Review report Tong et al. AMTD 2022

In this study, Tong et al. used the capability of Positive Matrix Factorisation (PMF) analysis to combine data from multiple sources in one dataset for analysis. They used the very detailed molecular composition information obtained from an Extractive Electro Spray Ionisation mass spectrometer (EESI-TOF) together with data from simultaneous Aerosol Mass Spectrometer (AMS) measurements, which provide almost no molecular information but instead enables the quantification of the measured OA signals. As each factor obtained in this combined PMF (cPMF) contains both AMS and EESI-TOF signals, apparent sensitivities could be derived for the EESI-TOF data. This revealed that without considering the compound specific sensitivity for this instrument, the contribution of specific sources (i.e., the identified factors) may be strongly over- or underestimated and thus alter the interpretation of the measurement data.

The underlying principle (combining variables from different instruments) is a basic feature of PMF in general, but the authors provide a clever way of using an established method in a new way to improve the interpretation of EESI-TOF data. As this instrument is becoming more and more important for atmospheric measurements, this manuscript provides very valuable suggestions for the analysis and interpretation, especially for source apportionment. But the implication of the derived apparent sensitivity are also very relevant.

I recommend publication in AMT after some minor issues are addressed.

General Comments:

1) In general, the authors do a good job linking their new analysis results to the already published ones for the two data sets used here. However, it would be easier for the reader if a few more details would be repeated in the main manuscript and not just given by reference.
    a. It remains unclear why some of the factors were constrained. Yes, the previous studies provide explanations for their decisions. But constraining a factor in the single instrument PMF to enhance its separation so that a lower factor number could be used, may no longer be necessary in the combined data set. Did the authors test if the factor constraining was really necessary in cPMF? How did they determine if a factor had to be constrained in cPMF?
    b. How was it determined if a factor was “mixed”?
    c. It would be beneficial to emphasise to the reader a bit earlier, that the chose solution for single instrument PMF was based on the considerations done for the two previous studies and that also the reference spectra are related to that.
    d. Were the same AMS and EESI-TOF instruments used in both studies? Do the authors expect changes in the instrument behaviour (e.g. change in Pieber effect for AMS)? The change in the NO^+ and NO_2^+ ratio for the AMS calibration with Ammonium Nitrate seems to suggest some instrumental differences.

2) The authors claim that they did not observe any relevant fragmentation or clustering with solvent molecules in the EESI-TOF. I find that hard to believe since other studies reported strong fragmentation for specific ions (Bell et al., 2021). Also, how could it be determined that no clusters with the solvent occurred? Especially with acetonitrile, the danger would be to interpret the N from the solvent molecule as a nitrated organic compound.
3) I wonder how computationally intensive this is. There are 2 single instrument PMF runs (with bootstrap, rotations etc). Then the exploratory cPMF run. Then at least 2 more bootstrap cPMF to constrain the additional parameters like C_{EESI} (or the 2D-scan for the a values). Noting that two very short dataset were chosen for this proof-of-concept study, I really wonder how feasible this is for a 2 or 3-month long campaign data set.
4) The authors show that for each data set a new set of parameters (a- constraints, C_{EESI}, AS_k) have to be determined. However, it would be good to really clearly state that once more in the conclusions. Lately I have come across publication which took data set specific parameters from older studies (e.g., for instrument calibrations) and blindly applied them to their data sets. While that is of course the shortcoming of these people and not the original authors, we can try to emphasise that it is really the method that is being presented and that every new data set needs its own careful exploration of the parameter space to provide reliable data interpretation.
5) This is just a suggestion: The manuscript is very long with a lot of important details about how to conduct this new version of PMF analysis. A long manuscript is not per se a problem – especially if a "new" analysis method is introduced. But the authors should consider if some of the more technical aspects could be shifted to the Supplement Material – or be presented as an Appendix. That would put a bit more emphasis on the interpretation of the cPMF results like the changes in factor contributions depending on the apparent sensitivity, which is currently a little bit hidden under all the (important) technical details.

Specific comments:

1) P4 L18f: in addition to the PMF studies Lee et al. (2014) could be mentioned here as another study investigating the sources and formation processes of OA. They used FIGAERO-CIMS spectra obtained in dedicated chamber experiments to reconstruct ambient measurements as linear combinations of them.
2) P4 L38: typo: wind speed (WD) -> (WS)
3) P5 L14: typo: "by the massed base method" -> with the mass based method
4) P6 L9: What was the schedule for the switching between direct sampling and background measurements? I.e. how long between each background measurement? Were there strong changes observed between adjacent background measurements?

