

Response to reviewers for “A functional group oxidation model (FGOM) for SOA formation and aging” by X. Zhang and J. H. Seinfeld

We thank both reviewers for their constructive comments, which have helped to note areas of ambiguity. Our specific responses can be found below, with reviewer comments in black and our responses in blue.

Response to Referee # 2 (Prof. N. M. Donahue)

First I must apologize and accept public shaming for the amount of time it took to complete this review. Also, while I am editorializing I will take this opportunity to point out that I have not read my much more prompt colleague’s review, and as a general rule I favor this and suggest that ACPD develop some mechanism to keep initial reviewers blind from each other’s comments (though as a several month tardy reviewer this seems a poor time to bring that up).

1. General Comments

This paper describes a much needed and carefully conceived model framework for evolving organic aerosol chemistry. The Functional Group Oxidation Model is a semi-empirical model of organic-aerosol evolution where the kinetics of functional-group addition to carbon backbones are constrained by a detailed chemical mechanism (the Master Chemical Mechanism in this case) but key uncertain parameters such as the fragmentation probability (the probability that a given reaction step involves C-C bond cleavage) and aspects of condensed-phase association reactions are left as fitting parameters for a least-squares optimization to chamber data. The fitting is split into two cases. The first case allows for only gas-phase and heterogeneous oxidation, with a fragmentation probability and a condensed-phase “slow down” factor left as the two fitting parameters. The second case adds to this first case a phenomenological condensed-phase (oligomerization) process with four new free parameters – a second-order rate constant and the n_C , n_H , and n_O of the quasi non-volatile product.

In general, the FGOM even with only 2 oxidative parameters can do a very good job reproducing chamber data for Secondary Organic Aerosol formation from alkane

oxidation, but it has trouble with the composition data, overestimating both O:C and H:C. Consequently, adding the oligomerization parameterization allows the model to (eventually) match those observables fairly well. Because both O:C and H:C are lowered via this parameterized reaction, the authors focus on the plausible possibility that condensation (dehydration) reactions are responsible and important for organic aerosol development.

Here is my one serious concern with this work. While the hypothesis that condensation reactions may be important for SOA evolution is certainly plausible – indeed backed up by theoretical and experimental evidence – I am not at all convinced that the FGOM results make that case persuasively. There is an old saying in Chemical Engineering (I am told by old chemical engineers...) that runs roughly “give me enough free parameters and I can fit an elephant.” Here, the elephant in the room is that the oxidative portion of the FGOM overpredicts both O:C and H:C, so a mechanism with C:H:O as free parameters will with certainty be able to fit that elephant, to a point. However, the authors have been intellectually honest and also included a rate constant for this process. Even with that rate constant as a free parameter, the FGOM fails miserably with the timing of the O:C and H:C data. As shown in Figures 6 and 7, it takes many hours – almost a day – for the mechanism to draw the purely oxidative results down to the data. For much of this period, the optimized mechanism gets the sign of the trends wrong – while the observed O:C is rising, for example, the model O:C is falling (because it started out far too high). Because of this, I would much rather conclude that the hypothesized condensation reactions can not explain the observations. Finally, this comparison between oxidative and non-oxidative processes emerges slowly in the paper, culminating in a very strong conclusion that dehydration / oligomerization reactions are very important in SOA chemistry. While this figures prominently in the conclusion, it is almost hidden in the abstract “The sensitivity of the model prediction to variation of the adjustable parameters allows one to assess the relative importance of various pathways involved in SOA formation.” Given my reservations about the stronger conclusion, I am OK with what is written in the abstract, but I feel the authors should soften the conclusion about condensation reactions substantially.

1. Match of model output to AMS data?

Wall-loss corrected chamber SOA yield data (i.e. yields computed accounting for particle deposition on chamber walls) have been used as a standard for the fitting of empirical models, such as the 2-product model and the 1-D VBS. The subtleties of using AMS derived atomic ratios (O:C and H:C) as well lie in the uncertainties in the AMS elemental analysis, which arise from variations in the ionization and fragmentation of compounds in the AMS and uncertainties in analysis of high-resolution mass spectra (Chhabra et al., 2011). The uncertainty estimates for O:C and H:C are 31% and 10%, marked as gray error bars in Figures 6 & 7. A transient set of data points for a particular experiment serves as the basis for carrying out the fitting processes (Here these comprise the AMS derived O:C and H:C). When comparing the optimal model fit with experimentally measured O:C and H:C, the model output can be considered to reasonably match the experimental ratios as long as the prediction falls within the gray region, which represents the 31% and 10% uncertainties, as shown in Figures 6 & 7. In this respect, the model output can reach the “experimental standards” within 7 hours of photooxidation. The reason that it still takes 7 hours of photooxidation to reach the gray region (uncertainties of O:C and H:C) is that the oligomer formation takes time to be competitive with the oxidation reactions in both gas- and particle-phase, which are dominant at the beginning of the oxidation.

