

Reply to Referee #1's comment

We would like to thank Referee#1 for the thoughtful and useful comment. Below are our point by point responses (in blue) to the comment (in black).

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.

We have addressed these issues as detailed below.

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?

We thank the reviewer for pointing out the temperature sensitivity issue. We are currently using the model to simulate the SOA formation and continuous aging as a function of OH exposure under a constant temperature (298 K) and comparing the results with temperature-corrected C_{OA} . We agree that the temperature dependence of the saturation concentrations should be included in the model itself. However, the effect of temperature on C_i^* as a function of OH exposure is unknown. Alternatively, we now adjust the temperature in the model to match the measured temperature in the PAM chamber, shift the saturation concentrations of the volatility basis set based on the enthalpy of vaporization estimated in Epstein et al. (2010) (C_i^* -dependent ΔH_{vap}) and Pathak et al. (2007) (effective $\Delta H_{vap}=30 \text{ kJ mol}^{-1}$), and re-run the model several times to obtain O:C and C_{OA} at measured levels of OH exposure. The select case ($\Delta \text{VOC}=281 \mu\text{g m}^{-3}$) with measurements at six levels of OH exposure is used here to probe the impact of

temperature change. We now add two paragraphs in the text to discuss the impact of temperature as below:

“The temperature dependence of C_i^* is represented by the Clausius-Clapeyron equation (Donahue et al., 2006):

$$C_i^*(T) = C_i^*(T_{\text{ref}}) \frac{T_{\text{ref}}}{T} \exp\left[\frac{\Delta H_v}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right] \quad (1)$$

where T_{ref} is the reference temperature, ΔH_v is the enthalpy of vaporization, and R is the universal gas constant. A constant effective ΔH_v of 30 kJ mol⁻¹ was used in Pathak et al. (2007) for the VBS parameterization of the SOA yields from α -pinene. However, Epstein et al. (2010) proposed a semi-empirical correlation between ΔH_v and C_i^* . Since ΔH_v is an uncertain parameter, a constant temperature of 298 K was used in the base-case model. Because UV lamps in the PAM chamber lead to temperature increases (measured temperature $T_{\text{obs}} = 21\text{-}36^\circ\text{C}$) and hence less SOA formation, the modeled C_{OA} is hence compared with measurements corrected at -0.02 per degree K of temperature increase (Stanier et al., 2008) relative to 298 K, which typically varies by 10-15%. Additional model simulations were performed at measured temperature T_{obs} with either $\Delta H_v = 30$ kJ mol⁻¹ or the C_i^* -dependent ΔH_v as in Epstein et al. (2010) to explore the temperature sensitivity of the model (see Section 3.3.1).”

“3.3.1 Temperature sensitivity

To probe the impact of temperature and ΔH_v variations on the model-measurement agreement, twelve additional simulations were run for the select case ($\Delta\text{VOC} = 281 \mu\text{g m}^{-3}$) at six measured temperature T_{obs} (295-307 K) with either a constant effective ΔH_v (30 kJ mol⁻¹) or C_i^* -dependent ΔH_v (Epstein et al., 2010). The model results show that the model with the constant ΔH_v does not produce a significant variation in modeled C_{OA} (within 6%) and O:C (within 1%) for the range of T_{obs} . For the model with C_i^* -dependent ΔH_v , the modeled C_{OA} decreases by up to 35% at higher temperatures (303-307 K) and higher OH exposures, as a result of the shift of C_i^* . Meanwhile, the modeled O:C only varies within 3%, compared to the model results at 298 K. Therefore the model performance was compared by the model-to-observed ratios of C_{OA} only, using the uncorrected measurements for the additional model results (Fig. S2). In general, relatively consistent model-to-observed ratios (within 7%) were obtained while the model accounts for the temperature increasing up to 303 K. For the temperature at 307 K and a high OH exposure of 2.1×10^{12} molec cm⁻³ s, C_{OA} predicted by the model with C_i^* -dependent ΔH_v is in better agreement with the measurement (model-to-observed ratio decreases from 3.0 to 2.3), although significant overprediction remains. Therefore the temperature correction used in this work gives results comparable to more detailed treatments of temperature for OH exposures up to 1.4×10^{12} molec cm⁻³ s. For higher temperature and OH exposure, the discrepancy caused by the constant temperature correction can partially explain the overprediction of C_{OA} .”

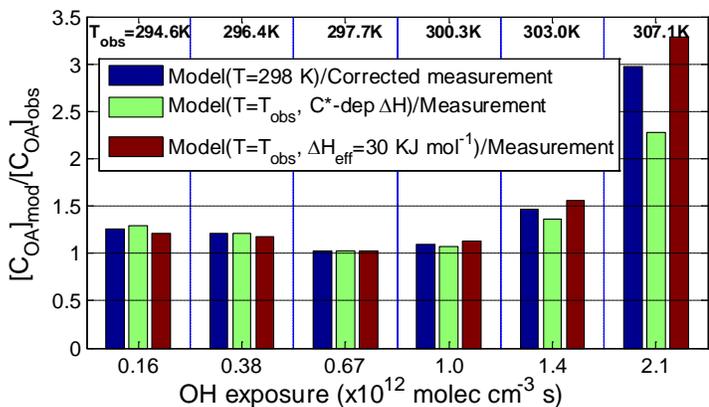


Fig. S2 The modeled-to-observed ratios of C_{OA} modeled under 298 K and under measured temperature T_{obs} with a constant effective ΔH_v or C_i^* -dependent ΔH_v as in Epstein et al. (2010) ($\Delta VOC = 281 \mu g m^{-3}$).

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?

The original Fig. 4 (now Fig. 5) shows the model results from the original model (OM) in which all fragments have the same O:C of the reactants, the modified model (MM) in which lighter products of fragmentation reactions were assumed to have higher O:C than the reactants, and the MM with adjusted model parameters (adjusted MM). For both OM and MM, the upper limit of O:C greater than 2 will produce the same modeled C_{OA} and O:C since the unrealistic products with O:C>2 will be lumped into the products with O:C of 2. Because the O:C of the light products in MM were assigned in a way that it moves diagonally to the O:C boundary (higher end), modeled O:C by MM is much more sensitive to the O:C boundary than that by OM. Hence for the MM, we applied a relatively high upper limit of O:C at 1.8 to probe its impact (Fig. 5). But for the global sensitivity analysis which considered the OM as the model of interest, we varied the highest O:C from 1.0 to 1.4, which is up to two bins difference with respect to the original 12 O:C bins. Additional OM model runs for the select case with $\Delta VOC=281 \mu g m^{-3}$ indicated that, compared to modeled O:C of 0.89 at high OH exposure (2.0×10^{12} molec cm⁻³ s) by the original model (O:C_{max}=1.2), varying the highest O:C to 1.0, 1.4 and 2.0 predicts O:C of 0.81, 0.93, and 0.97, respectively. We now add a sentence in section 3.3.3 about the upper limit of O:C as below:

“Additional sensitivity runs indicate that modeled O:C at high OH exposure (2×10^{12} molec cm^{-3} s) increases from 0.81 to 0.93 and 0.97 by varying the highest O:C from 1.0 to 1.4 and 2.0, respectively. Therefore the upper limit of O:C of at least 1.4 is needed to avoid artificially lowering the O:C prediction by the original base-case model.”

