Response to Reviewer for manuscript titled:

Organic vapors from Savannah and European Boreal fire emissions: Insights from photochemical and dark aging experiments in a smog chamber

Response to reviewer: We thank the reviewer for their insightful comments and suggestions for improvement. We have addressed their comments and concerns through appropriate changes and additions made in the revised manuscript. The replies/responses (in blue) to the comments are discussed below as point-by-point rebuttal. All line numbers referred to in the responses pertain to the resubmitted manuscript, unless otherwise specified.

Reviewer 2- General comments:

The manuscript presents a comprehensive laboratory study investigating the chemical profile and evolution of volatile organic compounds (VOCs) emitted from the combustion of biomass fuels characteristic of poorly studied biomes: European Boreal forest ground fuels and African Savannah fuels. Utilizing advanced high-transmission Vocus PTR-TOF-MS instrumentation allowed for the tracking of a vast array of ions (436 species). The research attempts to bridge a critical geographical data gap and introduces high-resolution metrics. However, there are fundamental methodological assumptions, limitations regarding lab-scale representation, and data treatment choices that must be thoroughly discussed and clarified before the manuscript can be recommended for final publication in ACP.

Major comments:

1. Representation of real-world biomass burning (field vs. laboratory scale)

The authors collected biomass samples directly from field sites (forests and savannahs) and transported them to the ILMARI facility for laboratory burn tests. While controlled environments are essential for chamber studies, this transition introduces serious artifacts that are not sufficiently addressed in the manuscript: - The harvesting, transport, and storage process inherently alters the natural moisture content of fuels. Ground-layer vegetation and soil organic horizons are extremely sensitive to these shifts, directly influencing the resulting MCE, temperature, and primary volatile organic emission profiles. - Burning small, isolated quantities in an open-stack configuration lacks the macro-dynamics of actual wildfires. Real fires feature strong local turbulence, wind vectors, and crucial interactions with the soil profile (underground pyrolytic processes and moisture distillation). - In a real wildfire front, intense radiant heat devolatilizes the adjacent vegetation and litter layer before active ignition occurs, injecting a unique cocktail of unburned pyrolytic vapors into the plume. This sequence cannot be replicated by small batch laboratory burns. The authors must introduce a dedicated "Limitations" subsection where these macro-scale and environmental boundaries are explicitly and critically discussed, dampening any generalized extrapolations to real-world wildfire plumes.

We thank the reviewer for this valuable suggestion. We agree that controlled laboratory combustion experiments can not fully reproduce the complexity of natural wildfires. The objective of the BASFAA campaign was to investigate the evolution of BB emissions under well-controlled laboratory conditions. We have therefore expanded the discussion of the study limitations in the revised manuscript (Lines 720-730) to explicitly acknowledge the limitations associated with laboratory combustion experiments and to clarify that our findings should be interpreted as mechanistic insights obtained under controlled laboratory conditions, with appropriate caution when comparing them with natural wildfires. The revised limitation paragraph now reads as follows:

Lines 720-730: *Certain limitations should be considered when interpreting the results of these chamber*

experiments in context to real atmospheric BB plumes. Chamber studies allow controlled investigation of aging processes but may not fully capture the complexity of real atmospheric conditions. Variability in fuel composition and moisture content, plume dilution rates, temperature, background aerosol concentrations, and potential chamber wall losses may affect the emission chemistry. In addition, although representative biomass fuels were collected from the field, combustion was performed under controlled laboratory conditions. Consequently, the experiments cannot fully reproduce the complexity of natural wildfires, including fire spread, plume dynamics, interactions between the fire and the surrounding vegetation and soil, and variability in dilution rates, all of which may influence BB emissions under ambient conditions (Akagi et al., 2011; Hodshire et al., 2019). Therefore, the findings should be interpreted as mechanistic insights obtained under controlled laboratory conditions, and caution should be exercised when comparing them with natural wildfire plumes.

2. Smog chamber aging conditions and chemical simplifications

Simulating multiple days of atmospheric oxidation within a 29 m3 chamber within a few hours introduces unavoidable chemical stresses, which should be acknowledged in the manuscript: - Injections of massive precursor levels or sharp generation of high hydroxyl radical/ozone concentrations force an accelerated reaction regime. This heavily biases the dynamic balance between fragmentation and functionalization pathways, potentially over-producing small organic acids/carbonyls that wouldn't necessarily dominate under slower, ambient atmospheric dilution rates. - The dark aging experiments focus almost entirely on ozonolysis. In real night-time wildfire plumes, the chemistry is heavily driven by nitrate radicals originating from background NOx and ambient ozone interactions. Simulating dark aging predominantly through O3 chemical tracks represents a significant oversimplification of the real nocturnal boundary layer chemistry. - Even in a 29 m3 Teflon chamber, the surface-to-volume ratio is high. Semi-volatile (SVOC) and low-volatility organic compounds (LVOC) produced during aging readily partition into the chamber walls. The authors should quantify or at least critically evaluate how these wall losses affected their absolute mass recoveries and total secondary yields.

