**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "The influence of semi-volatile and reactive primary emissions on the abundance and properties of global organic aerosol" *by* S. H. Jathar et al.

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Responses to the Comments of the Reviewers

Reviewer 1

(1) I felt that the authors did a very nice job of testing some of the key uncertainties with their sensitivity studies. However, I was surprised that this did not include a test of the aging mechanism. They did briefly contrast in the text the approach of Pye and Seinfeld (2010), but it would have been informative to see a simulation with no aging included to identify the importance of this mechanism to the total mass of OA simulated. While I hate to suggest that another model simulation is necessary I urge the authors

to seriously consider adding this. I think it would really complete the set of simulations performed and add to the citability of the paper as a comprehensive global sensitivity study. ———- We have added the 'no aging' scenario to the simulation list (Section 3, Table 3, Table 4 and Table 5) and discussed model predictions from that scenario in Sections 4.1.2 (OA budgets) and 4.2.1 (Surface OA concentrations). The context for introducing the 'no aging' scenario is setup in the Section 2.1.4 where photochemical aging is described. Model predictions from the 'no aging' scenario are also added to the panels in Figure 6 and 7. The text that is added to the relevant sections is listed below in the order it appears in the manuscript.

Section 2.1.4 – Photochemical aging: "Although we know very little about how aging proceeds, we believe it has a large influence on the OA budget and the ability of the model to reproduce observations. To illustrate its influence, we run a simulation where the POC is treated as semi-volatile but not allowed to age."

Section 3 – Simulations: "NOAG (NO AGing): To investigate the influence of gas-phase POC aging on OA burdens, we run the NOAG scenario where POC is treated as semi-volatile but the vapors are not allowed to age to form SI-SOA."

Sections 4.1.2 – OA budgets: "In addition, the difference between the BASE and NOAG scenarios (1.61 Tg) emphasizes the large contribution that POC oxidation or "aging" has on the OA burden."

Section 4.2.1 – Surface OA concentrations: "Model predictions from the NOAG scenario suggest that the model-measurement comparison worsens as the OA mass concentration decreases. The model does well in polluted locations (high OA mass concentration) presumably because the OA is very close to the source and is still fresh. This implies that as the OA moves away from the source regions, there is an enhancement in the OA mass that the NOAG model is not able to represent. It is clear, when compared to the BASE scenario, that aging the POC emissions is an essential process that needs to be modeled in order to enable a better model-measurement comparison."

————-

(2) Terminology: I have a query here about the comparison of OOA with SOA and HOA with "traditional" POA. Should the comparison not be done with OOA=SOA+POA_hydrophillic and HOA=POA_hydrophobic? Given that the crude aging mechanism of traditional models moves "aged" POA into the hydrophilic category, it seems sensible to imagine that it is a proxy of aged-POA or would appear OOA-like to an AMS. Thus, your assumptions inaccurately disadvantage "traditional" models in the comparisons. I think this is key in Figure 8 for example. On a related point, throughout the text OOA:OA and SOA:OA are used interchangeably. For clarity I would recommend referring to the observations ONLY as OOA:OA as not all future studies will convene to your definitions. ————- There has been a tremendous amount of ambiguity and confusion regarding what traditional models mean by their "aging" process. On the one hand, they may refer to evolution of the aerosol mixing state to a more internally mixed aerosol, something that would certainly not show up as OOA in the AMS. On the other hand, they may refer to heterogeneous oxidation of organics in the condensed aerosol phase, something that could show up as OOA in the AMS. In either case, "aging" in traditional models refers to different processes than here, where we mean oxidation of organic vapors to form lower volatility products. Moreover, recent evidence suggests that heterogeneous oxidation is too slow compared to the "aging" process represented in this model. Based on the reviewer's comment, we have added the following text to Section 2.1.4 and Section 4.2.2:

Section 2.1.4 – Photochemical aging: "Previous studies that have modeled POA as non-volatile have considered a hydrophobic to hydrophilic conversion of POA, which has been referred to as "aging" without being very precise about what processes were being represented. Although, it was initially meant to represent the evolution of POA from an externally mixed to an internally mixed state (Cooke et al., 1999), it has also been interpreted to represent a heterogeneous oxidation of OA to more hydrophilic products. In either case, "aging" in traditional models is different than "aging" here,

which is defined as ongoing oxidation of organics in the vapor phase. Moreover, we argue, based on the arguments by Kroll et al. (2011), that heterogenous chemistry appears to be a much slower process than the photochemical aging described in this section."