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 COA 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 ($\text{OH} \sim 10^{10}$ molec cm^{-3}) make diffusive limitations important enough to add a correction to the model?

The treatment of the heterogeneous OH reactions in the model is consistent with previous studies, including the very recent ones (e.g., Donahue et al., 2012). Alternative treatments are beyond the scope of current study and are suitable for further research in the light of the sensitivity analysis results which suggest increasing importance of heterogeneous reaction rate at high OH exposure.

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?

We agree that either more parameters should be varied for the global sensitivity analysis or the model formulation could use some improvement, as partially discussed in the section 4. We thank the reviewer for pointing out that the stoichiometry for the homogeneous and heterogeneous reactions could be different. The model will be modified accordingly and the model sensitivity to this modification will be investigated in future work. We now revise the related text and add more possible reasons for the model-measurement in the text as below:

“While the modeled and observed SOA O:C increase with OH exposure, the magnitude and functional form of the increase differ significantly. This discrepancy is probably not specific to the highly oxidizing environment in the PAM chamber because the same general trends were also observed in two large environmental chambers (Ng et al., 2007; Donahue et al., 2012a). Thus it is likely that this discrepancy emerges from the model framework. A global sensitivity analysis has the potential to indicate the cause. The most important parameters for modeled C_{OA} and O:C were found to be associated with the highest C_i^* and O:C values used to define the boundary of the 2D-VBS space, the initial mass yields and O:C ratios of the products from the first-generation oxidation,

particle-phase OH uptake rate and the probability of adding oxygen atoms during the functionalization process.

However, none of the Monte Carlo simulations were able to reproduce the measured curvature of O:C, suggesting that either more parameters should be varied for the global sensitivity analysis or the model formulation should be changed. In addition to the 13 model parameters listed in Table 2, the model sensitivity to more parameters will be explored in future work, such as (1) alternative first-generation product yields representations (e.g., RH-dependent yields), (2) varied magnitudes of C_i^* reduction following functionalization reactions, and (3) alternative representations of fragmentation coefficient (e.g., as in Cappa and Wilson (2011)).

For the model formulation, it is possible that some assumptions made for current model are too simplified to represent the trajectory of SOA aging accurately. For instance, some of the model parameters such as the probability of adding oxygen or fragmentation could be a function of carbon number, molecular structure, volatility, and/or oxidation state of the reactant products. In addition, the widely used assumption of instantaneous equilibrium partitioning may lead to overprediction of C_{OA} (Shiraiwa and Seinfeld, 2012) if the SOA is characterized by a solid phase state (Virtanen et al., 2010; Perraud et al., 2012; Saukko et al., 2012). Other assumptions that deserve more scrutiny include OH and O_3 reactions causing the same products or using a gas-phase reaction rate coefficient to simulate heterogeneous chemistry instead of including microphysics as well as chemistry and using the same mechanisms for gas-phase and heterogeneous oxidation reactions. For example, the fragmentation branching ratios in the heterogeneous reactions may be different from gas-phase reactions (Kroll et al., 2009). These assumptions will be tested in future work.”

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?

We would like to clarify that the probability of adding 3 oxygen atoms (P_{3Os}) was not included in the computation of the global sensitivity since it directly relates to the probability of adding 1-2 oxygen atoms (P_{1O} and P_{2Os}), i.e., $P_{3Os}=1-P_{1O}-P_{2Os}$, as stated in section 2.3. Therefore the importance of P_{2Os} does not rule out the importance of P_{3Os} , since we could not vary the P_{2Os} without changing P_{1O} or P_{3Os} . In fact, the importance of P_{2Os} reflects the potential importance of P_{3Os} . The fact that P_{2Os} (average S_i of 0.07) was found to be more influential than P_{1O} (average S_i of 0.03) for C_{OA} can be explained by the separate probability functions for the change in volatility when 1-3 oxygen atoms are added to the organic compounds (Roldin et al., 2011). That is, compared to the C_i^* of the reactant, when 1 oxygen atom is added, the C_i^* of the products can be reduced by 1-3 decades (centered at 2 decades); when 2 oxygen atoms are added, the C_i^* of the products can be reduced by 2-5 decades (centered at 3-4 decades); when 3 oxygen atoms are added, the C_i^* of the products can be reduced by 3-7 decades (centered at 5 decades). Therefore adding more oxygen atoms leads to greater shift of the products to the lower volatility direction, which covers a larger range in volatility variation, and hence has more impact on modeled C_{OA} .

We now add a sentence to clarify this in section 2.3 as below:

“For the probability of oxygen addition during functionalization process, a broad range of 0-0.5 was assumed for both adding one (P_{1O}) and two atoms (P_{2Os}) while the probability of adding three atoms (P_{3Os}) was simply calculated by $1-P_{1O}-P_{2Os}$. Therefore only the independent P_{1O} and P_{2Os} were included in the sensitivity analysis.”

We also add the explanation to section 3.3.3 as below:

“The probability of adding more oxygen atoms is more influential (average S_i of 0.07 and 0.02 for P_{2Os} and P_{1O} , respectively) since adding more oxygen atoms leads to a greater shift of the products to lower volatilities, which also covers a larger range of the volatility reduction (e.g., 1-3 and 2-5 decades reduction in volatility by adding 1 or 2 oxygen atoms, respectively).”

We now modify the sentence about the coupling of n_x and k_{OH_hetero} as below:

“As the particle is further oxidized and more mass of oxidation products condenses to the particle phase, C_{OA} becomes more sensitive to the heterogeneous oxidation rate. Note also that C_{OA} becomes sensitive to the coupling between the n_x and k_{OH_hetero} (S_{ij} up to 0.07) since n_x is critical in determining the mass of oxidation products in particle phase, which react with OH at the effective rate constant of k_{OH_hetero} .”

