Response to All Reviewers and Comments:

We thank the anonymous reviewers and Jathar and Robinson for their thoughtful and constructive comments. We have greatly revised our manuscript, taking into account all of the reviewers comments. The conclusions have been narrowed substantially. Reviewer comments are shown below in *italics*, and our responses are indented.

Response to Reviewer #1:

The many simplifications and assumptions in the modeled chemistry need to be discussed much more thoroughly. While these are certainly necessary for the construction of simple chemical schemes, it's important to note that they may have a major effect on the modeled results. However in the paper a large number of important simplifications/ assumptions are never explored, and for the most part are not even identified, and yet some major conclusions about SOA chemistry are drawn and stated rather strongly. Several specific concerns are listed below.

- the SOM ignores the effects of carbon skeleton. The manuscript includes some discussion of the possible effect of double bonds, but all but ignores the effects of cyclic, aromatic, and branched carbon skeletons. These can have a governing effect on the oxidation of organic compounds, mostly via affecting alkoxy radical reactivity [3]. By not including these effects, the SOM in its current form essentially simulates the chemistry of only n-alkanes, species which are probably not a good surrogate for most atmospheric SOA precursors.

- An important reaction in the chemistry of n-alkanes is formation of dihydrofurans, whose subsequent chemistry has been shown to play a central role in SOA formation[4]. This leads to the formation of a ring and a C=C double bond; thus even n-alkane chemistry may not be well-simulated by the SOM.

While the fragmentation probability (P_frag) is allowed to change over time (as the products become more oxidized), several key parameters (dIVP and P_func) are not. Yet we know these change with oxidation as well – for example the curvature in the van Krevelen plot with oxidation [5] strongly suggests that dIVP is an evolving parameter.

The point of the above list is not to point out the shortcomings of the model; the complexity of SOA chemistry requires that many simplifications be made. Instead the point is that it is very possible (even likely) that "real-world" SOA (from a range of precursors and conditions) may be substantially different from what is simulated by the SOM in its current form, even when only known gas-phase chemistry is involved. As a result, several strongly-worded conclusions (IVOCs and SVOCs cannot make OOA, the pumping mechanism is an inefficient oxidation channel, fragmentation reactions cannot increase O:C) are simply not well-supported by this work. A much wider range of compounds need to be examined, and much more chemical detail needs to be included in the model, before such broad conclusions can be made with any confidence. Thus these conclusions need to be removed, or at least softened considerably, with all the above caveats added.

Addressing the overall reviewer concern, we have revised the manuscript significantly, making clearer both the structural and parametric uncertainties of the model. We have revised ("softened") our conclusions substantially. Responses to specific comments in the above list are given below.

The model, as formulated, assumes that all reactions in the reaction scheme proceed along the same path with respect to oxygen addition, fragmentation probability and changes in vapor pressure. We are essentially determining a mean solution and all of the actual chemical complexity, including differences in reactivity of different "species," is essentially wrapped up into the 6 adjustable parameters. No structure of the reacting molecules or products is assumed and we do not suggest that we capture all of the fine details of the chemical pathways involved (which we hope is apparent since we are only dealing with "molecules" in a vague sense, but we have worked to clarify this point). As noted by the reviewer, the SOM is a simplification of the complex chemistry that governs oxidation of a given hydrocarbon. In principle, the reaction scheme (in particular the matrix of rate coefficients) could be modified to account for differences in the reactivity of the parent species vs. the product species. We emphasized this point for reactions of compounds with double bonds, but this could similarly be done, in principle, for branched compounds. This is now discussed in Section 2.1.

We believe that the discussion regarding curvature in the van Krevelen diagram overlooks the data presented in Figure 3 of Heald et al. (2010), which actually suggests minimal curvature for some individual field studies, especially the SOAR study. The curvature evident in the Figure 2 in Heald et al. (2010) may therefore arise from consideration of results from multiple studies/locations (including laboratory studies) together (although the clear curvature in the squalane heterogeneous oxidation experiments should not be overlooked). That there might be the appearance of curvature when different studies are combined is not particularly surprising and likely results from each location/study having different predominant SOA precursors, NO_x levels, etc. Nonetheless, we do not disagree that the SOM parameters might change with time/oxidation extent. That said, we note that the SOM can be explicitly fit to chamber data and thus the derived parameters can be constrained by experiment (although this obviously does not apply to the more exploratory aspects of our manuscript).

Throughout: The paper would be improved if the ultimate aims of the SOM were made clearer. It's not clear whether it's intended to be a conceptual framework to think about SOA formation and aging, or a module for incorporation in 3D models, or an approach for fitting laboratory data (the focus seems to change throughout the paper). Much of the discussion focuses on the advantages of the SOM (over the 2-product model and VBS) for fitting chamber data. However, this fitting is done only at the very end of the paper, and the results of the fits are not used to inform the model itself. (This in my view is one of the strengths of the VBS, which is parameterized by chamber experiments)

We agree that the purpose of the model could have been made clearer throughout, and we have revised with this in mind. Ultimately, we hope that the sequential oxidation model (SOM) can be used in all of the ways mentioned by the reviewer. We have moved the discussion of fitting to laboratory data closer to the beginning of the manuscript, as we believe this to be an integral part of future development of the SOM. We have also added discussion/text that attempts to make clearer how the SOM can be used at the end of the introduction. We have tried to provide more balanced comparison with the 2-product and VBS models. We now note explicitly in multiple locations (e.g. near the end of the introduction, section 2.3, in section 3.2 now titled "Fitting of Laboratory Data", and in the conclusions) that the SOM can (and should) be parameterized by chamber experiments.

