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***Interactive comment on* “Understanding evolution of product composition and volatility distribution through in situ GC×GC analysis: a case study of longifolene ozonolysis” by G. Isaacman et al.**

G. Isaacman et al.

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The reviewer has provided many opportunities to improve the flow and clarity of this manuscript. The author's agree with most of the comments, and hope that the responses below satisfy the curiosity and rigor of the reviewer. In reorganizing this manuscript, please note that many figure numbers have changed; the numbers in this response refer to the figure numbers in the discussion paper.

General comments:

As suggested by the reviewer, TAG has great benefits for tracer-based source analysis

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as well as significant limitations as far as the level of oxygenation that can be studied with this method. Currently, TAG is mostly limited to compounds in the SV-OOA range (or less oxygenated), though future work aims to include derivatization, which should greatly extend the range of compounds measurable with TAG. However, this limitation does not significantly curtail the utility of TAG when it comes to tracer-based analysis. TAG has been demonstrated as a powerful tool for source attribution and factor analysis using tracers (Williams et al. 2010). Williams et al. were able to separate SOA into several factors containing various levels of oxygenated compounds, suggesting an ability to measure tracers for many types of OOA. Similar data analysis using 2D-TAG data is underway, but the limitations and capabilities of 2D-TAG are not inherently different than those of TAG. We therefore do not feel that a significant discussion of the use of 2D-TAG for this purpose is necessary in this manuscript as it is discussed in detail by Williams et al. However, a discussion of the RTC method as it applies to SV-OOA and LV-OOA is important and useful for this work and has been added to the conclusions: “Currently this method is limited to systems with levels of oxygenation lower than is observed in most ambient environments, such as sesquiterpene or monoterpene smog chamber ozonolysis; chamber experiments generate aerosol with levels of oxidation similar to semi-volatility oxygenated organic aerosol (SV-OOA), while more oxygenated low-volatility OOA (LV-OOA) is observed to be a significant factor in ambient aerosol (Jimenez et al. 2009). The study of this transition from SV-OOA to LV-OOA is consequently difficult in laboratory settings. However, 2D-TAG is useful for studying the first few generations of VOC oxidation and the subsequent evolution of the OA, providing an opportunity to understand the aging and processing of SV-OOA. Analysis using the RTC method and 2D-TAG can therefore be used to inform models and improve understanding of the SV-OOA to LV-OOA transition. Future work expanding the O/C range of gas chromatography through use of derivatizing agents may also broaden the applicability of this method for use on LV-OOA and ambient systems.”

Both reviewers are correct that a list of compounds used should be available. The list of the compounds was intended to be attached as Supplementary Information and has

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therefore been attached to this comment. This list includes the O/C of all compounds used. Furthermore, in this attachment is presented a comparison of calculated to modeled vapor pressures and associated error analysis.

Some reorganization of the manuscript is detailed in the comments below. Most importantly, the discussion of results has been removed from the methodology section. We hope that the new organization of the manuscript improves flow and readability.

Specific comments:

1. What I understand from the manuscript is that there are indeed a large number of minor products formed in this system, but they only make up for approximately 20% of the total SOA. The reviewer is correct that the compounds comprising the final 20% of the peak area are fairly negligible. However, the statements referenced by the reviewer suggest that 12 compounds account for only 30% of the total peak area; we consequently consider these products to be "minor" (on average each accounts for less than 3% of the peak area). With this wording, we mean to imply that it is these 12 or so compounds that are minor but that their total contribution is non-negligible.
2. The use of "sesquiterpenes" is perhaps a bit over-reaching as suggested, and has been changed to "longifolene"
3. A reference to Figure 4 has been put into the discussion of TAG timing. We hope that drawing the reader's attention to this figure in this section makes the sample timing more clear.
4. This sentence has been changed to read "This retention time correlation (RTC) method is applied here using volatility and polarity separation, but a different column set could be used that separates based on different properties, extending the utility of this method." We hope this avoids confusion.
5. Compounds used in this method are now provided in the attached Supplementary in-

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formation. We apologize for the inconvenience that these were not attached in the first place as intended. The language of this sentence has been changed as follows: "We characterized the chromatographic plane by analyzing a standard mixture of 25 known compounds commonly found in ambient aerosols, as well as 10 confidently identified compounds observed in ambient data; these compounds are listed in the supplementary information." 25 compounds are from known standards, while the remaining 10 have been confidently identified from ambient data; we are therefore confident in the identification of all compounds used.

