RC1: 'Comment on egusphere-2026-1023', Anonymous Referee #1

We sincerely thank the referee for the helpful and constructive comments.

1. PMF factor number selection

I understand that interpretation becomes increasingly difficult as the number of PMF factors increases. However, this alone is not sufficient justification for not exploring higher-factor solutions more explicitly. The revised manuscript still states only that both four- and five-factor solutions were reasonable and that the five-factor solution was selected to better capture structural characteristics. I suggest that the authors provide a clearer and more explicit rationale for the final factor choice. For example, it would be helpful to explain whether higher-factor solutions mainly split factor time series without producing meaningfully distinct mass spectra, or whether they resulted in physically uninterpretable factors. A more transparent explanation would strengthen confidence in the selected five-factor solution.

We added Fig. S4g to compare the quantified concentration time series of the five-, six-, and seven-factor solutions across the HP-WSOM, HULIS, and WISOM fractions. As shown in Fig. S4g, increasing the number of factors to six or seven does not substantially change the dominant temporal patterns or the distributions of the major factors among the three OA fractions compared with the five-factor solution. The main changes are considered to be factor splitting or addition of minor factors as explained below.

In the six-factor solution, both the mass-concentration time series and the spectral profiles of F1, F2, F3, F4, and F6 (where F*i* denotes factor *i*, *i* = 1, 2, 3, ...) closely resemble those of F1, F2, F3, F4, and F5, respectively, in the five-factor solution. For each factor in the five-factor solution, its corresponding factor in the six-factor solution shows the highest correlation on a mass-concentration basis ($r > 0.938$) and the highest mass-spectral correlation ($r > 0.996$) among all possible factor pairings, and a similar annual mean mass contribution (91.9–101.4% of that of the corresponding factor in the five-factor solution). Factor F5 in the six-factor solution accounted for only 4.4% of the total reconstructed OA concentration on average, indicating that this additional factor had a limited influence on the overall mass budget. The factor profile of F5 in the six-factor solution was dominated by low-m/z fragments, with a particularly strong signal at m/z 29. This mass spectral pattern is not similar to common mass spectral patterns associated with a specific source in conventional AMS analysis. Therefore, the six-factor solution was not selected for further analysis. It should be noted, however, that F5 should not be considered meaningless solely on the basis of its mass spectral pattern, because a PMF factor may represent a group of molecular substructures rather than a group of intact compounds. The abundance of CHN-family ions (5.2%) suggests that F5 is related to a specific type of BBOA, although this relationship cannot be conclusively established.

In the case of the seven-factor solution, F4 is similar to F5 in the six-factor solution, with the highest correlation on a mass-concentration basis ($r = 0.963$) and the highest mass-spectral correlation ($r = 0.988$) among all possible factor pairings. Hence, as in the case of F5 in the six-factor solution, F4 cannot be clearly associated with a known source. F1, F2, F3, F6, and F4 in the seven-factor solution correspond most closely to F1, F2, F3, F4, and F5, respectively, in the six-factor solution, showing the highest mass-concentration correlations ($r > 0.917$) and the highest mass-spectral correlations ($r > 0.982$) among all possible individual-factor pairings, as well as similar annual mean mass contributions (81.7–121.8% of those of the corresponding factors in the six-factor solution). The sum of F5 and F7 in the seven-factor solution showed the highest mass-concentration

correlation with F6 among all factors in the six-factor solution (r = 0.997) and had a similar mean fractional contribution (112.8% of that of F6 in the six-factor solution). Further, the O/C ratios of six-factor F6 and seven-factor F5 and F7 were 0.15, 0.16, and 0.20, respectively, all of which were relatively low and comparable to that of HOA in the five-factor solution (O/C = 0.15). Taken together, we considered F6 in the six-factor solution to be mainly split into F5 and F7 in the seven-factor solution; the two split factors cannot be explicitly attributed to different known sources. For the reasons above, the seven-factor solution was not selected for further analysis.

The explanations on six- and seven-factor solutions above have been added to Text S3.

In relation to the factor contributions explained above, we have revised Section 2.5 (Lines 276-279) to report the extent of which the raw PMF-reconstructed OA signals for the three OA fractions explain the measured OA signals and to clarify the method used for calculating the atmospheric concentrations of the individual factors.

We do not deny that higher-factor solutions may contain additional information on submolecular structures. The five-factor solution is accountable as explained in the main manuscript, and was thereby selected for further analyses. This solution is considered conservative because the number of resolved factors was close to those reported in previous PMF studies at Hyytiälä (Table 1).

2. Identification of the BBOA-like factor

The revised manuscript explains that the BBOA-like factor was identified partly using CHN-family ions because the traditional levoglucosan-related marker (m/z 60) may be diminished during atmospheric aging. This is a reasonable possibility, but I think the discussion still needs to be more balanced. Since nitrogen-containing organic species can also evolve during photochemical processing, the manuscript should discuss more clearly the extent to which CHN-family ions can be expected to remain robust tracers in aged biomass-burning aerosol, compared with levoglucosan-related signals. I am not asking for a full kinetic treatment, but some discussion of the relative stability and possible aging-related limitations of these tracers would strengthen the interpretation.

CHN-family ions in AMS spectra represent a broader group of nitrogen-containing organic fragment ions. Therefore, even when individual CHN-containing molecular species undergo chemical transformation, the resulting products may still remain within the broader CHN-containing chemical class (Li et al., 2024). Conversely, although levoglucosan is not the only contributor to the m/z 60 ion signal (Lee et al., 2010), if this signal originates primarily from the chemical structures of anhydrosugars, atmospheric degradation of these structures would be closely associated with the loss of the m/z 60 signal (Hennigan et al., 2010).

