**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol in the Mexico City region" by A. Hodzic et al.

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As someone who is interested in model performance of OM/OC ratios using traditional SOA modeling, I was pleased to see this article in which O/C ratios are explicitly evaluated in the VBS framework. The model inter-comparison provided a good perspective on the differences in these model scenarios while making use of a rich dataset of ambient measurements for model evaluation. However, after reading the discussion paper I am left with some concerns.

Comparisons between different model formulations show that each scenario outperforms the others in regards to at least one metric:

1)REF- under-predicts SOA mass but has the best correlation for temporal variability of TOA. O/C was not evaluated.

2)ROB – has reasonable agreement on SOA mass (within a factor of 2 according to section 3.2.2), low correlation for temporal variability at T0 and T1, poor agreement for O/C.

3)GRI – over-predicts SOA mass (factor of 2 too high at T1 site every day), low correlation for temporal variability in TOA (at T1 and at T0 if you consider compensating errors mentioned in section 3.2.3), very good agreement for O/C.

Based on these results, the authors might critically evaluate whether VBS offers an improvement in model performance over traditional OA treatments? In section 4, it is mentioned that REF produces SOA concentrations that are too low by a factor of 5-10. However, the authors should be clear that the REF scenario does not represent the most up-to-date traditional modeling. Evaluations of other traditional SOA models have found much better agreements with ambient estimates (Yu et al, 2007).

I have additional concerns about the treatment of O/C in the GRI and ROB scenarios.

1)A description of how O and C are modeled for each OA category (V-SOA, S/I-SOA, POA) should be added to the model formulation section. It is not clear from the current paper how these are being treated.

a)Section 3.4.1 mentions that O and C are modeled explicitly for S/IVOC and that the O/C ratio is calculated directly from modeled O and C. The addition of oxygen from OH reactions (9% per reaction in ROB and 40% per reaction in GRI) is discussed, but this approach also requires an assumption about the O and C contents of the initial S/IVOCs. What O/C ratio is assumed for emitted S/IVOCs?

b)A single O/C ratio based on chamber measurements is used for each of V-SOA, Ant POA, and BB POA. Does this mean that O and C are not explicitly modeled for these other types of OA? This seems to introduce inconsistency in the model treatment of

OA from different sources given that the VBS was intended to represent a unifying framework for treating OA so that OA from all sources (POA, SOA etc.) is modeled using the same processes.

c)If O and C are not explicitly modeled for V-SOA and POA, does that mean that aging (addition of 9 or 40% mass with OH reaction) is not included for these OA subcategories?

2)The addition of 40% mass from a single oxidation step seems physically implausible. Although the authors acknowledge that no mechanism has been proposed to explain this parameterization (page 668, lines 26-27), this finding might be repeated in the conclusions section. The fact that such an assumption is necessary to achieve realistic O/C values suggests that this modeling framework might be missing some key physical/chemical processes (aging, condensed-phase reactions etc.). A more indepth exploration of this problem is needed since it has the potential to undermine the approach being used.

I have one final technical comment. The employed Hvap values in this work appear to be overestimated. Though the values are based on published work by Robinson et al., (2007), recent laboratory findings report Hvap values in the range of 11-44 kJ/mol for SOA formed from a variety of gas-phase precursors (Offenberg, et al., 2006). [Note that the highest value here is lower than the lowest value used in this work.] SOA model predictions are very sensitive to Hvap values (Tsigaridis and Kanakidou (2003) and Henze and Seinfeld (2006)), e.g., diurnal SOA profiles are opposite of observations when the applied Hvap is too high (Pun and Seigneur, 2008). If temperatures in Mexico City were high during the modeled period, an unrealistically high Hvap value could help to explain the over-predictions of POA evaporation at the T1 site.

Yu, S., P. Bhave R. L. Dennis, and R. Mathur. Seasonal and Regional Variations of Primary and Secondary Organic Aerosols Over the Continental United States: Semi-Empirical Estimates and Model Evaluation. Environmental Science & Technology.

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