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Atmospheric
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Interactive comment on "Evaluating simulated primary anthropogenic and biomass burning organic aerosols during MILAGRO: implications for assessing treatments of secondary organic aerosols" *by* J. D. Fast et al.

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The authors would like to thank the reviewers for their thoughtful comments and suggestions. Our responses are given in the order they were listed, and we have included the comments in our response for completeness. The major changes include the removal of Section 4.5 on TOOC since we agree that a more comprehensive analysis using other sites is needed, the addition of source attribution for simulated POA that changes the discussion of biomass burning sources of organic matter, and additional discussion throughout the text regarding details of the model configuration. Many of the figures have also been altered. We believe that the revised paper has responded to all of the reviewer's comments.

Major comment 1: The major weakness of the paper was the lack of information and lack of discussion of the emission inventory. Given that the simulated meteorology appears reasonable, the problems in the model predictions of POA, CO, EC are likely due to the emission inventory. This is not a surprise, but this means that the papers needs a lot more discussion on how the inventories were developed and a discussion of what parts of the inventory may be causing the problems for model performance.

Response: To clarify issues raised by all the reviewers associated with the emissions, the material in Section 3.3 has been reworded to more clearly indicate 1) 2002 MCMA inventory included particulate speciation and this was used in the model runs, 2) the "average speciation" from the 2002 MCMA inventory was applied to NEI 1999 PM2.5 estimates, 3) VOC changes were made by Lei et al. and that gas phase emissions are either from 2002 MCMA as modified by Lei et al. or from 1999 NEI, and 4) VOC speciation and adjustment profiles were performed by Lei et al. We assume that the reviewer's comment on "what parts of the inventory" means differentiating between mobile, area, and point sources for anthropogenic emissions as well as differentiating between anthropogenic and biomass burning sources. It is difficult to separate out these components, because they are not simulated separately in the model (or by most chemical transport models) and measurements cannot necessarily be attributed to one or more sources. We have added discussion regarding missing components in the emissions inventories that affect the conclusions from our simulations.

Major comment 2: Are the gas phase inventories the ones from Lei et al. (2007)? Although Lei et al. started with a traditional bottom-up emission inventory, they tuned the inventory using ambient measurements to improve model performance. If this paper is using the tuned inventories, then the good model performance for CO may be an artifact of this tuning and not the underlying MCMA emission inventory. This is an important point to clarify. The "reasonable" agreement for TOOC might also be the result of tuning. The paper needs to provide more detail on how the VOCs were speciated (what source profiles were used) and whether there was any tuning done using ambient data. Was the same set of profiles used for both inventories (NEI and MCMA)? If any adjustments were made based on ambient data, were the same adjustments made to both inventories?

Response: We have revised Section 3.3 to provide more details on the emission inventory. We did employ the gas phase emissions from Lei et al (2007). They modified only the VOC emissions, but CO (as well as other quantities) was not modified. The total CO emissions summed over the metropolitan area agreed with the reported emissions in the official MCMA 2002 documentation. We have provided more information on the VOC emissions and their speciation, including how the speciation was extended to the National Emissions Inventory; however, this material is no longer relevant since the TOOC section has been removed at the suggestion of other reviewers.

Major comment 3: Inventories are also critical for understanding the POA results. The model treats the POA as non-volatile. The “reasonable” agreement of the predicted POA with the HOA and BBOA PMF factors (at least in the city) seem to suggest the non-volatile POA assumption is ok, which appears to contradict the recent paper by Robinson et al. (2007). Of course uncertainties in inventories probably make it difficult to state anything definitively on this issue of volatility (e.g. Lei et al. report biases in the MCMA VOCs emission inventories that were greater than a factor of 2). There is a brief paragraph in the discussion section on the issue of volatliity. It states that any evaporation in the city would cause larger underpredictions, suggesting that Robinson et al. overestimates volatility. However, some evaporation would improve predictions in downwind areas. The question about whether or not some of the POA should evaporates depends critically on how the inventory was constructed. If it is bottom up inventory based on emission factors and emission profiles measured using dilution samplers at high concentrations then the Robinson et al. (2007) results indicate that a substantial fraction of the POA should evaporate (and one would expect the model to overpredict

