

Review of ACPD-9-12207-12281-2009 by Hodzic et al., entitled: «Modeling organic aerosols during MILAGRO: application of the CHIMERE model and importance of biogenic secondary organic aerosols».

First of all, the authors would like to thank referee #1 for his constructive comments and suggestions. We have addressed all of the reviewer's concerns as described below. The main addition to the revised manuscript concerns the assessment of the model predictions against independent estimates of biogenic SOA derived from measurements. We believe that this has strengthened our conclusions and demonstrated that the biogenic secondary organic aerosols are present in Mexico City.

Responses to Referee #1

R1.0) 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, 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?

A1.0) We agree that SOA formation pathways are highly uncertain and that a good comparison of modeled vs. measured SOA is not proof that the model is producing SOA for the right reasons. Other precursors with similar lifetimes and overall yields could

also explain the observed SOA levels. We have clarified the paper by adding the following text (page 12250, line 17)

« Obtaining perfect agreement with the observed SOA values is extremely challenging, and it is beyond the objectives of this paper, because of large uncertainties involved at every step of the SOA modeling. We have shown the importance of biogenic precursors in the formation of SOA in this region, but there are many more areas of uncertainties and directions for improvement to be considered, such as the formation of SOA from S/IVOCs (Robinson et al., 2007), in clouds (Lim et al., 2005), by reactions in the aerosol water phase (Volkamer et al., 2009), etc. One should keep in mind that other precursors with similar lifetimes and overall yields could lead to similar results and explain the observed SOA levels. The results of the present work have an important impact on the way the future modeling studies in this region should be designed.»

We agree that there are many competing mechanisms being proposed to explain the fact that SOA measurements in polluted areas such as Mexico City are much higher than those predicted by traditional SOA models. However testing all of the new theories is beyond the scope of this first paper, which is already quite long. If we added additional mechanisms the paper would become too long and confusing, and the conclusions of the current study would be harder to appreciate. We have chosen in this paper to limit our discussion to the role of traditional anthropogenic and biogenic precursors in the SOA formation within Mexico City, and the uncertainties related to the partitioning assumptions. Our results show for the first time that biogenic precursors in the Mexico City region are important contributors to the SOA formation, and cannot be neglected in modeling studies. We do plan to follow this work with an additional publication on SOA formation from SVOC/IVOC.

With respect to glyoxal or water-soluble species, with our current model formulation the fraction of the SOA that is formed by partitioning into the water phase is small, as it has been documented in previous studies (e.g. Pun et al., 2003, cited in the manuscript).

In order to consider not just partitioning but also chemical reactions on the water phase, we could only do this for glyoxal as this is the one system that has been parameterized (Volkamer et al., 2007). This is a very interesting suggestion but it would require much additional work, in particular because glyoxal is not represented explicitly in the chemical mechanism used in CHIMERE. Thus any attempt to implement a realistic glyoxal uptake would require major changes to the chemical mechanism, which are beyond the scope of this paper. In addition Volkamer et al. (2007) and Dzepina et al. (2009) estimate the contribution of glyoxal SOA as ~15% of the total SOA, so based on our current understanding although an important contributor, this is not the main missing piece to close the budget of SOA formation in Mexico City.

R1.1) 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 (CMB) analysis). Considering the combined uncertainty in the ^{14}C measurements (e.g, 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.

A1.1) The main criticism of the reviewer #1 concerns the lack of experimental proof to support our conclusions on the role of biogenic precursors in the SOA formation in Mexico City. We want to make several points in response:

(a) We agree that the measurements summarized in our ACPD paper do not provide direct evidence for the impact of biogenic SOA in Mexico City. However neither do they provide direct evidence against this impact. The citations to the Marley and Aiken papers refer to the surprisingly high fraction of modern carbon which is observed in Mexico City even during periods in which biomass burning is suppressed. The OC measurements from one of the ^{14}C analysis (PSI) have been compared to other OC measurements and found to be consistent (Aiken et al., 2009b). Since the enhancement of modern carbon is observed during periods in which regional biomass burning is suppressed, this conclusion is not affected by the uncertainties in the AMS quantification of BBOA.

(b) The strong piece of evidence for BSOA arises indeed from the model. We have used the MEGAN emissions model which is thought to provide at least the right order-of-magnitude for biogenic emissions, and modern biogenic SOA yields. Tunved et al. (2006) and Chen et al. (2009) show that the SOA yields of biogenic hydrocarbons under low-

NO_x conditions are in reasonable agreement with observations in Finland and the Amazon, respectively. Capes et al. (2009) show that the yields may underestimate the biogenic SOA in Africa, although their conclusions are less certain due to the difficulty in evaluation the amount of reacted precursors on a given air mass in their study. Thus if isoprene emissions are thought to be reasonably captured by MEGAN and isoprene SOA yields are thought to be reasonable or perhaps underestimated, the amount of SOA predicted by our model is consistent with the current knowledge in the field. Thus we think that the model results by themselves are sufficient evidence to postulate the importance of BSOA as a contributor to the background SOA in Mexico City at the ~1.5 $\mu\text{g m}^{-3}$ level.

