Response to Reviewers 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 reviewers: We thank the reviewers 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 1- General comments:

This manuscript presents a characterization of gas-phase emissions from laboratory biomass burning experiments. In particular, the gas-phase analysis is of high quality and constitutes a clear strength of the study. However, important sections lack sufficient detail, such as methodological explanations and the interpretation of results. The absence of reported concentration values is a significant limitation that makes the overall manuscript difficult to follow. There are also concerns regarding the methodology. The approach of calculating emission factors and interpreting them through aging is not appropriate as presented. While the treatment of primary emissions appears appropriate, the way that aging-related processes are presented in the paper requires reconsideration. In particular, primary and secondary contributions should be distinguished, and the methodology used to separate these components must be explicitly described. The terminology "emission factors" should then be revised at the aging processes. Additionally, there are multiple parts where the writing lacks clarity, and the intended meaning is not immediately understandable. Considering these concerns, I recommend major revisions before the manuscript can be considered for publication.

Specific comments:

1- The authors should provide a more detailed description of a representative experiment. Additionally, the presentation of the results requires improvement. Currently, results are expressed only in terms of equivalent time, which makes it difficult to assess the actual duration of experiments within the chamber. The time series of at least one experiment should be showed.

We thank the reviewer for this valuable suggestion. The Material and methods (Section 2) has been revised to provide a more detailed description of a representative experiment. Additional information on the biomass fuels has been included in the Supplementary Information (Table S1).

The experimental procedure now includes details on the chamber mixing period prior to primary measurements and the wall-clock duration of the aging experiments. Furthermore, representative time series of one photochemical and one dark aging experiment for the savannah grass biomass fuel have been added to the Supplementary Information (Figure S2), showing the evolution of the experiments as a function of actual chamber time.

The revised text now reads:

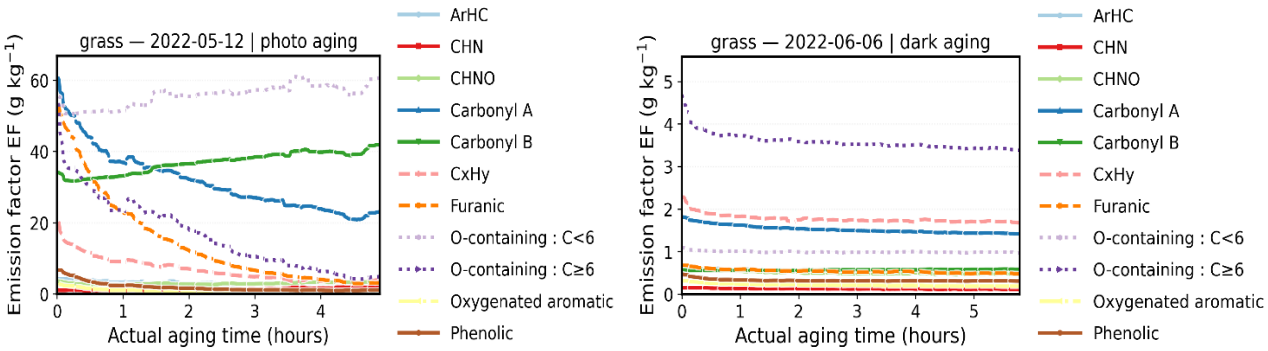
Lines 155-157: *The moisture content was analysed at an accredited laboratory (Eurofins Environment Testing Finland Oy) and was 9.4% for savannah wood, 8.6% for savannah grass and 9.6% for the boreal forest surface, representing dry conditions. More detailed information on the biomass samples is provided in the Table S1.*

Table S1. Description of biomass samples used in the BASFAA campaign

Biomass fuel type	Collection	Species included

Savannah Wood	Grassland savannah environment	Asparagus laricinus, Celtis africana, Euclea undulata, Gymnosporia buxifolia, Pavetta zeyheri, Searsia pyroides, Senegallia caffra, Vachellia erioloba, V. karroo, Vangueria infausta, Zanthoxylum capense and Ziziphus mucronata
Savannah Grass	Grassland savannah environment	Anthephora pubescens, Cymbopogon caesius, Cynodon dactylon, Digitaria argyrograpta, Elionurus muticus, Eragrostis chloromelas, E. lehmanniana, Heteropogon contortus, Setaria sphacelata and Themeda triandra
Boreal forest surface	An experimental fire area located in an even aged 75-year-old Scots pine stand	Mixed surface vegetation, litter and organic soil material

Lines 188-200: *After injection into the chamber and approximately 15 minutes of thorough mixing, a 45-minute period of primary measurements was conducted. After primary measurements, oxidant (O3) was injected into the chamber, and aging experiments were conducted in both photochemical and dark conditions. 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 O3 concentration was used to simulate a full night of atmospheric oxidation over a shorter experimental period. In photochemical aging experiments, O_3 was injected to an initial concentration of 50 ppb to represent regional daytime background atmospheric conditions. Externally added O3 (50 ppb) and H_2O_2 (0.5 mL of 30% v/v solution) in the presence of UV-lights resulted in the formation of OH·, thereby simulating realistic daytime atmospheric oxidation conditions. The aging experiments continued for about 4.5 hours of wall-clock time after the oxidant injection was completed. Representative time series of one photochemical and one dark aging experiment for savannah grass biomass fuel are shown in the Figure S2 in the Supplement.*



2- Lines 146-148: The instrumentation is described in previous work, however, the manuscript would benefit from the inclusion of a general schematic illustrating the experimental setup. In particular, the configuration of the "open-stack setup" is not clearly explained. The reference to Christian et al. (2003) is not sufficient in this regard, as it does not provide a schematic either.

We thank the reviewer for this helpful suggestion. A general schematic illustrating the experimental setup used in the BASFAA campaign, including the open-stack combustion system, smog chamber and sampling instrumentations, has now been included as Supplementary Figure S1 (shown below). Section 2.1 has also

been revised to directs readers to this schematic in Line 175.

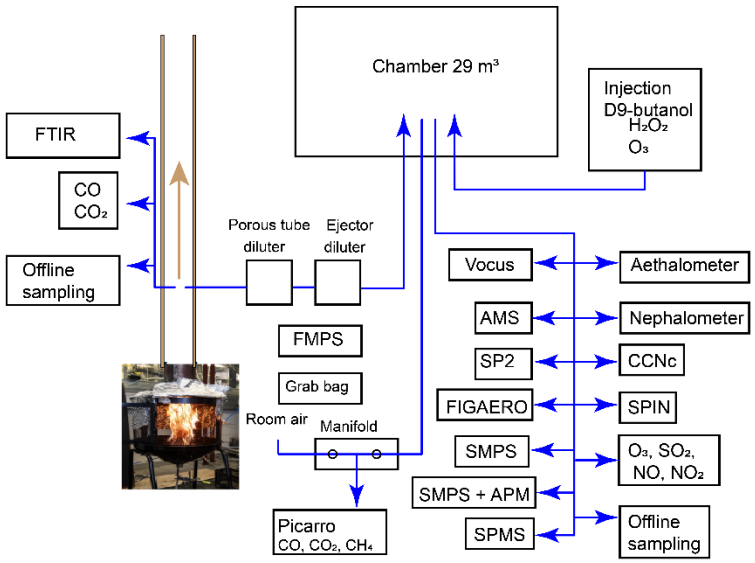


Figure S1. Schematic of the measurement setup in BASFAA campaign (Adapted from (Mukherjee et al., 2025). Savannah grass flaming combustion is pictured as an example.

