

Interactive comment on “Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS” by M. C. Woody et al.

Anonymous Referee #1

Received and published: 2 December 2015

Review of “Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS” by Woody et al.

The authors present results from simulations using the CMAQ model coupled with a VBS representation of SOA formation to investigate organic aerosol in southern CA, specifically in and around Los Angeles. They compare their model results with an alternative model, that uses the “standard” SOA treatment in CMAQ (referred to as CMAQ-AE6). They find that the CMAQ-VBS predicts substantially more SOA than the CMAQ-AE6, but that both substantially underpredict the observed SOA amounts. They find that the predicted primary OA (POA) concentrations are more similar to the observations, although generally miss an observed mid-afternoon peak. They conclude that the SOA underprediction is driven by a few different factors: too slow of photochemical

C10014

oxidation, too low of “intrinsic SOA formation efficiency” (i.e. yields) and either too low of emissions or too great of dispersion, justifying these conclusions through a variety of different comparisons. Overall, I find this to be a well-done study, but at times find the presentation to be difficult to follow due to imprecise and variable terminology and to the high density of the writing. I think that greater use of tables to summarize some of the results could be helpful in the cases where many different things are compared. I have a number of specific comments, many of which can be addressed through a greater focus on clarity in the presentation. I believe that this paper should be publishable once the comments are addressed.

Specific Comments (chronological)

P26746, L12: What is meant here by “semi-explicit OA treatment” and “SOA lumped by parent hydrocarbon”? The products forming SOA in this model are semi-volatile, as they are in the VBS model, correct? And are not most species treated via a 2-product framework, with the exception of isoprene?

P26748, L2: The authors seem to be implying that an O:C > 0.3 indicates a large contribution from SOA. If this is their intention, this thought should be made explicit.

P26751, L4: I do not entirely follow the arguments resulting from the statement that fragmentation is more important for biogenic SOA than for POA. I would think the appropriate comparison is between biogenic SOA and anthropogenic SOA from aromatic compounds, which are the species to which ageing is applied by default. The comparison between biogenic SOA and POA does not seem relevant here.

P26751, L8: It would be could if the authors could clarify further what they mean when they say that “a portion...of the OA mass [is] shifted from the POA to the SOA set.” It would seem more appropriate to me to have the “SOA” set include all vapors and the “POA” set to include only condensed-phase material.

P26751, L10: It is not clear here what is meant by “oxidized POA”. Does this refer

C10015

to “POA” vapors that are oxidized? It would be useful if the authors were to clarify the distinction between gases and condensed-phase material more explicitly. I am finding the POA/SOA distinction here to be somewhat difficult to follow. Along these same lines, the terms SVOC and IVOC could be more explicitly defined for the reader (especially in the context of P26751, L6-14 and how this relates to the information on the previous page). I think that it could be helpful to move the paragraph starting on Line 15 on P26752 to earlier in this section, probably before discussion of the SOA treatment.

P26753: The discussion of some of the caveats associated with estimating S/IVOC emissions, especially source-specific emissions, is very helpful, although it would be even better if the authors were to put this in the context of more recent measurements and constraints on S/IVOC emissions in addition to the relationship with other model treatments. Some of this is provided later in the manuscript (P26763), but it would seem appropriate to include some discussion here.

Figure 1: It would be useful if the authors were to put a box around the LA area to guide the reader to that location.

Table 3: It would be useful if the authors were to provide the equations used to calculate the statistical metrics.

Regarding the supplemental figures, it would be useful if the authors were to (a) have the figures included in the main text in order and (b) to include mention of all supplemental figures in the main text. The reader should be made aware of the content of the supplemental within the main text.

P26755, L27: The authors note that larger model-measurement gaps were seen during photochemically active periods when OOA concentrations were higher. In looking at Fig. 2, this is not abundantly apparent to the reader. After estimating some numbers off of the figure, it seems to me that this is not universally true. For example, the observed/model ratio on 4-June (when OOA is higher) is only ~ 2.3 but is ~ 3.3 on 8-

C10016

June when OOA is lower. It would be useful if the authors were to formalize this thought through an explicit demonstration, for example by plotting the observed/model ratio as a function of observed OOA concentrations.

Fig. 4 vs. Fig. S8: To facilitate comparison, it would be useful if the Fig. S8 were modified to separate the CMAQ HOA and CIOA.

