

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

Christian Mark Salvador et al.

We are grateful for the efforts of the Reviewers of our study. The comments of the Referees substantially improved our study, and the authors addressed each statement carefully. Our point-by-point responses to the Reviewers' 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.

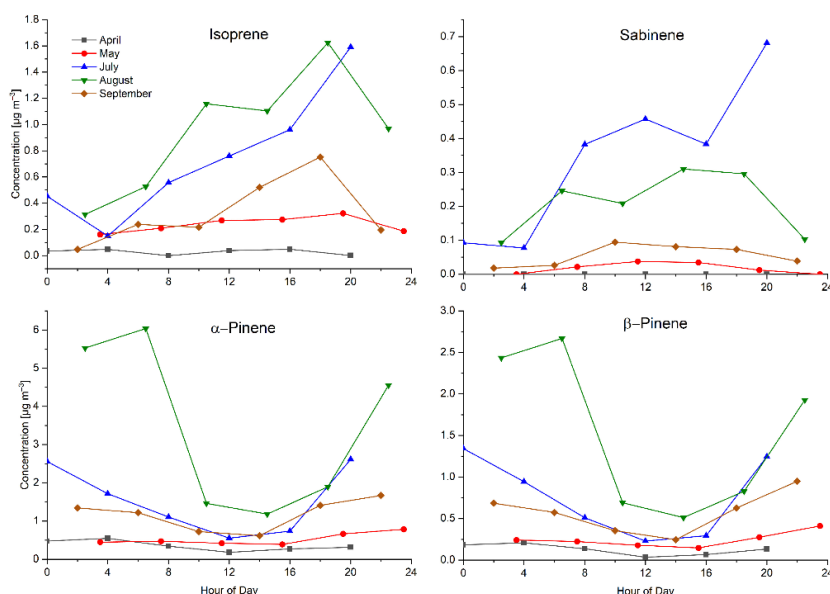


Figure R1. Seasonal and diurnal of isoprene and monoterpenes in a coniferous forest in Germany. Adapted from: Borsdorf, H., Bentele, M., Müller, M., Rebmann, C., and Mayer, T.: Comparison of Seasonal and Diurnal Concentration Profiles of BVOCs in Coniferous and Deciduous Forests, *Atmosphere*, 14, 1347, 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 NO_x, the transportation of fire plumes could bring NO_x 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 for Reviewer #1 Responses

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.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5, 1471-1492, 10.5194/gmd-5-1471-2012, 2012.

Hu, L., Millet, D. B., Baasandorj, M., Griffis, T. J., Turner, P., Helmig, D., Curtis, A. J., and Hueber, J.: Isoprene emissions and impacts over an ecological transition region in the U.S. Upper Midwest inferred from tall tower measurements, *J. Geophys. Res. Atmos.*, 120, 3553-3571, <https://doi.org/10.1002/2014JD022732>, 2015.

McGlynn, D. F., Frazier, G., Barry, L. E. R., Lerdau, M. T., Pusede, S. E., and Isaacman-VanWertz, G.: Minor contributions of daytime monoterpenes are major contributors to atmospheric reactivity, *Biogeosciences*, 20, 45-55, 10.5194/bg-20-45-2023, 2023.

Nagalingam, S., Seco, R., Kim, S., and Guenther, A.: Heat stress strongly induces monoterpene emissions in some plants with specialized terpenoid storage structures, *Agricultural and Forest Meteorology*, 333, 109400, <https://doi.org/10.1016/j.agrformet.2023.109400>, 2023.

Selimovic, V., Ketcherside, D., Chaliyakunnel, S., Wielgasz, C., Permar, W., Angot, H., Millet, D. B., Fried, A., Helmig, D., and Hu, L.: Atmospheric biogenic volatile organic compounds in the Alaskan Arctic tundra: constraints from measurements at Toolik Field Station, *Atmos. Chem. Phys.*, 22, 14037-14058, 10.5194/acp-22-14037-2022, 2022.

Reviewer #2

General Comment (GC)

GC 1: The work presented here reports the change in mixing ratio and distribution of several biogenic and anthropogenic VOCs (measured by CIMS) in a forest as a response to increased temperature and transported biomass burning plumes. The authors underscore the variability of VOCs as a result of heat and wildfire and claim to present a comprehensive analysis of the whole mass spectra performed in this study. While the subject matter of how the VOC distribution changes in response to extreme wildfire and temperature events in the context of future climate scenarios is highly relevant, the surface level results presented here unfortunately do not do well to support the conclusions and claims made by the authors. In its current form, the (sometimes incorrectly) drawn conclusions do little to further current knowledge. On this basis, and described in more detail in specific comments below, I recommend rejection.

Response: We appreciate the thorough evaluation of our work and understand the initial decision provided by the reviewer. In response, we carefully considered each comment and suggestion. The manuscript has been substantially revised to improve the readability and enhance the scientific impact of our research. Below are some of the major additions and revisions made to the manuscript:

1. **Chemical Reactivity** – The original manuscript made several claims regarding the modification of atmospheric chemical reactivity due to changes in the overall distribution of VOCs caused by elevated temperatures and transported combustion plumes. However, the initial version lacked the supporting data or calculations for those claims. In response, we calculated the OH reactivity of each compound with an identified molecular formula to assess the alteration of chemical reactivity due to extreme atmospheric events. More details regarding the calculation of OH reactivity is provided in our response to specific comment (SC) 20. Statements about reactivity in the revised manuscript are now based on the results of the reactivity calculations. We added the time series profile of the total reactivity in Figure 5.

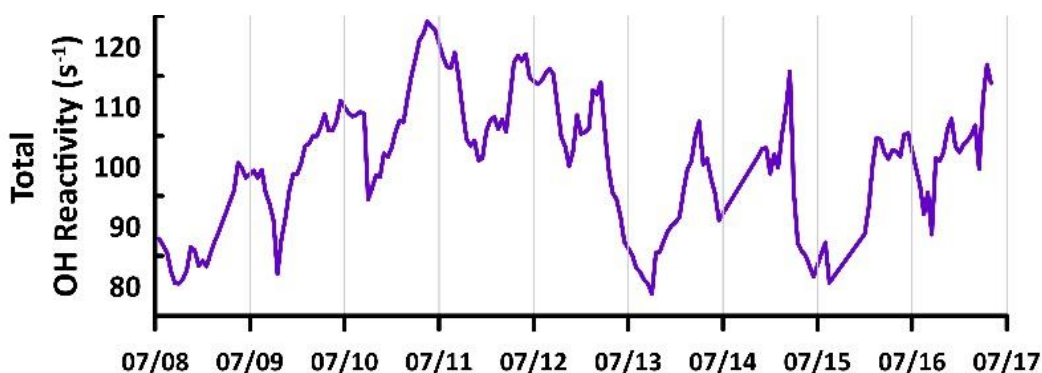
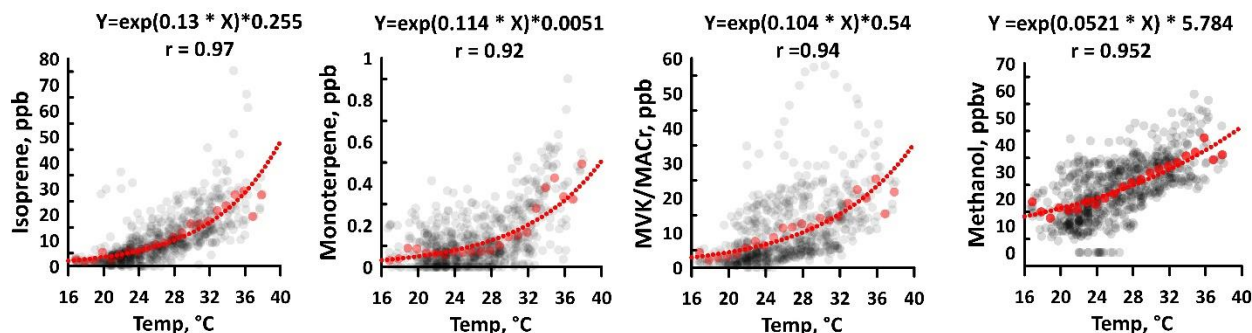


Figure R1. Time series profile total reactivity between July 8 to 17.

2. **Linear fit of Temperature and VOC Concentration** – One significant error in the earlier version of the manuscript was the fitting of a linear trend line to the correlation between

ambient temperature and BVOC mixing ratios. We apologize for this oversimplification, and the revised version of the manuscript now correctly demonstrates the exponential relationship between temperature and VOCs, consistent with several previous studies. We have also presented the statistical analysis of the exponential fitting, highlighting the merits of this approach. The coefficients derived from this analysis can be used by modelling studies to evaluate the current and future influence of temperature on temperate forests.