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.

We have corrected the equation. We have also added the other equation and referred to i , ξ_i and C_i^* in the text as below.

“The model also assumes instantaneous absorptive equilibrium with a gas-to-particle partitioning so that the mass fraction in the particle phase in each volatility bin (Donahue et al., 2006) can be defined by a partitioning coefficient ξ_i for species i with a effective saturation concentration C_i^* :

$$\xi_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1}; C_{OA} = \sum_i C_i^* \xi_i \quad (2)''$$

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.

We assume that the reviewer meant page 2762. We now remove the “moving the products to higher volatility” from the sentence as below:

“Functionalization refers to a net addition of oxygen without change of carbon number by adding oxygenated functional groups to a reactant, moving the products to lower

volatility and higher oxidation states; fragmentation refers to a net loss of carbon due to carbon-carbon bond cleavage (Kroll et al., 2011).”

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

We now add a sentence to summarize how we estimate the uncertainty in measured C_{OA} as below:

“The averages of SOA mass concentrations (C_{OA}) measured by the SMPS and AMS were used. The uncertainty in C_{OA} was estimated to be $\pm 25\%$ (1σ confidence level), which combines the uncertainties in both SMPS and AMS measurements, the AMS ionization efficiency calibration, and calculated effective density.”

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.

We now add the reason to choose upper limit in O:C, $(O:C)_{max}$ at 1.2 as below:

“The O:C of the organic products ranges from 0.1 to 1.2 while linearly separated by 0.1 (i.e., 12 bins of oxygenation, $n_y = 12$), consistent with the previous studies (e.g., Murphy et al., 2011, 2012).”

As discussed above (reply to major comment 2), higher $(O:C)_{max}$ was tested in sensitivity analysis and the lowest $(O:C)_{max}$ needed to avoid artificially lowering the bulk O:C prediction was suggested.

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.

We now add a figure (Fig. S1) in the supplement to show the difference in the two fragmentation pathways on the 2D-VBS space as below:

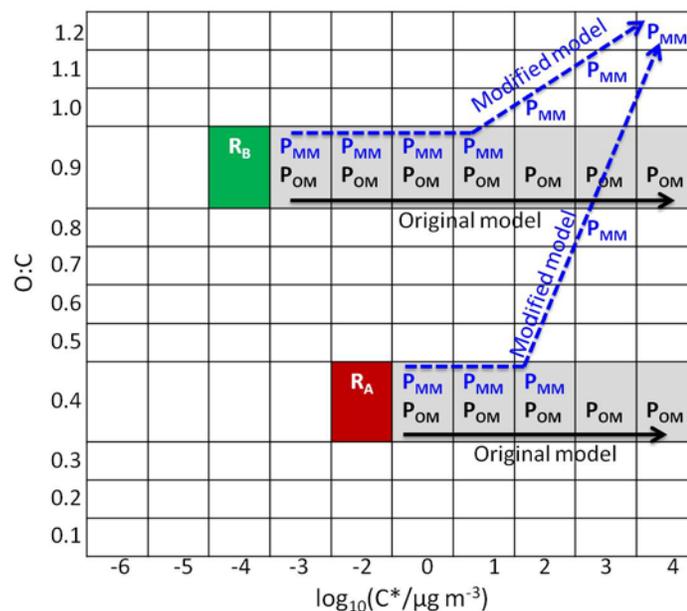


Fig. S1 The distribution of the fragments formed from two example reactants, R_A and R_B . P_{OM} denotes the fragments based on the assumptions in the original model (OM, the same O:C as the reactant). P_{MM} denotes the fragments based on the assumptions in the modified model (MM, higher O:C for the lighter fragments).

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.

We now revise the sentence and add the data of bulk O:C and branching ratio as below:
 “This SOA decrease along with the increase of the O:C from 0.61 to 0.77 suggests the importance of the fragmentation reactions that increase product volatility and decrease the yield of LVOCs and SVOCs, while the fragmentation coefficient f_c is greater than 0.92.”

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 COA 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.

We now revise the sentence as below:
 “Adjusting this parameter to a lower specific value (e.g., 0.2) increases the modeled C_{OA} by 43% and decreased the modeled O:C by 13% since more products are produced with lower O:C, which also decreases the fragmentation branch ratio.”

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

We now add some quantification data as below:

“Applying this alternative model configuration (MM) and adjusting these model parameters does not improve model-measurement agreement for C_{OA} or O:C relative to the base-case model. In many cases, the agreement is worse (e.g., average relative error of MM is higher than OM by a factor of 1.6 and 3.3 for C_{OA} and O:C, respectively).”

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 $10^6 \mu\text{g m}^{-3}$ 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?

The compromise solution suggested by the reviewer is actually equivalent to using $n_x=12$ (i.e., highest C_i^* of $10^6 \mu\text{g m}^{-3}$) in the model. Model simulation with $n_x=12$ (other model parameters hold the same as in the base-case model) shows that generally higher C_{OA} (except for lower OH exposure) and O:C are predicted, leading to worse model-measurement for C_{OA} (average relative error increases from 21% to 61%) and similar model-measurement for O:C (average relative error increases from 30% to 34%).

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 semivolatility saturation concentrations. The authors should address in a sentence or two the coupling between the sensitivity of COA to the homogeneous reaction rate and to the parameterized volatility of the first-generation products. Is this something to be worried about?

For the parameterized volatility of the first-generation products and the homogeneous reaction rate used in the model, the coupling between these two parameters is very weak based on the sensitivity analysis (i.e., the sum of higher-order sensitivities S_{ij} and S_{ijk} involving k_{OH_hetero} and α_i is not larger than 0.02), even if we run one more sensitivity analysis for the early aging (OH exposure $\sim 5 \times 10^{10} \text{ molec cm}^{-3} \text{ s}$).

Technical Comments:

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

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

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

We now revise the text as suggested above.

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...”

We now remove “mass” and just keep “In addition to volatility”.

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 2DVBS 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.”

We now revise the sentence as below:

“Products of the oxidation of organic precursors are classified by both C_i^* and O:C and mapped onto the 2D-VBS space. Further chemical processing 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.

We now replace “an aerosol” with “a particle”.

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

We now correct this typo.

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⁻³s. 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.

We now split this figure to Fig.1 and Fig. 2, as suggested by reviewer #2. We also change the lower x-axis ticks for the consistency and identify/reference the subplots in the caption.

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

We now add error bars to the measurement data points.

Reply to Referee #2's comment

We would like to thank Referee#2 for the thoughtful and useful comment. Below are our point by point responses (in blue) to the comment (in black).

