Response to RC1

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

General Comment #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.

1) *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?*

2) *How was it determined if a factor was "mixed"?*

3) *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*

4) *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 NO2+ ratio for the AMS calibration with Ammonium Nitrate seems to suggest some instrumental differences*

Response:

Thanks for this comment. We address the issue raised point-by-point:

1. We attempted both unconstrained and constrained runs, empirically arriving at the constraint strategy described herein. Although we have only investigated two datasets, our results suggest that factors appearing only in one instrument (here HOA, InorgNit) are difficult to separate without constraints. This may be because their contribution to Q is reduced relative to the single instrument case, similar to previous studies showing that low-mass factors are difficult to resolve accurately from unconstrained PMF (Ulbrich et al., 2009). For InorgNit and HOA, specifically, these factors often require constraints in standalone AMS PMF; with no additional tracers for these factors coming from the EESI-TOF but other unrelated variables added in, it would be very surprising if constraints were not required. COA is a more complex case, and whether or not it requires constraints is likely to rely on the characteristics of the specific dataset (e.g., fractional contribution to total signal, degree of temporal correlation with other factors

2. A factor is determined as mixed in any of the following cases: 1) the mass spectrum from one and/or both instrument in factor shows chemical evidence of influences from other sources; 2) increasing the

number of factors, splits a single factor into two factors with similar mass spectral features but different temporal features (e.g., the several MABB factors in Qi et al. (2019)); and/or 3) inconsistency between the AMS and EESI-TOF components of the factor profile.

3. This part is moved to Text S2, and we emphasise this point in the Text S2 as:

To determine the $F_{overlap}^*$, the EESI-TOF-only PMF was re-run on only the period when both AMS and EESI-TOF were operating based on the same configuration and mass spectra in Stefenelli et al. (2019) and Qi et al. (2019)

4. Although the same instruments were used in the two studies, measurements were conducted approximately half a year apart, so there is no guarantee of identical instrument tuning and performance. Further, the EESI-TOF used a different working solution in the two studies: 1:1 water:methanol in summer and 1:1 water:acetonitrile in winter. As a result, all analysis and corrections were performed separately for the two campaigns. We clarify this for the Pieber effect (Pieber et al., 2016), specifically, as follows (P5 L26-28):

The contribution of nitrate ions to CO_2^+ was estimated separately in each campaign from their respective NH_4NO_3 calibrations.

We further note that the differences in ambient NO^+/NO_2^+ values observed in the summer and winter campaigns are not explainable by instrument differences and are attributable instead to NO_3 from different inorganic cations, e.g., NH_4NO_3 vs. KNO_3

General Comment #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.

Response:

The extent of clustering observed in the EESI-TOF depends strongly on instrument settings, i.e., the collision energy in the quadrupole guides. The settings in these field campaigns appear to have led to relatively energetic collisions, such that clustering with solvent molecules is disfavoured. This is supported by comparisons of the ambient data with selected chamber measurements (e.g., terpene oxidation), where we identified ions giving the largest signal from clusters and verified that they were not significant in the field data. It is possible that some minor signals from cluster ions remain, but they do not appear to greatly influence the data.

Fragmentation due to the transfer of excess energy during ionisaiton has not been observed in the EESI-TOF and is not expected. However, molecular decomposition, possibly from hydrolysis reactions in the ESI droplets, has been observed in the EESI-TOF for certain molecular classes We cannot rule out the possibility that such reactions affect the data, although these are not expected to affect the majority of the signal (Bell et al., 2022).

General Comment #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 CEESI (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.

Response:

This is an excellent point, and we agree that the computational costs are worth considering. For our study, the cPMF on summer data and winter data 1) for 2D-scan costed us 3 days and 1 week, respectively, and 2) for bootstrap costed about 1 and 2 weeks, respectively. Nevertheless, we consider the cPMF outputs to be of sufficiently high value to be worth the computational investment. In terms of dataset size, SoFi/ME-2 are capable of handling datasets of the scale mentioned by the reviewer, although of course the computational time will be considerable. With that said, we would strongly support efforts to make PMF solvers faster and/or more compatible with large datasets. We also note that the trend of increasing chemical resolution in atmospheric measurements (and thus dataset size/complex) suggests that the need for such software improvements will become increasingly urgent in the future.

General Comment #4

The authors show that for each data set a new set of parameters (a- constraints, CEESI, ASk) 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.

Response:

Thanks for this suggestion. We state it once again in the second paragraph of the conclusion part in P34 L12:

Note that while these methods provide a general procedure for cPMF analysis, the specific parameters employed (i.e., the number of factors (p), instrument weighting parameter (C_{inst}), and the factors to be constrained and the tightness of constraints (a value ranges)) are dataset-specific and should be determined independently for each new analysis.

General Comment #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.

Response:

We appreciate the reviewer's suggestion. We have chosen to keep section 2.3, which describes the cPMF method in the main text, as the introduction of this method constitutes a central advance of the paper. However, we have moved the (old) section 3.1, which presented the details of the application of the cPMF to the present datasets (e.g., discussion of individual instrument solutions, construction of dataset-specific profiles, exploration of the solution space in terms of C and p, selection of the base case) to the supplement as section S2. We have also moved the discussion of the method used to organonitrate contributions to NO^+ and NO_2^+ (old section 3.2) to the SI as section S3.

Specific Comment #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.

Response:

We have added the results of Lee et al. (2020) as follows P3 L18):

Another source apportionment study from Lee et al. (2020) using FIGAERO-CIMS spectra successfully distinguished ambient SOA formation and ageing pathways in two forested regions.

Specific Comment #2

P4 L38: typo: wind speed (WD) -> (WS)

Response:

Now the typo is corrected in P4 L38:

Gas-phase species, e.g., nitrogen dioxide (NO_2), nitrogen oxide (NO) and sulfur dioxide (SO_2) and meteorological data, e.g., temperature (T), relative humidity (RH), radiation, wind speed (WS) and wind direction (WD) are recorded by the monitoring station.

Specific Comment #3

P5 L14: typo: "by the massed base method" -> with the mass based method

Response:

Now the typo is corrected in P5 L14:

At the beginning and end of the both campaigns, the instrument was calibrated for ionisation efficiency (IE) using 400 nm NH_4NO_3 particles using the mass-based method (Jimenez et al., 2003; Canagaratna et al., 2007).

Specific Comment #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?

Response:

The detailed operation and evaluation of instrument performance is discussed in Stefenelli et al. (2019) and Qi et al. (2019). To avoid making the paper too lengthy, we include information about the measurement cycle here but refer the reader to the original manuscripts for more detailed discussion. During both campaigns the EESI-TOF alternated between direct sampling for 8 min and background sampling for 3 min. Adjacent background periods were similar. The transition period from direct sampling to background sampling and from the background sampling to direct sampling was excluded in both campaigns (Qi et al., 2019; Stefenelli et al., 2019). The revised text reads P6 L15:

The EESI-TOF alternates between direct sampling (8 min) and sampling through a particle filter (3 min) to provide a measurement of instrument background (including spray). No major changes between adjacent background measurements were observed in either campaign (Qi et al., 2019; Stefenelli et al., 2019).

Specific Comment #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?

Response:

For the AMS, ions with low SNR were indeed treated as suggested by the reviewer, consistent with the recommendations of Paatero and Hopke (2003). This information has been added to the manuscript as follows (P5 L24):

Ions with signal-to-noise ratio (SNR) smaller than 0.2 were excluded in the further analysis, whereas ions with an SNR between 0.2 and 2 were downweighted by a factor of 2 (Paatero and Hopke, 2003)

For the EESI-TOF, we have empirically found that "weak" ions can be affected by fluctuations in the electrospray and/or instrumental background. The more strict SNR threshold was chosen in Stefenelli et al. (2019) and Qi et al. (2019) to compensate for this, and we retain their approach for cross-comparability here.

Specific Comment #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.

Response:

We agree with the reviewer that the performance of the two models is similar, with the main difference being an offset. For simplicity, we have removed the LRR results and include only the GBR, because it is expected to perform better at handling possible interactions in the feature space.