3. **Interpretation of O:C ratio During Transport of Combustion Plume** – Changes in the O:C ratio was observed during biomass burning transport to MOFLUX, but the initial explanation provided was inaccurate. We appreciate the reviewer for suggesting a more plausible explanation, which has now been incorporated into the revised manuscript.
4. **Missing Supporting Data for Claims and Conclusions** – Several statements in the original manuscript were made without sufficient supporting evidence. These include the assertion that mass 93 is a fragment of monoterpene and that benzene enhancement is due to biomass burning. Plots have now been included in the supplement to substantiate these claims in the main text. Any statements that could not be supported by our data, calculations, or results have been completely removed from the revised version of the manuscript.
5. **Interpretation of Smoke** – The Smoke parameter was extensively used in this research to indicate the extent of biomass burning's influence on the atmosphere in the temperate forest. However, the original manuscript lacked an in-depth explanation and data basis for this parameter. The revised manuscript now provides a clearer explanation of the Smoke parameter and includes a reference study for readers interested in further investigating or utilizing this biomass burning parameter.
6. **Formatting and composition guideline** – The original version of the manuscript has been carefully revised to comply with the formatting and composition guidelines of ACP. Specifically, the figures were updated to include letter notations that are referenced in the corresponding captions. Additionally, uncertainties in some graphs were addressed by integrating error bars to provide a clearer representation of the data.

These are just some of the major revisions made to our research work. We sincerely hope that the reviewer appreciates our comprehensive response and the modifications outlined in this document and reconsider the decision regarding the publication of our work in ACP. We very

much appreciate the amount of time and effort the reviewer has spent in bringing these issues to our attention. We remain grateful for their contribution to improve the quality of our research product.

GC 2: Despite the above, the manuscript has potential to be highly novel and impactful should the authors take steps to further the analysis and provide additional clarification in the methods. A refinement of the results would also allow for comparison to regional and global assessments, which would make the work far more reaching and useful. A review of recent literature would be beneficial in relating the relevance (and significance) of the work presented here to work already published.

Response: Several new statements were added in the recent version manuscript to compare our results with similar prior studies. For instance the following text was incorporated to compare our O:C ratios and acetonitrile levels with previous studies that showcased the influence of biomass burning:

This is consistent with a prior study that reported low O:C ratio (0.25) during intense biomass burning plume, compared to the measurement period when the smoke became diluted and impact of biogenic emission was enhanced (O:C =0.7) (Brito et al., 2014).

Additionally, the observed acetonitrile levels are beyond the mixing ratio range (0.047 to 1.08 ppb) recorded in Asian, US, and European regions (Huangfu et al., 2021), indicating the severe impact of biomass burning (BB)

GC 3: Broadly speaking, the difference in quantitative metrics (for example estimated OH reactivity, estimated reactive organic carbon, change in species abundance, etc) between typical conditions and high temperature and smoke impacted conditions are lacking and could be better analyzed and presented. Several of the figures are missing estimates of error and need to be further refined. Results presented and implied conclusions are missing context or relevance. The comparison to previous studies and literature is lacking and needs to be elaborated on. For instance, it would be useful to know how many of the species measured here by the CIMS are not included in climate predictions (e.g models). Presumably, it's quite a few given that global prediction models lack the complexity of emissions measured here. For models that discuss the importance in certain VOCs, it would be useful to know what those VOCs are and if they were also measured here. These are just a few examples of how the manuscript can be improved and resubmitted. Additional comments are provided below.

Response: We concur with the reviewer and we integrated the OH reactivity data as an important quantitative metric to showcase the impact of future climate events. The comprehensive calculation was performed for all 275 compounds with assigned molecular formulas. A total reactivity value is now presented in the manuscript, which highlights the potential influence of biomass burning and elevated temperatures. Additionally, key conclusions are supported by evidence such as correlation plots between VOCs and linear trends of tracers, paired with observations of atmospheric events. Insights without appropriate proof have been removed to prevent confusion and misinformation for the readers.

While we recognize that major compounds such as isoprene, monoterpenes and methanol are commonly included in climate projections, we are not familiar with previous studies that extensively list all species that could be referenced in our study.

Specific Comments (SC):

SC 1: Prior to resubmission I highly encourage and recommend the author review formatting and composition guidelines presented by ACP.

Response: The revised manuscript has been formatted according to the guidelines of ACP, with particular attention to the panel labels in the figures. Multi-plot figures are now labeled with letters, and the corresponding notations have been included in the figure captions.

SC 2: The background is fairly general and could benefit from more specificity when referencing literature. Specifically, elaboration on how the reviewed literature fits into the context of this study could help strengthen the results presented.

Response: The introduction has been revised to provide insights into the future climate conditions, particularly extreme temperatures and the increased frequency of global wildfires. During our measurement period, the MOFLUX site experienced such events, providing relevant data that can be used to explore the variability of atmospheric parameters and components. This was emphasized in the first and second paragraphs of the introduction.

The third paragraph highlights previous studies that investigated the impact of future conditions on VOCs. We also included reaction schemes and discussed the contribution of these compounds in the atmosphere. While we provided information on the influence of temperature on VOC emission and transformation, the section lacked a discussion on the impact of increasing wildfire events on VOCs. To address this, the following statements regarding previous studies on the influence of BB on VOCs have been added in the revised manuscript.

Moreover, BB events such as wildfires are considered as the second-largest source of VOCs globally, further influencing air quality and climate (Jin et al., 2023; Yokelson et al., 2008). Benzene, a common compound emitted during wildfire events, has been found to be more than ten times the typical concentration in metropolitan areas, thereby posing elevated health risks (Ketcherside et al., 2024).

SC 3: Coordinates need a degree sign and space when naming the direction. There are a few spots in the methods where the authors only added the lat, long in parentheses. This needs to be corrected.

Response: We concur with the reviewer. All coordinates presented in the manuscript have been converted to degrees minutes seconds (DMS) format. Here are the updated texts:

Measurements were conducted at the Missouri Ozark AmeriFlux (MOFLUX) site (latitude: 38° 44' 38.76" N, longitude: 92° 12' 0" W) in central Missouri, United States

Figure 1 shows the time series profile of hourly averages of temperature and relative humidity collected from Columbia Regional Airport (latitude: 38° 49' 1.2" N, longitude: 92° 13' 15.6" W) approximately 8.5 km from the MOFLUX site.

Global solar radiation data were measured at a weather site in Ashland, MO (latitude: 38° 43' 19.2" N, longitude: 92° 15' 10.8" W), 5.22 km from the MOFLUX tower.

SC 4: For methods, It would be useful to know how tall the tower is and where the instrument was situated.

Response: The height of tower and location of the PTR-TOF-MS were added in the methodology section. The following statements were added:

The PTR-ToF-MS was located in a climate-controlled cabin shed at the base of the MOFLUX tower.

Ambient air was sampled from the MOFLUX tower with the height of 32 meters.

SC 5: L44: Not sure what is meant by “components”, consider rewording for clarity.

Response: The word component was replaced with **constituents**, which indicates traces gases that are influenced by warming of the atmosphere.

SC 6: L53: Current wording of this sentence is awkward. Consider rephrasing to, “One potential effect of overall atmospheric warming is the change in global wildfire frequency”

Response: Done. Thank you for the suggestion. The first sentence of 2nd paragraph now reads:

One potential effect of overall atmospheric warming is the change in global wildfire frequency.

SC 6: L55: Cite Juang et al., 2022 as a reference to enhancements in wildfire and soil moisture/aridity: <https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2021GL097131>

Response: Done. Juang et al., 2022 was referenced in the discussion soil moisture evaporation.

SC 7: L63/64: Do you have a reference that provides evidence of this? Please cite.

Response: The atmospheric process indicated in L63/64 were previously discussed in two studies, which are:

Juang, C.S., Williams, A.P., Abatzoglou, J.T., Balch, J.K., Hurteau, M.D., Moritz, M.A. (2022). **Rapid Growth of Large Forest Fires Drives the Exponential Response of Annual Forest-Fire Area to Aridity in the Western United States.** Geophysical Research Letters 49, e2021GL097131. <https://doi.org/https://doi.org/10.1029/2021GL097131>

Liu, T., Hong, Y., Li, M., Xu, L., Chen, J., Bian, Y., Yang, C., Dan, Y., Zhang, Y., Xue, L., Zhao, M., Huang, Z., Wang, H. (2022). **Atmospheric oxidation capacity and ozone pollution mechanism in a coastal city of southeastern China: analysis of a typical photochemical episode by an observation-based model.** Atmos. Chem. Phys. 22, 2173-2190. <https://doi.org/10.5194/acp-22-2173-2022>

SC 8: L66: Change to say, “the abundance of volatile organic compounds are expected...”