Throughout: Much of the discussion is focused on contrasting the SOM with the VBS, with the VBS usually lumped together with the Odum two-product model as examples of "static" descriptions of SOA (e.g., P3302 L15, P3315 L11, P3334-35). While there are some references to kinetic parameterizations of the VBS, the casual reader would have no idea that an important aspect of the VBS is that it explicitly allows for aging (in contrast to the 2-product model). A more fair assessment of the literature and the current state of the science is thus necessary. It is true that the initial C distribution in the VBS, taken from fitting chamber data, must assume an initially static population of SOA, but it is not at all clear what sort of error (in calculations of C_oa, O:C, etc.) this introduces, at least relative to the SOM (which is not constrained by chamber data, and, as stated above, does not fully consider distributions in volatilities for a single generation). After the initial SOA formation, the VBS then allows for aging of this SOA, using a general scheme that is quite similar to the new one adopted in the SOM. Of course, when implemented in a chemical transport model, this kinetic implementation of the VBS naturally includes the statistical distribution of generations. None of this is apparent from the text as currently written; thus these sections need to be made more balanced in content and tone.*

We have revised the manuscript to clarify the distinction between the static and kinetic versions of the VBS and to provide a "more fair assessment" of the literature, especially in the beginning of Section 2 and in the conclusions. We note, however, that we did state clearly in Section 2 that our model "shares some similarities with kinetic implementations of the VBS." We now elaborate on this point. A few other considerations: (1) although the SOM does not *need* to be fit to chamber data, it *can* be and *was* in a few example cases. Thus, it is not correct to say that the SOM is *not* constrained by chamber data. (2) We believe the reviewer is oversimplifying in stating that the SOM "does not fully consider distributions in volatilities for a single generation." For a fixed value of ΔLVP, by using an array of oxygens added (the P_{func} array) we effectively produce species with a distribution of volatilities (i.e. different numbers of oxygen groups). What is not captured is differences in volatility that are the result of different functional group addition, since the SOM employs an average approach. This will lead to additional spread in the actual distribution of volatilities. So the reviewer is correct in saying that such distributions are not considered "fully", but we believe this statement to be an oversimplification of the actual SOM framework. Further, the excellent agreement between the SOM and chamber data presented in our manuscript suggests that, to first order, the combination of the ΔLVP and P_{func} captures sufficiently these distributions of volatilities of products from a single generation. (3) Only the "1st" generation VBS products yields have traditionally been constrained by chamber data; the ageing scheme has, as best we can tell, not been explicitly constrained by chamber data, but only compared with observations in an approximate way (Shrivastava et al., 2008) (at least until recently; see Jathar et al., Submitted to ACP).

3300, L17-21 and P3316 L28 – P 3317 L3: These discussions do not accurately reflect the Ng et al work [6]. That study involved compounds with one or more double bonds, allowing for good kinetic separation of generations: the first double bond reacts quickly (a large value of kOH), the next double bonds react quite a bit slower, and then after that the H-atom abstractions go slower still. This is in stark contrast with the n-alkane system modeled in the present paper, in which kOH's are all roughly the same, leading to generations mixing together as described by Wilson et al [2]. For the system studied by Ng et al, it is (to first order) correct to ascribe the different sections of the growth curve to different generations (in contrast to what is stated on P3300), just as it is correct (to first order) to interpret the data in terms of first- vs. second-generation products (in contrast to what is stated on P3316). Generalizing this result for nonalkenes does indeed require going beyond "second-generation products", but this has been recognized for some time (see discussions of "later-generation products" [7] or "subsequent-generation products" [8]).

In the first case referred to by the referee (page 3030), we have removed mention to Ng et al. (2006). Instead, we now state:

"In photo-oxidation experiments the oxidation products themselves are reactive towards OH. As a result, products with relatively large numbers of oxygen atoms always have some probability of being formed, even early on in the reaction. This is simply a consequence of statistical oxidation in a well-mixed system. For example, for the case where all molecules react with OH with the same rate coefficient (kOH), the distribution of oxidation products at any point in the reaction can be described as a simple Poisson distribution, as recently shown by Wilson et al. (2012). Note that "generation" is equal to the number of times that a molecule has reacted, starting from the initial SOA precursor. Further, because more than 1 oxygen-containing functional group can be added per reaction, the number of oxygens per molecule is not necessarily equal to the number of "generations" of oxidation. Understanding of the evolution of these later generation products is challenging, although chemically explicit models such as the GECKO-A (Camredon et al., 2007;Lee-Taylor et al., 2011;Valorso et al., 2011) have provided useful insights."

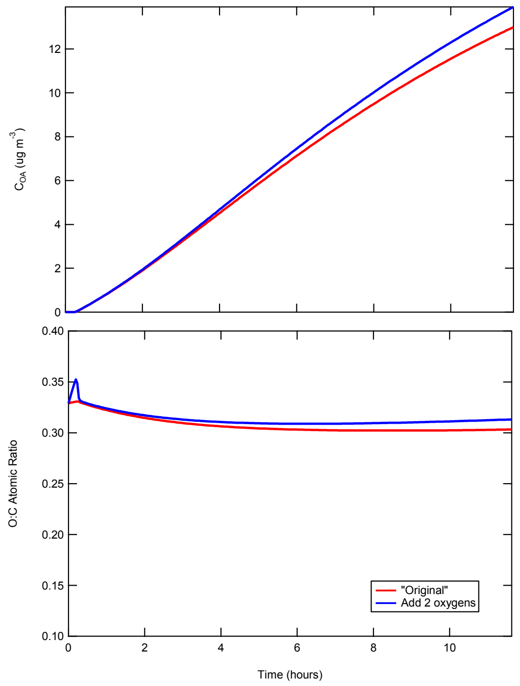
In the second case (p3316), we have added/modified the following for clarification: "While this may be approximately true for the specific reactions considered by Ng et al. (ozonolysis and photo-oxidation of compounds containing two double bonds) it should be kept in mind that in experiments where the reactivity of the oxidation products is not substantially different from that of the precursor compound at any point in the reaction there is a distribution of multiple generations of products in photo-oxidation experiments."

