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

Barreira et al.

We thank the reviewers for their constructive comments regarding the paper. Below we address the specific issues point by point. The reviewer's 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 1:

1. 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.

The FIGAERO-CIMS measurements of this study provided signals for more than 3000 potential molecular formulas. However, a significant fraction of their signals were noisy or consisted of very small mass spectral peaks (or parts of peaks) that degrade the accuracy and precision of the analysis. The experimental errors in FIGAERO-CIMS measurements are commonly determined for PMF analysis, assuming a Poisson type distribution of the counting error and considering the electronic background noise (Buchholz et al., 2020). This method could be potentially used to develop a procedure for limit of detection (LOD) or limit of quantitation (LOQ) determination. However, a well-stablished procedure for the determination of LOD and LOQ in FIGAERO-CIMS measurements is currently unavailable. To our knowledge, any LOQ has not been reported for FIGAERO-CIMS. Recently, Siegel et al. (2021) have determined the LOD for FIGAERO-CIMS measurements in Arctic ocean as 1 standard deviation of the field blank´s average signal of all ions.

In our study, we tried to determine the LOD based on the calculation commonly used with conventional analytical techniques such as GC-MS/LC-MS (3 times the standard deviation of the noise), but this method was not sufficient to eliminate noisy signals/erroneous thermograms

efficiently. For example, when plotting thermograms for some selected analytes with low signal we observed that they still were dominated by noise. Due to the lack of a well-stablished procedure for LOD/LOQ determination and since its development was beyond the purpose of this study, we focused on obtaining a threshold value that would efficiently eliminate most of the low and noisy signals and accelerate the data processing time. Yan et al. (2016) have shown that the analytical uncertainty is independent of the m/z range of the instrument and the specific ion. For that reason, we calculated threshold values from the instrumental noise at a mass range where no significant contribution to the overall signal is expected (800-1000 Th). The threshold values were then determined by integrating the background noise, averaging those values during the full desorption period, and multiplying by a factor of 10. With this method, the low signals were efficiently excluded, the number of molecular formulas was reduced to less than 1400, and the data processing time was greatly reduced (note that only compounds that were always below the threshold value were excluded from the analysis). Since the signals of the excluded molecular formulas were consistently low, they did not contribute significantly to particle mass concentrations and, therefore, will have a minor influence on the conclusions of this study. We agree that the term LOQ is confusing since quantification was not performed. The term was changed to threshold value throughout the manuscript.

P6 L162. Threshold values for FIGAERO-CIMS concentrations were derived as 10 times the average values of 15 randomly chosen ions from the mass range of 800 – 1000 Th. More details can be found in the supplement material (Sect. S4).

P9 L268. During this study, a total of 1375 formulas of chemical compounds were tentatively identified in gas phase and 1380 in particle phase measurements by FIGAERO-CIMS (above the threshold values, Sect. 2.3).

SM P18 L153. Threshold values were determined to eliminate noisy signals and restrict the analysis to the most prevalent compounds by averaging, for each sample cycle, the signal (ions s^{-1}) obtained for 15 masses randomly chosen from 800-1000 Th and multiplying the obtained values by a factor of 10.

SM P18 L156. All ions that were constantly below the threshold values during the entire campaign period were not considered for this study.

SM P19 L163. The threshold values for particle phase were calculated with the same method used for the gas phase measurement mode, but by using the average of the values obtained from the integration of signal (ions s^{-1}) over the full desorption duration (s).

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 ~ 50%, while in a similar biogenic-dominant environment, this work has a mass closure of only ~ 20%. More discussion of the potential issues with the quantification approach is needed.

We agree that the sensitivities of different oxidation products can differ greatly. This was pointed out in section 2.3 of the manuscript (L.168) and is one of the reasons why we presented the results as semi-quantitative (even though they were often called concentrations). All other issues that can impact on FIGAERO-CIMS quantitation are discussed in the text and in Sect. S5 of the manuscript. In Lopez-Hilfiker et al. (2016), the declustering scanning for mass closure attempt was not employed due to difficulties in its application to ambient data. Instead, a collision limit (i.e., a single maximum sensitivity value) was used for all ions. In practise, the same was done in this paper by using glutaric acid as a calibrant. In the referred paper, similar compounds to glutaric acid (e.g. succinic acid and malonic acid) were detected at the collision limit. In fact, the sensitivity of glutaric acid in our study, when desorbed from the FIGAERO filter, corresponded to a gas phase sensitivity of 11 normalized counts per second per pptv (ncps pptv^{-1}), which was close to the sensitivity of 16 ($\pm$ 6) ncps pptv^{-1} obtained for the same compound in Lee at al. (2014) (note that Lopez-Hilfiker et al. (2016) refer to the maximum sensitivity shown in Lee et al. (2014)). In the same paper, the maximum sensitivity was ~19 ncps pptv^{-1} (obtained for malonic acid), which shows that glutaric acid is indeed detected close to, if not at, the maximum instrumental sensitivity. The differences between our maximum sensitivity and the one obtained in Lee et al. (2014) may be attributed to analytical uncertainties arising from differences in the sampling setups (e.g. Lee et al. (2014) has not used FIGAERO and analyte losses may occur during thermal desorption), to differences in IMR geometries and operation, and also to differences in transmission efficiency between both instruments. Even though quantitation is challenging, particularly during field measurements, we believe that FIGAERO-CIMS is a valuable technique for semi-quantitation of oxidation products in the atmosphere and that it was able to show the importance of sesquiterpene oxidation products for SOA formation/production during spring in our study. In fact, the R^2 between summed particle constituents measured by CIMS and particulate mass determined by SMPS was 0.72 (Fig. S3). By using maximum sensitivity, a low mass closure is expected as lower sensitivities certainly apply for some compounds but are not considered. The text was modified to:

P6 L165. The concentration of analytes was determined using the obtained calibration coefficients, with the assumption that all analytes have the same instrumental response and that sensitivity was close to the maximum (the sensitivity for glutaric acid in particle phase corresponded to a gas phase sensitivity of 11 normalized counts per second per pptv (ncps pptv-1); see additional information in the supplemental material (Sect. S4)). The main reason for this approach is the multitude of analytes that are measured in ambient air and the difficulty in finding authentic standards for most of those analytes. Besides molecular functionality, CIMS sensitivity depends on several instrumental factors, including the instrument parameters (e.g. inlet temperature and pressure), transmission efficiency, declustering strength, and IMR (ion-molecule reaction unit) water vapor pressure (Lee et al., 2014); the latter may also change in response to environmental factors. In particular, for iodide-adduct CIMS, the instrument response depends on the analyte polarity (sensitivity increases with the addition of a polar group), hydrogen bonding capacity, molecular geometry and molecular size (Iyer et al., 2016; Lopez-Hilfiker et al., 2016). The ensuing considerable variations in sensitivity for compounds detectable in ambient samples and the susceptibility of some analytes to thermal decomposition are further reasons why we present results as semi-quantitative, even though we often report them as concentrations. Additional limitations associated to the analytical method used in this study are discussed in the supplemental material (Sect. S5).

P8 L244. The determination coefficient R^2 between both techniques was 0.72 (Fig. S3, note that SMPS hourly median values were used for comparison with CIMS data).

SM P19 L173. As mentioned in the publication (Sect. 2.3), the sensitivity for glutaric acid in the particle phase obtained in this study corresponds to a gas phase sensitivity of 11 normalized counts per second per pptv (ncps pptv^{-1}). Similarly, Lee et al. (2014) has obtained a glutaric acid sensitivity in the gas phase (without the FIGAERO unit) of 16 ($\pm$ 6) ncps pptv^{-1}. In the same study, a maximum sensitivity of 19 ncps pptv^{-1} has been determined for malonic acid, which shows that glutaric acid is detected at least close to the maximum sensitivity. The differences in sensitivity comparatively to our study may be attributed to analytical uncertainties (e.g. analyte losses during the thermal desorption process) and to differences in the ionization and transmission efficiencies between both instruments. When comparing the gas phase sensitivity obtained for acetic acid in both studies, we obtained a sensitivity of 0.34 ncps pptv^{-1}, while Lee et al. (2014) has reported the value of 0.1 ncps pptv^{-1}. This difference is on the same order as the differences between Lopez-Hilfiker et al. (2016) and Lee et al. (2014), where sensitivities differed by a factor of 2, and is expected considering the operational differences between CIMS instruments.

2. 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?

The o-highH1 and o-highH2 groups were created for compounds that have an unusually high H:C ratio. They seem unlikely to occur and their formation pathway is unclear, but yet they have been reported previously in other studies as well. Due to the limited resolution of FIGAERO-CIMS, they might actually be misidentified monoterpene or sesquiterpene oxidation products. For these reasons, these compounds were studied independently. The division into o-highH1 and o-highH2 was based on number of carbon atoms and consequently the division did relate to the possibility to originate from monoterpenes or sesquiterpenes. However, the actual differentiation between monoterpene oxidation products or sesquiterpene oxidation products, or also dimers products, is challenging for these high hydrogen compositions, especially since the possible formation mechanisms are unknown. Thus, we decided to name them as highH1 and highH2 instead of using monoterpenes and sesquiterpenes in the naming. The C11 species with high H were included in the o-highH1 group as we think that they were unlikely to be (monomeric) sesquiterpene products. Most C11 species featured 24 H, already suggesting a similar origin as the C10 species in this group, which mostly featured 22 H. Also, we are not aware of mechanisms in sesquiterpene oxidation that would lead to a loss of 4 C while retaining 24 H. The text was modified to:

P7 L207. This grouping was based on previous publications showing that the most characteristic and prevalent monoterpene and sesquiterpene oxidation products consist of C_{7-10} and C_{13-15}, respectively (Yee et al., 2018; Chan et al., 2011; Kundu et al., 2017; Hammes et al., 2019; Hamilton et al., 2011; Zhang et al., 2015).

