

Interactive comment on “Evaluation of new secondary organic aerosol models for a case study in Mexico City” by K. Dzepina et al.

Anonymous Referee #1

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This article provides an evaluation of existing SOA modeling approaches for formation of SOA in Mexico City. The modeling approach is based on AMS measurements. All the individual SOA modules used have been previously published, and the structure of the model is the volatility basis set approach. Thus, the word “new” in the title needs to be removed and the title should be “Evaluation of secondary organic aerosol models for a case study in Mexico City”.

Specific Comments:

1. Division between HOA and OOA.

HOA is used as a surrogate for POA, and OOA is used as a surrogate for SOA. The authors use the measured HOA for an estimate of the POA concentration in the model.

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It is unclear whether NT-SOA (the SOA formed from the oxidation of gases traditionally associated with POA, i.e. low volatility organic carbon) is more consistent with HOA or OOA.

Modeled NT-SOA (at least the early generations) may be more similar to HOA than OOA, and thus a strict comparison of SOA (which includes NT-SOA) to OOA may not be warranted. Conceptually, NT-SOA starts out very similar to HOA, as there is only a small reduction in volatility and small addition of mass to represent oxidation. As time progresses, and further generations of NT-SOA form, the NT-SOA probably resembles OOA more and more.

Certain model characteristics of NT-SOA indicate it may be more like HOA than OOA:

- The NT-SOA volatility from the kinetic calculation (Figure 10b) indicates that NT-SOA resembles HOA more than OOA as it tends to be more volatile.
- The O/C ratio of NT-SOA (about 0.1) is closer to the O/C of HOA (~ 0.05) than OOA (~ 0.4).
- According to Figure 7, the presence of NT-SOA leads to an over-prediction of OOA in the early morning (6:00 to 9:00 am) before OOA rises.

Are the above similarities to HOA just a result of the model framework or should NT-SOA actually be more like HOA or OOA?

2. Box model method.

Equation 11 may under-predict the amount of VOC oxidized if the oxidation reaction depletes the VOC in the atmosphere unless emissions (solving equation 4 with the emission and loss terms) are taken into account. Are any emission estimates for VOC precursors (for example, benzene) used?

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3. Page 4426. This section describes mixing of air from aloft with a background concentration of $1.4 \mu\text{g}/\text{m}^3$, which implies there should be a term in equations 4 and 5 to represent this addition of mass to the box. The mixing of air aloft was implemented by addition of a constant $1.4 \mu\text{g}/\text{m}^3$ background instead of a flux term through the top of the box. Clarify this approach in this section.

4. Page 4429, Eqn. (9), the authors introduce product VOC (PVOC) and CO_x terms in the mass balance equation in the updated traditional model (UT-SOA). Later, the authors show that the PVOC is the major SVOC in the UT-SOA and is likely the potential source of additional organic mass. On page 4439, line 1, “Figure 5c shows that UT-PVOC comprise by far the largest fraction of the mass arising from the reaction of these VOC precursors.”. The value of α_0 of the model species in UT-SOA is not given in the paper. How was the value of α_0 determined for the model species?

5. Page 4434, line 6-8. Awkward sentence, rewrite. “The OH reactivity is under predicted from that calculated from all measured species...” should be something like “The OH reactivity based on all measured species under predicts the observed OH reactivity...”

6. Page 4438, line 26, “The measured OOA is several times larger than total SVOC (SOA+gas SVOC) mass in this model, indicating that even if all UT-SVOC mass would partition to particle phase and form SOA, the UT-SOA would still be too small to explain measured SOA by a factor of 3.1.” From Table SI-1, for the one-product precursors, the $c^*(300\text{K})$ of the model species are low (around $1\text{--}5 \mu\text{g}/\text{m}^3$). Also, the mass yields of the model species are small. It is not surprising that there is only a small portion of the model species in the gas phase (i.e., UT-SVOC_g is small). Why are the volatilities of the model species so low?

7. Page 4442, line 4. The authors point out that about 20% of the total organic species present in Mexico City’s atmosphere are accounted for in any of the models considered in this paper. On page 4439, line 23, Since a relatively small portion of organic species

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is being accounted for in the models, how can the total model still predict the SOA mass loading in the case study?

8. Page 4446, line 21-24. Awkward sentence, rewrite. “the evaporation is closer to the actual residence time” should be something like “the evaporation is closer to the evaporation in the actual residence time”.

9. Page 4447, 4.5.2 O/C ratio section, it is not clear how the authors calculate the model SOA O/C ratio. The O/C ratios of the model species in UT-SOA model and of the volatility bins in the particle and gas phases in different oxidation generations in the NT-SOA model are not given in the paper. How were the O/C ratios of model species and volatility bins determined? What is the sensitivity of the model SOA O/C ratios to the assigned O/C ratios of model species and volatility bins? Page 4448, line 11, “Finally, the average model SOA O/C ratio is ~ 0.3 , which is ~ 0.1 below the observations, indicating that this combination of models produces SOA which is somewhat less oxygenated than the OOA measured O/C ratio, but within the uncertainty of the model and measurements.” What are the uncertainties of the O/C ratios measurements using the AMS and model SOA O/C ratios?

10. Page 4449, line 27 to page 4450 line 1: Authors assert correlation with primary anthropogenic pollutants implies hydrocarbons are of anthropogenic origin. One doesn't necessarily imply the other. There could be an urban enhancement effect that allows biogenic precursors to form SOA more efficiently in anthropogenic environments. The model could be missing this anthropogenic enhancement. The key factor is that the UT-SOA precursors that formed SOA were of anthropogenic origin and the origin of the POA is somewhat unknown but likely anthropogenic. The 14C section could be shortened as there no direct 14C measurements for the day modeled and the model doesn't predict 14C.

11. Page 4453, line 6, “The total model SOA O/C ratio after 3-days of aging is ~ 0.34 . OOA O/C ratios observed for aircraft measurements during MILAGRO-2006 range from

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0.64 for OOA-2 to 1.02 for OOA-1 (Aiken et al., 2008a; DeCarlo et al., 2008) indicating that aged OOA has much higher oxygen content than our model SOA." Do the authors have any explanation for this? What is the range of the O/C ratios of the model species in the UT-SOA model and the volatility bins in the NT-SOA model before and after aging?

12. Table 1: make T1-SOA, T2-SOA, etc as rows to be more consistent with Figure 4.

13. Figure 5: Pie chart too small.

14. Supp. Info lines 222-224 missing.

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