P3302, L9-11: Similarly, the wording here makes it sound as if it is still generally believed that yields are a static quantity; but many papers over the last several years (going back at least to Donahue et al 2005 [9]) have discussed that this is not the case. I suggest changing "interpreted" to "fitted" to avoid implying this.

Done.

P3307: It is not clear from the text how the number of O atoms added to the fragmented products is determined; this needs to be clarified. From P3299 L9-10 ("the total number of carbon and oxygen atoms are conserved") it sounds as if some oxygen atoms are first added (via the P_func array) and then are divided up randomly into the two fragments. If this is the case, it can lead to the addition of only one oxygen total to both fragments, which is chemically nonsensical. Since each fragment must end up with at least one O atom, fragmentation necessarily leads to the net addition of more O atoms than does functionalization. (This difference can be quite large, given that acid groups may be introduced via fragmentation reactions.) If O atoms are indeed computed by the above method (application of P_func), it will lead to an underestimate of the O:C (and overestimate of volatility) of the fragments, and can give a misleading impression of the role of fragmentation in SOA chemistry. This would need to be corrected.

We thank the reviewer for raising this important point. We have modified our model to account for this. Specifically, we assume that the probability of obtaining a species with zero oxygen atoms upon fragmentation is zero. To account for the additional oxygen addition that accompanies a fragmentation reaction (as opposed to a non-fragmenting functionalization reaction), we assume that one additional oxygen atom is added to one of the fragments, although this may slightly underestimate oxygen addition to the fragmented molecules if more than one oxygen is added from the fragmentation pathway. For example, if the $C_{12}O_2$ species reacts to add 1 oxygen (via functionalization) but also fragments with half the carbon going to each fragment, the following resulting species are possible: $C_6O_3 + C_6O_1$ and $C_6O_2 + C_6O_2$. A figure illustrating the general difference from our original formulation is shown below, run for a C_{12} hydrocarbon using ΔLVP = 1.6, P_{func} = [0.25,0.25,0.25,0.25] and c_{frag} = 0.25 with $[HC]_0$ = 15 ppb and [OH] = $1.95\text{x}10^6$ molecules cm^{-3}. In general, the calculated C_{OA} and O:C are slightly increased above our original formulation. However, the overall influence of this change is small and thus this change has had minimal impact on the model output and leads to no changes in our general conclusions.



P3324, L14: The relevance of examining SOA vs OPOA for a single pure compound is not clear to me. How is a comparison of the two meaningful when they are made up of the exact same species, formed by the same chemistry? A more useful test of the pumping mechanism would be to have some amount of a single SVOC present alongside an unreactive absorbing medium, and examine the evolution (partitioning and O:C ratio) of that SVOC. (Also, in this section the parameters of these simulations (dlVP, degree of fragmentation etc) need to be given.)

> We have actually removed this section from the manuscript so-as to maintain a tighter focus, as suggested by Reviewer #2.

Section 4 (P3328-30): The agreement between the data and the fitted SOM is not surprising given that there are six fitted parameters. Since these are likely not unique solutions, it is risky to ascribe chemical meaning to the results. For example, for a-pinene the fitted parameters suggest 20% of the time only one oxygen is added per reaction (Pfunc(1)=0.20), which is not chemically realistic for the oxidation of a cyclic alkene. Similarly, growth data were reported without consideration of gas-phase SVOC loss to chamber walls, an effect which can be substantial [10] and should lead to a model measurement discrepancy if the model accurately describes gas-phase chemistry and gas-particle partitioning of the system.

> The reviewer raises an important point about the uniqueness of the SOM solutions and the ability to attribute chemical meaning to the parameters. With 6 parameters available for tuning, it is possible that the there are multiple best-fit solutions, for example perhaps different with respect to the relative values of ΔLVP and the fragmentation parameter. We have tried starting our fitting routine from multiple points (i.e. initial parameter guesses) to assess whether a

solution is at least approximately unique. Interestingly, we find that, in general, the solution appears to be reasonably unique in that if we start with initial guesses far from the final answer the solution (typically) converges to a single best-fit set of parameters. Certainly this does ensure that the solution obtained is unique, but it does give some justification to the interpretation of the derived parameters in terms of physical properties (at least to the extent that the model structural formulation captures in sufficient detail the SOA formation process). Further, we note that the SOM need not only be fit to C_{OA} data, but can also be fit to O:C data. Fitting simultaneously to C_{OA} and O:C data can help to place much tighter constraints on the best-fit solution, although this is not done in this study. In the revised MS we suggest that simultaneous fitting to O:C data could provide for tighter constraints. We additionally have added some discussion regarding solution uniqueness at the end of Section 3.2.1 (Fitting of Laboratory Data: Time evolution of aerosol growth).

Now, considering the reviewers particular concern regarding the results from the α-pinene experiments, we have now obtained the time-dependent growth data from Sally Ng (from Exp. 1 in Ng et al. (2007)) and explicitly fit the SOM to the data (i.e. where previously we had been *matching* the yield vs. Δ[HC], now we *fit* the C_{OA} vs. time). Using the revised model formulation (with respect to fragmentation and the corrected k_{rxn}, see below) and time-dependent growth data from Prof. Ng, the best-fit SOM provides results that are more in line with the reviewers expectations based on the chemical mechanism. Specifically, we find that $\Delta LVP = 1.93$, $c_{frag} = 0.20$ and $P_{func} = [0.03, 0.55, 0.32, 0.10]$.

