

Measurement Report: Extreme Heat and Wildfire Emissions Enhance Volatile Organic Compounds in a Temperate Forest

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We appreciate additional comments of the handling editor of our manuscript, and we provided here a detailed response that addresses the handling editor's concern. Our point-by-point responses to the Editor's general and specific comments are presented below. The Editor'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.

General Comment:

The authors have an important dataset that captures changes in emissions sources and meteorological conditions in a location that has seen previous study. The results provide some insight in changes in atmospheric composition and reactivity driven by changes in source and/or meteorological conditions that generally contribute to our understanding of atmospheric chemistry. The methods are appropriate, with some minor comments and suggestions given below. These strengths demonstrate that this manuscript is appropriate for consideration as a measurement report in ACP. Following minor comments and suggestions on the methods are broader scientific comments and concerns that should be address in the revision stage. Some of these comments and concerns will naturally resolve with the change in format for manuscript type, and a tighter focus on the campaign and results.

Comment: We welcome the suggestion of the editor to convert the manuscript into a measurement report type under the ACP publications. The authors have revised the manuscript to place greater emphasis on the results of the field measurements rather than the broader implications of the research. In addition to addressing the editor's comments and suggestions, we have also changed the title of the manuscript to meet the requirements for measurement reports. The new title is as follows:

Measurement Report: Extreme Heat and Wildfire Emissions Enhance Volatile Organic Compounds in a Temperate Forest

Another requirement for measurement reports is the accessibility of the data presented. The data availability section was modified according to the data policy and regulations of ACP:

The data used in this publication are available to the community and can be accessed in ORNL's Terrestrial Ecosystem Science Scientific Focus Area - Data Products and Tools website under the Volatile Organic Compounds and Meteorological Conditions in the Missouri Ozark AmeriFlux (MOFLUX) Site, 2023 data product which can be accessed via the DOI: <https://doi.org/10.25581/ornlsfa.033/2409393>

The DOI is already functional and can be accessed by anyone without the need for registration or a license.

Several statements have been modified or removed to better highlight the results of the measurements. These changes are detailed in response to Broad Comments (BC) number 9 (BC 9).

Minor Comments, MC (with a focus on Methods)

MC 1: Line 89-Several **hundreds** of compounds have been identified in wildfire smoke (see for example Hatch et al. <https://doi.org/10.5194/acp-15-1865-2015>, Koss et al. <https://doi.org/10.5194/acp-18-3299-2018>, Selimovic et al. <https://doi.org/10.5194/acp-18-2929-2018>, Binte-Shahid et al. <https://doi.org/10.5194/gmd-17-7679-2024>).

Response: The authors cited the studies that detailed the compounds identified in wildfire smoke. The text now reads:

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; Hatch et al., 2015; Koss et al., 2018; Selimovic et al., 2018; Binte Shahid et al., 2024).

MC 2: Line 94-While it is true that there are significant uncertainties due to the huge variability inherent in fires and emissions, there are a lot of studies that have looked at the influence of wildfire emissions on atmospheric chemistry and reactivity that should be cited here (see for example Gilman et al. doi:10.5194/acp-15-13915-2015, Liu et al. doi/10.1002/2016JD025040, Kumar et al. <https://www.nature.com/articles/s41598-017-19139-3>, Permar et al. <https://pubs.rsc.org/en/content/articlehtml/2023/ea/d2ea00063f>).

Response: The authors are grateful for the suggestion. The studies were cited in the new version of the manuscript.

However, the relative importance and contribution of volatile organic compounds (VOCs) from wildfire activities to atmospheric reactivity remain uncertain, even with several studies tackling the problem (Gilman et al., 2015; Kumar et al., 2018; Permar et al., 2023).

MC 3: It might be useful to include a map of the measurement location, particularly showing the influence of biogenic emissions and smoke transport during the study period.

Response: We agree. The manuscript now includes a map that displays the measurement location along with a 50 km radius surrounding the site. This figure clearly shows the interstate and forested areas, which may contribute to the sources of anthropogenic and biogenic VOCs in the temperate forest. Additionally, the impact of transported wildfire smoke is highlighted in Figure S5 in the supplementary file.