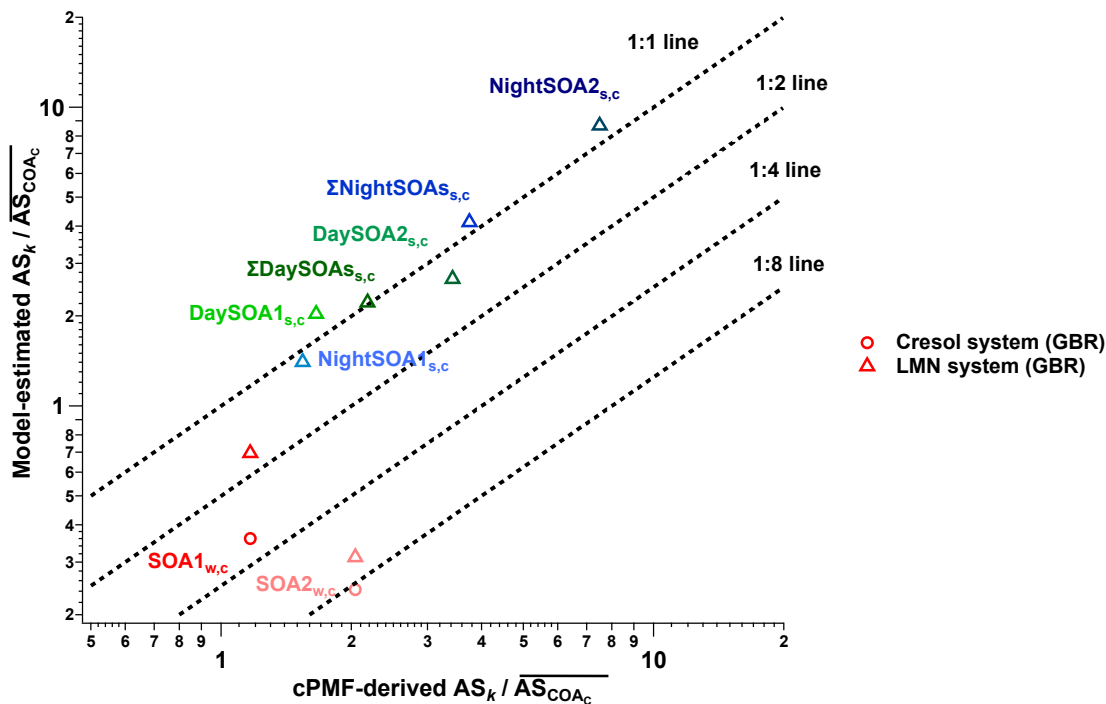The updated Figure 10 (now Figure 8) and the caption is shown below:

Figure 8. The estimated relative apparent sensitivity to COA ($AS_k/\overline{AS_{COA_C}}$) from the gradient boosting regression (GBR) model as a function of cPMF-derived $AS_k/\overline{AS_{COA_C}}$). The symbols indicate the different oxidation-precursor system (LMN for SOA produced from oxidation of limonene by ozone, cresol and TMB for SOA produced from oxidation of *o*-cresol and 1,3,5-trimethylbenzene by OH radicals, respectively).

Specific Comment #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)

Response:

We have moved this part of presentation and corresponding discussion to Text S2.1, including the figures comparing the result from this conventional PMF to the published result in Stefenelli et al. (2019) and Qi et al. (2019). This discussion is referenced in the manuscript as (P15, L32):

We re-ran the conventional PMF on the summer and the winter data, obtaining results similar to Stefenelli et al. (2019) and Qi et al. (2019), as discussed in Text S2 in the supplement.

Specific Comment #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?

Response:

There are 257 ions that are both found in PMF input matrices for both the summer and winter datasets. Here we attach the common ion list.

m/z	ion identity	m/z	ion identity	m/z	ion identity
148.07327	C7H11ONNa	227.12538	C10H20O4Na	282.05841	C10H13O7NNa
150.05255	C6H9O2NNa	228.08424	C8H15O5NNa	282.1312	C12H21O5NNa
151.07295	C7H12O2Na	229.03188	C7H10O7Na	283.07883	C11H16O7Na
152.03181	C5H7O3NNa	229.06825	C8H14O6Na	283.1152	C12H20O6Na
153.05222	C6H10O3Na	229.10464	C9H18O5Na	283.15158	C13H24O5Na
155.03148	C5H8O4Na	230.02711	C6H9O7NNa	283.18799	C14H28O4Na
157.01074	C4H6O5Na	233.07843	C11H14O4Na	284.07407	C10H15O7NNa
157.04713	C5H10O4Na	234.11006	C11H17O3NNa	284.18323	C13H27O4NNa
163.03656	C7H8O3Na	234.14645	C12H21O2NNa	285.05807	C10H14O8Na
163.07295	C8H12O2Na	235.09409	C11H16O4Na	285.09448	C11H18O7Na
163.12297	C10H15N2	236.08932	C10H15O4NNa	285.13086	C12H22O6Na
165.05222	C7H10O3Na	238.10498	C10H17O4NNa	286.05334	C9H13O8NNa
166.04745	C6H9O3NNa	238.14136	C11H21O3NNa	286.08972	C10H17O7NNa
166.08385	C7H13O2NNa	239.05261	C9H12O6Na	286.1261	C11H21O6NNa
167.03148	C6H8O4Na	239.08899	C10H16O5Na	287.16177	C16H24O3Na
167.06786	C7H12O3Na	240.12064	C10H19O4NNa	289.17743	C16H26O3Na
169.04713	C6H10O4Na	241.03188	C8H10O7Na	290.17267	C15H25O3NNa
170.04237	C5H9O4NNa	241.06825	C9H14O6Na	291.19308	C16H28O3Na
170.07877	C6H13O3NNa	241.10464	C10H18O5Na	292.15192	C14H23O4NNa
176.06821	C8H11O2NNa	242.02711	C7H9O7NNa	293.13593	C14H22O5Na
177.05222	C8H10O3Na	242.09988	C9H17O5NNa	293.17233	C15H26O4Na
177.08859	C9H14O2Na	243.04752	C8H12O7Na	293.20871	C16H30O3Na
178.08385	C8H13O2NNa	243.08391	C9H16O6Na	294.09482	C12H17O6NNa
179.06786	C8H12O3Na	243.12029	C10H20O5Na	294.1312	C13H21O5NNa
179.10425	C9H16O2Na	244.04277	C7H11O7NNa	294.20395	C15H29O3NNa
180.06311	C7H11O3NNa	244.07916	C8H15O6NNa	295.1152	C13H20O6Na

181.04713	C7H10O4Na	244.11554	C9H19O5NNa	295.15158	C14H24O5Na
181.08353	C8H14O3Na	245.11482	C13H18O3Na	295.18799	C15H28O4Na
182.07877	C7H13O3NNa	245.1512	C14H22O2Na	296.14685	C13H23O5NNa
183.09917	C8H16O3Na	247.09409	C12H16O4Na	297.09448	C12H18O7Na
184.05803	C6H11O4NNa	247.16685	C14H24O2Na	297.13086	C13H22O6Na
185.04204	C6H10O5Na	248.08932	C11H15O4NNa	297.16724	C14H26O5Na
185.07843	C7H14O4Na	248.12572	C12H19O3NNa	297.20364	C15H30O4Na
187.05769	C6H12O5Na	249.10973	C12H18O4Na	298.1261	C12H21O6NNa
189.08859	C10H14O2Na	249.14612	C13H22O3Na	298.16248	C13H25O5NNa
190.08385	C9H13O2NNa	251.05261	C10H12O6Na	299.11011	C12H20O7Na
191.10425	C10H16O2Na	251.08899	C11H16O5Na	299.18289	C14H28O5Na
192.0995	C9H15O2NNa	251.12538	C12H20O4Na	300.069	C10H15O8NNa
193.04713	C8H10O4Na	252.04787	C9H11O6NNa	300.10538	C11H19O7NNa
193.08353	C9H14O3Na	253.03188	C9H10O7Na	300.14175	C12H23O6NNa
194.04237	C7H9O4NNa	253.06825	C10H14O6Na	301.05301	C10H14O9Na
195.02638	C7H8O5Na	253.10464	C11H18O5Na	302.08463	C10H17O8NNa
195.06277	C8H12O4Na	253.17741	C13H26O3Na	302.12103	C11H21O7NNa
195.09917	C9H16O3Na	254.13628	C11H21O4NNa	303.06866	C10H16O9Na
197.00566	C6H6O6Na	255.04752	C9H12O7Na	303.10504	C11H20O8Na
197.04204	C7H10O5Na	255.08391	C10H16O6Na	303.14142	C12H24O7Na
197.07843	C8H14O4Na	255.12029	C11H20O5Na	304.10028	C10H19O8NNa
198.07368	C7H13O4NNa	256.07916	C9H15O6NNa	304.13666	C11H23O7NNa
199.05769	C7H12O5Na	256.11554	C10H19O5NNa	307.1152	C14H20O6Na
199.09409	C8H16O4Na	257.06317	C9H14O7Na	307.15158	C15H24O5Na
200.01656	C5H7O6NNa	257.09955	C10H18O6Na	307.18799	C16H28O4Na
200.05293	C6H11O5NNa	258.05841	C8H13O7NNa	308.18323	C15H27O4NNa
200.08932	C7H15O4NNa	258.09482	C9H17O6NNa	309.13086	C14H22O6Na
201.03696	C6H10O6Na	258.1312	C10H21O5NNa	310.16248	C14H25O5NNa
203.01622	C5H8O7Na	261.09448	C9H18O7Na	311.14651	C14H24O6Na
203.05261	C6H12O6Na	265.14102	C13H22O4Na	313.08939	C12H18O8Na
204.06311	C9H11O3NNa	266.06351	C10H13O6NNa	313.12576	C13H22O7Na
205.08353	C10H14O3Na	267.04752	C10H12O7Na	313.16217	C14H26O6Na
206.07877	C9H13O3NNa	267.1203	C12H20O5Na	314.19379	C14H29O5NNa
206.11514	C10H17O2NNa	267.15668	C13H24O4Na	317.17233	C17H26O4Na
207.02638	C8H8O5Na	268.07916	C10H15O6NNa	321.13086	C15H22O6Na
207.06277	C9H12O4Na	268.18832	C13H27O3NNa	321.16724	C16H26O5Na
207.09917	C10H16O3Na	269.02679	C9H10O8Na	321.20364	C17H30O4Na
208.09441	C9H15O3NNa	269.06317	C10H14O7Na	325.08939	C13H18O8Na
209.04204	C8H10O5Na	269.09955	C11H18O6Na	325.12576	C14H22O7Na
209.07843	C9H14O4Na	269.13593	C12H22O5Na	325.16217	C15H26O6Na
209.11482	C10H18O3Na	270.05841	C9H13O7NNa	325.19855	C16H30O5Na
210.11006	C9H17O3NNa	270.09482	C10H17O6NNa	325.23492	C17H34O4Na
211.05769	C8H12O5Na	271.07883	C10H16O7Na	326.15741	C14H25O6NNa