With respect to the reviewers second point (that wall losses are not accounted for), we note first that the SOM does not accurately describe the gas-phase chemistry and gas-particle partitioning *a priori*. Although we have explored the general behavior of SOA within the SOM framework by considering the influence of changing the various parameters, the SOM must ultimately be fit to chamber (or other experimental) data. Wall loss, in this case, will be wrapped up in the derived fit parameters. This will not lead to a model/measurement discrepancy per se, however it will (possibly) lead to derived parameters that may only approximately describe the evolution of the same chemical system in the absence of wall losses, i.e. in the atmosphere. Of course, similar challenges/limitations apply when fitting chamber data using (non-kinetic) equilibrium partitioning theory (i.e. the 2-product model or static VBS) and are not unique to the SOM. This is a current limitation of the SOM modeling framework, and is now discussed at the end of Section 2.2. It may be possible in the future to account for wall-losses within the SOM framework given the time-dependent nature of the model.

P3300, L10: "Structure" should be replaced by "formula" (or some similar word). "Structure" refers to connectivity of atoms, something that is not simulated in the SOM.

Done.

P3301, L3: There seems to be an error in this expression; I think it should be tau=1/(k[OH]).

Corrected.

P3302, L18: The term “two constants and one array” is more precisely described as “six parameters”. But it is also worth mentioning that the strength here is that those six parameters include aging parameters, not just the initial distribution.

This has been clarified. We appreciate the reviewer noting that the parameters do explicitly include ageing as part of the fundamental formulation as this is key.

P3303: I don’t see how the SAR of Kwok and Atkinson leads to equations 1a-5b. This should be explained in greater detail (perhaps in a supplement). Also, it appears that these were computed for straight-chain organics only; this needs to be stated in the text.

The derivation of the “structure”-reactivity relationships in Eq. 1a-1e are now extensively discussed in a new Supplemental material. Further, we have revised the SOM “structure”-reactivity relationships, as is discussed in the Supplement. We now also state that the relationship was derived with a straight-chain organic in mind, but we also provide some discussion of how the general relationship(s) can be modified for use with non-straight-chain species.

P3303, L22-23: The units for these rate constants are in error or are missing.

Fixed.

P3310, L18: The expression for yield is incorrect: the denominator should be -delta[HC], not [HC]o. The two are the same only when all the hydrocarbon has reacted away, which is not the case here (since only one lifetime has elapsed).

Fixed.

P3313, L11: If the simulation in question involves the addition of only one O atom is added per reaction, the finding that O:C doesn’t increase with fragmentation is not really that surprising.

This result is generally unchanged if more than one oxygen is assumed added per reaction, although as we show later in the manuscript (revised Fig. 12) the result does depend on how long the model is allowed to run (i.e. how many oxidation lifetimes are simulated).

P3316 L1, Fig 6: The simulation apparently includes fragmentation (since it is from case 2b, from section 3.1.2), but the figure shows no signs of fragmentation (i.e., compounds that are more volatile than the parent). Why is this?

The graph was accidentally truncated too low in volatility. We have corrected this to show higher volatility bins.

P3321, S3.2, Fig 9: It’s not clear to me how this section and figure contributes to the overall paper. The main results have either been shown already (O:C, shown in Fig. 2b) or, as mentioned in the text, are *expected based on partitioning theory (volatility, with C*=C_oa). Related to this last point, the section/figure would be much more informative if [HC]o rather than C_oa were held constant. (Also, the circles at the bottom of the figure are confusing, since their size implies substantial aerosol formation.)*

> First, we have replaced the circles at the bottom of the figure with x's. Second, we believe that the discussion in this section and the associated figure are important contributions to the overall manuscript as we now consider the *mean volatility of the SOA*, in addition to the O:C. Figure 2b only captures the N_C dependence of O:C with no consideration of particle volatility. We have revised this section to emphasize the new information regarding mean particle volatility. Related to this, we have merged the discussion in this section with the "Formation of oxidized organic aerosol" section, as these naturally go together, and we have revised accordingly. With respect to holding $[HC]_0$ constant vs. C_{OA} constant, we believe that either is useful, as the results are relatively insensitive to this assumption. However, if $[HC]_0$ is held constant, then the amount of OA formed (after reaction under given conditions w.r.t. time and [OH]) increases rapidly with N_C due to the increasing yield with N_C. We find that this leads to a somewhat more confusing graphical presentation than if a constant target C_{OA} is used.

P3323 L26: This appears to be the incorrect reference for describing the pumping mechanism.

> First, this section has been removed from the manuscript. Second, with respect to pumping influencing OA in biomass burning plumes, this is the correct reference. In their paragraph 29 they state:

> "There is a clear, and consistent transformation in all the mass as a function of distance from the source region; the addition of oxygenated mass fragments at the relative expense of long-chain aliphatic mass fragments indicates oxidation is important and can be expressed as an increase in O/C. When combined with the fixed OM/CO ratio this shows that net carbon loss occurs throughout the lifetime of the aerosol in the region, and must mean that both chemical processing and evaporation are happening. The processing is an undetermined combination of: (1) condensation of additional secondary material and (2) a chemical transformation of the primary organic aerosol. Ozone concentrations during SLRs within biomass burning layers were on average 10 ppb higher than background values, suggesting photochemical activity within the plumes. Condensable products could result from this, in line with hypothesis 1. Either way the increase in O/C must be balanced by evaporation in order for the mass to remain constant."

> Although they do not use the term "pumping" this is what they are describing.

P3324 L18, P3327 L17: is the "x" in the [OH] expressions a typo?