2. Gap between modeled and measured O:C and H:C during the first 14 h of reaction

The gap in O:C and particularly H:C ratios between measurements and simulations reflects the unresolved discrepancy between our current understanding of gas-phase photochemistry that leads to SOA formation and the actual SOA chemical trajectory measured in the chamber. Consider the dodecane low-NO_x case (Figures 6 and 7) as an example. The starting point of the O:C ratio measured by the AMS is ~ 0.2, which implies that a typical compound that is present in the particle phase with a C₁₂ carbon chain has, on average, 2.4 oxygen atoms. However, based on the vapor pressure prediction models (SIMPOL.1 or EVAPORATION), such a “compound” does not have sufficiently low vapor pressure to be predominantly in the particle phase soon after the beginning of the oxidation. The starting H:C ratio measured by the AMS is ~ 1.8, which implies that a typical compound that is present in the particle phase with a C₁₂ carbon chain has, on average, 21.6 hydrogen atoms and thus two unsaturated carbons in one

molecule. Based on the current gas-phase chemical reaction mechanisms for dodecane, it takes at least ~ 20 h ($1/(1 \times 10^6 \text{ molec cm}^{-3} \times 1.4 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})$) to completely lower the H:C ratio from 2.17 (dodecane) down to 2 (mostly due to the formation of $\text{C}=\text{O}$). If the measured H:C values are perfectly accurate, based solely on gas-phase photochemistry, the simulated H:C curves can not even reach the upper limit of the measured values after 20 hours of reaction. One infers that other reaction pathways are contributing, for which one possibility is particle-phase chemistry. The esterification from carboxylic acids or inorganic acids and alcohols or amines is considered to be a potentially important dehydration reaction channel in the particle phase. Esters, acid anhydride, and organosulfates have been widely observed in chamber studies (Gao et al., 2004 a, b; Surratt et al., 2006, 2007 a, b; Hamilton et al., 2006; Szmigielski et al., 2007; Iinuma et al., 2007 a, b). Other dehydration reactions, such as acetal formation from the reaction of alcohols and hemiacetals and peroxyhemiacetal formation from the reaction of peroxyhemiacetals and peroxides, have also been proposed to potentially occur within the lifetime of ambient aerosols (Ziemann and Atkinson, 2012). Acetals have been identified in SOA formed from methylglyoxal uptake recently (Yasmeen et al., 2010).

3. Modeled O:C trend

The simulated O:C trend reflects a competition between gas-phase oxidation and particle-phase accretion chemistry. As shown in Figure 6, the gas-phase chemistry alone leads to an increase in O:C, in agreement with our understanding of the atmospheric aging of semivolatile compounds. The particle-phase accretion reactions, however, lead to a dramatic decrease in O:C. Indeed, the modeled O:C without the accretion reaction channel better matches the measured O:C trend. This is mainly because the modeled starting points are usually considerably higher than the measured ones. In order to match the measured values, the modeled O:C is dragged down to the measured one at the beginning.

The reviewer is correct that the conclusion that oligomerization in the particle phase plays a significant role in the SOA formation and aging needs to be qualified. We have rewritten the Section 3.2 (Elemental aerosol composition) and Section 5 (Conclusions) in the revised draft accordingly.