211.09409	C9H16O4Na	271.1152	C11H20O6Na	326.19379	C15H29O5NNa
215.05261	C7H12O6Na	271.15158	C12H24O5Na	329.24509	C20H34O2Na
215.08899	C8H16O5Na	273.1825	C16H26O2Na	336.17813	C16H27O5NNa
217.06825	C7H14O6Na	275.12537	C14H20O4Na	337.16217	C16H26O6Na
220.05803	C9H11O4NNa	275.16177	C15H24O3Na	337.19855	C17H30O5Na
220.09441	C10H15O3NNa	276.12064	C13H19O4NNa	337.23492	C18H34O4Na
221.07843	C10H14O4Na	276.15701	C14H23O3NNa	339.2142	C17H32O5Na
223.02132	C8H8O6Na	277.17743	C15H26O3Na	340.17307	C15H27O6NNa
223.05769	C9H12O5Na	279.08392	C12H16O6Na	340.24582	C17H35O4NNa
223.09409	C10H16O4Na	279.1203	C13H20O5Na	345.20364	C19H30O4Na
224.08932	C9H15O4NNa	279.15668	C14H24O4Na	345.24002	C20H34O3Na
225.03696	C8H10O6Na	279.19308	C15H28O3Na	345.2764	C21H38O2Na
225.07333	C9H14O5Na	280.07916	C11H15O6NNa	349.16217	C17H26O6Na
225.10973	C10H18O4Na	280.15192	C13H23O4NNa	351.2142	C18H32O5Na
226.10498	C9H17O4NNa	281.09955	C12H18O6Na	373.23492	C21H34O4Na
227.05261	C8H12O6Na	281.13593	C13H22O5Na	389.26624	C22H38O4Na
227.08899	C9H16O5Na	281.17233	C14H26O4Na		

Specific Comment #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)?

Response:

The approach taken in this paper actually aligns with the reviewer's suggestion. We found that setting the values to 0 caused instabilities in the ME-2 solver, for reasons unknown. Therefore, to propose a generalised strategy that can be applied regardless of differences in the measurement units between instruments, we based this "same intensity" on the factor sensitivity, AS_k. This is based on Eq. 11, repeated here for clarity:

$$\frac{\left(f_{k,j}\right)_{j=all,ref}}{1 \ \mu g \ m^{-3}} = \begin{cases} \dfrac{\left(f_{k,j}\right)_j}{\sum_j \left(f_{k,j}\right)_j}, & j \in AMS, ref \\[3ex] AS_k \cdot \dfrac{\left(f_{k,j}\right)_j}{\sum_j \left(f_{k,j}\right)_j}, & j \in EESI, ref \end{cases} \tag{11}$$

For the case where the EESI-TOF is insensitive to the profile, we calculate the profile as follows:

$$\frac{\left(f_{k,j}\right)_{j=all,ref}}{1 \ \mu g \ m^{-3}} = \begin{cases} \dfrac{\left(f_{k,j}\right)_j}{\sum_j \left(f_{k,j}\right)_j}, & j \in AMS, ref \\[3ex] AS_k \cdot \dfrac{1/n_{EESI}}{\sum_j \left(f_{k,j}\right)_j}, & j \in EESI, ref \end{cases} \tag{S1}$$

Here n_{EESI} denotes the number of ions in the EESI-TOF dataset and assume $AS_k = 0.01$ cps (ug m^{-3}). This value is chosen to reliably yield and appropriately small numbers (again, regardless of instrument measurement units) while avoiding the 0-based solver instability. This value for AS_k is approximately 4-5 orders of magnitude lower than the lowest factor sensitivities, and thus implies species well below the EESI-TOF detection limit. This latter equation has been added to the SI, as Text S1 (Eq. S1).

We refer to the new text in the manuscript as follows (P12, L13):

In the case that a factor is undetectable by the EESI-TOF (e.g., non-oxygenated hydrocarbons comprising traffic-related factors), a value of AS_k is assumed that fixes the EESI-TOF contribution near zero, as discussed in the Supplement in Text S1.

The new Supplement section (Text S1) is as follows:

Text S1. Profile construction for factors to which the EESI-TOF is insensitive

In the Sect. 2.3.2, Eq. (11) proposes a generalised strategy for constructing reference factor profiles, that can be applied regardless of differences in the measurement units between instruments. Here we discuss the special case of a factor measured by the AMS but to which the EESI-TOF is insensitive, In this case, all variables in the EESI-TOF component of the profile are set to a low value based on an assumed $AS_k = 0.01$ cps (ug m^{-3}), which is orders of magnitude lower than the AS_k of detectable factors. This approach is preferred to simply setting the EESI-TOF variables to zero, as this was empirically observed to create instabilities in the ME-2 solver. The full profile is then calculated as follows:

$$\frac{(f_{k,j})_{j=all,ref}}{1\ \mu g\ m^{-3}} = \begin{cases} \dfrac{(f_{k,j})_j}{\Sigma_j (f_{k,j})_j}, & j \in AMS, ref \\[2ex] AS_k \cdot \dfrac{1/n_{EESI}}{\Sigma_j (f_{k,j})_j}, & j \in EESI, ref \end{cases} \tag{S1}$$

Here n_{EESI} denotes the number of ions in the EESI-TOF dataset and as noted above we assume $AS_k = 0.01$ cps (ug m^{-3}).

Specific Comment #10

P19: where the factor profiles constrained for the C_{EESI} analysis in section 3.1.3?