In this work, the authors modeled the evolution of α -pinene SOA in a flow chamber using the recently developed 2-dimensional volatility basis set (2D-VBS) framework. The experiments cover a wide range of OH exposure, which is a feature of the PAM chamber. Their model agrees qualitatively with measured values of organic aerosol concentrations and O/C, but cannot reproduce the temporal trend of O/C. The authors also examined the sensitivity of the model to each individual oxidation and partitioning parameter using global sensitivity analysis techniques. The paper is well written and the analysis is novel and carefully thought out. I recommend publication in ACP upon considering the following comments.

Major comments:

1. My main take - home message from the results is that although 2D - VBS is a step forward in predicting OA chemical properties by incorporating O/C, the representation is still too simplistic to be able to capture evolution of O/C. This is not simply because of poor estimates of parameter values, as demonstrated by the sensitivity analysis shown in Figs. 4 and 5. The authors did in fact point out that some parameters can change with oxidation state but did not investigate further. I believe the above result points out very clearly that the constant values for some parameters is the major deficiency in the model. I suggest the authors explore this further using the model. For example, I imagine that PO1, PO2 and PO3 changes with oxidation. How would it need to change in order to better fit the data? Is such a trend physically justifiable? How does oligomerization (which has been proven to happen in the α - pinene SOA system) change the picture? In general, I would link the results to more mechanistic understanding of the chemistry.

We now extend the discussion about the poor prediction of O:C as copied below. There are generally two possible reasons: more parameters should be varied for the global sensitivity analysis or the model formulation could use some improvement. These possibilities will be examined in future research based on more chamber data.

As shown by the sensitivity analysis, the probabilities of adding oxygen atoms are relatively less influential than other model parameters (n_x , n_y , k_{OH_homo} , k_{OH_hetero} , and O:C_i) for O:C prediction. Therefore more complex and/or realistic values are needed for these parameters, such as the boundary condition of 2D-VBS which defines the limit of volatility and oxidation state of the products involved in the continuous aging, the heterogeneous reactions which may behave differently from their gas-phase analogues, and the probability of adding oxygen atoms as discussed in the text. Therefore the model formulation should be more complex before the fitting can be performed.

Oligomerization is expected to move relatively volatile products toward the low volatility direction and hence enhance the C_{OA} , depending on the fractions of SOA with aldehyde groups and partitioning conditions such as temperature and SOA concentrations for the

SOA without oligomer formation (Pun and Seigneur, 2007). The effect of oligomerization on O:C was considered to be little (e.g., as shown in the O:C-volatility space of Jimenez et al. (2009) and \overline{OS}_c-n_C space of Kroll et al. (2011)). Therefore we believe that the oligomerization might not be able to explain the different trend of O:C predicted by the model.

“While the modeled and observed SOA O:C increase with OH exposure, the magnitude and functional form of the increase differ significantly. This discrepancy is probably not specific to the highly oxidizing environment in the PAM chamber because the same general trends were also observed in two large environmental chambers (Ng et al., 2007; Donahue et al., 2012a). Thus it is likely that this discrepancy emerges from the model framework. A global sensitivity analysis has the potential to indicate the cause. The most important parameters for modeled C_{OA} and O:C were found to be associated with the highest C_i^* and O:C values used to define the boundary of the 2D-VBS space, the initial mass yields and O:C ratios of the products from the first-generation oxidation, particle-phase OH uptake rate and the probability of adding oxygen atoms during the functionalization process.

However, none of the Monte Carlo simulations were able to reproduce the measured curvature of O:C, suggesting that either more parameters should be varied for the global sensitivity analysis or the model formulation should be changed. In addition to the 13 model parameters listed in Table 2, the model sensitivity to more parameters will be explored in future work, such as (1) alternative first-generation product yields representations (e.g., RH-dependent yields), (2) varied magnitudes of C_i^* reduction following functionalization reactions, and (3) alternative representations of fragmentation coefficient (e.g., as in Cappa and Wilson (2011)).

For the model formulation, it is possible that some assumptions made for current model are too simplified to represent the trajectory of SOA aging accurately. For instance, some of the model parameters such as the probability of adding oxygen or fragmentation could be a function of carbon number, molecular structure, volatility, and/or oxidation state of the reactant products. In addition, the widely used assumption of instantaneous equilibrium partitioning may lead to overprediction of C_{OA} (Shiraiwa and Seinfeld, 2012) if the SOA is characterized by a solid phase state (Virtanen et al., 2010; Perraud et al., 2012; Saukko et al., 2012). Other assumptions that deserve more scrutiny include OH and O_3 reactions causing the same products or using a gas-phase reaction rate coefficient to simulate heterogeneous chemistry instead of including microphysics and well as chemistry and using the same mechanisms for gas-phase and heterogeneous oxidation reactions. For example, the fragmentation branching ratios in the heterogeneous reactions may be different from gas-phase reactions (Kroll et al., 2009). These assumptions will be tested in future work.”

2. Following on the last point, the authors suggest that O/C depends on kOH_{homo} more strongly at low OH exposures, and on kOH_{hetero} more strongly at high OH exposures. It is unclear to me if that was an attempt to explain the poor correlation with measured values. If so, is there some combination of kOH_{homo} and kOH_{hetero} that will better fit the measured data?

The sensitivity analysis results provide the guidance about how to improve the model

performance. The one thousand additional simulations with different combinations of the 13 model parameters cannot reproduce the measured O:C curve as a function of OH exposure. For the current model formulation, there is no combination of $k_{\text{OH_homo}}$ and $k_{\text{OH_hetero}}$ that better fit the measured data. More complex values and/or different model formulation (as discussed above) might need to improve the model performance.

Minor comments:

1. P. 2761 Line 13 and 20: The term “mass yield” is confusing. It can refer to total SOA/HC reacted. I suggest using the term “stoichiometric yield” or “aerosol mass fraction” (Donahue et al., 2006).

We now use replace “mass yield” with “stoichiometric yield”.

2. Pg. 2763 Line 19: I disagree that 0.14 cm^{-1} is a “small” S/V ratio. It is much higher than those of smog chambers.

We now revise the sentence as below:

“The PAM chamber is a horizontal 13.1 L glass cylindrical chamber (46 cm length \times 22 cm diameter) with a surface-to-volume (SA/V) ratio of 0.14 cm^{-1} .”

3. Pg. 2763 Line 25: How was OH exposure varied? Was it achieved by varying the residence time in the flow tube, or by changing the UV intensity? If it is the latter, does that affect the particle phase processing of OA (photolytically induced oxidation in the particle phase)? That could be related to the higher O/C increase at higher O/C exposure.