Response: We appreciate the suggestion; the statement now reads:

Among the chemical components of the atmosphere, the abundance of volatile organic compounds (VOCs) is expected to respond to extreme heat and wildfire emissions.

SC 9: L74-75: Can you specify what “future” refers to here, or provide a time frame? The cited study is nearly 20 years old now, so it would be useful in context.

Response: We added the years (2070-2099) used in the calculation of future emission scenario indicated in the study cited in the introduction section. The statement now reads:

For instance, a global estimate of isoprene emissions with temperature and land-cover drivers under future scenario (year: 2070-2099) was 889 Tg yr⁻¹.

SC 10: L109-110: Not sure what the significance is of including averages from January and July? Consider removing if not relevant

Response: We concur with reviewer that January data is not relevant in this section, however, we kept the average temperature of July since it overlaps with our period of measurement (i.e., June 25 to August 12). The new sentence is as follow:

Long-term measurements of meteorological parameters (1981–2010) at a nearby airport (~10 km) indicated that the average temperature for July was 25.2°C.

SC 11: L111: Specify if this is an annual average, and change units to cm.

Response: The precipitation value presented is annual average. The sentence was improved to better convey the information. The unit was changed to cm as well.

Typical precipitation (annual average: 108.2 cm) is fairly evenly distributed through the yearly cycle.

SC 12: L139: Specify what “calibrated regularly” means. How often and for how long? (e.g every 5 days for 20 minutes, daily for 20 minutes, etc).

Response: The mass spectrometer was calibrated every two weeks for 50 minutes. This information is now included in the methodology section.

The PTR-ToF-MS was calibrated regularly every two weeks for 50 minutes using a 110-ppb mixture of gases.

SC 13: L141: Are the mixing ratios for the entire mixture or for each compound?

Response: The standard gas supplier (Airgas) prepared a gas mixture with each compound at concentration of 110 ppb. The range of mixing ratios during the calibration also applies to every compound. The statement was modified to account the reviewer’s comment.

The linear calibration curve for each standard compound consisted of eleven data points, with mixing ratios ranging between 1.89 and 50.9 ppb.

SC 14: L141-142: It’s unclear what is meant by the sentence, “The same compounds were used to calculate the mixing ratio of other compounds using the transmission efficiency and first-order kinetic reaction.” Please elaborate or reference to a manuscript that explains the method further.

Response: PTR-ToF-MS can provide quantitative measurement of compounds without standard gas available using mass dependent transmission analysis. The conversion of raw signals (counts per second) to mixing ratio (ppb) of an uncalibrated gas VOC can be performed using the following equation:

$$[VOC, ppb] = \frac{1}{k\Delta t} \times \frac{I(VOC^+)}{T(VOC^+)} \times \frac{I(H_3O^+)}{T(H_3O^+)}$$

Where RH^+ is the protonated gas compound, k is the proton-transfer-reaction rate coefficient, Δt is the reaction time, $I(VOC^+)$ and $I(H_3O^+)$ are the measured ion count rates for the RH^+ and the hydronium ion (H_3O^+), respectively. $T(VOC^+)$ and $T(H_3O^+)$ are the transmission efficiencies for RH^+ and H_3O^+ ions, respectively (Worton et al., 2023; Taipale et al., 2008). All the values are readily available except for transmission efficiency value, which can be determined by generating a mass dependent transmission curve from compounds with known concentrations and reaction rate. The transmission is an instrument-specific parameter that depends on the transmission efficiencies of the lens system/ion guide, the mass filter (TOF), and the ion detector. Transmission Tool provided by the instrument developer (IONICON) was used to generate the transmission efficiencies of gas standards.

The following statements regarding the conversion of raw signals to mixing ratio were added to the Methods section:

PTR-ToF-MS can provide quantitative measurement of compounds without standard gas available using mass dependent transmission analysis. The conversion of raw signals (counts per second) to mixing ratio (ppb) of an uncalibrated gas R can be performed using the following equation

$$[VOC, ppb] = \frac{1}{k\Delta t} \times \frac{I(VOC^+)}{T(VOC^+)} \times \frac{I(H_3O^+)}{T(H_3O^+)}$$

Where RH^+ is the protonated gas compound, k is the proton-transfer-reaction rate coefficient, Δt is the reaction time, $I(VOC^+)$ and $I(H_3O^+)$ are the measured ion count rates for the RH^+ and the hydronium ion (H_3O^+), respectively. $T(VOC^+)$ and $T(H_3O^+)$ are the transmission efficiencies for RH^+ and H_3O^+ ions, respectively (Worton et al., 2023; Taipale et al., 2008). All the values are readily available except for transmission efficiency value, which can be determined by generating a mass dependent transmission curve from compounds with known concentrations and reaction rate. The transmission is an instrument-specific parameter that depends on the transmission efficiencies of the lens system/ion guide, the mass filter (TOF), and the ion detector. Transmission Tool provided by the instrument developer (IONICON) was used to generate the transmission efficiencies of gas standards.

SC 15: L150-152: How tall was the tower? How long was the measurement sample line or inlet? Was a filter applied for particles?

Response: Ambient air was sampled from the MOFLUX tower with the height of 32 meters. The air was drawn at the top of the tower using a 65-meter overall length with ½ in. OD PFA tube. A Teflon filter with 47 mm diameter was attached to inlet to prevent particles from entering the sampling line. All of this information was added to the recent version of the manuscript.

Ambient air was sampled from the MOFLUX tower with the height of 32 meters. The air was drawn at the top of the tower using a 65-meter overall length with ½ in. OD PFA tube (McMaster-Carr) and a GAST compressor/vacuum pump with a mass flow controller (Alicat Scientific, Inc) set at 20 L min⁻¹. A Teflon filter with 47 mm diameter was attached to inlet to prevent particles from entering the sampling line.

SC 16: Figure 2: Please specify the time resolution of the averaged data. Is this hourly, daily, etc? It would be useful to also have some estimate of error or variability on the graphs of diurnal cycles.

Response: The VOC data were collected with a 100-millisecond time resolution and averaged into hourly data for processing and reporting. This statement has been added to the manuscript. Moreover, the authors added error bars, represented by standard error, to graphs in Figure 2.

