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Interactive comment on “Simulation of Atmospheric Organic Aerosol using its Volatility-Oxygen Content Distribution during the PEGASOS 2012 campaign” *by* Eleni Karnezi et al.

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(1) *Summary/recommendation: This paper seeks to model total OA concentrations and O:C ratios from ground and airborne measurements from the PEGASOS field campaign. A number of chemical aging schemes were used, and although several schemes performed well, no one chemical aging scheme yielded superior model-measurement fits. This is a well-conducted study and I recommend that this paper be in published in ACP but with revisions, as discussed below.*

We do appreciate the constructive comments and suggestions of the referee. We have done our best to address them and revise the paper accordingly. Our responses follow the comments of the referee (in italics) below.

General Comments:

(2) *Pg 3 lines 65-67: is this paper also using all those classifications of OA? Not clear from the “Lagrangian CTM description section”. How do you distinguish SOA-sv and SOA-iv from and/or between aSOA-v and bSOA? In general, this work assumes a knowledge of the Murphy et al. 2011 and 2012 papers and model that the modelling work was built upon. As a reviewer not familiar with the model used in this work, it was difficult to follow some of the more complicated nuances of how the model treats different OA types. I suggest that more details about the model be added to assist the reader.*

Yes, we use the classification proposed by Murphy et al. (2011) to address the complexity of components of OA. The following five OA components are resolved: (1) aSOA is OA formed from the oxidation of anthropogenic VOCs (aromatics, alkenes, and alkanes); (2) bSOA is OA formed from the oxidation of biogenic VOCs (isoprene, monoterpenes and sesquiterpenes); (3) POA is fresh emitted OA which may evaporate and recondense during its atmospheric lifetime, but once it reacts with OH it becomes secondary OA; (4) SOA-sv which is SOA formed from the oxidation of semivolatile organic compounds, that is POA that has evaporated and reacted and (5) SOA-iv that is SOA formed during the oxidation of intermediate volatility organic compounds. We have followed the suggestion of the reviewer and added more information about the simulated OA components and their simulation in the revised manuscript.

(3) *Sec 2.2.2: Need to give clear justification as to why there are two aging schemes of bSOA, and not any other type of SOA. These details need to be included.*

Please note that the fundamentals of the aging scheme are the same for all compounds: it is assumed that homogeneous reactions with OH radicals are the main chemical aging pathway. The effect of these reactions on the volatility distribution of the secondary compounds is allowed to be different between biogenic and anthropogenic SOA components. This is due to the available findings that suggest that there is significant second and later generation production of SOA from anthropogenic precursors (e.g., Hildebrandt-Ruiz et al., 2015), while the corresponding later production of SOA from biogenic precursors may or may not be a lot smaller (Ng et al., 2006; Szidat et al., 2006; Tritscher et al., 2011; Gilardoni et al., 2011; Yttri et al., 2011; Zhao et al., 2015). As a result, we have treated the chemical aging of anthropogenic and biogenic compounds independently following previous modeling efforts (Murphy and Pandis, 2009; 2010; Murphy et al., 2012). This independent treatment allowed us to explore better the effect of the various assumptions used in the various chemical aging schemes. We have added some additional information about this issue in the Introduction and we have added as well more information in the Section 2.2.2 describing the bSOA aging parameterizations.

(4) *Pg 6, simple scheme description: were any sensitivity studies done on the rate constants used for reactions with OH? A comment should be included about this assumption.*

Murphy et al. (2011) have investigated the sensitivity of the results of the 2D-VBS scheme to a number of assumptions in the framework including the assumed rate constants with OH. The sensitivity of the results was small to moderate. We have added a reference to that work in the end of Section 2.2.1.

(5) *Pg 10, Lines 299-300: There could be a brief discussion here of the potential problems of basing best-fit model conclusions on just one flight.*

Please note that the conclusions for altitudes lower than 700 m here are based on the measurements of all seven flights. We have clarified this point. Only the three data points for the higher altitudes are based on one flight. Potential problems with the use of data from just one flight include the existence of a pollution layer aloft that day that

was not captured by the model or some other relatively rare event that took place at that time. We have added a brief discussion about this in the manuscript.