6. Extrapolation is performed through a simple linear extension of the planar O/C fit; in the text "extrapolation" has been changed to "linear extrapolation" to highlight this. The relative standard deviation of the slope of the O/C fit is 17%, suggesting an error from this extrapolation of under 20%. This has been included in the manuscript: "This extrapolation unavoidably increases uncertainty, but relative standard deviation of the slope of this fit is less than 20% and will be increasingly better constrained as identification efforts improve and 2D-TAG becomes more widely applied."

7. Figures 3 and 7 should indeed be discussed in the same section, as suggested by the reviewer. To improve the flow, references to Figure 3 have been removed from Section 3 (Methodology) as this figure show results. Figures 3 and 7 are now discussed primarily in Section 4.2.2, with the bulk of the results. However, we feel that Figure 2c is very much a continuation of the theory of the RTC method, building off of and giving an example of the methods illustrated in Figures 2a and 2b, so we have chosen to leave Figure 2c in Section 3.

8. The reviewer presents a good question: is longifolene fully reacted at the end of particle formation? Unfortunately we have no definitive answer to this question as no instrument capable of quantifying longifolene was present in this experiment. TAG is capable of observing longifolene and does indeed show a small amount of the compound even in later samples, but this cannot be used as a reliable quantitation. As the reviewer suggests, the absence of significant particle formation would indeed suggest

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that most longifolene has been reacted though we cannot be certain.

9. The explanation of f_{44} evolution at the beginning the experiment has been rephrased to address the reviewer's concerns: "When particle formation begins, f_{44} is high due to the partitioning into the particle phase of highly oxygenated, and therefore less volatile, compounds (Kroll and Seinfeld 2008). As aerosol loading increases, f_{44} decreases because more volatile, less oxygenated compounds partition into the particle phase (Odum et al. 1996; Donahue et al. 2006)." We hope this more clearly explains changes in f_{44} .

10. The reviewer is understandably concerned that the evolution of f_{44} we have interpreted as increasing oxidation is actually simply caused by partitioning as particles are lost to the walls. We believe that while partitioning may contribute to the apparent increase in f_{44} , this is unlikely to be the sole explanation. Most notably, as the reviewer points out: in similar systems, particles lost to the walls continue to partition. It is in fact possible that if this were not that case - that is, if wall loss fully removed particles from the system - f_{44} would be decreased because the most oxygenated products are also the least volatile and are therefore likely the compounds responsible for homogeneous nucleation and therefore present in the smallest particles (Figure 5). These small particles have the fastest wall loss rates (Pierce et al. 2008) so with time oxygen would be preferentially removed from the system. Between TAG #2 and #3 an increase in average O/C is observed (added to Section 4.2.2 of the revised manuscript) as well as an increase in the complexity and relative peak area of more oxygenated regions of the 2DVBS, supporting the conclusion that oxidation is continuing.

We thank the reviewer for the suggestion to plot f_{44} vs. organics (attached). The trajectories of increasing f_{44} and decreasing f_{44} are similar but they do not follow quite the same pathway. This further suggests that the increasing f_{44} observed throughout the experiment is not solely a function of partitioning, though that may be a factor.

If increasing f_{44} does in fact imply oxidation as we state in this work, the reviewer is

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right to be puzzled by its source. No OH scrubber (i.e. cyclohexane) was present in the chamber during these experiments, so it is possible that some OH was produced as this has been observed in the ozonolysis of exocyclic double bonds (Winterhalter et al. 2002). Though this is unlikely to be a continued source of oxygenation (OH has a short lifetime, after all), it may result in the formation of hydroxyketones that can form double bonds upon later dehydration (Lim and Ziemann 2005) and may subsequently react with O₃. In general, hydration and/or dehydration in the particle phase may allow for complex chemistry resulting in increased oxidation levels; the presence of water in the chamber may serve as a source or slow but continued oxidation. Because we have had trouble identifying the compounds in this experiment, and the complexity of the potential chemistry, the possible oxidative pathways are speculative. Continued evolution of ozonolysis SOA has however been seen in previous studies to be dependent on the absence of an OH scrubber (Engelhardt et al. 2008). As the reviewer is undoubtedly aware, understanding particle-phase and heterogeneous chemistry has only recently become a focus of significant research, so the details of these processes are not yet well-understood. However, based on the data discussed above, we do believe the continued oxidation is a real phenomenon and we hope to study it further in the future.