P7 L219. Due to the limited CIMS resolution, their presence could not be definitely confirmed (Sect. S5), and thus these compounds were grouped and evaluated separately as $C_{9-11}H_{(>1.8xC)}O_z$ (o-highH1 group) and $C_{>=12}H_{(>1.8xC)}O_z$ (o-highH2 group). This division was performed to evaluate the possibility of these groups to represent monoterpene or sesquiterpene oxidation products, respectively, broadly based on their carbon numbers. However, the differentiation between monoterpene oxidation products, sesquiterpene oxidation products, or monoterpene dimers is more challenging for these compounds since their mechanism of formation is unknown. Some of the major contributors to the o-highH1 group, such as $C_{10}H_{20}O_6$, $C_{10}H_{20}O_7$ and $C_{10}H_{22}O_7$, have been previously connected to wet and acidic isoprene-derived SOA (Riva et al., 2016) and/or assigned as monoterpene SOA (Zhang et al., 2018). The major C_{11} species feature even more H, e.g. $C_{11}H_{24}O_7$, and hence are more likely related to the high-H C_{10} species rather than products of sesquiterpene oxidation. Therefore these C_{11} species were also grouped into o-highH1. Provided that the species grouped into o-highH1 and o-

highH2 were correctly identified, the chemical pathways to those highly to fully saturated compounds require more investigation in the future.

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.

Some C10 species can indeed be sesquiterpene oxidation products, and possibly also fragments from sesquiterpene oxidation products thermal decomposition. However, previous publications show that the most characteristic and prevalent monoterpene and sesquiterpene oxidation products consist of C_{7-10} and C_{13-15}, respectively (Yee et al., 2018; Chan et al., 2011; Kundu et al., 2017; Hammes et al., 2019; Hamilton et al., 2011; Zhang et al., 2015). Considering the purpose of this study, more important than to accurately group each compound as o-MT and o-SQT was to obtain representative groups of these oxidation products, and the major measured constituents from each group (Fig. 6) were clearly associated with an increase of MT and SQT (e.g. Fig. 4). These major constituents have been also identified as major products in previous oxidation studies from the corresponding terpenes (e.g. Yee et al., 2018; Li et al., 2011; Hammes et al., 2019; D'Ambro et al., 2018). I.e., we are convinced that our major conclusions, as based on our performed grouping, are robust, despite the limitations of our methodology. This statement is also supported by preliminary results from an elaborate statistics-supported source-apportioning approach that is currently being developed using this dataset, and which will be the subject of an upcoming publication. We clarify our main reason in the text:

P7 L205. Specifically, we presumed that $C_{7-10}H_{<=(1.8xC)}O_z$ compounds originated mostly from oxidation of monoterpenes (o-MT group) and $C_{13-15}H_{<=(1.75xC)}O_z$ compounds mostly from oxidation of sesquiterpenes (o-SQT group). This grouping was based on previous publications showing that the most characteristic and prevalent monoterpene and sesquiterpene oxidation products consist of C_{7-10} and C_{13-15}, respectively (Yee et al., 2018; Chan et al., 2011; Kundu et al., 2017; Hammes et al., 2019; Hamilton et al., 2011; Zhang et al., 2015).

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 relative concentrations of SQT vs MT increased with o-SQT, particularly during events B and C (Fig. 4). The text was modified to:

P12 L366. The concentration of gas phase SQT relative to MT also increased with o-SQT, corresponding to the observed increase in particle phase o-SQT compared to o-MT (Figs. 4 and 5).

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?

The dominant o-highH1 formulas during event B were $C_{11}H_{24}O_6$, $C_{10}H_{22}O_7$ and $C_{11}H_{24}O_7$. These compounds have similar m/z as e.g. o-SQT group species $C_{15}H_{24}O_3$ (379.0623 vs 379.0776), $C_{14}H_{22}O_4$ (381.0416 vs 381.0568) and $C_{15}H_{24}O_4$ (395.0572 vs 395.0725), respectively, which constituted the top 10 compounds during event B. Since all of these were higher during event B, and due to limited mass resolving power, it is likely that at least some of the signal attributed to the o-highH1 formulas actually belonged to those SQT oxidation products, at least in our study. The dominant o-highH2 were quite similar in the different events. For example, during event A they consisted of $C_{12}H_{24}O_8$, $C_{13}H_{26}O_9$ and $C_{13}H_{26}O_8$, while during event B the prevalent compositions were $C_{13}H_{26}O_7$, $C_{12}H_{24}O_8$ and $C_{13}H_{26}O_8$. However, we opted for limiting speculation and leave their closer investigation for future studies.

3. 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.

We agree that off-line techniques are prone to sample modification/losses during collection, and that these effects are likely to increase with the collection time. The selection of the collection time was based on rough estimates of the minimum aerosol mass required to overcome the instrumental detection limits considering the maximum flow rate that could be used with our sampling setup. The sampling time could be greatly reduced by using a high-volume sampler, but unfortunately one was not available for this study. It is then conceivable that some reactions did occur, which would affect the semi-quantitative/quantitative comparison between both techniques.

The off-line techniques with higher mass-resolution were mostly employed in this study to support the FIGAERO-CIMS compound´s identification, which we now acknowledge more clearly in the manuscript. In Sect. S6, several of the molecular formulas dominating the FIGAERO-CIMS measurements were also present among the respective dominant ones in LC-QToF-MS (in negative mode) (cf. Figs. 6, S10, S11). These results seem to indicate that at least most of the important compounds from FIGAERO-CIMS measurements were correctly identified and still present in

significant amounts in the collected filters. The off-line techniques also provided an idea of what type of compounds present in SOA were likely missed by FIGAERO-CIMS due to its higher sensitivity for oxygenated species. Furthermore, off-line measurements also seemed to support the misidentification of o-HighH1 and o-HighH2 groups. Therefore, we think it was beneficial to employ higher resolution techniques to support the identification of molecular formulas attributed in FIGAERO-CIMS analysis. The FIGAERO-CIMS and off-line results were considered more carefully in Sect. 3.2.3, the effect of sampling and storage time on sample modification was referred, and the previous Fig. 8 was moved to supplement. The text was modified to:

P14 L427. Off-line filter measurements of SOA particle composition by Q-ToF mass spectrometry provide higher mass resolution when compared to FIGAERO-CIMS. For that reason, off-line measurements were also performed by GC-QToF-MS and LC-QToF-MS to support the investigations with chemical formulas attributed in the FIGAERO-CIMS analysis.

