

## ***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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We thank the reviewer for a careful reading of this work. We hope that many of the technical comments from the reviewer will be well addressed by the attached supplementary information. Most of the typos and awkward sentences highlighted by the reviewer have indeed been changed, as detailed below.

The authors have reorganized parts of this manuscript to improve flow and clarity. Please note that many figure numbers have changed; the numbers in this response refer to the figure numbers in the discussion paper.

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### **Technical Comments:**

*“A list of those compounds did not seem to be available, which made the results presented in Figure 2 difficult to completely understand”*

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 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. As mentioned in the paper, the error is within half an order of magnitude. If the editor feels that this information should be presented in the main body of the text, that can be accommodated, though we feel that the concepts presented may be of broader interest, while those interested in the detailed error analysis can readily turn to the supplemental information

*“the acids appear to have the same O/C ratios as the ketones”*

Indeed, this is a difficulty of the O/C fit. The secondary retention time is most strongly a function of polarity, not strictly of O/C. However, the relative standard deviation of the O/C fit is under 20%, suggesting that despite this issue the fit is relatively good. O/C is only one potential parameter for the second dimension and was selected to allow this work to draw on and contribute to models presented by Donahue et al. However, other potential parameters have been suggested, including a sum of functional group dipoles, or the difference of the enthalpies of vaporization for the carbon backbone vs. the functionalized compound. These potential parameter fits are still under study and consideration by us and draw fundamentally on the principles presented in this work.

*“Less clear are the reported shift in O/C ratio (Fig. 3) and the agreement between the O/C mapping in Fig. 3 and the AMS results in Fig. 6”*

Figure 3 has been modified to include all three TAG samples on separate 2D-VBS plots

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(attached). We hope this improves the clarity of the plot, allowing easier comparison between the TAG samples. In addition to addressing the reviewer's comments, we feel this allows easier comparison to Figure 7. The modified Figure 3 makes it somewhat clearer that the products in the more oxygenated regions are getting larger and more numerous while the products in the less oxygenated regions get somewhat smaller. The number of less oxygenated peaks is also increasing, but somewhat less significantly and those new peaks are mostly very small. The wording of the paragraph discussing Figure 3 has been changed to more clearly reflect these statements. The increased oxidation is further illustrated in Figure 7a,b by the increased complexity of Regions 2 and 3: "Regions 2 (Figure 7, dotted circle) and 3 in this early sample contain relatively few peaks. However, as the experiment progresses, the number of peaks in these regions increases significantly, indicating an aerosol of increasing complexity and increasing oxygenation." The final phrase "and increasing oxygenation" has been added to state this trend more clearly.

Comparison between AMS and RTC O/C values was meant to validate the RTC method, and as well as corroborate the observed AMS  $f_{44}$  trend of increasing oxidation. The AMS measures bulk values while we measure individual compounds, so our measurements cannot be directly compared, so the word "agreement" has been removed to avoid confusion. To more clearly discuss comparison between AMS measurements of O/C and RTC calculations, average O/C values for each sample have been calculated and discussed in the manuscript: "Average O/C based on peak area increases from 0.21 to 0.23 from TAG #2 to TAG #3. This increase in average O/C and shift in peak distribution from TAG #2 to TAG #3 is consistent with the trend suggested by the evolution of AMS  $f_{44}$  shown in Figure 5: that oxidation and aging continue during the period of stable aerosol concentration. Average O/C calculated using the RTC method is expected to be lower than that determined using AMS  $f_{44}$  because of low response factors to oxygenated compounds. However, approximately half of the peak area as well as the largest peaks in all samples fall within the AMS  $f_{44}$  O/C range of 0.24 to 0.30, and average O/C falls only 15-25%, suggesting that O/C values calculated

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using the RTC method are reasonable."

We hope that this addition both supports the RTC O/C values and clarifies that both the accepted AMS methods and this method suggest a similar oxidative evolution. We also believe that this addition clarifies not only these comments, but also the discussion above about whether or not a perceived increase in O/C is real.

#### **Editorial Comments:**

In chromatographic literature, GC x GC is often referred to as "multi-dimensional" chromatography (one could imagine mass separation as a third dimension). However, we agree with the reviewer that the use of "multi" in this manuscript may be confusing for this audience, so we have changed "multi-dimensional" to "two-dimensional."

