

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

Christian Mark Salvador et al.

We appreciate the referee's detailed review of our manuscript, and we provided here a detailed response that addresses the referee's concern. 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.

Response to Reviewer 1

Major Comment:

Thanks to the authors for their efforts in addressing my concerns as well as those raised by the other reviewer. The manuscript quality has improved following the authors' revisions, and many changes have been incorporated into the updated manuscript. However, there are still some remaining issues that need to be addressed.

Response: We thank the reviewer for the thoughtful feedback and for acknowledging the authors' efforts in revising the manuscript. The reviewers greatly contributed to enhancing the quality and clarity of our work. In this version of the manuscript, we have thoroughly addressed the remaining issues based on the reviewers' suggestions.

Comment 1: I think the current Introduction is quite scattered and lacks focus. The topic of this paper is the impact of heatwaves and wildfires on VOC concentrations. Because the measurement site is a rural temperate mixed forest, one focus of the paper is biogenic VOCs, and the other is wildfires. However, the authors did not clearly present what has already been investigated or identify the specific knowledge gaps their paper could address. For instance, BVOCs are temperature dependent, which is why understanding the impact of high temperatures on BVOCs is important. Additionally, two field campaigns focusing on BVOCs have previously been conducted at the MOFLUX site (Potosnak et al., 2014, and Seco et al., 2015). However, the authors did not include this background information in their Introduction. The same issue applies to their discussion of wildfires.

Response: We concur with the reviewer. The third paragraph of the introduction section was modified to offer an overview of volatile organic compounds (VOCs), their atmospheric reactivity, and response to future climate scenarios. The initial introduction also identified knowledge gaps, emphasizing the need to understand the influence of extreme temperatures and wildfires on VOC emissions. To explicitly highlight this scientific information and address these research questions, we have added several statements in the third paragraph. The new statements discuss the exponential dependence of biogenic VOCs (BVOCs) on temperature, the typical VOCs emitted during wildfire activities, and the subsequent impact of the enhanced concentration of these VOCs on atmospheric chemical reactivity. The new third paragraph 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. VOCs, particularly the unsaturated compounds, interact with oxidants such as hydroxyl (OH) and nitrate (NO₃) radicals, which subsequently create ozone and oxidized molecules (Hakola et al., 2012; Ramasamy et al., 2016; Spirig et al., 2004; Vermeuel et al., 2023). Further reaction products such as highly oxidized molecules also

participate in the formation of particles that subsequently act as cloud condensation nuclei (Chen et al., 2022; Hallquist et al., 2009). The emission and transformation of VOCs highly depend on environmental parameters such as temperature, relative humidity, and solar radiation. For instance, biogenic volatile organic compounds (BVOCs) exhibit an exponential temperature dependence, whereby an increase in temperature accelerates both their production and release from plant tissues. (Guenther et al., 1993; Rinnan et al., 2020). However, the degree of changes under future climate is still uncertain (i.e., suppression or enhancement) (Daussy and Staudt, 2020). A global estimate of isoprene emissions with temperature and land-cover drivers under future scenario (year: 2070-2099) was 889 Tg yr⁻¹, substantially higher compared to that expected using current climatological and land-cover conditions (522 Tg yr⁻¹) (Wiedinmyer et al., 2006). Moreover, CO₂, which is expected to rise in the future climate, can substantially decrease the emission of isoprene from vegetation (Lantz et al., 2019a). On the other hand, empirical results and modeling efforts suggest that future elevated temperatures could suppress the impact of CO₂ on isoprene emissions, thus increasing the uncertainty of future climate's influence on the emission of isoprene (Lantz et al., 2019b; Sahu et al., 2023). 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). During wildfire events, the combustion of vegetation and other biomass induce the pyrolysis of plant materials which ultimately release several VOCs during the process (Ciccioli et al., 2014). Typical VOCs emitted from wildfires include acrolein, acetonitrile, pyrrole, styrene, guaiacol, toluene, phenol, and catechol (Liang et al., 2022; Jin et al., 2023). 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). Beyond their health impacts, the emitted reactive carbon- and nitrogen-containing compounds can significantly alter several critical atmospheric processes, including ozone formation and particle formation events. However, the relative importance and contribution of VOCs from wildfire activities to atmospheric reactivity remain uncertain. A comprehensive understanding of the interactions between future abiotic factors and VOC emissions is essential for accurately predicting future air quality and climate scenarios.

The initial version of the manuscript included information regarding results from previous measurements at the MOFLUX site. Some of these statements were moved to the introduction section to provide more background information about the site. The fourth paragraph now reads:

The Ozark Plateau (Wiedinmyer et al., 2005), and this site in particular, is a known hotspot for emissions of BVOCs such as isoprene and monoterpene. Drought is a critical event at MOFLUX, as such environmental stress induced the highest ecosystem isoprene emission ever recorded for a temperate forest in 2011 (53.3 mg m⁻² h⁻¹) (Potosnak et al., 2014). Field measurement campaign in 2012 in MOFLUX reported isoprene reaching a maximum concentration of 28.9 ppbv, while monoterpenes peaked at 1.37 ppbv over half-hour intervals (Seco et al., 2015). Moreover, the site is about 5 km away from a major highway, thus anthropogenic VOCs (AVOCs) such as benzene and toluene from vehicle exhausts are expected to persist in the forest. Given these strong emitters of BVOCs and the evident transport of AVOCs into the forest, the study area proved to be a good test bed for measurement of the overall response of VOCs to abiotic stress in a way that simulates possible future atmospheric conditions.

