Response to Referee #2

We thank the reviewers for their insightful comments and efforts to improve the manuscript. We provide point-by-point response to each comment as follows. In the following text, the **reviewers' comments** are in **black**, **authors' response** are in **blue**, and **changes to the manuscript and supplement information** are in **dark red**.

General Comments

This study presents a detailed investigation into the real-time measurements of biogenic volatile organic compounds (BVOCs) and their oxidation products in both gas and particle phases in a stressed pine forest near a biogas power plant. The authors performed comprehensive measurements using two advanced mass spectrometers and analyzed the influence of various factors including meteorology, local emissions, and chemical transformation processes. This study provides valuable information, but it has a more limited scope than typical research articles. Several major and minor comments need to be addressed before the manuscript can be considered for publication.

Major Comments

The authors emphasize in the title and discussion that this forest is stressed. However, there are no details about the nature of this stress (e.g., when it occurred, to what extent, any dead trees, etc.). A discussion about potential changes in emissions due to this stress would be beneficial.

Response: We have provided more details about the stress status of the Eifel Forest in the subsection of "2.1 sampling site". Moreover, we have included the discussion on meteorological and physical (e.g., leaf area and soil moisture) conditions during the sampling period, emphasizing that the Eifel Forest was under stress during our measurement period.

Lines 116-134: "2.1 Sampling site

"In this study, a three-week field campaign was conducted at a site in the northern Eifel Forest (50.72° N, 6.40° E) during June 2020 as a part of the "Heat and Drought 2020" campaign of the Modular Observation Solutions of Earth Systems (MOSES) project of the Helmholtz Association of German Research Centers. The Eifel Forest was suffering from severe droughts, heatwaves and severe bark beetle infestation in the last years (Weber et al., 2022b; Ghimire et al., 2016). Within two years (2018-2020), 14% of the spruce in the Northern Eifel region were removed due to summer droughts and only 28.3% remained in good condition (Montzka et al., 2021). Therefore, the Eifel Forest can serve as an example of a stressed temperate coniferous forest.

As shown in Fig. 1, the measurement site is situated directly next to a stand of Norway spruce with a few shrubs and blueberry plants also surrounding the area. To the south and southeast of the measurements site, there were some clear-cut areas due to bark beetle infestation in the years of 2018-2020. Additionally, the measurement site was located ~400 m southeast of a football field in the small village Kleinhau belonging to the municipality of Hürtgenwald, Germany (population about 9000) and ~250 m east of a BPP (BioEnergie Kleinhau GmbH). The biomass substrate used for the biogas production in this BPP consisted mainly of crop waste (e.g., corn stover). The measurement site was affected by the BPP emissions especially for westerly wind directions."

Lines 290-296: "). The leaf area index of the Eifel Forest during our measurement period was determined to be ~2.5 ± 0.02 m^2 m^{-2} based on the ERA5 reanalysis data. The soil moisture was measured to be 0.3 ± 0.04 m^3 m^{-3} at a station located ~150 m southwest of the sampling site. In addition, the spatial distribution of soil moisture in the northern Eifel Forest also showed low values (<0.3 m^3 m^{-3}) in most areas covering our sampling site (Fig. S7). Therefore, the Eifel Forest was under relatively dry condition during our measurement period."

The authors identified two organic acid factors using PMF based on VOCUS-PTR data. However, these could be fragments of larger parent ions and not necessarily acids. Additionally, the choice of identifying 6 factors instead of 5, 7 or more needs justification. Figure S6d suggests that 6 factors may not fully explain the measured signals. For source apportionment, the correlation analysis between the factor and its dominating species seems unnecessary and does not support source identification convincingly.

