**Atmospheric
Chemistry
and Physics
Discussions**

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.

Anonymous Referee #2

Received and published: 8 March 2011

This study illustrated a method for predicting the volatility and polarity of aerosol composition through the use of a GC x GC Thermal Desorption Aerosol Gas Chromatograph/Mass Spectrometer (2D-TAG) and a quadrupole Aerodyne Aerosol Mass Spectrometer. The ozonolysis of longifolene is used as a case study. It is found that the SOA composition continues to evolve even after aerosol formation stops, with an increasing number of less volatile, more oxygenated products being formed. The vapor pressures and O/C ratios of these products were estimated based on their chromatographic retention times relative to standard compounds.

This is an interesting study and the results are original. I only have a few main com-

ments. First of all, while the authors did mention the pros and cons of chromatographic approach in the introduction, the implications of the results from longifolene ozonolysis on ambient aerosols were not discussed in this context. As the authors stated in the manuscript, owing to the limitations of chromatographic columns, generally only compounds with O/C less than 0.3 (i.e., f44 up to $\sim$ 6%) will elute through the columns. The longifolene ozonolysis SOA fall well within this range. The O/C of longifolene SOA is more similar to the semi-volatile oxygenated organic aerosol (SV-OOA) component obtained from the factor analysis of ambient AMS datasets (Jimenez et al., 2009, Ng et al., 2010). However, it has been found the ambient low-volatility OOA (LV-OOA) are generally more oxidized than chamber SOA. Does this mean that the 2D-TAG approach will be limited to only detecting products in the SV-OOA range? In this regard, the authors need to include more discussions about the application of the 2D-TAG approach for studying ambient aerosols which tend to have higher levels of oxidation. On the other hand, the ambient SV-OOA components represent the fresher OA, and have different properties owing to their different sources and formation pathways. In this context, the 2D-TAG technique can be a great tool to better characterize the composition of these fresher SV-OOA by identifying specific tracers that can be used to provide more information about their sources.

The other comments are more related to the methodology and the organization of the manuscript. The authors characterized the chromatographic plane by analyzing a series of standard compounds. However, the details of these standard compounds are not available. Since the results from these standard compounds form the basis of the C* fit and O/C fit, such information should be included in the manuscript. Secondly, the discussions of the methodology and results seem convoluted. The authors first described the methodology but also included the longifolene results in the methods section, which the authors then returned to and further discussed again in the results section. I think the organization of the manuscript can be tighten up to make it flow better.

Overall, I recommend the manuscript to be published in ACP after the following comments are addressed.

Specific comments:

1. Page 54, lines 21 and 26. The sentences "the most abundant 3 compounds accounted for only half of the total observed peak area and 80% of the peaks are spread across 15 compounds" and "minor products contribute significantly to SOA from the ozonolysis of sesquiterpenes" seem a bit contradictory. I would think that if the 3 compounds make up for 50% of the total SOA and 15 compounds make up for 80% of the total SOA that means the other minor products are not contributing that much to total SOA. 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 ∼20% of the total SOA.

2. Page 54. Last line. I think it is more appropriate to change "sesquiterpenes" to "longifolene".

3. Page 60, line 15. I think Fig. 4 should be moved to the discussion here so that the readers can have a better idea of when the different TAG samples were taken.

4. Page 62, line 6. The last sentence "This retention time correlation method is widely applicable because a different column set could be selected and different properties estimated from the resultant retention times" is confusing and needs to be re-written.

5. Page 62, line 9. Information about the 35 standard compounds needs to be provided in the manuscript. The authors mentioned that 25 of those compounds are commonly found in ambient aerosols, and 10 of those can be confidently identified. What do the authors mean by "confidently identified"? Does it mean that the other 25 compounds are not "confidently identified"?

6. Page 64, line 17. How is this extrapolation performed? How much uncertainty does this extrapolation results in?

7. Page 64, line 20. I think the discussion of Fig 2c, Fig. 3, and Fig. 7 should all go together to make the paper flow better. For instance, in this version, the authors first discussed Fig. 3 on this page, and then returned to this again on Page 68, this makes all the discussions seem a bit convoluted.

8. Page 65, line 9. Does the longifolene all reacted away within 30min too? Since longifolene has only one double bond, there should be no more aerosol formation after all the initial hydrocarbon is all reacted away.

9. Page 66, line 12. The observation of high initial f44 does not necessarily mean that there is only formation of highly oxygenated products at the beginning of the oxidation. The high f44 observed at the beginning of the experiment is a direct result of partitioning; at the beginning the aerosol loading is very low, hence only the most nonvolatile products will partition into the aerosol phase (semi-volatile products are still formed, but they may not partition at this stage). The sentence "When particle formation begins....." should be rephrased to clarify this. 10. Page 66, last few sentences. It is very puzzling for me how this further oxidation in the particle phrase proceeds. As the authors pointed out, longifolene has only one double bond so reaction should cease after the first oxidation step. Towards the end of the experiment, when loading decreases due to wall loss, it is possible that the semi-volatiles would partition back into the gas-phase and lead to an increase in f44. However, this has not been observed in one double bond systems such as a-pinene ozonolysis and that it seems that the particles lost to the wall actually still participate in partitioning (Weitkamp et al., 2007; Hildebrandt et al., 2009; Ng et al., 2010).

The authors can potentially gain more insights into this by plotting f44 vs. organics loading (NOT wall loss corrected) – after the peak SOA growth, the f44 continues to increase, but does it follow the same trajectory of decreasing f44 with increasing loading (but just go backwards)? Or, it follows an entirely different trajectory in this space?

Also, how does the size distribution of the aerosols change over the course of the experiment? Did the authors observe any decrease in the size distribution that may indicate that the particles are vaporizing?

Overall, I think it is really unclear and puzzling of how the further oxidation proceeds in the longifolene ozonolysis system. The authors need to be more cautious and provide more discussion in the manuscript regarding this.

11. Page 67, line 12. What are the three compounds? Longicamphenylone, longifolenaldehyde, and what is the third compound?

12. Page 67, line 24. Why is longifolenaldehyde identified but longicamphenylone is not? Simply owing to differences in structures?

13. Fig. 2a: It would help to put "polarity" and "volatility" on the y and x-axis, respectively. Same for other figures.

14. Fig.7: What are the scales of the y and x-axis? What is the color scale, is it the number of compounds detected? The total number of compounds detected in each case (cases a-c) should also be included in the figure.

15. Overall, I find that the figure captions are not very informative (the authors often just refer to the main text). Please include more description of the figures in the captions.