain according to the findings of Vega et al. (2001), in contrast to our previous study where the global average mineral dust composition was used.

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Specific comments :

(2) *In the abstract, the authors used lots of numbers for the predicted and measured inorganic aerosol concentrations that are overly loaded with details and are lacking in the important conclusions. For example, at page 21996, line 21-23, the authors listed the predicted and measured sulfate, nitrate, ammonium and chloride concentrations without any comments on the difference of the modeled vs observed values (e.g., the model underestimates nitrate, ammonium and chloride at the T0 site, etc), which makes the abstract tedious and verbose.*

A thoroughly discussion about the differences between the model predictions and the observations exists in section 5 of the manuscript. However, after the recommendation of the reviewer, we have also included a brief summary of these results in the abstract of the revised paper.

(3) *From the context, the authors evaluated model prediction against measurements at two sites (i.e., T0 and T1). However, only the results at T0 (model vs observation) is concluded in the abstract.*

A brief discussion of the results from the model evaluation at the T1 site has been added to the Abstract.

(4) *The brief conclusion from the sensitivity with respect to the hybrid method versus the equilibrium method is also missing in the abstract.*

A discussion of the sensitivity of model results to inorganic aerosol dynamics has been added to the abstract.

(5) *In the section of introduction, the authors used lots of vague statements when referring previous studies, for example, a. page 21998, line 22-23, "a general agreement although some differences were found"; b. page 21998, line 27-28, "an overall agree-*

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Discussion Paper

ment was reported although some discrepancies were found at Long Beach"; c. page 21999, line 15, "general agreement was found"; d. page 21999, line 27- 29, "similar results in model predictions for total PM although some differences over species concentrations and RH regimes are reported." The statements like "an overall agreement although some difference" are too general and uninformative when comparing the model predictions to the observed data. General agreement on what? Differences on what? It's unclear. The question is: how different or similar previous model studies are compared to the observations? What are advantages of your model compared to numerous previous model studies since the prediction of the partitioning of the semi-volatile inorganic aerosol components is one of the most challenging tasks? The authors need to clarify that.

More details about the results of the previous studies, summarized in the introduction section, 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. 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.

(6) *Page 21998, line 25-27, if "the MILAGRO campaign was designed to follow the urban plume originated in Mexico City" as stated, it might be more interesting to compare the vertical profile from the model prediction of inorganic matter versus the measured*

ones by taking advantage of both 3D CTM and observed data.

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. There have been other modeling studies focusing on the evolution of the Mexico City plume and these are referenced now in the revised paper.

(7) *Page 21999, line 2-3, "An analysis of model performance against measurements has been performed" is needed to be changed to "An analysis of model performance against measurements with respect to the particulate matter has been performed".*

Corrected.

(8) *Page 22002, line 22-25, the authors stated that "The concentrations of the aerosol components at the boundaries of the domain were chosen based on results of the GISS-II global CTM for the month of March". Do you mean March 2006 or climatology March? I am curious how the model predictions on the inorganic PM are sensitive to these boundary conditions. For example, the predicted PM1 chloride seems sensitive to the south boundary conditions shown in Figure 2(d).*

The GISS-II results generated a climatological background of aerosols in the area around the PMCAMx model domain with the aerosol values representing a 5-year average for the month of March. In order to estimate the effect the boundary conditions (BCs) have on the predicted inorganic aerosol concentrations, we have conducted a sensitivity simulation where the only source of aerosols is through the BCs (zero emissions). Based on the results of the base case and the BC-sensitivity case simulation, at T0 site, the percentage of the predicted PM_{10} 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 getting higher close to boundaries and meaningless 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 very important in relatively small modeling domains, they seem to have small impact close to sources and thus they do not affect the conclusions of this study significantly. Sodium and chloride are considered an exception as they are significantly influenced from the imposed south BC.

(9) *This study used meteorology fields outputted from the WRF model. What's the time interval of CTM as well as the meteorology field? Did you use the meteorology fields corresponding to March 2006? The model setup needs to be described in details. It's unclear how the model setup as well as the emission inventories used in the current work differs with that in the previous study (Karydis et al., 2010) although the authors stated the current work is based on previous efforts.*

The maximum time step in CTM is 10 minutes and the CTM output frequency is one hour and the simulations were specific for March 2006. 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

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Discussion Paper

setup are described by Song et al. (2010). This information has been added to the revised manuscript.

Regarding the emission inventory, we have added the following to the last paragraph of Section 3: "The anthropogenic emissions were constructed based on the official inventory for the year of 2006 for the Mexico City Metropolitan Area (MCMA), and the area emissions outside the MCMA were estimated based on the population distribution. Biogenic emissions were estimated using the WRF-driven MEGAN v2.04 model (Model of Emissions of Gases and Aerosols from Nature) developed by Guenther et al. (2006). The anthropogenic emissions were evaluated and adjusted based on the comprehensive data from the field campaign and the routine ambient air quality monitoring network. Details of the anthropogenic emission estimation are described in Song et al. (2010). The dust emissions were calculated based on the algorithm of Draxler et al. (2001) and the dust and sodium chloride emissions were improved based on the approach of Karydis et al. (2010)".