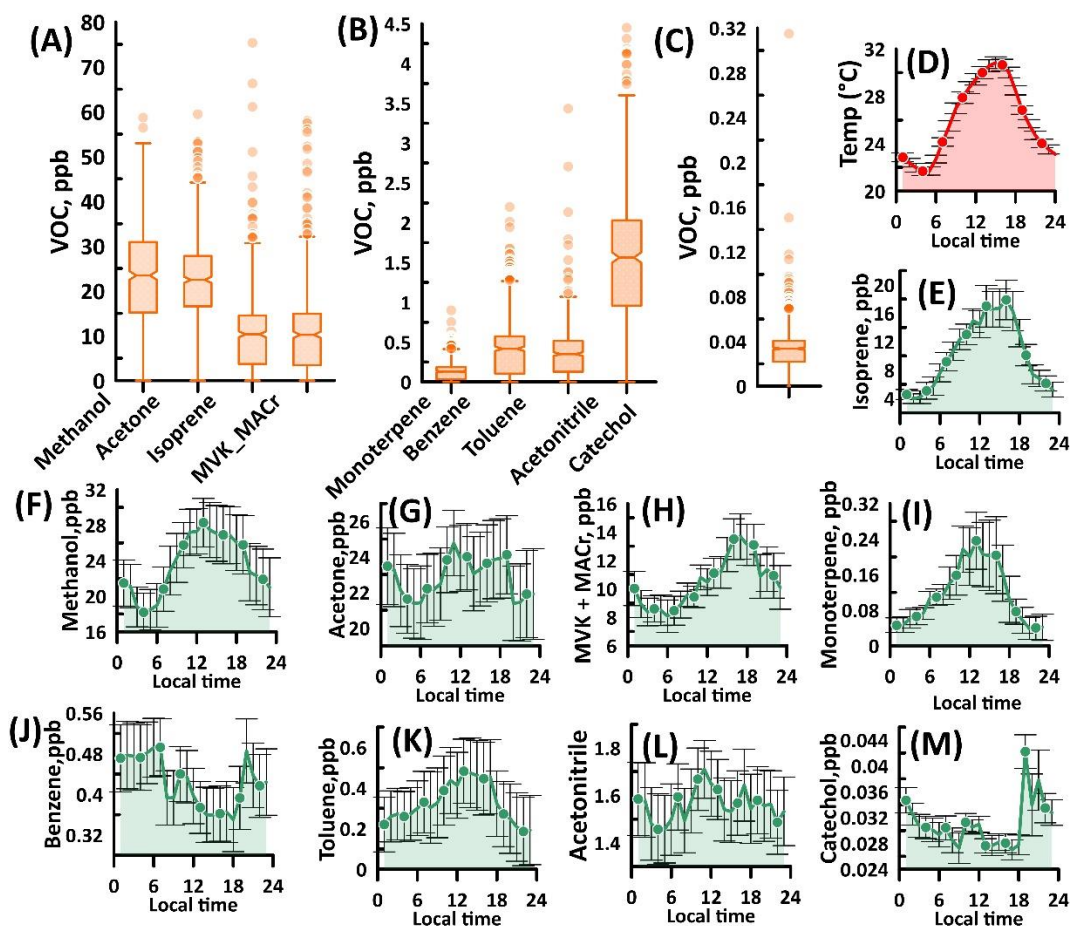


Figure 2. (A-C) Average mixing ratio in ppb and (E-M) average diurnal profile of major VOCs at MOFLUX. Also included here is the diurnal profile of (D) temperature for reference. Time reported here is the local daylight time. The center lines of the box and whisker plots are the mean mixing ratio. Box edges are quartiles, and lower (upper) corresponds to 25th (75th). Whiskers represent 1.5 times the interquartile range. Symbols outside the box plot are outliers. Diurnal profiles have a unit of ppb mixing ratio. MVK and MACr are methyl vinyl ketone and methacrolein. The error bars are represented by standard error.

SC 17: L190: How many is several? Define.

Response: The number of VOCs (n=275) was added in the text.

Many VOCs (n = 275) were detected in the ambient air throughout the three-month measurement period

SC 18: L206: What is BB? Don't think the abbreviation has been defined yet.

Response: We thank the reviewer for noticing this error. We have defined BB in this section of the manuscript

Besides the photochemical oxidation of isoprene, MVK and MACr have other sources, such as Biomass Burning (BB) and gasoline vehicular emissions.

SC 19: L236: It's unclear if the particle diameter is supposed to be greater than or less than 50 nm.

Response: This error was corrected by adding the appropriate mathematical sign in the text.

Relatively large particles (i.e., particle diameter > 50 nm) were observed with no apparent aerosol growth.

SC 20: L264-267: While acetonitrile was more enhanced at this site during the BB event compared to other studies, it is not necessarily fair to say that the increase in acetonitrile alone 'highlights the severe impact of BB on atmospheric VOC distribution and reactivity.' It would instead be more appropriate to change the language to "implying the severe impact of BB..." or even better, providing a metric to confirm this. One idea is to compare the estimate average OH reactivity (O_{Hr}) of the measured VOC species during ambient times and compare it to the O_{Hr} during BB impacted times when acetonitrile is elevated. This would also help to strengthen the message of the manuscript.

Response: We concur with the reviewer regarding the addition of OH reactivity data, which provides supporting evidence to our claim about the impact of VOCs on the overall atmospheric reactivity in the temperate forest. To calculate the total OH reactivity (R) based on the measured concentration of VOCs, we used the following equation similar to a prior study (Wang et al., 2021):

$$R = \sum k_{VOC_i+OH}[VOC_i]$$

where [VOC_i] is the concentration of the volatile organic compounds measured by the PTR-ToF-MS and k_{VOC+OH} (cm³ molecule⁻¹ s⁻¹) is the rate constant of the reaction between the OH and VOC. The rate constants were obtained from the National Institute of Standards and Technology (NIST) Chemical Kinetics Database which compiles kinetics data on gas phase reactions (<https://kinetics.nist.gov/kinetics/>). All molecular formulas identified from more than 250 ions were subjected to Reaction Database Quick Search Form. The calculation of the reaction constant accounted for the hourly temperature conditions measured during the field campaign. Only records with temperature range (20-36 °C) similar to the observed conditions in the temperate forest were considered in the calculation. The kinetic search procedure yielded 428 record matches for 82 ions. The median value of rate constants was used for molecular formulas with multiple records.

The authors added the following statement in the methodology and results and discussion section of the revised manuscript.

The total calculated OH reactivity (R) was obtained from the measured concentration of the VOCs using the following equation similar to a prior study (Wang et al., 2021):

$$R = \sum k_{VOC_i+OH}[VOC_i]$$

where [VOC_i] is the concentration of the volatile organic compounds measured by the PTR-ToF-MS and k_{VOC+OH} (cm³ molecule⁻¹ s⁻¹) are the rate constant of the reaction between the OH and VOC. The rate constants were obtained from the National Institute

of Standards and Technology (NIST) Chemical Kinetics Database which compiled kinetics data on gas phase reactions (<https://kinetics.nist.gov/kinetics/>). All molecular formulas identified from more than 250 ions were subjected to Reaction Database Quick Search Form. The calculation of the reaction constant accounted the hourly temperature conditions measured during the field campaign. Only records with temperature range (20–36 °C) similar to the observed conditions in the temperate forest were considered in the calculation. The median value of rate constants was used for molecular formulas with multiple records.

We also rephrased the statement in focus to the suggested wording by the reviewer.

Such values are beyond the mixing ratio range (0.047 to 1.08 ppb) of acetonitrile recorded in Asian, US, and European regions (Huangfu et al., 2021), implying the severe impact of BB.

SC 21: L268-272: Is it possible to estimate an age of the BB event using a back trajectory or the abundance of compounds? For instance, furan containing species are often associated with fresh combustion and can be used to estimate smoke age. This would help to contextualize the compounds reported here.

Response: Due to the sporadic nature of the biomass burning events observed during the field campaign, we were unable to estimate the age of the combustion plumes that arrived at our sites.

SC 22: L274: Instead of saying “During some parts” it would be useful to have a quantitative measure (e.g number of days/hours). You could reference the supplemental histogram here.

Response: The number of hours when the temperature exceeded over 32 °C occurred more than 100 times during the measurement in the temperate forest. This was mentioned in the following statement in the revised text.

*The extreme temperature, defined by an hourly mean temperature exceeded 32 °C, was based on the projected climate scenarios that temperature will increase by 2–4 °C by 2100 (Collins et al., 2013). The extreme temperature occurred for **more than 100 hours** (see Figure S1 for histogram). The strong impact of the elevated temperature in the region ultimately altered the vegetation’s physiological functions*

SC 23: Figure 3: Error bars should be added to the bar charts. It’s unclear why a linear regression was used to fit the correlation between isoprene and temperature when the relationship is known to be exponentially related. This needs to be corrected. Equations should be added to the correlation analysis figures and errors. Units are needed on the y axis. For linear regression, consider orthogonal regression over linear regression, as orthogonal distance regression takes into account error in both the x and y axis.

Response: The authors agree with the reviewer. The bar charts now include error bars, which represents the calculated standard errors. The major flaw of the manuscript regarding the linear relationship between isoprene and temperature has been corrected by the fitting exponential curve instead. Additionally, the statistical merits of the fitting, which include the equation of the line and correlation coefficient (r), are provided in Figure 3. The authors have retained the linear regression fitting for benzene. The caption of Figure 3 has been updated to reflect the changes in the figure.

The new Figure 3 and the corresponding caption are as follow:

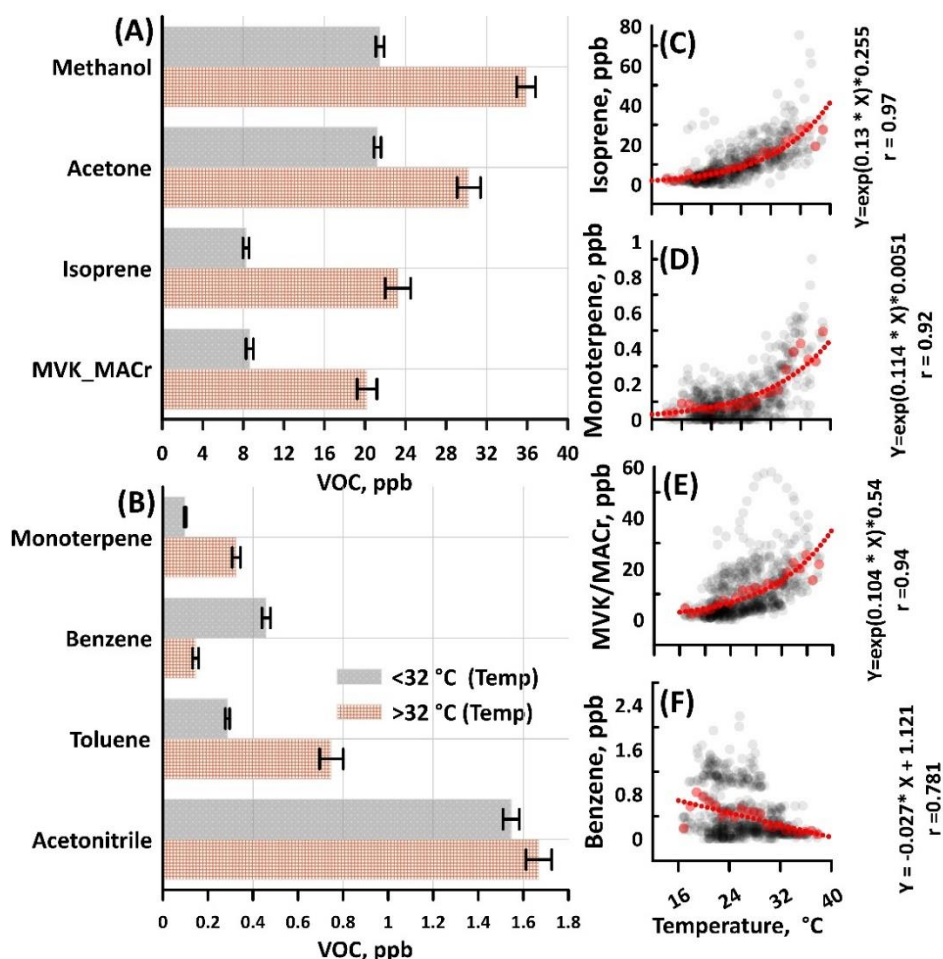


Figure 3. (A-B) Comparison of VOC mixing ratios for temperatures below and above 32°C. Catechol, not shown here, showed no evident difference between the two conditions (~30 ppt). The error bars in the bar chart are represented by standard error. (C-F) The correlation analysis of temperature with biogenic VOCs and benzene mixing ratios (in ppb). Correlation analysis of other major VOCs is provided in the supplement. Black symbols are the hourly data, whereas the red lines indicate the best-fit line of the binned mixing ratio of VOCs according to 1.0°C of temperature. The equation of the exponential fit line and correlation coefficients are given on the right side of the plot.

SC 24: L290-L291: It is inappropriate to use a linear regression for isoprene and temperature. The relationship is known to be exponential. There several papers in the literature that show this. (Guenther et al., 1993, 2006; Rasulov et al., 2010; Hu et al., 2015; Selimovic et al., 2022; etc).

Response: We apologize for the error of using linear regression between temperature and isoprene, thank you kindly for pointing this out. The statements in this paragraph were updated to reflect the evident exponential relationship between temperature and the BVOCs.

The major BVOCs, isoprene and monoterpene, responded well to variations in temperature, as shown in Figure 3. Under extreme temperatures, 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 25: L292: It's simpler to just say "was three time higher than conditions..."

Response: Done. Statement was revised accordingly.

SC 26: L293-297: See my earlier comments about which fit to apply for monoterpenes. Also the authors state, "the tenfold increase ... had several implications for the distribution and chemical reactivity in the forest," but then provide no evidence or metric for reactivity to support this. An estimate of the change to reactive organic carbon (ROC) or OHr as a result of the increase would support this statement.

Response: The authors calculated the changes in OH reactivity due to enhancement of isoprene and monoterpene at elevated temperature conditions. We added the following statement

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.

SC 27: L300-301: Why? What is the significance of calculating this ratio? The wording could be changed.

Response: A comprehensive plant chamber analysis indicated that the suppression of new particle formation was dependent on the ratio of isoprene carbon to monoterpene carbon (Kiendler-Scharr et al., 2009). This impacts the aerosol formation events in the temperate forest. However, due to limited information and supporting data to explain our statements at L300-303, the authors have completely removed the aforementioned statements and the corresponding plot in the supplementary information.

SC 28: L302-L303: This statement lacks specificity. What values needs to be exceeded in which aerosol formation is suppressed? What is the optimum temperature? Why is it interesting or relevant that this occurs?

Response: See our response to the prior comment.

SC 29: L307-L311: What is the enhancement range in values for the temperature increase reported here? Would be useful to report so that a direct comparison can be made to previous literature.

Response: In the main text, the authors indicated that the measured MVK/MACr during the enhanced temperature conditions doubled compared at low temperatures. To explicitly highlight the impact of temperature on the concentration of MVK/MACR, the following statement was added to the main text.

As shown in Figure 3, the concentration of MVK/MACr doubled during extreme temperature conditions compared at low temperatures.

SC 30: L306-L314: Can you report the ratio of isoprene to MACr+MVK during “low” temperatures and elevated temperature? This would provide an assessment of the lifetime and a metric for how oxidation changes between the two events. It would also be useful to compare during BB and non-BB events. See Hu et al., 2015, and Selimovic et al., 2022 for a discussion of this metric.

Response: We calculated the ratio of isoprene to monoterpene to assess the impact of degree of oxidation of isoprene to its primary oxidation products. During elevated temperature conditions ($>32\text{ }^{\circ}\text{C}$), the average ratio was 1.21, while the value increased under low temperatures conditions ($<32\text{ }^{\circ}\text{C}$, 1.27). Both values suggest transport time shorter than one isoprene lifetime, as indicated in previous studies (Selimovic et al., 2022; Hu et al., 2015). However, the higher values recorded at low temperatures are in stark contrast to the expected trend of decreasing ratio due to enhancement of MVK/MACr production from isoprene. As a result, the following statements were removed from the manuscript

Moreover, several of the reaction mechanisms during the oxidation of isoprene are temperature dependent (e.g., 1,6- and 1,5-H shift isomerization reactions of isoprene), which further augmented the formation of the first-generation products of isoprene (Navarro et al., 2013).

Instead, the elevated concentration of the primary oxidation products was primarily attributed to enhancement of concentration of isoprene. The following statements were added in the manuscript.

The ratio between isoprene and MACr + MVK indicates the lifetime of the isoprene and degree of oxidation of isoprene to MVK and MACr. At elevated temperature ($>32\text{ }^{\circ}\text{C}$), the average ratio was 1.21 while it increased at low temperatures ($<32\text{ }^{\circ}\text{C}$, 1.27) conditions. Both values suggest transport time shorter than one isoprene lifetime, as indicated in the previous studies (Selimovic et al., 2022; Hu et al., 2015). However, the higher values recorded at low temperatures are in stark contrast to expected trend, where the ratio should decrease due to enhanced production of MVK/MACr from isoprene. The elevated concentration of the primary oxidation products was primarily attributed to enhancement of concentration of isoprene.

SC 31: L319: AVOCs has not been previously defined.

Response: Anthropogenic VOCs (AVOCs) was already defined in the introduction section (L91)

SC 32: L319-320: It's not clear why a negative correlation between colder nighttime temperatures and AVOC would exist, especially when in the previous sentence the authors seem to imply the opposite is true, and that AVOCs are enhanced when the boundary layer is reduced (presumably at colder temperatures)?

Response: We recognize that the statements were confusing and do not have supporting information. Thus, the said texts were removed from the main text.

SC 33: L32gr1-322: I see no direct evidence to confirm this is due to higher temperature. A plot would be useful.

Response: Our apologies for the confusion. We meant to clarify that mass 93 is a fragment of monoterpene. We have improved the text and added a correlation plot between monoterpene and mass 93 in the supplement.

This result further supports our initial claim that the compound occurring at mass 93 originates from the fragmentation of monoterpene. The correlation plot in the supplement shows a direct relationship between the two compounds.

The following graph was also added to the supplement:

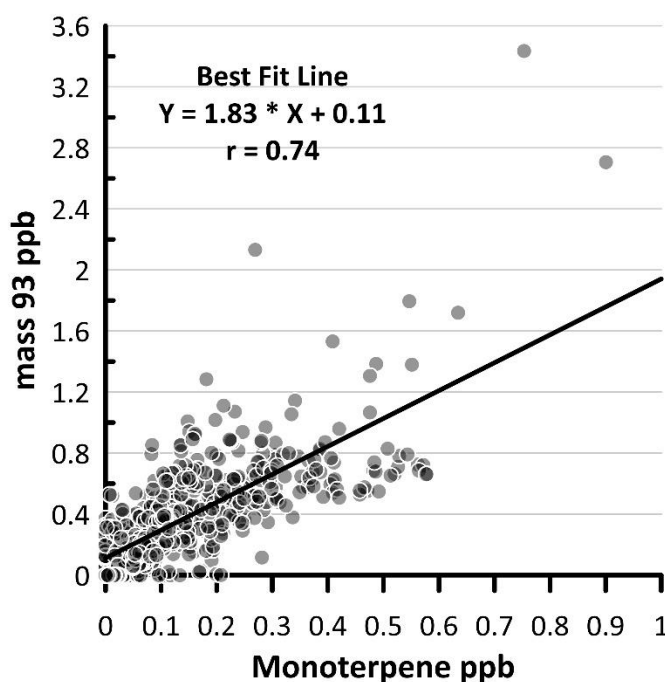


Fig S4: Correlation plot of mass 93 and monoterpene at mass 137.