3- Lines 162-163: Specific information is missing, such as: the injected mass concentration, the dilution ratio, the size distribution of the injected particles, the mass concentration after the oxidation.

We thank the reviewer for pointing this out. We have modified the Supplementary Table S2, which now includes dilution factor, injected mass concentration (Primary OA, µg m^{-3}), primary rBC concentrations (µg m^{-3}), CO_2 and CO concentration (ppm) for each experiment. The median primary size distributions for each biomass fuels, grouped according to MCE ranges, have also been added to the Supplementary Information and is presented in Figure S3. Section 2.2 (Lines 178-182) has also been revised to directs readers to added information. Details regarding OA mass concentrations before and after oxidation are discussed in the response of the following comment 4.

Table S2. Overview of BASFAA experiments including biomass, modified combustion efficiency (MCE), dilution factor, injected mass concentration (POA, µg m^{-3}), primary rBC concentrations (µg m^{-3}), CO_2 (ppm), CO (ppm) and type of aging performed in the chamber

Exp. No.	Date (M.D.Y)	Biomass	MCE	Dilution factor	POA	rBC	CO_2	CO	Aging type
1	05.06.2022	Savannah grass	0.756 ± 0.005	180	16.1	0.381	3.23	1.04	UV light + O_3
2	05.09.2022	Savannah grass	0.943 ± 0.001	490	21.4	0.139	3.64	0.222	UV light + O_3
3	05.10.2022	Savannah grass	0.803 ± 0.004	580	5.7	0.009	0.866	0.213	UV light + O_3
4	05.11.2022	Blank	No combustion	160	0.0	4.14e-05			UV light + O_3
5	05.12.2022	Savannah grass	0.852 ± 0.002	4260	7.1	0.015	0.198	0.034	UV light + O_3
6	05.13.2022	Savannah	0.969 ±	1900	5.0	0.301	2.53	0.080	UV

		grass	0.0005						light + O_3
7	05.16.2022	Savannah grass	0.952 ± 0.001	840	26.2	0.357	2.85	0.145	UV light + O_3
8	05.17.2022	Savannah wood	0.589 ± 0.055	380		0.120	0.090	0.062	UV light + O_3
9	05.19.2022	Savannah wood	0.886 ± 0.003	440	23.0	0.229	0.579	0.074	UV light + O_3
10	05.23.2022	Savannah wood	0.929 ± 0.001	1030	12.7	1.287	2.72	0.207	UV light + O_3
11	05.24.2022	Savannah wood	0.935 ± 0.001	800	29.8	1.564	3.24	0.226	UV light + O_3
12	05.25.2022	Boreal forest	0.763 ± 0.009	140	41.6	0.255	1.22	0.380	UV light + O_3
13	05.31.2022	Savannah wood	0.672 ± 0.022	350	32.0	0.083	0.204	0.099	O_3
14	06.01.2022	Savannah wood	0.950 ± 0.001	200	16.1	0.703	2.18	0.115	O_3
15	06.02.2022	Savannah wood	0.892 ± 0.002	340	47.1	0.335	1.15	0.140	O_3
16	06.03.2022	Savannah grass	0.843 ± 0.002	770	38.3	0.219	1.35	0.251	O_3
17	06.06.2022	Savannah grass	0.973 ± 0.0004	1590	19.7	0.773	4.90	0.134	O_3
18	06.07.2022	Savannah grass	0.895 ± 0.002	290	49.9	0.365	2.76	0.322	UV light + O_3
19	06.08.2022	Boreal forest	0.743 ± 0.006	290	52.6	0.011	0.787	0.272	O_3
20	06.09.2022	Boreal forest	0.839 ± 0.003	310	15.2	0.443	0.926	0.178	UV light + O_3
21	06.10.2022	Boreal forest	0.758 ± 0.009	170	22.5	0.681	0.722	0.230	O_3

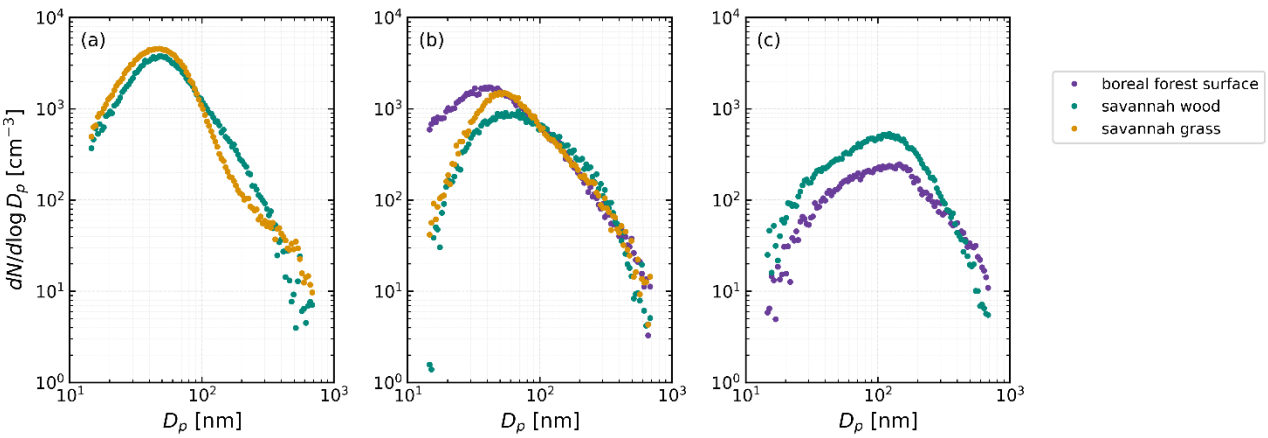


Figure S3. The median primary size distributions grouped according to MCE ranges for savannah grass, savannah wood and boreal forest surface

4- The paper provides a strong analysis of the gas phase, however, it would benefit from including some basic information on the particle phase. In particular, the OA mass before and after oxidation should be reported, as it is currently unclear whether additional mass was produced during these experiments. Also, it would be useful to include BC concentrations. Finally, the manuscript would benefit from a metric or indicator demonstrating that consistent burning conditions were maintained across all experiments.

We thank the reviewer for this comment. BC concentrations for each experiment have also been added to the Supplementary Table S2 as presented in the response of comment 3.

The new/secondary OA formation was studied in detail in Kommula et al. 2026. Their analysis shows that multiple experiments showed an initial increase in total OA mass concentration followed by a decrease to values similar to the OA concentration during the primary period. In brief, new OA is formed, at the same time, primary OA is lost via evaporation and/or reactions in the particle phase. For most experiments, these two processes balanced each other so that after 0.5 eqv. days of atmospheric aging, very little change in net OA is observed.