(6) *Sec 3.4 How valid is it to tune fragmentation to the measurements with just 7 cases?*

Obviously the validity of this scheme that was tuned to the measurements in a specific area and period will need to be tested in future work. For the time being, this can be viewed as a parameter fitting exercise showing that there are multiple sets of 2D-VBS parameters that can give predictions consistent with the measurements. This is now discussed in the end of the paper.

(7) *It's confusing in general how many cases were used and how the averaging was done with the model and measurements, especially between ground based and zeppelin measurements, since many of these didn't match in time/date. This should made clear throughout the manuscript.*

Regarding the specifics of the optimization, the fragmentation probability was varied from 0 to 1 for all cases examined. Examples are shown in Figure S5 in the Supplementary Information. The optimum value was selected minimizing the error for the predicted OA mass concentration. Please note that all model predictions discussed in the paper were matched in time with the measurements (either ground or aloft). The details of the fitting are discussed in more detail in the revised manuscript.

(8) *It would be good to include a brief discussion of uncertainty related to model emission inventories, if any details of this are known (e.g. other model-measurement validation studies).*

This is always a tricky issue. We have performed detailed evaluation of the three-dimensional chemical transport model PMCAMx using the same pan-European emissions inventory for other periods, stations, and chemical species (Fountoukis et al., 2011). However, especially for organic aerosol, it is difficult to determine if discrepancies between measurements and model predictions are due to the emissions, the chemical transport model itself or the meteorological inputs. Even worse, assessment of the uncertainties of highly resolved (in space and time) emission inventories is non-trivial. We have added citations to the evaluation of the 3D PMCAMx in the same domain using the same inventory.

(9) *Ultimately, aging schemes are tuned to fit the measurements and 7 different aging schemes are found to well-reproduce the measurements. However, this paper did not provide any or enough discussion about measurement uncertainty, number of measurements, or the other uncertainties I brought up above (emissions, rate constants) to allow the reader to firmly conclude anything about the validity or transferability of these tuned best-fit schemes.*

The uncertainties of the AMS measurements used in this study are the typical AMS measurement uncertainty due to a large part to the estimated collection efficiency (for absolute concentrations) and the fragmentation table for the O:C. We have added citations to papers discussing these AMS uncertainties. We have added also information about the number of measurements performed and used in the model evaluation. We agree that the degree of transferability of the schemes that worked well in this study will need to be determined in future applications using them in other areas and periods and we now clarify this in the Conclusions section in the end of the paper.

(10) *I feel that it would be of interest to the community to provide a brief discussion about the pros/cons of the different aging parameterizations used in this study. E.g. the simple functionalization scheme could be implemented into a more computationally intense model (e.g. a global CTM) but potential could have biases from leaving out Y; the detailed functionalization scheme provides X extra information but is likely unrealistic in Z, and so forth.*

We have followed the suggestion of the referee and added some discussion of the positive and negative computations features of the different parameterizations. For example, the simple parameterization scheme has the advantage that it can also be implemented in the 1D-VBS reducing a lot the computational cost. In that case, the predictions of OA mass concentrations and the volatility distributions remain the same, but one loses the ability to predict the O:C. The other schemes can be simplified for the 1D-VBS without introductions of errors.

Figures/Tables:

(11) *Figure 5: is the average OA from the ground measurements or does it include the Zeppelin measurements? Caption and text should state this clearly.*

This is the average OA from the ground measurements. We added the missing information in the caption.

(12) *Figure S3: it would be helpful to each SOA type (ASOA-v, bSOA, etc) and the case types redefined either in the caption or in a brief section before the figures redefining both the SOA types and the case types. The case types are defined nicely in Figure S5 but that doesn't help out Figure S3.*

We added the information about the seven aging cases under the caption of Figure S3 and more information redefining the OA types in the corresponding sections.

Technical comments

(13) *Line 233: what is Figure C.4?*

This was a typo. We changed Figure C.4 to Figure S5 in Section 2.3.

(14) *Line 272: no comma after "predictions"*

Corrected.

(15) *Line 311: no comma after “scheme”*

Corrected.

(16) *Line 400: finish parenthesis*

Done.

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