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Atmospheric Chemistry and Physics Discussions

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) *This paper describes the simulation of ground-based and vertical profile measurements of organic aerosol mass loading and O:C ratio during the PEGASOS campaign. The multiple simulations use a variety of different parameterizations of functionalization and fragmentation, different for anthropogenic and biogenic SOA, and also vary assumed vaporization enthalpy. The offsetting nature of functionalization, fragmentation, and vaporization enthalpy result in no unique simulation scheme having clearly superior prediction skill metrics.*

We have done our best to address the various suggestions and comments of the referee. Our responses follow the corresponding comments of the referee (in italics) below.

General comments:

(2) *In the introduction, you describe the Murphy et al modeling studies and point out that they found the simplest approach to parameterization (for anthro compound aging) did better than the more complex formulation (lines 72-75). It seems like this is your conclusion, too, based on your figures focusing on your simplest 1-bin parameterization. But, I didn't see that stated clearly as the conclusion. I suggest to explain somewhere why you focused on that 1-bin model for the figures, and if you conclude it was the best, make that clearer. In the end I came away feeling that no parameterization was necessarily superior but then was confused by your focus on the one in the figures. (Also in that discussion of Murphy 2011 and 2012: I would have found it easier to make the comparison between parameterizations if you included some metrics from each model on average volatility reduction and O addition at each step.)*

Murphy et al. tried a few parameterizations without try to select optimum parameters (e.g., the fragmentation probability) and concluded that the simplest approach performed better. In this study, the different parameterizations with fitted parameters perform a lot better and their performance is quite close to that of the simple parameterization. The performance metrics shown in Table 2 and 3 indicate that different parameterizations perform better than the others depending on the metric. For example, the detailed functionalization scheme (DET with b=0.3) has the lowest mean square error for OA mass concentration, while the 2-bin shift with bSOA aging an b=0.4 scheme has the lowest fractional bias for O:C. Given that the performance of the seven best performing parameterizations is quite close to each other and that this is based on just one measurement set, we do not think that it makes sense to try to declare a winner. So, we agree that no parameterization (from the seven best) is superior. We have added the above discussion in the paper.

We had to choose one set of simulations based on one of the parameterizations to illustrate the results of the model. Figures 2-4 were quite messy with the results of all 11 or even 7 parameterizations. We have chosen the results of the simple scheme because they are discussed first in the paper. To avoid confusion, we clarify in the revised paper that this is just an example and the results of the other six best performing parameterizations are quite similar to those shown.

(3a) *The discussion of temperature dependence / enthalpy of vaporization confused me. In the introduction (lines 97-103), can you comment a bit on the stark difference between the Sheehan and Bowman and Murphy results you report? Because you also find a surprising result, it would be useful to understand what is known about why this has not been found to have consistent results in past studies.*

The main difference is the chemical aging process. Sheehan and Bowman (2001) focused on the first generation of SOA production. They found (as expected) that temperature affected significantly the partitioning of the mostly semivolatile SOA components and therefore the predicted SOA concentration was quite sensitive to the assumed enthalpy of evaporation. Murphy et al. (2011) simulated both the first and later generation of reactions in the system. The inclusion of the chemical aging processes reduced dramatically the sensitivity of the predicted SOA concentration to the enthalpy of evaporation. This explanation has now been added to the introduction.

(3b) *Related, around lines 431-434: I don't understand your result. Why would aging mechanism change in response to deltaHvap? Or is this just that your optimization will adjust fragmentation correspondingly? This discussion could be clearer.*

The aging mechanism did not change (the fragmentation probability is fixed in these tests), the amount of SOA produced from these later generation reactions did. When a high evaporation enthalpy was used, the first generation SOA evaporated more at high temperatures and its concentration was reduced. However, now there were more semivolatile vapors available for the aging reactions with the OH. So, these reactions produced more later-generation SOA. The reduction of first generation SOA (due to evaporation) was offset by the higher SOA from the chemical aging reactions, so the total SOA did not change much. The opposite happened when a lower enthalpy was used. This interplay between the two processes (first generation production/partitioning and chemical aging) resulted in a small sensitivity of the predicted SOA to the enthalpy of evaporation. We have added the above explanation to Section 3.6.