Regarding the burning conditions, we would like to clarify that the objective of BASFAA campaign was not to maintain identical combustion conditions across the experiments. Rather, the experiments were intentionally designed to span a range of combustion conditions, from smoldering to flaming combustion, in order to investigate how combustion characteristics influence primary emissions (Vakkari et al., 2026) and their atmospheric aging.

5- Line 165: The authors could add an explanation for their choice to add O3 into the photochemistry experiments in addition to H2O2.

Thank you for mentioning this. We have expanded the description of the photochemical aging protocol in Section 2.2 (Lines 196-198) to clarify the rationale for adding O_3 in addition to H_2O_2. The revised text reads as follows:

Lines 196-198: *externally added O_3 (50 ppb) and H_2O_2 (0.5 mL of 30% v/v solution) in the presence of UV-lights resulted in the formation of OH·, thereby simulating realistic daytime atmospheric oxidation conditions in which multiple oxidants co-exist.*

In addition, its important to note that several VOCs, including monoterpenes such as myrcene and oxygenated monoterpenes such as linalool are degraded at similar rates by O_3 and OH·, while α-terpinene reacts even more rapidly with O_3 than with OH·(Atkinson and Arey, 2003).

6- Lines 166-167: The manuscript could be benefited by a small discussion of the reason why different quantities of O_3 were injected for night vs day experiments. Also, the O_3 concentrations could be added for every experiment.

Thank you for this suggestion. We agree that the small discussion on injection of different O_3 quantities in night vs day experiment will improve the manuscript. Specifically, an initial O_3 concentration of 50 ppb was used during photochemical aging experiments to represent regional daytime background of atmospheric oxidation conditions, whereas 100 ppb was used during dark aging experiments to simulate a full night of atmospheric oxidation over a shorter experimental period. This has been added in the revised text as follows:

Lines 193-196: *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. In photochemical aging experiments, O_3 was injected to an initial concentration of 50 ppb to represent regional daytime background atmospheric conditions.*

Additionally, O_3 concentrations for the dark aging experiments have now been added to the Supplemental

Table S4 as follows:

Table S4. Overview of O_3 concentration (molecules cm^{-3}) and O_3 exposure (molecules cm^{-3} s) at the end of dark aging experiment

Date (M.D.Y)	**Biomass**	**Aging type**	**O_3 concentration (molecules cm^{-3})**	**O_3 exposure (molecules cm^{-3} s)**
05.31.2022	Savannah wood	O_3	2.48e+12	5.02e+16
06.01.2022	Savannah wood	O_3	2.38e+12	4.60e+16
06.02.2022	Savannah wood	O_3	2.57e+12	5.34e+16
06.03.2022	Savannah grass	O_3	2.70e+12	5.34e+16
06.06.2022	Savannah grass	O_3	2.36e+12	5.25e+16
06.08.2022	Boreal forest	O_3	2.28e+12	4.91e+16
06.10.2022	Boreal forest	O_3	2.38e+12	4.87e+16

7- Lines 179-182: It is not clear why this averaging happened.

We thank the reviewer for this comment. For primary emissions, data were averaged over a period of 30 minutes before the addition of oxidants to represent the fresh emission after the chamber mixing. For aged emissions, data were averaged over the interval corresponding to 0.5 equivalent aging days because the extent of aging varied between different experimental days under different oxidant exposure. Hence, using a common equivalent aging reference point allowed for a direct comparison on how different chemical classes responded to photochemical and dark oxidation regimes. The corresponding text has been revised in Section 2.2 to state that the averaging provides ‘‘a standardized reference point for comparing photochemical and dark aging experiments conducted on different days under different oxidant exposures” (Lines 215-216).

8- Lines 250-253: The reason for performing an outlier analysis is not clear. This type of analysis may be useful for field measurements, but its use in controlled laboratory experiments needs to be better explained. The authors should clarify why outliers would be expected in this case and which were the ones that were identified.

We thank the reviewer for this comment. Although the experiments were conducted under controlled laboratory conditions, isolated instrumental spikes can still occur in PTR-MS measurements. To identify such outliers in the measurement, outlier detection was performed using a Hampel filter (median ± median absolute deviation) (Pearson et al., 2016)for each detected ion. At each time step, a robust z-score was calculated as the absolute deviation from the local median divided by 1.4826×MAD. Data points with a robust z-score larger than the threshold ($k \approx 5$) were flagged as candidate spikes. Isolated spikes were removed only when they occurred as short excursions (<3 points); longer changes were retained as genuine temporal variability. Overall, the filter identified only 0.28% of all measurements as outliers, leaving 99.72% of the measurements unchanged. We have clarified this in the revised manuscript in Line 298.

9- Lines 259-263: The authors should clarify why certain carbonyl compounds increase while others decrease. It would be helpful to identify any common characteristics within each group (e.g., molecular weight, carbon number, or chemical structure) and to discuss whether a systematic pattern can be observed.

We thank the reviewer for this comment. We have clarified that the Carbonyl A/B classification was initially based on the observed temporal trends during the photochemical aging, but the two groups also show chemically interpretable differences. For e.g. Carbonyl A class are generally dominated by reactive primary carbonyls, including unsaturated carbonyl compounds such as acrolein, crotonaldehyde and methyl-vinyl ketone (MVK), which are depleted during OH-driven oxidation (Line 456-457). On the other hand, Carbonyl B class contains a larger contribution from oxygenated compounds, particularly organic acids and other

secondary oxidation products (Line 470-471), which are formed as result of oxidation of reactive biomass burning precursors.

10- The use of the term "emission factors" in the context of aged or secondary products is not appropriate and may be misleading. I recommend that the authors both clarify their methodology for distinguishing primary and secondary processes and revise the terminology accordingly.

We thank the reviewer for this comment. We would like to note that the use of emission factors (EFs) for species quantified after aging is an established approach in laboratory combustion studies. For example, (Heringa et al., 2011)reported EFs for primary organic aerosol (POA) together with secondary organic aerosol (SOA) expressed in terms of gkg^{-1} wood burned. Likewise, Tiitta et al. (2016) quantified SOA EFs (mg kg^{-1} fuel), and Miersch et al. (2019) calculated SOA EFs using the same carbon mass balance approach as primary EFs. More recently, Kokkola et al. (2026)reported EFs for fresh and photochemically aged combustion aerosols. Accordingly, we consider the term "emission factors" appropriate in this manuscript.

11- Section 3.2: The manuscript could be benefited by adding how much the OH was in each experiment.