P26756, L21: I find the meaning of this sentence to be somewhat unclear in terms of what is meant by “theoretical partitioning” in the context of “AMS measured OA”. Do they mean that the larger CIOA concentrations lead to lower concentrations of semi-volatile vapors due to enhanced partitioning? I think this is the case, but it could be stated more explicitly.

P26757, L3: The authors conclude that the underprediction of CIOA even using non-volatile CIOA indicates that emissions were low. Couldn't an overestimate of the boundary layer height, especially at night, also be a contributing factor when considering absolute values? The authors might consider normalizing by background corrected CO, as they do with the SOA, to account for issues of dilution.

P26757, L18-21: The authors conclude based on the nighttime underprediction that low emissions are likely the reason for the underprediction during the daytime, rather than photochemistry. However, if the diurnal emissions profile is incorrect, it may be that the daytime underprediction is due to photochemistry (and low emissions) while the nighttime underprediction is due to low emissions alone. I suggest that the authors need to make a stronger argument as to how the nighttime underprediction truly constrains the reason for the underprediction during the daytime given an uncertain emissions timing. It is argued that the slower growth of the CIOA during the daytime compared to SV-OOA is suggestive of low emissions, as opposed to photochemical influence, but isn't it possible that the reaction rates are different, leading to differences in the timing when coupled with transport?

Figure S11: The meaning of “POA” in this figure is unclear. Is this CIOA + HOA (to-

C10017

tal POA) or just the HOA-type? In the main text, “POA” seems to be used to mean “non-CIOA POA” (Section 3.2.2). Similarly in Fig. S12 This should be clarified and terminologies used consistently throughout. Perhaps the authors could adopt the terminology “oPOA” to indicate “other POA” aka non-CIOA POA.

P26759, L2: The “opposite” behavior of the modeled non-volatile oPOA compared to the observed HOA is similar to that of the semi-volatile oPOA, correct? As stated, this makes it seem that such “opposite” behavior is only for the non-volatile treatment, but Fig. 4 suggests that there is a similar “opposite” behavior for the semi-volatile case.

P26759, L17: Is this discussion associated with “ageing” in the context of POA indicating that including some SOA as POA would help? This is not entirely clear to me, I think in part due to my not entirely understanding the model definitions of POA and how/whether the “POA” category includes SOA (here, I think, referred to as oxidized POA). It would be useful if this could be clarified here and/or within the methods section.

P26759, L26: Regarding the conclusions associated with the NEI, again I think that it would be helpful if the authors were to more explicitly define their categorizations of what counts as POA. I find it somewhat difficult to understand how underestimates of SVOCs leads to underestimates of POA, unless oxidation of SVOCs produces POA. I think that it does in this model, but the I am finding the terminology to be difficult to follow. I think that the authors could make this work more easily readable by adopting more precise language. For example, if their POA really equals POA + some fraction of oxidized SVOCs, then a better name would be POA+SVOCOA (or something like that, as I realize that is a cumbersome terminology). But even that might not be sufficient, because if I am understanding correctly some fraction of SVOCs contributes to a different SOA category. Ultimately, I strongly encourage the authors to rethink their overall terminology to make it more easily accessible to the reader.

P26760, L9: It would be useful if the authors were to point the reader to a figure or

C10018

table at this point. Perhaps Fig. 3 and Fig. 4. Along these same lines, it would be useful if the authors were to move some of the additional information (specifically the LV-OOA and SV-OOA diurnal profiles) in Fig. S8 to Fig. 4b.

P26760, L12-13: It would be useful if the authors were to note that the cited studies were not for LA but for other urban regions.

P26762, L2: The authors use $-\log(\text{NO}_x/\text{NO}_y)$ to estimate photochemical age and compare observed values at Pasadena to their modeled values. They conclude that the modeled photochemical age was too small by a factor of 1.5. However, doesn't this analysis also rely on the spatial distribution of NO_x emissions being correct? NO_x is converted to NO_y over time, but if the NO_x inputs are too low or too high along the transport pathway then the photochemical age will be incorrect. It could potentially be useful to also consider the NO_x/CO ratio. Or, potentially, the toluene/benzene ratio (although the timescales may be too short for this to be a useful photochemical clock). Also, I find the second half of this sentence to be difficult to follow, in particular the section starting “. . .but not on SOA.” I suggest the authors might be more explicit here.