Response:

Note that this comment refers to section 3.1.3, which is now moved to the supplement as Text S2.3. Yes, factor profiles were constrained during the C_{EESI} analysis, as noted in the original text ("the *a* values of all constrained factor profiles were set to zero during this initial exploration"). We now additionally present the anchor profiles for all constrained factors in the new Fig. S5.
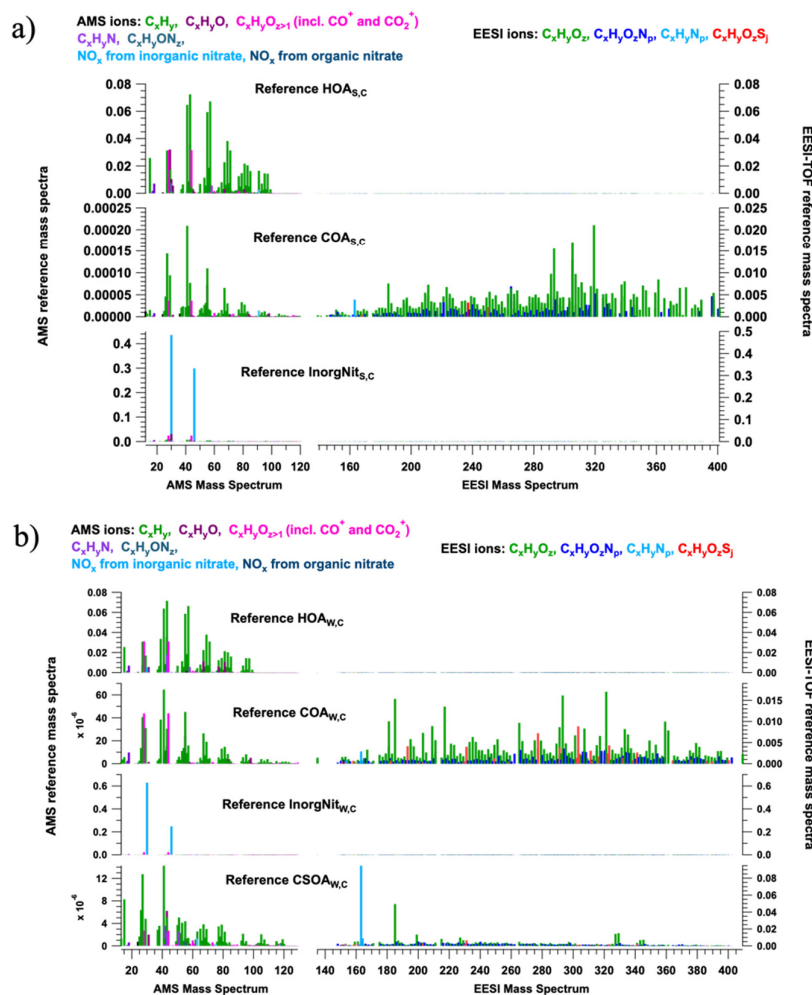
Figure S5. Normalised reference factor profiles for all constrained factors in (a) summer and (b) winter, coloured by different ion families.

Specific Comment #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?

Response:
Because C_{EESI} is a weighting parameter, the expectation is that the residuals (e_{ij}/s_{ij}) of the EESI-TOF monotonically decrease with increasing C_{EESI}, while the AMS residuals, if they are perturbed at all, would move in the opposite direction. This means that for a given p, $F^*_{overlap}$ is expected to monotonically decrease with increasing C_{EESI}, reach a minimum at some dataset-specific value of C_{EESI}, and then monotonically increase with increasing C_{EESI}. Such

behaviour is observed for summer (Fig. S6a). However, Fig. S6b shows 2 local minima for F^*_{overlap} as a function of p and C_{EESI}. The precise reason for this is unknown but is likely related to the general complexities of the PMF solution space, in which the possibility of multiple local minima is well-established.

Specific Comment #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)?

Response:
The reasons for this are not entirely clear, but likely relate to one or more of the following: 1) different instrument configurations, which can change the sensitivity of EESI-TOF to different ions, 2) different solvents used in two campaigns, which causes the different background value, and 3) different numbers of ions resolved by EESI-TOF.

Specific Comment #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.

Response:
We agree, and now note that the lunch time corresponds to approximately 11:30-13:30 and dinner to 18:30-20:30 in the manuscript.

Specific Comment #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).

Response:
We thank the referee for this suggestion.
We have added Kroll diagrams for Figure S32 and Figure S33 (previous Fig. S29 and S30), as the referee suggested. We also add scatter plots of the PMF vs. cPMF factors where 1:1 correspondence can be established. These are shown below.
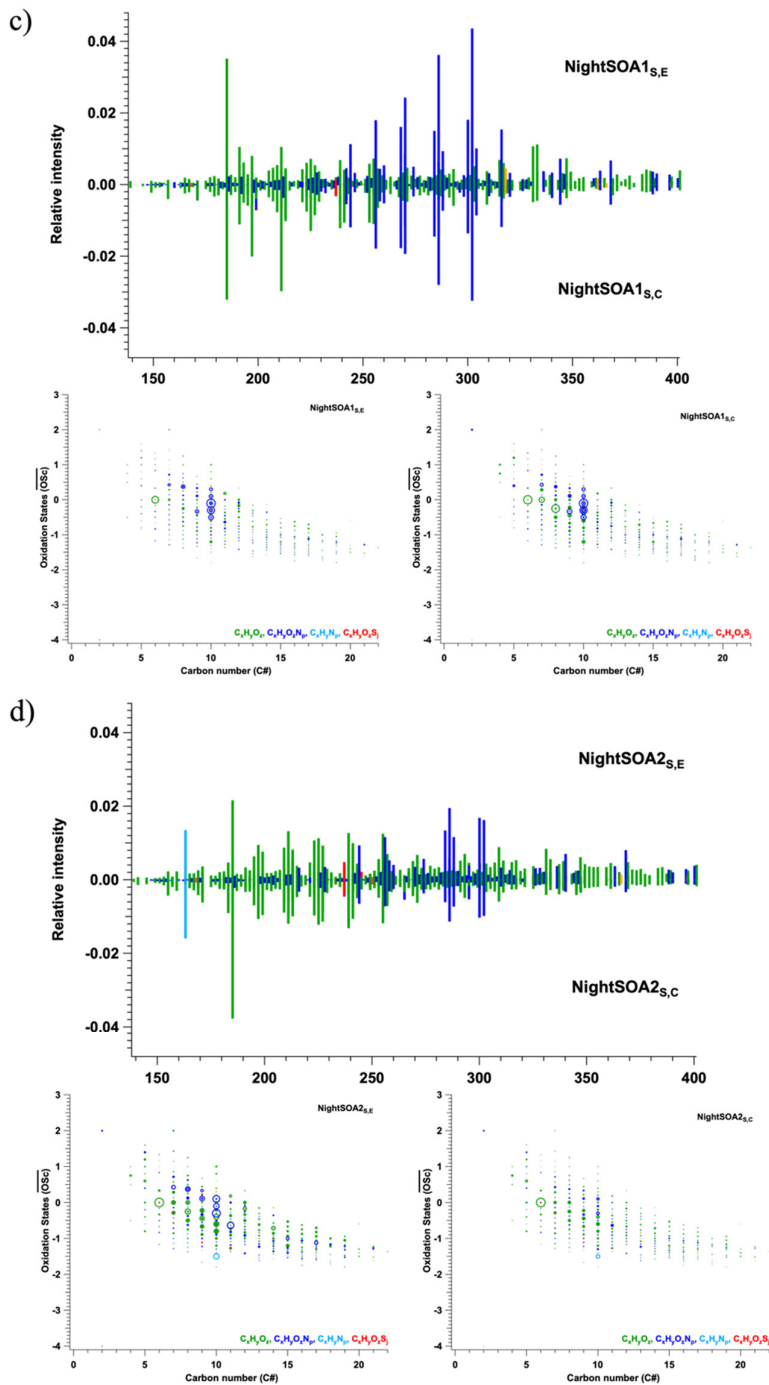
We also show below the modified Kroll diagrams suggested by the reviewer (i.e., marker size as base case signal, color as difference to compared factor). Although interesting, we find the side-by-side Kroll diagrams simpler to understand in illustrating the strong similarity between corresponding factors and use these in the supplement.