SC 34: L327-328: This needs to be reworked on the basis of extensive literature historically showing exponential relationships with temperature.

Response: Agree. The new statement is as follow:

On the other hand, BVOCs such as isoprene, MVK+MACr, and monoterpene showed exponential relationship with temperature but at varying rates.

SC 35: L328-L332. It would be useful to know what VOC compounds the literature refers to here and whether or not they were also measured in the results reported in this manuscript.

Response: Agreed. We indicated in the main text the specific VOCs investigated in the oxidation of the mixed precursor system performed in previous studies.

Recent laboratory chamber studies have shown that unexpected interaction of individual VOCs (e.g., isoprene, monoterpene, toluene, xylene, and trimethylbenzene) during the oxidation process produced intermediates and products that impacted the yields, volatility, and other physiochemical properties of aerosols (Voliotis et al., 2021; Takeuchi et al., 2022; Chen et al., 2022).

SC 36: L335: Do you have a reference for this?

Response: We were unable to find a literature that can support our statements regarding the integration of cross-reaction of precursors in regional and climate models. Thank you for pointing this out and we have removed these statements.

SC 37: Some of the information in Section 3.3 would be better introduced prior to discussion of BB impacts in Section 3.1 and 3.2. Earlier introduction would help to provide context.

Response: We understand the reviewer's concern regarding the proper introduction of biomass burning events and transport observed at our site. However, rather than relocating the introductory statements from section 3.3 to earlier paragraphs, we opted to compile all discussion related to biomass burning tracers in section 3.3 to enhance the readability of our manuscript. The following statements have been moved to section 3.3.

At MOFLUX, typical gas phase BB tracers were observed in substantial amounts. Acetonitrile, one of the prominent BB markers (Huangfu et al., 2021), had mean and maximum mixing ratios of 1.56 ppb and 4.45 ppb, respectively. Such values are beyond the mixing ratio range (0.047 to 1.08 ppb) of acetonitrile recorded in Asian, US, and European regions (Huangfu et al., 2021), implying the severe impact of BB. Acetonitrile did not follow a typical daily cycle, which is consistent with the sporadic nature of the emissions from a distant source and subsequent transport. Another prominent BB marker measured at the site was catechol, an aromatic compound directly emitted from combustion processes. At MOFLUX, catechol had a mean level of 30 ppt but increased significantly to 300 ppt on some days. Catechol had a minor peak during the daytime, which can be attributed to the photochemical processing of phenol (Finewax et al., 2018), another aromatic VOC emitted during BB events. Moreover, acetonitrile ($r = 0.53$) and catechol ($r = 0.017$) also did not follow the trend of temperature, which is consistent with the infrequent emissions of BB plumes.

SC 38: L343-L345: Specificity on how wildfire smoke pollution periods were determined and separated would be beneficial. Were there times when both temperature was high >32 and BB was present? If so, how did the authors handle these in their comparisons?

Response: Wildfire plume transports were estimated using the NOAA's High-Resolution Rapid Refresh (HRRR) model at 3-km resolution, which generates the weather forecast for the entire continental US. The HRRR-Smoke model is based on single smoke tracer, plume rise parametrization, and satellite fire radiative power processing (Chow et al., 2022). Considering the intensive period between July 8 to 17 (see figure 5), there's limited overlap between the two extreme events. This made the delineation of response of the VOCs to elevated temperature and transport of combustion plume easier.

To provide further clarity regarding the estimation of Smoke, the following statements were added to the Methods section:

Smoke concentrations (in mg m^{-3}) were estimated from the High-Resolution Rapid Refresh (HRRR) 3 -km weather model for Missouri at 6-hour intervals for the duration of the VOC data measurement period. The HRRR model generates weather forecast for the entire continental US. The Smoke model is based on single smoke tracer, plume rise parametrization, and satellite fire radiative power processing (Chow et al., 2022).

SC 39: L345: What defines stronger enhancement between the two? Can you provide some metric (e.g PM2.5, acetonitrile mixing ratios, etc?)

Response: The enhancement was based on the estimated Smoke concentrations shown in Figure 4, which revealed substantial concentrations between July 15-18 (~180 mg m⁻³) compared to the observation between June 25 to July 1.

SC 40: L348-L351: How old is the air mass based on these trajectories? How long are the trajectories? What inventory was used? What is the resolution? What heights were the runs initialized at?

Response: The backward trajectories were calculated based on single trajectory, 500 m above ground level height, 24-hour duration and model vertical velocity as the motion calculation method. The meteorology used for the calculation was based on 1-degree Global Data Assimilation System (GDAS1).

This information was added in the methods section.

Backward air mass trajectories estimation was performed using was calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) Model (Stein et al., 2015). The backward trajectories were calculated based on single trajectory, 500 m above ground level height, 24-hour duration and model vertical velocity as the motion calculation method. The meteorology used for the calculation was based on 1-degree Global Data Assimilation System (GDAS1).

SC 41: Figure 4: What is “smoke” in the figure? Is this a combination of VOCs? Is this PM2.5? There is no definition for what is included in the smoke measurement.

Response: Please see our response to SC 38 regarding the estimation of Smoke parameter.

SC 42: L360-363: How many non-BB days were compared? How were non-BB days defined? Did non-BB days include extreme temperature events? If so, how was this separated?

Response: The figure was based on the recorded values during July 16, when a strong combustion plume was observed, and July 12 with no low concentration of smoke. As shown in Figure 5, the two extreme events did not overlap during these days.

SC 43: L363-L364: Not sure how the authors came to this conclusion?

Response: Prior to July 15, the typical concentration of benzene was around 0.4 ppb, which was accounted to automobile emissions. Between July 15 to July 17, benzene concentrations followed the variability of the estimated Smoke (see figure S), indicating the impact of transported combustion plume on benzene levels. The following statement was added in Section 3.3

The major source of benzene shifted from vehicular emissions to BB, highlighting the diverse anthropogenic activities influencing the variability of benzene at the temperate forest, as shown in the time series profile of benzene and Smoke (see Figure S in supplement)

The time series profile of benzene and smoke between July 8 to 17 was also added in the supplement.

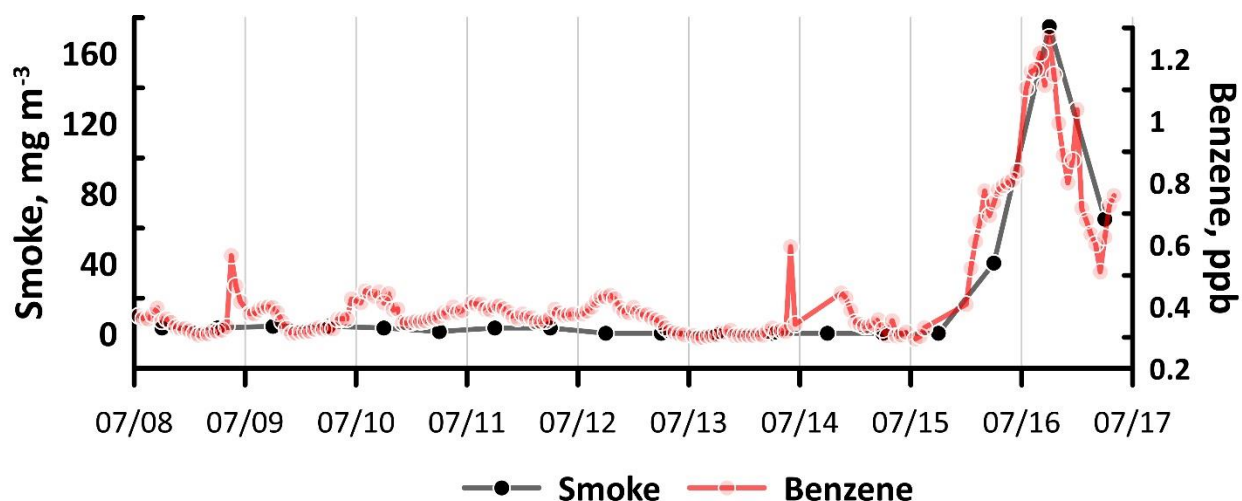


Figure S: The time series profile of benzene and smoke between July 8 to 17

SC 44: L366-L368: This seems to be only for one day? Can you expand this analysis for the observation period to strengthen your results? This is also only benzene and ozone, so it's not fair to say that this one measurement is evidence of change to the overall chemical reactivity in the forest. On this note, it would be beneficial to have a measure of the regional applicability based on landscape and emission sources. Further, transported smoke plumes can also reduce the amount of sunlight getting to vegetation, impacting photolysis and potentially altering emissions of BVOC (notably isoprene) due to light and temperature reduction. This is an important consideration in the context of changing BVOC profiles due to changes in environmental factors. Based on Figure 5 it looks like the peak of smoke occurred during an extreme temperature event. Given the known relationship between ozone and temperature, how were the authors able to separate increases in ozone due to temperature versus the increase due to enhancements in VOC and BVOC precursors (e.g isoprene?)