We thank the reviewer for this suggestion. The final OH exposures ranged from 1.3×10^{11} to 2.57×10^{11} molecules cm^{-3} s (assuming 24-hr average ambient [OH] = 1.5×10^{6} molecules cm^{-3}). We have further added OH· concentration and exposure for each photochemical aging experiment in the Supplemental Table S3 as follows:

Table S3. Overview of OH· concentration (molecules cm^{-3}) and OH· exposure (molecules cm^{-3} s) at the end of photochemical aging experiment

Date (M.D.Y)	**Biomass**	**Aging type**	**OH· concentration (molecules cm^{-3})**	**OH· exposure (molecules cm^{-3} s)**
05.06.2022	Savannah grass	UV light + O_3	8.70e+06	1.52393e+11
05.09.2022	Savannah grass	UV light + O_3	1.17e+07	2.5054e+11
05.10.2022	Savannah grass	UV light + O_3	8.27e+06	1.46373e+11
05.12.2022	Savannah grass	UV light + O_3	8.65e+06	1.48994e+11
05.13.2022	Savannah grass	UV light + O_3	1.06e+07	1.99796e+11
05.16.2022	Savannah grass	UV light + O_3	8.87e+06	1.56482e+11
05.17.2022	Savannah wood	UV light + O_3	8.65e+06	1.54601e+11
05.19.2022	Savannah wood	UV light + O_3	8.33e+06	1.62959e+11
05.23.2022	Savannah wood	UV light + O_3	9.24e+06	1.81906e+11
05.24.2022	Savannah wood	UV light + O_3	8.92e+06	1.60554e+11
05.25.2022	Boreal forest	UV light + O_3	7.40e+06	1.2604e+11
06.07.2022	Savannah grass	UV light + O_3	7.38e+06	1.27031e+11
06.09.2022	Boreal forest	UV light + O_3	8.36e+06	1.66065e+11

Section 2.2 (Lines 210-212) has also been revised to directs readers to added information.

12- It is unclear whether blank experiments were performed to assess the background contributions of each gas species after aging.

We thank the reviewer for pointing this out. Yes, blank experiments were performed to assess the background contributions of each gas species before and after aging. We have added this information in Section 2.2 (Lines 182-185). The revised text now reads as follows:

Lines 182-185: *A blank experiment was conducted on 11 May 2022 following the same experimental procedure as the BB experiments, except that no biomass fuel was burned (Table S2). No measurable background signals were observed for the monitored gas species either before or after aging during the blank*

experiment.

13- Lines 453-458: Have the authors checked the volatility of the fresh vs aged gases? Wall losses can reduce the gas phase but not as significantly as the particle phase (for Teflon chambers), so it could not be the main reductor. How much time did each experiment last?

We thank the reviewer for this comment. While the volatility of the aged gas-phase composition was not evaluated in this study, the volatility of the fresh emissions from the same BASFAA campaign was characterized in detail in the companion paper by Vakkari et al. (2026), where effective saturation vapor concentrations (C*) of the primary gas- and particle-phase emissions were determined using a Filter Inlet for Gases and AEROsols (FIGAERO) coupled to a time-of-flight chemical ionization mass spectrometer (TOF-CIMS).

Regarding the wall losses, our statement was not intended to imply that the gas-phase wall losses were the dominant cause of the observed decrease in organic vapor EFs, but rather one potential contributing process. 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.

After injection of the smoke and about 15 mins of mixing in the chamber, the primary emission experiments were made for about 45 minutes by sampling from the chamber. Aging emission experiments lasted for over 4.5 hr each day. This information has been described in the Section 2.2 Line 188 and Lines 198-199 of the revised manuscript.

14- Lines 470-479: The introduction of O_3 in the OH experiments complicate the attribution of observed reactivity. It is not clear why the authors chose to study mixed chemistry. In addition, key information is missing: OH and O_3 concentrations for each experiment are not reported, which limits the ability to interpret the relative oxidation processes and access the reactivity.

Thank you for this comment. The objective of photochemical aging experiments was to investigate the evolution of BB emissions under realistic atmospheric oxidation conditions using a mixture of oxidants rather than a single oxidant. We have addressed this point in our response to comment 5, and revised the manuscript accordingly (Lines 190-193).

We agree with the suggestion of the reviewer. At the end of photochemical aging experiments, the final OH exposures ranged from 1.3×10^{11} to 2.6×10^{11} molecules cm^{-3} s (Lines 202-204). Similarly, 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 (Lines 208-209). This information has been added in the revised manuscript.

We have now added the OH and O_3 concentrations (molecules cm^{-3}) and exposure (molecules cm^{-3} s) for all experiments to the Supplementary Information (Table S3 and Table S4). A corresponding reference to this table has also been included in the revised manuscript in Lines 211-212.

Table S3. Overview of OH· concentration (molecules cm^{-3}) and OH· exposure (molecules cm^{-3} s) at the end of photochemical aging experiment

Date (M.D.Y)	**Biomass**	**Aging type**	**OH· concentration molecules cm^{-3}**	**OH· exposure molecules cm-3 s**
05.06.2022	Savannah grass	UV light + O_3	8.70e+06	1.52393e+11
05.09.2022	Savannah grass	UV light + O_3	1.17e+07	2.5054e+11
05.10.2022	Savannah grass	UV light + O_3	8.27e+06	1.46373e+11
05.12.2022	Savannah grass	UV light + O_3	8.65e+06	1.48994e+11
05.13.2022	Savannah grass	UV light + O_3	1.06e+07	1.99796e+11
05.16.2022	Savannah grass	UV light + O_3	8.87e+06	1.56482e+11

05.17.2022	Savannah wood	UV light + O_3	8.65e+06	1.54601e+11
05.19.2022	Savannah wood	UV light + O_3	8.33e+06	1.62959e+11
05.23.2022	Savannah wood	UV light + O_3	9.24e+06	1.81906e+11
05.24.2022	Savannah wood	UV light + O_3	8.92e+06	1.60554e+11
05.25.2022	Boreal forest	UV light + O_3	7.40e+06	1.2604e+11
06.07.2022	Savannah grass	UV light + O_3	7.38e+06	1.27031e+11
06.09.2022	Boreal forest	UV light + O_3	8.36e+06	1.66065e+11

Table S4. Overview of O_3 concentration (molecules cm^{-3}) and O_3 exposure (molecules cm^{-3} s) at the end of dark aging experiment

Date (M.D.Y)	**Biomass**	**Aging type**	**O_3 concentration molecules cm^{-3}**	**O_3 exposure molecules cm-3 s**
05.31.2022	Savannah wood	O_3	2.48e+12	5.02e+16
06.01.2022	Savannah wood	O_3	2.38e+12	4.60e+16
06.02.2022	Savannah wood	O_3	2.57e+12	5.34e+16
06.03.2022	Savannah grass	O_3	2.70e+12	5.34e+16
06.06.2022	Savannah grass	O_3	2.36e+12	5.25e+16
06.08.2022	Boreal forest	O_3	2.28e+12	4.91e+16
06.10.2022	Boreal forest	O_3	2.38e+12	4.87e+16

15- The manuscript would benefit from reporting the concentrations of key species such as carbon monoxide (CO) and carbon dioxide (CO_2) for each experiment. In addition, the presence and levels of levoglucosan should be specified.

Thank you for this valuable suggestion. We have added background subtracted carbon monoxide (Δ CO, ppm) and carbon dioxide (ΔCO_2, ppm) concentrations for each experiment to the Supplementary Information (Table S2, presented above in the response of comment 3). A reference to this table has also been included in the revised manuscript (Section 2.2, Line 181).