(3c) *And, lines 472-484: these conclusions could use more discussion. Why is the low sensitivity surprising? Is this result mainly a function of not having explored a wide enough temperature range because of the season? If so, could say this at the end: e.g., "wintertime predictions would explore a larger range of temperature and thus better constrain delHvap."*

The low sensitivity is surprising because all the SOA models rely on the partitioning of the semivolatile organic vapors between the gas and particulate phases. In any simulation of the atmosphere, this process is very sensitive to the evaporation enthalpy and changing temperature. The fact that in the SOA model used in this work, there is a quite different process (chemical aging) that cancels to a large extent this sensitivity is unexpected. This is now clarified in the paper.

The suggestion of the referee about exploring the sensitivity of the model to the enthalpy of evaporation during winter is quite interesting. This interplay should still be present, but the chemical aging should be slower. We will try to explore this suggestion in future work.

(4) *I also had some confusion about the exact use of the back-trajectories. On line 115, are you simulating along the clustered average back-trajectory, or each one? Perhaps a bit more additional explanation of how the CTM incorporates the back-trajectories would be helpful. At line 142, I suggest to begin this paragraph with stating that these* *are 72-hour back trajectories (you mention this much later), and clarify that the ground site is the trajectory receptor – the list of times at the beginning was confusing. At line 161: "receptor site around Po Valley"-does this refer to the Zeppelin flights? Were 72-hr back-trajectories run for a series of points along the flight trajectory too? Or did you only use zeppelin measurement above the ground site and thus use the same back trajectories? At the end of this paragraph, maybe segue to the next section with a brief recap of how they are fed into the chemistry schemes. (If you discuss this more above it may not be necessary to do much here).*

We have followed the reviewer's suggestion and added information about the calculation and use of the back-trajectories. We are simulating along the clustered average back-trajectory in this work and not along each one of the individual trajectories. We now clarify in the beginning of the paragraph that these are 72-hr back trajectories with the ground site as their end point. The Zeppelin trajectories were based on the actual Zeppelin position every hour, so that we could use all the measurements from all the flights. We have added a couple of sentences in the end of this paragraph explaining that the trajectories are used to select the corresponding emissions from the emissions inventory files and also the meteorological parameters (temperature, humidity, rain, etc.) from the meteorological input schemes.

(5) *Around lines 178-182: What is the reasoning for using different aging rate constants for some classes of OA and not others? Explain choices.*

We now explain in the revised paper that these choices of different rate constants by Murphy et al. (2011) were based on the average size of the corresponding organic compounds, with higher values for bigger organic molecules.

(6) *Around line 208-209: Why would aging of bSOA result in negligible change in volatility and an increase in O:C? And around line 215: why would bSOA be different than other OA aging?*

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 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. A similar comment was made by the second reviewer (see Comment 3).

(7) *Fragmentation parameterization, around lines 223-224 and following section: Were fragmentation probabilities simulated separately per time step or at all times, or at endpoint, or at "average" timestep? Why would b not be dependent on O:C? At line 233: what is Figure C.4?*

In all tests described in this work a constant fragmentation probability was assumed during the full corresponding simulation. In principle this probability should depend on O:C. However, the fact that the model could reproduce the observations with a fixed value, discouraged us from using a more complicated parameterization in which the b would be a function of O:C introducing more free parameters in the scheme. Clearly, this fragmentation probability should be better constrained in all similar schemes. These points are clarified in the revised paper. We have corrected the typo and Figure

C.4 is now Figure S5.