(c) Importantly, independent estimates of daily-average biogenic SOA concentrations at T0 and T1 during MILAGRO became available to us recently (after our paper and its reviews had been posted in ACPD) from the work of Stone, Schauer et al., (2009). Specific tracers for different types of biogenic SOA were measured as described in Kleindienst et al. (2007) and used to estimate biogenic SOA concentrations arising from each precursor using SOA/tracer yields measured in the laboratory. Based on this method, 1.14 $\mu\text{g/m}^3$ (+/- 0.22) of biogenic SOA was found at T0, and 1.35 $\mu\text{g/m}^3$ (+/- 0.24) at T1, which compares reasonably well with predicted BSOA levels and provide independent and specific experimental evidence for the presence of non-negligible amounts of biogenic SOA in the Mexico City area during MILAGRO. The following modifications have been included in the manuscript:

Abstract p.12209: «Model sensitivity results suggest that observed nighttime SOA concentrations are strongly influenced by a regional background SOA (~ 1.5 $\mu\text{g/m}^3$) of biogenic origin which is transported from the coastal mountain ranges into the Mexico City basin. The presence of biogenic SOA in Mexico City was also confirmed by SOA tracer-derived estimates that have reported 1.14 (+/-0.22) $\mu\text{g/m}^3$ of biogenic SOA at T0, and 1.35 (+/-0.24) $\mu\text{g/m}^3$ at T1, which are of the same order as the model. Consistent with other recent studies, we find that biogenic SOA does not appear to be majorly underestimated by traditional models, in strong contrast to what is observed for anthropogenic pollution.»

Manuscript Section 5.4.1: «The predicted concentrations of biogenic SOA from our CHIMERE/MEGAN model have been compared with the measurement-based estimates of biogenic SOA that recently became available from the work of Stone et al. (2009). The Stone et al. estimates are based on measurements of specific tracers of different biogenic SOA precursors from 24-hr filter measurements at T0 and T1. The total SOA arising from each biogenic SOA precursor is then estimated as the tracer concentration multiplied by the SOA/tracer concentration average from chamber experiments as reported by Kleindienst et al. (2007). Figure 11 shows that the model daily-averaged BSOA levels are of the same order as the measured ones for both T0 and T1: tracer-derived (model predicted) BSOA values range from 0.3 to 1.8 $\mu\text{g/m}^3$ (0.7 to 2 $\mu\text{g/m}^3$) at T0, and from 0.4 to 2.1 $\mu\text{g/m}^3$ (0.5 to 1 $\mu\text{g/m}^3$) at T1, respectively. The total model BSOA and also the precursor-specific model BSOA are generally within a factor of 2-3 of the observations. This contrast with the strong underprediction of the anthropogenic SOA reported here and in previous studies in Mexico City. It is also consistent with other studies which have

reported that biogenic SOA models typically predict the right levels of SOA observed in the field and do not show order-of-magnitude underpredictions (Tunved et al., 2006; Chen et al., 2009).»

The figures have been renumbered accordingly after the addition of Figure 11.

R1.2) 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 Figs, 5 and 6 (the time series plots) are of very low resolution and quality).

A1.2) We agree that a real uncertainty analysis on measured and predicted values would be useful, however a reasonably rigorous uncertainty quantification and analysis of the causes of uncertainty in the model output is a project by itself that would require an additional paper. Such a study can only quantify the uncertainty of the models that we have implemented, and cannot quantify the bias due to systematic problems in model structure, e.g. the omissions of some important mechanisms, which likely dominate the total uncertainty here and are impossible to completely quantify at this stage.

Regarding the request for scatter plots, in our opinion the paper already contains statistical indicators that quantify the strength of the model/observation agreement in addition to the time-resolved plots (time series – Fig. 6) and daily-averaged profiles. From the existing plots, the reader can already appreciate the model performance in simulating the day-to-day variability of observed species under various meteorological conditions and time of the day. The uncertainty interval is given for modeled and observed diurnal profiles, and indicate the variability associated with the comparison results. Statistical indicators such as bias, RMSE, and correlation coefficient give a quantitative indication on the strength of this comparison. Scatter plots will only provide information on the overall bias (slope of the linear regression) and the scatter/correlation between model and observations, parameters that are already available in the paper. Therefore, we feel that adding scatter plot won't bring additional information on the quality of the model/observation comparison and decided not to include it in the paper.

We agree that unfortunately the time series plots appear to be of very low resolution in the ACPD version and we apologize for our oversight of that detail during the ACPD-proofing stage. We will make sure that the plots included in the final ACP version are of high quality.

Other Comments.

R1.3) 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.