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.

Information regarding the instrument was also added in section 2.2 VOC Measurement and Identification

The mass resolution of the technique (6000 m/ Δ m) provided an extended list of VOCs, beyond the usual routinely evaluated compounds (e.g., methanol, isoprene, and monoterpene).

MC 5: Line 111-why are vehicle emissions expected to persist in the forest?

Response: Indeed, the word “persist” was inappropriate for the statement. Thus, it was replaced with “transported”, consistent with the proximity of the interstate highway to measurement site. The statement now reads:

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 be transported into the forest .

MC 6: Line 144-while it makes some sense to use the HRRR forecasts to identify periods with smoke influence (which need to be more clearly defined in the methods-i.e., what periods met the established threshold?), it would strengthen the paper to use measurements to confirm impacts of smoke during these periods (e.g., using PM_{2.5} and/or CO data, or even acetonitrile or other known fire tracers measured during the campaign).

Response: Acetonitrile was already utilized to confirm the impacts of wildfire emissions during our measurements. This was highlighted in statements in section 3.3.

Among the major VOCs, acetonitrile and benzene appeared to be associated with the transport of the combustion plumes. These two VOCs had day average mixing ratios of 2.15 (acetonitrile) and 0.34 (benzene) ppb on July 16, corresponding to increases of 139% and 269%, respectively, compared to July 12, which is non-BB day.

This was also highlighted in Figure S6, which showed the time series profile of benzene and smoke between July 8 to 17, when enhanced transport of wildfire emissions were observed in MOFLUX.

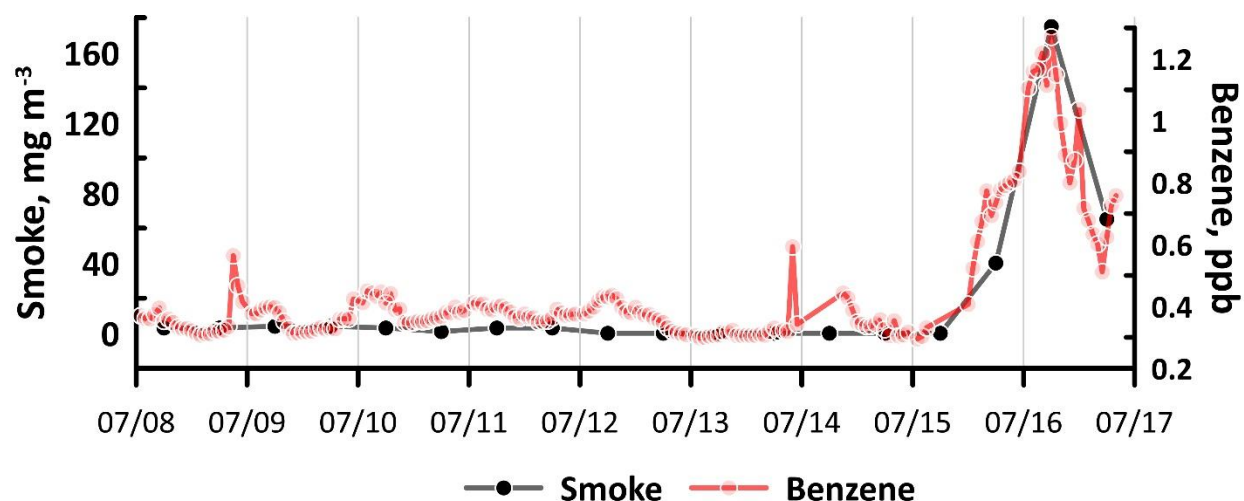


Figure S6: The time series profile of benzene and smoke between July 8 to 17.

MC 7: There are a lot of details about operation of the PTRMS that could be moved to the SI (e.g., equations 1-3 and associated text). The authors may want to include additional references on the use of PTRMS for measurement of monoterpenes and known challenges/interferences if relevant

Response: Agreed. Several statements regarding the operation of the PTR-ToF-MS were moved to supplementary information.