P14 L449. The use of chromatographic separation and truly higher resolution instrumentation, such as the LC-QToF-MS used in this study, can possibly provide better chemical formula identification of compounds. However, off-line techniques are also prone to sample modification, i.e., the analytes might undergo chemical decomposition/losses/transformations during sample collection, preparation, or storage. These effects are likely to increase with the collection and storage time, and to influence the comparison between FIGAERO-CIMS and off-line techniques.

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).

We totally agree with the referee. The text was modified as:

P14 L429. The LC-QToF-MS measurements performed in negative ionization mode detect mostly polar and oxygenated species, being particularly sensitive to carboxylic acids. Most of the compounds in this group are also detected by FIGAERO-I-CIMS that is highly sensitive to many oxygenated species, in particular most species with -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, due to their different analytical principles (e.g. ionization mechanism), they could contribute to understanding the potential presence of SOA constituents that FIGAERO-CIMS might not be enough sensitive.

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.

We agree with the referee. The text was modified to:

P15 L454. Also, for GC-QToF-MS, a direct analysis of larger oxygenated compounds is not suitable without employing a derivatization technique, since the polarity of these compounds can cause low volatility, poor thermal stability, and/or their adsorption in the injector.

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.

We agree that a direct comparison between techniques using different collection time spans is often not suitable, especially for performing quantitative/semi-quantitative comparisons of field measurements. For that reason, the title of Sect. 3.2.3 was modified, part of the text was removed and the discussion of chemical composition measured by off-line techniques and FIGAERO-CIMS considered more carefully (see modifications referred in the answer to the comment above about potential artifacts). The title was also modified to:

P14 L426. 3.2.3 Evaluation of chemical compositions measured by FIGAERO-CIMS, GC-QToF-MS and LC-QToF-MS

Minor comments:

4. 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?

Our goal here was to assess how plausible different possible conclusions are, regarding local vs. transported BSOA sources, even though a detailed source apportionment was not the purpose of this study. We do think that BVOC oxidation products were mostly produced locally, due to their low O:C ratios (likely indicating less processed aerosol). We pointed out that the higher presence of low oxygenated products in the particle phase could be additionally caused by more volatile compounds partitioning into the particles due to cooler temperatures during night-time. However, the analysis of wind directions and back trajectories was insufficient to clarify the sources of measured constituents.

For that reason, we were more careful when speculating about the sources and the text was modified to:

P9 L263. The chemical composition measured by FIGAERO-CIMS appears to support an influence from locally produced BVOC oxidation products since a decrease in concentration-weighted O:C was generally observed in particle phase (Fig. S4) during night. However, the higher presence of low oxygenated products in the particle phase could be also caused by more volatile compounds partitioning into the particles due to cooler temperatures observed during that period of the day.

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

The Fig. 4 was removed.

6. 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.

The text was modified to:

P15 L454. Also, for GC-QToF-MS, a direct analysis of larger oxygenated compounds is not suitable without employing a derivatization technique, since the polarity of these compounds can cause low volatility, poor thermal stability, and/or their adsorption in the injector.

7. 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.

We believe that we agree with the reviewer regarding that thermal decomposition leads to artefacts in both methods. However, the effect will be stronger for the parameterization method. When using the parameterization method, the volatility of a fragment is assigned by the composition of the fragment. So, e.g. CH_2O_2 will always contribute to the IVOC group. With the thermogram method the desorption temperature at which the fragment was created becomes relevant. If the majority of the CH_2O_2 signal stems from thermal decomposition at >100 °C, this signal will be classified as (E)LVOC instead of IVOC. Hence, the C* values derived from the thermograms are also an upper limit but are generally closer to the real volatility of the thermally decomposing compounds than the values from the parameterization. We revised these sentences to hopefully make the statements clearer:

P6 L190. As P_{sat} can have significant uncertainties, an appropriate fitting method should be chosen that accounts for errors in both a and b variables. In our study, we used the bivariate least squares

method (York et al., 2004; Ylisirniö et al., 2021), which was implemented in MATLAB as shown in Pitkänen et al. (2016). The applied fit and its uncertainties are shown in Fig. S15.

P15 L464. When deriving C^* purely from the assigned elemental compositions by employing the parameterization method (Eq. (3); Li et al., 2016), the majority of measured SOA particle constituents were classified as SVOCs and IVOCs (Fig. 7, left), whereas when C^* was derived from thermograms (Eq. 1) a clear dominance of LVOCs was observed (Fig. 7, center) with very little contribution from SVOCs and ELVOCs. The thermograms reflect mostly the volatility of aerosol composition based on their volatilization from the aerosol state (Lopez-Hilfiker et al., 2014), even though thermal decomposition also plays a role. Since thermal decomposition will lead to the detection of fragments of the original molecule, the parameterization method will then assign a higher volatility C^* to these fragments than that derived from their thermograms. Furthermore, the estimation of volatility from parameterization method using Eq. (3) may be inaccurate for certain compounds whose properties are less studied and were not part of the parameter determination (e.g. some highly oxygenated compounds). The C^* value derived from the thermogram will also tend to be higher than the true volatility of the decomposing compound, but it will be closer to the true value than the one derived from the composition of a possibly much smaller molecule fragment. For that reason, the thermogram-based method likely constitutes a more direct and realistic approach for determining C* (Lopez-Hilfiker et al., 2015; Schobesberger et al., 2018).

