Extreme Heat and Wildfire Emissions Enhance Volatile Organic Compounds: Insights on Future Climate

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We are grateful for the efforts of the Reviewer of our study. The comments of the Referee substantially improved our study, and the authors addressed each statement carefully. Our point-by-point responses to the Reviewer's general and specific comments are presented below. The referee's comments are in **black,** and our answers are in red. Modified or new statements integrated into the revised manuscript are indented. All changes can be seen in the revised version of the manuscript in red font

Reviewer #1

General Comments (GC)

The authors reported the volatile organic compound (VOC) concentrations measured at a temperate forest site. The research highlights the impact of high temperatures and wildfires on VOC concentrations from various sources. This topic is important due to the increasing frequency of heatwaves and fire events, and it fits within the scope of ACP. The results from this study are interesting and could contribute to understanding the impact of these events on air quality and climate. The paper is generally well-written, and the analysis conducted is reasonable and solid. However, the manuscript still requires additional adjustment in the format and clarification before it is ready for publication.

Response: The authors appreciate the kind words from the reviewer.

GC 1: According to the requirements of ACP (https://www.atmospheric-chemistry-and-physics.net/submission.html#figurestables), figure panel labels should be included. This is currently not the case throughout the manuscript, including the figures in the supplementary materials.

Response: Done. All figures with panels, including in the supplementary file, have been modified with alphabetically labeled panels. The corresponding captions were also modified according to the changes in the figures.

GC 2: The method section (Section 2.3) is not clear enough. The content in Lines 173-177 should be expanded with more detailed explanations. For example, the authors mentioned, "The NNMF was applied for a 10-factor series with 30 replicates, 1000 iterations, and a multiplicative update algorithm," which is too vague for readers.

Response: We added the following statements in section 2.3 to explain the parameters and algorithm used in the NNMF procedure.

> *Replicates are the number of times the program will perform the factorization, with every replicate starting with random values for W and H. Iteration is the input value for the maximum replicate performed in the optimization for convergence purposes. The NNMF at Matlab can be performed either as alternating least square (als) or multiplicative update algorithm (mult). This study implemented the mult factorization algorithm as it has faster iterations and is more sensitive to starting values.*

GC 3: Some content from the first paragraph of Section 3.4 should be placed in the methods section, as it should not be mixed with the results.

Response: Done. We appreciate the reviewer for raising the concern. We moved the following statements from section 3.4 to section 2.2 in the methodology.

> *The volatility of the extended list of VOCs was assessed by estimating the effective saturation mass mixing ratio (C_{sat}). The parameterization of the volatility, based on the number of carbon, oxygen, and nitrogen atoms (Donahue et al., 2011; Mohr et al., 2019), was calculated using the following equation:*
>
> $$log(C_{sat}) = (n_{O*} - n_C)b_C - (n_O - 3n_N)b_O - 2\frac{(n_O - 3n_N)n_C}{(n_C + n_O - 3n_N)}b_{CO} - n_N b_N \quad (3)$$
>
> *where n_{O*} = 25, b_C = 0.475, b_O = 0.2, b_{CO} = 0.9, and b_N = 2.5. The terms n_C, n_O, and n_N are the number of carbon, oxygen, and nitrogen atoms, respectively.*

Specific Comments (SC)

SC 1: Line 231: When monoterpene shows a peak during the day, it implies that the emission of monoterpenes from plants is also light-dependent, similar to isoprene (e.g., Kuhn et al., 2004). This is not necessarily related to the isomers of monoterpenes.

Response: Recent studies have shown that isomers of the monoterpenes can be categorized as light-dependent or independent. In an extensive measurement in a coniferous forest in Germany, isomers of monoterpene showed different diurnal profiles. Both pinene isomers (α- and β-) recorded daytime peaks while sabinene had an apparent enhancement during nighttime as shown in Figure R1 (Borsdorf et al., 2023). This observation was consistent across different months/seasons of the year.