Operation of PTR-ToF-MS 6000X2, Conversion of Raw Signals, and Definition of Mixing Ratio

In PTR-ToF-MS, hydronium ions are utilized to charge the VOCs through a non-dissociative proton transfer in the reaction chamber of the instrument. This technique can identify a wide range of compounds (e.g., carboxylic acids, carbonyls, and aromatic hydrocarbons) if the target compound has a proton affinity higher than water (691 kJ/mol). The protonation occurs as follows:



The conversion of raw signals (counts per second) to mixing ratio (ppb) of an uncalibrated gas VOC can be performed using the following equation:

$$[VOC, ppb] = \frac{1}{k\Delta t} \times \frac{I(VOC^+)}{T(VOC^+)} \times \frac{I(H_3O^+)}{T(H_3O^+)} \quad (2)$$

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 (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 PTR-ToF-MS was operated with 2.6 mbar and 80°C drift tube pressure and temperature, with an E/N value of ~119 Townsend. The mass range was set up to 500 m/z. The single spectrum time was set to calculate the fluxes of the VOC, the results of which will be reported in subsequent works. One of the limitations of the PTR-ToF-MS technique is that it cannot distinguish isomers (e.g., α -pinene, β -pinene, and limonene) because of their identical exact mass (Blake et al., 2009).

The term mixing ratio used in this manuscript is defined as the ratio of the moles of target analyte to the moles of all of atmospheric gases (i.e., N_2 and O_2). This can be expressed as the following equation:

$$R_i = \frac{n_i}{n_\Sigma - n_i} \approx \frac{n_i}{n_\Sigma} \quad (3)$$

Where R_i is the mixing ratio, n_i is the moles of gas analyte, and n_Σ is the total moles of atmospheric gases. The amount of organic gases in the atmosphere is significantly lower than the total gases.

MC 8: It is not clear what value was used for the reaction rate constant of the summed monoterpenes with OH and how that was calculated or what assumptions were made.

Response: The reaction rate constant for monoterpenes was determined using literature values for α -pinene, β -pinene, 3-carene, limonene, camphene, and β -ocimene. The median reaction constant for all these monoterpenes was then used to calculate the OH reactivity. This information has been incorporated into the updated version of the manuscript.

To address molecular formulas with multiple records, the median value of the rate constants was employed. For example, the reaction rate constant for the class of monoterpenes was derived from literature values of several compounds, including α -pinene, β -pinene, 3-carene, limonene, camphene, and β -ocimene. The median reaction constant across all these monoterpenes was then utilized to calculate the OH reactivity.

MC 9: Line 430-log saturation “mixing ratio” should be log saturation vapor concentration

Response: Thank you for noticing the error. The new text now reads:

The average log saturation vapor concentration for all the compounds was $7.50 \mu\text{g m}^{-3}$, and 100 and 136 compounds were classified as intermediate and volatile organic compounds, respectively.

Broader Comments on Science and Scope, BC

The mechanisms by which climate change and climate extremes affect biogenic, anthropogenic, and wildfire emissions are very different, and that complexity is not clearly or adequately addressed in the manuscript as currently written. For example, in the abstract

lines 17-18 describe the “...response of VOCs to future conditions such as extreme heat and wildfire events...”. It is well documented that biogenic emissions can be temperature dependent, with compound- and species-specific differences. It is also well documented that some anthropogenic emissions can also be temperature dependent, e.g., asphalt emissions, but that strong temperature dependence is typically more indicative of biogenic emissions. In addition, reaction product formation can also have some dependence on temperature (as temperature can influence oxidant levels and reaction rates). This is addressed to some extent in section 3.2, but some refinements are needed.

BC 1: The authors state the at the BVOCs “respond well” to variations in temperature. What does this mean? They behave as expected/consistent with other studies?

Response: The authors modified the statement to be consistent with our results. The new statement now reads:

The major BVOCs, isoprene and monoterpene, increased with temperature, as shown in Figure 4.

