acp-2013-23
Comment on ”Modeling organic aerosol from the oxidation of α-pinene in a Potential Aerosol Mass (PAM) chamber”

Anonymous Review

This paper applies the 2D-VBS model framework to predict organic aerosol formation in the high-oxidizing environment of the PAM chamber. The unique nature of the experimental setup allows the authors to probe long-term, multigenerational aging of organic aerosol and evaluate the ability of the VBS to represent this aging. The model configuration and general setup has been used before with some success, but the clear contribution of this paper (beyond the interesting experimental data) is the multi-variable sensitivity analysis presented. Specifically, Figures 5 and 6 and the associated discussion provide quite valuable, quantitative insights that are much-needed for the 2D-VBS. The paper is well-written in general, but I have some concerns regarding the assumptions the authors have chosen to include, as well as the lack of discussion of some of their model's results. These issues should be addressed before this paper is published.

Major Comments:

1. Page 2764, Line 11-15: Could the authors please discuss the applicability of this temperature correction to their measurements? First, I think the authors mean to cite Stanier et al. (2008) rather than (2007). The (2007) measurement study did not report such a precise recommendation. More importantly, these studies focused on first-generation ozonolysis products; they included an OH scavenger in their experiments. Given arguments like that of Epstein et al. (2009) and the connection between volatility and enthalpy of vaporization, how can the authors be confident that this temperature sensitivity will hold throughout the intense aging in the PAM chamber? If the system is heating up along the flow, a discrepancy here could help account for the overprediction in C_{OA} at high OH exposure and underprediction of O:C at high OH exposure (assuming higher O:C for less volatile material). More importantly, if there is a temperature change along the flow, it should be accounted for in the model. Did the authors account for shifting of the saturation concentrations with temperature in the model itself?

2. Page 2773, Line 20: It is disturbing that increasing the range of modeled O:C bins significantly increases the prediction of O:C. It is mentioned again (Page 2776, Line 19-21), but never fully discussed. It is also confusing why the authors chose to run one sensitivity case with the upper limit at 1.8 and then run the global analysis with upper limit at 1.4. Specifically, if the bulk-average O:C can change by a factor of 1.5 (from about 0.9 to 1.4 at high OH exposure; Figure 4), simply by changing the model's O:C boundaries, something seems to be wrong. In general, this problem would suggest either that the O:C range should be made larger (large enough so that it no longer impacts the results), or that the model is not behaving well numerically. If the latter is the case, then a high enough choice of upper limit for O:C (i.e. > 2) would allow physically unrealistic molecules to be formed. Could the authors please acknowledge and discuss briefly in the text this apparent weakness in the model, or show with an additional sensitivity what upper limit on O:C is necessary to avoid artificially lowering the bulk O:C prediction?

3. Heterogeneous OH reactions are treated a little too lightly here, given the fact that the sensitivity analysis suggests the rate is very important for predicting both C_{OA} and O:C at high OH exposure. The major concern is whether or not the gas-phase reaction formulation is valid. The authors do mention briefly in the conclusions that this assumption deserves more scrutiny but I think considering the context of the PAM chamber, it deserves some here as well. Specifically, does the high-oxidizing environment of the PAM chamber (OH~10^{10} molec cm^{-3}) make diffusive limitations important enough to add a correction to the model?

4. The fact that the global analysis was not able to capture the shape of the O:C evolution curve is problematic. This either means that the model formulation is definitely wrong, or that not enough of the parameters were varied. Did the authors consider adjusting the stoichiometry (probability of adding oxygen atoms, fragmentation branching ratio, etc) for the homogeneous and heterogeneous reactions independently for their sensitivity study? In most chamber experiments, analysis is difficult since the high OH exposure limit is not probed significantly. However, here there is a unique opportunity to investigate the contributions of heterogeneous oxidation to high observed O:C. Are there other specific problems with the model framework that the authors could attribute this discrepancy to?

5. Page 2776, Line 6-10: There are several very interesting results here but the authors simply report them, rather than giving some analysis. Please add some thoughts, for instance, about why the probability of adding 2 oxygen atoms is important, but adding 1 or 3 of them is not. The coupling between number of C* bins the heterogeneous reaction rate is also surprising. What is causing this, in the authors' opinion?

6. Page 2765, Equation 2: This is wrong. The authors need to include the inverse exponent. Please explicitly refer to i, ξ_i and C^*_i in the text. The authors may also consider, for completeness, adding the other equation used in Donahue et al. (2006) that shows the other relationship between aerosol mass fraction and total organic aerosol mass used for solving the system.