2. Representation of the 2D-VBS

The 2D-VBS descriptions are mostly accurate in this paper, but not universally so. That is almost entirely because we have yet to publish a single, coherent description of the 2D-VBS. There are a few points however where I disagree with the authors' description. First, when the authors are discussing vapor-pressure estimation, they assert "The molecular vapor pressure prediction method used also plays an important role in the overall SOA yield predicted (Valorso et al., 2011), although this is the case for any SOA model." I disagree with this statement. Fully empirical models, including the Odum 2-product model and the original VBS, have no intrinsic sensitivity to estimated vapor pressures. They rely on empirical fitting of chamber data to deduce the volatility distribution of SOA formed in a chamber, but not on vapor pressure estimation; there are no molecules in those models, just material of some volatility. Even the 2D-VBS is not overly sensitive to vapor pressure estimation uncertainty – it enters only in the average change in volatility caused by addition of a functional group (taken to be 1.7 decades per O on average, but as much as 2.5 decades per O, as in an -OH group, or as little as 1 decade per), as in an =O group). The uncertainty in the 2D-VBS arises when we attempt to figure out the typical composition of molecules in a given C*,O:C bin.

We agree with the reviewer. We have rephrased the sentence in question, see below. The point here is that the predictions of SOA yield from current models incorporating specific gas-phase photochemistry such as MCM and GECKO-A depend strongly on the vapor pressure of species estimated in the model.

"...The molecular vapor pressure prediction method used also plays an important role in the overall SOA yield predicted (Valorso et al., 2011), although this is the case for any SOA model incorporating specific or lumped gas-phase photochemical mechanisms."

Second, I don't understand the statement "The 2D-VBS and SOM do not require an explicit VOC oxidation mechanism, although [sic] the chemical intuition is required in the choice of the adjustable parameters." The actual process of parameter estimation in the 2D-VBS goes beyond chemical intuition – the oxidation kernel described in Donahue et al., PNAS, 2012 is based on an assessment of typical functional groups added during oxidation reactions adding 1-6 oxygen atoms to a carbon backbone (really a distribution

of -OH and =O groups taken to be on average about evenly distributed because of the Van Krevelen constraints presented by Heald et al). That is not so very far from the FGOM.

We agree and have revised that sentence in question, see below. The point here was that the 2D-VBS and SOM do not require actual molecules or specific chemical structures (e.g. functional groups) in the model, although they rest on the current understanding of SOA formation chemistry.

“...The 2D-VBS and SOM do not explicitly incorporate specific chemical structures of VOC oxidation products, although they rest on the current understanding of SOA formation chemistry.”

The discussion of fragmentation in the 2D-VBS in Section 2.2, line 22ff is incomplete. The authors correctly describe the first step in the fragmentation process, where randomly fragmented compounds are distributed in a “dog leg” extending from the reactant toward higher volatility (and ultimately higher oxidation state), but half of these products are assumed to be radicals that can further functionalized. This is shown for an example cell in the supplementary material for Donahue et al., PNAS, 2012. As an example, the triacid MBTCA shown in Figure 4 of Jimenez et al., Science, 2009 is technically a fragmentation product of cis-pinonic acid (also shown in the figure), though it is orders of magnitude less volatile. While the 2D-VBS doesn't describe condensed-phase association reactions, there is no reason it can't. However, nobody to my knowledge has implemented oligomerization in the 2D-VBS.

We have rewritten this part:

“...The 2-D VBS assumes that the C-C bond scission from the precursor is randomly distributed along the carbon backbone. The distribution of products over the OS_{C-n_C} space is computed in such a way that the less volatile bins to the left of the midpoint (nominally $C_{n/2}$) have the same O:C as the precursor, while the more volatile bins to the right of the midpoint progress diagonally towards the bin with highest O:C (i.e., $C^=10^9 \mu\text{g}/\text{m}^3$, O:C = 1.0). Half of the products formed from the first-step fragmentation are assumed to be intermediates that can undergo further functionalization. As a result, a number of heavy fragments with similar C^* and O:C as their precursors are produced,*

filling a wide area in the 2D-VBS space.”

Finally, I don't at all understand the statement in the second paragraph of Section 4 “As a result, a number of free parameters representing the stoichiometric amount of product bins need to be assigned manually after each generation of oxidation.” (it is also not clear to me why a paragraph about the 2D-VBS is in a section entitled “Comparison of FGOM with SOM”. Whatever this is intending to say, there is no manual adjustment after any generations in the 2D-VBS. It is fully recursive and conserves carbon while allowing H and O to evolve based on inference of the average composition in each bin. I believe the authors are referring to the distribution of functionalization products in various C*,O:C bins whose average composition (carbon number) differs from the carbon number of the reactant bin. However, while the 2D-VBS mechanism is informed by the average composition, it does not require any information about it – the chemistry moves carbon about in the 2D space. No renormalization is required.

