**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Simulating the oxygen content of ambient organic aerosol with the 2D volatility basis set" *by* B. N. Murphy et al.

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Received and published: 12 June 2011

1. *The FAME-08 data are not a stringent test of model performance of aging given the consistency of observed of O:C and OA mass concentrations. It's not clear that the model would capture the variability in these parameters, as they might exist in a region influenced by a variation of air mass ages. Now clearly there are not many alternate datasets available at this time, and I am not suggesting that additional cases should be added to this study. However I think this aspect of a weak test case with limited dynamic range should be (strongly) emphasized in the discussion.*

The referee correctly points out that this exercise does not completely constrain the various uncertainties in the model framework we have chosen. We view this study instead as a test of the utility of this approach to analyze further datasets as they become

available. It is true that little variability exists in the FAME-08 observations of O:C ratio. However, it is still a challenging case for the model given that the O:C is constant for all the air masses arriving at the site. We therefore consider the agreement between model predictions and observations to be an important early step in this model's on-going development and evaluation. The fact that the model's O:C predictions also lack temporal variability is quite interesting. Future work will focus on testing the ability of the model to capture site-to-site variability and further constrain these uncertain properties. We have added some discussion to the revised manuscript to make this point clear.

2. *Given the complexities of simulating all OA formation processes, including those (very reasonably) not included here, but discussed by the authors in the text, there is at times an inappropriate degree of confidence in the current results. This should be toned down. For example, fragmentation processes (ignored here) could lead to reductions in OA mass and likely increases in O:C. This could compensate for the high OA simulated when both aSOA and bSOA are aged. Overall, I think it should be emphasized that though you have pursued a nice series of sensitivity tests here, your system is under-constrained and you cannot definitively conclude regarding model performance. Text should be modified throughout Sections 4 and 5, specifically*

a. Page 8554, lines 23-25

b. page 8574, lines 21-24

c. page 8575 line 28 through page 8576 line 6.

We did not intend to convey such a high degree of confidence on the model given its simplified description of the various OA processes. We are currently pursuing the implementation of these added complexities, like fragmentation processes, from the perspective of smog chamber experiments. The mentioned lines have been changed to make this uncertainty more clear.

3. *On a related point, it seems completely arbitrary to age aSOA but not bSOA. The text suggests that this approach is considered in the best case solely because it is the "best fit" to the measurements. If not, please provide some justification. If so, please refer to above point.*

We should first clarify that in the current model both the aSOA and the bSOA are chemically aged. We explain in lines 22-24 of page 8653 that "For bSOA, the model does simulate the oxygenation of this mass as it reacts with OH, but assumes that these reactions increase the O:C ratio without a net change of the volatility of the products." Therefore, the model assumes that the chemical aging of aSOA results in an increase of both the O:C and a reduction of the volatility of the surrogate OA components. On the other, hand it assumes that the chemical aging of the bSOA components does not result in a net change of their volatility.

This is a complicated issue and is closely related to the practical aspects of smog chamber studies upon which the first-generation stoichiometric yields are based. There is evidence to suggest that bSOA does age in the atmosphere as discussed in the text. However, it may be possible that first-generation yields from smog chamber studies of bSOA tend to include more aged mass than their counterpart studies of anthropogenic precursors like the aromatics due to the relatively fast reactions of the biogenics. If this is true, then explicitly aging bSOA after applying those particular yields would double-count OA production from aging. Further, previous studies using the 1D volatility basis set with 3D chemical transport models (where we first employed this simplification) have shown better agreement with measurements when aSOA is aged and not bSOA. We agree that there is still great uncertainty in the effects of this important process on OA from anthropogenic and biogenic sources. We have added some discussion emphasizing this point to the discussion in the text.

4. *It's unclear why so many of the plots are represented as diurnal means given the very, very small degree of variability in the time dimension. While it is interesting to see*

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the modeled difference in O:C throughout the day in Figure 3, others (such as Figure 4, 6 and even 2) are not particularly informative as shown.

