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Comment on acp-2021-8

Anonymous Referee #2

Referee comment on "The importance of sesquiterpene oxidation products for secondary organic aerosol formation in a springtime hemiboreal forest" by Luis M. F. Barreira et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-8-RC2>, 2021

In this manuscript, the authors measured the detailed molecular composition of gas- and particle-phase organic compounds in a boreal forest. Many of the compounds observed were related to terpenoid oxidation products. After examining 3 events of high mixing ratios, they argue that sesquiterpene (SQT) oxidation products are important contributors to secondary organic aerosol (SOA). The manuscript describes a remarkable set of measurements with rich details, and shows careful analytical work to identify and quantify a large set of organic compounds. The work is an important contribution to knowledge around oxidation chemistry in a forest. I raise some concerns about the interpretation and the conclusions of this manuscript that should be addressed. In particular, the arguments about sesquiterpene oxidation products being "underestimated" or "substantial" are not well supported by the available evidence. In my opinion this manuscript should be accepted after addressing some of the limitations, which I would consider to be minor corrections.

The central argument to support importance of o-SQT (oxidation products of sesquiterpenes) in SOA is based on one (or maybe two) of the three event days, out of a total of more than 30 days throughout the measurement campaign. Throughout the campaign, O-MT (oxidation products of monoterpenes) are significantly higher (by >1 order of magnitude based on Table 1). In fact organic nitrates are also important, but were not examined in detail. How representative are these "event days"? They are clearly interesting and worthwhile to pursue detailed investigation. What are the conditions that led to these anomalously high mixing ratios? Without proper understanding, caution should be taken about drawing major conclusions. e.g. Are the temperatures lower? (It does not appear so.) Are the air masses coming from a location different from the rest of the campaign? (Something like a back-trajectory analysis will be helpful)

Along similar lines, what is different between events that leads to differences in o-MT and o-SQT (more specifically, events A and B)? It seems like the ratio of MT to SQT measured by PTR-MS is about the same between the two events, but yet there is a large difference in o-MT to o-SQT ratio? It is unlikely due to differences in oxidation rates (otherwise MT/SQT ratio would change too). It is not clear if it is a partitioning issue, because the authors did not examine the relative fraction between gas/particle phase. It might be, as the authors suggested, a difference in dry deposition efficiencies between o-MT and o-SQT. It will be useful to look into this further.

The authors opt to group the observed formulas by chemical structures, and they are useful to distinguish between precursors, but, as the authors pointed out, there can be confounding effects from fragmentation. One possible method to disentangle these effects is to use statistical methods, such as clustering or positive matrix factorization, to identify covarying species. Depending on the size of the data set, different methods may be possible. I suspect that the data size might be too small for PMF, but clustering or principal component analysis might work.

The use of multiple characterization techniques to confirm the findings is a major strength of this work. I wonder if the differences between the techniques are due to the ionization method. The discussion seems to allude to the steps prior to mass spectrometry (e.g. sample storage, chromatographic separation, thermal decomposition) as determining what compounds each technique is sensitive to, but the ionization steps are very different (GC: methane negative CI, LC: ESI+ and ESI-, FIGAERO: iodide negative CI). These ionization methods have drastically different ionization efficiencies between different compound groups.

The relationship between chemical formulas and observed volatility from thermograms is an interesting one. The authors opt to suggest that this is evidence for thermal decomposition, which I believe is likely. At the same time, how good is Equation (3) in describing vapor pressure? Could the results suggest that Equation (3) may overestimate vapor pressure, especially for the highly oxygenated compound measured here? Group contribution methods of vapor pressure tend to use commercially available compounds as calibration data sets, but these methods might not perform as well for more oxygenated compounds which are not commercially available, or vapor pressures are not well known.

If thermal decomposition is really the explanation for the discrepancy shown in Figure 9, it might be useful to see if the discrepancy between predicted and observed T_{max} shows some trend (e.g. with number of carbon atoms, or oxygen atoms). It is still unclear why o-SQT is more volatile than o-MT, despite what the chemical formulas suggest. Figure 10 seems to suggest that volatility is only dependent on oxygen atoms, but there is a large difference in number of carbons between o-MT compounds and o-SQT compounds that should be very important. Also, the gas phase data show the relative particle fraction of o-SQT is lower (Table 1), which suggests that based on gas-particle partitioning, o-SQT is less volatile. Are there formulas measured in both the gas and particle phase and can be used to calculate relative volatilities? This can be compared to the desorption temperature trends. Perhaps some clarification would be useful.

Other comments:

Abstract line 17-20: Sesquiterpenes have been studied for a long time too, since 1990s. I would not characterize the field as focused on isoprene and monoterpenes only.

Abstract line 33: I do not agree that this work necessarily suggests that sesquiterpene contributions are underestimated. (There were no comparison to current estimates.) In fact, the contribution relative to monoterpenes (10x lower than monoterpenes) is quite in line with many other studies. There are 1 event where o-SQT is dominant, but, as mentioned before, it is unclear how common that is.

Line 51: another important factor about terpene diversity is their ring structures, in addition to double bonds. Not a critical comment, just a suggestion to mention ring structures.

Line 161: why is the sensitivity dependent on water vapor pressure?

Line 171: Tmax is not defined. How is Tmax determined from the thermograms? Why not use median temperature? (I have seen Tmax used in other FIGAERO papers too.)

Line 185: how is the optimization done for N- and S- compounds? Is this specific to this work, or there is an established method available from other papers?

Lines 200-205: are the abundances of these high H compounds greater during wetter periods? Hydration reactions could add H atoms.

Line 223: It is not clear (from Figures 2 and 5) that 13/5 – 18/5 had the highest temperatures and PAR, and PAR is not shown for other days outside of this period (Figure 5). Maybe show the 24-hour average, or 12-hour average for each day or night? It seems that later days also had higher temperatures, but perhaps the plant growth period is over by then?

Line 264: should be "high molecular weight", not "weighted"

Line 277-278: to be more precise, sesquiterpene oxidation products partition favorably to

the particle phase, not necessarily quickly. (Difference between kinetics and equilibrium)

Line 285: perhaps acetonitrile from PTR-MS data can shed some light on this as well?

Line 288: should be a period after Fig

Line 294: maxima instead of maximums

Lines 309-320: It appears that SQT concentrations during the event days drop very rapidly, but O-SQT seems to drop more gradually, and the relative decrease is not as obvious as SQT concentrations. I wonder if daytime oxidation of SQT also contributes to O-SQT as well.

Line 346: This sentence appear contradictory to earlier CIMS-SMPS comparison. Only $\sim 1/4$ of the particulate mass is accounted for by CIMS, but it is the correlation between CIMS and SMPS that allows the authors to argue that the CIMS is measuring compounds that are representative of the full OA mass. This is a nuanced argument that should be clarified whenever making statements such as this one here.

Lines 379-385: Are there smaller (C10 or less) molecules that form from sesquiterpene

oxidation?

Section 3.2.3: Given that the filter collection is 4 days long, are there any tests of stability of compounds on filters? Could there be on-filter ozone reactions?

Line 465: regarding "lower O:C ratios", does that also account for the fact that SQT have more carbons, so, to the first order, the same extent of reaction would result in a lower O:C ratio than something smaller, e.g. isoprene or monoterpene?

Line 468: Are the plots for smaller compounds shown anywhere? I cannot seem to find them in the Supplemental Material.