(8) *Lines 243-253: Aren't these skill metrics pretty standard definitions? Is it necessary to include the equations in the body text, or could they be in the supplemental info, or referenced?*

We have moved the definition of the metrics to the Supplementary Information.

(9) *On the binning of model results (lines 269-270): why 4 hours? Did you try single hours and how did it look? If 4 hours is all that works from the model perspective, why not bin your data onto the same time base as the model output that you are comparing too? It looks awkward to have the difference. The wording also made me wonder if you binned over the same hour of the day on multiple days – clarify how you did the averaging, how many days averaged, etc.*

The use of 4 hr long time bins was a compromise between keeping the computational cost of the hundreds of simulations performed and maintaining most of the variability of OA and O:C. We tried the single hour simulations for selected schemes and the differences were marginal. We did bin the measurements in exactly the same time base as the model output. This is now clarified in the paper and the comparisons to avoid confusion. Please note that the diurnal averages are shown for illustrative purposes in Figures 2 and 4. We have added additional text to explain our choice of the number of trajectories per day and the corresponding model evaluation.

(10) *A big question I have about the observations is why the error bar suddenly changes above 700 m (the top 3 points in the vertical profiles), and there is a striking discontinuity in the data at those points as well. This needs to be addressed in the text (around lines 279-287, caption for Fig. 3) – what could explain this unusual behavior? You mention it is a single flight – how many flights do the other points represent? How were the locations different? Are those points truly better known (as suggested visually by* *the smaller error bars) or were the others just spatially or temporally more diverse? If the latter, maybe rethink how you determine your error bars, or how you portray the different points to show this. One thought: Are the top 3 points at lower temperature? Although, this would suggest a stronger delHvap sensitivity.*

The measurements below 700 m represent averages from all flights. Given that these took place during several different days they have a higher variability. The three data points above 700 m are from a single flight (June 20). The measurements suggest that there was a layer with higher OA levels at these altitudes during that day that cannot be explained by the model. It is difficult to draw any reliable conclusions from such an event without additional information. We have added some additional explanation about these three data points in the corresponding section.

(11) *Around line 314: It doesn't make sense to me that aggressive functionalization would underpredict O:C – would it oxidize faster?*

This is one more relatively counterintuitive result due to the interplay of different processes. The aggressive reduction of the volatility of the organic compounds in this parameterization moves them rapidly to the particulate phase where they cannot be oxidized further (at least in this modeling scheme). So the scheme moves the compounds to the left of the 2D-VBS but with a small slope, so the final predicted O:C is low and actually lower than observed. This additional discussion has been added to the paper.

(12) *Around lines 347-354: The range in b's you find optimized for the various parameterizations is enormous – it seems to just be a correction factor you can use to tune your model. Can you contextualize what would be a reasonable value for b, e.g. by citing some experimental results that might help one choose? Same questions generically at the end of section 3.5 (line 412) about bSOA parameterizations – these also span a huge range. How could we decide which assumptions are more reasonable?*

If no data exists to constrain this, might you suggest some experiments that should be done?

We do agree that the resulting range for the “optimal” average fragmentation probability (0.1 to 0.7) is large and the model appears to use it as a correction factor to reduce the SOA produced by the most aggressive schemes. However, both the low and high values of this range are reasonable for lightly and highly substituted organic compounds (Donahue et al., 2012). There have been a number of studies that have tried to constrain this process for selected systems like squalene particles (Kroll et al., 2009) and a series of alkanes, ketones, aldehydes and acids (Chacon-Madrid et al., 2010; Chacon-Madrid and Donahue, 2011). While these studies have provided useful insights we are far from constraining this parameter. Additional emphasis on the production of volatile organic compounds (including small organic molecules) during the aging process will clearly help. These issues related to the fragmentation probability are discussed in a new paragraph in the paper.