We now add how we varied OH exposure in the text as below:

“The OH exposure was varied by changing the UV light intensity and typically measured at 2.0×10^{10} to $2.2 \times 10^{12} \text{ molec cm}^{-3} \text{ s}$, roughly corresponding to 0.2-17 days of atmospheric oxidation at an equivalent ambient OH concentration of $1.5 \times 10^6 \text{ molec cm}^{-3}$ (Mao et al., 2009).”

However, UV-induced degradation in the PAM chamber has a minor effect on SOA composition since the timescales are probably too slow relative to OH oxidation (Lambe et al., submitted to *Environ. Sci. Technol.*). To produce an OH exposure of $1.5 \times 10^{12} \text{ molec cm}^{-3} \text{ s}$, a flux of UV photons of $\sim 10^{14} - 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ was estimated from ozone measurements in the presence and absence of UV lights. Based on literature values of absorption cross section for several oxidation products (1×10^{-20} to $4 \times 10^{-17} \text{ cm}^2$), UV photolysis life times were hence estimated to be ~ 25 to $1 \times 10^5 \text{ s}$, which is generally much longer than the gas-phase and particle-phase OH oxidation life times ($\sim 6.7 \text{ s}$ and $\sim 67 \text{ s}$ from the OH rate constants assumed in the base-case model).

4. Pg. 2764 Lines 11 – 14. Is this temperature correction a function of c^* ? The heat of vaporization (and hence, temperature dependence of partitioning) should depend on c^* .

We now have additional simulations and show the impact of temperature change on the model results as below:

“The temperature dependence of C_i^* is represented by the Clausius-Clapeyron equation

(Donahue et al., 2006):

$$C_i^*(T) = C_i^*(T_{\text{ref}}) \frac{T_{\text{ref}}}{T} \exp\left[\frac{\Delta H_v}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right] \quad (2)$$

where T_{ref} is the reference temperature, ΔH_v is the enthalpy of vaporization, and R is the universal gas constant. A constant effective ΔH_v of 30 kJ mol⁻¹ was used in Pathak et al. (2007) for the VBS parameterization of the SOA yields from α -pinene. However, Epstein et al. (2010) proposed a semi-empirical correlation between ΔH_v and C_i^* . Since ΔH_v is an uncertain parameter, a constant temperature of 298 K was used in the base-case model. Because UV lamps in the PAM chamber lead to temperature increases (measured temperature $T_{\text{obs}} = 21\text{-}36^\circ\text{C}$) and hence less SOA formation, the modeled C_{OA} is hence compared with measurements corrected at -0.02 per degree K of temperature increase (Stanier et al., 2008) relative to 298 K, which typically varies by 10-15%. Additional model simulations were performed at measured temperature T_{obs} with either $\Delta H_v = 30$ kJ mol⁻¹ or the C_i^* -dependent ΔH_v as in Epstein et al. (2010) to explore the temperature sensitivity of the model (see Section 3.3.1)."

“3.3.1 Temperature sensitivity

To probe the impact of temperature and ΔH_v variations on the model-measurement agreement, twelve additional simulations were run for the select case ($\Delta\text{VOC} = 281 \mu\text{g m}^{-3}$) at six measured temperature T_{obs} (295-307 K) with either a constant effective ΔH_v (30 kJ mol⁻¹) or C_i^* -dependent ΔH_v (Epstein et al., 2010). The model results show that the model with the constant ΔH_v does not produce a significant variation in modeled C_{OA} (within 6%) and O:C (within 1%) for the range of T_{obs} . For the model with C_i^* -dependent ΔH_v , the modeled C_{OA} decreases by up to 35% at higher temperatures (303-307 K) and higher OH exposures, as a result of the shift of C_i^* . Meanwhile, the modeled O:C only varies within 3%, compared to the model results at 298 K. Therefore the model performance was compared by the model-to-observed ratios of C_{OA} only, using the uncorrected measurements for the additional model results (Fig. S2). In general, relatively consistent model-to-observed ratios (within 7%) were obtained while the model accounts for the temperature increasing up to 303 K. For the temperature at 307 K and a high OH exposure of 2.1×10^{12} molec cm⁻³ s, C_{OA} predicted by the model with C_i^* -dependent ΔH_v is in better agreement with the measurement (model-to-observed ratio decreases from 3.0 to 2.3), although significant overprediction remains. Therefore the temperature correction used in this work gives results comparable to more detailed treatments of temperature for OH exposures up to 1.4×10^{12} molec cm⁻³ s. For higher temperature and OH exposure, the discrepancy caused by the constant temperature correction can partially explain the overprediction of C_{OA} .”

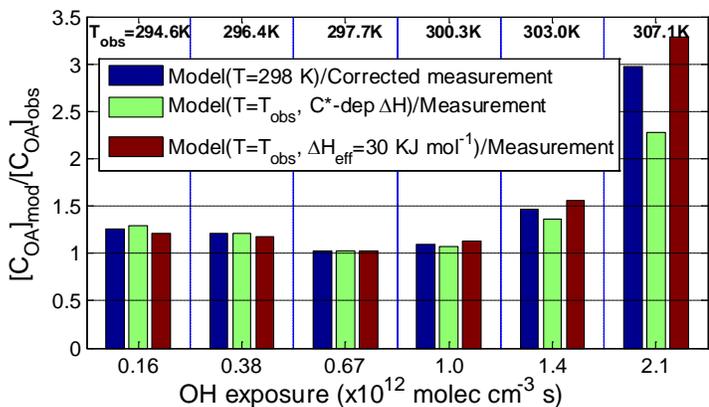


Fig. S2 The modeled-to-observed ratios of C_{OA} modeled under 298 K and under measured temperature T_{obs} with a constant effective ΔH_v or C_i^* -dependent ΔH_v as in Epstein (2010) ($\Delta VOC = 281 \mu g m^{-3}$).

- Pg. 2766 Line 5:O3 reacts with alkenes only, so this rate constant should decrease very significantly beyond the first generation. Any products of a - pinene would react with O3 with a $k_{O3} \ll 1E - 17$.

We constructed the SOA model to be used for different organic precursors. Therefore the general assumption of O₃ reactions was applied. As shown by the global sensitivity analysis, this O₃ reaction rate constant is not influential for the modeled results of interest from the oxidation of α -pinene.