> Yes, this is a typo that was introduced during copy-editing. We have confirmed that there is only one "x" in the original word document and will watch out for typos introduced during copy-editing.

P3333 L20: I'm unaware of any evidence (including in the papers cited) that OA can be truly "non-absorbing"; submicron particles made up of material in which diffusion is incredibly slow (D of _1e-15 cm2/s) still allow for absorption over timescales of hours. "Viscous" might be a better word.

> As the reviewer notes, "non-absorbing" is perhaps an imprecise term. We now use the term "viscous" or "highly-viscous".

Response to Reviewer #2

The main problem with the manuscript in its present form is that it dramatically overreaches in some of its conclusions. Strong conclusions are made about the importance of some species on SOA formation in the real world based on a very simplified model that has undergone very little experimental verification, and likely also due to some confusion about the results of field studies.

> Per the comments of all of the reviewers and commenters, we have revised our manuscript to narrow the conclusions and add caveats, as appropriate.

It is true that SOA is observed to form quickly in field studies, especially in urban areas. It is also true that SOA of high O:C is observed in field studies. However these are not typically observed together. O/C of bulk OA peaks at ~0.4 in the afternoon in Riverside, CA (when SOA represents ~90% of the OA and some very aged background OA is present, Docherty et al. ACP 11:12387-12240, 2011) and at 0.55 in Mexico City on a typical day (Aiken et al. 2008). However SOA formed over a few hours of oxidation in Mexico City has an O/C~0.37 (Dzepina et al. ACP 9:5681, 2009, their Fig 11). Similarly the SV-OOA factors that are associated with fresh SOA have O/C~0.35 across many locations (Jimenez et al., Science 326: 1525-1529, 2009). Precursors with many carbon numbers can contribute with SOA with those ranges of O/C according to the results of the SOM model, especially if it is taken into account that a mixture of precursors is always present. With a mixture of precusors, some will lead to SOA of lower O/C (such as IVOCs) and others of higher O/C (such as toluene, or glyoxal via accretion reactions that are ignored here), so that intermediate O/Cs result for the total SOA. This was clearly illustrated by e.g. Chhabra et al (ACP 11: 8827-8845, 2011, their Fig. 9) who showed that no individual precursor produces SOA that matches the chemical properties of total ambient SOA, and that a mixture of precursors is essential. The fact that an individual precursor produces SOA with O/C~0.2 does not mean that it cannot substantially contribute to fresh ambient SOA with O/C~0.35 if e.g. some smaller precursors and glyoxal are also present. Thus the very strongly stated conclusions about IVOCs not being important contributors to ambient SOA are unwarranted and should be removed from the paper.

The very high O:C observed in some field studies and OOA factors (such as the LVOOA with O:C~0.75 reported by Jimenez et al. 2009) is more frequently observed in rural and remote areas. It appears to be the result of multi-day oxidation and perhaps aqueous chemistry, but to my knowledge it has not been observed for fresh SOA in ambient air. The authors somehow appear to be assuming that it has, and this potential confusion may lead to the overstated conclusions about IVOCs. Although higher values of O:C approaching 1 have been reported for very aged OOA, they are less frequently observed. But the authors *seem to assume (for ex. P3311 line 22) that for an SOA precursor to be relevant, it needs to reach O:C > 0.8 in 1 day.*

> The reviewer makes many important points, in particular that mixtures of compounds do matter greatly. We did not appropriately consider the potential importance of contributions from species such as glyoxal, which can form SOA with very high O:C. We have adjusted our conclusions accordingly.

Another reason why the conclusions about ambient SOA should be stated much less strongly is that the structural and parametric uncertainties in the SOM are very large at this point. As in other models, in the SOM there are multiple tunable parameters. These parameters are fitted to a-pinene and pentadecane experiments presented in the paper, with very different results, adding an important caveat about the generality of the numerical values of the parameters. It is also a strong assumption that parameters such as DIVP and cfrag are constants and not distributions, and are the same for all precursors, molecular sizes and structures, degrees of unsaturation and oxidation, presence or absence of aromatic structures, functional groups, high vs low NOx chemistry, etc. Although the model focuses mostly on alkanes, important chemistry about the formation of hemiacetals and dihydrofurans which is important for SOA formation from these species (Lim and Ziemann, PCCP 11: 8029-8039, 2009) is ignored. While simple assumptions are necessary to construct the model and start exploring its behavior, the authors should not forget that those strong assumptions have been made when comparing the results with observations.

> Again, we agree with the reviewer in general and have adjusted our conclusions accordingly. However, we do note that by considering the output of the SOM for a range of model configurations (e.g. the magnitude of ΔLVP, number of oxygens added per reaction, extent of fragmentation), we are able to gain insights into whether consideration of e.g. ΔLVP as a distribution will strongly change the model results (and thus what the influence of the parametric uncertainties are). What we can conclude with reasonable confidence is that the predicted aerosol mass is sensitive to any of the parameters but the predicted O:C is predominately controlled by the parent species carbon number and the ΔLVP. Such insight will allow for continued development of the SOM and, in particular, future application (i.e. fitting) to a variety of laboratory experiments will further help to constrain and understand the variability in the derived parameters. Finally, we note that although we assume the parameters to be constants for a given precursor, we make no such assumption that the parameters are or should be the "same for all precursors." We believe that the different values for the α-pinene vs. pentadecane systems demonstrate this clearly. It is our hope that, upon future consideration of many different systems, that we are able to find some generalizations with respect to the best-fit parameters, but do not suggest presently that some sort of universally applicable solution is possible.

In addition the model is based on partitioning theory, which has recently been suggested by several groups (including the authors themselves in Cappa and Wilson ACP 11:1895-1911, 2011) to be insufficient to capture SOA formation processes due to potentially large mass transfer kinetic limitations.

