Review of "Quantification of primary and secondary organic aerosol sources by combined factor analysis of extractive electrospray ionisation and aerosol mass spectrometer measurements (EESI-TOF and AMS)"

Brief summary

In "Quantification of primary and secondary organic aerosol sources by combined factor analysis of extractive electrospray ionisation and aerosol mass spectrometer measurements (EESI-TOF and AMS)" the authors take on the challenging task of not only performing positive matrix factorization (PMF) source apportionment on a relatively new measurement method, EESI-TOF-MS, but also combine that dataset with AMS data to present a new application of PMF they call "combined PMF (cPMF)". In great detail the authors outline the procedure they followed to perform cPMF. They present a PMF factor-based approach to estimating sensitivities from the EESI-TOF and describe how they use bootstrapping to estimate uncertainties for the PMF factors. After reading the paper I have an appreciation for the challenging of appropriately preparing and evaluating the data input to and produced from the cPMF analysis. I suspect any researcher utilizing this technique in the future would have to apply a similar level of rigor. This paper is appropriate for the journal and should be published with minor revisions.

While thorough, rigorous, and interesting, this paper is very long and has a very long supplement. I think it is useful to consider how very long papers can impact the accessibility of a manuscript. For many scientists, including myself, this is a very challenging task in addition to the great effort of doing quality research. I acknowledge the supplement is long mostly because of the 34 supplemental figures, but one way to decrease the length of the main manuscript is to partition some of the information that is highly detailed—but is not absolutely necessary to understand the main points of the manuscript—to sections in the supplement for the advanced reader.

Major comments

Major comment 1: At the end of section 2.2.2 the apparent sensitivity application informed by the AMS mass is introduced and then said it will be discussed later. Section 2.2.3 basically does the same thing. Can it be briefly mentioned here that two methods of applying EESI-TOF sensitivities were tested in the study and they'll be discussed and evaluated in a different section? In its current state the authors review the methods then say they will discuss them further later.

Major comment 2: (page 8, line 13) I'm unclear about what residuals are used and how the residuals are used as a reference to help retrieve a balanced solution from the AMS/EESI-TOF joint PMF. Are the residuals the total residual (basically the Q value) of the "best" stand-alone AMS and EESI-TOF PMF runs? What does it mean to use these residuals "as a reference to retrieve a balanced solution"? Instead of "(step 4)" could you replace that with "(procedure described in step 4)"? It's unclear if, when reading this, the reader should skip to step 4.

Major comment 3: Can the authors consider changing the title of section 2.3 to "combined PMF method" or something similar? It would describe the section better as this section is a set of instructions for researchers who would want to apply an identical or similar method to their datasets.

Major comment 4: I'm finding the presentation of section 2.3 hard to follow. There's description of some unique things that were done for the PMF analysis in this paper and there's description of PMF generally that have been published many times. I have some suggestions for clarification.

(1) Change figure 2 to figure 1.

(2) Combine the ideas from (page 8, lines 1-9) and (page 9, lines 6-24) with each other and use it to introduce section 2.3. Trim it down considerably. Can say "We used PMF and in one sentence this is what it is and what it does. We combined the mass spectral time series from the EESI-TOF and AMS to create the input matrix for the PMF analysis. We performed PMF on the combined input matrix and we call this "combined PMF" (cPMF). A conceptual schematic is shown in Figure 1." Two additional things to keep that the authors mentioned that I thought was useful was the respective units of the AMS and EESI components and the inclusion of NO+ and NO2+.
(3) Remove (page 10) lines 7-19 and reference either the Paatero papers or Ulbrich's review.
(4) More or less remove (page 9) lines 11-19 and equation 5 for the same reason.
(5) In a new paragraph make the major points "We present an overview of the cPMF through a series of steps listed below. Details corresponding to each step are outlined in subsequent sections. The overall procedure is outlined in Figure 2, with the main steps as follows: …".
(6) Title subsections as 2.3.# where # = 1-6 (representing each step in cPMF) and include the relevant information to perform that step in that section. For example, the first subsection would be Section 2.3.1 with a title of "Step 1: Conventional PMF". In this section you'll say PMF was performed on the AMS and EESI-TOF datasets independently. You'll also explain how constraints on factor profiles were applied. Section 2.3.2 with a title "Step 2: Creating input matrix for cPMF". Maybe consider combining steps 2 and 3.