[Point well taken. This part has been removed from the paper.](#)

Finally, finally, the retardation factor or effective OH rate constant for heterogeneous uptake is described in Lambe et al., ES&T 2009, 3, 8794–8800.

[This reference has been added.](#)

3. Walls

The model is being employed to simulate a chamber experiment, and yet there almost no discussion of the chamber walls. The sole mention in the first sentence of section 3.1 is that the simulations consider wall-corrected data; to me this is a curious choice. Wall loss corrections are themselves a model, and there are numerous assumptions about mass transfer behavior either implicitly or explicitly included in the correction. The wall loss correction should be discussed here (or at least the method should be cited), but it would be far better in my opinion to actually include mass transfer to (and possibly from) the walls in the simulation. This way, all or most of the current hypotheses about wall behavior could be included in the chamber model and the sensitivity to these assumptions could be explored.

[We have added the following section to the Supplementary Material describing protocols](#)

for particle wall loss correction:

“The particle wall loss corrected SOA mass data were used as the basis for model fitting. Additional details about particle wall loss correction protocols can be found in Loza et al. (2012). Two limiting assumptions can be made for the interactions between particles on the wall and suspended vapor: 1) particles deposited on the wall are assumed to interact with the suspended vapors as if they had remained suspended and 2) particles deposited on the wall are assumed to cease interaction with the suspended vapors. The first assumption gives the upper bound limit on SOA mass concentration. To invoke this assumption, one applies the time-dependent organic to sulfate ratio measured by AMS to the seed volume concentration measured by DMA. We do not usually use this assumption considering the fact that the presence of organics enhances the collection efficiency of sulfates in AMS. The second assumption is applied in the present study. In this case, particles deposited on the wall remain the same size and do not undergo continued organic growth. In order to calculate the total particle mass lost on the wall as a function of time, the size-dependent particle wall loss rate parameter (β) needs to be determined. Wall loss calibration experiments were carried out by atomizing 1.0 M and 0.015 M ammonium sulfate solution ($(\text{NH}_4)_2\text{SO}_4$) into the chamber and monitoring the decay of particle number distribution using a DMA. The size-dependent wall loss rate parameter (β) can be obtained by fitting equation S1 to the data for pure wall loss:

$$n_{i,s} = n_{i,0} \times \exp(-\beta t) \quad (\text{Equ S1})$$

where $n_{i,s}$ is the suspended particle number distribution in size bin i at time t , and $n_{i,0}$ is the initial particle number distribution in size bin i . The β values so derived were then applied to the C_{12} alkane chamber experiments. For each size bin i at each time step j , particle number distribution deposited to the wall ($n_{w,i,j}$) is calculated as:

$$n_{w,i,j} = n_{s,i,j} \times [1 - \exp(-\beta \Delta t)] \quad (\text{Equ S2})$$

where $n_{s,i,j}$ is the suspended particle number distribution in size bin i at time step j , and Δt is the difference between time step j and time step $j + 1$. The deposited particle size distribution ($n_{w,i,j}$) is added to the suspended particle size distribution ($n_{s,i,j}$) to give the total particle distribution ($n_{\text{tot},i,j}$):

$$n_{tot,i,j} = n_{w,i,j} + n_{s,i,j} \quad (\text{Equ S3})$$

The total number concentration in size bin i at time step j ($N_{tot,i,j}$) can be calculated by converting the particle size distribution based on $d(\ln D_p)$ to $d(D_p)$:

$$N_{tot,i,j} = n_{tot,i,j} / D_{p,i} \ln 10 \times (D_{p,i+} - D_{p,i-}) \quad (\text{Equ S4})$$

where $D_{p,i}$ is the median particle diameter for size bin i , $D_{p,i+}$ is the upper limit of particle diameter for size bin i , and $D_{p,i-}$ is the lower limit of particle diameter for size bin i . Assuming spherical particles, the total volume concentration at time step j ($V_{tot,j}$) is:

$$V_{tot,j} = \sum_i^m \frac{\pi}{6} D_{p,i}^3 \times N_{tot,i,j} \quad (\text{Equ S5})$$

The total organic mass growth ($\Delta M_{o,j}$) at time step j is:

$$\Delta M_{o,j} = \rho (V_{tot,j} - V_{seed}) \quad (\text{Equ S6})$$

where ρ , the density for a specific C_{12} alkane SOA under high- or low- NO_x conditions, is obtained from seed free nucleation experiments.”

