Response to RC3

We thank the reviewer for the helpful comments. Below we provide a detailed point-by-point response to the issues raised by the reviewer. Reviewer comments provided in *italics* and our responses follow in normal text. Changes to the manuscript are denoted in blue font. When our responses reference other comments, we use the formalism R#C#, such that R1GC5 and R1SC5 would refer to General Comment 5 by Reviewer 1, and Specific Comment 5 by Reviewer 1. When indicating the page and line, we use the formalism P#L#, such that P10L5 would refer to Page 10 Line 5.

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.

Response:

We appreciate the reviewer's suggestion and have clarified this in the manuscript as follows.

In Section 2.2.2 (P7 L11, following Eq. 3), we discuss the method based on cPMF outputs:

"Equation (3) is used to determine the apparent factor-specific sensitivities from cPMF outputs by defining the AMS contribution to the factor profile (μg m^{-3}) as $Mass_x$ and the EESI-TOF contribution (cps) as I_x."

In Section 2.2.3 (P8 L2, following Eq. 4), we present the GBR-based method used for comparison:

"The factor-specific sensitivities derived from cPMF (Eq. 3) and from the GBR model (Eq. 4) are compared in Sect. 3.2."

Major Comment #2

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.

Response:

We have clarified several issues here. First, the general reference to "residuals" is specifically to scaled residual distributions (e_{ij}/s_{ij}), as discussed in detail in Section 2.3.3. Second, we have clarified what is meant by using the residuals "as a reference to retrieve a balanced" solution and the associated reference to step 4. The revised text reads (P8L27):

"1) PMF analyses are conducted on the standalone EESI-TOF and AMS datasets with synchronised time resolution, including constraints on factor profiles as necessary. Residual distributions from the optimised solutions are used later in step 3 as a criterion for assessing relative instrument weight."

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.

Response:

Thanks for this suggestion. We change the title of this subsection to "Combined Positive Matrix Factorisation (cPMF) Method".

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

Response:

We appreciate the reviewer's suggestions, and have made the following improvements to the manuscript:

1. We condensed the introduction to PMF and cPMF, roughly following the lines suggested by the reviewer in points 1 and 2.
2. We clarified the old Figure 1 (now Figure 2) and linked it more closely to the related text by labelling the corresponding steps in boxes.
3. Sect. 2.3.0 to 2.3.4 are numbered to align with steps of the same number in the new Fig. 2 and related text. In Sect. 2.3.0, the basic principle of PMF, and *a*-value approach is introduced, we also mentioned its capability in cPMF analysis. Sect 2.3.1 demonstrates how the combined dataset is constructed. In Sect. 2.3.2, we introduced the general method to construct the reference profile for cPMF analysis. It Sect. 2.3.3, the instrument weighting method and corresponding evaluation process are introduced. Finally, in Sect. 2.3.4, we introduced the case-specific criteria for solution selection and bootstrap analysis.
4. We decided to keep Eq. (5) and Eq. (6) in the manuscript, because Eq. (5) is the basic principle of PMF and Eq. (6) introduces the concept of scaled residual scaled residual (e_{ij}/s_{ij}). Although well known, both define symbols and quantities that are critical for later discussion. Equation (7) has been deleted as suggested.

Major Comment #5

I apologize, I might have missed some information; why is 1 ug m-3 used as a reference value?

Response:

This is used for convenience in representing the factor profiles. It is similar to the traditional presentation of AMS-only PMF data (dimensionless factor profiles normalized such that the sum is 1), while providing an easy means of visually separating profiles of factors to which the EESI-TOF is not sensitive vs. those to which it is. It also simplifies some of the governing equations used to separate EESI-TOF and AMS components of the cPMF solutions.

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.

Response:

We appreciate the reviewer's support and agree this is a complex analysis. We have tried to make the discussion easier to follow by moving dataset-specific details to the Supplement, as discussed in response to RC1GC5.

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.

Response:

We have moved this section, which introduces the method from Kiendler-Scharr et al. (2016) to estimate the contribution from organonitrate and inorganic nitrate to individual factors, to the SI as Text S3.

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?

Response:

We certainly agree with the reviewer on the need for continued evaluation of cPMF results and performance. In our view, the most useful strategy at present is simply the application of cPMF to additional datasets. We are currently in the process of doing this for both laboratory measurements and ambient datasets from different geographical areas, although consider it premature to comment on this in the current manuscript.

Another useful approach would be the replacement of the EESI-TOF with another instrument having high chemical resolution but semi-quantitative outputs, such as the FIGAERO-CIMS. This is noted in the Conclusions.

Minor Comment #1

P3 L3: "*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.

Response:

These words are removed and the revised text reads (P3L4):

The corresponding decrease in chemical resolution, particularly for multifunctional and/or highly oxygenated SOA components (e.g., multifunctional acids, peroxides, organonitrates, organosulfates, oligomers), limits the resolution of SOA source apportionment.

