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Interactive comment on "Quantification of solid fuel combustion and aqueous chemistry contributions to secondary organic aerosol during wintertime haze events in Beijing" *by* Yandong Tong et al.

Anonymous Referee #1

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The manuscript presents analysis of EESI-TOF-MS and AMS measurements carried out in Beijing during autumn and winter 2017. It aims to address important questions surrounding haze formation and is within the scope of ACP.

The authors use positive matrix factorisation (PMF) to identify factors corresponding to primary and secondary organic aerosol measured by AMS and use these factor time series to constrain a PMF analysis of the EESI-TOF-MS observations. Factor composition and time series are compared between heating and non-heating seasons, identifying varying contributions from aerosol components observed by the two instruments.

The authors identify solid fuel combustion and aqueous chemistry to be particularly important in the build-up of winter haze events.

The paper provides extensive technical recommendations for operation of the EESI-TOF-MS in highly polluted field measurement campaigns which will be a valuable contribution to the instrument user community. The analysis gives potentially useful information on sources and formation of organic aerosol, but I have some concerns about the approach taken. In addition, I think that the presentation and discussion of results requires significant improvement for publication in ACP so I would recommend major revisions. Major issues identified are discussed below, followed by detailed comments and suggestions.

General Comments:

PMF of the EESI-TOF-MS has been constrained by the time series derived from PMF of AMS measurements. This has the potential to introduce significant biases in the results, which should be addressed in the manuscript. EESI-TOF-MS detects a similar range of compounds to those detected by FIGAERO-CIMS and previous studies have shown distinct differences in the time series of CIMS factors compared with those derived from AMS (Chen et al. 2020). The additional chemical composition provided by the EESI-TOF-MS should enable more factors to be derived on the basis of chemistry occurring across the measurement period which the AMS does not have the chemical resolution to identify. Therefore the approach taken to constrain the time series of EESI-TOF-MS PMF factors could have influenced the identification of factors. The PMF of the AMS factors forms the basis of the results presented in the manuscript, and the use if EESI-TOF-MS data is supplementary and used simply to show the composition of the EESI which corresponds to the AMS factors. This is different to a true PMF analysis of the chemically insightful EESI-TOF-MS data and should be discussed accordingly. What are the correlations between the EESI-TOF-MS and AMS factor time series? How sensitive are the time series to the constrains. I understand that carrying out a separate PMF of the EESI-TOF-MS without constraining the time series is a large body of work, however, you should try to discuss how not doing this could have influenced your results and interpretation.

The discussion of ions identified by EESI-TOF-MS is limited and needs to be referenced more extensively. Mass spectra from EESI-TOF-MS should be labelled and a more detailed list of ions provided in the supplement along with their potential sources. Correspondences drawn between AMS and EESI-TOF-MS ions should be better justified through a more thorough evaluation of the ions contributing to each factor. Time series of dominant ions contributing to each factor should be compared with that of the factor profile itself and its corresponding AMS factor in a Figure to show the validity of constraining the EESI-TOF-MS factor profiles by the AMS time series. CIMS and AMS factor time series should also be presented on the same axis for comparison.

Presentation, discussion and interpretation of factors is confusing and hard to follow, particularly with respect to comparison between AMS and EESI-TOF-MS factors due to their identical naming. Additionally, many of the figures need to be improved and should be referenced better throughout the manuscript. It would be useful if the haze events of interest and heating/non-heating periods were labelled in each figure. Figure 9, in particular, needs to be overhauled in favour of something much more easy to interpret. Perhaps stacked bars could be used to compare the contributions of different factors during different haze events. Interpretation of figures also requires some attention, with diurnals interpreted based on the time series' of their standard deviations as opposed to their average values. As presented, the figures hinder the interpretation of the manuscript and should be improved to emphasise conclusions.

Structure and language throughout the manuscript need to be improved. Placeholders for data values and figure numbers remain throughout. In addition, there are figures referenced which are not included, and those which are included are not referenced in the text thoroughly making the paper challenging to follow. Several sections including the introduction and methods and not well-structured and clear. The introduction needs to be streamlined and made clearer and referencing needs to be improved throughout,

particularly in the results section where it would be useful to discuss where ions identified by EESI-TOF-MS have been previously observed.

Specific Comments

Introduction:

The introduction is currently very hard to follow and lacks a coherent structure. The author begins by introducing organic aerosol in the first paragraph in which its key sources are outlined, and then in paragraph 2 they mix health effects with sources and instrumentation. This structure should be streamlined into a narrative which provides the information required to contextualise the results presented in the manuscript.

Lines 8-12 on page 2 are not referenced and mention uncertainties in quantification due to instrumentation, however, instrumentation is not introduced until line 48 of the same page. The few sentences about health impacts of ROS seem out-of-place in this paragraph.

Results from the AMS are mentioned in paragraph 2 on page 2, while several sentences describing it are on page 3 (lines 9 -16). I would suggest that the author introduces instrumentation first before talking about observations with those instruments in Beijing. The introduction should be re-written to better contextualise the more detailed aerosol source characterisation which the EESI provides, this is currently disjointed, with the key AMS factors the EESI is expected to better constrain being described on lined 25 - 42 of page 2, while the EESI itself is not described until page 3.