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POA if there are not other inventory problems). However, if the inventory is based on ambient measurements or has been tuned using ambient measurements similar to what Lei et al. (2007) did with VOCs then the evaporation predicted by Robinson et al (2007) is already included in the POA fluxes (and one would not expect the model to grossly overpredict POA if there are not other problems). In this second scenario, the non-volatile assumption is not too bad because it eliminates the big problem of partitioning bias in source tests but will not capture the second order effect of changes in partitioning as ambient temperature and concentration change. My understanding is that the MCMA PM2.5 emission inventories are not speciated and that previous modeling studies have used ambient measurements to determine speciation (Tsimpidi, A. P.; Karydis, V.; Zavala, M.; Lei, W.; Ulbrich, I.; Jimenez, J. L.; Molina, L.; Pandis, S. N. In Organic Aerosols in Mexico City: Sources, Formation Processes and Responses to Emission Controls, AAAR 27TH Annual Conference, Orlando FL, October 20–24, 2008; Orlando FL, 2008.). If the POA inventories have been tuned with ambient data, then the reasonable agreement would not contradict the results of Robinson et al. The details on how the POA inventory (both the NEI and the MCMA inventory) were constructed must be described to correctly interpret the results.

Response: The emission inventory is based on a bottom-up approach. Tuning of VOCs was then applied by Lei et al (2007). As stated in the previous comment, the primary particulate emissions were not “tuned”. The MCMA inventory was speciated by Lei et al. into elemental carbon, organic matter, other inorganic material, and crustal material, although they do not describe in great detail the particulate matter emissions in that paper. We have significantly modified the description of the emissions section to address this and other comments.

Major comment 4: In the discussion the paper states that “The degree of POA evaporation is unclear at present since the ambient measurements suggest a volatility much lower than that in the Robinson et al. (2007) model (Dzepina et al., 2009).” This is not correct. Robinson et al. (2007) and Dzepina et al. (2009) are measuring somewhat different things. Robinson et al. shows that substantial amounts of POA evaporate when you dilute it from high concentrations (1000s ug/m3) to ambient like conditions (10 ug/m3). Dzepina et al. shows that when you heat ambient OA (_20 ug/m3) it evaporates. Therefore, the Dzepina et al. says nothing about whether or not POA evaporates when you dilute it from high concentration conditions. They do say that Robinson et al. somewhat underestimates the amount of very low volatility material in the POA, but that will have not bearing on whether or not POA predictions are biased.

Response: We partially disagree with the reviewer on this point. Robinson et al. (2007) propose a volatility distribution for POA which includes information for the lower c* bins which are relevant under ambient concentration conditions, and Dzepina et al. (2009) applied a kinetic thermal denuder model to that distribution and found higher evaporation than in the measurements. However this was worded too strongly. The reviewer does have a point in that the Dzepina comparison does not allow the evaluation of the Robinson volatility distribution at concentrations much higher than ambient. Thus we have revised that sentence to read “The degree of POA evaporation is unclear at present. Ambient measurements suggest a volatility somewhat lower than that in the Robinson et al. (2007) model at ambient concentrations (Dzepina et al., 2009), but the volatility under higher concentrations which are most relevant for the evaporation of fresh emissions remains poorly characterized.”

Major comment 5: I found Figure 2a very interesting. The difference between the NEI and MCMA inventories striking. The NEI inventory suggest that all of the regional emissions are completely dominated biomass smoke? Is that correct? I realize that on some days there are significant fires in the regional inventory, but Figure 2a suggests that fires appear to dominate on essentially all days. Some pie charts comparing the relative importance of different source categories of POA (gas, diesel, biomass smoke, etc) for the NEI and MCMA inventories would be very useful. An alternative explanation is that there is something fundamentally different about how the NEI and MCMA inventories were constructed. For example, is there a partitioning bias in the NEI inventory

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and not in the MCMA inventory (i.e. if the MCMA inventory had been tuned but the NEI had not). Of course the differences here could be due to CO emissions and not the POA emissions.

Response: Indeed, there is likely something fundamentally different on how the two emission inventories were constructed, and the purpose of that figure was to show that difference.

