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Atmospheric
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Discussions

Interactive comment on "Simulations of organic aerosol concentrations in Mexico City using the WRF-CHEM model during the MCMA-2006/MILAGRO campaign" *by* G. Li et al.

Anonymous Referee #2

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Review of of Li et al.: "Simulations of Organic Aerosol Concentrations in Mexico City Using the WRF-CHEM Model during the MCMA-2006/MILAGRO Campaign" submitted to ACP.

This paper describes a modeling study of organic aerosol (OA) concentrations in Mexico City during the MCMA-2006/MILAGRO campaign. The paper compares two different secondary organic aerosol (SOA) modeling frameworks that were implemented into the WRF-CHEM chemical transport model. The models are evaluated using ambient concentrations of OA factors inferred from positive matrix factorization (PMF) analysis of Aerosol Mass Spectrometer (AMS) data. One model is a more traditional approach that assumes primary organic aerosol (POA) is non-volatile and non-reactive and treats SOA formation using an Odum 2 product framework applied to traditional SOA precursors (VOC). The second SOA modeling approach treats the POA as semivolatile and reactive as well as uses some more recent parameterization for traditional SOA. The paper examines the sensitivity of the model predictions to a number of inputs. The paper concludes that the second approach better predicts the observed OA concentration, but that many uncertainties remain.

This is a topic that is of interest to the readers of ACP. Chemical transport models appear to chronically underpredict SOA and this paper critically evaluates some new approaches for simulating SOA. Although other recent papers in ACP have evaluated these SOA frameworks against the Mexico city data, this model adds some new dimensions to this analysis. The following comments need to be addressed before the paper should be published ACP.

Major comments

There have been some other recent papers in ACP (Hzodic et al. and Tsimpidi et al, both cited in the paper) that also apply this non-traditional SOA model to Mexico City. The paper needs to clearly state what it is doing differently than those previous papers (different episode, different composnent of model ,etc). It also needs to more directly compare the conclusions of these different papers with its conclusions. My sense is that the predictions here are pretty similar to Hzodic, but not as similar to Tsimpidi which attributed less SOA to the non-traditional SVOC and IVOC precursors. Highlighting the similarities and differences between this and previous attempts to use these models to simulate OA in Mexico City would help the community start to focus in on the strengths and uncertainties of the new approach.

Definitions – A challenge in this paper is that the NT-SOA model that blurs the traditional definitions of SOA and POA which can create confusion. At points my head was swimming with acronyms and terms, not sure what they mean (SVOC, IVOC, POA, POG, OPOG, etc) plus all the acronyms for the cases. Examples of problems include – “POA” appears to refer to the primary organic particles and to the combination of the primary SVOC vapors and particles. The also paper uses the term anthropogenic precursors to refer to both traditional anthropogenic precursors and the new SVOC and IVOC precursors. There are other examples of definitional problems (POG ,OPOG). A reader who is not intimately familiar with the approach is likely to be very confused. The paper needs to precisely define the different parameters and clearly describe how these concepts related to terms used in other papers (e.g. Hzodic, Tsimpidi, Shrivastava, etc). Getting the terms and definitions straightened out is a key need in this area.

Sections 2.2.1 and 2.2.2 A major different between the two model is that different yields are used for the traditional SOA precursors (e.g. pg 23957 says “updated based on laboratory results from recent smog-chamber” for NT-SOA model). That difference needs to be clearly stated. How different are those yields than those in the T2-SOA model. Please provide a table in the supplemental information with the stoichiometric yield coefficients and the rate constants for the different lumped species used in both models (NT-SOA and T2-SOA) for the traditional SOA precursors. For the NT-SOA what are yields for low and high NOx and how do you branch between. In addition, to providing the yield data (stoichiometric coefficients and rates) in a table, the authors need to provide a plot of yield curves in the supplemental material comparing the parameterizations for the traditional SOA would be very helpful. In addition, one could also simply say at a COA of 10 ug/m3 the yield of the NT-SOA model for some precursor is some multiple of the T2-SOA model in the main text to emphasize this issue here.