Accretion reactions are also ignored, when there is evidence (e.g. Hall and Murray, 'Oligomer content of alpha-pinene secondary organic aerosol', Aerosol Sci. Tech. 45: 37-45, 2011) that oligomers often represent over 50% of the SOA mass, at least for some precursors. Heterogeneous oxidation is also ignored, even though the authors have also done significant work on this topic and it starts to be important for timescales of several days which are considered in some parts of the manuscript. Given the extremely limited experimental verification of the model structure and parameters and the important processes that have been omitted, strong conclusions about ambient SOA are simply not warranted and should be removed from the manuscript before it can be accepted into ACP.

> Again, the conclusions have been adjusted to reflect the limitations and assumptions of the SOM. We certainly agree that heterogeneous chemistry and accretion reactions are important. We now include explicit discussion and results from a new heterogeneous chemistry module in the revised manuscript.

3298n23, Kroll et al proposed a framework for representing organic species but not a model per se

> We will clarify, as this is what we meant in our statement.

3300n10, it is not the 'structure' but the elemental composition of the molecules that is specified by the SOM. This should be reworded for clarity.

> Done.

3305n23, here the authors say that DlVP is 0.74 for nitrates, however in most of the rest of the manuscript they ignore this value and emphasize that 1 is the lowest reasonable value. This needs more explanation as nitrates are thought to be important components in fresh SOA in urban areas where alkanes are important (see for example Lim and Ziemann, AST 43: 604-619, 2009).

> It is true that nitrates can be important components of SOA. However, the likelihood that they comprise 100% of the functional groups is low. Using 1 for the approximate lower-limit of ΔLVP likely represents a (somewhat) more realistic balance of actual functional groups that is appropriate given that the SOM reflects mean values. Nevertheless, we have de-emphasized 1 as a lower limit.

3308n4, my understanding is that oxygen may be added more rapidly upon fragmentation than if no fragmentation occurs, however the model does not appear to consider this.

> As discussed in our reply to Reviewer 1, we now account for additional oxygen upon fragmentation.

3308n14, I would call that a 2d space, as in a 2d data structure with a value (abundance) at each point in the structure, and not a 3d space.

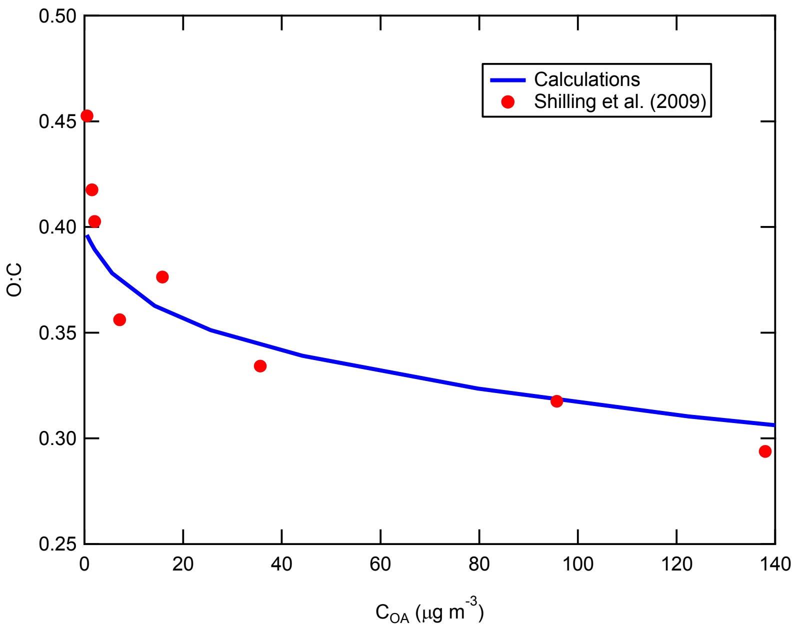
We have changed the text accordingly and use the term “multi-dimensional space”, allowing the reader to decide the dimensionality (which is not the truly important criteria; the important aspect is the number of required parameters and we state what these are).

3310n20, although here the model has been run for low Coa, there is no reason for not simulating the results of the experiments that have been reported at higher concentrations to verify that the experimental trends are captured by the model. Although this may be left for a latter paper, an extended exercise along those lines is needed to build confidence that the model represents reality with a reasonable degree of approximation.

We have confirmed that we obtain similar results when running to higher concentrations. We now include explicit and much expanded discussion of the yield vs. N_C data from Lim and Ziemann (revised section 3.2.2).

3311n12, the results presented here contrast with the experimental results of Shilling et al. (ACP: 9, 771-782, 2009) who measured a much larger change on O/C over this range of Coa.

The Shilling et al. results were obtained for ozonolysis of α-pinene, not photo-oxidation, which is what is discussed in this section. This is key since during ozonolysis of a compound with a single double bond multi-generational chemistry is minimized (to the extent that OH produced from the O_3 + alkene reaction is efficiently eliminated). Thus, the evolution of the SOA composition is primarily governed by the 1^{st} (and only) generation products. Results from Chhabra et al. (2011) indicate that the variability of O:C of SOA with C_{OA} from photo-oxidation vs. ozonolysis are different. However, we understand the reviewers point that a larger range of variability of O:C with C_{OA} is at least possible. The SOM is able to approximately capture the strong dependence of O:C on C_{OA} that was observed by Shilling et al. if we modify the model to deal with ozonolysis (which requires adjusting the rate coefficient of the parent species and setting the reaction rates of the product species to zero). Below, we show the results of a calculation of O:C vs. C_{OA} for different $[HC]_0$ values, having assumed ΔLVP = 1.9 and P_{func} = [0,0.84,0.07,0.09]. Note that these values were not derived from a fit to the data, and have only been selected to give approximate agreement for illustrative purposes (i.e. we have not made a specific attempt to fit the Shilling observations). Thus, we see that our results are *not* in contrast to the Shilling et al. observations and, in fact, are in reasonably good agreement.