Minor comments:

Page 2672, Line 4: This is not always true. The products may go to higher volatility after fragmentation. However, if the C-C cleavage occurs such that one of the resulting radical intermediates contains essentially the same number of carbon atoms as the parent, it can easily form products of lower volatility than the parent after it is functionalized and stabilized.

Page 2764, Line 15: Where does this 25% uncertainty in C_{OA} come from? Is this an addition of the previous sources of uncertainty in some other measurement technique source?

Page 2764, Line 25: Why stop the upper limit in modeled O:C at 1.2 for the base case? If this is just for consistency with previous models, please say so. However, Figure 5 shows that portions of products formed in the PAM chamber could reach higher O:C than 1.2.

Page 2766-2767: The authors' explanation of fragmentation processes is difficult to understand. Admittedly, it is difficult to describe. Could the authors consider adding a figure with two panels illustrating the movement of fragments in the 2D-VBS space under the two methods? This might help readers understand the effects of this choice on the results.

Page 2772, Line 1-2: Instead of relying on the decrease in SOA mass to suggest the increased role of the fragmentation pathways, could the authors present quantitative data or a figure showing the value of the "bulk-average" branching ratio as a function of OH exposure (related through O:C as a function of OH exposure)? This would help give some solid characterization of the sensitivity of the mass decrease to the branching ratio.

Page 2774, Line 6: This statement is confusing. It seems clear that when the O:C of first-generation products is lowered, fewer of them fragment due to the relationship with the branching ratio (thus C_{OA} rises). O:C then decreases because more products are formed through the functionalization pathway from the early aging steps and because the O:C of the first-generation products are lower. Is this a correct analysis? If so, the authors' explanation does not seem to agree, or it is written somewhat awkwardly.

Page 2774, Line 4: The statement "the agreement is worse" could use some quantification or specific data for support.

Page 2775, Line 23-25: The authors' point is clear, but it would make a stronger case if they had just assigned all of the material higher in volatility than the upper limit to the highest volatility bin instead of excluding it. Of course this would lead to overprediction since the most volatile vapors would be artificially kept at semi-volatile saturation concentrations. A compromise might be to exclude vapors above 10^6 µg m^{-3} after calculating the fragmentation but keep the lower ones. Is there a reason the authors did not consider exploring this a little more since the number of C* bins seems so critical?

Page 2776, Line 3-5: It could also be the case that the gas-phase reaction rate has little impact because the first-generation yields have already put a lot of the material at semivolatile saturation concentrations. The authors should address in a sentence or two the coupling between the sensitivity of C_{OA} to the homogeneous reaction rate and to the parameterized volatility of the first-generation products. Is this something to be worried about?

Technical Comments:

Page 2761, Line 5: Please remove "Pankow" to read just "(1994)"

Page 2761, Line 20: Please specify the typical units of µg m^{-3} used for effective saturation concentration.

Page 2761, Line 20: Please add parentheses around α to read "for each bin (α_i) can"

Page 2671, Line 22: Please consider removing “mass” to just read “In addition to volatility.” I understand what the authors are trying to say here, and it is clear that OA mass has an effect on partitioning, but I think it’s confusing to some audiences to call it a “property” of “organic material” when material and mass are very similar words in this context. Another alternative might be to write “In addition to volatility and particulate-phase mass concentration, other properties of the organic aerosol system…”

Page 2671, Line 26-29: This sentence is also somewhat awkward. Perhaps try “Products of the oxidation of organic precursors may be classified by both C^* and O:C and mapped onto the 2D-VBS plane. Further chemical processing, it has been argued (Jimenez et al., 2009), can then be viewed to proceed through two competing pathways: functionalization and fragmentation.”
Page 2762, Line 21: Please consider replacing “aerosol” with “particle” since aerosol refers to both the gas and particle together. This is usually not a big deal, but since the authors are specifically talking about the removal of particles and not the gases and particles, I think it’s worth being precise.

Table 3: Typo. The 12th parameter should read “Adding 1 O probability”

Figure 1: The broken x-axes on panels (b) and (d) are ok, but please consider changing the lower axis ticks to 0.1 and 0.2 molec cm^{-3} s. Having the broken axes and the magnitude change is a little too crowded. Also, please explicitly reference and identify panels (a) and (c) in the caption.

Figure 4: Please add error bars to the measurement data points for help in comparing accuracy of model representations.