Response: We have provided the time series of 5-7-factors from the PMF analysis in the revised supplement. Compared to the 5-factor solution, a new factor F6 was resolved in the 6-factor solution. However, with 7 or more factors, we were unable to separate the terpene-dominated factor into two distinct sources related to biogenic emissions and BPP emissions. Instead, the 7-factor or higher-factor solutions led to factor splitting, resulting in additional uninterpretable factors. Therefore, we have retained the 6-factor solution as the most interpretable result.
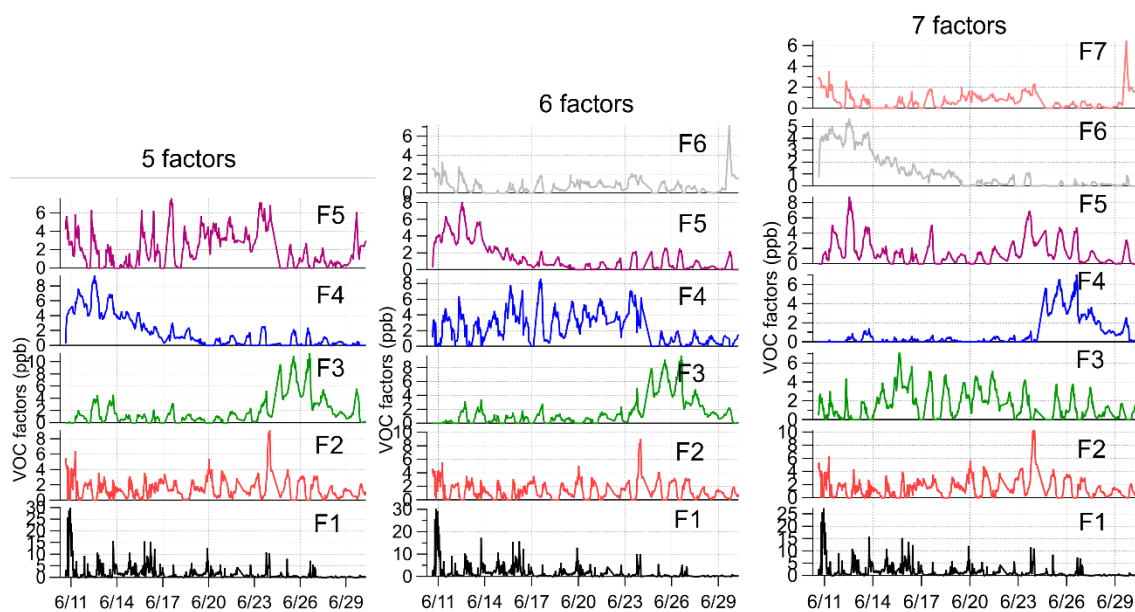
Figure S5. Time series for 5-7 VOC factors resolved from the PMF analysis of Vocus-PTR-ToF-MS data. Compared to the 5-factor solution, a new factor F6 was resolved in the 6-factor solution. Further increasing factor number to 7 only led to the factor splitting, resulting in uninterpretable factor time series.

It is important to avoid assigning factors solely based on correlation analysis between the factor and its dominating species. To ensure a robust and interpretable result, we have rephrased the source apportionment of VOCs, identifying the factors based on their profiles and temporal variations. We have revised these two original factors related to

organic acid to two factors related to BVOC oxidation during daytime (day-SecVOC2 and day-SecVOC3).

Lines 535-570: "In this study, we also resolved three factors related to the oxidation of BVOCs during daytime denoted as day-SecVOC1, day-SecVOC2 and day-SecVOC3. The factor profile of day-SecVOC1 was characterized with high fractions of acetic acid ($C_2H_5O_2^+$) as well as isoprene and its oxidation products (e.g., $C_5H_9^+$, $C_4H_7O_{1-4}^+$ and $C_5H_9O_{2-4}^+$). This factor was also dominated by stronger oxidized products of monoterpenes with oxygen atom numbers >3 (e.g., $C_{10}H_{17}O_{4-5}^+$) compared to other factors in the higher mass range. The diurnal variations of day-SecVOC1 factor showed high concentrations during daytime. Therefore, the day-SecVOC1 factor can be mainly attributed to the photochemical oxidation of isoprene and monoterpenes during daytime. Li et al., (2021) resolved one factor representing isoprene and its oxidation products and another factor representing stronger oxidized products of monoterpenes from the binPMF analysis for a low-mass (*mz*50-200) and a high-mass range (*mz*201-320), respectively, for two European forest sites. They found that these two factors had a similar diurnal pattern with high daytime concentrations. In our study, we performed the PMF analysis for the full mass range (m/z40-220) of the major VOC ions and resolved the day-SecVOC1 factor containing high fractions of oxidized products of isoprene and monoterpenes. This suggests that isoprene oxidation products and higher oxidized products of monoterpenes were mainly related to the daytime oxidation processes. The factor profiles of both day-SecVOC2 and day-SecVOC3 were characterized with high fractions of acetone ($C_3H_7O^+$) and acetic acid ($C_2H_5O_2^+$). Acetone and acetic acid could be contributed by biogenic and anthropogenic secondary sources (Khare et al., 1999; Jacob et al., 2002). The factor profile of day-SecVOC2 also had high fractions of $C_2H_7O_3^+$ (acetic acid water cluster), $C_3H_7O_2^+$ (propionic acid), $C_4H_9O_2^+$ (butyric acid) and $C_3H_9O_2^+$ (e.g., propylene glycol). These gaseous organic acids could be formed from the oxidation of BVOCs like monoterpenes (Friedman and Farmer, 2018). In addition, the factor profile of day-SecVOC3 showed higher fractions of $C_4H_7O_4^+$ (e.g., succinic acid) compared to other factors. The time series of day-SecVOC3 showed the highest correlations with $C_2H_7O_3^+$ (acetic acid water cluster, r = 0.79), $C_2H_5O_2^+$ (acetic acid, r = 0.63) and $C_3H_9O_3^+$ (propionic acid water cluster) compared to other factors. The time series of day-SecVOC3 factor also showed strong correlations with $C_4H_6O^+$ (r = 0.90, **Fig. S10**) and $C_2H_5O_3^+$ (r = 0.89), which can be assigned as the isoprene oxidation product as deprotonated $C_4H_7O^+$ (MVK+MACR) and glycolic acid, respectively. In addition, O_3 was only weakly correlated with day-SecVOC2 (r = 0.27), but much better correlated with day-SecVOC3 (r = 0.57). Moreover, a better correlation was found between O_3 and the sum of these two factors (r = 0.70). The diurnal variations of both factors showed higher concentrations during daytime. Based on these results, we identified day-SecVOC2 and day-SecVOC3 as representing low-molecular weight oxygenated organic compounds produced from the daytime photooxidation of BVOCs."