3313n9-10 and again 3314n22-24 and other places, this is true if accretion reactions are ignored as they are in the current version of the SOM. This needs to be explained here and throughout the paper. It could be that other formulations of Pfrag may work better once accretion is represented in a realistic manner in the model.

> Accretion reactions would allow for compounds that have condensed to stay condensed (i.e. not evaporate in response to gas-phase reactions). However, this may not have a strong influence on the actual initial condensation step: molecules must have sufficiently low volatility (or sufficient solubility, in the case of aqueous phase reactions that are not considered as part of the SOM) to condense in the first place. To the extent that fragmentation limits formation of products with sufficiently low volatility to condense in the first place our comments are valid. In the context of chamber experiments, which are typically performed at low RH, consideration of aqueous phase reactions and solubility of high volatility species in the aqueous phase is not likely to be important.

3313n24, shouldn't this probability be the product of Pfrag and not of (1-Pfrag)?

> Yes. Fixed.

3315n6 and other places, although the model uses the word 'statistical' in its name, there is nothing new from an statistical point of view compared with the mechanism of Robinson et al. (2007) and several other VBS implementations, where individual precursors also underwent a variety of reaction generations. What is newest here is the implementation of a simplified SOA model on a Nc-No grid as opposed to the variety of other representations proposed in the literature. Although the statistical aspect not being novel for SOA models is mentioned (somewhat unclearly) towards the end of the paper, I suggest that this is clarified early in the paper.

> This will be done.

3319n20, again this is only true if accretion with some of the small molecules resulting from fragmentation is ignored.

> Again, accretion reactions involving small, highly volatile molecules are likely primarily important when there is an aqueous phase present. We now comment on this aspect, which is not treated by our model (in revised sections 3.1.2 and in the conclusions). However, we again note that in chamber experiments, where RH is usually low and aqueous phase reactions unimportant, we believe our conclusion as to the role of fragmentation to be generally valid.

3320n25, dilution does not always proceed at a constant rate in the real world, so that less time always means less dilution. When the boundary layer rises in the morning very rapid dilution can be achieved in very little time, of the order of 100% per hour, compared with a few percent per hour during horizontal transport in the free troposphere. Once this is taken into account, some of the conclusions in this paragraph do not hold.

> We have removed this section, as it is not crucial to the current SOM development.

3322n11-13, I think their Fig 9 contradicts the conclusions that the authors make here. A mixture of different precursors can easily produce material in the SV-OOA range in the figure after ONLY ONE oxidation generation. With additional oxidation generations, accretion, aqueous processing, it does not seem too difficult to reach LV-OOA over realistic timescales of a few days.

> We agree that a mixture of compounds can potentially produce SV-OOA. We have revised this section (and our conclusions) extensively to provide further discussion of the role that condensed phase reactions might play.

3323n11, unless the measurement is proven wrong, this type of disagreement should give the authors pause about the completeness of their model and the generality of the conclusions that can be extracted from it at this level of development.

> The section in which this discussion occurred has been completely revised, and the specific discussion regarding this particular measurement no longer naturally fits in. Therefore, we have removed this discussion from the manuscript. However, despite the fact that we have removed this discussion, we believe that it is important to address this point as we do not want it thought that we have removed this in order to hide any deficiencies in the SOM.
>
> Currently, the differences between the SOM and this particular observation cannot be reconciled. The reason for this model/measurement discrepancy is unknown. This may indicate a limitation of the SOM, although the ability of the SOM to simulate aerosol growth in some chamber experiments (Section **Error! Reference source not found.**) at least suggests that the model/measurement discrepancy here is outside the range of likely uncertainty of the SOM (to the extent that condensed phase reactions do not have a dramatic influence on the O:C for these chamber experiments). Further, the SOM results are consistent with the O:C observed for

low-NOx, low-C_{OA} experiments presented in the same study (observed O:C = 0.17) (Presto et al., 2009). In a separate study, Presto et al. (2010) carried out experiments for heptadecane photooxidation under similar high-NO_x conditions, although with a final C_{OA} (or $[HC]_0$) somewhat larger than in Presto et al. (2009). In these later experiments, they observed the fraction of the *m/z* 44 signal from their aerosol mass spectrometer (f_{44}) to be ~0.04 when C_{OA} ~ 2 μg m^{-3} (*c.f.* their Figure S6), which can be compared with the f_{44} ~ 0.12 at the same mass loading reported in their earlier work. Using the Aiken et al. (2008) relationship, f_{44} = 0.04 corresponds to O:C = 0.22, which is in reasonable agreement with the SOM results. It is possible that the differences between the Presto et al. studies indicates a particularly strong sensitivity of the O:C to the exact experimental conditions that is not captured by the SOM. Certainly, further experiments that investigate the N_C dependence of OA O:C, especially at low C_{OA}, would be illuminating. Finally, we note that in a manuscript recently submitted to ACP, Aumont et al. use their chemically explicit GECKO-A model to simulate SOA formation for pentadecane and other n-alkanes and find very similar results we report here. Admittedly, the GECKO-A model does not include aqueous phase chemistry, heterogeneous chemistry or accretion reactions (as with the SOM), but the fact that the SOM model and the chemically-explicit GECKO-A model lead to generally the same conclusions gives us confidence that the simplifications made in the SOM are indeed reasonable.