Comment 2: I don't think the definition of an extreme temperature threshold as 32 °C is appropriate. A temperature of 32 °C is quite common. I understand that temperature conditions can vary significantly by

region. Typically, heatwave studies define thresholds using the 95th or 99th percentile of historical temperature records. Therefore, I suggest the authors use the 95th percentile of hourly July temperatures over the past 10 years as the threshold for defining heatwaves.

Response: We thank the reviewer for suggesting the use of heatwaves as a basis for defining extreme temperature, which provides strong complementary evidence for our initial definition. In our study, extreme temperature was defined as an hourly mean temperature exceeding 32 °C, which aligns with projected climate scenarios indicating a temperature increase of 2–4°C by 2100 (Collins et al., 2013). During the measurement period, the average temperature was 26°C; therefore, the defined extreme temperature is at least 5°C above the average temperature.

Heatwave events are defined as periods when the maximum daily temperature exceeds the 90th percentile calculated from a smoothed 15-day moving average (Perkins and Alexander, 2013; Perkins-Kirkpatrick and Gibson, 2017). To qualify as a heatwave, this occurrence must persist for three consecutive days. For our analysis, the calculated 90th percentile temperature for the month of July from 2015 to 2024 was 32°C, which was the same extreme temperature threshold defined for our case.

We added the following statement to substantiate our definition of extreme temperature.

The extreme temperature defined in this study aligns with the heatwave definition (Perkins and Alexander, 2013; Perkins-Kirkpatrick and Gibson, 2017), wherein the 90th percentile temperature for the month of July from 2015 to 2024 is 32°C.

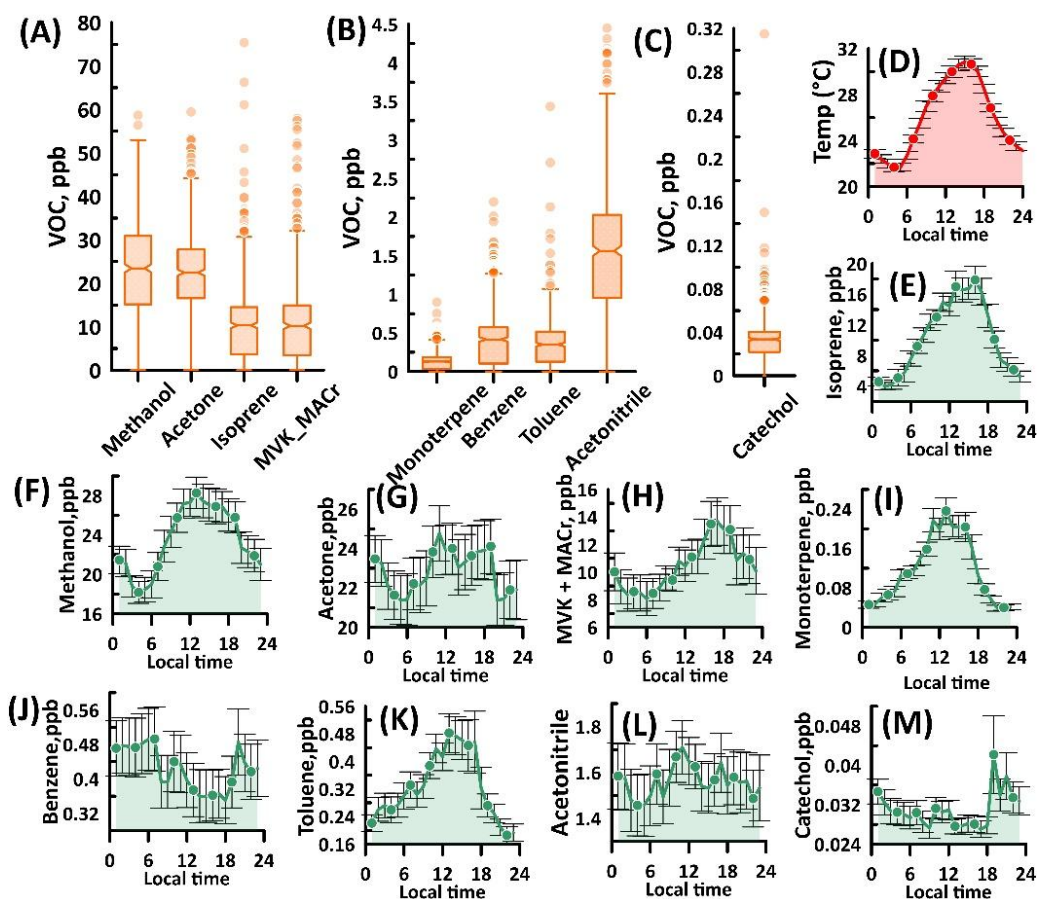
For reference, the 95th percentile of temperatures over the past 10 years is 33°C, which is near our established threshold for extreme temperature conditions (32°C). However, the authors chose to maintain the 32°C cut-off to remain consistent with our initial definition and classification of heatwaves.