Section 4.2.2 – Oxygenated organic aerosol: "Based on our discussion in Section 2.1.4, for the TRAD model, we consider all non-volatile POA to be "unaged" and therefore as HOA and V-SOA to be OOA."

We have made changes wherever necessary to refer to the observations as OOA/OA and the model predictions as SOA/OA. Most of the changes were made in the abstract and in Section 4.2.2. ———-

(3) The model evaluation of isotopic composition inherently is based on the simulation of OC & EC mass concentrations. You clearly need to add an evaluation of simulated EC concentrations to the discussion in Section 4.2.4, particularly in light of your modifications to the relative emissions of EC/OC to correct the isotopic values. A comparison at the IMPROVE sites should be added. ———- To address the comment, we have added a plot in the supplementary material that compares model-predicted EC concentrations for the BASE and LOEM scenarios to those measured at the IMPROVE sites. We have referred to them in the text in Section 4.2.4. The revised text now reads:

"For summer, the observed contemporary fractions vary from 0.8 to 1.0, which the BASE model slightly under-predicts (0.62 to 0.85). In winter, the observed contemporary fractions vary between 0.67 to 1.0 which are significantly under-predicted by the BASE model (0.35 to 0.55). There are two possible reasons for the shortcoming of the model in predicting the contemporary fraction in winter. First, for the observations, the EC on average, accounts for 15% of the total carbon (TC) in summer and 22% of the TC in winter. In comparison, the BASE model predicts that EC on average, accounts for 22% of the TC in summer and 60% of the TC in winter. Hence, the BASE model predicts the correct EC:TC ratio in the summer but over-predicts EC concentrations

in the winter, which are mostly fossil in origin (80% of US EC emissions), at all locations except Mt Rainier (refer to Figure S1 in supplementary material). Second, the BASE scenario under-predicts OC concentrations in winter, which are mostly contemporary in origin (78% of US OC emissions), at all locations except Grand Canyon. This leads to a larger fossil fraction and a smaller contemporary fraction in winter. Therefore, lower predicted EC concentrations and higher predicted OC concentrations will likely improve wintertime comparisons. To that effect, we take EC concentrations from the LOEM (LOw EMissions) scenario and pair them with OC concentrations from the LOVL (LO VoLatility) scenario to predict the contemporary fraction. This combination, labelled 'BASE revised' modestly improves the comparison during the winter months."
———-

(4) Abstract, line 21: typo "lied" should be "lie" ———- Lied has been changed to lie.
———-

(5) Introduction, line 8: insert "non-refractory" or remove 20-90% quantifier. ———-
We removed the 20-90% 'quantifier'. ———-

(6) Introduction, line 20: Park et al., 2006 – useful to mention where/what obs were used since the conclusion is so different from other studies. Also, could you later bring us back to this study in contrast to your results? Why does Park et al., 2006 "traditional" simulation of IMPROVE obs look relatively unbiased?

The study by Park et al. (2006) compares model predictions to observations from the IMPROVE network. It is comforting to see that their results are very similar to our TRAD case (non-volatile POA) where we see very little bias in the summer and winter months (Table 5). We believe that the comparison is unbiased because the concentrations have been adjusted by increasing the OC emissions (Park et al., 2003). The text in Section 4.2.1 is revised as follows:

"For the BASE scenario, both the fractional bias and error are smaller in summer than in winter. The TRAD model, in comparison, has similar metrics in summer but better

metrics in winter than the BASE model. So on an absolute OA mass concentration basis, the TRAD model performs better than the BASE model due to differences in wintertime results. In the BASE model, reduced photochemistry in winter results in reduced aerosol formation through gas-phase oxidation of POC emissions. The TRAD model, on the other hand, predicts higher OA concentrations because none of the POC emissions evaporate. We are not surprised by the performance seen with the TRAD model because Park et al. (2006), using the same emissions inventory and IMPROVE observations, arrived at a similarly good model-measurement comparison. Park et al. (2006) achieved the better model performance by increasing the fossil and biofuel OC emissions over North America by a factor of $\sim$2."

(7) Table 2: list that GFED2 is for 2005 in the caption

We have added '2005' to the table.

(8) Page 5503, line 22: typo reference on Figure number

It is a typesetting mistake and we will notify the ACP staff about it.

(9) Section 2.1.4: Please clarify in the text that your aging scheme does not add additional mass.

We have added the following text to Section 2.1.4:

"Although oxidation might result in additional mass being added to the products, we are conservative in our aging scheme and do not add any additional mass."

(10) Page 5505, line 19 & page 5511 line 23: Heald et al. 2005 is not a reference for North American emissions (it is the ACE-Asia manuscript).