4 OS_C vs O:C

One of the less appreciated advantages of OS_C is that it is insensitive to dehydration ($\delta(2O - H)/C = 0$ when H₂O is eliminated). This is potentially very important here, because OS_C is also insensitive to assumptions about production of the $m/z = 18, 17, 16$ fragments in the AMS. Actual dehydration of organics in the instrument is incredibly uncertain, and strange things have happened to the AMS “fragmentation tables” over the past few years as estimates of $m/z = 28$ (CO⁺) have evolved. Thus, depending on both the treatment of the air beam in the AMS (which influences how accurately 28 can be recovered from the interfering N₂ signal) and assumptions about 18, the O:C and H:C can vary systematically. Furthermore, the standard fragmentation tables are thought to be reasonable for ambient sampling, but there is no reason to believe that they will apply for any given single precursor chamber experiment. Because of the prominent role that O:C and H:C from the AMS play in this paper, this should be discussed.

We have added the paragraph below to the Supplementary Materials:

“All AMS data were processed with “Squirrel”, the ToF-AMS Unit Resolution Analysis Toolkit (<http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/index.html>), in Igor Pro Version 6.22A (Wavemetrics, Lake Oswego, OR). The ToF-AMS High Resolution Analysis software tool PIKA (Peak Integration by Key Analysis) was employed for high-resolution analysis (Decarlo et al., 2006). O:C and H:C ratios were computed using the computation toolbox “Analytical Procedure for Elemental Separation”, which applies elemental analysis to the W-mode data. The interference of chamber air on the particulate spectrum was corrected by adjusting parameters in the fragmentation table based on the “filter run” (AMS is collecting chamber air with a particle filter in-line) before each alkane photooxidation experiment (Chhabra et al., 2010; Craven et al., 2012). Briefly, the ion CO_2^+ signal from ambient CO_2 , which is estimated to be 370 ppm in the chamber, is removed to determine the organic contribution of CO_2^+ to m/z 44. The ion CO^+ (m/z 28), which is considered to be a common fragment of organic species, can be overwhelmed by ion N_2^+ signal derived from ambient N_2 . In this study, we used the particle-phase ratio of $\text{CO}^+/\text{CO}_2^+$ to be unity as the default value to calculate the contribution of CO^+ to the total organic signal. We also checked W-mode, which has higher resolution than V-mode, to separate the CO^+ signal from N_2^+ signal. The C_2H_4^+ ion signal was removed because of its interference with the N_2^+ signal. The signals from H_2O^+ , OH^+ , and O^+ can be biased by water from both gas and particle phase. We use fragmentation table parameters in Aiken et al. (2008) to estimate the organic contributions ($\text{H}_2\text{O}^+ = 22.5\%$, $\text{OH}^+ = 5.625\%$, and $\text{O}^+ = 0.9\%$). For the high- NO_x alkane data, NO^+ and NO_2^+ signals were included in the O:C calculations because they trend with the organic mass so that they might come from organic nitrates. Including both of these ions increases O:C but does not increase the oxidation state of the carbon backbone (Kroll et al., 2011).”

5. FGOM SOM Comparison

This comparison is extremely interesting but yet extremely vexing. The mechanisms appear as two ships passing in the night. It should be pointed out that the Kroll et al. paper in Nature Chemistry includes a fair amount of experimental data that appears qualitatively consistent with the SOM trajectory in this space, while the FGOM feels the pull of the oligomers in Figure 9. The performance of the FGOM in Figure 10 also

deserves much more discussion. If the data evolve in the direction of the SOM (as they appear to do), this would seem to be inconsistent with significant dehydration chemistry, which will indeed tend to decrease both H:C and O:C as shown by the FGOM trajectory. However, I also don't understand how the FGOM continues downward from the data between 20 and 30h (the red part of the trajectory in Figure 10), whereas in Figures 6 and 7 the FGOM appears to have locked onto the observed O:C and H:C (as it should, being empirical). I don't understand this deviation. The location of the oligomers in the top panel of Figure 9 are fascinating. As discussed above, condensation (dehydration) is non-oxidative and thus conserves OS_C , and yet the oligomer is more oxidized than most of the condensed-phase products at higher C^* . This would not be surprising if the oligomers derived from glyoxal or other highly oxidized monomers, but as far as I understand the chemistry presented here the oligomers are presumed to derive in some way from the existing condensed phase. The chemistry thus appears to be an oxidative process. This leaves me somewhat confused as I don't fully understand how it can lower both O:C and H:C while being oxidative...