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

The point in observation (b) is that we will only observe thermal decomposition if the compound decomposes before it evaporates. The likelihood for that increases with decreasing volatility. For our study, a decrease in volatility is typically following an increase in MW and an increase in functionality (as that increases MW and intermolecular interactions).

The thermal lability is linked to thermally labile bonds in the molecule. These can be from functional groups (e.g. COOH groups -> decarboxylation). Then an increase in functionality (=number of functional groups) is indeed most likely directly coupled to the tendency for thermal decomposition. Additionally, the presence of some functional groups may have a stabilizing effect for the intermediate state and thus further enhance the decomposition. But the coupling bond in dimers is potentially fragile as well. The thermal stability of dimers depends more on the type of coupling bond (e.g. hemiacetal vs ester) than the additional functional groups in the molecules. Speculating about the detailed thermal decomposition processes are beyond the scope of this study. Hence, we refrain

from postulating a direct general link between increase in functionality and thermal lability and instead only refer to the statement that compounds with lower volatility are more likely to be detected as thermal decomposition products in FIGAERO-CIMS measurements. The sentence was modified to:

P16 L488. Also (b), less volatile organic compounds are often highly functionalized and, therefore, generally more likely to decompose prior to evaporation.

Reviewer 2:

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 significant 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).

As pointed out in Sect. 3.2, an in-depth analysis of aerosol particle composition and volatility was performed for the periods with higher aerosol mass loadings (3 events described in the paper). The main reason for this approach, besides the already referred high mass concentrations, was because the relative contribution of o-SQT vs o-MT varied greatly during these days, which allowed us to compare in detail these atmospheric constituents. However, SQT and o-SQT were also measured in significant amounts during many other periods of the campaign. In total o-MT did predominate over o-SQT (by about an order of magnitude on average), but o-SQT disproportionally contributed to the condensed phase, with typically smaller difference.

The concentration of o-SQT was particularly high from 6.5.-24.5. (e.g. Figs. 4 and S6). This shows that some phenomena occurring in spring are causing important increases in concentrations of SQT in the atmosphere that are being oxidized and contributing to particle mass. For that reason, we believe that the increase in both SQT mixing ratios and particulate o-SQT is not directly linked to atmospheric conditions but to a certain plant phase in spring. Our study did not cover a detailed investigation of the biosphere, and for that reason we cannot precisely determine when the spring recovery period started. However, the active plant growth period (daily average air temperature consistently above 10

°C) in Jõgeva (75 km NW from Järvselja SMEAR station) has started on 6th of May (Keppart, 2018). This consistent increase in temperature was also observed in our data (e.g. Fig. S6), as expected due to the proximity of Järvselja SMEAR station to Jõgeva. This warm period most probably is of particular importance for the biosphere's spring-time recovery, and hence could have triggered the observed high emissions (known as emission bursts and associated to spring recovery, e.g., Vanhatalo et al. (2015)) and possibly caused the terpene mixtures. It is the importance of SQT to SOA formation/production during that phase in spring that has in particular been underestimated. Note that while the absolute concentrations of SOA may not be as high after that initial burst, the composition after event C still differed from the composition observed before the events and was comparable to the three events.

Due to the limitations associated with the used techniques, in particular for obtaining absolute concentrations, the main purpose of this study was to compare SOA compositions, including relative amounts of SOA material attributable to MT vs. SQT oxidation, and volatility. However, we also compared the variations in concentration over time since the correlation with particulate matter PM_1 calculated from SMPS measurements was reasonable (R^2=0.72). We did not explore organic nitrates in detail because their variation during the events was not as clear. The organic nitrates concentration was also lower during the events than e.g. in the beginning of the campaign when sesquiterpenes were low. For these reasons, we think that their relative importance is not strongly related to the spring phenomena but to long-range transport or to local production, e.g. when NO_x concentrations increase at the site. The text was modified to:

P1 L30. Overall, this study demonstrates that sesquiterpenes may have an important role in atmospheric SOA formation and oxidation chemistry, in particular during the spring recovery period.

P9 L280. The o-MT was the dominant constituent during the campaign, reaching a maximum particle phase concentration of 3.1 µg m^{-3} (Table 1, Fig. 3). However, important concentrations of particulate o-SQT were also measured during a significant period of the campaign (6.5-24.5), with maximum concentrations of 1.6 µg m^{-3}.

P9 L287. The changes in ON concentration were then likely dependent on long-range transport or periodic episodes of anthropogenic pollution.