We do understand the point of the referee however this lack of variability given the variability of the air masses reaching is site was one of the most surprising results of FAME-08 (Hildebrandt et al., 2010). We consider the ability of the model to reproduce this observed lack of variability one of the most important results of these simulations. As we explore other sites throughout the EUCAARI field campaign, variation in along this axis will become more important. Here, the model performs well for a site where limited variability is observed despite significant variability in source location. We would prefer to keep the figures in their current form.

5. *Page 8562, line: 28-29: Can you provide some chemical justification for the addition of one or two oxygen atoms per reaction with OH in the text?*

To justify this assumption, we refer to Atkinson (2000) and assume oxidation aging by OH is carried out similarly to hydrogen abstraction from alkanes. These reactions form first the alkyl radical, followed quickly by oxygen addition to form the alkyl peroxy radical. This species can undergo a number of reactions that reduce it to the alkoxy radical (by reacting with NO, NO_3, or another peroxy radical) and then may be stabilized to form a product species with one more oxygen added. However, the alkyl peroxy radical also may undergo reaction with HO_2 to form a hydroperoxide with two added oxygen atoms. We take both of these pathways into account in this initial study. A more detailed model can semi-empirically estimate the magnitude of these branch points by using the predicted concentrations of HO_2 and NO among other reactants. We have added this clarifying argument to the text.

6. *Page 8563, lines 27-28: Can you tell us in the results what the average increase in mass in your model simulations is to compare with the prior assumptions by Lane et al. and Grieshop et al.?*

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Yes, the increase in OA mass for one generation of chemistry fluctuates between 14 and 18 percent, depending on the proximity to fresh emissions sources but averages to about 16 percent according to this model. This information has been added to the text.

7. *Page 8568, lines 7-8: Are MEGAN emissions calculated online in your model or taken from an offline calculation (if so, please specify).*

The MEGAN emissions are calculated offline. This is now clarified in the text.

8. *Page 8568, lines 10-13: You need a reference for the sea spray source function parameterization (O'Dowd et al. is the partitioning of sea spray reference only).*

The reference (Geever et al., 2005) has been added to the text.

9. *Page 8569, lines 1-2: How much chemical uncertainty is associated with clustering these back trajectories? I assume little given the consistency of the aged air masses, but it would be worth testing this for a day (run the chemical model for all the back trajectories and look at the variability) and stating so in the text.*

We have performed this exercise and found the mass to vary by as much as ± 0.5 μg m^{-3} and O:C by much less, ± 0.01. This important result has been added to the text.

10. *Page 8569, lines 4-5: Please specify in the text whether the initial conditions from PMCAMx are matched for the same date and time of the back trajectories or a climatological mean.*

The initial conditions are matched to the same date and time of the back trajectories. These are values predicted by PMCAMx. We have edited the corresponding lines to be more clear.

11. *Page 8569, lines 20-21: Please provide more information on the simulated bcOA. Is this a constant advected in from all directions? What are the likely sources?*

The assumed bcOA concentration is constant in time and along horizontal directions. However these concentrations do vary in height consistent with observed vertical profiles. Likely sources are long-range transport of OA from other continents as well as marine-source OA. This is explained in the revised paper.

12. *The supplementary materials are brief and should be re-integrated into the main text. Figure S3 is unnecessary given the discussion in the text. You could perhaps add a mean map of emissions for the region to underly Figure S2.*

We have made the suggested changes.

REFERENCES

Atkinson, R.: Atmospheric Chemistry of VOCs and NOx, Atmos Environ, 34, 2063-2101, 2000. Geever, M., O'Dowd, C. D., Ekeren, S., Flanagan, R., Nilsson, E. D., Leeuw, G., and Rannik, U.: Submicron sea spray fluxes, Geophys. Res. Lett., 32, L15810, 10.1029/2005GL023081, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8553, 2011.