1. Comparison of oxidation trajectories between SOM and FGOM

Four oxidation trajectories in Figure 4 in Kroll et al. (2011) represent the heterogeneous oxidation of pure organic particles, which were conducted in flow tubes. Significant fragmentation was found for these four systems when particles are exposed to a high OH concentration. In the chamber where the OH exposure is considerably lower, the functionalization channel was found to be dominant for the photooxidation of long-chain alkane systems (Lambe et al., 2012). This correlation is also confirmed by a recent explicit modeling study (Aumont et al., 2012).

The SOM model describes SOA formation as a statistical evolution in the space of numbers of carbon and oxygen atoms, n_C and n_O . It is assumed that the properties of the n_C / n_O pair can be represented by mean values that account for the actual distribution of functional groups within the group of molecules that make up an SOM species. There are 7 adjustable free parameters in the SOM model: (1) The average number of O atoms added per reaction, which is represented as an array of probabilities of adding 1, 2, 3, or 4 oxygen atoms, (2) The decrease of the logarithm of vapor pressure upon the addition of

an oxygen atom (ΔLVP), (3) The probability of fragmentation ($P_f = (\text{O:C})^f$), and (4) The H-atom loss per O-atom added. The SOM model has been applied to the same dataset of alkane SOA formation as used in the present study (Cappa et al., 2012). Consider dodecane low- NO_x as an example. The best-fit values of the seven free parameters in the SOM are: (1) [0.79, 0.17, 0.03 0.0], (2) 2.20, (3) 0.077, and (4) 1.7. From the values in (1), the average number of oxygens added upon one generation of oxidation is 1.22. From the optimal values in (1) and (2), the decrease of vapor pressure on a log scale per generation of oxidation is 2.7, which equals the contribution of the addition of approximately 1.3 $-\text{OH}$, 1.2 $-\text{OOH}$, 1.2 $-\text{ONO}_2$, or 2.4 $-\text{C}=\text{O}$ groups to the decrease of vapor pressure, according to SIMPOL.1. From the value of (3), i.e., $P_f = (\text{O:C})^{0.077}$, fragmentation is intense: For example, for a compound such as hydroxycarbonyl ($\text{C}_{12}\text{H}_{24}\text{O}_2$), 87% of the reactions of the compound are fragmentation. Based on the best-fit values of the free parameters, the “species” predicted by the SOM that eventually reside in the particle phase are relatively small molecules with fewer carbon atoms and more oxygen atoms, and very low vapor pressure. Therefore, the trajectory of SOM in Figure 9 creeps towards the upper right of the $\text{OS}_\text{C}\text{-n}_\text{C}$ space. One can conclude that “species” predicted by SOM are not necessarily consistent with compounds produced based on the dodecane gas-phase photochemical mechanism, although they can perfectly describe the general properties, yield, O:C and H:C, of dodecane SOA.

The trajectory of the O:C / H:C ratio generated by the SOM in the van Krevelen diagram is due to the data fitting processes in SOM. In SOM, the measured van Krevelen slope is used to determine the H-atom loss per O-atom added with other six parameters held at their best-fit values adjusted by C_{OA} and O:C, as opposed to fitting all of the free parameters together to C_{OA} , O:C, and H:C in FGOM. One can understand that fitting SOM to both organic mass and O:C is done first, and then the one parameter left (H-atom loss per O-atom loss) was fit to the measured van Krevelen slope using the best-fit parameters obtained from the first step.

The oxidation trajectory of dodecane photooxidation from FGOM is a result of two principal pathways: C-C bond cleavage and particle-phase accretion reactions. Here oligomerization in the particle phase dominates to predict, in particular, the evolution of the O:C and H:C. The O:C vs H:C trajectory of dodecane photooxidation in Figure 10 are

the same data from Figure 6 and 7 located at small scales.