Page 29358 “The total amount of material (POA+SVOC+IVOC) introduced in the NT-SOA model is 7.5 times of the particle phase POA emissions.” This is presumably about modifying inventories. This needs to be greatly expanded. A factor of 7.5 is much larger than what was used in the original Robinson et al. (2007) Science paper. It is also much larger than the range of cases consider in Shrivastava et al. 2008. JGR paper. What is the basis for the 7.5. Are there any data that support using this or was it chosen because it made the POA calculations basically work. In addition what volatility distribution was used for the primary emissions? What is the particle phase POA emissions? This needs to be at least a paragraph, and presumably a short section since inventories are a key issue for the NT-SOA approach. Note that there is some description of the inventories for more traditional species in section 2.3. This should be pulled together. Have the earlier studies that have applied the NT-SOA model to Mexico City also used a factor of 7.5. It seems like this is a critical uncertainty. I was surprised that it was not considered in the sensitivity studies. The paper would be greatly improved if there was sensitivity runs done with this parameter.

Comments on Section 3.1.2 I was surprised the paper only compared predictions to the PMF factor. The paper should at least have some comparison (before comparing to the factors) about how well it does reproducing the overall OA. Note that total OA profile is shown in Figure 16, but is never really discussed in the paper.

Alot of the discussion in section 3.1.2 related to diurnal profiles, which are eventually shown in Figure 11 (etc). It is very hard to see things like two peaks in long time series such as the ones shown in Figure 4. The paper should move Figure 11 up much sooner and discuss it in section 3.1.2 (one can wait on discussing he sensitivity results later in the paper). It would be good to get that figure earlier.

Page 29363 “Although an updated 2006 MCMA inventory has been utilized in this study, our POA simulations are comparable to those reported by Hodzic et al. (2009) and Fast et al. (2009) when the POA is considered as non-volatile.” Presumably this is true because you bumped up the POA emissions by a factor of 7.5 in this paper. I.e. if you didn’t increase emissions a lot of POA would have evaporated and the comparisons with the non-volatile model would not look so good. These issues need to be discussed and they tie back closely to what you are doing with the inventory.

“The SOA production from anthropogenic precursors is increased by 33% in the NT-

SOA model compared to the T2-SOA model, indicating the high formation of SOA from anthropogenic aromatics in the NT-SOA model" Presumably this is because you are using different (and higher) yields than in the T2-SOA model. This needs to be pointed out as the explanation for this change. Since you are using different yields than it is not necessarily a fair comparison. Presumably a second factor of partitioning, in that the NT-SOA forms more OA than the T2-SOA model so even if the yield curves were the same the amount of SVOC in the condensed phase would be higher in the NT model.

Section 3.2.1 – Seems like a big uncertainty that is not considered is uncertainty in emissions of IVOC/SVOC.

Page 23970 "NT2-SOA model generally produces less POA mass than the NTSOA model at T0 and T1, especially during nighttime and rush hours, which is caused by the decrease of the enthalpy of vaporization of POG in the NT2-SOA model." I do not understand this. You are using Clausius Calpeyron to describe T dependence of C*? The greishop formulation has lower delta hvaps so should have lower temperature sensitivity.

Page 29376 – "The underestimations of SOA concentrations are principally caused by the OH treatment, emissions, aging of the SOA from anthropogenic precursors, and boundary conditions." What about aging of SVOC and IVOC? That mechanism is very uncertain.

Table 1 – Please also provide the same statistical measures for performance for O3 and CO so that the reader can directly compare how the model does at these sites against these pollutants in addition to SOA. Also adding statistics for total OA (in addition to those for POA and SOA).

This paper has 16 Figures. That seems like too many. For example, Figures 8 and 10 seem somewhat duplicative with Figure 4. Maybe just show figure 4 with total time series for the two base cases and then use the average diurnal patterns (e.g. Figure 11)? I thought Figure 11 was more useful in assessing model performance and should be discussed more prominently and earlier in the paper.