Levoglucosan was not discussed separately in this paper but was included within the O-containing compounds with C≥6 class. The ion $C_6H_{11}O_5^+$ (m/z 163.06), tentatively assigned as levoglucosan and presented in Table S6 in Supplementary Information, was detected in the gas-phase. However, it's important to note that levoglucosan is a semi-volatile compound close to the low-volatility organic compound (LVOC) boundary, and hence its gas-phase contribution is expected to be low. Therefore, gas-phase EFs represent only a small fraction of the total levoglucosan emissions. A detailed discussion of levoglucosan as a particle-phase BB marker from the same research campaign is provided in the companion paper, which focuses on the characterization of organic aerosol using a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) (Kommula et al., 2026).

16- Figure 3 is difficult to follow in its current form

We thank the reviewer for pointing this out. To improve its readability, we have increased the overall figure size and enlarged the font sizes of the axes, labels, colorbar labels, and annotations which has now improved the overall clarity of the figure in the revised manuscript.

17- Line 572: "29-35% in savannah grass » it seems like a range when it should show as from x to y%. Also, I have some concerns about how this part is presented. First, the increases are not so big (in figure 5, the image does not change much between the different cases). Secondly, how much is the uncertainty of those percentages? And thirdly, I would like to see the differences in absolute concentrations rather than only in percentages.

We thank the reviewer for this valuable comment. We agree that the original wording was not clear and have revised it to state that the relative contribution changed from x% to y%, rather than presenting the values as a range (Lines 623-624).

The relative class contributions were calculated from pooled measurements within each biomass and aging condition. To better account for experiment-to-experiment variability, we recalculated the class contributions separately for each independent experiment and then determined the mean relative contribution and standard deviation across experiments. We have updated Figure 5 accordingly. The revised analysis resulted in only minor changes to the reported mean percentages while providing a statistically more appropriate estimate of the variability across experiments. The updated Figure 5 is as follows:

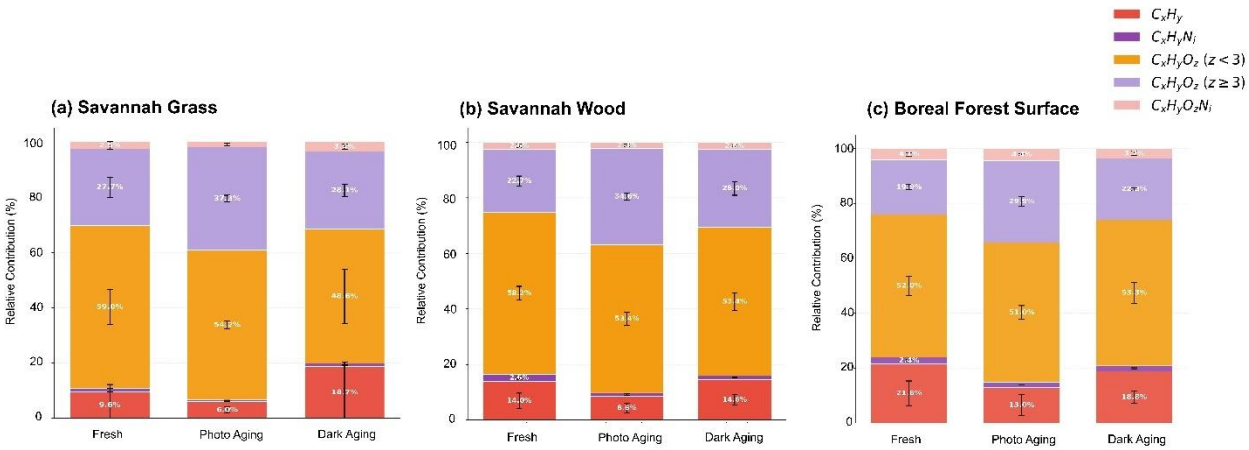


Figure 5. Stacked bar plots showing the mean relative contribution (%) of compound classes (CxHy, CxHyOz (z<3), CxHyOz (z⩾3), CxHyNi and CxHyOzNi) to the total mean mixing ratio (ppbv) for (a) savannah grass, (b) savannah wood and (c) boreal forest surface under fresh, photochemical aging and dark aging conditions. Error bars indicate the standard deviation; n = 9, 7 and 2 (savannah grass); n= 7,4 and 3 (savannah wood) and n= 4, 2 and 2 (boreal forest surface) for fresh, photo aging and dark aging conditions.

We additionally checked the absolute class-resolved mixing ratio based on elemental composition. However, these showed experiment-to-experiment variability and did not show any consistent trend across biomass fuel and aging conditions for this kind of classification. We have therefore revised and clarified in the text that the discussion here (Lines 620-624) refers to changes in relative class contributions rather than absolute mixing ratios.

18- Boreal forests are located in Scandinavia. So, the argument in the introduction linking climate change impacts on boreal forests is not particularly strong. For instance, regions such as the Mediterranean are expected to be more significantly affected by climate change. A brief revision in this presentation statement would strengthen the introduction section.

We thank the reviewer for this helpful suggestion. We have revised the Introduction to strengthen the motivation for including boreal forest BB and its implication in the context of climate change (Lines 53-61). The revised text reads as follows:

Lines 53-61: *Global warming has increased the frequency, intensity and behavior of wildfires in recent decades, making wildfires an important source of atmospheric pollution over time (Rogers et al., 2020). Recent evidence shows over twofold increase in frequency and magnitude of extreme wildfire events, with the largest increases occurring in the carbon-rich boreal and temperate conifer forests of the Northern Hemisphere (Cunningham et al., 2024). The long-range transport of wildfires from northern boreal regions like Siberia is known to affect the radiative balance and aerosol composition in the sensitive ecosystem of the Arctic region (Calì Quaglia et al., 2022; Schneider et al., 2024). Moreover, long-range transport of wildfire emissions in Canada substantially decreased the air quality in metropolitan areas of the US East Coast (Kolden et al.,*

2024). These findings highlight the increasing importance of understanding emissions from boreal forest wildfires and their atmospheric impacts.

19- Lines 461-466: The manuscript would benefit from reporting the concentration of NO2 in this study, as together with O3 they can create NO3 that can be a significant oxidant for dark chemistry

We thank the reviewer for this comment. NOx concentrations were monitored and remained below 10 ppb and under these low-NOx conditions, formation of NO_3 radical is expected to be limited during the dark aging experiments as mentioned in Section 2.2 (Lines 205-207). We have checked the response of phenolic compounds to dark aging, as they react rapidly with NO_3 radical, and we found that the phenolic compounds showed negligible or only minor reductions in EFs in dark aging experiments (Lines 512-515). Together, the low NOx concentrations and limited changes in the phenolic compounds support our interpretation that the NO_3 radical formation was limited and dark aging was primarily driven by O3 oxidation.

