

Interactive comment on “Modeling organic aerosols during MILAGRO: application of the CHIMERE model and importance of biogenic secondary organic aerosols” by A. Hodzic et al.

Anonymous Referee #1

Received and published: 18 June 2009

This paper presents a sophisticated model that attempts to predict both primary and secondary organic aerosol (POA and SOA) mass over the Mexico City metropolitan region, and compares the results with extensive measurements made at various sites during the MILAGRO 2006 experiment. In my view the main conclusion reached by this analysis is that POA is predicted reasonably well by the model, but relative to POA, SOA is not. These results are consistent with other published studies from data collected in Mexico City and other locations. Thus, in this regard the paper makes a contribution to the large and growing body of evidence suggesting that SOA production, based on yields from environmental chamber experiments, is not accurately described in current models. The paper, however, goes on to make some further conclusions,

C2008

which in my view are interesting, but largely unsupported and must be highly qualified. Generally, given the staggering level of uncertainty in many aspects of this area of research, I think the authors should view the model results with more skepticism and provide some type of uncertainty analysis. It is not clear to me that the model is really doing that great of job since even some form of general agreement between model and measurements is not proof that the emissions and physicochemical processes are correctly represented in the model. For example, general agreement in diurnal SOA trends can be simply due to reasonably correct meteorology and OH trends. Overall, to me it would be most insightful if the philosophy of this work was to explore model sensitivities to SOA predictions, such as biogenic SOA, enhanced partitioning (as done, but expand on this), instead of the goal that seems to be to get the model to match the data. For example, why not test or break down partitioning to liquid water (ie, the glyoxal-type) route vs partitioning to OA; how do they compare as a function of time of day, what type of VOC (say glyoxal or generic water-soluble VOC) level would be needed to explain all the observed OOA when partitioning to water vs OA is important, what type of VOC level would be need for partitioning to OA, how do these compare to masses of all aromatics, etc. There are many competing SOA theories, why not test these in some rudimentary ways and try to see what, or what combination, is most plausible?

One of the main new results espoused by the authors is the importance of biogenic SOA to the overall levels of measured organic aerosol in Mexico City. This is even noted in the paper's title. I believe this assertion is greatly overstated: the authors really show no direct proof in either in the measurement data or the model results to support this. First, two references are cited to support that there is evidence for extensive contributions of biogenic SOA, Aiken et al, (2009b, in preparation) and Marley et al, (2009). The Aiken paper, which I have not seen since it is in preparation, I presume is based on AMS PMF analysis and AMS biomass burning tracers, which is likely based on or “verified” from the source apportionment study of Stone et al (based on 12 or 24h HiVol samples, levoglucosan as a biomass burning tracer, and a Chemical Mass Balance

C2009

(CMB) analysis). Considering the combined uncertainty in the 14C measurements (eg, artifacts from HiVol samples, etc, were for example the HiVol OCEC compared to online data?) and uncertainty in AMS-predicted biomass burning SOA mass, is there conclusive data to show evidence for biogenic SOA. This has not been provided in this paper. The Marley reference appears to be wrong. The Marley paper I believe the authors are wanting to reference, as far as I can tell, makes no conclusion on biogenic SOA mass. Some type of confidence level should be provided to support the statement that experimental data provides evidence for biogenic SOA in Mexico City. Despite this lack of quantitative data proving biogenic SOA, the authors have added biogenic emissions and SOA formation routes to the model, achieved somewhat improved comparison to the data (especially at night) and conclude that they have made a significant new finding. Uncertainties in measurements aside, the large uncertainties in predicting SOA mass alone makes this conclusion suspect. More specifically, given the models are missing a great portion of the SOA (i.e., much is unknown), just because known SOA mechanisms (eg aromatics, nighttime nitrate radical chemistry) can't explain the data, and regional biogenic SOA adds some improvement, this does not prove that biogenic SOA is important. In summary, the biogenic SOA hypothesis may be correct, but I don't think the authors have made a scientific case for this conclusion, they have only come up with a plausible explanation; the paper currently overstates this result.

A real uncertainty analysis for both the data and model predictions throughout the paper would provide more confidence in the results (i.e., comparisons). For example, I would find scatter plots of predicted vs measured, including some error bars, for the various components compared very useful. These could be further broken down into night or day, or time period during the study under different emission/weather conditions, etc. The time series plots showing comparisons are too coarse to be useful (although they do give an indication of temporal agreement), and comparisons based on average diurnal profiles don't provide a quantitative assessment (much useful information is averaged out). The authors do give statistical results, eg, bias, correlation etc, but it would be more useful when combined with scatter plots. (Note, some of the

C2010

Figs, 5 and 6 (the time series plots) are of very low resolution and quality).

Other Comments.

Pg 1220 lines 19-22, why not discuss 14C data here – it is the only direct measurement of biogenic vs anthropogenic C, I don't think the ref. cited here are direct measurements.

Pg 12224 line 23-24, discuss errors associated with size miss-match between model and measurements, which could be especial high for biomass burning aerosols with significant mass above 0.6 um.

Pg 12232 line 17-18 . . . mid-day production of SOA that starts around 12:00LT. . . Are the authors really stating that this is typically when SOA production begins? There are a number of published papers from Mexico City that shows SOA production consistently begins roughly an hour after sunrise (following OH). This brings up the issue of the discussion dispersed throughout the paper of "afternoon" or late afternoon SOA production. It would be helpful if the authors gave more precise times (more on this in next comment).

Pg 12236 line 15-16, this sentence is not clear – why is the morning SOA production compared to the afternoon production rate? It is then stated that there is similarity in SOA production between modeled and measured? Furthermore, conclusion (IV) seems to contradict this. Conclusion (IV) is also unclear: when discussing the factor of two, is this in regard to concentrations or production rates. I find the whole discussion of morning vs afternoon comparisons confusing. Similarly, conclusion (VIII) is also unclear. Why not pick a period of 2 days or so that demonstrate that morning SOA predictions agree better than afternoon and plot predicted and observed (maybe highlight the difference). Include error bars. This would also reduce confusion on what times are exactly meant by morning and afternoon. Comparing diurnal averages from the whole study are highly suspect and in my view do not show much.

C2011

It would have been helpful to me if the meaning of Corr was defined in the figure captions (eg, r^2 or r) instead of trying to hunt it down in the text (which is not easy to find).

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 12207, 2009.

C2012