Summary

In this preprint, the authors utilized excitation-emission matrix (EEM) fluorescence spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to examine the molecular composition and formation mechanisms of water-soluble organic carbon (WSOC) in atmospheric aerosols gathered from Karachi, Pakistan. They identified three parallel factor (PARAFAC) components, consisting of two humic-like (C1 and C2) and one protein-like (C3). They further investigated the connection between PARAFAC components and possible brown carbon (BrC) fluorescent species, along with absorbance characteristics, which could aid in broadening our knowledge of BrC in the atmosphere. With a few adjustments, clarifications, and a thorough language revision for clarity, this study has the potential to contribute to the field and be suitable for publication in ACP.

Strengths

The authors leveraged a blend of advanced analytical techniques, such as EEM spectroscopy and FT-ICR MS, to characterize WSOC in aerosols.

By identifying three PARAFAC components and examining their molecular relationships, the study provides a more in-depth understanding of the formation processes and properties of fluorescent species in the atmosphere.

The insights gained on the molecular compositions and formation mechanisms of atmospheric fluorescent components can prove valuable for future investigations that employ EEM-PARAFAC to study atmospheric BrC.

Areas for improvement

The study focuses on aerosols from Karachi, Pakistan, so the conclusions might not represent other geographical areas. Although there are comparisons with results from Bakersfield and Guangzhou (among others), it would be beneficial for the authors to critically discuss the broad applicability of their overall findings to other locations in the conclusion, or suggest future studies using their methodologies to include aerosols from diverse regions.

In Section 3.3, the authors attempt to explain the differences in oxidation pathways (depending on precursor types) for the formation of C1 and C2 components. It would be helpful if the authors could elucidate this explanation (Lines 520-522) and incorporate a more detailed summary in both the conclusion (Lines 586-587) and abstract.

Although the study identifies molecular families associated with each of the three components, their specific molecular formulas are not detailed, potentially limiting the study's replicability. Providing more information on abundant (in terms of MS signal intensity) molecular formulas associated with each component would allow other researchers to expand upon these findings. In addition, based on Lines 537-540 (Section 3.4) and Figure 5, the reviewer is particularly interested in knowing the molecular formulas of major (potential) BrC species (nitro-aromatics, CHO species) within the C2 component.

Line 562: It may be worthwhile to include an alternate version of this figure that represents the number of carbon and nitrogen atoms (C+N) on the *x*-axis, and discuss any discrepancies with the current version. This alternate figure might be more pertinent to BrC, as nitroaromatic groups (if present) in CHON are potential chromophores. When considering C+N, the data points for N-containing compounds in this figure would shift to the right.

Several sentences are difficult to understand, and their meanings are unclear. The authors should rectify any remaining language issues to enhance the manuscript's readability. After these improvements, another review might be required to ensure the precision of all statements in the revised manuscript.

Additional comments and suggested edits

Lines 1-3: Consider rearranging the title for clarity: "Molecular signatures and formation mechanisms of water-soluble chromophores in particulate matter from Karachi (Pakistan) in South Asia."

Line 56: Change to "originates."

Line 58: Change to "formation processes, such as aqueous-phase reactions from anthropogenic or biogenic emissions."

Lines 60-61: Change to “Light-absorbing organic (or brown) carbon (BrC) is an important component of WSOC…”

Line 74: Change to "...absorb light at certain wavelengths..."

Lines 115-116: Could you elaborate on whether primary or aged biomass burning emissions are anticipated and how they might influence the interpretation of BrC results?

Line 126: Change to "Total suspended particulate matter (TSP) was collected..."

Line 148: Change to "PARAFAC."

Line 285: Please clarify what the error bars signify in panels (c) and (d).

Lines 310-312: Could the authors provide insights as to whether the molecular formulas that showed no correlation with any PARAFAC component are predominantly aliphatic and sugar compounds, which are not typically expected to exhibit light absorption or fluorescence?

Line 362: Change to "saturated."

Line 364: Change to "lower."

Line 604: Summarize Text S7 briefly.

<u>Comments on the SI</u>

Text S3: Please explain why liquid chromatography was not employed for the separation of compounds prior to the MS analysis, and discuss any potential effects this decision might have on the current study.

Lines 149 & 154: Please elucidate the distinction between the carbon oxidation state and the nominal oxidation state of carbon. Also, provide a rationale for the application of both these metrics in this manuscript.

Line 209: Remove "using."

Line 232: Remove the first "that."

Line 233: Change to "may not have the same character as in..." or similar.

Lines 249-251: Rewrite the sentence for clarity.

Line 380: Correct "streams" in the figure legend.