Review of Karbach et al. (2026): Non-Target Analysis of Atmospheric Organic Aerosols as a Tool to Discriminate Anthropogenic Contribution in Mixed Air Masses during the ACROSS campaign

Overall Assessment

This manuscript presents a wind-informed non-target LC-HRMS analysis of organic aerosol collected during the ACROSS 2022 campaign and applies a K-means clustering framework to organize molecular signatures associated with anthropogenic and biogenic source influences. However, in its current form, the manuscript requires substantial revision before it is suitable for publication in ACP. While the results are promising, the manuscript currently sits somewhat between a methodological contribution and a measurement/report study, without fully developing either aspect.

If the primary contribution is methodological, additional analyses are needed to demonstrate the specific advantages of the proposed wind-informed clustering framework relative to simpler approaches, such as direct enrichment-based classification or clustering performed without wind-based source partitioning. In particular, it remains unclear what information is uniquely gained from the K-means step, given that source-associated behavior is already quantified through the wind-based feature construction. The manuscript would benefit from a clearer discussion of the role of clustering in the overall workflow and evidence demonstrating its added value relative to alternative approaches. Furthermore, while the reduced-sample clustering exercise suggests internal consistency of the derived cluster assignments, it does not constitute an independent validation of the framework. Consequently, claims regarding the applicability of the method to determine cluster contributions in "truly unknown organic aerosol samples" appear overstated and would require validation using independent datasets or a more rigorous predictive evaluation strategy.

Alternatively, if the primary contribution is the chemical characterization of anthropogenic and biogenic molecular signatures, the discussion would benefit from a more comprehensive comparison with published ACROSS studies. In particular, the manuscript does not discuss results from Pereira et al., 2025 (https://doi.org/10.5194/acp-25-4885-2025), which reports LC-HRMS measurements conducted during the same campaign and sampling periods, including observations at both the suburban-forest site and the Paris site that is interpreted here as the dominant anthropogenic source region. Such comparisons could provide important validation of the cluster assignments, place the findings within the broader ACROSS context, and substantially strengthen the atmospheric interpretation of the identified molecular signatures. Given the regional nature of the dataset, these comparisons are also important for demonstrating how the reported findings advance or extend existing knowledge, which is a key consideration for ACP studies with a predominantly local focus.

Specific Comments

Scientific Language and Organization

The manuscript would benefit from careful editing to improve clarity, consistency, and precision throughout. The examples provided below are illustrative rather than exhaustive, and a thorough review of the manuscript is recommended with these issues in mind.

Sentences such as *"Mixed anthropogenic biogenic environments add a layer:"* (line 72); *"…which prioritizes abundant precursors however."*(line 92)*; "After exporting the data, the blank was subtracted from the data three times…"* (line 140); and *"The concentration of those compounds is strongly increased…"* (line 327); could be rewritten for clarity and scientific formality. Many claims would benefit from literature citations. For instance, lines 70-79 discuss organic markers in atmospheric aerosols but without any references. Several acronyms and abbreviations are introduced without prior definition (e.g., lines 46, 58, 66, 67, 85, etc.), and terminology is not always used consistently. For example, non-anthropogenic sources are variously described as biogenic, natural, and mixed, while sampling periods are alternately referred to as day/night and daytime/nighttime. Figure references are also inconsistent, with panels labeled alphabetically in the figures but described as left and right in the text.

The sample nomenclature is also difficult to follow. There is currently no clear reference linking the filter identifiers presented in Table S1 and the backward trajectory figures in the Supplement to the sample identifiers (S1, S2, etc.) used throughout the manuscript. It is therefore unclear whether F1 corresponds directly to S1 or whether the samples were renumbered after the exclusion of six filters. This ambiguity becomes particularly apparent when discussing time series, where the x-axis extends to 43 despite only 37 samples being included in the analysis. I recommend using a single, consistent naming convention (e.g., "samples" or "filters") throughout the manuscript and clearly explaining in the main text how the excluded filters were handled. In addition, Section 2.1 is titled Sample Preparation but also includes sample collection procedures. Consider revising the section title or separating collection and preparation into distinct subsections.

More importantly, most statements describing differences between groups remain qualitative. Where possible, differences should be quantified and accompanied by appropriate statistical metrics. Similarly, statements regarding significance, enrichment, or separation should be supported by suitable statistical analyses rather than qualitative descriptions alone.

The introduction in its current form is overly descriptive and method-oriented and does not yet clearly establish a focused scientific hypothesis, knowledge gap, or study objective. As a result, the reader is left uncertain about the central scientific question being addressed. Several sections read more as methodological background than scientific motivation, which weakens the conceptual framing of the study. In addition, the connection between the ACROSS campaign and the specific objectives of the manuscript is not sufficiently explicit, making the scientific purpose of the work somewhat diffuse. The introduction is also organized as a series of largely independent thematic sections rather than a coherent narrative that progressively develops toward a clearly articulated research question. Consequently, the broader atmospheric significance, novelty, and expected scientific advances of the study are not sufficiently evident from the introduction.