BC 2: It appears the isoprene and monoterpenes have the same exponential response to temperature. I do not think that this is completely consistent with other studies (or for example the temperature response as would be predicted in a biogenic emissions model), as isoprene typically shows a much stronger response to temperature. There may be some studies that show very strong dependence of monoterpene emissions in extreme temperatures, but this is not clear as this section is currently written. It is suggested that the temperature sensitivity of isoprene and monoterpenes be discussed separately in this section, including context from references that are specific to isoprene and to monoterpenes. The authors state that the enhanced emissions of monoterpenes “can also be linked to”, suggesting that at least one other mechanistic reason for enhanced emissions has already been discussed, but this is not the case. One suggestion is to more generally summarize (with appropriate citations) (and not to get into any specific mechanisms).

Response: We welcome the suggestion of the editor to separate the discussion of temperature sensitivity of isoprene and monoterpene. We also concur with providing a more general summary. New texts were added in the manuscript:

Furthermore, Figure 4 shows the evident exponential relationship between temperature and the major BVOCs, consistent with previous studies in which temperature controls the emission of isoprene and monoterpene (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, respectively. The emission of isoprene is linked to plant thermotolerance, which is the ability of plants to endure and adapt to high temperatures without experiencing detrimental effects on their growth (Sharkey et al., 2007; Duncan et al., 2009). While the dependence of monoterpene emissions on temperature appears similar, based on the empirically determined coefficients calculated in this study, the mechanisms for monoterpene release from vegetation differ from those of isoprene. This variation is primarily due to

plants' ability to store monoterpenes and their high- water solubility and elevated temperature leads to vaporization of stored monoterpenes. (Loreto and Schnitzler, 2010; Malik et al., 2019; Malik et al., 2023)

BC 3: The discussion of MVK and MACr is confusing as written. The discussion seems to be mixing the effects of temperature on emissions of isoprene (and therefore its oxidation products) with the effects of temperature on lifetime (which could alter the ratio as a function of temperature). These effects need to be more clearly differentiated in this section and this distinction should be considered throughout the manuscript when discussing temperature effects particularly when the compounds can be oxidation products.

Response: The authors agree. We simplified the discussion on the impact of temperature of yields of MVK/MACr from Isoprene. The new paragraph now reads:

MVK and MACr produced from the oxidation of isoprene showed a strong association with temperature. MVK and MACr reached a 20-ppb average mixing ratio during extreme temperature conditions. As shown in Figure 4, the concentration of MVK/MACr doubled during extreme temperature conditions compared at low temperatures. This is consistent with a prior study that showed the yield of MVK increased with temperature (Navarro et al., 2013).

The discussion on lifetime of isoprene based on the ratio was moved to section 3.1. These statements are now included in the general results of MVK/MACr

Furthermore, The ratio between isoprene and MACr + MVK indicates the lifetime of the isoprene and degree of oxidation of isoprene to MVK and MACr. Greater than value of 1.0 observed in MOFLUX suggests transport time shorter than one isoprene lifetime, as indicated in the previous studies (Selimovic et al., 2022; Hu et al., 2015).

BC 4: Toluene is also emitted from biogenic sources. The discussion around toluene (including attributing everything to interference/fragmentation of monoterpenes) needs to be reconsidered and revised accordingly in this context.

Response: We agree. The possible contribution of toluene from biogenic emission is now added in the new version of the manuscript.

Interference of para-cymene fragmentation in the drift tube of the PTR-ToF-MS at mass 93 (Ambrose et al., 2010) might have impacted the observed concentrations at MOFLUX although we also do not discount the emission of toluene from vegetation (Heiden et al., 1999) .

Remarkably, the toluene mixing ratio (0.73 ppb) doubled at higher temperatures, unlike the benzene and xylene. This result further supports our initial claim that the compound occurring at mass 93 originates from the fragmentation of monoterpene or from the emission of toluene from biogenic activities.