Minor Comment #2

P3 L47: "...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)**

Response:

The reference list has been updated to include:

Wang, D. S., Lee, C. P., Krechmer, J. E., Majluf, F., Tong, Y., Canagaratna, M. R., Schmale, J., Prévôt, A. S. H., Baltensperger, U., Dommen, J., El Haddad, I., Slowik, J. G., and Bell, D. M.: Constraining the response factors of an extractive electrospray ionization mass spectrometer for near-molecular aerosol speciation, Atmos. Meas. Tech., 14, 6955-6972, https://doi.org/10.5194/amt-14-6955-2021, 2021.

Minor Comment #3

P4 L22: "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.

Response:

Now these words are deleted, and the sentence is corrected in P4 L25 as:

The present study is the first application of cPMF to a joint EESI-TOF/AMS dataset, and the first quantitative EESI-TOF-driven source apportionment.

Minor Comment #4

P5 L20: "...from highresolution mass spectral analysis..."

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

Response:

We now use "high-resolution" throughout the manuscript.

Minor Comment #5

P16 L2: Is "(2.54)" a ratio value? If so can you change it to read (NO+/NO2+ = 2.54)? It's unclear what (2.54) means as is.

Response:

Yes, it is the ratio of NO^+/NO_2^+. Now we have changed this here and throughout out the manuscript wherever appropriate.

Minor Comment #6

P30 L2: 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...".

Response:

This text was modified in response to RC1SC17, where the use of "qualitatively" was found unclear. The revised text (P21 L1) reads:

"This factor is dominated by the $C_nH_{2n+1}^+$, and $C_nH_{2n-1}^+$ series, consistent with *n*-alkanes and branched alkanes, with lower CO^+ and CO_2^+ content than the $HOA_{S,C}$. The $HOA_{W,C}$ time series correlates strongly with $HOA_{W,A}$ (r^2 of 0.913)."

Minor Comment #7

P33 Paragraph2: I think using the COA profile as a reference is an appropriate solution to a tough problem.

Response:

We appreciate the reviewer's support. In the future, we intend to use the sensitivity of a reference compound (levoglucosan) from on-site calibrations to facilitate cross-campaign comparisons.

Minor Comment #8

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?

Response:

We have corrected this formatting error. The figure appears below.

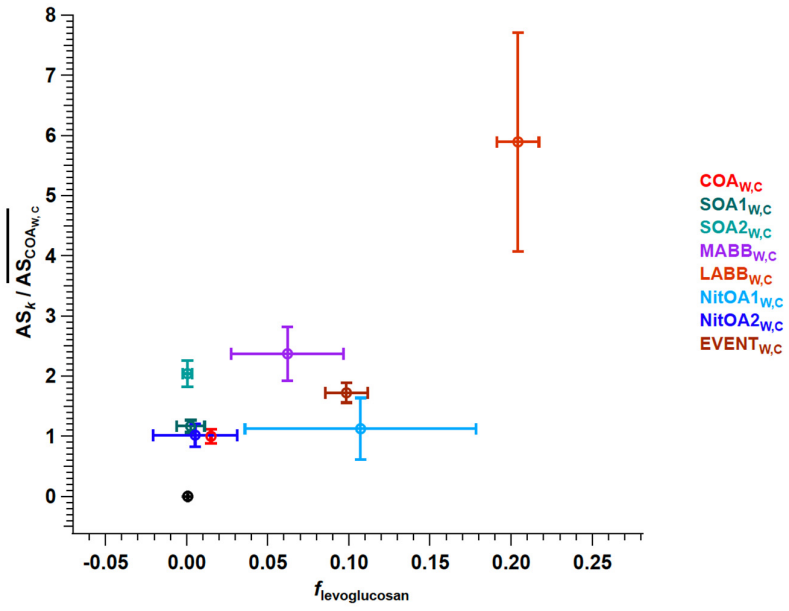

Figure 6. Relative apparent sensitivity $AS_k/\overline{AS_{COA_{W,C}}}$ as a function of levoglucosan fraction for all factors resolved from the cPMF of the winter dataset except $CSOA_{W,C}$. Error bars denote standard deviation.

Minor Comment #9

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 25th and 75th percentiles?)

Response:

Now the maximum value for y-axis for summer is set to 0.5. We have clarified the caption and also expanded the explanation by adding the 25th and 75th percentiles. The revised text reads:

"The box-and-whisker diagram shows the mean (open/filled circle), median (horizontal bar), interquartile range (rectangle, the 25th percentile is the lower edge and the 75th is the upper edge), and minimum/maximum values (whiskers)."