(10) *Page 22001, line 6-8, the authors stated the purpose of this study is to "evaluate our current understanding of the atmospheric processes responsible for the spatial, temporal and seasonal variability of fine inorganic PM over the Mexico City Metropolitan Area". This statement is not appropriate since only observations on March 2006 during the MILAGO campaign were used. I could not find any results related to seasonal variation with respect to either fine or coarse inorganic aerosols.*

We agree with the referee's comment. We have removed the reference to the seasonal variability from the statement.

(11) *Page 22004, line 3, what's the MCMA 2006 official emission inventory? What's the frequency of the emissions of precursor species emitted into the CTM?*

The MCMA 2006 official emission inventory can be found in the following web address: http://www.sma.df.gob.mx/sma/links/download/archivos/ie06criteriopw.pdf. A

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Interactive Discussion

Discussion Paper

reference to this has been added. The pollutant emissions are introduced in the model every hour during the simulation. This is now explained in the revised paper.

(12) *Page 22004, line 12-14, the authors stated that "There is also a little ammonium in the coarse mode because the coarse dust particles are alkaline". I do not understand this explanation since the formation of ammonium (i.e., NH4+, cation species, needs to be associated with anion.) favors the acidic condition (e.g., H2SO4, HNO3, or HCl). The authors further explained "The soluble crustal elements increase the PM water content and thus favor the ammonium nitrate formation". This is also confusing statement without supportive justification from neither the context nor figures. Actually the presence of crustal elements (Ca2+, Na+, K+, Mg2+) may compete with NH4+ for available HNO3 gas. What's the corresponding relative humidity near the dust region (Texcoco lake, where is it? Could you mark it in Figure 1)? How's aerosol water content predicted by the model?*

Our sentence has been misinterpreted. We do not state that ammonium exists in the coarse mode *because* the coarse dust particles are alkaline. Small amounts of ammonium exist in the coarse mode *even if* the coarse dust particles are alkaline. We have rephrased this sentence to avoid confusion.

The statement about the effect of water on ammonium nitrate formation is based on fundamental aerosol thermodynamics. A reference to a textbook (Seinfeld and Pandis, 2006) has been added to support this point. The aerosol water content near Texcoco lake and near the Tolteca cement plant increased by 45

Phase equilibrium between the gas and aerosol-phases (Seinfeld and Pandis, 1998) results in the equality between the water activity, α_w, and the ambient fractional relative humidity, RH (expressed on a 0.0 to 1.0 scale). The water content of aerosols is calculated using the ZSR relationship (Robinson and Stokes, 1965). The addition of the soluble crustal elements, especially magnesium, increases the water content in the coarse mode (under the same RH) which eventually shifts the reversible reac-

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Interactive Discussion

Discussion Paper

tion of NH_3 with HNO_3 towards the aerosol phase producing more ammonium nitrate (Nguyen et al., 1997; Finlayson-Pitts and Pitts, 2000). Appreciable amounts of aerosol water (hence ammonium nitrate) is present even at moderate RH, given that some of the mineral salts deliquesce at low to moderate RH (e.g., 33 percent for $MgCl_2$ and 54 percent for $Mg(NO_2)_2$ at 298 K). We have added the corresponding explanations regarding this point to the text.

(13) *In the section 5, the authors compared the inorganic particulate matter concentrations (i.e., sulfate, nitrate, ammonium, chloride and dust components) between model predictions and observations. In the entire section, the authors listed a lot of average values with respect to the inorganic PM when comparing to the observations. Comparing the mean values only is not very helpful to understand the discrepancy between the model predictions and observations. The inclusion of uncertainty analysis (e.g., standard deviation, relative difference, absolute difference, root mean square, etc) might be more informative than the mean value from the statistic point of view. It's easier for readers to follow with a neat table.*

The mean absolute gross error, mean bias, normalized mean error, normalized mean bias, and root mean square error are also calculated and included in the discussion of Section 5 in the revised manuscript. These metrics are also summarized in a new table.

(14) *In Figure 4, the authors used PM2.5. What's your definition of PM2.5 here? How is it related to or deduced from PM1-10 in the model shown in Figure 3? Why do you use the PM1 for T0 site but use the PM2.5 for T1 site? This issue needs to be clarified.*

PM_1 and $PM_{2.5}$ are defined as particulate matter with diameter less than 1 and 2.5 μm respectively while PM_{1-10} is defined as particulate matter with diameter between 1 and 10 μm. PMCAMx distributes aerosols in ten sections, depending on their diameter, varying from 40 nm to 40 μm (Karydis et al., 2007). The sum of the first 5

sections corresponds to PM_1, the sum of the first 6 sections corresponds to $PM_{2.5}$, and the sum of the sections 6, 7, and 8 corresponds to PM_{1-10}. We used PM_1 for T0 and $PM_{2.5}$ for T1 because of the availability of the corresponding measurements. At T0, a high-resolution time-of flight Aerosol Mass Spectrometer (ToF-AMS) was used, which measures aerosols up to approximately 1 μm, while at T1, a Particle Into Liquid Sampler (PILS) was used which measured the $PM_{2.5}$ ion concentrations. This has been also clarified in the revised manuscript.

