Journal: *Atmospheric Chemistry and Physics (ACP)* / EGUsphere

Title: Unraveling the chemical structures and sources of biomass-derived organic aerosols through a year-long offline analysis in Hyytiälä, Finland

Recommendation: Major Revisions

General Comments:

This manuscript presents a year-long offline high-resolution aerosol mass spectrometry (HR-AMS) analysis of PM samples collected in the Hyytiälä boreal forest. The authors utilize a polarity-based fractionation method (HP-WSOM, HULIS, WISOM) combined with Positive Matrix Factorization (PMF) to untangle sources of organic aerosols, particularly focusing on differentiating biogenic secondary organic aerosols (BSOA) from biomass-burning organic aerosols (BBOA).

The dataset is valuable, and the approach of combining offline fractionation with HR-AMS to increase chemical resolution is an interesting contribution. However, prior to publication in *Atmospheric Chemistry and Physics*, several major methodological and interpretive issues must be critically addressed. In particular, the mathematical assumptions underlying the concatenated PMF analysis, the potential for sample extraction artifacts, and the apparent contradiction regarding key tracer ions (e.g., m/z 60) require substantial clarification. I recommend **Major Revisions**. Detailed comments are provided below.

Major Comments:

1. Physical Assumption of PMF Matrix Concatenation:

In Section 2.5, the authors state that the mass spectra of HP-WSOM, HULIS, and WISOM were "processed together". It is fundamentally unclear how the data matrices were combined (e.g., were they appended into a single concatenated matrix?). More importantly, concatenating chemically fractionated samples into a single 2D PMF model inherently assumes that a resolved source factor (e.g., BBOA-like) possesses the exact same mass spectral profile regardless of the polarity fraction it resides in. Chemically, this is highly unlikely. Since fractionation physically separates molecules by polarity, the BBOA components in the HP-WSOM fraction should have a higher degree of oxygenation (higher O/C) and a different fragmentation pattern than the BBOA components in the non-polar WISOM fraction. Forcing a static factor profile across fractions of varying polarities may lead to significant mathematical distortion. The authors must explicitly justify the validity of this physical assumption and explain how ion contributions were handled across fractions.

2. The Discrepancy Regarding the C2H4O2 (m/z 60) Tracer:

In Figures 9 and 10, the authors use C2H4O2+ as a marker for BBOA based on its strong temporal correlation. However, it is highly contradictory that the corresponding BBOA-like mass spectrum (Figure 10) shows little to no contribution at m/z 60. If m/z 60 perfectly tracks BBOA temporally, why did the PMF algorithm fail to allocate this ion into the BBOA factor profile? This is likely a direct consequence of the PMF concatenation issue mentioned above: levoglucosan is highly water-soluble and may have partitioned exclusively into the HP-WSOM fraction, while the bulk mass of the BBOA factor was driven by HULIS/WISOM. This glaring contradiction between temporal correlation and spectral absence must be critically explained.

3. Chemical Artifacts during Offline Extraction (pH Adjustment):

In Section 2.2, the authors describe acidifying the WSOM to pH 2 using 1 M HCl before Oasis HLB solid-phase extraction, followed by elution with methanol. Subjecting a complex mixture of organic aerosols to highly acidic conditions combined with methanol can induce significant chemical alterations, such as acid-catalyzed esterification, hydrolysis, or the ring-opening of biogenic epoxides (e.g., IEPOX-derived SOA). Furthermore, at pH 2, basic compounds like amines (proposed as CHN tracers for BBOA) will be heavily protonated , drastically altering their retention on a reverse-phase SPE column. Since this study heavily relies on specific HR-AMS structural fragments to identify sources, the authors must explicitly discuss the potential that some structural features or O/C ratios are artifacts of the aggressive sample preparation.

