

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

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General comment:

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.

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 NO_x 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.

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.

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.

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 ($k \approx 5$) 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.

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.

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.

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.

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.