(15) *Page 22005, line 21-29, the authors ascribed to the spike on March 18th predicted by the model not coincident with the observations to the same emission for SO2 every day as well as errors in meteorology. The authors did not explain the discrepancy of the sulfate concentration between the model predictions and observations occurred for the first 3 days at T0 as well as the spikes on March 14th at both T0 and T1. Clearly, the model predicted sulfate is much larger than the observed ones for the first 3 days at T0 site.*

Sulfate peaks at T1 and T0 sites are the result of transport of sulfur emissions from the area around Tula. There are no major sources of SO_2 around T0 and T1 to produce these sulfate spikes (i.e. during 14th and 18th of March). Therefore, we attribute the inability of the model to capture these spikes to errors in meteorology. In the manuscript, we just focused on one of these spikes (during March 18th) to illustrate the problem, but discrepancies between predicted and observed values on March 14 or during the first three days of simulation are also due to a large extent to errors in the meteorological input.

(16) *Page 22006, the authors tried to use the underestimated OH during the early morning to explain the underprediction of nitrate at T0 and T1. What about the temperature and relative humidity at T0 and T1 during this period of time? Note that the partitioning of semi-volatile species is also highly sensitive to these two parameters. Actually Figure 5d suggests that the underprediction of nitrate from the model*

occurred in the afternoon at T1 site while the overprediction happened in the early morning, which results in the slight overestimation from the model vs the observation if comparing the average values at T1 site. Do you have justification for this discrepancy in the afternoon that is different with what happened at T0 site?

Temperature and relative humidity can indeed affect the partitioning of nitric acid between the aerosol and the gas phases. Nevertheless, as we stated in the manuscript, the underestimation of aerosol nitrate during morning hours is not a result of errors in the partitioning of nitric acid as the model underpredicts not only the aerosol nitrate but the total nitric acid too (the mean bias is -1.3 ppb). The total nitric acid produced in the center of Mexico City is transported to the north and is observed in T1 site during afternoon hours. Therefore, the underestimation of nitrate during morning hours at T0 is observed 3 to 6 hours later at T1 site. The corresponding explanation of this point has been added to the paper.

(17) *Page 22007, the overestimation of dust components as stated by the authors may partially explain the overestimation of PM2.5 nitrate at T1 site shown in Figure 5c.*

We agree that the overestimation of dust components, especially calcium which originates from the Tolteca cement plant close to T1, can affect the partitioning of nitric acid to the aerosol phase resulting in an over-prediction of nitrate early in the morning and late at night. This explanation has been added to the manuscript.

(18) *The authors conducted sensitivity test by comparing hybrid approach (HYB) versus equilibrium (EQ) approach. Which method (i.e., HYB vs EQ) is more close to the observations during the MILARGO campaign (e.g., at T0 and T1 site)?*

At T0 the average measured concentration of PM_1 nitrate is 3.5 μg m^{-3}. Using the hybrid approach for aerosol dynamics, the model underpredicts the average PM_1 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 the size distribution or in the

partitioning 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 PM$_{2.5}$ nitrate by 1.2 μg m^{-3}. This discussion has been added in Section 6.

(19) *In the section 7, the authors conducted the sensitivity test by arbitrarily reducing half of SO2, NH3 and NOx emissions to see the change of inorganic PM. What about the situation if there is 50 percent increase of SO2, NH3 and NOx emissions for the case we do not have emission control in future? What do you expect if there is 50 percent reduction of SO2 with 50 percent increase of NOx for the case we only control the sulfur emission? Although the authors claimed that these sensitivity tests "do not correspond to actual emission control strategies", more discussion about the indication from these sensitivity tests might be more insightful for the design of future emission control strategies since "a major component of the MILAGRO campaign was the use of the observed data to evaluate the performance of three dimensional chemical transport models and then used them for the design of emission control strategies" as stated by the authors in page 21998 line 3-6. I think this is also the major motivation of the current study.*

We have focused on simple emission reduction scenarios because this is the expected direction of change of the emissions in Mexico City in the next several years (Molina et al., 2010). These simple tests provide thus some information about the effectiveness of these reductions. Investigation of the effects of significant increases of emissions would be of some academic interest, but would have little to do with the future air

quality in this area. We agree that a lot more is needed in the investigation of the effects of the different emission control measures. This of course should cover organic PM that is the major component of fine PM in the area and was not discussed in this study. We are planning such a detailed study for the immediate future.

(20) *In the section of conclusion, the conclusion by comparing the hybrid method versus the equilibrium method is missing. The section of "conclusions" needs to be revised by including more discussions of your findings replacing the summarized list given in the present manuscript.*

After the recommendation of both reviewers, we have replaced the summarized list in the Conclusions section with a comprehensive discussion of the main findings of this study. The main results from the comparison between the hybrid and the equilibrium approaches have been added to this discussion.

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