- Figure 1: This is a very busy and confusing figure. First, the subpanel labels should be clearer (larger). Second, the explanation for the legend should appear inside the legend itself, not in the captions. Third, the split x - axis on the right panel should have the same exponent(e.g. 0 - 0.2E12 and 0.2-5E12). Alternatively the authors should consider using log scale. Lastly I think this figure is trying to demonstrate too many messages, such that each is lost behind the myriad of plots. I recommend splitting this into two figures, one demonstrating the correlation between modeled and observed data, and the other looking at detailed evolution of one particular case. I also suggest making all markers the same for the left panels, as it does not seem to depend on RH or starting concentration, and using different markers serve as an unnecessary distraction.

We now split this figure to two figures. We also revise the legend and x-axis tick labels as suggested.

Reply to Referee #3's comment

We would like to thank Referee#3 for the thoughtful and useful comment. Below are our point by point responses (in blue) to the comment (in black).

This work provided a modeling framework based on 2D-VBS to simulate SOA formation from α -pinene photooxidation/ozonolysis in the PAM flow reactor. The modeled and observed Coa and O/C are compared. It is found that the modeled Coa and observed Coa agreed within uncertainties, but the modeled O/C has a different trajectory (with increasing OH exposure) compared to the observed O/C. The sensitivities of Coa and O/C to different model parameters are investigated. I think the paper is well-written and the results are interesting and original. One of the main concerns I have is regarding the global sensitivity analysis. As shown in the manuscript, even when the 13 parameters are simultaneously perturbed, the authors still cannot reproduce the trajectory of changes in O/C with OH exposure. It is not very clear what this implies. Does this mean the formulation is “wrong” and that none of the 13 parameters is as important in predicting O/C as the authors might have suggested? Or, perhaps not enough simulations have been performed? Or, perhaps the range that the parameters are allowed to vary is not large enough? If so, the authors need to perform further simulations with a larger range of parameter values. All these need to be carefully addressed to support the usefulness of the modeling framework proposed in this work.

The SOA model was constructed based on recently proposed 2D-VBS model frame with a series of model parameters consistent with previous studies. One thousand simulations were run with conservative estimates of the possible ranges of the model parameters. We believe that these ranges are sufficiently large for the sensitivity analysis of the current model. The sensitivity results are able to provide guidance for future studies on the important model parameters and suggest that the refining of these parameters is essential to reduce the model uncertainty, especially for the modeled C_{OA} which agrees with the measurements within uncertainty ranges. For the O:C modeling, we now expand the discussion for the possible reasons in section 4 as below:

“While the modeled and observed SOA O:C increase with OH exposure, the magnitude and functional form of the increase differ significantly. This discrepancy is probably not specific to the highly oxidizing environment in the PAM chamber because the same general trends were also observed in two large environmental chambers (Ng et al., 2007; Donahue et al., 2012a). Thus it is likely that this discrepancy emerges from the model framework. A global sensitivity analysis has the potential to indicate the cause. The most important parameters for modeled C_{OA} and O:C were found to be associated with the highest C_i^* and O:C values used to define the boundary of the 2D-VBS space, the initial mass yields and O:C ratios of the products from the first-generation oxidation, particle-phase OH uptake rate and the probability of adding oxygen atoms during the functionalization process.

However, none of the Monte Carlo simulations were able to reproduce the measured curvature of O:C, suggesting that either more parameters should be varied for the global sensitivity analysis or the model formulation should be changed. In addition to the 13 model parameters listed in Table 2, the model sensitivity to more parameters will be

explored in future work, such as (1) alternative first-generation product yields representations (e.g., RH-dependent yields), (2) varied magnitudes of C_i^* reduction following functionalization reactions, and (3) alternative representations of fragmentation coefficient (e.g., as in Cappa and Wilson (2011)).

For the model formulation, it is possible that some assumptions made for current model are too simplified to represent the trajectory of SOA aging accurately. For instance, some of the model parameters such as the probability of adding oxygen or fragmentation could be a function of carbon number, molecular structure, volatility, and/or oxidation state of the reactant products. In addition, the widely used assumption of instantaneous equilibrium partitioning may lead to overprediction of C_{OA} (Shiraiwa and Seinfeld, 2012) if the SOA is characterized by a solid phase state (Virtanen et al., 2010; Perraud et al., 2012; Saukko et al., 2012). Other assumptions that deserve more scrutiny include OH and O_3 reactions causing the same products or using a gas-phase reaction rate coefficient to simulate heterogeneous chemistry instead of including microphysics and well as chemistry and using the same mechanisms for gas-phase and heterogeneous oxidation reactions. For example, the fragmentation branching ratios in the heterogeneous reactions may be different from gas-phase reactions (Kroll et al., 2009). These assumptions will be tested in future work.”

Secondly, one of the main features of the PAM reactor is the very high gas-phase OH concentration (many orders of magnitudes higher than ambient) used in the experiments. On one hand, this allows for the study of aerosol aging. On the other hand, heterogeneous reactions would be more prevalent in the PAM flow reactors than in ambient environments and this introduces the concern of whether these results are relevant to ambient environments. Coincidentally, the results in this manuscript showed that heterogeneous reaction is the only parameter that becomes progressively more important for both Coa and O/C with increasing OH exposure. Is this a direct result of the high OH concentration (and enhanced heterogeneous reactions) used in PAM reactor? The authors need to discuss this in more details and provide justifications on how their modeling framework is applicable to ambient conditions where heterogeneous reactions are probably not as prevalent compared to the PAM flow reactor conditions.

Potential heterogeneous reactions and their role in PAM experiments is a very important open question at the moment and one that needs to be addressed in future work, but is outside of the scope of what we can accomplish for this work. Please see our responses to Review #1, comments 2 and 3 and our reply to the specific comment #12 below.

Overall, I recommend the manuscript to be published once these issues are resolved. The authors can find more specific comments below.

Specific comments:

1. Page 2765, line 15. The experiments performed by Pathak et al used 2 butanol as OH scavenger to exclude the OH chemistry. Since both ozone and OH are present in the PAM experiments, what is the relative importance of OH vs ozone reaction with a-pinene in these experiments? Are the authors making the assumption that the yields from Pathak et al are applicable to their systems? If so, this needs to be stated clearly.

We state in section 2.2 that “For OH oxidation, the model assumes that the products are the same as those from O₃ oxidation of α -pinene.”

2. Page 2767, line 20. The authors chose a specific experiment (281 $\mu\text{g}/\text{m}^3$ of α -pinene) as a “typical case”. Is this typical case representative of all the PAM α -pinene experiments that have been performed? For instance, do all other PAM α -pinene experiments exhibit the same behavior in O/C, i.e., increases slowly at low OH exposure, and rapidly at higher OH exposure? The authors need to clarify this and provide more information regarding why the particular experiment (281 $\mu\text{g}/\text{m}^3$) is chosen as a “typical case” and how it is “typical”.