We thank the reviewer for this important comment and agree that environmental chamber have certain inherent limitations. We have discussed the limitations associated with chamber-aging in the revised manuscript and emphasized that the findings should be interpreted within the context of these experimental limitations (Lines 720-739).

Yes, we agree with the reviewer that our dark aging experiments represent a simplified nocturnal oxidation environment. However, the aim of our dark aging experimental conditions was to represent remote wildfire plumes with little anthropogenic influence. Accordingly, no additional NOx was added. NOx concentrations in all experiments remained below 10 ppb, and under such low-NOx conditions, dark aging experiments were primarily driven by O_3. This has now been clarified in Lines 205-207 of the revised manuscript. Furthermore, as discussed in the Results (Lines 512-515), phenolic compounds are known to react rapidly with NO_3 radical, however they showed negligible changes throughout the dark aging experiments. This observation provides additional evidence that NO_3 radical chemistry was limited in our dark aging experiments. To clearly state the focus and experimental conditions of the dark aging experiments, the text in the revised manuscript has been modified as follows:

Lines 190-194: *In dark aging experiments, the aim was to represent remote wildfire plumes with little anthropogenic influence, and therefore no additional NOx was added. Additionally, no OH· scavenger was added and no OH· formation was observed as indicated by constant butanol concentration. Initial concentration of approximately 100 ppb of O_3 was injected. The elevated O_3 concentration was used to simulate a full night of atmospheric oxidation over a shorter experimental period.*

Lines 205-210: *In dark aging experiments, NOx concentrations in the chamber were low, and under these*

low-NOx (<10 ppb) conditions, formation of NO_3· is expected to be limited, so dark aging was largely driven by O_3. The O_3 exposure was calculated by O_3 concentrations integrated over time, and at the end of dark aging experiments, the O_3 exposure ranged from 4.6×10^{16} to 5.3×10^{16} molecules cm^{-3} s. Ambient O_3 concentration of $7x10^{11}$ molecule cm^{-3} (Ziemann and Atkinson, 2012) was used to convert the exposure into eqv. atmospheric day for dark aging experiments.

Lines 512-515: *Phenolic compounds, which react rapidly with NO_3·, showed negligible or only minor reductions in EFs during dark aging experiments, similar to other organic vapor classes. This suggests that NO_3· formation was limited under our experimental conditions, and the observed evolution of organic vapors is dominated by weak O_3 oxidation for dark aging experiments*

Hartikainen et al. (2018) estimated that, owing to the considerably larger size and low surface-to-volume ratio (29 m^3) of ILMARI chamber, losses of organic vapor to the chamber walls are expected to be relatively small compared with condensation onto particles. We have clarified this now in the revised manuscript in Lines 503-505.

3. Emission Factors (EFs) metrics

Throughout the text, Emission Factors are reported in mass units per fuel mass (g kg−1). However, it is never clearly stated whether these factors are calculated based on dry fuel weight (dry basis) or as-received fuel weight (wet basis). Given that the moisture content varies heavily across the sampled spectrum (e.g., bone-dry savannah vegetation vs. damp European boreal soil organic horizons), this omission creates ambiguity. Relying strictly on cross-referencing past literature (e.g., Vakkari et al., 2025) is insufficient. The fuel moisture data and the explicit mathematical basis of the EFs must be stated transparently within the methods section of this manuscript.

We thank the reviewer for this comment. In this study, emission factors (EFs) were calculated on dry fuel weight (dry basis) and this has been explicitly mentioned in the revised text in Section 2.4 (Line 279). In addition, we have expanded the description of the carbon mass balance approach used for EF calculations by providing a more detailed explanation of equation 2 and its associated variable. The revised paragraph now reads as follows:

Lines 279-293: *The emission factors (EFs; g kg^{-1} dry fuel) of species i were calculated following a carbon mass balance approach (Yokelson et al., 1999), following the implementation described by Vakkari et al. (2026) as shown in Equation 2:*

$$EF_i \left(\frac{g}{kg}\right) = F_c \times 1000 \times \frac{MW_i}{12} \times \frac{ER_i}{\sum_{j=1}^{n} \frac{\Delta C_j}{\Delta CO}} \quad (2)$$