Response: The statements regarding the increase of ozone formation potential of benzene was removed in the revised manuscript based on the suggestion of the other reviewer. The reviewer indicated that the benzene is not a key factor for ozone formation in a temperate forest, where biogenic VOCs such as isoprene are more abundant.

We agree with the reviewer that the transported plume can modify the incoming radiation that can influence the emissions of BVOCs. However, we don't have the necessary supporting data to assess the changes in solar radiation due to transported biomass burning plume and the subsequent alteration of the variability of BVOCs.

The separation of the impact of elevated temperature and biomass burning was explained in-detail in our response to specific comment (SC) 50. Briefly, the influence of enhanced temperature was evident between July 8 at 1:00 to 15 at 6:00 while the contribution of combustion processes attributed primarily for the measurements between July 15 at 7:00 to July 17 at 20:00. The BB period only recorded one hour of extreme temperature conditions (>32°C), which was excluded during the calculations.

SC 45: An expansion of Section 3.4 to include references to previous literature would be beneficial in contextualizing the results. As it is currently written it's unclear what the significance

of the reported results is. Previous studies (Brito et al., 2014) have utilized the O:C and H:C ratios as a marker for aging and to characterize organic aerosol.

Response: Done. We referenced a prior study that showcased the variability of O:C during the transport of combustion plume.

This is consistent with a prior study that reported low O:C ratio (0.25) during intense biomass burning plume compared during the measurement period when smoke became diluted and impact of biogenic emission enhanced (O:C =0.7) (Brito et al., 2014).

SC 46: L396-397: It seems disadvantageous to exclude these compounds from the analysis, considering their global abundance and the importance that was placed on them in the earlier part of the manuscript

Response: We completely agree with the reviewer regarding the atmospheric significance of the acetone, isoprene, and MVK + MACr. However, integrating these VOCs to the multivariate analysis skews the results of the factorization methodology, which limits the contribution of the other VOCs with substantially lower concentrations.

SC 47: L397-L398: Is that the average VOC mixing ratio excluding those compounds? What is the standard deviation in the average VOC mixing ratio?

Response: The calculated average concentration of VOCs, including isoprene, acetone, and MVK + MACr is 97.8 ppb with standard deviation of 45.5 ppb. The three major VOCs contribute more than 35% of the total VOC concentration, which skews and impacts the matrix factorization analysis. The standard deviation of the average mixing ratio without acetone, isoprene and MVK + MACr is 31.5. This information was added in the main text.

During this period, the average VOC mixing ratio was 78 ppb with standard deviation of 31.5

SC 48a: L401-L402: This conclusion is fundamentally incorrect. VOCs become more oxygenated as they are aged away from the biomass burning source. The oxidation of VOCs is what produces ozone and secondary organic aerosol. Multiple studies show this. The more likely explanation for a decrease in the O:C ratio is the increase in reactive organic carbon as a result of enhancements in VOC abundance due to BB and BB aerosol, which is overwhelmingly organic in nature. Additionally, the higher temperatures noted during the smoke period likely induce gas-particle partitioning of transported BB aerosol, particularly VOC and IVOC compounds (classified in the manuscript) further contributing to a decrease in the O:C ratio.

Response: The authors agree. The statements were modified based on the suggestion of the reviewer. The new statement now reads:

However, the apparent transport of the combustion plume to the site decreased the ratio to less than 0.3 due to increase of reactive organic carbon.

SC 48b: L401-L402 Additionally, the higher temperatures noted during the smoke period likely induce gas-particle partitioning of transported BB aerosol, particularly VOC and IVOC compounds (classified in the manuscript) further contributing to a decrease in the O:C ratio

Response: We believe that the change in O:C ratio was primarily due to biomass burning as temperature during transport of the combustion plume on July 16 did not exceed the criterion set for extreme temperature conditions.

SC 49: Figure 6: It would be more useful to plot the VOC types as a fraction of the total, to assess the distribution and how it changes, rather than the total abundance. Does the analysis presented in Figure 6 exclude the compounds previously mentioned?

Response: The authors concur. The time series of the percent contribution of each VOC class was added in the supplement. Moreover, the analysis of the presented in Figure 6 excluded the concentration of isoprene, monoterpene, and MVK + MACr.

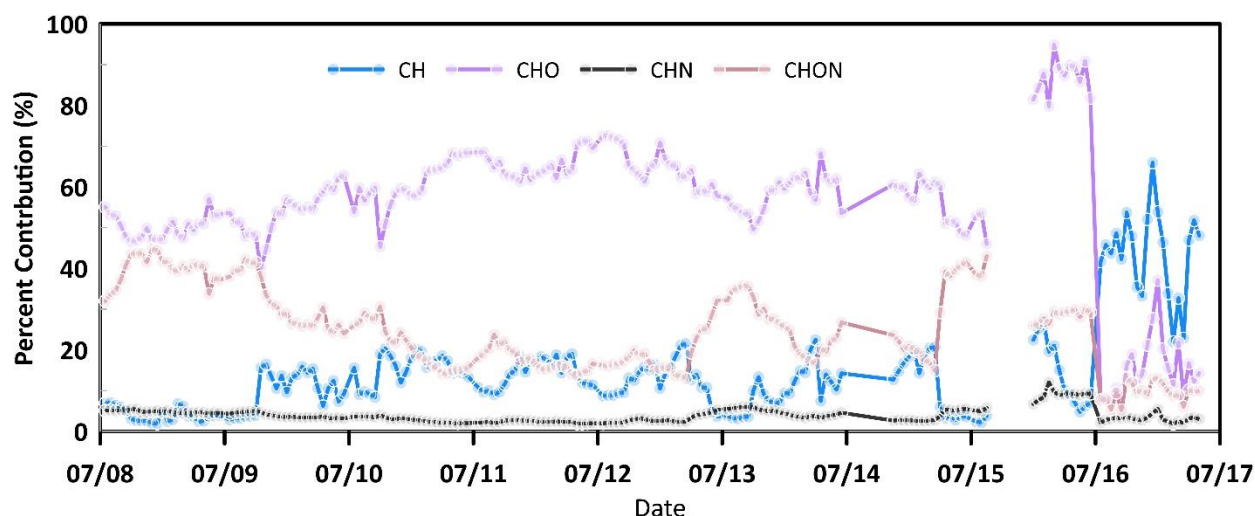


Figure S7: Time series profile of percent contribution of each VOC class to total concentration during the intensive observation period with enhanced temperature and combustion plume transport at MOFLUX. $C_xH_yO_wS_v$ compounds were not included due to low mixing ratio compared to other categories.

SC 50: L421-L423: The change in distribution in the extended list alone does not validate the substantial influence of temperature and BB on the overall chemical reactivity. A more appropriate measure of reactivity would be to calculate how the distribution of total reactive organic carbon (ROC) and OH reactivity (OHR) as a result of temperature and biomass burning influence.

Response: The authors agree with the reviewer and sincerely appreciate your feedback. Figure R2 presents the time series of calculated OH reactivity during the intensive period from July 8 to 17, which was influenced by extreme heat and combustion plumes. For reference, the time series of smoke and temperature are also included. Note that the calculation of reactivities included isoprene, acetone, and MVK+MACr.

During this period, the average OH reactivity was 91.30 s^{-1} , with notable contributions from isoprene, acetone, ethylamine, and ethenone. To assess the impact of elevated temperature and biomass burning on atmospheric reactivity, the data were categorized based on recorded ambient temperature and smoke concentration. The influence of biomass burning was evident from July 15 at 07:00 to July 17 at 20:00. Only one hour within this period had a temperature above 32°C , in which that data point was excluded from the average reactivity calculation.

Conversely, the effect of extreme temperatures was evaluated using data recorded from July 8 at 01:00 to July 15 at 06:00. Within this timeframe, 30 hours met the extreme temperature criteria, allowing an assessment of the potential impact of future warming on atmospheric reactivity.