The methodological description is incomplete and not presented in a sufficiently sequential manner. For example, the exact coordinates of the sampling site are not reported; the rationale for the OA molecular characterization approach and clustering framework, including the basis for selecting the number of clusters, is not clearly defined; the directional-dominance metric is introduced later without a clear description of its calculation; and the bootstrap validation

approach is insufficiently described, with key details such as the resampling strategy and number of iterations omitted. As a result, the workflow cannot be readily reproduced by an independent researcher based on the current description.

Finally, the selection of compounds highlighted for detailed discussion requires clarification. Given the large feature space (1894 biogenic and 1023 anthropogenic compounds), it is unclear on what basis four anthropogenic and one biogenic compound were chosen for further interpretation. Without a clearly defined and objective selection criterion (e.g., cluster membership strength, enrichment metrics, abundance, occurrence frequency, or statistical ranking), it is difficult to assess how representative these examples are of their respective clusters. As currently presented, the selection appears subjective and may bias the discussion toward compounds that are more readily interpretable from a chemical perspective. Providing transparent selection criteria or a more systematic summary of cluster composition would improve reproducibility and strengthen confidence in the atmospheric interpretation of the identified molecular signatures.

Presentation and Figures

Many figures and figure legends would benefit from revision. Font sizes are inconsistent across figures and within individual panels, which reduces readability. A more uniform graphical style throughout the manuscript would improve clarity and visual consistency.

A map showing the study region and sampling location would be helpful to provide geographical context for readers unfamiliar with the ACROSS campaign domain.

Figure 1. It would be helpful to add cardinal directions (e.g., N, NW, S, SW) alongside the degree scale on the y-axis, as wind direction is referred to in this format throughout the text rather than in degrees. In addition, the HYSPLIT trajectory plots are difficult to interpret due to small font sizes and limited geographical context. The sampling location is not immediately identifiable, which makes it challenging to assess air mass origins. It may be helpful to include a marker for the sampling site, an outline of the Greater Paris region, and a marker indicating the location of Paris.

Figure 2. It may improve comparability to use a common y-axis scale for panels (a) and (b). In addition, a more chemically resolved representation (e.g., stacked contributions of CHO, CHON, CHOS, CHONS, and related classes) could provide additional insight into how compound classes are distributed across m/z and retention time.

Figure 3. The Van Krevelen diagram is difficult to interpret due to the large legend occupying substantial plot space. The marker size is not defined, and the marginal distributions along the axes are not clearly explained. It may be useful to separate molecular formula classes into individual Van Krevelen plots to improve interpretability. The equation used for OSc should also be provided in the main text, figure caption, or Supplement.

Figures 3–6, 11. The acronym MCR is not defined in the manuscript, although the corresponding regions shown in these figures appear to be defined. These regions are not discussed in the main

text. The authors may wish to clarify their meaning and relevance, or consider whether they are necessary if they are not directly used in the interpretation of the results.

Figure 6. This figure is difficult to interpret due to relatively small panels, overlapping legends, and elements that are not fully described (e.g., clustering structure and axis subscripts). The discussion in Section 3.3.1 also appears somewhat limited relative to the complexity of the figure and could be expanded to better support interpretation.

Figure 7. It may improve interpretability to harmonize panel formatting using a common y-axis scale. A chemically resolved presentation of the directional-dominance analysis (e.g., by molecular formula class) could help identify which compound classes contribute most strongly to the observed patterns.

Figure 9. This figure is not explicitly referenced in the main text. If retained, it may be helpful to clearly define terms such as “XIC” and distinguish between identified peaks and observed time series. Improvements in font size and color contrast could also enhance readability.

Figure 10. It may be helpful to align the structure of this figure with Figure 9 to facilitate comparison.

Figure 11. It may improve clarity to separate the HYSPLIT trajectory plots from the Van Krevelen plots, as combining them contributes to visual congestion.

Line Comments

Line 11: The phrase *"particle phase of Earth's atmosphere"* is misleading, as particles are suspended within the atmospheric gas phase rather than constituting a phase of the atmosphere itself. Consider revising to clarify that organic aerosol is a major component of atmospheric particulate matter.

Line 34: Consider broadening the end of this sentence. Restricting the toxic components of OA to "combustion-related constituents" overlooks a wide range of other health-adverse organic species that comprise the OA mass.

Line 36: The sentence says OA is a source of uncertainty because it is complex and dynamically evolving. But the complexity itself isn't what causes the uncertainty; it's our incomplete understanding and poor modeling of that complexity. OA would still be complex even if we predicted it perfectly. Consider rephrasing to focus on these modeling and observational constraints, and add a few representative references to back it up.

Line 39: Instead of listing specific sources for POA, consider grouping them more broadly into anthropogenic and biogenic categories. Because new OA sources are continuously being identified, summarizing them this way will improve the long-term relevance of the text.