Here, EF_i refers to the mass (g) of species (i) emitted per unit mass (kg) of dry fuel burned, where i denotes the chemical species for which the EF (g kg^{-1} dry fuel) is being calculated. Fc is the fuel carbon fraction, MWi is the molecular weight of the species (i), and ERi is the emission ratio of species (i) relative to ΔCO. In the denominator, j denotes each carbon-containing species included in the carbon mass balance, and ΔCj is the excess carbon concentration of species j. The summation includes carbon emitted as CO_2, CO, CH_4, VOCs, OC, and BC (Vakkari et al., 2026). Background concentrations measured before sample injection were subtracted for each species. Fc, measured at Eurofins Environment Testing Finland Oy according to DIN EN ISO 16948:2015-09 protocol was 48.8% for savannah wood, 43% for savannah grass, and 42.8% for boreal forest fuel, with a measurement uncertainty of 2% (Vakkari et al., 2026)

To address the comment regarding fuel moisture content, we have also revised Section 2.1 (Lines 155-157) to explicitly report the measured moisture contents of the biomass fuels. The revised text now reads as follows:

Lines 155-157: *The moisture content was analysed at an accredited laboratory (Eurofins Environment Testing Finland Oy) and was 9.4% for savannah wood, 8.6% for savannah grass and 9.6% for the boreal forest surface, representing dry conditions.*

4. Instrumental transmission thresholds vs. data interpretation

In Section 2.3, the authors state that the ion transmission efficiency for low mass ranges below m/z 50 was compromised due to the settings of the quadrupole ion guide. Paradoxically, the results and discussion sections draw strong, definitive conclusions regarding light molecular weight species such as formic acid (CH2O2, detected at m/z 47). If transmission below m/z 50 is non-linear or attenuated, how was the absolute calibration and quantification of these lighter, crucial compounds secured? The authors must clarify the specific analytical uncertainty ranges for molecules under m/z 50.

We thank the reviewer for this comment. The reduced transmission below m/z 50 mentioned in the manuscript reflects the transmission efficiency of the quadrupole low-mass filter and does not imply that this mass range could not be reliably detected or quantified. During data processing, the mass transmission function, together with the ratios of measured and calculated sensitivities for a series of ions was used for data quantification and conversion of ion counts to mixing ratios (ppbv) (Lines 250-252). Therefore, the reduced transmission efficiency was accounted for during quantification. Additionally, detection not only depends on transmission efficiency but also on compound abundance and instrument sensitivity. In our measurements, formic acid (m/z 47) still produced sufficiently strong signals for data analysis.

We would like to clarify that to calculate uncertainties, the propagation of errors in instrumental precision, VOC calibration gas mixing ration (5%) and MFC (1% each) used for dilution were utilized and an uncertainty of 7.2% was obtained for acetone. Uncertainty in the sum of VOC concentrations from the Vocus was estimated to be 10%, which was in line with (Jensen et al., 2023) (Lines 263-266). For compounds that were not directly calibrated, including formic acid (m/z=47), the reported mixing ratios represent lower-limit estimates as they were quantified using acetone sensitivity factor. A separate analytical uncertainty was not determined specifically for compounds below m/z 50.

5. Statistical and data processing evaluations

a) The application of the Hampel filter on turbulent data

To clean the raw MS data, the authors applied a Hampel filter with a rigid threshold (k≈5) to eliminate "spikes." While appropriate for stable baseline monitoring, batch biomass combustion is inherently highly dynamic, flash-driven, and turbulent, particularly during ignition phases or sudden structural collapses of the burning fuel. A blind statistical filter risks wiping out real, short-lived kinetic bursts of chemical emissions by misinterpreting them as instrumental noise. The authors need to prove that this specific filtering step did not scrub away genuine combustion dynamics.

We thank the reviewer for raising this important comment. We agree that biomass combustion emissions are highly dynamic and that genuine short-lived emission events should not be removed as statistical outliers. In our study, the Hampel filter was applied solely to remove isolated instrumental outliers (single-points spikes) that occurred in PTR-MS signals using a robust outlier detection approach, similar to quality-control procedures previously applied to atmospheric time-series measurements (Aigner et al., 2026; Fernández Palomares et al., 2026; Pearson et al., 2016). To verify that the filtering did not affect genuine combustion dynamics, we quantified the fraction of data points identified as outliers. We found that the filter affected only 0.28% of all the measurements, meaning 99.72% of the measurements remained unchanged. Thus, the filter

removed only negligible number of isolated instrumental spikes and did not influence the temporal evolution of the measured concentrations. We have now clarified this in the revised manuscript (Lines 296-297).

b) Compositional unassigned mass and isomeric ambiguities

The manuscript reveals that only 61% of the total organic mass detected by the Vocus PTR-MS was successfully assigned to specific chemical formulas. This leaves roughly 39% of the volatile mass behaving as an unassigned "black box." This missing fraction compromises absolute mass closures and introduces uncertainties in the hierarchical clustering. The author must explicitly discuss how this unassigned ~39% mass might skew their conclusions regarding overall mass decay or growth during aging, and acknowledge the intrinsic limitations regarding structural isomer differentiation via PTR-MS.