(13) *On line 456, you refer to “more than a hundred” tested aging schemes, but your tables have a much smaller number. Do you mean the multiple tested b values in each scheme?*

This is correct. We count the different values of the fragmentation probability as a different scheme because additional simulations need to be performed for each value before we can arrive at the optimum b. A brief explanation has been added.

Specific comments / technical suggestions:

(14) *Line 26: define SOA (first instance)*

The definition has been added.

(15) *Line 28: “contribute around 5 percent”*

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The typo was corrected.

(16) *Line 29: define HOA, define (explain) PMF-AMS*

Done.

(17) *Line 32: "intricate interplay" is unclear, replace with something more descriptive?*

We have added a new paragraph to deal with this issue and added a brief explanation at this point.

(18) *Line 37: perhaps you meant to cite the IPCC 2013 WG1 report?*

The reference has been corrected.

(19) *Line 68: "(PMCAMx-Trj) as the" (this is one of several places where I think a comma should be removed or added)*

Corrected.

(20) *Line 75: "chemical aging assumed"*

Corrected.

(21) *Line 82: "(2012), formation"*

Corrected.

(22) *Line 98: "Bowman (2001) concluded"*

Corrected.

(23) *Line 99: are you refering to SOA mass yields increase? Or mass concentrations?*

This refers to an increase in SOA mass concentrations.

(24) *Line 106: “The Po Valley”*

Corrected.

(25) *Line 108: “evaluated by comparing the resulting 2D-VBS”*

Corrected.

(26) *Line 115: “2011; 2012) simulating the”*

Corrected.

(27) *Line 118-119:”aerosols, vertical turbulent dispersion, and area and”*

Corrected.

(28) *Line 132: “from terrestrial ecosystems”*

Corrected.

(29) *Line 133: “emissions, and wildfire emissions are included following Sofiev et al. (2008a,b).”*

Corrected.

(30) *Line 267: “ground level is”*

Corrected.

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(31) *Line 270: "concentrations of 4 hours instead of"? I think this is what you mean? But not clear why you chose 4 hours. See general comment above.*

We have rewritten this. The choice of 4 hours is explained in our response to Comment 9 above.

(32) *Line 278: "measurement in Figure 3a . . . predictions agree with"*

Corrected.

(33) *Line 299: "error for altitudes"*

Corrected.

(34) *Line 311: "scheme underpredicted the"*

Corrected.

(35) *Line 313: "; 2012) about the"*

Corrected.

(36) *Line 461-462: "with similar average"*

Corrected.

(37) *Line 464: "evaporation of primary OA and subsequent"*

Corrected.

(38) *Lines 479-480: "small temperature differences for altitudes up to 600 m . . . this low sensitivity to . . . evidence that the higher values (150 kJ mol-1) are"*

Corrected.

(39) *Fig 1: In caption, mention that these are 20 72-hour trajectories. On maps: can you make the map boundaries the same in both panels?*

We have added the suggested text. Unfortunately, it is not easy to make the map boundaries the same.

(40) *Fig. 2: As mentioned above, it feels strange to me that the binning is different for model and measurements – consider unifying? Maybe state in caption how many days of coverage this is to help contextualize the variability / error bars. And, could interrupt / truncate the y axis to miss all the white space up 0 – 0.4 and see the variation better.*

We prefer to keep the hourly resolution for the measurements because this provides an idea of the variability that the model is missing by using 4-hr bins. We do explain this difference in the new figure caption together with the number of days that have been averaged. The range used for the y-axis reflects the reasonable range for O:C of ambient aerosol.

(41) *Fig. 3: As mentioned, say something about the weird discontinuity at the top. Mention in caption how many measurements are averaged at each height (or find a way to show this with symbology in the figure).*

We have added the corresponding information in the figure caption.

(42) *Fig 2-4: somewhere, explain why you picked the 1-bin case for all comparisons.*

We mention now that this is shown as an example.

(43) *Fig 6 caption: “Diurnally averaged (a)”*

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Corrected.

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