Now an important question to answer here is why these two approaches that more or less equally capture the chamber-generated dodecane SOA properties such exhibit distinct oxidation trajectories in OS_{C-nC} space? Which model output is consistent with the actual makeup of dodecane SOA generated in chamber experiments? Further particle-phase speciation and quantification can help resolve the discrepancy between these two model outputs. Although these two models predict different progressive oxidation patterns in the OS_{C-nC} space, further analysis reveals that both models suggest the importance of accretion reactions in the SOA formation from dodecane. In SOM, the measured van Krevelen slope is used to determine the H-atom loss per O-atom added with other six parameters held as their best-fit values adjusted by C_{OA} and O:C, as opposed to fitting all of the free parameters together to C_{OA} , O:C, and H:C. As shown in Fig. 11 in the revised manuscript, the best-fit value of H-atom loss per O-atom added is 1.77 in SOM in the dodecane low- NO_x case, indicating the formation of an unsaturated carbon bond upon one step of oxidative reaction. The ΔLVP value per O-atom added (2.20), however, indicates that the functional group likely to be added is the $-OH$ group, with a van Krevelen slope of 1. This discrepancy reflects the fact that the best-fit parameters in the SOM can not reproduce the observed O:C or H:C ratios without a dehydration reaction channel.

2) Location of oligomers

The “oligomer” in the FGOM model is not an actual species and is represented by $[C_xH_yO_z]$, where the x , y , z values are obtained from optimization. Upper and lower bounds are set for the values of x , y , z during the optimization processes but there is no necessary correlation among them. The location of the oligomer is a result of fitting the model output to both measured O:C and H:C. The reason that the oligomers can lower both O:C and H:C while being oxidative is that more H-atoms are lost compared with O-atoms during oligomerization. Consider the AMS measured O:C and H:C data after 36 h of reaction for dodecane under low- NO_x conditions. We can calculate that the corresponding oxidation state ($OS_C = 2O:C - H:C = 2 * 0.3 - 1.7 = -1.1$), which is consistent with the oxidation state of the oligomers predicted by FGOM.

6. Notational Consistency

I had a difficult time working out the details of the two simulation cases (oxidation only and oxidation plus oligomerization). They are described in perfect detail, but they are not named in the text. In the caption of Fig. 4 they are named sim.1 and sim.2, but here we find out “Note that “sim.1” represents the full fitting of the six empirical parameters in the FGOM to the chamber data and “sim.2” refers to fitting by only two parameters, r_p and f_v , to the organic mass concentration.” That’s wonderful if the reader can immediately recall what r_p and f_v (or the other four parameters) are. This reader could not recall that at the time and had to go hunting. It would be far better to first describe sim.1 and sim.2 in the text and then add to the caption “Note that sim.1 refers to full fitting of both oxidation and oligomerization chemistry to the chamber data while sim.2 refers to fitting of only two oxidation parameters to the organic mass concentration.” or something like that.

Yes. We have added the description in the first paragraph of Section 3, also shown below:

“... Two simulations were run for each C_{12} alkane system: sim.1, the full fitting of the six empirical parameters in the FGOM to the chamber data, and sim.2, fitting two parameters “ f_v ” and “ r_p ” to the organic mass concentration”

7. Conclusions

The conclusions section (paragraph) right now reads like something Molly Bloom in Ulysses might have said. Ideas just tumble out one after another almost without punctuation. The first half of the paragraph is quite coherent, but the final half to third is a succession of almost unrelated statements. The authors should take a little more time and space with the Conclusions section and put distinct concepts in separate paragraphs.

We have removed the previous Conclusion Section, and focused the conclusions on a comparison of FGOM and SOM, as reveals key feature of each model.

8. Minor editorial comments

Table 2: Please explain what the parameters are in the caption.

Done.

Figure 3: I was confused for a time by the gray rectangle cutting of an $n_C = 12$. I still don't fully understand why the authors do this, but the statement in the caption 'the shaded region ... is taken to represent the combination of carbon number and volatility for which a molecule can appreciably partition to the particle phase.' is manifestly false, given that higher carbon number species with low C^* can obviously also condense. It might be nice to put dodecane on this figure – it should sit just above $C^* = 10^6$.

Done.

Figures 4: Please explain at least briefly what the omitted parameters are (as discussed above).

Done.

Figure 8: Please make a more informative legend or caption. It is impossible to guess what the various cases are without reading the text; it will help the casual reader if the r_p and k_a values are explained.

Done.

Figure 9: Please label the 2D spaces on the top panels – put a big FGOM to the left of the top row and a big SOM to the left of the middle row. Once I get used to it is easy to pick out the oligomerization product and thus the FGOM graphs, but please save me the trouble!

Done

Figure 10: Please describe the dashed black and cyan lines in the caption.

Done

References:

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