Comment 3: The authors insisted that “Regions dominated by emissions of α -pinene, β -pinene, and limonene typically have a nighttime peak, whereas daytime enhancements are observed for areas with sabinene and ocimene.” I cannot agree with this statement. The diurnal cycles of monoterpenes largely depend on whether their emissions are light-dependent. De novo monoterpenes typically peak during the day because their emissions are driven by light emissions (Jardine et al., 2015). Only temperature-dependent monoterpenes consistently show nighttime peaks due to the lower boundary layer height at night. The monoterpenes mentioned by the authors can be either light-dependent or only temperature-dependent. For example, α -pinene emissions from Scots pine is light-dependent (Tarvainen et al., 2005). Furthermore, the paper (Borsdorf et al., 2023), which the authors cited in response to my comment, also mentioned that “The atmospheric concentrations of monoterpenes, which are emitted in a temperature dependent manner, are often greatest during nighttime hours due to the shrinking of the planetary boundary layer,” and also noted that “Sabinene is obviously emitted in a light-dependent manner comparable with isoprene, while all the other monoterpenes are emitted by volatilization.” Therefore, assigning diurnal emission patterns based on monoterpene isomer type is not appropriate, as each isomer may exhibit either emission pathway.

Response: After careful consideration, the authors have agreed to remove the statements regarding the designation of the monoterpene isomer based on the diurnal profile. We appreciate the reviewer for their insightful suggestion.

Comment 4: Figures 2 and 3 contain obvious errors. Figure 2 lacks a label for the first panel and has no axis labels for panel (C). In Figure 3, the standard deviations shown in the histogram plots appear too small compared to the actual distribution of data points displayed on the right side of the figure.

Response: Thank you for bringing the error to our attention. We have updated Figure 2 to include the missing labels. The error bars in Figure 3 represent the standard error, which accounts for the total number of observations. This is why the error bars are relatively small.



Comment 5: According to the NNMF results, does this imply that there is always a fire plume near the site? Lines 501–503 state: “oxygenated hydrocarbons ($C_xH_yO_w$) and $C_xH_yN_z$ compounds were persistent in the early hours of the combustion plume.” However, as the second reviewer mentioned, “VOCs become more oxygenated as they age away from the biomass burning source,” which does not support the statement made here.

Response: Figure 7 shows that the oxygenated biomass burning factor experienced a significant enhancement on July 16, which is why the authors initially argued that it was persistent in the early hours of the combustion plume. However, the concentration of oxygenated compounds resulting from the oxidation of hydrocarbons should indeed increase afterward, not prior. To avoid any confusion, the following statement was excluded in the latest version of the manuscript.

This is consistent with the analysis based on atomic content: oxygenated hydrocarbons ($C_xH_yO_w$) and $C_xH_yN_z$ compounds were persistent in the early hours of the combustion plume.

Specific comments:

Comment 1: Figure 1. The term “Global solar radiation” used here is incorrect; the authors should use “Downward solar radiation” instead. In addition, UV refers to ultraviolet radiation, which is a portion of the whole solar radiation spectrum. Based on the values provided (around 1000 W m^{-2}), I believe the authors are referring to total solar radiation rather than UV radiation, as such a high UV radiation level would not be survivable for any life forms. In addition, did author consider the smoke impact on BVOC emission during by affecting the solar radiation?

Response: The authors appreciate the reviewer's suggestion. The term "UV radiation" has been replaced with "downward solar radiation" throughout the manuscript. Additionally, the authors investigated the impact of smoke on solar radiation and how it subsequently modifies the concentration of biogenic volatile organic compounds (BVOCs). Figure R1 below displays the time series of solar radiation and smoke during the period of significant transport of combustion plumes. It is evident that solar radiation was not substantially affected by the combustion plumes.

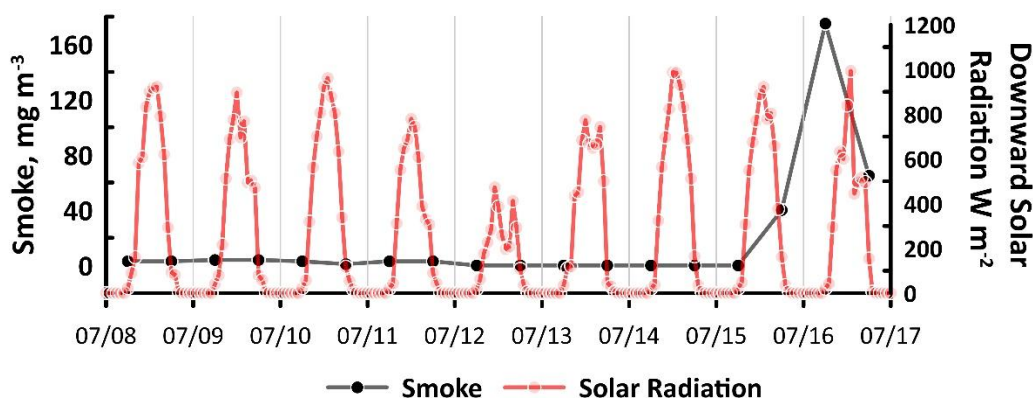


Figure R1. Time series profile of solar radiation and smoke during the period of evident transport of combustion plumes

Comment 2: Line 252: The word “global budget” is not accurate. Guenther et al. (2012) calculated the emission, which is just part of the “global budget”.