P11 L344. In our study, we observed sesquiterpene spikes during many mornings from May 6 until a break in PTR-ToF-MS measurements on May 21, so these spikes may be a common phenomenon possibly related to a certain plant phase in spring. A possible reason for the general increase in sesquiterpene emissions observed in May could be related to plant growth. The active plant growth

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period (daily average air temperature consistently above 10 ◦C) in Jõgeva (75 km NW from Järvselja SMEAR station) has started on 6th of May (Keppart, 2018). This temperature increase was also observed in our data (e.g. Fig. S6), as expected due to the proximity of Järvselja SMEAR station to Jõgeva. For that reason, it is likely that active plant growth in our study started at about the same time. Furthermore, the meteorological summer (daily average air temperature consistently above 13 °C) in Jõgeva has started on 10 May (Keppart, 2018). This consistent increase in temperature might have triggered the spring-time recovery period.

P12 L364. This practically immediate response of SOA particle loading and composition to the increase in sesquiterpene emissions reveals the importance of sesquiterpenes to SOA formation/production during spring and broadly verifies the classification applied in this study.

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 useful to look into this further.

The main difference between events that lead to differences in o-MT and o-SQT is the terpenoid composition in gas-phase, which will impact on atmospheric reactivity and SOA potential. However, the dry deposition is still a possible contributor to the differences in o-MT and o-SQT. The text was modified to:

P12 L366. The concentration of gas phase SQT relative to MT also increased with o-SQT, corresponding to the observed increase in particle phase o-SQT compared to o-MT (Figs. 4 and 5).

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 conflating effects from fragmentation. One possible method to disentangle these effects is to use statistic 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.

We agree with the reviewer. PMF is currently a particular valuable tool to identify covarying species and their sources and would be suitable for this data set. Other statistical tools are also available for

that purpose. However, we believe that even without those methods, our study here is comprehensive already and yields new insights into the detailed characterization of particle chemical composition and volatility. And, broadly at least, we think that our classification of o-MT and o-SQT is well supported by the precursor measurements: since o-SQT increased with SQT gas-phase concentrations, while o-MT were higher during increased MT concentrations. The application of statistical methods and their interpretation for source apportionment are also not trivial, as the reviewer indicates. However, we actually think that we do have a sufficient dataset size also for PMF, as each sample's thermal desorption yields a thermogram for each detected species, which can be exploited by PMF, as recently demonstrated (Buchholz et al., 2020). The use of statistical methods on our dataset is indeed currently work in progress. But given the scope (and novelty) of that work alone, and the ability to convey our main messages about the relationship of the distinct sesquiterpene chemical composition and volatility, we decided to publish those results in a separate publication. We indicate this work in progress in the text:

P18 L561. In addition, future studies of ambient SOA using FIGAERO-CIMS (including the dataset obtained here) will likely benefit from the currently on-going development of techniques to deconvolute and interpret thermogram data sets (Buchholz et al., 2020). The employment of analytical tools, such as Positive Matrix Factorization (PMF) method, could be beneficial for e.g. improved source apportionment, and we intend to explore and report on its capabilities in future 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 have drastically different ionization efficiencies between different compound groups.

We agree that the ionization method is certainly a major factor contributing to the differences in measured chemical composition between techniques. However, especially for GC-MS, the main difference was most likely caused by losing the fraction of high polarity compounds prior to ionization (see also answer to reviewer #1 main comment 3). The text was modified to:

P14 L429. The LC-QToF-MS measurements performed in negative ionization mode detect mostly polar and oxygenated species, being particularly sensitive to carboxylic acids. Most of the compounds in this group are also detected by FIGAERO-I-CIMS that is highly sensitive to many oxygenated

The relationship between chemical formulas and observed volatility from thermograms is an interesting. 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.

We agree that the Eq. (3) may overestimate vapor pressure for some compounds, especially for the highly oxygenated ones whose properties are less studied due to difficulties in obtaining commercially available standards and/or to produce them in laboratory. This is another reason why we think that the study of volatility based on obtained thermograms is likely providing values that are closer to the "true" volatility of the measured compounds. Group contribution methods would probably work better than this simple parameterization. However, for group contribution methods the functional groups have to be identified from the sum formulas, which is very challenging. The text was modified to:

P15 L471. Furthermore, the estimation of volatility from parameterization method using Eq. (3) may be inaccurate for certain compounds whose properties are less studied and were not part of the parameter determination (e.g. some highly oxygenated compounds). The C^* value derived from the thermogram will also tend to be higher than the true volatility of the decomposing compound, but it will be closer to the true value than the one derived from the composition of a possibly much smaller molecule fragment.

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 Tmax 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.

Regarding Fig 8, the apparent dependency on only the O number stems from the grouping by C number. Within each group (o-MT and o-SQT) the C number varies by 3/4 (7-10 and 13-15) while the O number is 3 - 14. The sequential addition of oxygen, which increases MW and the functionality, will then directly correlate with the observed volatility. If the compounds were grouped by a narrow range of O numbers, trends with C number would appear. However, as visible in Fig S12, the trends of C^* with C number or O number are not as straight forward when using the thermogram-based method than with the composition-based method. This in itself is a strong argument for the importance of thermal decomposition as this will sever the direct link of detected sum formula and volatility of the original (intact) compound.

The data in Table 1 also supports our interpretation when considering that thermally decomposed low volatility compounds will be detected with the same sum formulas as high volatility compounds. The o-SQT group in the particle phase contains a large fraction of SVOC and LVOC compounds (using the thermogram based method). The O number is not very high, but the C number seems to compensate that and create compounds with low enough volatility to strongly partition into the particle phase. This product distribution is possible for "fresh" SQT SOA, i.e. SOA from not very strongly oxidized SQT precursors. This is in agreement with the observed partitioning between gas and particle phase as reported in Table 1.