5) P6 L25ff: For AMS PMF analysis, signals with SNR = 0.2 – 2 are usually considered as "weak" and downweighed by a factor of 2-3. Only signals with SNR < 0.2 are removed. Why did the authors choose to remove signals with SNR <2?
6) P7 L23 & Fig 10: The authors do not explain anything about the two chosen methods (GBR vs LRR). Later in section 3.3 they also do not provide any more information about what these two methods mean, why they were used, or what the different values mean. As the paper is already very long as it is and only a qualitative comparison is conducted anyway, I recommend that the authors decide which of the methods they want to use here. To me the trends seem identical with just a general offset between LRR and GBR.
7) P15&16: Here the similarities of the single instrument PMF with the new data set are described and compared to the original ones (although only for AMS). The information presented here is not really used in the rest of the manuscript. This could be a section that could be moved to the supplement and replaced by a sentence stating that the new factors are similar enough to the old ones so that all the interpretations from the previous studies are still valid (see SI for details).
8) Table 1: out of curiosity, how many "common ions" are there in the two EESI-TOF data sets? I.e., how many of the 892 ions identified for the winter data were also present in the summer data?
9) P18 L22: It is not clear to how the authors handled the HOA and InorgNit factor reference spectra for the EESI-TOF part of the combined dataset. What was the "same intensity" to which all ions were set? Why was 0.01 cps (ug m^{-3})$^{-1}$ chosen? Why did they not just set the values to 0 (or a very small number, e.g. 1e-6)?
10) P19: where the factor profiles constrained for the C_{EESI} analysis in section 3.1.3?
11) P19 L29f: The authors state that the summer data follows the "expected" trend of the overlap values with C_{EESI}. But why is that trend expected? And what does it mean that the winter data does not follow the same trend (i.e. having the low values for p=7 and $C_{EESI} = 0.5$)? Could it be connected to the change in EESI background due to using a different solvent?
12) P20: Do the authors have any idea why the C_{EESI} value was so different for the two data set? I assume the AMS sensitivity can be considered as constant. Which changes may have occurred to the EESI to cause this value to change by 2 orders of magnitude (2 -> 0.05)?
13) P26 L9: Will the world may agree on the time for lunch, dinner time is very culture specific (just ask an Italian and a Finn ;-). It may be more specific to give the time of day in the description of the COA factor and then clarify that those times correspond to lunch and dinner in Switzerland.
14) P26 & Fig S28, S29: It is very good that the authors provide the factor mass spectra for comparison. But the chosen visualisation may not be the best. As this is HR data, sticks may overlap and not be distinguishable (especially for EESI-TOF). The authors could try using a modified Kroll diagram (OSC vs carbon number) with showing the signal intensity of the base case as the size of the symbols. Then a colour code could be used to show the difference to the compared factor. That would also highlight if certain groups of compounds are different (e.g. dimers).

15) P27 L14. Hereafter the notation "Sum_BB" etc is used. It is clear what the authors mean, but it may enhance readability if the Greek Σ were used instead of Sum_ (e.g., Σ BB). Especially in Fig 7 and Fig 10, this would highlight at these values are something different from the after bars/markers.
16) P29 L22: It feels a bit odd that one of the arguments to constrain individual factor profiles was to prevent factor splitting. But now the authors recombine two factors which they deem to have been split artificially. Since I am not a fan of overly constrained PMF, I do not want to recommend constraining LABB. But it makes me wonder if using the same constraints in cPMF as in single PMF is the right approach here.
17) P30 L 1 & 29: The authors have used correlations for almost everything to express similarity. But now for the factors they use "qualitatively similar". What does that mean here? Is there a reason why the authors do not use a mathematical measure for the similarity of their factors (e.g., uncentered R or contrast angle)? How can they be qualitatively similar if one contains ON and the other does not?
18) P30 L 1ff: Also, how meaningful is it to compare the factor mass spectrum of the constrained factors here? How much could e.g. HOA really vary with the set constraints? E.g. how big are the differences of HOA for summer and winter?
19) P30 L 9 "consistent with other studies" If the authors use the PMF factor from Qi et al. to create a constrained factor, they cannot claim that this factor than is in good agreement with Qi et al. (unless the constraint was so loose that a strong variation was truly possible)
20) Section 3.3: I find it difficult to follow in this section when the authors are talking about the Fig S32 and S33 and when they are using the "scaled" values in Fig 34 in their arguments. I also do not understand what the benefit is of Fig 34. The spread of the AS_k values are already visible in S32&33. For me the additional scaling was more confusing than enlightening.
21) p33 L43: how is COAs,c multimodal in Fig S32?
22) p 34 L 7ff I find the predictive value of levoglucosane/C6H10O5 very limited. It only works for BB factors in which the ion associated with levoglucosane is not disturbed by anything. If the origine of the factors have not yet been interpreted, this value may be misleading.
23) P35 L1f & Fig 9: I find the correlation of H:C and relative AS_k rather poor. 5 markers fall into the square H:C 1.58 – 1.66 and AS 1-2 without any clear trend in my eyes. Also, why was H:C chosen? How would this look with O:C or OSc?
24) Section 4: In my opinion the authors could put a bit more emphasis on this part of the manuscript. The implications for the interpretation of the factor contributions for the EESI-TOF data are big while the AMS part as not affected as much. To me, that is an important message for any PMF analysis of instruments which lack detailed sensitivity information (so also FIGAERO-CIMS). Already for one instrument applied at the same location but in two different seasons, such big differences are observed. How careful should we then be when comparing factors obtained for different locations.

25) Fig 11-13: Although I would like to see a bit more emphasis on the Atmospheric Implications section, I do think that the authors should decide if they prefer Fig 11 or Fig 13 as they do show the same information. One of them could go to the supplement information. Also Fig 12 is not providing that much exiting visual information. I take from Fig 12 that for AMS pmf factors, the sensitivity does not matter (as could be expected).

26) P39 Fig 9 The summer and winter symbol are both circles in the legend. I think you need a square for winter.

27) P 42 L13f: “optionally constraining factor profiles for one or both instruments” I did not find the place where a factor was constrained for one of the instruments but not for the other. As I understood the method, that is not possible. One a-value is applied for a factor containing both EESI-TOF and AMS ions. Hence a factor is either constrained (to a certain degree) or not.

References

Bell, D., Wu, C., Bertrand, A., Graham, E., Schoonbaert, J., Giannoukos, S., Baltensperger, U., Prevot, A., Riipinen, I., El Haddad, I. and Mohr, C.: Particle-phase processing of α-pinene NO3 secondary organic aerosol in the dark, Atmos. Chem. Phys. Discuss., 1–28, doi:10.5194/acp-2021-379, 2021.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R. and Thornton, J. A.: An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic and organic compounds, Environ. Sci. Technol., 48(11), 6309–6317, doi:10.1021/es500362a, 2014.