We realized that the correct reference was Heald et al., JGR, 2006 and have changed the manuscript accordingly.

(11) Page 5505, line 25: Chung and Seinfeld, 2002 and Liao and Seinfeld 2005 used an enthalpy of vaporization of 42 kJ/mol not 30 kJ/mol as cited.

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The statement in Section 3 was changed to:

"To represent the dependence of COA on temperature, we use a ΔHv value 30 kJ mole-1, a value that has been used by Farina et al. (2009).'"

(12) Section 4.1.1: re-order figure numbering. Figure 8 is discussed in the text following Figure 5 (before Figures 6 and 7 are introduced)

Figure 8 was changed to Figure 6 and figures after 6 were renumbered.

(13) Section 4.2.1, Rest of the World comparisons: suggests that the model has very little skill in reproducing the variability in observed OA! A little depressing after the efforts to include all these additional volatilization/aging mechanisms. How much do you think coarse grid scale could contribute to this?

The IMPROVE data-set represents rural and remote continental sites for which the BASE model makes reasonable predictions. This would imply that, despite the coarse resolution, the model is able to capture variability in OA concentrations within the United States. The measurement dataset used for 'rest of the world', similar to the IMPROVE data-set, represents rural, remote and marine sites. Hence, it would be hard to imagine that the scatter in the 'rest of the world' plots arises from the model's coarse resolution when the IMPROVE comparison is so much better. Rather, the poor comparison could be blamed on the uncertainty in the POC emission inventory in those regions and the lack of standardization in the measurements.

(14) Section 4.2.2: A little strange to re-introduce Figure 8 here when previously discussed in Section 4.1.1. Consolidate the discussion.

We have made a deliberate attempt to separate the discussion of model predictions from the discussion on model comparison. At the same time, we have also made an attempt to reduce the number of figures. The current figure setup is a compromise between the two.

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(1) Page 5498, line 2: The explanation of SOA aging that appears in page 5504, lines 20-21 should also appear here.

The text on page 5498 has been changed to read as follows:

"The OA model is based on the work of Farina et al. (2010). Farina et al. (2010) implemented the VBS to simulate the formation and gas-particle partitioning of SOA produced from the oxidation of VOC precursors (isoprene, monoterpenes, sesquiterpenes, alkanes, alkenes and aromatics). In addition, they also used the VBS to model the gas-phase aging of anthropogenic SOA. They assumed that POA was non-volatile and non-reactive and also did not account for IVOCs. In this paper we modified the model of Farina et al. (2010) to account explicitly for semi-volatile and reactive POA and IVOCs."

(2) Section 2.1.5: The authors made no sensitivity runs for the Henry law selected. This is a major uncertainty, given the rather high value selected (which is common among model studies). Why not selecting a varying value based on volatility? Volatility bins can also describe the degree of oxidation, which should be related to the solubility. This also applies to the choice of 80% scavenging efficiency for all organic particles, regardless of volatility.

No sensitivity simulations were run for the Henry's law constant because the effect was previously explored by Farina et al. (2010). Also, we are not aware of any robust data to model the Henry's law constant or the scavenging efficiency as a function of volatility. To make the discussion complete, we have revised and/or added to Section 2.1.5 as follows: "The solubility of gases is determined by their effective Henry's law constants and all organic gases are assigned a Henry's law constant of 105 M atm-1. It is likely that higher volatility products on account of being less oxygenated have a lower Henry's law constant and vice-versa but in the absence of any robust data, we consider it to be constant across volatility.

The previous version of the unified model (Farina et al., 2010) divided POA into hy-

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drophobic and hydrophilic categories to distinguish between their wet deposition characteristics (Chung and Seinfeld, 2002). By assuming that the organic particulates form a single phase (Section 2.1.1), we use the same wet deposition characteristics for all OA and hence avoid this additional categorization all together. Following Chung and Seinfeld (2002) all organic particles are assigned a scavenging efficiency of 80%. Again, it is likely that the scavenging efficiency, just like the Henry's law constant, is a function of volatility but in the absence of any robust data, we consider it to be constant across volatility."

(3) Page 5506, lines 19-20: Why not changing the dH values for SOA formation as well, for consistency with the HVAP scenario?

The SOA yields for various VOC precursors have been independently derived by different groups and published in various papers. It would take a significant effort to acquire the raw data and re-work those yields with the heat of vaporization values prescribed by Epstein et al. (2010). Moreover, it would be beyond the scope of this paper. Further, most SOA smog chamber experiments are done quite close to 298 K, which is the reference temperature for the volatility basis set. Hence, the revised heat of vaporization values will probably not have a huge effect on the SOA mass yields. The text is revised to read as follows:

"One needs to exercise caution when interpreting results from the HVAP scenario as yields for SOA formation have been derived using a single value for the heat of vaporization ($\Delta Hvap$ in the range of 30-60 kJ mole-1 depending on the study). However, given that most SOA chamber experiments are done quite close to 298 K - the reference temperature for the VBS - using the revised heat of vaporization values will probably not have a huge effect on the SOA mass yields."