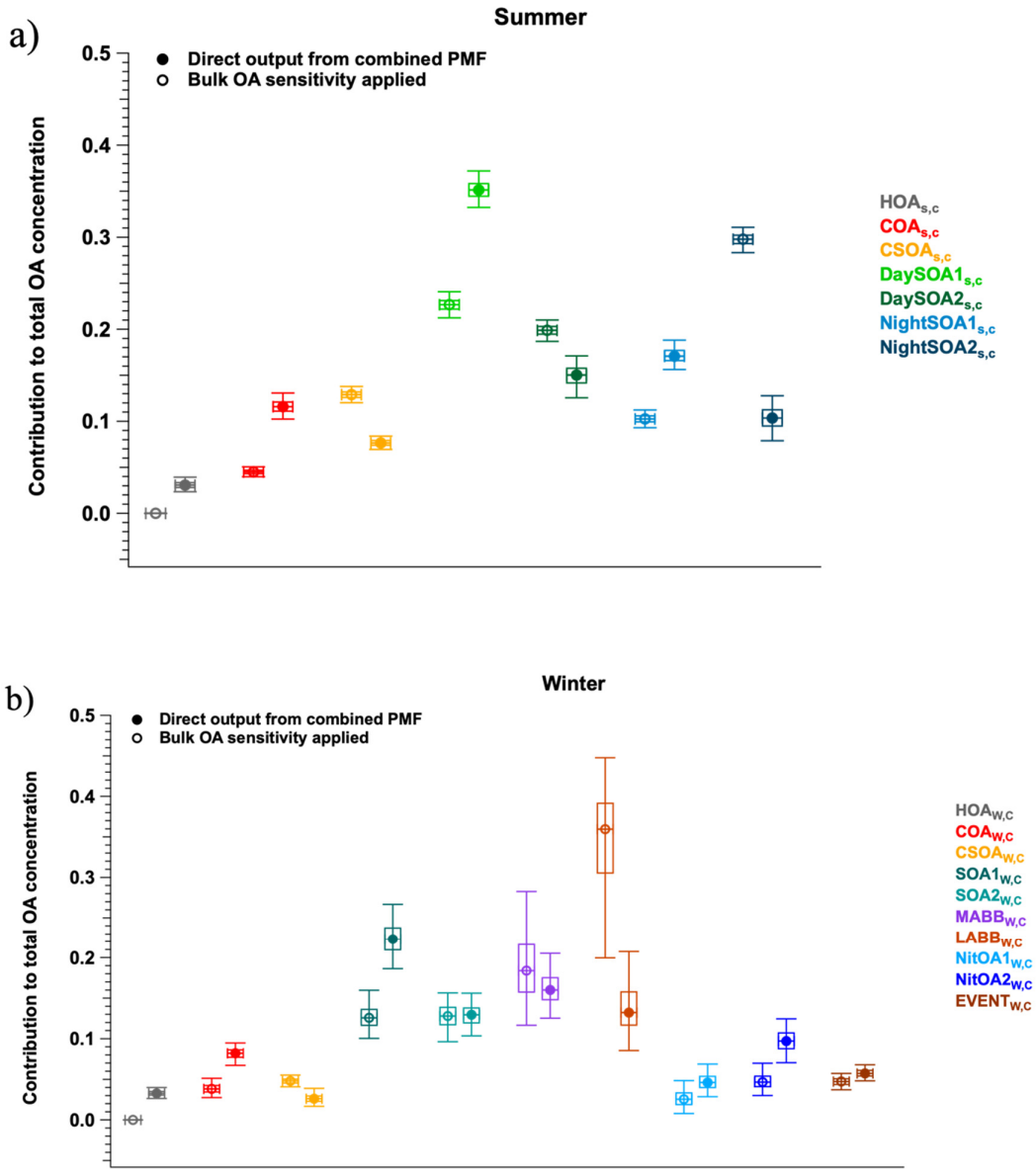

Figure 13. Box-and-whisker diagrams of factor contribution to total OA with/without applying the factor dependent sensitivities, for summer in a) and winter in b) within accepted solutions. For each pair of factors, the contribution without factor-dependent sensitivity applied is shown in the left box (open symbols), whereas the contribution corrected by factor-dependent sensitivity is shown in the right box (full symbols). The box-and-whisker diagram shows the mean (open/filled circle), median (horizontal bar), interquartile range (rectangle, the 25th percentile is the lower edge and the 75th is the upper edge), and minimum/maximum values (whiskers). Note that here the contribution of InorgNit factor and contribution of NO^+ and NO_2^+ from inorganic nitrate in each factor are excluded.

Minor Comment #10

*P43 L1: "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.

Response:

The typo has been corrected.

Reference

Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prevot, A. S. H., Aijala, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H. C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, Geophys. Res. Lett., 43, 7735-7744, https://doi.org/10.1002/2016gl069239, 2016.