The conclusion about the impact of relative humidity (RH) on gas-to-particle phase partitioning should consider the influence of temperature changes (about 10-15°C difference), which could not be excluded here.

Response: We agree. The ambient temperature was anticorrelated with RH. Therefore, increasing RH and decreasing temperature promoted the gas-to-particle partitioning of these weakly oxidized monoterpene products. We have revised this conclusion in the abstract correspondingly.

Lines 39-41: "Furthermore, increasing relative humidity and decreasing temperatures promoted the gas-to-particle partitioning of these weakly oxidized monoterpene products, leading to an increase in nighttime OA mass."

Minor Comments

More details about the tree species are needed.

Response: We have added the information of tree species.

Line 98: "Norway spruce (*Picea abies* (L.) Karst.)"

Lines 54-55 & 390-394: Discuss the temperature and light dependency of monoterpene emissions. Are they emitted in higher amounts during the daytime? The authors should discuss the different synthesis, storage, and emission mechanisms of isoprene (de-novo) and monoterpenes (mainly pool emissions from boreal pines).

Response: Thank you for the comment. Yes, the emissions of monoterpenes are higher for Norway spruce-dominated forest during daytime due to higher temperatures and radiation. We have included the temperature and light dependency of monoterpene emissions in the introduction. Although we cannot demonstrate the impact of different emission mechanism on isoprene and monoterpenes in this study, we have mentioned this possibility in the revised manuscript.

Lines 64-73: "The diurnal pattern of isoprene concentrations in forests shows typically higher values during daytime (Yáñez-Serrano et al., 2021; Li et al., 2020; Hakola et al., 2012), since isoprene emissions increase with temperature and sunlight intensity as result of increased de-novo production and direct release. In contrast, monoterpenes are mainly released from storage pools of boreal pines. The emissions and composition of BVOCs from trees varies with abiotic and biotic stresses such as high temperature (Teskey et al., 2015; Kleist et al., 2012), drought (Peron et al., 2021; Bonn et al., 2019) and herbivore attack (Jaakkola et al., 2023; Kari et al., 2019; Faiola and Taipale, 2020). It has been reported that these stresses can alter the emissions of BVOCs, especially of terpenoids (Ghimire et al., 2016; Jaakkola et al., 2023; Byron et al., 2022)."

Line 133: Add the diameter of the sampling tube (also for other relevant sections).

Response: We have added the diameter for the sampling tube in the revised manuscript.

Lines 154-155: "perfluoroalkoxy tube (1/4 inch inner diameter)"

Lines 227 & 302-304: Clarify how many compounds were detected and identified by both instruments, and how many were excluded from further analysis due to low signal. Explain what is meant by "missing".

Response: With the Vocus-PTR-ToF-MS measurement, 287 VOC ion peaks within the mass range of m/z 40–445 were quantified after background correction. Following selection, 157 VOC ion peaks with assigned chemical formulas (primarily mainly $C_xH_y^+$ and $C_xH_yO_z^+$) were used for the PMF analysis. For the CHARON-PTR-ToF-MS measurement, 939 ion peaks were automatically identified using IDA software, and 388 of these were assigned chemical formulas (mainly $C_xH_y^+$ and $C_xH_yO_z^+$). After background correction, 112 VOC ions measured by the CHARON-PTR-ToF-MS were considered for comparison with those simultaneously measured by the Vocus-PTR-ToF-MS.