A1.3) It is unclear to us why the reviewer is making this suggestion. At this point of the paper we are discussing some additional biogenic SOA mechanisms that are used in our study, in addition to the ones that we have already described earlier in section 3.2. It is not clear why the 14C results would be more relevant to these specific biogenic SOA mechanisms than to the ones we have discussed already at this point. The motivation to investigate the potential impact of biogenic SOA based on the modern carbon analyses was already given earlier in the paper (p.12214 L1-3) with the following text: "However, the high fraction of modern carbon observed even in periods with low biomass burning (Aiken et al., 2009b) provides additional motivation to investigate this topic."

R1.4) 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 μm .

A1.4) We have added the following text to address this point:

"The size cut of the model is larger than that of the measurements, and this introduces some additional uncertainty in the comparisons, but it should provide an upper limit of the expected SOA concentration."

The reviewer states that biomass-burning aerosols tend to have significant mass above 0.6 μm , but does not provide any reference for this statement. First we note that the size cut of the AMS under the conditions of Mexico City is approximately 0.7 μm in physical diameter (~ 1 μm in vacuum aerodynamic diameter) and not 0.6 μm , as described in detail in Fast et al. (2009). Second, our understanding from the literature both in Mexico City and elsewhere is that biomass-burning aerosols are dominantly in the submicron mode. For example Yokelson et al. (2007) report on their paper about the emissions of the forest fires around Mexico City that "Both the measured and previously published particle size distributions show that particles of diameter below 1 micron account for nearly all the fine particle (PM_{2.5}) mass emitted by biomass fires (Radke et al., 1991)." Indeed size distributions of primary BB particles typically show a peak around 200-400 nm (e.g. Dubovik et al., J. Atmos. Sci., 2002; Reid et al., ACP 2005; Clarke et al., JGR 2007) and thus should be squarely in the AMS measurement range. Primary biogenic aerosol particles (PBAP; e.g. Spracklen and Heald, GRL, 2009) may have a much larger fraction of their mass above 1 μm , however PBAP are not represented in CHIMERE at present.

R1.5) 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).

A1.5) We thank the reviewer for catching this mistake. Indeed as shown in Fig. 7 SOA production in the model starts between 7 & 8 am local time, and peaks around noon LT, depending on the site. We have modified the text as follows to clarify this point:

“(Figure 7) shows that the model correctly replicates the gradual increase in TOA concentrations during the day caused by both early morning primary emissions (13UTC, i.e. 7LT) and the increase of SOA concentrations starting at sunrise (7-8LT) with SOA concentrations peaking around mid-day (18UTC, 12LT).”

R1.6) 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.

A1.6) We again thank the reviewer for catching this additional error, due to our confusing the UTC afternoon (which is the local morning) with the local afternoon. We have rephrased the sentence on P12236 L15-16 to read:

“As illustrated in Figure 7, the predicted morning average SOA production rate of $4 \mu\text{g m}^{-3} \text{hr}^{-1}$ is only a factor of 2 lower than the intensity of the observed increase at the urban site in the morning, although the discrepancy in the observed concentrations grows to a factor of 5-10 by 20UTC (i.e. 14LT), consistent with the findings of Volkamer et al. (2006), Kleinman et al. (2008), Dzepina et al. (2009), and Tsimpidi et al. (2009).”

Conclusion (IV) is in agreement with the revised text, and refers only to concentrations except for the morning rise in SOA.

Conclusion (VIII) has been rewritten for clarification as:

“The comparison of daily SOA profiles suggests that the model model/measurement discrepancies could arise from too high volatility of the model SOA, which would lead to the model’s inability to retain more permanently the freshly formed secondary organic aerosols inside the particulate phase during the afternoon hours. Although sensitivity

runs with enhanced partitioning toward the aerosol phase provided more realistic daily average SOA concentrations, the large afternoon discrepancies remained. The model inability to simulate this persistent SOA fraction could be explained by missing processes that reduce the vapor pressure of semivolatile organic species, such as oligomerization. However the discrepancies can also be due to missing precursors, rather or in addition to missing processes for the precursors that are represented in the model.”

We disagree on the need to show a 2-day comparison, as this information is already available in the time series comparisons (which we will ensure are reproduced at full page width in ACP) and the diurnal cycles. We have also added gray stripes for nighttime periods (18:00h – 5:00h LOC) to aerosol time series plots to allow the reader to better evaluate the discrepancies vs. time of the day.

R1.7) 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).

A1.7) This is a commonly used abbreviation for the correlation coefficient. Its meaning is now defined in the figure captions.

Additional Remark:

The authors would like to change the main title of the paper to: «Modeling organic aerosols during MILAGRO: importance of biogenic secondary organic aerosols». There is no need to be specific on the modeling tool that has been used here to derive the conclusions concerning the SOA production. Actually it is rare to have the model (or instrument) name mentioned in the title (e.g. Simpson et al., 2007; Fast et al., 2009; Tsimpidi et al, 2009, etc...) unless the paper is a technical description of these tools. This new title is also more concise and focused on SOA and BSOA.