Response: The word “budget” was replaced with “emission”.

Comment 3 : Line 322: What kind of vegetation’s physiological functions?

Response: This statement is generally applicable to several physiological functions of plants; however, our results do not support this claim. Therefore, this sentence has been removed from the latest version of the manuscript.

Comment 4: Line 354: I think that biogenic VOCs are temperature dependent.

Response: The statement was corrected. The new text reads:

Anthropogenic tracers such as benzene and xylene did not show dependence on temperature, unlike some BVOCs.

References

- CICCIOLI, P., CENTRITTO, M., and LORETO, F.: Biogenic volatile organic compound emissions from vegetation fires, *Plant, Cell & Environment*, 37, 1810-1825, <https://doi.org/10.1111/pce.12336>, 2014.
- Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K., and Fall, R.: Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses, *J. Geophys. Res. Atmos.*, 98, 12609-12617, 1993.
- Jin, L., Permar, W., Selimovic, V., Ketcherside, D., Yokelson, R. J., Hornbrook, R. S., Apel, E. C., Ku, I. T., Collett Jr, J. L., Sullivan, A. P., Jaffe, D. A., Pierce, J. R., Fried, A., Coggon, M. M., Gkatzelis, G. I., Warneke, C., Fischer, E. V., and Hu, L.: Constraining emissions of volatile organic compounds from western US wildfires with WE-CAN and FIREX-AQ airborne observations, *Atmos. Chem. Phys.*, 23, 5969-5991, 10.5194/acp-23-5969-2023, 2023.
- Liang, Y., Stamatis, C., Fortner, E. C., Wernis, R. A., Van Rooy, P., Majluf, F., Yacovitch, T. I., Daube, C., Herndon, S. C., Kreisberg, N. M., Barsanti, K. C., and Goldstein, A. H.: Emissions of organic compounds from western US wildfires and their near-fire transformations, *Atmos. Chem. Phys.*, 22, 9877-9893, 10.5194/acp-22-9877-2022, 2022.
- Perkins-Kirkpatrick, S. E. and Gibson, P. B.: Changes in regional heatwave characteristics as a function of increasing global temperature, *Scientific Reports*, 7, 12256, 10.1038/s41598-017-12520-2, 2017.
- Perkins, S. E. and Alexander, L. V.: On the measurement of heat waves, *Journal of climate*, 26, 4500-4517, 2013.
- Rinnan, R., Iversen, L. L., Tang, J., Vedel-Petersen, I., Schollert, M., and Schurgers, G.: Separating direct and indirect effects of rising temperatures on biogenic volatile emissions in the Arctic, *Proc Natl Acad Sci U S A*, 117, 32476-32483, 10.1073/pnas.2008901117, 2020.

Response to Reviewer 2

General Summary:

The work presented here reports the change in mixing ratio and distribution of several biogenic and anthropogenic VOC measured in a forest, as a response to increased temperature and transported biomass burning plumes. The authors emphasize the variability of VOCs and associated reactivity due to heat and smoke. This study investigating how the VOC distribution changes in response extreme events is highly relevant, and the authors have done quite a bit of work to improve upon the analysis from initial submission. The appropriate temperature responses have been added, and a section on reactivity has been included to expand the discussion of VOC variability and reactivity under extreme conditions. There are some minor adjustments that need to be made, but overall the reviewer is pleased with the additions and corrections the authors have made to help improve the manuscript. I recommend publication of the manuscript, after these small issues (addressed below) are rectified or clarified.

Response: The authors would like to thank the reviewer for their kind words. We have revised the manuscript in accordance with the reviewer's recommendations.

Minor comments:

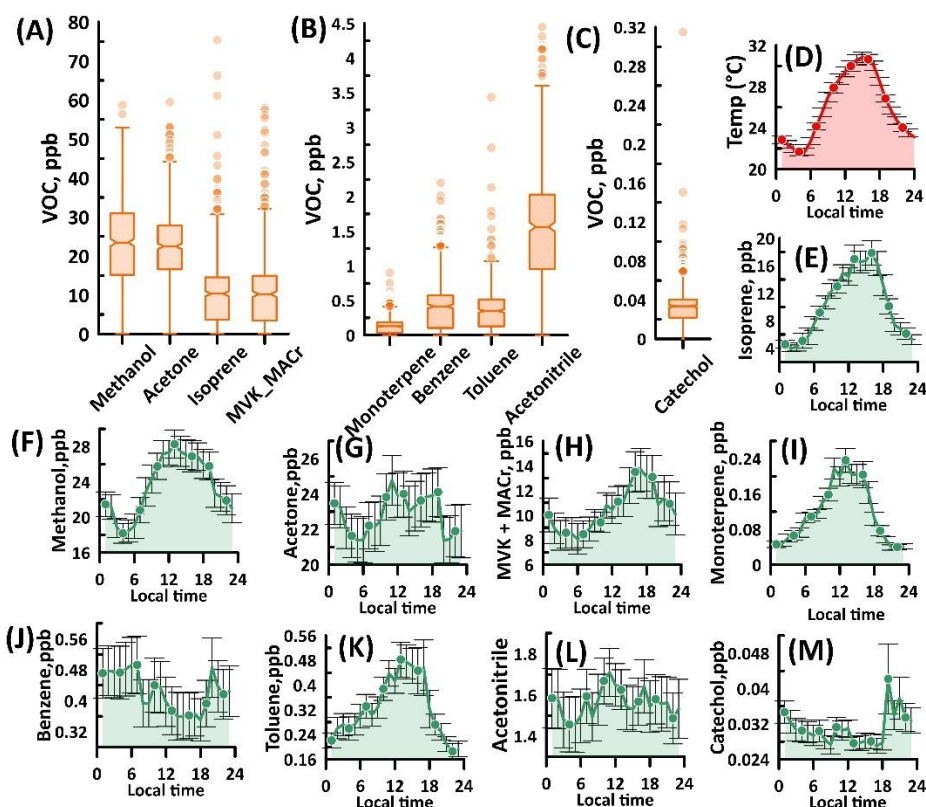
Comment 1: I recommend abstract explicitly state the estimated and increased OH reactivity due to these exceptional events. This is a significant and informative addition that is highly relevant. The authors should do well to emphasize this!

Response: Agreed. The following sentence was added in the Abstract.

The calculated OH reactivities during extreme temperature condition and transport of biomass burning plumes were $106.37 \pm 4.27 \text{ s}^{-1}$ and $106.22 \pm 5.15 \text{ s}^{-1}$, respectively, which are substantially higher than the background level of $98.78 \pm 1.16 \text{ s}^{-1}$.

Comment 2: Figure 1 is missing (A), Figure 1C is missing a label for the x-axis, not sure what this is representing?

Response: Thank you for bringing the error to our attention. We have updated Figure 2 to include the missing labels. The error bars in Figure 3 represent the standard error, which takes into account the total number of observations. This explains the relatively small size of the error bars.



Comment 3: L285 to L287: Minor point, but I would caution against the authors using “large” to broadly refer to particles >50 nm. Based on the geometric mean diameter shown in the supplementary information Fig. S2B, the particles fall into the accumulation mode and are technically “fine mode” aerosol. Large particles typically refer to particles in the coarse mode (e.g. >2500 nm or 2.5 microns). Suggest removing ‘large’ in lines 285 to 287, and instead simplify to say “..Particles >50 nm in diameter were observed...” and “...for the presence of these particles...” You could also consider stating the average (+/-) geometric mean of particles throughout the study for reference.

Response: We agree with the reviewer's feedback and have revised these statements. The updated statements now read:

Particles >50 nm in diameter were observed with no apparent aerosol growth (see Figure S2). The average geometric mean diameter in MOFLUX site was 85.53 ± 16.68 nm.

The most probable reason for the presence of these particles was the isoprene-rich condition of the temperate forest that impacted the aerosol nucleation, even with enough monoterpene and ozone available for particle formation.

Comment 4: L381-383: It's both interesting and intriguing that catechol also has a sharp peak after 6 PM in the diurnal cycle shown in Fig 2M. Is there some process responsible for this, or is that just an artifact from data averaging smoke impacted days? The lines here mention that it increased significantly to 300 ppt on some days, so it could just be that the timing of the smoke impact corresponded with that sharp increase?

Response: The authors are uncertain about the reason for the sharp peak observed after 6 PM. These enhancements did not occur during the days impacted by smoke. The research team has attempted to

identify a likely explanation for the elevated concentration, but we are unable to provide a definitive suggestion at this time.

Comment 5: Comment: L388: Make sure to specify/reiterate that smoke concentration is derived from HRRR. (E.g. “Figure 4 shows the HRRR-derived smoke concentration...”

Response: The authors concur. The new statement reads:

Figure 4 shows the HRRR-derived smoke concentration measured at MOFLUX.

Comment 6: Figure 4B: It's difficult to read/see the trajectory as an inset in the figure. Is it possible to make it its own separate panel, or move it to the supplement as part of figure S5?

Response: The authors have provided a larger image with higher pixel resolution in Figure S5. The following statement has been added to the caption:

A larger image with higher resolution of the trajectory is presented in Figure S5.

Comment 7: L437-438: Are there units on this value of 8.5? Is this different from Csat?

Response: This value is saturation concentration (Csat). Unit ($\mu\text{g m}^{-3}$) was added to the statement.

Comment 8: L450-451: Presumably “low temperature” means <32 C and extreme is >32 C? Suggest defining/stating this in parenthesis next to the statements to prevent ambiguity. Is the low temperature and corresponding reactivity in reference to the selected time period (July 8 to 17) or is that the average for non-impacted/non-extreme temp outside of that date range as well? Please clarify.

Response: Agreed. The numerical values for the temperature conditions have been added to the text. Additionally, the atmospheric reactivity mentioned in these statements is based solely on the selected time period from July 8 to 17. We have rephrased this statement for clarity. See new statements in our response to Comment 9.