Technical comments:

Add a small explanation of what MCE is

We have modified and added the explanation of MCE in Section 2.4, Lines 274-279. The revised text reads as follows:

Lines 274-279: *MCE provides a measure of combustion characteristics that reflects the relative contributions of flaming and smoldering combustion and is defined as the ratio of CO2 to sum of CO2 and CO emissions (Ward and Radke, 1993;Akagi et al., 2011). Flaming combustion is typically associated with MCE values larger than 0.1, whereas smoldering combustion is associated with MCE values smaller than 0.9 (Akagi et al. (2011); Yokelson et al., 1999).MCE values between 0.8-0.9 represent a mix of flaming and smoldering combustion (Jen et al., 2019). In this study, MCE was calculated as a function of time using primary CO_2 and CO concentrations following Akagi et al. (2011).*

Line 65: Please rephrase. Either/or

We thank the reviewer for this suggestion. The sentence has been rephrased accordingly (Lines 66-68).

Line 67: Please add a reference. Are these in the emission inventories high?

We thank the reviewer for this comment. We have revised the statement and added references from global fire emission inventory studies (van der Werf et al., 2017, 2025) which shows that savannah fires account for nearly half of global fire-derived carbon emissions (Lines 69-71).

Line 69: Part the explanation is because in US there are a lot of boreal forests, while in Europe not so much. The surface area of these forests in the 2 continents is very different.

We thank the reviewer for this helpful comment. We agree that the greater spatial extent of North American boreal forests contributes to their more extensive representation in the literature. We have therefore revised the text to acknowledge this point and to distinguish the contrasting fire regimes between North American and European boreal forests. The revised text reads as follows:

Lines 72-78: *North American boreal forests have been studied more extensively (Boby et al., 2010; Zhao et al., 2021), partly because of their greater extent and the prevalence of high-intensity crown fires. In contrast, European boreal forests, which are dominated by lower-intensity surface fires, remain comparatively understudied (Köster et al., 2024). Since boreal forests form a continuous circumpolar belt from Scandinavia across European Russia to Siberia, results from Finnish biomass-burning emissions are also relevant for eastern high latitudes as a representation of the boreal fire regime, although there can be regional differences in fuel moisture and fuel/stand composition expected along an eastward gradient.*

Lines 70-71: Please add all the processes. Heterogeneous reactions and dilution are part of the story but so is

evaporation and gas-phase oxidation. I can see that these are mentioned later in line 76, so maybe this part could be changed to be more easily followed.

We thank the reviewer for this suggestion. The paragraph has been revised to provide a more comprehensive description of the key processes governing the atmospheric evolution of biomass burning plumes. The revised text now reads as follows:

Lines 79-86: *The atmospheric evolution of the BB plume is a complex process governed by several interacting processes including gas-phase oxidation, heterogeneous chemistry, evaporation and condensation of semi-volatile compounds, and plume dilution. Functionalization and oligomerization reactions produce low volatility gas-phase species that gradually condense to form SOA; however, continued oxidation promotes fragmentation reactions, resulting in lower SOA yields (Kroll et al., 2009; Lambe et al., 2012). Plume-dilution can cause condensed semi-volatile compounds to evaporate, reducing the organic loading (Pagonis and Ziemann, 2018; Palm et al., 2020) These evaporated compounds may recondense after further oxidation, continuously altering the composition and properties of organic vapors (Akagi et al., 2012; Garofalo et al., 2019; Mason et al., 2001).*

Lines 79-81: Part of this is that in the atmosphere these transformations happen fast so bbOA is part of the SOA

We thank the reviewer for this comment. We agree that rapid atmospheric oxidation of BB plumes can lead to the early formation of BB-derived secondary organic aerosol (SOA), making it increasingly difficult to distinguish between primary organic aerosol (POA) and SOA in the atmosphere. We have revised the introduction (Lines 88-92) to acknowledge this when discussing the discrepancy between ambient observations and laboratory smog chamber studies. The revised text reads as follows:

Lines 88-92: *There exists a discrepancy between ambient wildfire plumes and those aged in laboratory smog chambers with respect to net SOA formation with aging, smog chamber studies generally indicating stronger SOA formation (Hodshire et al., 2019). This discrepancy may partly arise from rapid atmospheric oxidation of ambient BB plumes, which promotes the early formation of BB-derived SOA and makes it increasingly difficult to distinguish between primary organic aerosol (POA) and SOA.*

Lines 147-148: Please rephrase for clarity

We thank the reviewer for this suggestion. The text has been revised for improving clarity by separating the description of the open-stack combustion setup, fuel bed dimensions, and sample holder sizes for the different biomass fuels. The revised text now reads as follows:

Lines 160-163: *Combustion was conducted under an open-stack setup designed to mimic natural burning and dilution conditions, following the approach by Christian et al., 2003, but on a smaller scale. The fuel bed had a diameter of approximately 50 cm. A 6 cm diameter sample holder was used for savannah biomasses, whereas a 23 cm diameter sample holder was used for the boreal forest surface to accommodate larger fuel load.*

Lines 148-149: Please explain why different diameters were used for the different fuels

We thank the reviewer for this comment. Different sample holder diameters were used because the physical characteristics of the biomass fuels differed. The boreal forest surface fuel consisted of a bulkier and more heterogenous fuel bed i.e. vegetation, litter and organic soil horizon (Line 152), and required a larger sample holder to accommodate the larger fuel load (described in revised manuscript Line 163) while preserving the representative fuel bed structure during combustion. In contrast, savannah biomass fuels were more compact and therefore, were burned in the smaller sample holder.

Line 150: Parenthesis opens and never closes

We thank the reviewer for noticing this. The typographical error has been corrected in the revised manuscript (Line 164).

Line 157: Please explain why different RH was used. Could the differences in RH affect the chemical results?

We thank the reviewer for this comment. The manuscript has been revised to clarify the rationale for using different relative humidity (RH) conditions. Specifically, the RH was selected to replicate the characteristic RH conditions for each environment during active fire season. The revised text reads as follows:

Lines 171-174: *The relative humidity inside the chamber was maintained at 20% for savannah grass and savannah wood experiments and 50% for boreal forest surface experiments to replicate characteristic daytime relative humidity conditions for each environment during active fire seasons, using the humidification setup described in (Leskinen et al., 2015).*

We acknowledge that differences in RH can potentially influence the atmospheric oxidation chemistry and SOA formation, and previous smog chamber studies (Chen et al., 2021; Hu et al., 2011) have specifically investigated the effects of RH on these processes. However, the objective of our study was not to investigate RH-dependent chemistry, but rather to investigate the evolution of BB emissions under characteristic daytime RH conditions for each ecosystem during active fire seasons.

Line 171: Please add reference for the average OH.

We thank the reviewer for this suggestion. References supporting the average ambient OH concentrations used to calculate the equivalent photochemical age (Cheung et al., 2025; Mukherjee et al., 2025) have been now added in the revised manuscript (Lines 204-205).

Line 238: “flue-gas” seems to be a typo here

We thank the reviewer for pointing this out. This has been corrected in the revised manuscript (Line 278).

Line 238: “as per” Please rephrase for clarity

We thank the reviewer for this suggestion. The text has been rephrased for improved clarity in the revised manuscript (Lines 278-279).

Line 244-246: Please add a better explanation. It is not mentioned what is “i” and what is “j”.