The 281 $\mu\text{g m}^{-3}$ of α -pinene case was chosen because (1) it has measurements of C_{OA} and O:C at six different levels of OH exposure to be compared with (other cases generally have measurements at 3-4 different levels of OH exposure) ; (2) it has the representative behavior in modeled and measured C_{OA} and O:C as a function of OH exposure, i.e., acceptable agreement for C_{OA} but different trend in O:C prediction for most cases.

We now revise the sentence as below:

“The model results of $\Delta\text{VOC} = 281 \mu\text{g m}^{-3}$ case, which have representative behavior in C_{OA} and O:C prediction, are shown in Fig. 2.”

3. Page 2767, line 20. For the parameters in Table 2, is the effect of RH explicitly accounted for in the model? Many previous studies have found that RH affects SOA formation from α -pinene ozonolysis (e.g., Jonsson et al., 2006). How does the difference in RH affect the results of this study and are they consistent with literature? Please address this in the revised manuscript.

Although RH was included in the model (so that it has impact on the modeling of OH and OH exposure), the same yields of the first-generation products (α_i) was applied for the experiments with different RH levels since the data of α_i under the specified experimental conditions (RH of 20-25% and 30-40%) are not available. Hence the effect of RH on the yields α_i and hence the SOA formation was not accounted. We now revise the sentence about α_i in section 2.2 to state this assumption clearly:

“To simulate the formation of the products from the first-generation oxidation by O₃, the stoichiometric yields α_i derived by Pathak et al. (2007) for low NO_x with UV light and dry conditions (Table 1) were used for all experiments. The effect of RH on yields α_i was not accounted due to limited available data.”

We also add the possible RH effect on yields α_i in section 4 to be included in future work as below:

“In addition to the 13 model parameters listed in Table 2, the model sensitivity to more parameters will be explored in future work, such as (1) alternative first-generation product yields representations (e.g., RH-dependent yields), (2) varied magnitudes of C_i^* reduction following functionalization reactions, and (3) alternative representations of fragmentation coefficient (e.g., as in Cappa and Wilson (2011)).”

4. Page 2768, line 3. How is the uncertainty of 15% determined?

This uncertainty of n_C was estimated based on a rough estimate of n_C accuracy of ± 1 . We now revise the sentence as below:

“The uncertainty of n_C was estimated to be $\pm 15\%$ (i.e., greater than ± 1 carbon number for $n_C \geq 7$).”

5. Page 2769, discussion of Figure 1.

a. Lines 14-16. Do the authors have any insights why the model-measured discrepancy of these three experiments is much larger than other cases? Please comment.

Please see the reply to comment #5c below.

b. Lines 19-20. The authors noted that “...the model tends to over-predict the SOA concentration at high OH exposure by a factor of ~ 2 ”. This is not obvious from Figure 1. Please explain. I suggest the authors to color the points in Figure 1a by OH exposures (and use different symbols for different α -pinene initial concentrations).

We now re-plot this figure (see Fig. 1) with different symbols for different α -pinene initial concentrations and color the symbols by OH exposure levels.

c. In Figure 1a, there is a wide range of observed Coa even for experiments with similar initial α -pinene concentrations (e.g., the two pink diamonds to the right, and the two blue diamonds in the middle). Why? Also, while the difference in the observed Coa is about 100 $\mu\text{g}/\text{m}^3$ for these cases, it is curious that the modeled Coa is actually in better agreement. (e.g., the modeled Coa values for the blue diamonds in the middle are both around 200 $\mu\text{g}/\text{m}^3$). Please comment and address this in the revised manuscript.

As shown in the new Fig. 1, the modeled and measured C_{OA} were compared at different levels of OH exposure. For ΔVOC of 833 $\mu\text{g m}^{-3}$, measured C_{OA} at high OH exposures of 1.1 and 1.6×10^{12} $\text{molec cm}^{-3} \text{ s}$ ($> 270 \mu\text{g m}^{-3}$) is much higher than the modeled results ($\sim 200 \mu\text{g m}^{-3}$). For ΔVOC of 695 $\mu\text{g m}^{-3}$, measured C_{OA} at low OH exposures of 0.8 and 2.8×10^{11} $\text{molec cm}^{-3} \text{ s}$ ($\sim 100 \mu\text{g m}^{-3}$) is much lower than the modeled results ($\sim 200 \mu\text{g m}^{-3}$), although modeled C_{OA} at high OH exposures of 1.1 and 2.2×10^{12} $\text{molec cm}^{-3} \text{ s}$ are generally in agreement with the measurements (modeled-to-observed ratio of 1.06-1.18). It seems that there is a discrepancy of the C_{OA} measurements at high OH exposure between these two cases. That is, the C_{OA} measured for $\Delta\text{VOC} = 833 \mu\text{g m}^{-3}$ case is much higher than $\Delta\text{VOC} = 695 \mu\text{g m}^{-3}$ case (e.g., $C_{\text{OA}} = 359$ and $171 \mu\text{g m}^{-3}$ at 1.14×10^{12} OH $\text{cm}^{-3} \text{ s}$, respectively) with comparable initial concentrations of α -pinene. The reason for this measurement discrepancy remains unknown.

7. Page 2770, description of CIT results. The modeled CIT results (both Coa and O/C) appear to be extremely similar to the modeled PAM results, even though the CIT and PAM experiments are performed under very different conditions. Are all the parameter inputs (Table 2) the same for CIT and PAM data, perhaps except for the initial α -pinene concentration?

The parameter inputs associated with the 2D-VBS functionalization and fragmentation processes (Table 2, except RH) are the same for both the CIT and PAM models. But both models are run with different chamber conditions (α -pinene, RH, O_3 , OH), based on the measurements. The major difference between the two models are the different levels of OH and simulation time, i.e., the CIT model was run with OH of $\sim 3 \times 10^6$ molec cm^{-3} for a

much longer simulation time.

8. Page 2770 and 2771. The authors stated that the differences between modeled and observed C_{OA} for both CIT and PAM results could arise from experimental uncertainties. What “experimental uncertainties” are the authors referring to? When taking experimental conditions into account (Page 2771 line 3), it appears that the discrepancy between modeled vs. observed C_{OA} is even worse. Please explain.