In response to the reviewers comments about awkward language, we have changed the wording in the final paper of many of the discussed sentences:

Abstract: Wording has been changed

Page 56, line 2: "in the using chamber" has been removed. Line 6: Sentence has been changed.

Page 57, 58: The reviewer is correct in interpreting the flexibility of the Pankow and Barsanti model; the model is "multi-product", not "five-product." With reference to the end of the paragraph, we intended to make a point that both of these recently developed models include a polarity parameter that was not present in the original two-product model, highlighting the growing interest in the effects of functionality on partitioning. The word "functionality" has been changed to "polarity" to more clearly make this point.

Page 60, line 15: We have followed the reviewers suggestion to reverse the order of this paragraph.

Page 60, line 11: "firmly" as has been removed.

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Page 65, line 1: "a variety" has been changed to "any" as suggested by the reviewer. Line 8: "meant that" has been changed to "caused." Line 17: The repetition has been removed.

Page 66, line 10: Redundant first "from" has been removed. Line 19: "particle phase oxidation" in this case is meant to refer to the level of oxidation of the particle, not to the process of oxidation occurring in the particle phase. This confusing language has been changed to "particle oxidation level"

Page 67, lines 1-5: The reviewer is correct in the assessment that Figure 4 should be presented earlier. This figure is now referenced in the experimental section, during the description of the TAG samples. The opening paragraph of section 4.2.2. has been changed to read "Though TAG #2 was collected immediately following particle formation, and TAG #3 and #4 were collected later in the experiment, wall loss corrected aerosol concentrations were stable across all three samples (Figure 4)." The authors hope that this moves the description of the system into the experimental section, as is proper, while retaining a meaningful introduction to this section and discussion of this figure.

Page 68, lines 4-5: We agree with the reviewer that this is a confusing sentence: the intention was to suggest that a few of the peaks may be less-polar doubly oxygenated compounds, such as diketones. However, most of these peaks, based on location in the second dimension as well as mass spectral data, are likely to be singly oxygenated, so the confusing "or double" language was removed

Figure 1: The authors feel that Figure 1 is useful in reading the introduction, where formation of the Criegee Intermediate is discussed in detail. Furthermore, longifolene is selected as a model compound in large part because of its structure, so we believe it is useful to provide an illustration of this structure as in Figure 1.

Please also note the supplement to this comment:

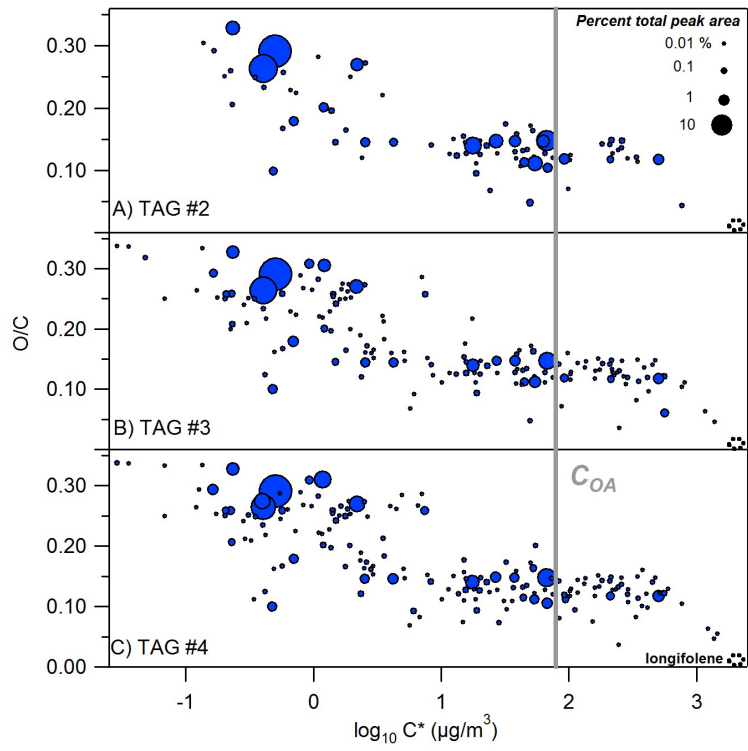
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<http://www.atmos-chem-phys-discuss.net/11/C2000/2011/acpd-11-C2000-2011-supplement.pdf>

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

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**Fig. 1.** Revised Figure 3: all TAG samples are shown as separate sub-figures

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