The o-MT group in the particle phase is mostly detected in the LVOC and ELVOC range (based on the thermograms). As the reviewer notes, this seems contradictory to the values given in Table 1. But while the same sum formulas of o-MT "compounds" were detected in the gas and particle phase, this does not mean that these are indeed the same real compounds. A dimer compound formed from MT precursors will most likely partition mostly into the particle phase while the corresponding monomer stays mostly in the gas phase. But due to the thermal decomposition in FIGAERO-CIMS, we will detect this dimer with the sum formula of the corresponding monomers. Using the sum formula of the thermal decomposition product will greatly overestimate the volatility. The broad shape of the thermograms strongly suggests the occurrence of thermal decomposition for many ions grouped into o-MT (Fig 8). If the o-MT group does indeed contain such lower volatility, thermally labile dimers in addition to a larger fraction of monomers with a range of volatilities, we would observe a large contribution of o-MT in the gas phase (higher volatile monomers). The lower volatile monomers and

dimers will partition into the particle phase. These o-MT in the particle phase may then easily have a lower volatility than the o-SQT group in the particle phase.

We can only speculate why o-MT could contain so much more of thermally labile dimers than the o-SQT group. The MT reaction precursors may favor dimer formation. Or this could be connected to the overall concentrations of reaction products from SQT and MT.

In light of this explanation we modified the text at several places to strengthen our arguments:

P13 L411. In fact, in Li et al. (2011), the first was found as a major first-generation ozonolysis product, which seems to indicate a recent atmospheric formation.

P15 L477. The main difference between o-MT and o-SQT dominant events, respectively A and B, for the thermogram method was the higher fraction of SVOCs for o-SQT event. This can also possibly indicate that o-SQT oxidation products were "fresher" than those of o-MT, which would explain the higher weighted C* values during the o-SQT event. In fact, as stated previously in this publication, the o-SQT analytes with a molecular formula of $C_{15}H_{24}O_3$, which have been found as a major first-generation sesquiterpene products in another study (Li et al., 2011), increased from 3.2 % on o-MT event A to 20.7 % on o-SQT event B. The presence of first-generation o-SQT products might explain why the o-SQT products were more volatile than the o-MT ones.

P16 L517. As expected from the results in Fig. 8, some trends in volatility follow expectations from the observed compositions, also for the thermogram-based C* although they are lower throughout. The discrepancy between composition and thermogram-based volatilities was higher for o-MT than for o-SQT (Fig. S12). Considering that the tailing in Fig. 8 was broader for o-MT than o-SQT, thermal decomposition is the most probable cause of volatility differences between both methods. The plots from Fig. S12 also indicate generally high T_{max} for small compounds (for example with #C < 5), which is strong evidence for thermal decomposition as the origin of those analytes.

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.

The text was modified to:

P1 L16. Atmospheric SOA particulate mass yields and chemical composition result from a complex mixture of oxidation products originating from a diversity of BVOCs. Many laboratory and field experiments have studied SOA particle formation and growth in the recent years. However, a large

uncertainty still remains regarding the contribution of BVOCs to SOA. In particular, organic compounds formed from sesquiterpenes have not been thoroughly investigated, and their contribution to SOA remains poorly characterized.

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.

The text was modified to:

P1 L30. Overall, this study demonstrates that sesquiterpenes may have an important role in atmospheric SOA formation and oxidation chemistry, in particular during the spring recovery period.

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.

The text was modified to:

P2 L49. Terpenes have high structural diversity, such as distinct ring structures and double bond amounts and positions.

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

The sensitivity to a given compound depends on the water vapor pressure inside the IMR. The reasons for that are a competition between the compound and water vapor for the iodide ion, thereby lowering the sensitivity, but also the capability of water molecules to stabilize the iodide-analyte cluster, thereby increasing the sensitivity (e.g. Lee et al., 2014). The text was modified to:

P6 L165. The concentration of analytes was determined using the obtained calibration coefficients, with the assumption that all analytes have the same instrumental response and that sensitivity was close to the maximum (the sensitivity for glutaric acid in particle phase corresponded to a gas phase sensitivity of 11 normalized counts per second per pptv (ncps pptv-1); see additional information in the supplemental material (Sect. S4)). The main reason for this approach is the multitude of analytes that are measured in ambient air and the difficulty in finding authentic standards for most of those analytes. Besides molecular functionality, CIMS sensitivity depends on several instrumental factors, including the instrument parameters (e.g. inlet temperature and pressure), transmission efficiency, declustering strength, and IMR (ion-molecule reaction unit) water vapor pressure (Lee et al., 2014); the latter may also change in response to environmental factors.

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.)