We have provided this information in the revised supplement **S2, Lines 56-57:** "With the Vocus-PTR-ToF-MS measurement, 287 VOC ion peaks within the mass range of m/z 40–445 were quantified after background correction. Following selection, 157 VOC ion

peaks with assigned chemical formulas (primarily mainly $C_xH_y^+$ and $C_xH_yO_z^+$) were used for PMF analysis. For the CHARON-PTR-ToF-MS measurement, 939 ion peaks were automatically identified using the IDA software, and 388 of these ions were assigned with chemical formulas (mainly $C_xH_y^+$ and $C_xH_yO_z^+$). After background correction, 112 VOC ions measured by the CHARON-PTR-ToF-MS were considered for comparison with those simultaneously measured by the Vocus-PTR-ToF-MS."

Missing data is misleading since we mean the data below the limit of detection. We have provided the detailed calculation method of data uncertainties in the revised manuscript.

Lines 251-256: The uncertainties were calculated with the following equations:

$$Unc. = \begin{cases} LOD \times \dfrac{5}{6} & conc \leq LOD \quad (1) \\ \sqrt{LOD^2 + (Error\ fraction \times conc.)^2} & conc. > LOD \quad (2) \end{cases}$$

where the concentrations of a VOC ion below the limit of detection (LOD) were replaced with half of the LOD and the associated uncertainties were set to 5/6 of the LOD using the Equation 1. The uncertainties of a VOC ion above the LOD were calculated using the Equation 2, assuming an error fraction of 10%.

Line 229: The explanation for excluding C4H9+ is unconvincing. Figure S5 shows a high contribution of C4H9+ from 6/11 to 6/14, but a low contribution outside this period despite relatively stable TVOCs signal (by CHARON-PTR). Was this due to instrument performance?

Response: Yes. The significant variation of $C_4H_9^+$ was attributed to the instrument performance of the Vocus-PTR-ToF-MS. We only observed the large contribution of $C_4H_9^+$ to the VOCs measured by the Vocus-PTR-ToF-MS during the measurement period of 6/11 to 6/14. During other measurement periods, the values of $C_4H_9^+$ were mostly below the detection limit. Therefore, we excluded this signal from the PMF analysis.

Lines 292-300: Discuss the potential impacts of fragmentation on the mass and O:C and H:C ratios detected by CHARON-PTR.

Response: A previous study has reported that the fragmentation of organic compounds in the CHARON-PTR-ToF-MS can result in a negative bias in the determination of bulk organic aerosol parameters. Therefore, the average O:C ratio of bulk OA measured by the CHARON-PTR-ToF-MS was lower than that measured by the AMS. We have added one sentence to clarify this point.

Lines 356-358: "Please note that the fragmentation of organic compounds in the CHARON-PTR-ToF-MS may result in lower average O:C values of bulk OA compared to those measured by the AMS (Leglise et al., 2019)."

Lines 310-312: It is also common to see C5-C8 compounds in boreal forest environments as oxidation products from monoterpenes. Compare these results with more field observations using CIMS with other reagent ions that cause less fragmentation and provide some conclusions.

Response: We agree that the oxidation of monoterpenes can produce C5-C8 compounds. Unfortunately, this study lacks concurrent measurements with a CIMS using a soft ionization source (e.g., iodide). To the best of our knowledge, no measurements with the CHARON-PTR-ToF-MS or other CIMS have been available for specific C5-C8 compounds in the boreal forest environment. Therefore, we are unable to make such comparisons. In the future, we plan to make such comparisons by concurrently measuring

of BVOC oxidation products with the CHARON-PTR-ToF-MS and the FIGAERO-iodide-CIMS in field observations.

Line 316: Have you done any correlation analysis between the parent ions and their potential fragment ions? How strong are these correlations?