Major comment 6: A final comment on inventories is that, given the problems with POA predictions, the paper would be improved if there was more discussion of what underlying components of the inventory may be causing the problems.

Response: By "components", we assume that the reviewer is referring to mobile, area, point, biomass burning, and biogenic sources. While we have modified the paper to examine POA from biomass burning and anthropogenic sources, we have not broken down the anthropogenic emissions into additional categories. Therefore, the figures now have broken down the POA between biomass burning and anthropogenic sources and the text has been modified accordingly. It would be difficult speculate further as to which sector in the anthropogenic emissions may contain the largest uncertainties.

Minor comment 1: At a number of points I thought that comparison of the model with the measured OA and the different PMF factors was unclear. For example, "Mean predicted POA was 2.3 μgm$-$3, while the mean observed total organic matter was 7.7 ugm$-$3. A somewhat better agreement is reached when predicted POA is compared with concentrations of HOA+BBOA (mean value of 4.7 ug m$-$3)." This sort of phrasing seems to imply that we would expect the POA to agree with the total OA. Given the substantial SOA that exists in Mexico City, I would expect that the model would almost always substantially underpredict the total OA. The paper would be improved if these comparisons with total OA and BBOA/HOA were more clearly laid out. Maybe have a short separate section which compares model predictions of POA to total OA. My perception is that for the most part the simulated POA was generally substantially lower

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then the observed OA consistent with there being lots of SOA that is not accounted for the in model. Periods such as that shown in Figure 15 (and places) where the model POA is greater than OA should be highlighted as suggesting major problems with the inventory. Once you have dealt with POA comparisons with total OA the paper could then focus on the comparison with the HOA and BBOA factors which should provide a better measure of model performance. Right now all this was woven together which I found confusing.

Response: We certainly did not intend that predicted POA was supposed to agree with total OA. At the suggestion of reviewer #1 we have greatly modified the figures on organic matter components. Now predicted POA is compared solely with total observed OA in one panel of plots to clearly show that predicted POA is less than total observed OA as one would expect.

Minor comment 2: The paper uses the term “dilution” to refer to dispersion of pollutants. This might be interpreted to imply changes in partitioning given the use of dilution samplers in the source community. Might be worth defining this term or using the word dispersion.

Response: “Dilution” has been replaced by “dispersion” or “vertical mixing” depending on the content of the sentence.

Minor comment 3: Abstract – “A much better agreement was found when modeled POA was compared with the sum of measured “primary anthropogenic” and “biomass burning” components on most days, suggesting that the overall magnitude of primary organic particulates released was reasonable” Not comparing with “measured” components, but to components derived using PMF

Response: The sentence in the abstract has been changed to indicate that the PMF components are not measured quantities, but are derived. We have also made similar changes elsewhere in the manuscript.

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Minor comment 4: “anthropogenic and biogenic precursors contribute to SOA formation is far from complete. It is therefore not surprising that simulated organic aerosol mass from recent modeling studies have been shown to be as much as two orders of magnitude lower than observed for photochemically aged air masses (e.g. Volkamer et al., 2006).” It is not clear that Volkamer is showing that the organic aerosol concentrations are being underpredicted by two orders of magnitude. My interpretation is that they are showing that the models underpredict the SOA formation by a factor of 10 or more.

Response: Volkamer’s figure 2 shows models underestimating SOA by a factor of 5 – 8 for photochemically “fresh” air masses when applied to MCMA 2003 that increases to a factor of 10 – 100 for photochemically “aged” air masses when applied to ACE-Asia 2001. So our phrasing refers to the upper bounds. We did not want to refer to a lower bounds because some recent studies after Volkamer’s work are achieving better agreement (e.g. Hodzic et al. 2009). Nevertheless, the text has been change to include the entire range in Volkamer’s figure. One must not be mislead by one figure, however, since local simulations of SOA are not necessarily a factor of 10 or more too low.

Minor comment 5: “The concentrations of most other species are produced primarily by local emissions rather than by long-range transport.” Local emissions confusing. Presumably this is emissions within the modeling domain versus outside the domain?

Response: Yes, we meant emissions within the modeling domain. The sentence has been changed to clarify.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4805, 2009.

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