BC 5: “Combustion” is used to describe anthropogenic emissions (as in this section) and wildfire emissions which is confusing and should be revised throughout. It is more typical to

refer to wildfire emissions as wildfire emissions, biomass burning emissions, or pyrogenic emissions. It is suggested to choose one of those more commonly used terms and use it throughout (right now there is some use of wildfire and biomass burning but it is inconsistent). Back to the line in the abstract, wildfire emissions don't "respond" to temperature in the same way that biogenic emissions or anthropogenic emissions do. There are complex relationships between ambient temperature and fuel moisture, and therefore fire ignitions, fire spread, fire, severity, fuel consumption, etc. that affect emissions. This complexity is not acknowledged in the manuscript (e.g., by saying that wildfire emissions "respond" to temperature) and the rationale for discussing the wildfire emissions in the context of temperature is not well supported.

Response: We agree with editor. The word combustion, all 24 of them, was replaced with wildfire to prevent confusion. Moreover, we concur with editor the word "respond" was unfit to describe the changes of the general physiochemical properties of the gases in the forest. The statement in abstract was modified into the following sentence:

Extreme heat and presence of wildfire plumes modified the overall volatility, reactivity, O:C, and H:C ratios of the extended list of VOCs.

BC 6: A related comment, on line 193, it is stated that acetonitrile and catechol don't follow the trend of temperature (presumably this means they do not increase with temperature like the BVOCs), which is not unexpected based the complexities noted above. However, in line 394 it is concluded that this is in fact because of the "infrequent emissions of BB plumes". It is not clear what is meant by that.

Response: The statement in question was indeed confusing, thus the 2nd part of the sentence was removed. The new statement is now:

Moreover, acetonitrile ($r = 0.53$) and catechol ($r = 0.017$) also did not follow the trend of temperature.

BC 7: As noted above, the discussion of wildfire emissions is not sufficiently differentiated from anthropogenic emissions throughout the manuscript. This leads to some confusion about the results and ultimately, the implications of this work.

Response: We concur with the editor. We modified several statements in the manuscript to differentiate anthropogenic emissions from wildfire activity.

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

However, several prior studies have shown that monoterpene can also originate from anthropogenic sources and wildfire events

During the measurement period, the forest included several sources of biogenic compounds and was influenced by short- and long-range transport of anthropogenic and wildfire emissions

BC 8: In addition, “monoterpene” is used throughout and described on line 285 as being composed of several organic species. This is not accurate or consistent with existing literature. Monoterpene specifically describes a class of organic compounds with the formula $C_{10}H_{16}$, of which there are several isomers (some of which are listed on line 285). The analytical technique being used can’t differentiate isomers (as noted in the methods), so what is being reported is the sum of monoterpenes (plural) and that needs to be clearer. The monoterpenes in that mixture can have very different reactivities, lifetimes, etc. and the manuscript should be revised with this in mind. For example, what was assumed for the OH reactivity of the monoterpene mixture?

Response: We agree with the editor. The current wording of monoterpene indicates a sum of all species instead of a class of compounds with molecular formula of $C_{10}H_{16}$. The new statement in the text are as follows:

Monoterpene, a critical contributor to ozone and secondary aerosol formation (Salvador et al., 2020a; Salvador et al., 2020b), is a class of organic compounds with the formula $C_{10}H_{16}$ such as α -pinene, β -pinene, limonene, δ -carene, ocimene, and sabinene, and its distribution varies significantly based on the vegetation species.

The limitation of the PTR-ToF-MS to resolve isomers is included in the discussion of the capabilities of the instrument. The following statement is now in supplementary information:

One of the limitations of the PTR-ToF-MS technique is that it cannot distinguish isomers (e.g., α -pinene, β -pinene, and limonene) because of their identical exact mass (Blake et al., 2009).

Moreover, the reactivity value used for monoterpene was based on the median value of the rate constants available for all monoterpenes. This was highlighted in the new statements in the most recent version of the manuscript.

To address molecular formulas with multiple records, the median value of the rate constants was employed. For example, the reaction rate constant for the class of monoterpene was derived from literature values of several compounds, including α -pinene, β -pinene, 3-carene, limonene, camphene, and β -ocimene. The median reaction constant across all these monoterpenes was then utilized to calculate the OH reactivity.

