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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Modeling the formation and aging of secondary organic aerosols in Los Angeles during CalNex 2010" *by* P. L. Hayes et al.

Anonymous Referee #2

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Review of Hayes et al.

Hayes et al. present results from box model simulations of in-basin SOA formation focusing on Pasadena, CA and measurements made during the CalNex 2010 study. Their box model is explicitly constrained by observations of ambient traditional VOC concentrations. The also include emissions of intermediate and semi-volatile organic compounds (I/SVOCs) that are not included in standard emissions inventories. They link their I/SVOC emissions to POA emissions and assume that all POA sources have identical volatility distributions. They also consider a first order estimate of the influence of chamber biases on SOA yields by multiplying their yields of semi-volatile VOC product species by 4. They have considered a number of different schemes for treating the oxidation of S/IVOCs and even of VOCs. They find that the various combinations all

exhibit a diurnal profile shape consistent with the observations, but that certain model formulations perform better than others when the model results are compared with observations of the semi-volatile oxygenated organic aerosol (SV-OOA) factor determined from PMF analysis of the ambient organic aerosol time-series. They conclude that, overall, there is a need for some contribution of I/SVOCs to allow for simulation of SOA levels that are consistent with the average SV-OOA diurnal profile. They find that biogenics from within LA ("in-basin") contribute negligibly to the total in-basin SOA, although biogenic-SOA may contribute to the background OA burden. They find when they extrapolate their simulations based on these literature parameterizations to longer times that they overestimate the amount of SOA that should be formed.

Overall, the authors do a good job explaining what they have done, describing the results, and comparing between the different literature model formulations. I believe that this work should be publishable after they address the comments below.

Model formulation

The authors apply a number of different model formulations, taken from the literature, for the simulation of SOA concentration diurnal profiles within a constrained box model. Each of these model formulations/parameterizations has particular limitations that ultimately lead to differences in the box model results. Some aspects of the model formulations are more constrained than others. For example, the VBS yields for the traditional VOCs are constrained from comparisons with chamber observations whereas the literature ageing scheme(s) applied have generally weak, or even no, constraints. The O/C parameterization for S/IVOCs are similarly underconstrained, while the O/C estimates for SOA from VOCs are guided by observations from laboratory studies. The S/IVOC emission scheme is linked to literature measurements of POA volatility, although connecting these observational constraints on the volatility distribution to actual emissions is challenged by a lack of knowledge regarding the conditions under which the emission inventory was determined. I therefore suggest that it would be useful if the authors were to note a bit more explicitly what aspects of the literature parameterizations are more/less constrained by previous observations. They already do a good job of describing the model formulations, but some minor addition regarding the nature of these formulations might facilitate greater understanding by the reader. I also suggest that, given the inherent uncertainties in the parameterizations, that the authors limit the scope of any conclusions regarding whether one particular parameterization is particularly better than another.

Some additional clarification regarding the specification of the BVOC emissions would be useful.

P32340: The authors should provide some brief discussion regarding their use of a constant [OH] in the simulations.

Section 2.6: Some clarification regarding the correction for "higher OA concentrations upwind of Pasadena" would be useful.

Questions and concerns regarding results and discussion:

I suggest that the introduction of the model variant that considers the influence of vapor wall losses be moved to methods.

P32347/L10: The authors conclude here that their simulation results point to the "importance" of S/IVOCs. "Importance" is such a cagey word. I suggest that the authors be more precise, stating that their results suggest that S/IVOCs contribute anywhere from X-Y% of the total SV-SOA.

Although the authors do clearly distinguish between SV-OOA and LV-OOA, in general, it could be useful if they take opportunities to work to remind readers more often that the SOA being investigated here excludes background OA, a fraction of which is likely SOA.

Fossil vs. Modern:

1. The fossil/modern carbon analysis was determined for samples collected over only

7 days, a small subset of the overall campaign. The authors should note whether this week was generally representative of the overall campaign. 2. The authors might point out more strongly that the fossil/modern split determined here is linked to the assumptions regarding the assumed I/SVOC volatility distributions and emissions of these same compounds between sources.

SOA Apportionment:

P32354/L14: I find the point associated with the mention of these PMF results from filters to be somewhat unclear. Are the authors simply saying that someone else said that diesel might contribute something?

Evolution for 3 days:

P32356/L12: I can see the concern raised regarding potential overestimates of OA downwind from urban regions in models. However, I think it is equally important to note that this is intimately tied to the model formulation that is used. Many models use very simple parameterizations that will not overpredict (necessarily), potentially even underpredicting (as shown with the WRF-CMAQ model). I think that the model dependency of this conclusion needs to be emphasized to a greater extent.

WRF-CMAQ box modeling:

I think that the comparison here can go even further than what is already noted by the authors. The non-ageing VBS treatment of VOCs in the primary box model is essentially equivalent to the 2-product model in CMAQ. The only difference is really that there are four products instead of two. Yet in the primary box model if only the VOCs are considered the underprediction is not a factor of 25, as is seen when using CMAQ in box model form. It is more like a factor of 5 or 6. While still substantial, I think that this also indicates that there is a fundamental difference in the basic model parameters used in the CMAQ 2product formulation vs. the VBS 4-product formulation. In other words, toluene in CMAQ does not equal toluene in VBS. The authors are encouraged to emphasize this upon revision. They may wish to refer to (Barsanti et al., 2013) who discuss issues associated with refitting data to determine 2 product parameters.

Oxygen content comparison:

The literature oxygenation (i.e. O/C) parameterizations used for S/IVOCs are particularly underconstrained. I suggest that the authors take care to note that, given these inherent uncertainties in the O/C model formulation, that the results here should not necessarily be taken as an indication that one model performs better than another.

The updated SOA budget:

I suggest that the authors focus this discussion on the anthropogenic SOA budget, with less consideration given to the BVOC SOA budget, given that the (non-cooking related) urban SOA here is predominately anthropogenic in origin.

Conclusions:

Given the differences between the different parameterizations regarding the relative contributions from S/IVOCs versus VOCs towards the urban SOA, I suggest that the authors further emphasize that the relative concentrations remain quite uncertain.

Figures:

Figure 1 is fantastic and is very helpful to the reader to understand how the model formulations work.

References:

Barsanti, K. C., Carlton, A. G., and Chung, S. H.: Analyzing experimental data and model parameters: implications for predictions of SOA using chemical transport models, Atmos. Chem. Phys., 13, 12073-12088, 2013.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 32325, 2014.