Response: Yes, we have performed correlation analysis between parent ions and their potential fragment ions for several organic compounds (e.g., $C_8H_{13}O_4^+$, $C_9H_{15}O_3^+$ and $C_{10}H_{17}O_3^+$) in the particle phase measured by the CHARON-PTR-ToF-MS. Good correlations were observed between $C_8H_{13}O_4^+$ (norpinic acid) and $C_8H_{11}O_3^+$ ($r = 0.97$) as well as between $C_9H_{15}O_3^+$ (norpinonic acid) and $C_9H_{13}O_2^+$ ($r = 0.73$). However, no correlation was found between $C_{10}H_{17}O_3^+$ (cis-pinonic acid) with $C_{10}H_{15}O_2^+$, likely due to the strong fragmentation of cis-pinonic acid, resulting in low concentrations of the parent ion $C_{10}H_{17}O_3^+$. In addition, we found a good correlation for $C_{10}H_{15}O_2^+$ and $C_4H_7O^+$ ($r = 0.72$), both of which were likely produced from the fragmentation of cis-pinonic acid.

We have added this figure in the supplement (now Figure S9).
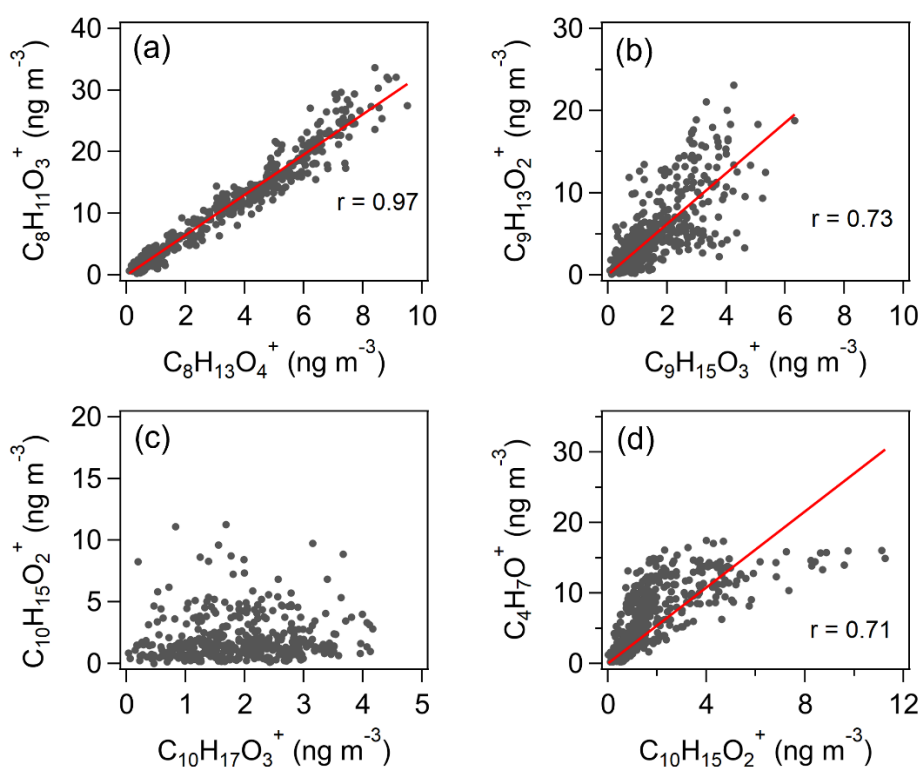
Figure S9. Scatter plots of parent ions and their potential fragment ions: (a) $C_8H_{13}O_4^+$ (norpinic acid and its isomers) vs. $C_8H_{11}O_3^+$; (b) $C_9H_{15}O_3^+$ (norpinonic acid and its isomers) vs. $C_9H_{13}O_2^+$ and (c-d) $C_{10}H_{17}O_3^+$ (cis-pinonic acid and its isomers) vs. $C_{10}H_{15}O_2^+$ and $C_{10}H_{15}O_2^+$ vs. $C_4H_7O^+$.

Lines 598-599: Are there also spruce and beech trees at the sampling site?

Response: Yes. Our sampling site was located adjacent to an intact forest stand dominated by Norway spruce.

Technical Corrections

Line 391: Add a space between "values" and "during".

Response: Added.

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Figure S9, panel (b): Confirm if the isoprene signal was also multiplied by 10, as in panel (a). Double-check the legend.

Response: The legends are correct in both panels. The scale of y axis in panel (a) is larger than that in panel (b), so the isoprene signal was scaled by a factor of 10 in panel (a) for a better visualization.

Line 155: Correct to "pink and grey" instead of "grey and pink".

Response: This figure is removed.

References

Friedman, B. and Farmer, D. K.: SOA and gas phase organic acid yields from the sequential photooxidation of seven monoterpenes, Atmos. Environ., 187, 335-345, https://doi.org/10.1016/j.atmosenv.2018.06.003, 2018.

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