3323n section 3.4, I find this section confusing and unclear. I suggest that it is removed from the manuscript to allow a tighter focus on the more fundamental topics being explored.

We have removed this section.

3331n21, I strongly disagree with the statement that 'gas-phase mechanisms have been shown unable to form OOA'. With a mixture of compounds such as in Figure 9, they seem perfectly capable of forming fresh SOA with the O:C of SV-OOA (_0.35) observed in the atmosphere.

Our discussion was perhaps too focused on the LV-OOA category, not the SV-OOA category. We now provide a much narrowed discussion and have removed this statement.

3333n19, if SOA is converted to a non-absorbing phase upon condensation then O:C would be lower than in the current implementation of the model. So while that may be the case, it does not seem like a suggestion to produce SOA of higher O:C in the model.

We discussed the potential for formation of a non-absorbing (or, more precisely, highly viscous) phase not as a pathway to high O:C, but as a pathway to low aerosol volatility. We will revise to clarify this point. In future work, we will explicitly consider the impact of treating OA as a highly viscous medium.

Reply to Jathar and Robinson

SOA O:C in addition to being a function of the carbon number of the precursor, is also dependent on the molecular structure of the precursor. For instance, aromatics have a much higher O:C (Chhabra et al., ACP, 2010) than similar carbon-number n-alkanes (Presto et al., ES&T, 2010). This would imply that different structures (alkanes, alkenes, aromatics) could have very different oxygen addition kernels which could result in very different product O:Cs.

> We do not disagree that molecular structure undoubtedly plays some role in determining the SOA O:C. However, we believe that in saying that "different structures (alkanes, alkenes, aromatics) could have very different oxygen addition kernels" Jathar understates the importance of the relationship between oxygen addition and volatility that must also be considered. There is a limit to the range of O:C that can be obtained starting from a compound with a given O:C, despite potentially different pathways for compounds with the same carbon number but different structures. We explicitly addressed this in our (previous) Figure 7, where we showed the model results for various "oxygen addition kernels" of sorts. Additionally, we do not see where in Presto et al. (2010) the O:C for any of the precursors were actually reported, although discussion of the AMS f_{44} fraction is provided. This is likely because the Presto measurements were made using a Q-AMS, which cannot directly measure O:C for SOA. We assume that Jathar wants us to compare the Presto et al. decane SOA results to the naphthalene results from Chhabra et al., as both have 10 carbon atoms. From the figures in the supplementary material of Presto et al., we estimate from the f_{44} ~ 0.05 (at $C_{OA} = 6\ \mu g\ m^{-3}$) that the O:C for decane is 0.27 (based on the relationship in Aiken et al., 2008). It is not clear to us the accuracy of this conversion from f_{44} to O:C for decane under high NO_x conditions; the results from Chhabra (their Fig. 15) indicate that the $f_{44}\rightarrow$O:C conversion can be highly uncertain for certain species. Chhabra report O:C for naphthalene SOA to range from 0.3-0.74, depending on exact conditions. For high NO_x conditions (as in Presto), Chhabra report a max O:C = 0.57 for naphthalene SOA, with values obtained over a similar oxidation time as in Presto typically giving lower O:C values. Given the potential uncertainty in the $f_{44}\rightarrow$O:C conversion and the dependence of O:C upon specific reaction conditions, we believe that it cannot be ruled out that the decane and naphthalene results are more similar in terms of the O:C than is implied by Jathar.

Although n-pentadecane is a low-volatility organic, it is not clear how good a surrogate it is for the vast majority of SVOCs and IVOCs, which are very hard to speciate (Schauer et al., ES&T, 1999-2002). In fact, one thing we do know is the vast majority of SVOCs and IVOCs are not normal alkanes. SVOCs and IVOCs are likely a complex mixture of branched, cyclic and lightly oxygenated compounds (O:C between 0.1 and 0.2) that likely behave differently than a normal alkane. Lightly oxygenated SVOCs and IVOCs are smaller carbon-number compounds with volatility similar to hydrocarbons like n-pentadecane and therefore stand a much larger chance of forming SOA with higher O:C.

> This point is well taken: SVOC's and IVOC's are not restricted to saturated hydrocarbons. However, having a precursor with some oxygen (O:C > 0) does *not* necessarily lead to SOA with a

> substantially higher O:C. This is because there is a relationship between oxygen addition and volatility. One must add sufficient oxygen (of particular functional groups) to push a compound from the gas to the particle phase. This is (to first order) independent of whether the precursor does or does not contain oxygen. Unless the oxygen present fundamentally changes the chemical pathway available the O:C will not be strongly altered. We have added a section to our manuscript (new section 3.3.3) that explicitly makes this clear through modeling of SOA formed from precursor compounds that start out containing oxygen atoms.

The SOM is fit to SOA data for alpha-pinene and n-pentadecane photo-oxidation. Since the model fits 6 free parameters (too many in my opinion), I suspect that the fit is not very unique, i.e. there are multiple parameter-sets that are able to fit the data. Have the authors checked how different these fits are by predicting the evolution for these fits beyond the smog chamber data?

> We refer Jathar to our reply to Reviewer 1, where this is addressed. However, we now include an example in the manuscript that shows the extrapolation of the alpha-pinene and pentadecane experiments to oxidation lifetimes beyond the fit range (new Figure 10).

The authors state on page 3333: "IVOCs and SVOCs do not contribute substantially to the SOA burden. If these compounds comprised a significant fraction of the total OA mass, it would be very difficult to obtain mean O:C values as high as have been observed in the atmosphere (Aiken et al., 2008; Ng et al., 2011)." This conclusion is much too strong…

> As discussed above, we have revised our manuscript substantially to provide more balanced discussion.

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