Lines 43-48: The paragraph sets up a strict dichotomy where high temporal resolution is limited to bulk composition (e.g., AMS) and molecular speciation is restricted to offline filter analysis. This characterization overlooks significant advances in state-of-the-art in situ instrumentation.

Advanced online platforms, such as the Thermal Desorption Aerosol Gas Chromatograph (TAG), bridge this gap by providing molecularly speciated OA measurements at hourly resolution or better. Additionally, derivatization methods and online two-dimensional GC-MS aerosol system (i.e., 2D-Q-TAG, VAPS) allow for the measurement of polar species present in OA. Consider revising this section to acknowledge these advanced online speciation techniques, as the current text presents an overly simplified view of modern aerosol analysis capabilities.

Line 54: Consider omitting the description of the NTA workflow or move it to methods as it does not add significance in the introduction.

Line 55: The statement “Because OA datasets are high dimensional…” is overly broad. OA datasets are not necessarily high dimensional (e.g., bulk OA mass measurements), although chemically resolved datasets are often highly dimensional. Please revise to reflect this distinction.

Line 62: Please acknowledge the campaign coordinators in the Acknowledgements section.
Line 113: Please change the date format to the Copernicus standard: " dd month yyyy".

Line 200: It is unclear how nitrogen-containing compounds are included in the CHOS subset. Since nitrogen is not part of CHOS, please clarify whether CHON or CHONS compounds are intended here.

Line 207: The inference of a temporal evolution (“increasing time in the atmosphere”) from the Kroll plot is not justified, as the figure does not track air mass aging over time but instead shows a cross-sectional distribution of compounds with different oxidation states.

Line 226: The interpretation that differences between samples S6 and S22 can “solely be attributed to different meteorological conditions” is too strong. While wind direction suggests different air mass origins (W–SW vs NE), other factors such as chemical aging, boundary layer dynamics, and regional mixing may also contribute to the observed differences. The attribution should therefore be softened to reflect these additional uncertainties.

Line 264: The statement that *“similar clustering results”* were obtained compared to Thoma et al. (2025) is unclear, as it is not specified whether similarity refers to cluster structure, compound class distributions, or source attribution patterns. A more precise description of the basis for this comparison would be helpful, and, where possible, should be supported with quantitative or clearly defined criteria. In addition, a comparison with Pereira et al. (2025), which reports LC-HRMS measurements from the same ACROSS campaign and sampling periods, would be highly relevant.

Line 270: The rationale for selecting samples S6, S21, S22, and S38 for exclusion in the validation clustering experiment is not explained, and it is unclear whether this selection was based on predefined criteria, randomness or on inspection of the clustering results.

Line 325: Please correct the typo from "and likely related" to "and are likely related." Additionally, consider replacing the vague term "related" with a more precise descriptor, such as

"chemically related" or "members of a homologous series." As written, "related" is ambiguous and could refer to source origins, chemical structures, or transformation pathways.

Line 327: The term “concentration” should be re-assessed, as the reported values represent signal intensity rather than calibrated concentrations, and this should be corrected throughout the manuscript. The claim that these signals are “strongly increased” is not quantitatively supported, and the statement that this “validates the automatic clustering results” is too strong given the lack of statistical evaluation. The wording should be revised to more appropriately reflect a qualitative or semi-quantitative comparison.

Line 328: The interpretation of the fragmentation data for $C10H18NO8S^-$ would benefit from clarification. While the observed neutral loss of HNO3 is consistent with the presence of an organonitrate functionality, the terminology “nitro group” is chemically imprecise in this context (i.e., nitro vs. nitrate ester/organonitrate). In addition, the extrapolation that the “whole compound class” carries this functionality is not fully supported by a single MS/MS observation and should be stated more cautiously or supported with additional evidence.

Line 353: The interpretation of the C10 fragment evidence requires clarification. The parent ion is identified as $C11H17O6^-$, from which C10 fragments can arise through common fragmentation pathways, such as loss of small neutral or alkyl groups. Therefore, the presence of C10 fragments is not diagnostic of a monoterpene (C10) precursor, but rather a general and expected outcome of fragmentation of a C11-containing molecule. Although these compounds are assigned to the biogenic cluster, the conclusion that the observed fragments directly support a biogenic source attribution conflates structural fragmentation behavior with source identification and should be stated more cautiously or supported by additional diagnostic evidence.

Line 374: The proposed calculation of “anthropogenic influence” as the relative abundance of cluster-assigned compounds requires clearer methodological definition, as cluster membership in a non-target feature space does not directly translate into source apportionment. The reduced-sample clustering exercise provides a useful internal consistency check but does not represent an independent validation, as it is performed within the same dataset and analytical framework. Therefore, the interpretation that it validates “truly unknown organic aerosol samples” is overstated. In addition, it is unclear how the clustering step improves source attribution compared to the wind-based classification, which already appears to capture the primary source information.