We thank the reviewer for this comment. We agree that unassigned fraction limits complete organic vapor mass closure and should be considered while interpreting changes in total mass during aging. The Vocus PTR-TOF-MS used in this study had a mass accuracy of <5 ppm and mass resolving power of approximately 10,000 Th/Th, which enabled reliable separation of many isobaric ions and molecular formula assignment for the identified signals (Lines 252-254). However, confident assignment also depends on sufficient signal intensity, adequate separation from neighboring peaks etc. Upon cross-checking the peak fitting, we found that many of the unassigned peaks were either of low intensity of overlapped with neighboring peaks, which limited confident molecular formula assignment. Primary ions $(H20)_nH^+$, and ions containing deuterated hydrogen (^2H), water clusters, silicon (Si) and fluorine (F) were excluded from this assignment as mentioned in Lines 268-269.

The compositional data analysis, including hierarchical clustering, presented in this study was based on the chemically assigned fraction of the organic vapors rather than complete organic vapor mass closure. This has been explicitly acknowledged and clarified in the revised manuscript now. The revised text reads as follows:

Lines 268-271: *All detected and identified ions (n=436) except the primary ions (H20)nH+, and ions containing deuterated hydrogen (2H), water clusters, silicon (Si) and fluorine (F) were used for further analysis. Approximately 61% of the total organic vapor mass measured using the PTR-MS was assigned. The compositional analysis and discussion presented in this study are based on this chemically assigned fraction of organic vapors.*

Regarding structural isomers, this limitation is introduced in Section 1, Lines 125-127, where we have stated:

Lines 125-127: *High resolving power TOF-MS allows separation of compounds that are isobaric at unit mass resolution and enables molecular formula assignment, however, without an additional separation dimension (e.g. retention time), it cannot distinguish isomers that share the same chemical formula (Hatch et al., 2017).*

In the limitation subsection of Conclusion, the lines have been revised to acknowledge above limitations as suggested by reviewer. The revised text now reads as follows:

Lines 730-734: *Additionally, while PTR-MS provides high-sensitivity, real-time measurements of organic vapors, it cannot reliably distinguish between structural isomers, which may introduce some uncertainties in compound identification without complementary separation techniques. Furthermore, the compositional analysis and discussion presented in this study are based on the assigned molecular formulas. Therefore, the results should be interpreted within the context of these limitations.*

c) Statistical normalization artificially suppressing MCE trends

Based on PERMANOVA and Mantel tests, the authors conclude that the oxidation regime controls 73% of the absolute compositional variance, claiming that MCE had no structural influence on the relative gas composition (p=0.531). While mathematically true for their specific matrix, this statement contradicts decades of biomass burning literature demonstrating that MCE dictates the primary ratio of flaming vs. smoldering compounds (e.g., hydrocarbons vs. oxygenated species). By applying an aggressive column-wise normalization (z-score scaling per sample), the authors effectively erased the absolute magnitude shifts driven by MCE. The manuscript must clarify that this "independence from MCE" is a direct mathematical artifact of the chosen statistical normalization method rather than a real-world physical independence.

We thank the reviewer for this important comment. We completely agree that MCE is a key parameter dictating both the magnitude and initial composition of biomass burning emissions and this is well established in the literature and shortly discussed in our primary gaseous organic emissions section (Section 3.1, Lines 345-347), where we state *"The EFs of organic vapors varied based upon the biomass fuel type and MCE values, and generally lower MCE values corresponded to higher EFs of organic vapors, excluding two glowing-phase experiments (MCE 0.8 or less) with low EFs values (Vakkari et al., 2026)."* However, the primary objective of this multivariate analysis was not to reassess the influence of MCE on fresh emissions, but rather to evaluate the drivers of relative compositional changes during simulated aging. Because our dataset spans both fresh and aged samples, the statistical framework was specifically designed to isolate which factor governs the transformation of organic vapor profiles over time. While MCE dictates the initial baseline profile and absolute emissions of fresh smoke, the oxidation regime becomes the dominant driver once aging occurs. Column-wise standardization was therefore intentionally applied to compare the relative compositional trajectories across samples, explicitly controlling for differences in absolute emission loading (which scales strongly with MCE). The revised line now states *"Although there was a strong negative correlation between MCE and absolute* ΣEF_{VOC} *(Vakkari et al 2026), it did not structure the relative composition space used for clustering based on the normalized compositional data. "*

Minor comment and correction:

-Figures 1 & 3: The font sizes, labels, and sub-legends within these highly dense figures (especially the Hierarchical Clustering Heatmap) are extremely small and nearly unreadable in standard print. Please increase the font size of axes and colorbar labels for final publication.

