

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

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We appreciate the efforts of the handling editor in improving our manuscript, and we provided here a detailed response that addresses the handling editor's remaining minor concerns prior to publication. Our point-by-point responses to the Editor's 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.

Scientific Comment (SC)

SC 1: Lines 198-208, calculation of OH reactivity, is somewhat confusing. One suggestion is to be consistent with language and use “reaction rate constant” throughout. Line 202...does this mean that reaction rate constants were calculated for all compounds with hourly resolution using measured temperature? Please just reread for clarity.

Response: The authors agree. The term reaction rate constant was used all throughout for clarity in the revised manuscript. The hourly ambient temperature were indeed considered during the calculation of the reaction rate constant. The calculation also incorporated available activation energy (E_a) and pre-exponential factor (A) data. The new paragraph now reads:

*...where $[VOC_i]$ is the concentration of the volatile organic compounds measured by the PTR-ToF-MS and k_{VOC+OH} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are **the reaction rate constant** between the OH and VOC. The **reaction rate constant** were calculated based on the available data 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 rate constant** incorporated the hourly temperature conditions observed during the field campaign. **Only records with available activation energy (E_a) and pre-exponential factor (A), along with temperature range (20-36 °C) similar to the observed conditions in the temperate forest, were considered in the calculation.** 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 rate constant** across all these monoterpenes was then utilized to calculate the OH reactivity.*

SC 2: Lines 280-282: There are counter-examples of measured terpenes being highest at night, with clear daytime peaks. Bouvier-Brown et al., 2009; Pfannerstill et al., 2024

Response: The authors concur with the editor that the daytime peak can occur for some monoterpene. Thus, the statement was removed in the revised manuscript.

SC 3: Line 302: Do you mean that benzene can initiate new particle formation or just contribute to SOA formation? I am unfamiliar with the former (contribution of benzene to NPF).

Response: We refined this statement to specify benzene's role as a contributor to aerosol formation. The revised sentence now reads:

As benzene is a crucial precursor for ozone and a significant contributor to aerosol formation, the variability of such BB VOC should be incorporated into simulations of future atmospheric processes.

SC 4: Lines 350-354: Note that toluene also has a biogenic source, and appears as an emission in biogenic emissions models (e.g., MEGAN). This does not mean your conclusion is wrong, but you may want to rethink given that toluene can be biogenic.

Response: The authors acknowledge that toluene can have biogenic source. The paragraph includes the following statement:

...emission of toluene from biogenic activities.

Response:

Editorial Comment (EC)

EC 1: It is suggested to remove all exaggerated/non-quantitative/qualitative language. Some examples include: "grave implications" (line 49), "imminent implications" (line 359), remove "clearly" in Fig 1 caption.

Response: We agree with the editor. The following non-quantitative words were removed in the revised manuscript.

*Ultimately, results here underscore the **imminent** effect of extreme heat and wildfire emissions ...(Line 33)*

*...which will have **grave** implications for air quality, climate, and human cardiovascular health (Line 49).*

*The alteration of VOC distribution due to enhanced temperature has **imminent** implications on the formation of secondary aerosols (Line 358)*

*The figure **clearly** illustrates the interstate and forested areas... (Line 111)*

*Overall, the calculated averages during extreme heat and wildfires **clearly** altered atmospheric reactivity in the forest (Line 450).*

*The highly variable profiles of the extended list of VOCs measured at MOFLUX **clearly** indicated that species were impacted by a variety of emissions and processes (Line 567)*

EC 2: Line 66: suggestion to change “..ozone enhancement will lead to...” to “ozone enhancement may lead to...”

Response: Done. The new statement now reads:

Ozone enhancement may lead to elevated atmospheric oxidation capacity that can initiate more secondary pollutant formation.

EC 3: Line 88: “several VOCs” should be changed to “hundreds of VOCs”

Response: Done. The revised statement now reads:

*During wildfire events, the burning of vegetation and other biomass induce the pyrolysis of plant materials which ultimately release **hundreds of VOCs** during the process*

EC 4: Line 156: needs revision

Response: The authors agree. The following statement is included in the revised manuscript.

Backward airmass trajectories were estimated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model.

EC 5: Line 166: cabin or shed? (not clear what a cabin shed is)

Response: The term “shed” was removed from the statement

EC 6: Line 167: “can be” missing “found”

Response: Done. The line now reads:

*A detailed description of the general mechanism of the PTR-ToF-MS **can be found** in the supplementary file and elsewhere*

EC 7: Line 371-378: This section describes “sporadic...emission and transport” and “infrequent emissions”. During a fire, emissions and transport will be ongoing (and not sporadic or infrequent). It is more than the variability in emissions and transport lead to infrequent interception of the smoke at any given location. Suggestion to reword to make that clearer.

Response: The authors agree with the editor. The terms sporadic and infrequent emissions were removed to make the statement clearer. The new statement now reads:

Acetonitrile did not exhibit a typical daily cycle, aligning with the unpredictable emissions and transport dynamics characteristic of biomass burning events.

EC 8: Line 439: “accounted for” should be changed to “attributed to”

Response: Done. The line now reads:

The elevated reactivity calculated in this study **was attributed to** the notable contributions from isoprene, acetone, ethylamine, and ethenone.

EC 9: Lines 549-554: This paragraph is talking about biomass burning/wildfire emissions, but concludes with talking about “such AVOCs”. BB/wildfire emissions are not considered AVOCs. The specific compound, benzene, that you are describing has both pyrogenic and anthropogenic sources. Last sentence should be revised to make that clearer.

Response: We agree. The new statement now reads:

As benzene is a crucial precursor for ozone and a significant contributor to aerosol formation, the variability of such BB VOC should be incorporated into simulations of future atmospheric processes.