The calculated OH reactivity for low and extreme temperatures was 98.92 s^{-1} and 106.37 s^{-1} , respectively, indicating that elevated temperatures enhanced atmospheric reactivity. Additionally, transported combustion plumes increased reactivity to 106.00 s^{-1} due to elevated concentrations of biomass burning tracers such as acetonitrile and benzene.

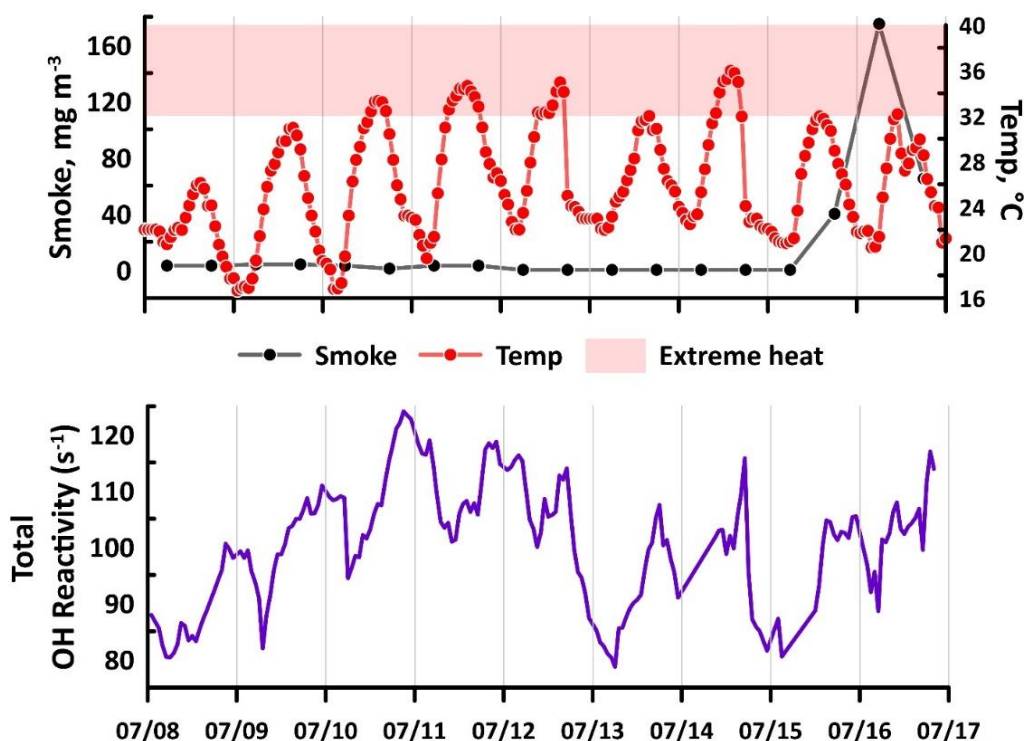


Figure R1. Time series profile total reactivity during the intensive operational period between July 8 to 17

The total reactivity plot was added in figure 5 and the following statements were added in section 3.4 to highlight the impact of extreme temperature conditions and transported plumes on reactivity.

Also in Figure 5 is the time series of the calculated OH reactivity during the intensive period influenced by extreme heat and combustion plumes between July 8 to 17. Note that the calculation of reactivities included isoprene, acetone, and MVK+MACr. During this period, the average OH reactivity was 91.30 s^{-1} , with notable contributions from isoprene, acetone, ethylamine, and ethenone. To assess the impact of elevated temperature and biomass burning on atmospheric reactivity, the data were categorized based on recorded ambient temperature and smoke concentration. The influence of biomass burning was evident from July 15 at 07:00 to July 17 at 20:00. Only one hour within this period had a temperature above 32°C , in which that data point was excluded from the average reactivity calculation. Conversely, the effect of extreme temperatures was evaluated using data recorded from July 8 at 01:00 to July 15 at 06:00. Within this

timeframe, 30 hours met the extreme temperature criteria, allowing an assessment of the potential impact of future warming on atmospheric reactivity. The calculated OH reactivity for low and extreme temperatures was 98.92 s^{-1} and 106.37 s^{-1} , respectively, indicating that elevated temperatures enhanced atmospheric reactivity. Additionally, transported combustion plumes increased reactivity to 106.00 s^{-1} due to elevated concentrations of biomass burning tracers such as acetonitrile and benzene.

SC 51: L426-L428: Many of the compounds listed here are tracers for (typically fresh <1 day old) wildfire emissions. That it increased with temperature is likely a result of concurrent “smoke” enhancements as well (evident in Figure 5). Given this fact it cannot be stated that they increased 100% a result of enhanced temperature conditions alone, especially given the concurrence of the two events.

Response: The statements were modified to reflect the possible impact of biomass burning in the enhancement of the compounds listed in these statements.

Besides the major compounds such as isoprene and monoterpene, VOCs such as formic acid (CH_2O_2), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$), isocyanic acid (HCNO), acrolein ($\text{C}_3\text{H}_4\text{O}$), furan ($\text{C}_4\text{H}_4\text{O}$), methylglyoxal ($\text{C}_3\text{H}_4\text{O}_2$), glycolic acid ($\text{C}_2\text{H}_4\text{O}_3$), and propanethiol ($\text{C}_3\text{H}_8\text{S}$) exhibited enhancement at the extreme temperature conditions, although it is equally possible that these compounds were also associated with transport of the combustion plumes.

SC 52: L488: This is presumably an average mixing ratio? Earlier the manuscript stated that isoprene reached a maximum of 75 ppb.

Response: *The value presented here is the average mixing ratio of isoprene. This was explicitly indicated in the new manuscript.*

Among the VOCs, isoprene had one of the highest recorded average mixing ratios (10 ppb), next to methanol (23 ppb) and acetone (22 ppb).

SC 53: L489-490: There are no measurements of light or photosynthetically active radiation to support this conclusion that temperature had a greater effect than UV.

Response: The statement was removed in the revised manuscript.

SC 54: L496-497: There is no metric (SOA formation potential, OHr, change to ROC) that supports this conclusion.

Response: Our new results regarding the chemical reactivity now supports this conclusion. However, no calculation of SOA formation potential was provided, thus it was removed from the statement. The new text now reads:

The varying enrichment of the major VOCs and their response to extreme temperatures influenced the atmospheric reactivity in the temperate forest.

SC 55: L497-498: It would be useful to know what VOCs these are and if there is overlap with the ones presented here.

Response: We agree with the reviewer. We added statements in this section regarding the VOCs studied during the oxidation of multiple coexisting VOC precursors.

For instance, the coexistence of isoprene and monoterpene led to reduced hydroxyl radical availability, leading to a limited oxidation process (McFiggans et al., 2019). The interactions of anthropogenic VOCs (AVOCs) such as toluene, xylene, and trimethylbenzene produced more secondary organic aerosols, but the addition of biogenic VOCs (BVOCs) reduced the yield through cross-reactions between the intermediates (Chen et al., 2022).

SC 56: L510: It's unclear why the authors all of a sudden switched to units of Kelvin? And what is smoke? How is it defined?

Response: Our apologies for the mistake. The temperature was converted to Celsius in the latest version of the manuscript. Smoke is defined earlier in this response.

The mixing ratios of which sum to as much as 78 ppb during a period with elevated temperature (>32 °C) and BB plumes (smoke > 100 mg m⁻³).

SC 57: L514-L515: There is no correlation analysis presented to support this conclusion.

Response: The statement regarding the formation of more unsaturated compounds due to enhanced temperature was disregarded in the revised manuscript.

SC 58: L518-L519: Some of these increases are likely associated with enhancement of wildfire emissions rather than temperature.

Response: The authors added the impact of the wildfire emissions on concentration of some VOCs in this statement.

The analysis of the entire spectra pinpointed an additional 40 compounds that have at least 100% enhancement in mixing ratio at extreme temperatures and/or during the transport of wildfire emissions.

SC 59: L525-527: This is likely broadly true but there is no evidence presented in the manuscript to support this conclusion. It would be useful to compare how the reactivity changes for each oxidant based on available kinetics data for the species measured.

Response: The total reactivity calculated during the intense biomass burning plume transport observed between July 15 to 17 increased the reactivity to 106.00 s⁻¹ compared at non-BB period (98.78 s⁻¹), based on our calculations in section 3.4. However, the calculation was only based on reaction with OH oxidant, thus NO₃ was removed from the statement. The statement now reads:

With the high reactivity of such compounds to OH radicals, it is expected that BB altered the normal forest-dominated atmospheric processes.

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