

Comment on “Evaluating the impact of new observational constraints on P-S/IVOC emissions, multi-generational oxidation, and chamber wall losses on SOA modeling for Los Angeles, CA” by Ma et al.

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General Comments:

Ma and coauthors present a follow-up to the work in Hayes et al. (2015), adding more recent parameterizations for I/S-VOC emissions and yields as well as very recent approaches to correcting chamber yields for wall losses. I am satisfied with the application of the box model to the Pasadena data given the lack of quantitative statistics presented. The important limitations of the aging mechanisms and over-exuberant IVOC formation pathways is demonstrated more qualitatively than quantitatively. Also, the authors are careful to avoid strong conclusions about the dominance of SOA from IVOCs over SVOCs or vice-versa. I do urge the authors to move toward a 3D-CTM analysis in the future, particularly since I’m pretty sure input datasets exist for all the major CTMs. Although the conclusions are not exactly novel (other studies have shown that the VBS functionalization mechanisms overpredict at long photochemical lifetimes), I appreciate the demonstration of the improved parameterizations, particularly the chamber wall-loss correction. I found some aspects of the experimental design to have unnecessary limitations. Moreover, I encourage the authors to consider improving several aspects of the presentation before I recommend publication of this manuscript.

Specific Comments:

- 1) My primary question/criticism is why do the authors not investigate aging mechanisms with fragmentation given the emerging global/regional model implementations of these pathways and the low computational overhead of their own box model? This would seem like an ideal application given the experimental data available to them from CalNex. Why not use measured AMS elemental ratios to help constrain the configuration choices here? Potentially, that analysis could give complimentary information to the analysis in Section 3.2 and Fig. 6.
- 2) The authors discuss extensively the problems with aging VOC oxidation products and the tendency for mechanisms to accumulate mass at long photochemical lifetimes. It is important that they emphasize (stronger than they already do) that this aging approach is likely problematic precisely because it does not consider fragmentation. One of the main conclusions I read from the paper is that wall-loss corrected VOC yields should be used and aging mechanisms turned off. Conceivably, a future study will conclude that turning off aging is a bad idea because even though the OA mass is better predicted at long time, the O:C is underpredicted. The models of the future will hopefully have both more accurate yields and probably aging with both functionalization and fragmentation adequately described. To avoid confusion in the meantime, I recommend the authors refer everywhere to the TSI aging as “aging by functionalization only” or something similar, with an appropriate acronym for readability.

- 3) L390-394 and L480-483: The authors repeatedly refer to the OFR work of Ortega et al. (2016) to justify not including fragmentation in any model case. This argument relies on the assertion that fragmentation only played a dominant role when the OA mass began to decrease after it had plateaued for a couple of days in photochemical age space. But the OA concentrations started leveling off in that study at about 1 day. As with any competition, the manifestation of a plateau indicates to me that fragmentation is playing a role equal to that of functionalization. So sentences like L477-480 and L482-483 are pretty confusing, if not misleading.
- 4) The application of the wall-loss corrected chamber yields seems problematic to me. First of all, many of the studies used to inform the Tsimpidi et al. (2010) yield set included seed aerosol in their experiment. As the authors point out multiple times, the data they have included in Table S4 should be considered an upper bound. However, I fear that their demonstration of this approach will encourage others to blanket apply the parameters of Krechmer et al. (2016) to historical chamber yields without considering the details and possible interferences. I encourage the authors to describe in detail the problems with applying the narrowly defined Krechmer C_w 's to existing data and repeat that paper's call for more detailed analysis of chamber data before the community gobbles this simple approach and then moves on to the next hot SOA formation topic.
- 5) Why is the SOA mass in Fig. 5 not also divided by CO concentrations to correct for dilution?
- 6) L257-258: Woody et al. (2016) proposed a meat cooking volatility distribution. Why not try this one in a sensitivity test?
- 7) Can the authors clarify more directly why the model with the Worton parameters for SVOCs gives more OA than that with the Robinson parameters? The volatility distribution and Fig. 2 show pretty clearly that the emissions are substantially higher in volatility. Is the difference really from the added 7.5% mass that comes with the 1-bin aging mechanism? If that's the case, please emphasize more clearly the uncertainty in this parameter/approach to put the differences in these two model runs into context.
- 8) Section 3.2 and Fig. 6: This analysis is an interesting idea but I don't think the slight differences among the model cases warrant such a long-winded discussion and detailed figure. It would be enough to add a comment to section 3.1 that the WOR cases give more SOA from precursors with k_{OH} in the range identified by Ortega et al. (2016). The abstract and conclusions would need to be correspondingly reduced.
- 9) L716-718 and L796-797: Why do the authors not discuss the limitations of their aging mechanisms that only reduce volatility by one bin at a time? It is possible that a compound can shift more than one generation in volatility upon oxidation; the more recent 2D-VBS approaches and the SOM methods allow for multi-decadal shifts in volatility. Approaches like these might push the products below the "oxidation-partitioning barrier" manifested when compounds are protected from gas-phase oxidation.

10) L760-762: How do these reaction rate constants compare to estimation methods developed for the 2D-VBS? If you used those approximations (based on C^* and assumed O:C) would you do better?

Minor Changes/Typos:

- 1) L48-50: This sentence should say something about how the two methods predict similar mass at short to moderate photochemical ages.
- 2) L82: Consider replacing “nucleate” with “form”.
- 3) L742-743: Make sure to also mention that Woody et al. (2016) cited excessive model dispersion as a potential complicating factor.
- 4) I recommend adding figures with SOA mass curves (not just the yields) for each of the VOC product species to the supporting information, thereby visually demonstrating the effects of the upper- and lower-bound yield parameterizations. It would be a good idea to assume a background concentration equal to 2.1 $\mu\text{g m}^{-3}$ (or greater if you just want to take an average of your total OA, model wide) like in the model so that you get relevant partitioning.
- 5) SI, L6-22: I found the derivation of the wall-loss correction confusing. First, the quantity in parentheses in equations 5 and 6 should be the reciprocal. I assume they used the correct form for the calculation because I calculated the adjusted ARO2 and it would have been way off using the equation as it is written. Also, [VOC] should be replaced with something more accurate like $[\Delta\text{ROG}]$ or $[\Delta\text{VOC}]$. It would be helpful to explain briefly why the mass of compounds on the walls, C_w , is a function of C^* alone and not C_{tot} , C_g or C_p . This is essentially a consequence of the equilibrium assumption in the chamber analysis, as I understand it.