EGUsphere, referee comment RC3
https://doi.org/10.5194/egusphere-2022-1319-RC3, 2023

RC2

Anonymous Referee #2

Referee comment on "Generalized Kendrick analysis for improved visualization of atmospheric mass spectral data" by Mitchell W. Alton et al., EGUsphere, https://doi.org/10.5194/egusphere-2022-1319-RC3, 2023

General Comments:

Overall, I think that this manuscript provides a valuable demonstration of a "Kendrick analysis" (using terminology from RC1) that can be applied to complex mass spectrometry data (in this case a VOCUS-PTRTOFMS) without knowledge of the ion elemental composition to improve data visualization towards assisting in ion assignment, revealing chemical homologues, and potential chemical trends. The manuscript is generally well-written and straightforward, thoughtful about introducing KMD, REKMD, and SKMD, and definitely proves through the figures the potential for using effective scaling for allowing greater insight into atmospheric chemical measurements (e.g. the separation of nominally odd/even IUPAC mass ions into odd nitrogen containing or no/even nitrogen containing formulas). That being said, I agree with RC1's concerns that the main formulation of SKM/SKMD not truly being novel per prior publication in Fouquet (2019) necessitates reframing how the manuscript is presented/worded. After this, I still see the manuscript being publishable and of interest to the atmospheric measurement community for bringing attention to a potentially valuable data processing method for the torrent of mass spectrometric data being collected in recent times.

Specific Comments:

- Line 172: the introduced term "reduced fraction" representing X/R_{IUPAC} is not the most intuitive given values of X (as exampled in the cases of $X=20, 24, 40$) with R_{IUPAC} as ^{16}O results in expanding the mass scale instead of contraction—this seems more like a scaling factor whether enlarged or reduced. Consider changing this term and revising throughout the rest of the discussion.
- Line 303: The text would be enhanced to include more information such as the caption for Figure 7. That is, explain here that these points in Fig. 7a are not just simply omitted in Fib. 7b, but they would not appear in Fig. 7b because they would not fall within the SKMD range after m/z transformation.
- Lines 241, Line 251, Line 296: By using "REKMD" in these section headings, it signals to the reader that co-authors intend SKMD to be a sub-method/type of REKMD, yet the language earlier in text introducing SKMD as a concept makes it seem that it should be distinct as it is used in the analyses in these sections. Thus, I would have expected these section titles to be "SKMD" instead of "REKMD". Given the comments from RC1 on nomenclature/reframing the paper generally as a "Kendrick analysis," just be consistent with the chosen framing in the revised version.

- General comment on Figures 3, 4, 5: For further connection with text and enforcing of how mass defect analysis allows for visualization of homologous series, it would be helpful for labels on the figures pointing out the chemical families and their generic chemical formulations if possible.

Technical Corrections:

- It would be helpful perhaps in Fig. S1 to include vertical lines associated with the bounds of X presented in Eq. (7), which brings more focus to the linearity and equivalency of the two methods within those bounds.
- Figure 2 captions for c and d have inconsistent *X* values with those in subpanels of figure. Caption text for c) should have $X = 24$, d) should have $X = 20$.
- Line 148: Extra space before period should be deleted.
- Line 180: Change "result" to "results".
- Line 278: Add period after "respectively."
- Figure S4: Add panel labels to figure

References:

RC 1: https://doi.org/10.5194/egusphere-2022-1319-RC1

Fouquet, TNJ. The Kendrick analysis for polymer mass spectrometry. *J Mass Spectrom*. 2019; 54: 933– 947.