Comment 9: L450-L453: The additional reactivity calculations do a lot to help develop the work and associated impacts! These calculations are a highly useful addition. However, I think this section could be worked on a bit to provide more clarity and help emphasize the significance of what is shown. Is it possible to include OH reactivity during “background” or typical conditions during times not influenced by temperature or combustion? Looks like July 9th to 10th could be a possible time-frame that would work for this? L443 earlier states that average reactivity between July 8 to July 17 was 91.30, but this average would presumably include days that experienced elevated temperature and BB impacts. What does the reactivity look like outside of these times? This would provide a useful benchmark for determining exactly how much the reactivity increased due to these extreme events. If it's not possible to calculate yourself, is there a study you can cite that might provide an estimate? I'm also confused as to how it's possible that the reactivity at low temperature (however that is defined) is higher than the average for this entire “impacted” period (98.92 low temp versus 91.30 s⁻¹ average July 8 to July 17)? Clearer wording and phrasing throughout the paragraph would strengthen this finding.

Response: We concur with the reviewer. We have redefined the periods with low temperature conditions as “background” since these durations experienced temperatures below 32°C and were unaffected by biomass burning. The average reactivity during the background conditions was $98.78 \pm 1.16 \text{ s}^{-1}$. Additionally,

we revisited the calculation of average reactivity from July 8 to 17, and the correct mean value during this period was $100.53 \pm 10.80 \text{ s}^{-1}$.

We modified the statement to clarify the "background" condition and corrected the average reactivity values. Furthermore, we included a comparison of our average reactivity with findings from other studies in response to the reviewer's subsequent comment.

During this period, the average OH reactivity was $100.53 \pm 10.79 \text{ s}^{-1}$, which was evidently higher compared to previous measurements in an urban environment in California, USA (Hansen et al., 2021), a sub-urban site in Shanghai, China (Yang et al., 2022), and forest environments in Finland (Sinha et al., 2010) and France (Bsaibes et al., 2020). The elevated reactivity calculated in this study was accounted to the 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 ($>32^{\circ}\text{C}$), allowing an assessment of the potential impact of future warming on atmospheric reactivity. Periods with temperature conditions below 32°C and not influenced with combustion plume were tagged as background. The average OH reactivity for periods with enhanced temperatures ($>32^{\circ}\text{C}$) and with transported plumes was $106.37 \pm 4.27 \text{ s}^{-1}$ and $106.22 \pm 5.15 \text{ s}^{-1}$, respectively, which are substantially elevated compared to background conditions ($98.78 \pm 1.16 \text{ s}^{-1}$). The comparable OH reactivities of the two future climate scenarios highlight the reactive nature of the BB gas phase species such as benzene and acetonitrile. Overall, the calculated averages during the extreme heat and wildfires clearly modified the atmospheric reactivity in the forest.

Comment 10: L451: It would be useful to compare your estimates of OH reactivity to other studies (SOAS, CalNEX, WE-CAN, etc.), for context.

Response: See previous response.

Comment 11: L453, & Figure 5: One thing not emphasized in the text that I think would benefit from more attention is that according to L453 and Figure 5, even though total VOC was lower during the BB event compared to extreme heat, total volatility increased (presumably due to presence of BB compounds like benzene and HCN as mentioned in text). Total reactivity under BB was comparable to reactivity under high temp conditions without any BB influence. Given the lower apparent tVOC, this really highlights how reactive BB gas phase species are! This should be emphasized, especially when considering the projected increase in BB and extreme temp events in the future, and also begs the question—under these future climate scenarios what will have more of an influence in this kind of environment: enhanced temperature, or enhanced BB?

Response: Indeed, the similarity in the calculated OH reactivity during extreme temperature conditions and during the transport of the combustion plume highlights the reactive nature of biomass burning gas species. This will be included in the new version of the manuscript.

Regarding which future climate scenario will have a greater influence, a more comprehensive characterization of VOCs over an extended measurement period, supplemented by modeling procedures,

will be necessary. The current limited dataset, which shows similar values of OH reactivity, is insufficient to draw a valid conclusion about which scenario will exert a greater influence.

We have added the following statement to the latest version of the manuscript:

The comparable OH reactivities of the two future climate scenarios highlight the reactive nature of the BB gas phase species such as benzene and acetonitrile.