Figure S32. Comparison of four summer SOA factors (DaySOA1$_{S,E}$, DaySOA2$_{S,E}$, NightSOA1$_{S,E}$ and NightSOA2$_{S,E}$) resolved from EESI-TOF-only PMF analysis to the corresponding factors (DaySOA1$_{S,C}$, DaySOA2$_{S,C}$, NightSOA1$_{S,C}$ and NightSOA2$_{S,C}$) resolved from the combined PMF analysis, shown in a), b), c) and d), respectively. Each subfigure contains the direct comparison of corresponding factors, and modified Kroll diagram sized by the ion intensities of the corresponding factor.
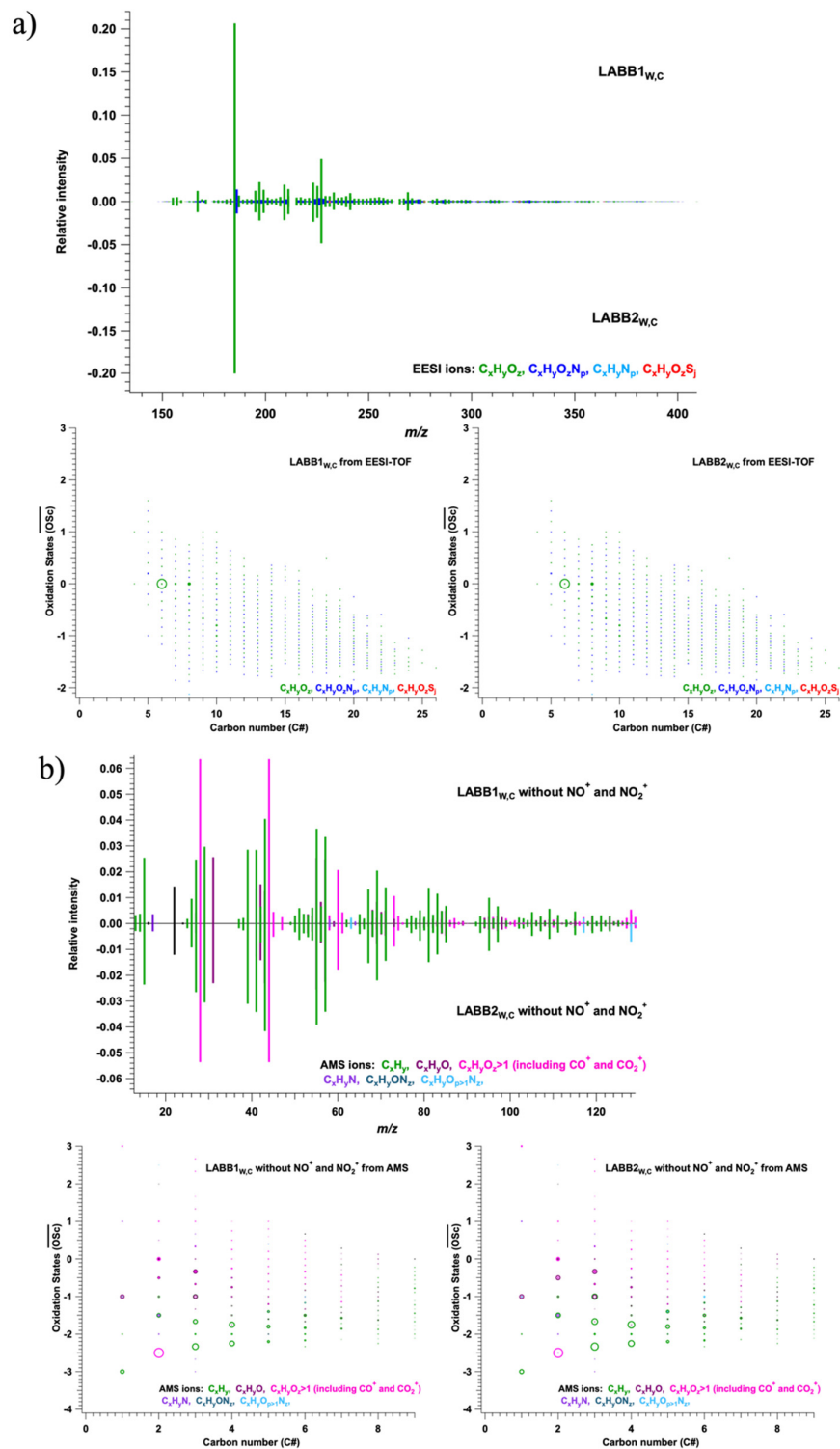
Figure S33. Comparison of two LABB$_{W,C}$ factors resolved from combined dataset in Zurich winter. Direct EESI part mass spectra comparison and modified Kroll diagram sized by the ion intensities are shown in a) and direct AMS part mass spectra comparison and modified Kroll diagram sized by the ion intensities without NO$^+$ and NO$_2^+$ are shown in b).

Figures suggested by the referee but not included in the manuscript.
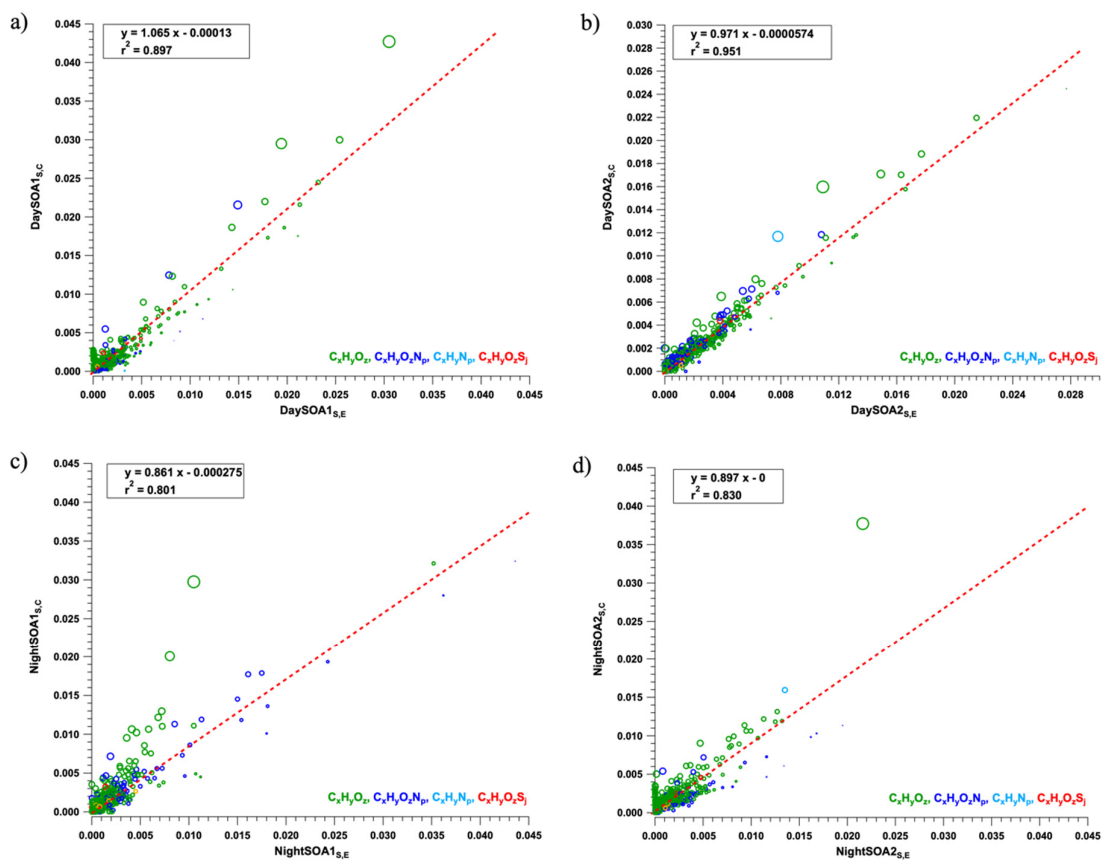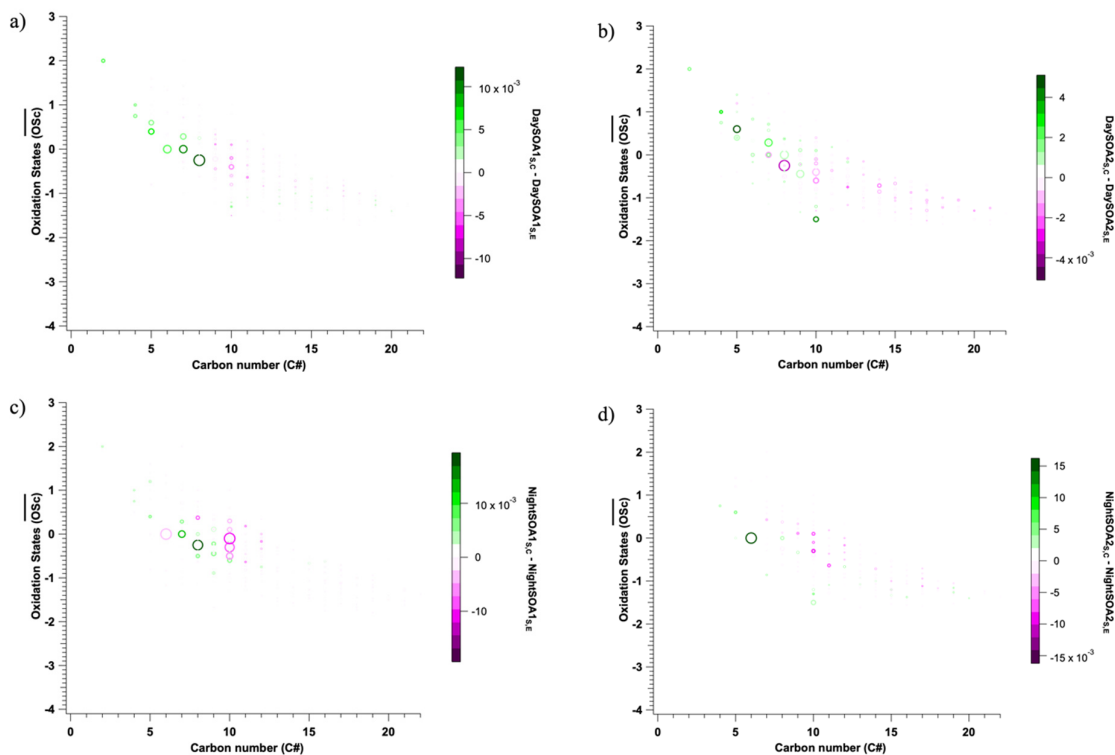
We also make the comparison between two LABB factors.
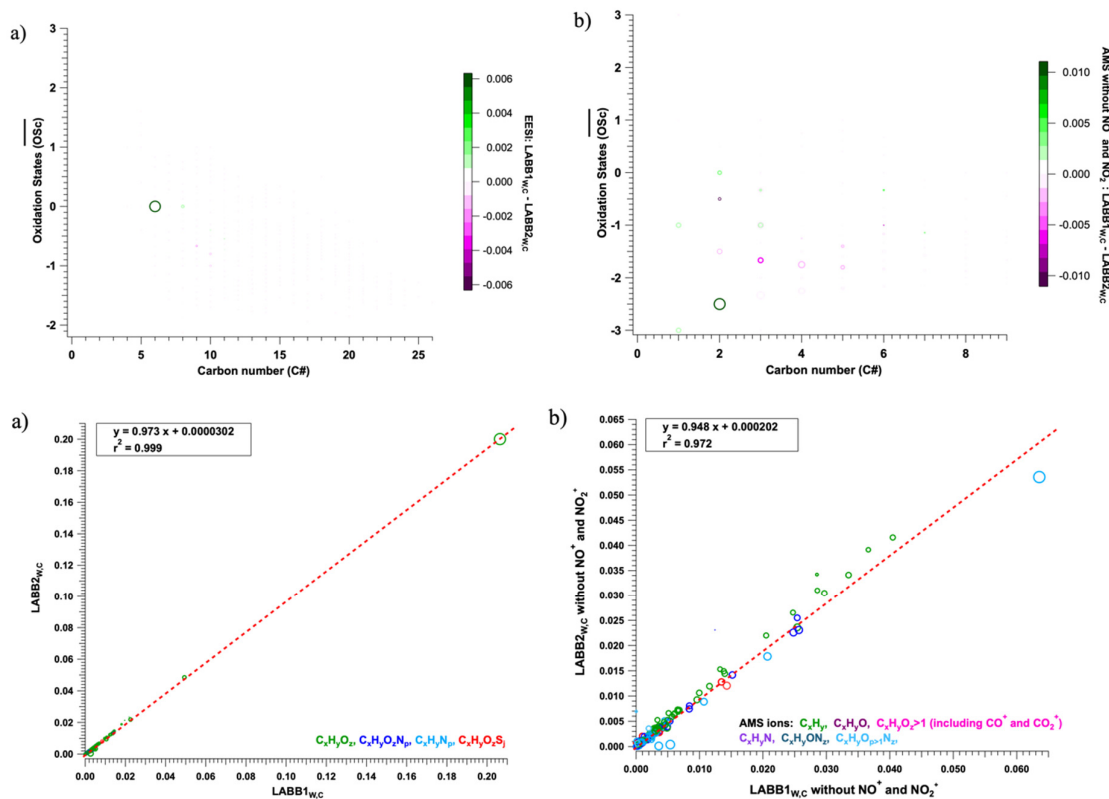
Specific Comment #15