(4) Page 5508, line 25: The difference of 0.89 Tg is lower than the one between BASE and HVAP. This means that the assumption of the volatility distribution and aging of IVOC is at least equally important compared to their sources. Nevertheless, HVAP

increased burden reflects the POC aging and volatility distribution as well. Can you quantify the contributions of each? Please comment.

The reviewer comment is a little ambiguous which makes it hard to answer. The difference of 0.89 Tg between the BASE and NOIV scenario reflects the influence that IVOCs exert on the OA burden. By comparing this difference to the difference between the BASE and HVAP scenarios, is the reviewer suggesting that IVOC aging might be as important as the heat of vaporization values for all of OA in the SVOC range? To answer the question that is posed, we would have to run the HVAP scenario without IVOCs.

(5) Last paragraph of section 4.1.2: SOA yields come from chamber experiments that do not necessarily capture the multi-day aging that might undergo in the atmosphere. Acknowledging the uncertainties related to introducing such an aging, is there a reason that you expect that SOA will not age like the other organic aerosols in the model? Why not introducing SOA in the volatility bins and allow them to evolve?

We do put all SOA into the volatility bins of the VBS. Moreover, we do allow anthropogenic SOA products to undergo further evolution/aging. We do not, however, allow biogenic SOA to undergo additional aging beyond the yields captured in smog chambers. This is the same as the earlier model built by Farina et al. (2010). Their assumption for not aging biogenic SOA is that the SOA mass yields represent completed reactions for biogenic VOCs. Although we realize that this is a big assumption, we do not yet have a good parameterization for aging biogenic SOA that works for global and regional OA models (Lane et al., 2008, Murphy and Pandis, 2010). We had added the following text to Section 2.1.4 and Section 4.2.1.

Section 2.1.4 – Photochemical aging: "Farina et al. (2010) assumed that the SOA mass yields for biogenic VOCs represent completed reactions and hence they do not need to be aged. We realize that this is a significant assumption that requires additional study that is outside the scope of this manuscript. However, simple "first guess" aging

parameterizations, when applied to biogenic SOA, lead to gross over-predictions in regional models (Lane et al., 2008, Murphy and Pandis, 2009). Hence, as per Farina et al. (2010), the biogenic V-SOG is not allowed to age while the anthropogenic V-SOG is allowed to age with a reaction rate of 4 x 10-11 cm3 molecules-1 s-1."

Section 4.2.1 – Surface OA concentrations: "Presumably, the wintertime comparison can also be improved by aging biogenic SOA. However, given that biogenic VOC emissions are higher (Guenther et al., 2006) and photochemical processing is stronger in the summer, aging biogenic SOA at the same rate as anthropogenic SOA would influence the summertime IMPROVE comparison much more than the wintertime IMPROVE comparison."

(6) Page 5511, lines 14-20: Maybe too efficient removal of gases can explain this as well? See also comment #2.

Although possible, the efficient removal of gases would affect both summer and wintertime results almost equally. Hence, a lower Henry's law constant or a lower scavenging efficiency would presumably improve wintertime results but worsen the summertime results.

(7) Page 5512, line 6: If you believe this set of heat of vaporization values is more realistic, why not using it in BASE?

Actually, we do not consider the set to be more realistic since the heat of vaporization values used in HVAP predicts too volatile an OA when compared to the OA volatility at Finokalia, Riverside and Mexico City. The intent of HVAP as a sensitivity simulation is to demonstrate that it works well in reproducing OA mass concentrations but fails to predict ambient OA volatility. We have revised the text in Section 4.2.1 to say:

"The HVAP scenario, using a wider range of heat of vaporization values, better reproduces the winter data with a slight over-prediction during the summer."

8) Section 4.2.3: Please mention and comment in the discussion how much traditional

SOA is present in these locations, since it does not age, which affects the volatility distribution. If there is plenty of traditional SOA, it might change the discussion considerably.