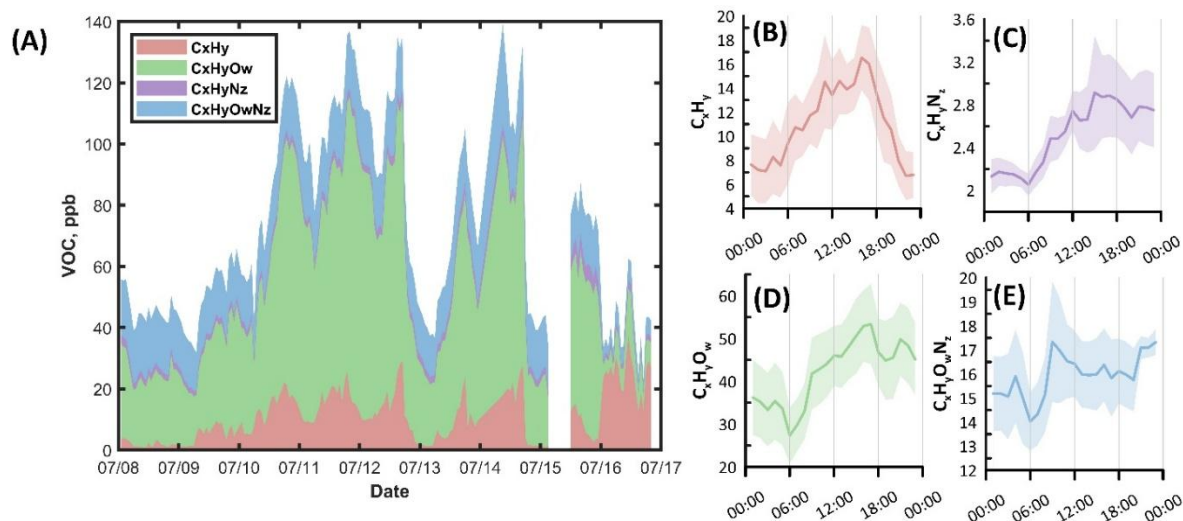
Comment 12: L466-L470: Do you have data that you can add here to support this? (E.g % change enhancement due to increased temperature, or make a table in the supplement). Without the values there the reader is left to take the author's word for it.

Response: The authors agree. Percent enhancement values calculated using average concentrations at low (<32°C) and high (>32°C) temperature conditions are now provided in this section. The statement now reads:

VOCs such as formic acid (CH_2O_2 , 8%), acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, 83%), acrolein ($\text{C}_3\text{H}_4\text{O}$, 62%), furan ($\text{C}_4\text{H}_4\text{O}$, 62%, 51%), methylglyoxal ($\text{C}_3\text{H}_4\text{O}_2$, 51%), and glycolic acid ($\text{C}_2\text{H}_4\text{O}_3$, 68%) exhibited enhancement at the extreme temperature conditions, although it is equally possible that these compounds were also associated with transport of the combustion plumes. Values inside the parentheses are percent enhancement calculated using average concentrations at low (<32°C) and high (>32°C) temperatures conditions

Comment 13: Figure 6: The $\text{C}_x\text{H}_y\text{N}_z$ category is a bit washed out and difficult to see. Can you make it a different color or make it darker? Same for the error shading in diurnal plot Figure 6C.

Response: We updated figure 6 to enhance the readability of the plot, particularly for $\text{C}_x\text{H}_y\text{N}_z$ category. Here is the new figure 6 integrated into the new version.



Comment 14: L496: Define what a substantial number is. N=?

Response: The number of compounds that contribute substantially to factor “others” is now provided. Here is the new statement.

The “others” factor, with a substantial number (N =137) of contributing compounds, remains unidentified.

Comment 15: L504-505: Can you remind the reader of the significance of LogCsat >6? What do values higher than this imply? Reiterate the message you want to convey.

Response: We apologize for the confusion. The statement was modified to indicate that compounds under O-BB and H-BB factors are volatile based on saturation mixing ratio.

Also, the O-BB and H-BB factors are classified as volatile ($\log C_{\text{sat}} > 6 \mu\text{g m}^{-3}$), based on the saturation mixing ratio values of 7.27 and $8.45 \mu\text{g m}^{-3}$.

Comment 16: L512-513: “This is unlikely due to the expected biogenic emission in the forest, although it came second with 34% contribution compared to 66% from the H-BB factor.” This sentence is worded strangely... Does “this” refer to the preceding sentence describing monoterpene and its fragment? Is “it” also monoterpene and its fragment? Not sure what This/it refers to here, can you please clarify?

Response: The statement was rephrased to provide more clarity. The new sentence now reads:

The inclusion of monoterpene to the H-BB factor is unlikely due to the expected biogenic emission in the forest, although the biogenic factor accounted for the second-largest contribution at 34%.

Comment 17: L514-L515: Hmmm, are BB events considered anthropogenic? I think this is the subject of ongoing debate and is a hot topic! The answer depends on where you are in the world. Suggest slight rephrasing to ...”originate from anthropogenic sources and BB events”

Response: The statement was rephrased according to the suggestion of the reviewer.

Comment 18: L525-526: Do you have a reference to support nighttime oxidation of NO₃ contributing to the formation of these species?

Response: Currently, there is no data available to support this statement; therefore, it has not been included in the latest version of the manuscript.

Comment 19: L528-529: “During the transport of BB plumes, the secondary factor had a relatively low increase in signal compared to both BB factors, which shows that oxidation compounds were generally locally...” I don’t think this is true, given that one of your factors is literally called, “oxygenated BB”, which implies that there was indeed some contribution from long-range transport... I think maybe what you mean to say is, “the secondary factor had... low increase... showing that secondary formation was predominantly locally generated...”

Response: We agree with the reviewer. The statement was modified to explicitly indicate that secondary formation is primarily generated locally. The new statement reads:

During the transport of BB plumes, the secondary factor had a relatively low increase in signal compared to both BB factors, which shows that secondary formation was predominately locally generated with little to no contribution from long-range transport

Comment 20: L530-531: Re-emphasize the change to chemistry during the BB impact to strengthen your messaging. What was the increase in reactivity during BB events compared to non-BB events (see earlier comment)? Add it here.