BC 9: The manuscript has a lot of detail that does not necessarily support or benefit from the measurements and results presented. For example, there is scattered mention of climate, climate forcing, future climate scenarios, and aerosols (including new particle formation). (One of the reviewers notes this of the introduction.) The connections between emissions composition, chemistry, aerosols, and climate could be made more generally, but the repeated mention does not strengthen the manuscript since the measurements and results are not clearly and sufficiently linked to these complex processes. Refining the focus to the measurements and results, including placing them in the context of similar studies, will help improve this aspect of the manuscript.

Response: Authors concur. Several statements from the original manuscript were removed or modified To shift the focus to the campaign and results instead of broad extended implication of the work. The following statements are either the modified or removed statements in the new version of the manuscript:

(Abstract – Modified) *Ultimately, results here underscore the imminent effect of extreme heat and wildfire emissions on the overall chemical properties VOC in a temperate forest.*

(Introduction – Removed) *The results presented here provide important information to assess possible future feedback loops of vegetation and atmospheric chemistry to regional- and/or global-scale climate changes (Introduction).*

(Results and Discussion – Removed) *Based on the results here, isoprene at MOFLUX is expected to increase more as the temperature increases compared to monoterpene. Thus, careful consideration of the oxidant chemistry and product speciation will provide valuable new insights into the impact feedback loop between aerosols and climate in temperate forests.*

(Results and Discussion – Removed) *The interactions of AVOCs such as toluene, xylene, and trimethylbenzene produced more secondary organic aerosols, but the addition of BVOCs reduced the yield through cross-reactions between the intermediates (Chen et al., 2022).*

(Results and Discussion – Removed) *Given the anticipated increased temperatures in the future due to increasing effects of climate change, addressing the enhancements of formic and acetic acid will be important for predicting future chemistry–climate interactions.*

(Summary and Conclusion – Removed) *The comprehensive analysis of the whole mass spectra performed in this study underscores the importance of unaccounted-for VOCs in the atmosphere. The results of this study highlight the possible unaccounted modifications in VOC distribution that might be expected in future climate scenarios with serious impacts on aerosol–climate interaction. With the growing but still limited insights on the effect of mixed precursors on aerosol formation, more information regarding the overall distribution and transformation of AVOCs and BVOCs and their response to different future climate scenarios are needed to realistically account for the climate forcing of organic aerosols.*

Header of section 4 was modified from Summary and Atmospheric Implications to **Summary and Conclusions.**

The current version of the manuscript compares results with previous studies with similar measurements. These are highlighted in the following statements:

Mean mixing ratios of methanol and acetone were 23 ppb, consistent with a prior study done in MOFLUX, in which half-hour averages of methanol ranged between 1.9 and 26 ppb (Seco et al., 2015)

Observed isoprene mixing ratios were substantially elevated compared to other similar temperate forests in the United Kingdom (~8 ppb) (Ferracci et al., 2020), deciduous forest in Michigan, USA (~1.5 ppb) (Kanawade et al., 2011), and mixed temperate forest in Canada (~0.01 ppb) (Fuentes and Wang, 1999). For MVK+MACr, prior measurements in similar environments reported mixing ratios below 2.0 ppb (Safronov et al., 2019; Shtabkin et al., 2019; Montzka et al., 1995) highlighting the intense production of MVK+MACr at MOFLUX.

Throughout the measurement duration, the maximum mixing ratio of monoterpene was 0.9 ppb. This ambient level is similar to a prior measurement at the MOFLUX site (Seco et al., 2015), as well as observations of monoterpene in other temperate forests in Wisconsin, USA, and Wakayama, Japan (Vermeuel et al., 2023; Ramasamy et al., 2016).

Furthermore, Figure 4 shows the evident exponential relationship between temperature and the major BVOCs, consistent with previous studies in which temperature controls the emission of isoprene and monoterpene (Hu et al., 2015; Selimovic et al., 2022; Guenther et al., 2012).

In 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.

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 urban environment in California, USA (Hansen et al., 2021), 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).