It's clear all the elements of the analysis are detailed in the subsections, but it's not clear at what points analyses are performed. For instance, (page 11) lines 1-21 describe the calculation of the apparent sensitivity for the EESI-TOF, but it's unclear at what step(s) in the cPMF method this is done.

Major comment 5: I apologize, I might have missed some information; why is 1 ug m^{-3} used as a reference value?

Major comment 6: In subsections 2.3.3 and 2.3.4 the authors do a very nice job of explaining how they treated and evaluated the data and solutions for the cPMF. I think I personally would have to actually go through the process to fully understand all the details.

Major comment 7: Consider putting the text between the title of section 3.2 and 3.2.1 as a supplemental section. I was finally excited to see some results with the title "cPMF results", but instead started reading more details of analysis.

Major comment 8: The authors have demonstrated the application of cPMF to a multi-season, complex mass spectrometry dataset from two instruments. Despite the thorough and rigorous development and evaluation of the method some curiosities and uncertainties still persisted like the contribution of high sensitivity species in contributing to a factor profile, multi-modality of sensitivity values in the COA and CSOA factors, and increasing uncertainty when sub-dividing factors like in the case of the aggregate BB factor. These uncertainties contribute in the overall uncertainty to a relatively complex data processing procedure. Can the authors briefly provide any laboratory experiments, calibrations, or "ideal" datasets in the conclusions section where this cPMF method could be applied in the future as test cases for improving the interpretability and quality of the cPMF analysis?

Minor comments

(page 3, line 3) "*The corresponding decrease in chemical resolution, particularly for ~~the~~ multifunctional and/or highly oxygenated SOA components ~~molecules of which SOA is comprised~~…*"

Reviewer: Please remove the words indicated above.

(page 3, line 47) *"…gas-phase concentrations measured by a Vocus proton transfer reaction-mass spectrometer (Vocus-PTR-MS) (Wang et al., 2021)"*

Reviewer: I didn't see the Wang et al. study listed in the references. Please list the following article in the references section **"Constraining the response factors of an extractive electrospray ionization mass spectrometer for near-molecular aerosol speciation" Wang, et al. (2021)**

(page 4, line 22) *"The present study is the first application of cPMF to a joint EESI-TOF/AMS dataset, and the first ~~attempt at~~ quantitative EESI-TOF-driven source apportionment."*

Reviewer: Please remove words indicated above.

(page 5, line 20) *"…from highresolution mass spectral analysis…"*

Reviewer: Replace "highresolution" with "high resolution" or "high-resolution".

(page 16, line 2) Is "(2.54)" a ratio value? If so can you change it to read ($NO^+/NO_2^+ = 2.54$)? It's unclear what (2.54) means as is.

(page 30, line 2) Replace "This factor ~~has a qualitatively a~~ profile similar to the summer campaign…" with "This factor qualitatively has a profile similar to the summer campaign…".

(page 33, paragraph 2) I think using the COA profile as a reference is an appropriate solution to a tough problem.

(Figure 8) Figure 8 has a line through the x-axis label. I assume this is a formatting/review feature accidentally carried into the PDF from Word?

(Figure 13) Can you set the maximum value for the y-axis in panel a = 0.5? In the caption can you note what defines the box and whiskers (i.e. are the boxes 25^{th} and 75^{th} percentiles?)

(page 43, line 1) "The cPMF method presented herein ~~is~~ can be utilised as-is not only for the AMS/EESI-TOF combination**…"**

Reviewer: Please delete the misplaced "is" in the sentence above.