Response: Agree. We added the following sentence in this section.

This was corroborated by the enhanced reactivity (106.22 s^{-1}) during the transport of combustion plume compared to background conditions (98.92 s^{-1}).

Comment 21: L533: What is meant by a “critical” VOC? Suggest removing this adjective and just saying, “VOCs have important contributions to several...”

Response: The word “Critical” was removed in this sentence.

Comment 22: L536: Change to “anthropogenic and fire emissions”. Anthropogenic emissions typically refer to things like traffic, shipping, home heating, etc. While it’s true that a significant portion of wildfires are started by humans, that’s not always the case. Factors contributing to fire ignition are dependent on location and time of year, among others.

Response: The authors concur. The new statement now reads:

...the forest included several sources of biogenic compounds and was influenced by short- and long-range transport of anthropogenic and fire emissions

Comment 23: L538-539: Some of these are also sourced from anthropogenic emissions (e.g. benzene, toluene), so I suggest removing “in the forest” after typical VOCs, especially when they are referenced as AVOCs later in the conclusions (L545). Add the error to the average total mixing ratio reported at the end of the line in L539.

Response: Agree. The phrase “in the forest” was removed and error was added to the sum of VOCs. New statement reads:

Typical VOCs, consisting of methanol, acetone, isoprene, monoterpene, MVK+MACr, benzene, toluene, acetonitrile, and catechol, had an average total mixing ratio of 69 ± 34 ppb.

Comment 24: L541-L542: Add the uncertainty or standard deviation with these averages.

Response: Uncertainty values were added in this sentence.

Among the VOCs, isoprene had one of the highest recorded average mixing ratios (10 ± 9 ppb), next to methanol (23 ± 10 ppb) and acetone (22 ± 9 ppb).

Comment 25: L557-L558: “...Increases could be significantly affected regionally by accompanying changes in atmospheric circulation.” I’m not sure what this means or is supposed to imply. Are you saying that the extent of predicted increases could be regionally impacted due to changes? Suggest rewording for clarity.

Response: Instead of rewriting, the authors decided to remove the statement in the recent version, thank you for pointing this out.

Comment 26: L565: Not sure what a typical VOC is. I think you mean to say background/typical conditions? “Typical VOC” likely changes based on location and environment.

Response: The word “typical” was removed in this sentence avoid confusion.

Comment 27: L567: Important to note that this is for all of the measured VOCs*. Estimates could vary if additional species are measured to include those beyond the list of 250+ you have.

Response: Agree. The word “all” was replaced with “measured” to constrain the statement to observed VOCs using our current instrumentation. The new statement reads:

The O:C and H:C ratios of the measured VOCs, as well as their volatility, provided insight into their response to future climate scenarios

Comment 28: L568: But you had a whole factor named “oxygenated BB” that showed enhancement so it’s not clear to me how it’s fair to say, “During BB plume transport, less oxygenated compounds were enhanced...”?

Response: The authors apologize for the mistake. The research team meant hydrocarbons (C_xH_y), instead of less oxygenated compounds. The new statement reads:

During BB plume transport, hydrocarbons (C_xH_y) with high volatility were enhanced.

References

- Bsaibes, S., Al Ajami, M., Mermet, K., Truong, F., Batut, S., Hecquet, C., Dusanter, S., Léornadis, T., Sauvage, S., Kammer, J., Flaud, P. M., Perraudin, E., Villenave, E., Locoge, N., Gros, V., and Schoemaeker, C.: Variability of hydroxyl radical (OH) reactivity in the Landes maritime pine forest: results from the LANDEX campaign 2017, *Atmos. Chem. Phys.*, 20, 1277-1300, 10.5194/acp-20-1277-2020, 2020.
- Hansen, R. F., Griffith, S. M., Dusanter, S., Gilman, J. B., Graus, M., Kuster, W. C., Veres, P. R., de Gouw, J. A., Warneke, C., Washenfelder, R. A., Young, C. J., Brown, S. S., Alvarez, S. L., Flynn, J. H., Grossberg, N. E., Lefer, B., Rappenglueck, B., and Stevens, P. S.: Measurements of Total OH Reactivity During CalNex-LA, *J. Geophys. Res. Atmos.*, 126, e2020JD032988, <https://doi.org/10.1029/2020JD032988>, 2021.
- Sinha, V., Williams, J., Lelieveld, J., Ruuskanen, T. M., Kajos, M. K., Patokoski, J., Hellen, H., Hakola, H., Mogensen, D., Boy, M., Rinne, J., and Kulmala, M.: OH Reactivity Measurements within a Boreal Forest: Evidence for Unknown Reactive Emissions, *Environ. Sci. Technol.*, 44, 6614-6620, 10.1021/es101780b, 2010.
- Yang, G., Huo, J., Wang, L., Wang, Y., Wu, S., Yao, L., Fu, Q., and Wang, L.: Total OH Reactivity Measurements in a Suburban Site of Shanghai, *J. Geophys. Res. Atmos.*, 127, e2021JD035981, <https://doi.org/10.1029/2021JD035981>, 2022.