We stated that the discrepancy between the modeled and measured C_{OA} observed in the CIT and the PAM might partially be due to the experimental uncertainties in both chambers and the uncertainty from the wall loss correction in CIT. The experimental uncertainties are referring to the measurement uncertainties ($\sim\pm 15\%$ in CIT and $\pm 25\%$ in PAM).

The discrepancy between modeled and measured C_{OA} in the CIT is worse if we apply the most recent parameterization for first-generation products based on measurements conducted at the Carnegie Mellon University (CMU) Smog Chamber (Henry et al., 2012), in which the experimental conditions (e.g., UV intensity, RH, etc. as discussed in Presto et al., 2005; Pathak et al., 2007; Henry and Donahue, 2011) were different from the CIT and PAM chambers.

We now move the sentence about the experimental conditions and replace “experimental uncertainties” with “measurement uncertainties” as below for clarity.

“The model-measurement agreement of C_{OA} in the CIT chamber can be further improved by adjusting some parameters in the model. For example, increasing the assumed gas phase OH oxidation rate coefficient from 1×10^{-11} to 4×10^{-11} $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$, which was the highest OH homogeneous rate coefficient assumed in previous VBS modeling studies (e.g., Robinson et al., 2007; Shrivastava et al., 2011), the model generally reproduces the C_{OA} in both CIT and PAM with average relative errors of 28% and 39%, respectively (Fig. 2a). However, with a more recent parameterization of first-generation product yields of α -pinene oxidation (Henry et al., 2012), which are sensitive to the experimental conditions (e.g., Presto et al., 2005; Pathak et al., 2007; Henry and Donahue, 2011), the model significantly over-predicts the C_{OA} in CIT (e.g., C_{OA} peak modeled at 48% higher than the measurement). It also should be noted that the C_{OA} measurements in the CIT were corrected for wall loss with first-order size-dependent coefficients (Ng et al., 2007). Therefore the uncertainty of this correction combined with measurement uncertainties in both the CIT and PAM might partially explain the discrepancy of the C_{OA} peaks.”

9. Page 2771, line 19. The typical case chosen is “ α -pinene = 281 $\mu\text{g}/\text{m}^3$, is there a reason why this “typical case” is not used to examine the trends in SOA volatility distributions as a function of OH exposure? (instead, an experiment with 443 $\mu\text{g}/\text{m}^3$ reacted α -pinene is chosen here).

The word “typical” was misleading and in our response to comment 2 above, we have removed this description from the manuscript. The reason we chose ΔVOC of 443 $\mu\text{g m}^{-3}$ for discussing the SOA formation and growth is simply that the initial concentration is close to the middle value of the ΔVOC range of 23 -833 $\mu\text{g m}^{-3}$, the model-measurement

comparison for this case is similar to the $281 \mu\text{g m}^{-3}$ cases, and to provide more examples of our data set rather than to just rely on the $281 \mu\text{g m}^{-3}$ case.

10. Page 2773 and 2774. Both the modified models and global sensitivity analysis do not reproduce the trajectory of evolution of O/C as a function of OH exposure. Does this mean that the parameters included in this study, even when all are allowed to vary, cannot capture this trend? If so, how do the authors justify the usefulness of all these parameters in predicting O/C?

The SOA model in this study was constructed based on the model parameters widely used in recent studies. However, the one thousand combinations of possible values of 13 model parameters within their assigned uncertainty ranges (Table 2) cannot reproduce the O:C trend as a function of OH exposure, suggesting that more complex/realistic model formulation is necessary to improve the model performance. The sensitivity analysis results provide the guidance about the model parameters that have great impact on the modeled O:C. For instance, the heterogeneous reaction rate becomes more important at high OH exposure. Although adjusting the heterogeneous reaction rate within current model formulation (the same mechanisms as the gas-phase homogeneous analogue with an equivalent gas-phase reaction rate coefficient) cannot produce better model performance, the sensitivity analysis does point out that modeled results are sensitive to this rate and hence more realistic formulation of heterogeneous reactions (e.g., different mechanisms from the gas-phase homogeneous analogue) could have great impact on the model performance, especially for high OH exposures.

11. Page 2776, line 3. The authors stated that "...gas reaction rate has limited impact on Coa". This appears to be contradictory with the results shown in Figure 1c, where changing the OH reaction rate in the gas-phase obviously leads to changes in Coa. Please clarify.

$k_{\text{OH_homo}}$ was found to have little influence ($S_i < \sim 0.03$) based on the global sensitivity analysis at six different levels of OH exposure in PAM chamber ($\sim (2-20) \times 10^{11}$ molec cm^{-3} s). For the comparison of modeled and measured C_{OA} in the CIT (original Fig. 1b, now Fig. 2), the OH exposure was only measured up to 1.3×10^{11} molec cm^{-3} s. That is, the changing in $k_{\text{OH_homo}}$ leads to obvious changes in C_{OA} for the low OH exposures. As shown in Fig. 2, the modeled result of C_{OA} is more sensitive to $k_{\text{OH_homo}}$ for low OH exposure ($< \sim 1.5 \times 10^{11}$ molec cm^{-3} s for the CIT condition) than high OH exposure ($> 1.5 \times 10^{11}$ molec cm^{-3} s for the PAM condition). This is consistent with the global sensitivity results, which indicate less sensitivity of C_{OA} to $k_{\text{OH_homo}}$ with the increase of OH exposure.

12. Page 2776, line 19. Heterogeneous reaction rate. One of the main differences between PAM reactors and laboratory chambers is the OH concentration in the gas-phase, in which the OH concentration in PAM is many orders of magnitude higher than ambient OH concentration. Among all the parameters, the KOH-hetero is the only parameter that becomes progressively more important for both Coa and O/C (Figure 6). With the very high OH concentration in the PAM reactors, is it possible that the role of heterogeneous reactions becomes more important than what it would be in the ambient environment? If so, would the results from this study be representative of

ambient conditions?

The role of heterogeneous reactions is probably less important in the PAM chamber than it would be in the ambient environment. Laboratory study of aerosol uptake kinetics by Renbaum and Smith (2011) had shown that it is appropriate to extrapolate results from flow tube studies (high OH concentration and short residence time) to ambient processes (low OH concentration and long exposure time), given the same OH exposure. However, they also observed that high O₃ concentrations (e.g., 50 times larger than ambient maximum of ~250 ppbv, i.e., ~12 ppmv) causes ~50% slower reaction rate for OH with 2-ocylododecanoic acid particles since O₃ affects the reactivity of OH by adsorbing to the surface of the liquid particles. Furthermore, the PAM chamber has a short residence time compared to the time scale of the heterogeneous reactions.

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