4. Filter Sampling Artifacts for Semi-Volatile OAs:

The aerosol samples were collected on filters over prolonged periods of one week. A 7-day sampling duration is highly susceptible to severe sampling artifacts, particularly the evaporative loss (negative artifact) of semi-volatile organic compounds (SVOCs) and the adsorption of gas-phase VOCs (positive artifact). Prolonged sampling likely volatilizes a large portion of fresh BSOA and BBOA, leaving behind only the highly aged, low-volatility OAs. The impact of this extended sampling duration on the reported PMF factor distributions and O/C ratios must be acknowledged as a limitation.

5. Ambiguity of CHN Family Ions as Exclusive BBOA Tracers:

The authors assign CHN family ions as exclusive tracers for fresh BBOA (protein-rich biomass combustion). However, the boreal forest emits significant amounts of Primary Biological Aerosol Particles and biogenic aliphatic amines, which are heavily involved in local new particle formation and also yield prominent CHN fragments. Assigning these nitrogen-containing ions purely to biomass burning without ruling out PBAP/biogenic amine partitioning, or without providing correlations with independent combustion tracers (like BC or CO), is a significant interpretative leap.

Minor & Specific Comments:

6. Motivation for Polarity-Based Fractionation:

The motivation for applying polarity-based fractionation would benefit from further clarification in the Introduction. While it is described as a means to improve source apportionment, it is not fully clear what additional insights this approach provides beyond conventional online AMS–PMF analysis. Please explicitly explain how polarity-resolved measurements contribute to understanding the chemical processing, structure–property relationships, or atmospheric behavior of OA.

7. Lines 221-222 (P1 and P2 events):

The manuscript highlights P1 and P2 as distinct periods because of their high HULIS concentrations. However, it is not entirely clear what makes these periods fundamentally different from the rest of the dataset. While P2 is associated with elevated absolute concentrations, the *relative* mass contributions of WISOM, HULIS, and HP-WSOM do not seem substantially different from adjacent periods. A more explicit discussion of both the compositional uniqueness during P1/P2 and the overall seasonal trends would improve clarity.

8. Figure S6 (Back trajectories):

It would be highly beneficial to include time markers (e.g., 12-hour or 24-hour intervals) along the backward trajectories to better indicate transport timescales. Based on the current figure, it is difficult to clearly distinguish whether P1 reflects long-range transport and whether P2 is influenced by more local/regional stagnant air masses.

9. Lines 302-320 (High-mass BSOA tracers):

While the authors acknowledge the low abundance and potential fragmentation of these high-mass ions , it remains unclear whether the observed correlations alone are sufficient to support their use as robust characteristic signatures. Given their relatively weak signal intensity in W-mode HR-AMS, further clarification on their signal-to-noise ratios and stability across samples is needed. Providing representative HR peak-fitting plots for these ions in the Supplement would strengthen this claim.

10. Line 316:

Please check whether “BBOA” should be corrected to “BSOA” in this context regarding $C_5H_7^+$ and $C_6H_9^+$.

11. Lines 425-430 (Temperature dependence of BSOA):

The interpretation of the temperature dependence of BSOA requires further clarification. While BVOC emissions are generally temperature-dependent, monoterpenes (the dominant emissions in boreal pine forests) typically have a different temperature-emission relationship compared to isoprene. It would be helpful to clarify whether the observed BSOA trend is primarily driven by isoprene-derived SOA or if monoterpene-derived SOA also contributes significantly, contextualized by the dominant vegetation types at the site.

12. Line 452 (Date Verification):

Please verify whether “15-22 December” should actually be “21-28 July.” Looking at Figure 12, the WISOM fraction of MO-OOA does not appear particularly elevated in December, whereas there is a massive spike during the July period.

13. Formatting:

There are inconsistencies in the formatting of subscripts and superscripts throughout the manuscript (e.g., PM0.95 vs PM_$_{0.95}$, C5H6O+ vs C5H6O^{+}). A careful proofread is recommended to ensure consistency in their presentation.