Fig. 5: What should the reader take away of the apparent intercept in Fig. 5a not being 0? If the fit were performed without constraining the fit to go through zero, a steeper slope would likely be obtained, correct? In Fig. 5b, is there a reason that the authors chose to not present the model results in the same manner as in Fig. 5a, i.e. using a Gaussian density kernel estimate to colorize the points? There seem to be a lot of points in the CMAQ-VBS simulations that fall along a line with much lower slope than the fit slope, which was forced through zero. The authors should also note in the main text (and/or the caption) that the fits were forced through zero.

P26763, L1-5: The authors concluded that the SOA production efficiency was under-predicted by a factor of 1.6-2. They note that Zhang et al. (2014) indicated a potential underestimate in SOA production by a factor of 2-4 from losses of SVOCs to chamber walls, but also that this was only for alkanes and toluene and was specific to the

C10019

chamber used. They then conclude that SVOC wall loss does not likely account for the entire underestimate of SOA production efficiency. I do not entirely see how this conclusion is justified based on the statements given. As a hypothetical, what if the losses were greater in other chambers? Also, a factor of 2-4 is greater than a factor of 1.6-2. I suggest that the authors revisit the justification for this conclusion.

P26763, L13: The authors note that the use of the results of Jathar et al. (2014) to update the IVOC emissions and parameterization in CMAQ-VBS could help to bridge the gap between model and measurements, and then go on to perform some sensitivity tests by scaling up the S/IVOC emissions. However, it would be useful if the authors were to more specifically make a connection with the Jathar et al. work. What does that work imply about what is correct? Are the test simulations consistent with those results?

P26764, L11: Are the measurements referred to here from Baker et al. (2015) or Zotter et al. (2014)? This should be clarified. Also, it would be useful if the authors could indicate (a) by how much >1 the non-fossil fractions were and (b) why contributions from a medical waste incinerator would lead to an estimated non-fossil fraction > 1 .

Section 3.3: After reading through this section a few times, I suggest that addition of a summarizing table could be quite helpful that has entries for the different combinations of species considered (e.g. CMAQ-VBS fossil fraction with EC and without EC).

Fig. 8: It would be very useful if the authors were able to split their "A_AGE" category into aged SOA originating from VOCs versus that from IVOCs. Also, I do not see the "B_IVOC" category in the figures, although one is indicated in the caption. To which species does this refer? Finally, it would be useful if the authors were to include the total AMS OOA on this figure, for comparison and reference to Fig. 4. Clearly, the predicted OOA is still greatly underpredicted even after addition of ageing of biogenic species.

P26767, L21: While I agree that the ageing scheme represents a "technique to in-

C10020

crease model SOA yields," I find the words "similar to" in the context of the Zhang et al. (2014) findings to be a bit awkward as these refer to different physical processes. Additionally, Zhou et al. (2015, ES&T, 49, 2245–2254) demonstrate that the addition of ageing on top of existing parameterizations leads to an overprediction of SOA concentrations in chamber experiments, suggesting that such increases in SOA concentrations may result for the wrong reason. I suggest instead the authors state something to the effect of "The results indicate the majority of SOA was formed from aging, representing a technique to increase model SOA yields. Although via a different process, the resulting outcome is similar to that obtained if SOA yields are increased to account for SVOC losses to chamber walls, as proposed by Zhang et al. (2014) and used with CMAQ-AE6 in Baker et al. (2015). Also, although the inclusion of ageing reactions leads to an increase in SOA concentrations, this may be for the wrong reason as recent model-measurement comparisons with chamber experiments suggest that including ageing reactions on top of existing parameterizations can lead to overprediction of SOA concentrations (Zhou et al., 2015)." In other words, I think that a similar caveat as was included for the scaling up of S/IVOC concentrations is required.

P26767, L25: I suggest that this is reworded. The models do not, in my view, "utilize comparable SOA yields." The yields from the models are not constant values, but the result of specification of semi-volatile product yields that produce SOA. I suggest instead that they simply change "utilize" to "produce." Here, also, the Figure numbers should be given and the figures reordered.

SIMPLE model: I suggest that a line for the SOA/CO slope from the simple model be added to Fig. 5.

General note on Figures: Many have relatively small axes labels. I encourage the authors to make sure that the labels are sufficiently large such that when formatted into a final article they remain easy to read.