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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #3

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This paper evaluates the performance of WRF-chem using data collected during the MILAGRO study in Mexico City. The evaluation considers meteorology, CO, primary organic aerosol (POA), elemental carbon, and total observed organic carbon. The model did a reasonable job reproducing the observed meteorology and CO concentrations. There were problems with the POA and EC results, especially outside of the city. Overall, I found the paper interesting, but a number of issues need to be addressed before the paper is suitable for publication in ACP.

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.

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?

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

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the Robinson et al. (2007) results indicate that a substantial fraction of the POA should evaporate (and one would expect the model to overpredict 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.

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 ($\sim$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

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not bearing on whether or not POA predictions are biased.

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 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.

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.

Minor comments

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

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most part the simulated POA was generally substantially lower 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.

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.

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

"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.

"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?

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