We thank the reviewer for pointing this out. We have revised the description of equation 2 to define the indices *i* and *j*, thereby improving the clarity for EF calculation. The revised text now reads as follows:

Lines 285-289: *Here, EFi 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) with respect 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.*

Line 248: Please add how Fc was calculated

We have included the details in Method section to clarify how the fuel carbon fraction (Fc) was determined. The revised text now reads as follows:

Lines 291-293: *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).*

Line 261: “Compounds with ≥80% experiments showing a negative slope” please rephrase for clarity

We thank the reviewer for this comment. The text has been rephrased for improved clarity. The revised text now reads as follow:

Lines 304-308: *For each compound, a robust Theil-Sen estimator was used to calculate the slope of its EF over the ageing period across biomass type. Compounds were assigned to carbonyl A class if they exhibited a negative slope (decreasing trend) in at least 80% of the experiments, whereas compounds exhibiting a positive slope (increasing trend) in at least 80% of the experiments were assigned to carbonyl B class.*

Line 303: What do the authors mean by glowing-phase?

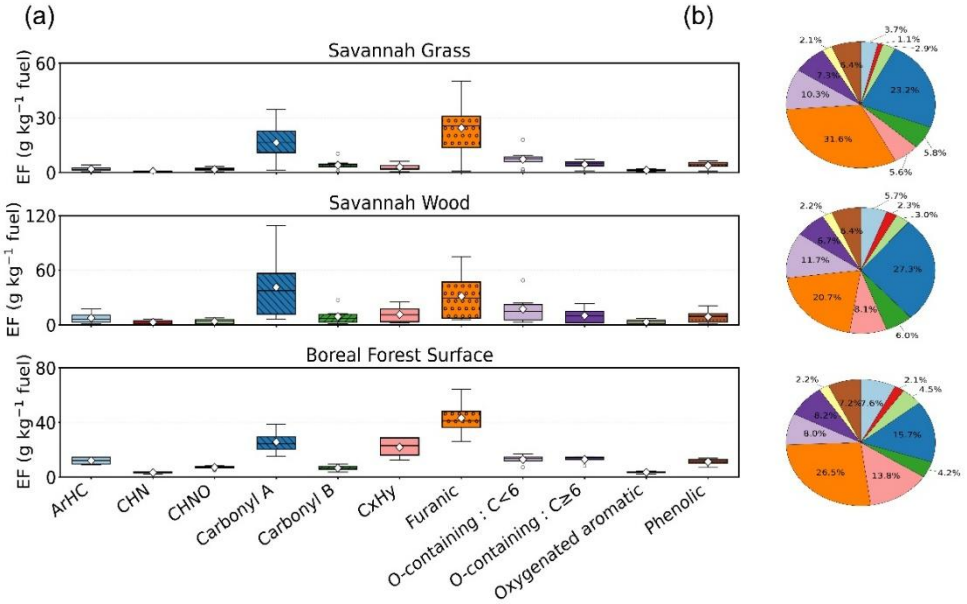
We thank the reviewer for this comment. Glowing combustion refers to the post-flaming combustion stage dominated by char oxidation. In this study, two savannah experiments with MCE 0.8 or less were identified as glowing phase experiments and represented the phase after flames had died down following the definition of Vakkari et al. (2026). This has now been clarified in the revised manuscript (Lines 348-349).

Line 319: IQR acronym name. Please name all the acronyms the first time you use them

We thank the reviewer for pointing this out. To improve readability, IQR (Interquartile Range) has now been defined in the figure caption (Line 364). In addition, the manuscript has been cross-checked to ensure that all acronyms are defined at their first occurrence.

Figure 1: Please add percentages to pie charts. Also write in the figure caption that different axes are used in EF. Also, were these gases measured with the PTRMS? If yes, how were the hydrocarbons measured?

We thank the reviewer for this suggestion. The requested percentages have now been added to the pie charts in Figure 1. We have also revised the figure caption to clarify that different Y-axes are used for the emission factor (EF) as follows:



Yes, these gases, including hydrocarbons (CxHy), were measured using Vocus PTR-MS. The high mass resolution of PTR-TOF-MS allowed molecular formula assignment of the detected ions, which were then grouped into various compound classes similar to previous combustion studies (Bhattu et al., 2019; Hartikainen et al., 2024; Wang et al., 2025). The CxHy class does not include alkanes, which are not efficiently detected by PTR-TOF-MS, as also clarified in the Lines 223-225.

Figure 2 is not helpful. Maybe one diagram per fuel type and the rest to the SI.

We thank the reviewer for this comment and we accept this suggestion. Figure 2 has been revised to include one diagram for each biomass fuel in photochemical and dark aging experiment each, and remaining diagrams

have been moved to Supplementary Information (Figure S2). The corresponding discussion in the Section 3.2 has been revised accordingly.

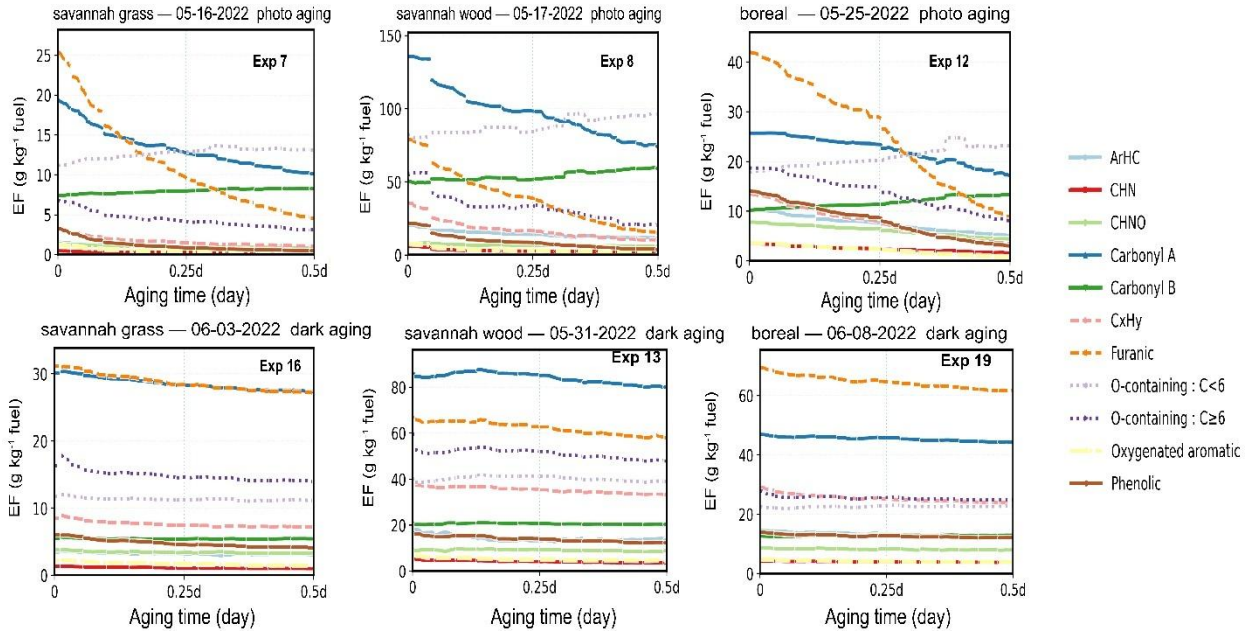


Figure 2. Chemical evolution of organic vapors categorized by functional groups during aging in the smog chamber. The x-axis shows equivalent aging time up to 0.5 eqv. Day, and y-axis represents emission factors (EFs; g kg^{-1} fuel). One selected photochemical aging experiment and one selected dark aging experiment are shown for each biomass fuel and the remaining experiments are provided in the Figure S4. Aging time t=0 represents when UV light was switched on for photochemical aging experiments or when O_3 was injected for dark-aging experiments.

