

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-8

Anonymous Referee #1

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-RC1>, 2021

Overall comment:

This work examined SOA formation from monoterpene and sesquiterpene oxidation in a spring-time hemi-boreal forest. The authors concluded that sesquiterpene oxidation could contribute largely to the total measured SOA during the field campaign. This manuscript contributes to the recent awareness of the importance of sesquiterpenes in forming atmospheric SOA and provides new information in that regard. However, there are a few major flaws with the manuscript (see below). The main concern is that the uncertainties regarding FIGAERO-CIMS quantification, formula assignment to specific precursors, and thermal decomposition's impacts were not clearly addressed. Whether the observation (only one event in the entire campaign showed large sesquiterpene SOA) could be due to the combination of these uncertainties was not fully discussed. In addition, the online and offline analysis are not directly comparable for the reasons detailed below. These issues need to be carefully addressed before considered publishable at ACP.

Major comments:

- Sensitivity and quantification of FIGAERO-CIMS.

First, the determination of the LOQ of FIGAERO-CIMS needs more reasoning in the main text, or some references using this approach could be cited.

Moreover, the FIGAERO-CIMS quantification is likely over-simplified. Sensitivities of different oxidation products could differ by 2-3 orders of magnitude. This might lead to low mass closure shown in Figure 1. Using a relatively more accurate approach, i.e., the Lopez-Hilfiker et al. (2016, AMT), the mass closure for SOAS and BAECC could be $\sim 50\%$, while in a similar biogenic-dominant environment, this work has a mass closure of only $\sim 20\%$. More discussion of the potential issues with the quantification approach is needed.

- Grouping of chemical formulas and relative contributions.

It is unclear what the groupings of o-highH1 and o-highH2 were based on. If the purpose is to separate MT vs. SQT products, why was C11 species grouped to o-highH1?

Second, can some of the C10 species be from SQT oxidation? For example, Yee et al. (2018, ACP) showed that C10H16O4 can be a SQT product.

In addition, the relative concentrations of MT vs. SQT during the three events appear very similar, it would be interesting to discuss possible reasons that their SOA relative contributions were so different.

The o-highH1 was only high during event B, throughout the entire campaign, while the o-highH2 had a few other days with high concentrations. What formulas contributed to the differences?

- Comparison between FIGAERO-CIMS and offline analysis.

First, four days of filter collection (Line 111) under ambient condition is likely too long. A lot of chemical reactions could occur on the filters. The authors should discuss some of the potential artifacts and how they could influence the results of this work.

Moreover, the LC-QTOF-MS measures polar and oxygenated species with the (-)ESI more

sensitive to carboxylic acids and (+)ESI more sensitive to the other functional groups. On the other hand, I-CIMS measured oxygenated species. Thus, it is inaccurate to state that "the obtained results with FIGAERO-CIMS are expected to be most comparable with those obtained by LC-QTOF-MS in the negative ionization mode" (Line 389).

In addition, the filter samples were not derivatized prior to the GC-QTOF-MS analysis and hence polar species may not survive the GC column. But most the formed particle-phase products (relevant to MT and SQT oxidation) are expected to be polar species. Thus, the use of GC-QTOF-MS analysis results in this manuscript is less meaningful.

Finally, as the authors claimed that each filter collection was for 4 days, while each of the event A, B, and C were for ~ 1 day. Thus, using filter analysis results representative of 4 days to compare with 1 -day event is not suitable.

Minor comments:

- Line 236 – 242. The authors first argued that the local BVOC contribution to aerosol is significant, in comparison to upwind influence, but then contradicted themselves by suggesting that the lower temperature might have caused the low O:C ratios at night. So, could regional transport of aerosols be ruled out or not? Can the wind directions be used to further examine the hypothesis?

- Figure 4 is unnecessary. Figure 3 and Figure 5 already have included the key information.

- Line 405. As pointed earlier, it is not that GC-QTOF-MS is not suitable for this analysis due to vapor pressure, but polar species need to be derivatized first to pass the GC column.

- Line 427 – 429. The potential thermal decomposition will cause artifacts to interpreting volatility from thermogram. Thus, this sentence is inaccurate. Also, when comparing the two methods, the validity of the thermogram-based empirical calculation (Eq. 1) is needed.

- Line 438 – 439. The readiness of thermal decomposition might be more linked to functional groups than volatility.