Our previous field study suggests that a considerable fraction of levoglucosan remained detectable after 4–5 days of wintertime transport, whereas substantial depletion occurred during summer transport (Mochida et al., 2010). Further, laboratory experiments estimated a particle-phase lifetime of 0.7–2.2 days under typical summertime OH exposure, while a global model estimated a mean atmospheric lifetime of 1.8 days (Li et al., 2021; Hennigan et al., 2010). For CHN-containing compounds, molecular-level characterization of laboratory -generated BBOA showed that, after approximately 7 days of atmospheric-equivalent aging, the overall CHN signal, remained at approximately 91–112% of the corresponding fresh-BBOA values (Li et al., 2024). These results indicate that the signals from broader CHN-containing compounds may be more resistant to aging, despite the transformation of individual compounds. However, we cannot exclude the possibility that the secondary formation of nitrogen-containing compounds during atmospheric transport introduces uncertainty

into the source apportionment. These points have been added to Section 3.2.4, Lines 486–502.

Hao et al. (2025) identified a CHN-rich nitrogen-containing OA factor (NOA) and mainly associated it with biomass-fuel primary emissions. The time series of NOA also showed a good correlation with levoglucosan (r = 0.75) (Hao et al., 2025). Therefore, this study also supports our use of CHN-family ions as potential complementary markers for the BBOA-like factor. To make our statement more precise, we have added the qualifier "in AMS-based PMF " to the Summary section (Line 645), which now reads: "This study also explored CHN-family ions as potential BBOA-like factor markers in AMS-PMF for the first time to our knowledge."

3. Discussion of PMF solubility analysis in Section 3.3.2

I still find Section 3.3.2 somewhat unconvincing in its current form. The manuscript now notes that several abrupt changes in the water-insoluble fraction in Fig. 12 occurred under very low factor concentrations and therefore should be interpreted with caution. If the fractional variation is strongly affected by low-concentration uncertainty, I do not see a strong justification for discussing the temporal variation in Fig. 12 in as much detail as is currently done. In my view, the main message of this section is already sufficiently conveyed by the mean distributions shown in Fig. 4b, and Fig. 12 does not appear to add robust additional insight beyond that. The authors may wish either to shorten this section substantially or to clarify more explicitly what unique information Fig. 12 provides beyond the annual mean pie-chart summary.

We revised Fig. 12 from a time-series plot to a factor-by-factor summary plot showing the annual mean ± standard deviation of f_{WISOM} for each PMF factor. This revised figure avoids overemphasizing short-term variations that may be affected by the uncertainties for low-concentration samples, while more clearly showing the factor-specific water-insoluble fractions. The main point of this section is to explore the solubility characteristics of the resolved PMF factors, which is generally difficult to obtain from conventional online PMF analysis without additional fractionation experiments. Fig. 12 provides complementary information to Fig. 4b by showing the water-insoluble fraction of each factor, which helps interpret the physicochemical characteristics of the compounds associated with the factors.

We have revised and shortened Section 3.3.2. In the revised text, we no longer discuss detailed temporal variations or individual abrupt changes. Instead, we focus on the mean factor-specific f_{WISOM} values and explicitly note that part of the variability may arise from uncertainties in PMF-derived fractional values at very low factor concentrations.

4. Connections between PMF factors and polarity distributions

I still find the connection between the PMF factors and the polarity distributions somewhat difficult to follow. The manuscript suggests that HOA is strongly associated with WISOM and that the BSOA-like factor contributes strongly to HULIS, but the relationship between these interpretations and the seasonal behavior shown in Fig. 12 and Fig. 13a is not yet explained clearly enough. In particular, the discussion seems to emphasize HOA–WISOM, while the corresponding links between PMF factors and HULIS or HP-WSOM are less clearly developed. I suggest that the authors make these connections more explicit and balanced across all three fractions. In addition, please match the colors of HP-WSOM, HULIS, and WISOM consistently in Fig. 13 between the bar chart and the pie chart to improve readability.

We have revised the first paragraph of Section 3.3.3 to make the connections between the PMF factors and the polarity distributions more explicit and balanced across the three fractions. Specifically, we added an description linking the dominant PMF factor in each fraction to the seasonal behavior of HP-WSOM, HULIS, and WISOM, as follows:

"This seasonality is linked to the dominant PMF factors in each fraction (Fig. 4b and 11). The BSOA-like factor was the largest contributor to the intermediate-polarity HULIS fraction, accounting for 54.2% on average, and this factor exhibited a clear summertime enhancement. The mean HULIS concentration increased by 1.1 μg m^{-3} from winter to summer, of which 0.97 μg m^{-3} (87.1%) was accounted for by the increase in the BSOA-like factor. HP-WSOM and WISOM were dominated by MO-OOA and HOA (Fig. 4b), with mean contributions of 73.7% and 63.0%, respectively. The seasonal mean concentrations of HP-WSOM and WISOM increased by 0.12 and 0.22 μg m^{-3} from winter to summer, respectively, with substantial increases of MO-OOA (0.11 μg m^{-3}) and HOA (0.11 μg m^{-3}). The other factors contributed only slightly to the changes from winter to summer (from -0.01 to 0.06 μg m^{-3}). Although HP-WSOM and WISOM and their dominant factors also increased in summer, the BSOA-related enhancement of HULIS was the primary driver of the winter-summer redistribution among the three fractions."

In addition, we have revised Fig. 13b so that the colors for HP-WSOM, HULIS, and WISOM in the pie charts are consistent with those used in Fig. 13a, the stacked bar chart.

Other changes

In addition to the revisions made in response to the reviewer's comments, we have corrected two incorrectly listed ions in the Abstract, have updated one author's name, have corrected the Author contributions section, and have added one project in the Acknowledgments section. Please see the track-changes version of the manuscript for details of all the changes made to the manuscript.

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