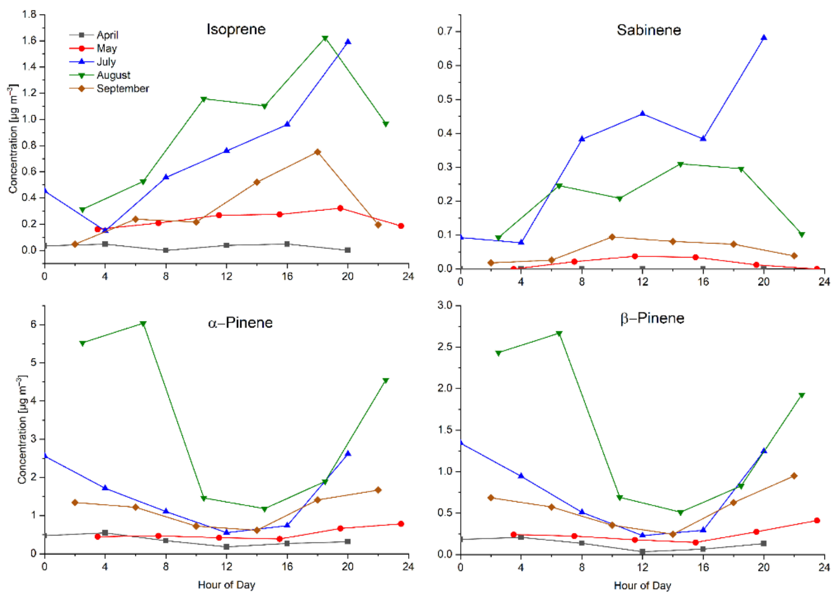

Figure R1. Seasonal and diurnal of isoprene and monoterpenes in a coniferous forest in Germany. Adapted from: Borsdorf, H., Bentele, M., Müller, M., Rebmann, C., and Mayer, T.: Comparison of Seasonal and Diurnal Concentration Profiles of BVOCs in Coniferous and Deciduous Forests, Atmosphere, 14, 1347, 2023.

Similar results were obtained in a Forest Research Lab in Virginia, USA where pinene isomers had minima during the daytime while sabinene had a clear peak around 15:00 (Mcglynn et al., 2023). Evidently, isomers of monoterpene had different diurnal profiles, which can be utilized as identifiers. Our measurements at a temperate forest in the Midwestern USA indicated elevated monoterpene concentrations during daytime, which implies that the dominant monoterpene might be sabinene and/or ocimene.

SC 2: Line 274: Align the paragraph.

Response: Done. The paragraph was aligned.

SC 3.1: Line 289: It is well-known that BVOC emissions increase exponentially with temperature. Why did you choose linear regression here? Could you try using the traditional exponential equation to fit the data?

Response: We thank the reviewer for the suggestion. The temperature-BVOC relationships were fitted with the exponential equation. The following statements were added to the main text.

> *The major BVOCs, isoprene and monoterpene, responded well to variations in temperature, as shown in Figure 3. Under extreme temperatures conditions, the isoprene and monoterpene mixing ratios were 23 and 0.32 ppb, respectively, which were three times higher than the concentrations observed at temperatures below 32°C. The enhancement of isoprene and monoterpene also increased the reactivity of the atmosphere in the temperate forest, based on the calculated 8.31 s^{-1} increase in OH reactivity. Furthermore, Figure 4 shows the evident exponential relationship between temperature and the major BVOCs, consistent with previous studies (Hu et al., 2015; Selimovic et al., 2022; Guenther et al., 2012). The empirically determined coefficients (β) for isoprene and monoterpene are 0.13 and 0.12.*

SC. 3.2 One interesting point I noticed in Figure 3 is that monoterpenes respond differently across different temperature ranges. This might be related to the stress response of monoterpenes. For example, monoterpene emissions may increase dramatically after surpassing a certain temperature threshold (Nagalingam et al., 2023). Therefore, I wonder whether the varying responses observed here are indicators of a stress response in plants or simply an artificial effect caused by the choice of fitting equation.

Response: Indeed, plants have mechanisms to adapt to heat stress and the emission of BVOCs is one of the physiological responses to mitigate heat stress. We agree with the reviewer that the varying responses of monoterpene to different temperature ranges in our temperate forest might be linked to plant thermotolerance.

We added the following statements to the main text.

> *The non-linear response, particularly the enhanced emission of monoterpene at elevated temperatures, can be linked to the thermotolerance physiological activities of plants during heat stress events. A previous study indicated heat stress evidently enhanced the emission of monoterpenes from sunflower, western redcedar, and American sweetgum by at least a factor of 22 (Nagalingam et al., 2023).*

SC 4: Line 364-368: From the perspective of ozone formation, the interactions between fire plumes and BVOCs could be more significant. Since rural regions are usually VOC-limited due to the lack of NOx, the transportation of fire plumes could bring NOx or PANs to the site and promote ozone formation (Xu et al., 2021). In this case, the increase in benzene is not a key factor for ozone formation at this site, which is abundant in isoprene. Additionally, even though the benzene concentration increased significantly, I wonder if the OFP of benzene could be as high as that of isoprene. I suggest either removing this part or providing a more comprehensive discussion.

Response: We agree with the reviewer that benzene might not be the primary contributor to ozone formation, even during the fire plume transport. The section, including the calculation of OFP in the supplementary material, was removed.

REFERENCES

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