The applied calibration procedure described by Ylisirniö et al. (2021) links the T_{max} values to P_{sat} (Eq. 1). It is possible to construct a calibration curve using T_{median} instead. But T_{max} is the characteristic temperature most accurately associated with P_{sat}, as the initial upslope and peak of the thermogram of a compound are determined chiefly by P_{sat}, and the vaporization enthalpy, which is connected to P_{sat} (Epstein et al., 2010). On the other hand, the "tail" of a thermogram is influenced more strongly by instrumental issues and thermal decomposition processes (Schobesberger et al., 2018; Thornton et al., 2020). The text was modified to include the definition of T_{max}:

P6 L182. The temperature at the peak of the thermogram of each detected ion (T_{max}) was converted to the corresponding saturation vapor pressure P_{sat} using Eq. (1):

$$P_{sat} = exp^a \, exp^{b \, Tmax} \; ,$$

where *a* and *b* are fitted parameters from calibration measurements with atomized polyethylene glycols of known saturation vapor pressure (Krieger et al., 2018). The used calibration values for the fit are shown in Sect. S3.

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?

We used a saturation mass concentration parameterization established previously also for N- and S-containing compounds. It was obtained by Li et al. (2016) using a multi-linear least-squares analysis of more than 30 000 organic compounds with different classes (CH, CHO, CHN, CHON, CHOS, CHONS) from the NCI open database. The text was modified to:

P7 L199. The equation is based on a previous parameterization developed by Donahue et al. (2011) for CHO compounds, but optimized in Li et al. (2016) to be applicable also for N- and S-containing compounds.

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

We agree that hydration reactions could contribute to the production of high-H compounds. However, we did not find any correlation between the abundances of high H compounds with RH/precipitation (e.g. Figs. 2 and 3).

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?

A complete time-series of available PAR and T data is presented in Fig. S6. In this figure, an increase in temperature followed by a slight increase in PAR was observed during consecutive events prior to the event days. As referred previously, this increase coincided with the starting of active plant growth observed at another experimental site located 75 km NW from the site of our study, and might have triggered the spring-time recovery period. High T and PAR values were also observed from 22-23 of May, but no PTR-MS and FIGAERO-CIMS measurements are available for that time period.

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

The text was modified accordingly.

Line 277-278: to be more precise, sesquiterpene oxidation products partition favorably to the particle phase, not necessarily quickly. (Difference between kinetics and equilibrium).

The text was modified accordingly.

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

It is true that acetonitrile is also a tracer of forest fires and indeed the concentration of acetonitrile increased with the one of levoglucosan in the referred event. However, the source of levoglucosan is a minor topic of discussion and for that reason the acetonitrile time series was not included in the manuscript.

Line 288: should be a period after Fig.

The text was modified accordingly.

Line 294: maxima instead of maximums

The text was modified accordingly.

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.

We agree that the oxidation can both occur during day- and night-time. However, we think that night-time oxidation was predominant because the o-SQT concentration was mostly increasing with a

decrease in O_3 during late-evenings and early-mornings. If day-time oxidation would be dominant, we would expect e.g. an immediate increase of o-SQT with the decrease in mixing heights (with a continuous increase in concentrations from late-afternoons), which was not observed in this study.

Line 346: This sentence appear contradictory to earlier CIMS-SMPS comparison. Only ~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.

The sentence was removed.

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

It is indeed possible that sesquiterpene oxidation lead to the formation of C_{10} or less molecules. That would greatly depend on the structure of sesquiterpenes since for example linear sesquiterpenes are more likely (or quicker) to fragment as a result of oxidation compared to ring-containing sesquiterpenes. However, we think that the formation of sesquiterpene-originated C_{13-C15} molecules was dominant over the formation of $C_{<=10}$ during the sesquiterpene event. In fact, the compositions assigned to o-MT products decreased during that event compared to C_{13-15}.

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?

We did not perform any tests of stability of compounds on filters since stability is highly dependent on the measured analyte and the chemical composition was unknown prior to the development of the collection method. Furthermore, the structure of the dominant o-MT and o-SQT products was also unknown, and it would be difficult to obtain authentic standards of the dominant o-MT and o-SQT products. For that reason, the chemical composition measured off-line was compared with the one from FIGAERO-CIMS. Since the composition was similar, especially considering the major analytes of this study, we concluded that the results from filter collection and subsequent measurements could also be used to support the results from FIGAERO-CIMS. However, it is conceivable that some on-filter losses/modifications did in fact take place and results were considered more carefully when comparing the referred techniques. The text was modified to:

P14 L451. However, off-line techniques are also prone to sample modification, i.e., the analytes might undergo chemical decomposition/losses/transformations during sample collection, preparation, or

storage. These effects are likely to increase with the collection and storage time, and to influence the comparison between FIGAERO-CIMS and off-line techniques.

P18 L559. The use of devices that allow to decrease the sampling time (e.g. high-volume samplers) can also greatly reduce the occurrence of sample losses/modification and facilitate the comparison between on-line and off-line techniques.

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?

The reviewer is correct regarding the general trends for O:C in products of SQT and MT. However, in this section we are referring to the change in O:C within the group of o-SQT. I.e. that the oxidation processes during the event B led to less oxidized compounds from SQT precursors. The most prominent atmospheric constituents have much lower #O during the o-SQT event than in the other events when o-MT were higher (Fig S12). The text was modified to clarify this:

P16 L515. However, during event B, an increase in C_{13-15} analytes with low #O was observed, again suggesting the increased contribution of more recently formed (hence less oxygenated) sesquiterpene oxidation products.

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

The text refers to plots from Fig. S12 depicting the relationship between T_{max} and carbon and oxygen number. The text was modified to:

P17 L521. The plots from Fig. S12 also indicate generally high T_{max} for small compounds (for example with #C < 5), which is strong evidence for thermal decomposition as the origin of those analytes.

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