Just to clarify, the SOA from anthropogenic VOCs is allowed to age while the SOA from biogenic VOCs is not. The amount of traditional SOA at the three sites discussed in Section 4.2.3 can be inferred from the TRAD curve (solid green) in Figure 9 by looking at the OA MFR at the highest temperature, i.e. traditional SOA accounts for about 30, 60 and 50% of the OA mass at the FAME, MILAGRO and SOAR sites. As the reviewer has pointed out, aging the biogenic SOA will make the OA less volatile which will result in all the curves shifting upwards. This, however, would worsen the TRAD predictions compared to the measurements and have little influence on the conclusion that the revised framework does better in predicting the OA volatility. To incorporate the reviewers comment, we have revised the text in Section 4.2.3 as follows:

"The initial decrease in the mass fraction remaining for the TRAD model is due to the evaporation of semi-volatile V-SOC. At higher temperatures, the flat response of the thermogram reflects the remaining POA, which is treated as non-volatile by the TRAD model and does not evaporate at any temperature."

(9) Same section: The use of thermograms is an extremely useful technique to validate the OA volatility in global models and it should be highlighted more in the iňĄnal manuscript.

We agree that it is extremely useful, but it is already highlighted in the conclusions section as written:

"We evaluated model performance by comparing predictions not only against ambient OA mass concentrations but also against observations that provide insight into the sources, chemistry and properties of OA. These additional observations include degree of oxygenation, volatility and isotopic composition. The revised versions of the model perform much better on all those additional observations than the traditional version

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of the model. This illustrates that by modeling POA as semi-volatile and reactive and the emissions and oxidation of IVOCs, we have improved the model's capability in predicting the sources, chemistry and properties of OA. For example, we are able to predict degree-of-oxygenation of OA. This has important implications for climate models that determine the effects of aerosols on radiative forcing as oxygenated OA have a higher propensity to uptake water and affect cloud formation. We are also able to predict the volatility of OA which is important in determining its lifetime and fate in the atmosphere."

We have revised the abstract to separate the contribution from the OOA/OA comparison and the volatility comparison as follows:

"Predictions of the revised model for the SOA fraction at 17 different locations compared much better to observations than predictions from the traditional model. Model-predicted volatility is compared with thermodenuder data collected at three different ïňA̧eld campaigns: FAME-2008, MILAGRO-2006 and SOAR-2005. The revised model predicts the OA volatility much more closely than the traditional model."

(10) Page 5515, lines 19-21: How does BC burden compares with that of OC in this fraction?

We have revised the text in Section 4.2.4 to read as follows:

"There are two possible reasons for the shortcoming of the model in predicting the contemporary fraction in winter. First, for the observations, the EC on average, accounts for 15% of the total carbon (TC) in the summer and 22% of the TC in the winter. In comparison, the BASE model predicts that EC on average, accounts for 22% of the TC in the summer and 60% of the TC in the winter. Hence, the BASE model predicts the correct EC:TC ratio in the summer but over-predicts EC concentrations in the winter, which are mostly fossil in origin (80% of US EC emissions), at all locations except Mt Rainier (refer to Figure S1 in supplementary material)."

(11) End of page 5515: The assumption that traditional SOA do not age affects these results. If it was allowed to age, I would expect that the model would calculate more contemporary OA. Please comment.

We have added the following text to Section 4.2.4:

"It is also possible that the model-predicted contemporary fraction in winter is low because the biogenic SOA, which is all contemporary, is not allowed to age. However, as mentioned in Section 4.2.1, this would badly over-predict the summertime OA mass concentration as seen by Lane et al. (2008) and Murphy and Pandis (2009). Hence, it is not clear whether the aging of biogenic SOA is important in predicting the correct contemporary fraction in winter."

(12) Linking in the text is broken. There are places that mention e.g. Fig. refvbssch

It is a typesetting mistake and we will notify the ACP staff about it.

(13) Page 5513, line 9: "predicts the correct fraction" should be something like "reproduces more accurately the fraction" or something similar. The word "correct" is too strong, given the uncertainties of the modeling approach.

The statement has been changed to:

"The BASE case reproduces more accurately the fraction of OOA with model predictions lying between -21 and +27% of observations."

(14) Epstein et al reference is from 2010, not 2009.

The reference has been corrected.

(15) Huffman et al reference is missing the initial H.

The reference has been corrected.

(16) Table 4 should include Kanakidou et al. 2005, if not some models from that paper, same with the discussion in page 5509, lines 2-3. Chung et al is Chung and Seinfeld.

We have added burdens from the following papers to Table 4: Griffin et al., GRL, 1999 Kanakidou et al., JGR, 2000 Derwent et al., JAC, 2003 Tsigaridis and Kanakidou, ACP, 2003 Lack et al., JGR, 2004

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Fig. 1. Figure 6

Fig. 2. Figure 7

Fig. 3. Figure S1