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.

Response:

We agree, and have modified the manuscript accordingly. Fig 7, Fig 9 and Fig 10 (now Figs. 5, 7, and 8) are also updated, as shown below.
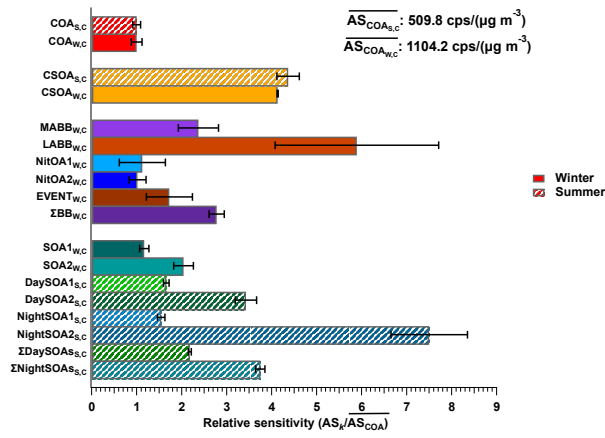
Figure 5. Comparison of $AS_k/\overline{AS_{COA_C}}$ of different factors resolved from the cPMF on the summer and winter datasets. Mean values are shown as bars, and error bars indicate the standard deviation over all accepted bootstrap runs. The following factor aggregations are also shown: $\Sigma BB_{W,C} = MABB_{W,C} + LABB_{W,C} + NitOA1_{W,C} + NitOA2_{W,C} + EVENT_{W,C}$; $\Sigma DaySOAs_{S,C} = DaySOA1_{S,C} + DaySOA2_{S\_C}$; and $\Sigma NightSOAs_{S,C} = NightSOA1_{S,C} + NightSOA2_{S,C}$.
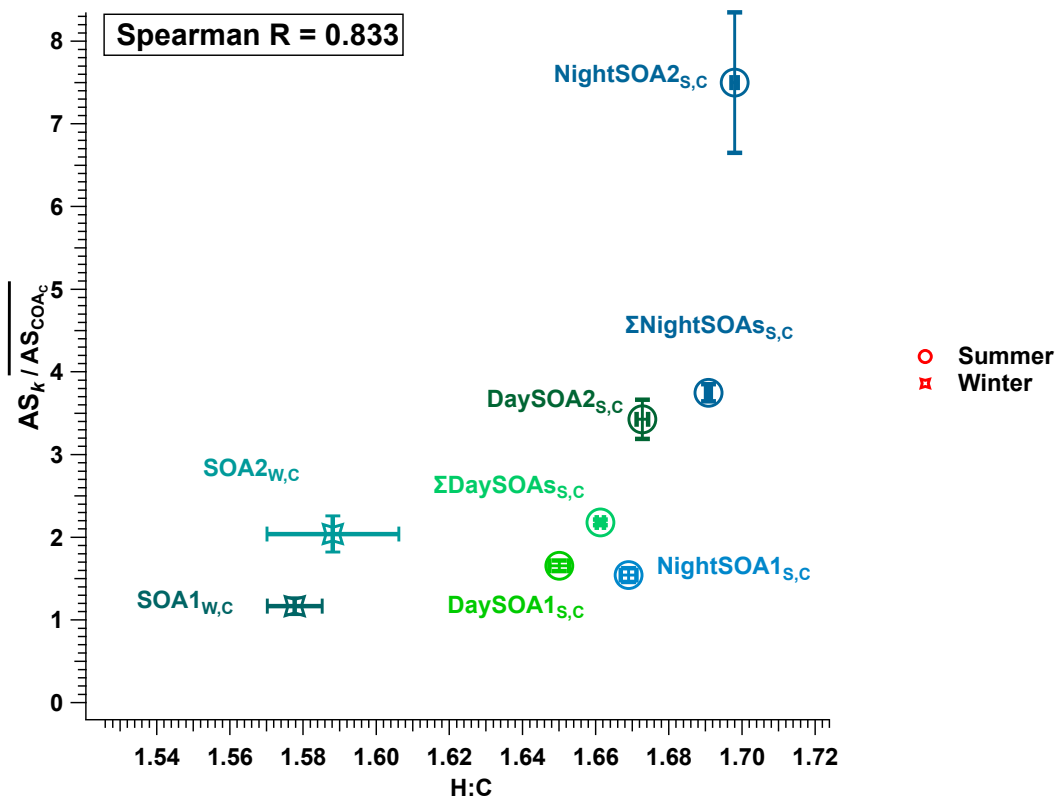