Figures 11-16 are different version of average diurnal profiles. Many of these are only briefly discussed in the text. It seems like combining these all of the OA (POA and SOA) into one multi-panel figure would help the reader get a quick overall sense of how the model performs for different cases.

Minor comments

Example of definitional problem – page 29356 "the oxidation of six primary organic gases (POG)" these are traditional SOA precursors. However on at bottom of page 29357 POG refers to the IVOC and SVOC vapors associated with the POA. Maybe POG is used for all primary organic gases, but this should be clarified. The paper then starts to discuss OPOG. . . A reader not very familiar with this approach will likely be very confused.

Page 23957 line 22 "In the base case, we assume that the organic condensable gases (OCG) produced from the oxidation of anthropogenic and biogenic VOCs do not react further with OH radicals to reduce the volatility. Tsimpidi et al. (2010) and 25 Murphy and Pandis (2009) have assumed that these first generation products continue to react and age. The importance of this anthropogenic SOA aging process will be explored in a sensitivity test in a subsequent section." This is out of place and belongs in the description of the treatment of traditional SOA (previous paragraph) and not the SVOC/IVOC SOA.

"The simulated organic aerosols in the WRF-CHEM model are compared with the AMS data analyzed using PMF at T0 and T1 (Aiken et al., 2009)." The paper should add one short paragraph summarizing what that analysis found for the period in question. OOA was X, HOA was Y, and BBOA was Z, etc.

Page 29362 –" The good agreement between the long-lived predicted CO and the corresponding measurements" there is only good agreement during the day? How well does the model reproduce the spatial variability of the CO?

Page 29364 “the saturation of the POG due to evaporation of POA” I don’t understand the word saturation?

Page 29364 – “With the significant decrease of POA emissions at T1, the NT-SOA model produces less POA than the T2-SOA model because most of the emitted POA evaporates to keep the saturation of the POG in the NT-SOA model.” Decrease in POA emissions? But you increased them by a factor of 7.5? There are also some definitional issues here. You are using POA to presumably refer to both the primary organic particles and the SVOC vapors? What is saturation of the POG?

Page 29366 – “anthropogenic precursors” this is another example of problems with definitions. Are anthropogenic precursors the traditional VOC precursors (e.g. single ring aromatic) or do they also include IVOC and SVOCs in the NT model. My sense is that the term is used different ways in different places. This needs to be made consistent.

Page 23957 line 1 – the “traditional” SOA formation . . . note that you have non-traditional SOA also formed in this model that is not represented using the four species basis set

Typo “in the basin are contributed to the development of high O3.”

Is all of the OA assumed to form a pseudo ideal solution?

Caption for Figure 4 (and other figures). “Diurnal variations” This is really the time series. Diurnal variations – or diurnal profile shown later.

Figure 10. Brown hard to differentiate from black. Change brown to some other color.

Caption for Figure 13 – labels for panels (a) and (b) are switched.

“the WRF-CHEM model underestimates the glyoxal concentrations” please be quantitative. By how much. A factor of 2, 5 . . .?

Page 29372 “At T1, the T2-SOA model significantly underestimates the observed POA concentrations but overestimates in the rest of the day.” I am not sure what this sentence is saying.

Page 29373 “One of the possible reasons for the daytime gap between the model and the observations is the underestimation of ARO2 during daytime,” This paragraph seems like it fits in the sensitivity study section. It is describing a new sensitivity study tweaking both inventories and glyoxal.

Page 29374 – “according to recent laboratory studies and model results” I am not aware of any laboratory studies that have looked at aging of anthropogenic SOA. All of the references given here are for modeling studies.

Page 29375 – “performs well in modeling the daytime O3 and CO,” How much better is the performance of the model for O3 and CO relative to POA and SOA. It seems like performs pretty well for POA?

Page 29377 – glyoxal contributing about 9.6% But in some formulations shown here it was much less. How about “at most 9.6%.”

Table 2 – It seems like you are repeating some of the cases here from Table 1. For example, the NT2E-SOA model is in both? But the numbers are different.

Figure 2 – It is impossible to see where the data are. How does the model do predicting the spatial variation of CO?

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