Both Section 4.2.1 and the conclusions (Section 5) have been modified to address the concerns of the reviewer.

Changes in size distribution are prone to artifacts and errors because wall loss is a function of particle size. However, size dependent wall loss correction suggests not particle vaporization, but rather a shift slightly toward larger sizes over the course of the experiment.

11 12. Questions around compound identification are difficult. As discussed in the manuscript, the very ideas surrounding the development of the RTC method stem from an inability to confidently identify these peaks due to a lack of candidate structures in available mass spectral libraries. Consequently, we cannot be certain of the structure of the major products. Longifolenaldehyde is labeled because it is the only peak for

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which we have a confident identification. In the case of longicamphenylone, several candidate peaks have been identified that have very similar mass spectra. Though it is likely that the largest peak is this compound, we cannot be certain and so have not definitively labeled any peak as such.

13 through 15. The reviewer makes a good suggestion to more clearly label each retention time as either volatility or polarity separation. These labels have been added to Figures 2 and 7. Adding a scale to the axes of Figure 7 has proven very difficult as it is already a very busy figure, so this information has been provided in the caption. In short, the x and y scales are equal to those of Figure 2 while z scale is detector response (total ion chromatogram in arbitrary units; red is highest, blue is lowest). Captions of most figures have also been expanded to provide more detailed description.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/11/C2007/2011/acpd-11-C2007-2011-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 53, 2011.

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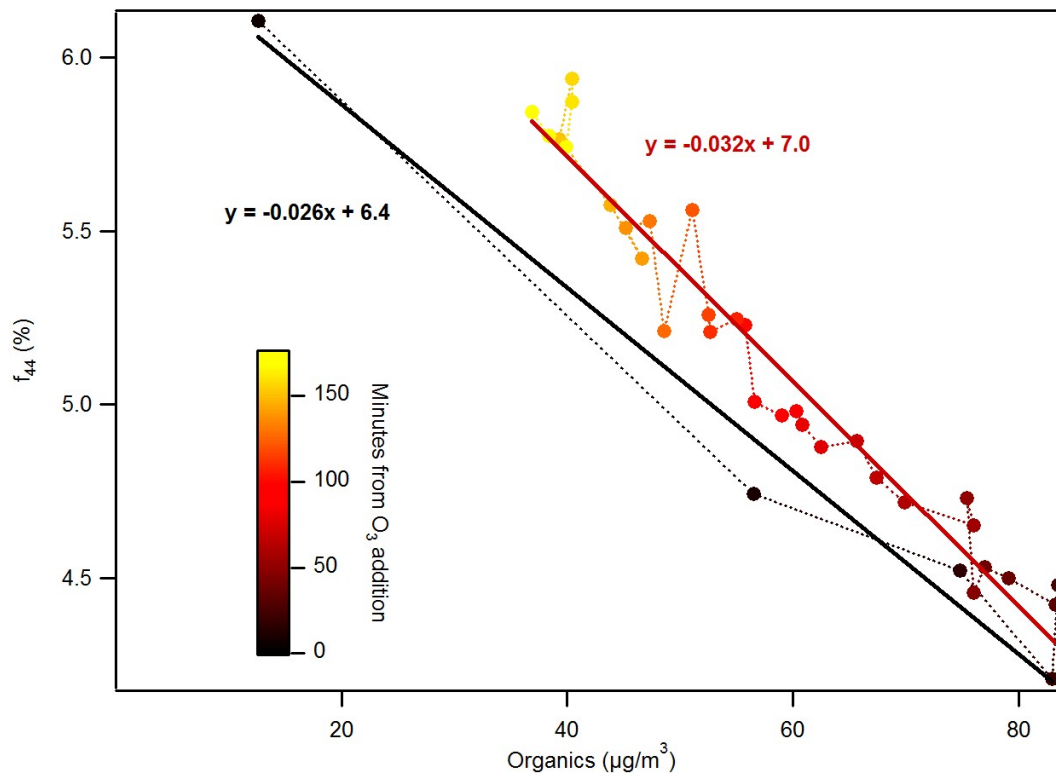
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Fig. 1. AMS f₄₄ vs. organics showing different trajectories during particle nucleation and later oxidation

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