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Comment

Interactive comment on “Second-generation products of β -caryophyllene ozonolysis are the dominant contributors to particle mass concentration” by Y. J. Li et al.

Anonymous Referee #2

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First of all, apologies both to the editor and to the authors for my very late review.

This chamber-based study presents molecular identification of a total of 15 first and second generation products of secondary organic aerosol generated by dark ozonolysis of gas phase beta-caryophyllene under conditions of excess ozone. Three of the products are being reported for the first time in the literature with one of them being proposed as a candidate for new particle formation in the atmosphere. The study identified the molecular formulas of the compounds and their O:C and H:C elemental ratios. The work is of good quality and the manuscript is well structured, well written and certainly within the scope of ACP. However, I have a number of concerns that I would like to ask

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Interactive Discussion

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the authors to address before this manuscript can be recommended for publication.

Main Comments:

The authors emphasized the point that providing excess ozone relative to beta-caryophyllene was key in terms of achieving atmospherically relevant conditions, allowing second generation products to form. Is this really what happens in the atmosphere? It is well established that ozone reacts very quickly with beta-caryophyllene, however whether the available ozone molecules will go on and react with the first generation products to produce second generation products (as illustrated in this study) will certainly depend on the reactivity of ALL available VOCs towards ozone. The conclusion that the second generation products are the dominant contributors to particle mass concentration may be correct for a single precursor compound under conditions of excess ozone, but is it really correct in the real atmosphere in the presence of a huge number of reactive VOCs? The authors should discuss this point in the revised manuscript and justify their main conclusion in this regard.

My other main concern with this study is the use of pinic and pinonic acids as calibration compounds for the semi-quantification mode (Page 17707, lines 4-8). The authors have not really discussed the rationale for this choice in any detail. This obviously has a large implication on the quantitative nature of the study. How representative are those typical monoterpene oxidation products of the range of first and second generation molecules identified in the produced SOA? In addition, it is not really clear in the manuscript, whether the estimated contribution of the second generation products (~90%) to the total SOA mass is calculated using these calibrations or not? This needs to be clarified. Again, this has a direct impact on the major conclusion of the study as summarised in its title.

Related to the previous point is the discussion comparing the surrogate method to the AMS measurements (page 17711 – 17712). I believe that the conclusion that the identified 15 compounds quantitatively account for most of the SOA mass is not

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convincing due to the following reasons:

1- The error associated with the use of pinic and pinonic acids as calibration standards (~30% as mentioned in the manuscript)

2- Artifacts related to filter sampling (~60% as mentioned in the manuscript)

3- The comparison with the AMS is not really conclusive giving that the AMS absolute concentration could change by a factor of 2 or so if the collection efficiency is not determined correctly. The discussion of the AMS data is not provided in this paper and only referenced as “in-preparation”. Hence, I am not in a position to evaluate this aspect of the data.

The current version of the manuscript is not really clear on the quantitative capabilities of the analysis methods and therefore, the claim that the second generation products are responsible for most of the SOA mass is not supported enough. The revised version of the manuscript needs to address this point and either make a stronger case for it or change the emphasis of the paper to focus on the product identification and their formation mechanisms.

Other Comments: Page 17702, Lines 17-19: What are the global emission estimates of sesquiterpenes and how do they compare to monoterpenes? i.e. how important are they as a source or SOA?

Page 17702, Lines 21-29: This section of the introduction mentions what other researches studied in regard to beat-caryophyllene SOA but it does not really provide any brief summary of the importance of the findings. For example, the authors mention that studies on mass yield were conducted. I think it would be a lot more informative to provide a one or two lines on the findings so that the motivation for this study becomes clear.

Page 17704: The introduction came to an abrupt ending. The authors should state the scope of the paper here and provide a summary of what will be presented.

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Page 17704, Line 9 -12: Why dry and not wet ammonium sulphate seed was used? Have the authors compared results under dry and wet conditions? Also, I think the authors should comment on the rationale of their choice of quasi-monodisperse particles (50nm).

Page 17704, Line 21 - 24: The initial beta-caryophyllene concentration ranged from 1.47 to 46.4ppbv, and ozone concentration was kept at 50ppbv. This means that the experiments at the high end of beta-caryophyllene concentrations were at approximately stoichiometric quantities with respect to the first double bond and unlikely to be leading to much second generation products (as per your discussion when reviewed previous work on beta-caryophyllene). This potentially has an effect on the results presented in Figure 6 and should be discussed.

Page 17705: Has the sample preparation and analysis methodology described in section 2.2 been evaluated previously? i.e. has this procedure been described elsewhere? If it can not be referenced, then a brief discussion of the suitability of the procedure for the type of organic mixture being analysed should be provided.

Page 17710, lines 8 - 20: The comparison to the results of the study by Winterhalter et al. (2009) attributed the differences to either detection limit or low yield. Could these differences be attributed, instead, to differences in the experimental conditions between the two studies? i.e. precursor concentration, ozone levels, aging times, humidity, etc.

Page 17712, section 3.3: The authors used one method for the estimation of vapor pressure for molecular structures (Hilal et al., 2003) and concluded that compound P302 has an estimated saturation vapor pressure low enough to make it a candidate compound for involvement in atmospheric new particle formation. Barley and McFiggans (2010) have recently shown that there can be a huge range of variability in the estimated vapour pressure depending on which method is used. Has these estimates been compared to any other methods?

REFERENCE: Barley, M. H., and G. McFiggans (2010), The critical assessment of

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vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol, *Atmos. Chem. Phys.*, 10(2), 749-767.

Page 17713, lines 16 - 18: It is suggested that most first-generation products of sesquiterpene ozonolysis are sufficiently volatile to remain in the gas phase. This appears to contradict the observations of extremely fast (i.e. within a couple of minutes) nucleation of new particles in beta-caryophyllene oxidation experiments as reported by a number of studies.

Page 17726, Figure 6: The mass fraction for the first and second generation products (shown in Figure 6) has not been explained. Is this a fraction of the sum of the total 15 products, a fraction of the total mass collected on a filter, or a fraction of the mass measured by the AMS?

Minor comments: Page 17705, line 19: replace 3d with 3 days. Page 17706, line 19: replace “and another” with “and the third mode”

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