Lines 370-372: 3 or 2 pathways? Seems like 2 are explained.

We thank the reviewer for pointing this out. The text has been revised to explicitly identify the three major OH reaction pathways, namely H-atom abstraction, OH addition to C=C bonds, and OH addition to the aromatic rings. Revised text now reads as follows:

Lines 416-419: *In general, OH· reacts with VOCs via three main pathways, including H-atom abstraction, OH· addition to C=C bonds and OH· addition to aromatic rings, which accelerate the depletion of unsaturated and aromatic classes and drive the formation of more oxygenated products (Ziemann & Atkinson, 2012).*

Line 414: please remove “by”

Thank you. Corrected.

Line 438: “R ranges” maybe R2? (R range in SI also)

Thank you. We would like to clarify that the reported values in Lines 487-488 and Supplemental Figure S7 refer to Pearson correlation coefficients (R) rather than R^2.

Figure 4: Please add percentages to the pie chart

We thank the reviewer for this suggestion. The percentages have now been added to the pie charts in Figure 4

in the revised manuscript.

Line 570: “>3” change to (z>3)

Thank you. Corrected.

Line 571: parenthesis open is in subscript

Thank you. Corrected.

Line 577: Please add what is DBE

Thank you. DBE (double bond equivalent) is defined at its first occurrence in Line 310 in the Section 2.4.

Figure 5: x,y, etc. Please make them subscripts.

We thank the reviewer for this suggestion. We have updated Figure 5 where x,y,z and i are now presented in subscripts.

Line 621: please rephrase for clarity

We thank the reviewer for this comment. The sentence has been rephrased for improved clarity in the revised manuscript and now reads as follows:

Lines 673-674: This fragmentation-dominated aging modulates radical (HOx) and O3 chemistry while generating oxygenated products that can undergo further oxidation and may contribute to SOA formation.

Lines 653-657: how much are the SOA yields of these compounds?

We thank the reviewer for this comment. We acknowledge that the SOA yields of individual precursor compounds or compound classes were not quantified in this study. However, Previous BB laboratory studies show that phenolic compounds have SOA yield in the range of 24-44% (Yee et al., 2013), while furanic compounds have been reported to produce SOA yields of upto 16% (Romanias et al., 2024). These references have now been included in the revised manuscript to support the role of these compounds as SOA precursors. The revised text now reads as follows:

Lines 708-712: *Previous BB laboratory studies show that phenolic compounds have SOA yield of 24-44% (Yee et al., 2013), while furanic compounds have been reported to produce SOA yields of up to 16% (Romanias et al., 2024). Together with the substantial depletion observed during photooxidation in our study, these findings support the need to account for non-traditional precursors, particularly furanic and phenolic compounds, in SOA models to more accurately represent SOA formation from BB emissions.*

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.

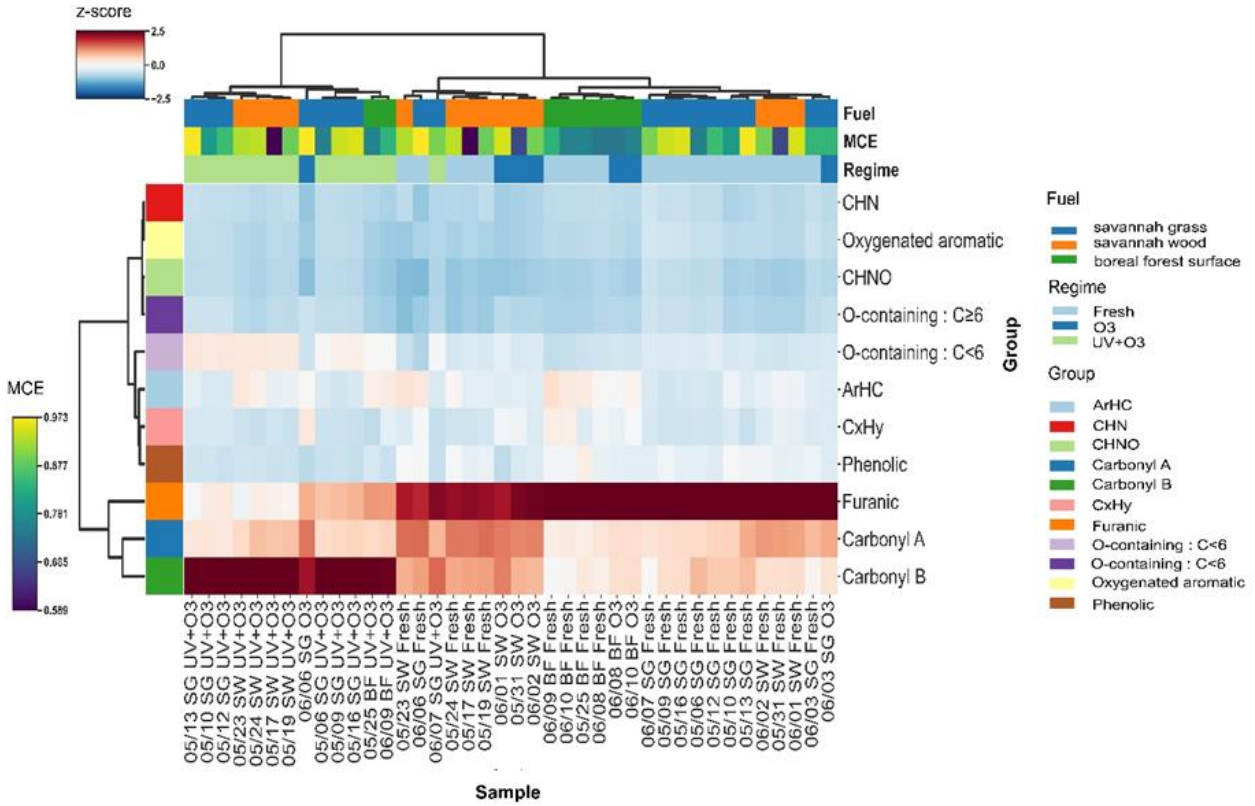


Figure 3. Hierarchically clustered heatmap of standardized mean mixing ratios grouped by compound groups (rows) and regime-resolved samples (columns; date x fuel x regime), with row and column dendrograms summarizing similarities among compound groups and regime-resolved samples, respectively.

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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