We thank the reviewer for pointing this out. Both Figure 1 and 3 have now been updated to improve the overall readability. We have increased the overall figure size, enlarged the font sizes of the axes, labels, colour bar labels and annotations for these figures, thereby improving the overall clarity of the figures in the revised manuscript.

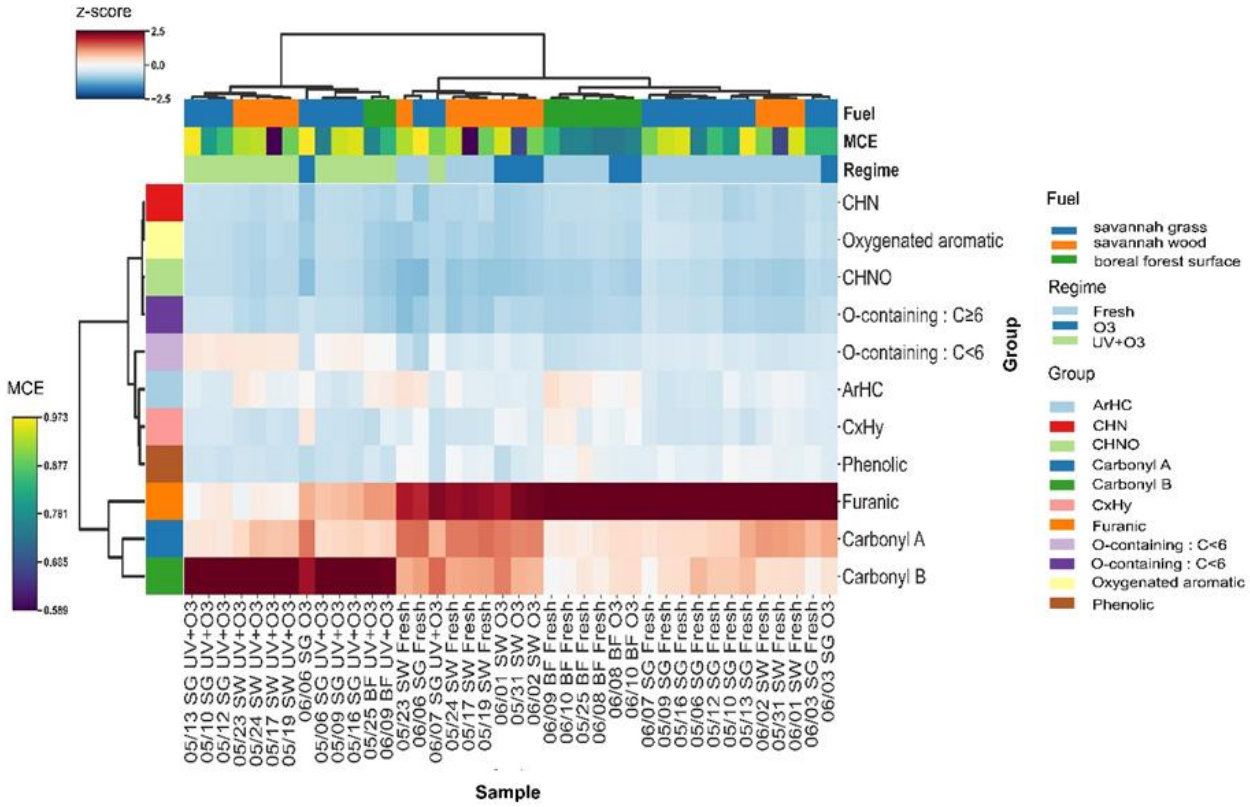

Figure 3. Hierarchically clustered heatmap of standardized mean mixing ratios grouped by compound groups (rows) and regime-resolved samples (columns; date x fuel x regime), with row and column dendrograms summarizing similarities among compound groups and regime-resolved samples, respectively.

Final comment:

The dataset collected via the Vocus PTR-TOF-MS is highly valuable and within the perfect scope of ACP. However, the manuscript requires a more rigorous, self-critical approach regarding laboratory boundaries, chemical simplification limits, and statistical biases before it is ready for publication.

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