Figure 7. $AS_k/\overline{AS_{COA_C}}$ of SOA factors retrieved from the summer and winter datasets as a function of the H:C ratio. Error bars denote standard deviation across all accepted runs. Spearman correlation is 0.833, as indicated in the top-left corner.
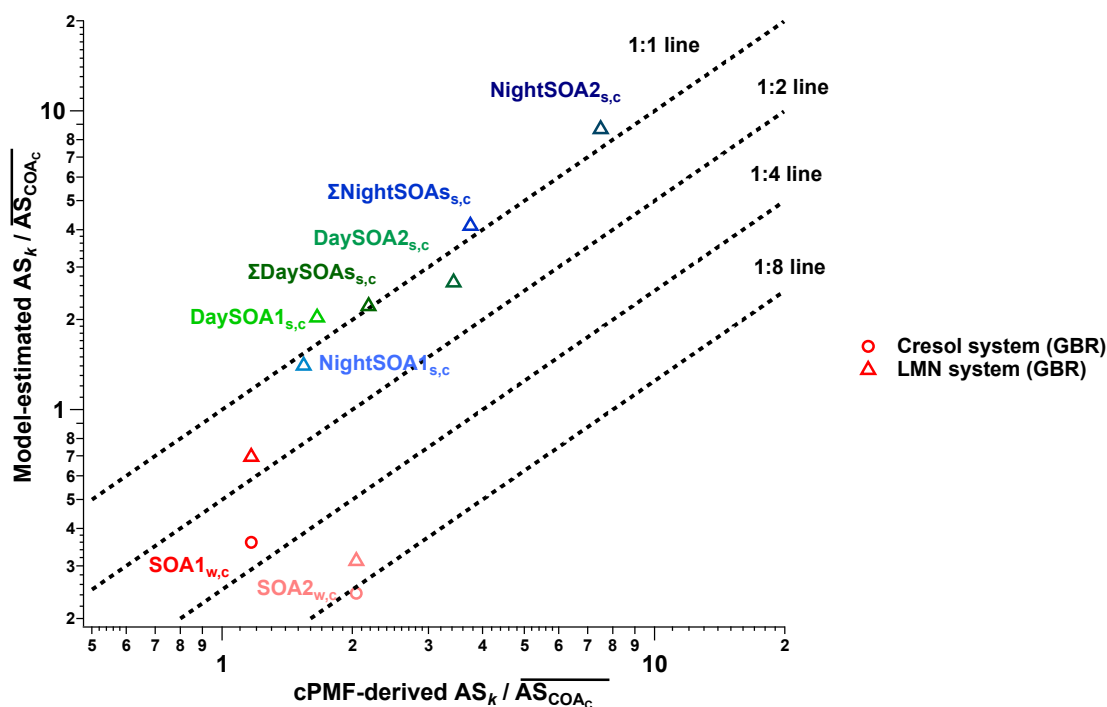
Figure 8. The estimated relative apparent sensitivity to COA ($AS_k/\overline{AS_{COA_C}}$) from the gradient boosting regression (GBR) model as a function of cPMF-derived $AS_k/\overline{AS_{COA_C}}$). The symbols indicate the different oxidation-precursor system (LMN for SOA produced from oxidation of limonene by ozone, cresol and TMB for SOA produced from oxidation of *o*-cresol and 1,3,5-trimethylbenzene by OH radicals, respectively).

Specific Comment #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.

Response:

There are three issues raised here, which we address separately (1) general motivation for applying factor constraints; (2) recombination of LABB factors; (3) relationship between cPMF and individual PMF constraints.

We are not sure from where the referee gained the impression that avoiding factor splitting was a motivation for constraining factor profiles, but would be happy to clarify the misleading text if identified. Indeed, constraints do not address factor splitting but rather the common problem of rotational ambiguity leading to mixed and/or unresolvable factors, as noted in the first paragraph of section 2.3.2.

In P20 L21, we state: "Because no significant chemical differences are apparent between LABB1$_{W,C}$ and LABB2$_{W,C}$, they are aggregated to a single LABB$_{W,C}$ for presentation." This practice of factor recombination is a well-known technique in unconstrained PMF, and indeed is performed here on unconstrained factors. It is not related to the use or lack thereof of constraints on other factors. As a result, we are unclear regarding the referee's concern.

The question of using the same constraints in single PMF vs. cPMF is an excellent point, and one that we fully agree deserves more investigation. There are two questions: (1) to what extent do factors of the "same type" (e.g., cooking-related aerosol) from individual PMF analyses by separate instruments represent the same aerosol fraction; and (2) even assuming they represent identical fractions, how to construct the joint profile in the current case when uncertainties in the quantification of one or both instruments exist. We attempt to address (1) by varying a values within the bootstrap analysis. This allows the cPMF to adapt to the case that the two instruments describe similar-but-not-quite-identical fractions of the aerosol. We consider this theoretically robust, although practical tests on additional datasets and/or synthetic data would be illuminating. Regarding (2), we now suggest that in future work, variation of the assumed AS_k values used to construct the reference profiles (Eq. 11) could be varied, as follows (P14, L21):

Since the constrained factors use reference profiles constructed with an estimated AS_k (see Eq. (11)), this combined bootstrap/constraint analysis allows recalculation of AS_k within PMF for any factor with a non-zero a value. As a result, the final reported solution is the average of all accepted bootstrap runs, with uncertainties in factor profiles and time series taken as the standard deviation. To minimise the effect of estimated AS_k on constrained factors, we suggest that in the future this method could be improved by initialisation of constrained factor profiles with randomised AS_k within a predefined range, in conjunction with the existing a-value/bootstrap routine.

Specific Comment #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?

Response:

In P30 L1, we refer to the presence of a characteristic set of features in the HOA profile, specifically the large contribution from the $C_nH_{2n+1}^+$, and $C_nH_{2n-1}^+$ series, consistent with *n*-alkanes and branched alkanes. This is now clarified in the manuscript (P21 L1) as:

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).

In P30 L29, the comment on profile similarity between SOA1$_{W,C}$ and SOA2$_{W,C}$ was included mistakenly, and has been removed.

Specific Comment #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?

Response:

All cPMF factor profiles are taken as the average of the bootstrap/a-value randomization results. For $HOA_{W,C}$, this includes a values as high as 0.9. As such, this is a loose constraint (recall $a = 1$ is unconstrained) and comparison of the profiles is meaningful.

Specific Comment #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)?

Response:

We agree, and have rephrased the text as follows (P21 L8):

"These are key features of the constrained reference profile ($0 \leq a \leq 0.3$) (Qi et al., 2019) and COA factors found in other studies (Stefenelli et al, 2019; Tong et al., 2021)."

Specific Comment #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.

Response:

We have deleted Figure S34 and now solely use the other figures to discuss the spread of AS_k values.

Specific Comment #21

p33 L43: how is COAs,c multimodal in Fig S32?.

Response: Although the overall width of the distribution of $COA_{S,C}$ is relatively narrow compared to most other factors, a close inspection indicates that is comprised of ~3 discrete peaks, centered at $AS_k = $ ~510 cps/(μg m^{-3}) (around 1 in Figure S35). Similar results are observed for $COA_{W,C}$. This has been clarified in the text as follows (P24 L44):

"Interestingly, the distribution of the sensitivities, of $COA_{S,C}$, $COA_{W,C}$, and $CSOA_{W,C}$ in Figs. S32 and S33 is clearly multi-modal despite a value constraints (although the overall $COA_{S,C}$ and $COA_{W,C}$ distributions remain relatively narrow), but the reason for this is unknown."

Specific Comment #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.

