Response to reviewer comments for manuscript: “The importance of sesquiterpene oxidation products for secondary organic aerosol formation in a spring-time hemi-boreal forest”

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We thank the reviewer for the constructive comments regarding the paper. Below we address the specific issues point by point. The reviewer comments are in black and our answers are in blue. Changes to the Manuscript or Supplement Information are highlighted in red (note that the lines referred in reviewer´s comments correspond to the ones in the previous version of the manuscript, while the lines in our answers and in the modified text refer to the updated version).

Reviewer 2:

1. Line 385 – 387. From Figs. 4 and 5, it is not convincing that the SQT/MT VOC intensity ratio increased with the o-SQT/o-MT intensity ratio proportionally. Could the authors provide some quantitative comparison (e.g., integrate the intensities in the three events and make comparisons). It appears that SQT/MT ratio might only be slightly higher in event B than event A, but the o-SQT/o-MT ratio increased more dramatically (from ~0.2 in event A to ~2 in event B!). Please explain/discuss the reason.

We agree that the increase in SQT/MT ratio is difficult to visualize in Figs. 4 and 5. A new figure showing the SQT/MT and o-SQT/o-MT ratios in the period of time preceding the increase in o-SQT during the events of this study was added to supplement (Fig. S7). Atmospheric VOCs photo-oxidation is a complex process that initiates before the resulting formation and partition of oxidation products into particle-phase. The atmospheric concentrations of VOCs are influenced by their reactivity with oxidants, and the concentration of corresponding oxidation products by their capability to partition into particle-phase. For that reason, a direct link between VOC concentrations and the concentration of particulate oxidation products is challenging. For example, MT has been found to dominate OH and NO_3 radical chemistry, but SQT can greatly impact O_3 chemistry and form a significant amount of oxidation products even at low SQT concentrations (e.g. Hellén et al., 2018). However, as can be seen in Fig. S7, the SQT concentrations relative to the ones from MT were significantly higher in event B than in Event A, which corroborates the importance of SQT for the aerosol formation during spring-time. The text was modified to:

P12 L367. The maximum SQT/MT ratio in the period of time when o-SQT increased was 0.018 for event A, 0.024 for event B, and 0.018 for event C, with the maximum occurring close to the peak in o-SQT for events B and C (Figs. 4 and S7a). The increase in gas phase SQT relative to MT started around 4 am for events B and C, which coincided with the referred increase in o-SQT particulate concentrations (Figs. 4 and S7a, b).

2. Line 451 – 460. This discussion is still inaccurate. First, LC-QTOF-MS in the negative ion mode only detect acidic compounds, not all polar and oxygenated species. Further, LC-QTOF-MS in the positive ion mode less selectively detects polar and oxygenated species and thus this mode should have more overlap with FIGAERO-CIMS measurements.

The text was modified to:

P14 L432. The LC-QToF-MS measurements performed in negative ionization mode detect mostly acidic species, including many carboxylic acids. These compounds are also detected by FIGAERO-I-CIMS, which is highly sensitive to acidic oxygenated species, and generally to most species with multiple -OH moieties (e.g. Lee et al., 2018). However, LC-QToF-MS measurements performed in positive ionization mode and GC-QToF-MS measurements performed in negative mode were also included in this study since, besides being capable to identify additional compounds measured by FIGAERO-CIMS, they can as well identify SOA constituents that FIGAERO-CIMS is less or not sensitive to. For example, LC-QToF-MS measurements in positive ionization mode are particularly suitable for the detection of basic compounds, while GC-QToF-MS performed in negative mode can measure several aromatic molecules in complex samples with high sensitivity. Therefore, the combination of the off-line mass spectrometry techniques employed in this study allowed the sensitive ionization and detection of a wider range of compounds.

References

Hellén, H., Praplan, A. P., Tykkä, T., Ylivinkka, I., Vakkari, V., Bäck, J., Petäjä, T., Kulmala, M., and Hakola, H.: Long-term measurements of volatile organic compounds highlight the importance of sesquiterpenes for the atmospheric chemistry of a boreal forest, Atmos. Chem. Phys., 18, 13839–13863, https://doi.org/10.5194/acp-18-13839-2018, 2018.