Response:

We agree that the $C_6H_{10}O_5$ content is not predictive in a quantitative sense. However, we consider the analysis useful in illustrating the effect that this single ion, which appears with moderate-to-high intensity in several primary factors, exerts on AS_k. The statement has been rephrased as follows (P25 L7);

"Therefore, despite the variation in composition of the POA-influenced factors, the effect of the $C_6H_{10}O_5$ content on the overall factor sensitivity is often considerable for cases where this ion is strongly influenced by levoglucosan."
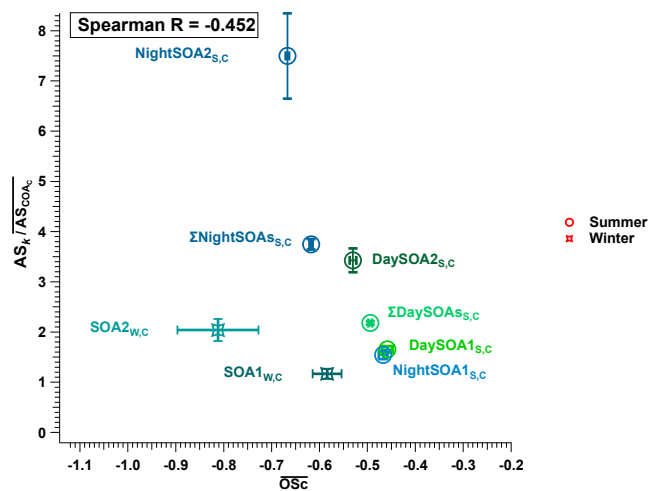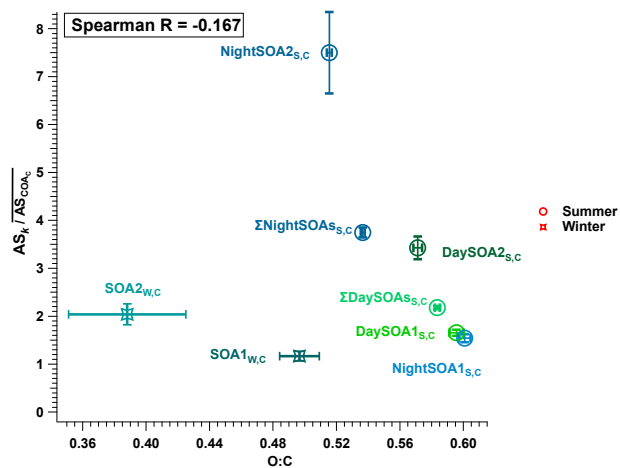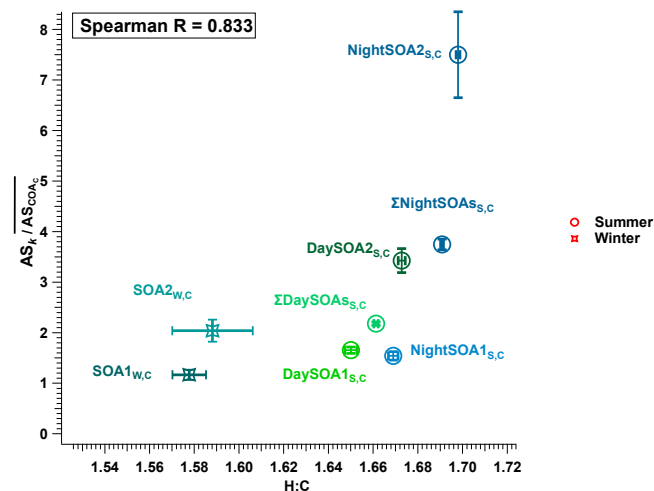
Specific Comment #23

P35 L1f & Fig 9: I find the correlation of H:C and relative ASk 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?

Response:

We select H:C for comparison due to two reasons. First, it was identified as a major predictor of molecular sensitivity in the study of Wang et al. (2021), in preference to quantities such as O:C and OSc. Second, the correlation of factor sensitivities with H:C in the present study is much stronger than with O:C or OSc, with Spearman's rank correlation of 0.833, -0.167 and -0.452 for AS_k vs H:C, AS_k vs O:C and AS_k vs OSc, respectively. This has been added to the manuscript as follows (P26 L2):

Consistent with Wang et al. (2021), H:C is found to be a better predictor of AS_k than either O:C or OSc, yielding Spearman's rank correlation of 0.833 for AS_k vs. H:C, -0.167 for AS_k vs. O:C, and -0.452 for AS_k vs. OSc.

The AS_k vs H:C, O:C and OSc plots are shown below :

Specific Comment #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.

Response:

We fully agree that the implications for interpretation of standalone source apportionment results from instruments such as the EESI-TOF and FIGAERO-CIMS are an important outcome of the study, and now highlight this in the Conclusions as follows (P34 L7):

These considerable differences in the source contributions between the uncorrected EESI-TOF and cPMF results highlight the challenges in interpreting standalone source apportionment results for instruments where ion-specific sensitivity information is not readily available, such as EESI-TOF or FIGAERO-CIMS. Although the time trends of such analyses are likely robust, interpretation of the relative composition requires caution. Therefore, if such interpretation is desired, it is advised to employ analysis strategies such as cPMF that are capable of integrating quantitative measurements from reference instruments.

In the present study, we consider the differences between the summer and winter results to be driven by real differences in the factor composition, as discussed in the manuscript. Because of this contrast in factor composition, we do not yet have enough information to assess the consistency of factors across different locations, or consistency of AS_k's for related factors retrieved across different studies. As a result, we cannot comment on this point.

Specific Comment #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).

Response:

Although there is some overlap in information between Fig.11 (now 9) and Fig. 13 (now 11), the first focuses on temporal variation in composition, while the second relates to the uncertainties in the cPMF results (i.e., differences in composition across solutions). Therefore, we consider both figures to be important (and complementary) and retain both in the main text.

Regarding Fig. 12 (now 10), our cPMF implementation implicitly treats the AMS as the reference instrument. As such, it is very unlikely that the total AMS OA concentration changes, as this would require a large and systematically positive or negative increase in AMS residuals.

Specific Comment #26

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

Response:

The legend has been corrected, and the revised figure is shown in response to RC1SC #15 and #23.
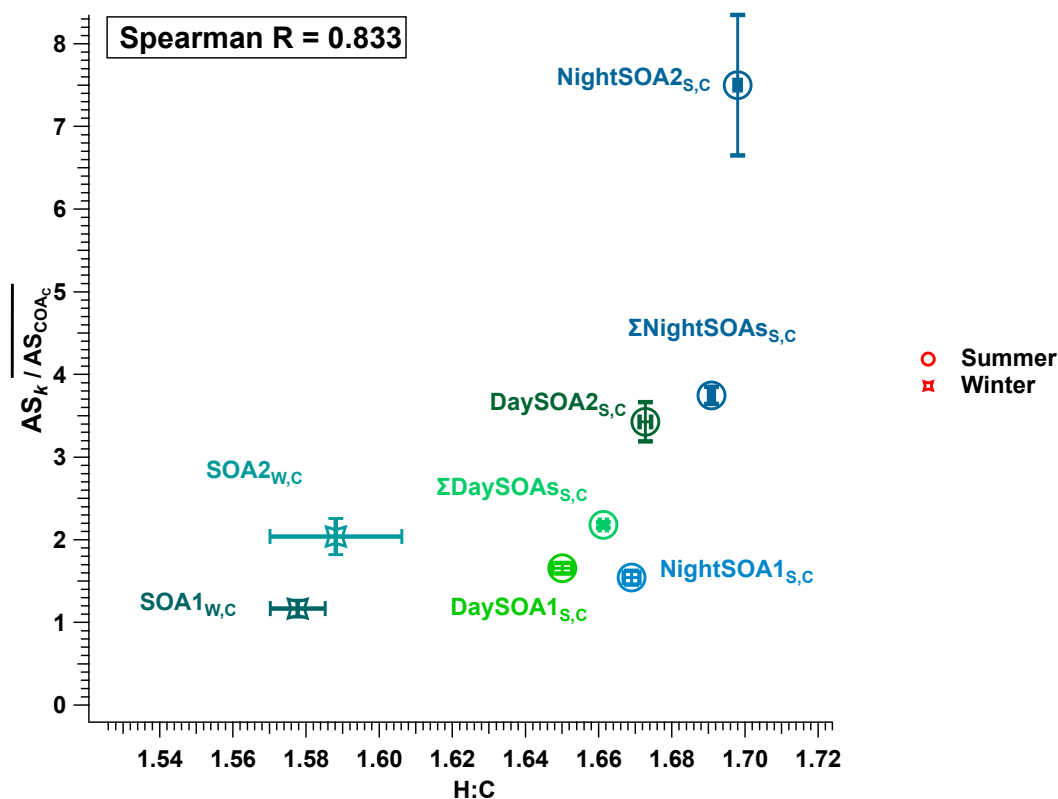
Specific Comment #27

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.

Response:

This was not stated clearly in the original text. We intended to refer to the case where a factor is detectable by only one instrument (e.g., our treatment of HOA and InorgNit), as opposed to the case where the factor is detectable by both instruments but has a constrained profile in only one (which the reviewer correctly notes was not addressed). We have clarified and emphasise the text as follows in the Abstract (P1 L28):

"…a method for optionally constraining the profiles of factors that are detectable by one or both instruments,…"

Reference

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