Consider splitting paragraph 2 on page 2 up with the discussion of Beijing separate from the broad discussion of AMS and ACSM capabilities. This should be made clearer.

Lines 32 - 33 on page 2 are not justified, there are a variety of previous studies in Beijing which study and apportion OA to different sources and formation mechanisms, inc. Bryant et al. (2020) and Wang et al. (2019).

The introduction of EESI on page 3 should explain better how it is able to capture detail which the AMS cannot, and which components of aerosol measured by the AMS are most poorly understood. Line 25 on page 3, include references.

Discussion of instruments on page 3 lacks accurate chronology, e.g. CHARON, FIGAERO and GC/MS-FID.

Page 3 lines 35 - 38 are contradictory, you first say that the EESI-TOF provides a hard-to-quantify response, then go on to say it has the potential to provide a quantitative measurement of OA.

Methodology: Again the structure of this needs to be corrected, you discuss the exact co-ordinates of the measurement location and then go on to talk about Beijing in the context of the NCP. This needs to be more focused. A better structure would start with Beijing, move to the location of the site and then talk about its surroundings and potential influences.

Page 4 lines 6 - 8, you suggest that highway traffic and industry do not influence measurements at the site. However, given that pollution in Beijing is regional, and it is well known that industrial air masses from the SE affect the air quality in Beijing, this statement needs to be removed or better justified. Surely the site is influenced by both local emissions and regional transport? Page 4 lines 9-10, can you explain why this period from October - December was chosen when measurements were carried out from September. No details are provided on sampling flow rates, these need to be added.

Lines 7-10 page 5 - could the sensitivity differences be related to changes in relative humidity?

Lines 42 -43 page 5 - why is there not expected to be any compound dependant effect? Is this backed up by any literature or an assumption? Why is it valid to make this assumption?

Lines 9 -12 page 5 - here you state a " a diagnostic species" is used, and below this you state "inorganic nitrate species" - these need to be clarified in more detail.

Lines 29 - 30 page 5 - provide more discussion of the assumption that the time-dependant changes in sensitivity are eliminated for organics.

Lines 30 - 33 page 6 - here you state that particle-phase signals tend to be less oxygenated than the background ions, while in supplement section S1 you state the opposite. This needs to be corrected.

Some of the details provided in this section may not be of interest to the typical reader and I would suggest moving more of the detailed instrument trouble shooting to the supplement as currently the paper is harder to follow as a result. The sections in the supplement are much clearer are will be easier to access for a technical reader who wants to understand the troubleshooting process. This level of detail in the main body of the manuscript itself shifts the focus from the results.

Line 42 page 6 - "as discussed in Sect. 2.3" - this should either be as "will" be discussed or should be removed.

Line 41 page 6 to line 9 page 7 - This discussion of PMF and its error seems to be out of place in this section, it should be moved to section 2.3.

Lines 15 -28 page 8 - explain and justify potential biases in the interpretation of EESI-TOF data by constraining time series' to those of AMS factors, given that EESI-TOF factors, similar to CIMS factors have previously provided factor TS which are distinctly different those from the AMS, e.g. Massolli et al (2018), Yan et al (2016) and Chen et al. (2020).

Check how you wish to refer to EESI through the manuscript, it varies between EESI-TOF and EESI-TOF-MS. Choose one.

Line 41 page 8 - determine should be "determination" Line 42 page 8 - "compare the" should be "comparison of" Line 44 page 8 - z-score is mentioned here, either do not mention or signpost the reader to where it will be discussed.

Major comment - AMS factors and EESI-TOF or CIMS factors are not expected to be directly related to one another, by constraining each EESI factor to an AMS factor solution is it not possible that you are introducing a bias which limits the extent to which you are describing chemistry in your interpretation and are instead biasing the results towards primary sources.

Throughout "as discussed" refers to past tense, it should be changed to "will be discussed in".

Results:

Page 10 lines 46-47 - criteria used to define "haze episodes" should be defined here rather than in figure caption for Figure 1.

Page 10 line 20 - 37 % is written twice. Needs to be corrected.

Figure 1 - Several corrections are needed. 1) y-ticks are overlapping between (b) and (c). 2) y-label for (c) should specify if this is PM2.5 mass, which I assume is the case, and also include units in brackets. 3) y-label for (d) should be changed to fractional factor contribution or something more clear 4) Colorscale of W_dir should be labelled as wind direction, which is what I assume it is? It would also be better not to use rainbow. 5) Legend for light and severe haze should be made clearer.

Page 12 lines 9-10 - it should be specified which HR ions were used and where UMR sticks were used. A table in the supplement would be a good way to record this.

Page 12 line 18 - page 13 line 8- Here you discuss that the apportionment of 4 OOA factors is unusual, and point the reader to section 3.3. for interpretation. Is it the case that 4 factors are chosen in the AMS data to better represent the EESI-TOF data? Or were there factors chemically or temporally distinct enough in the AMS data alone that the EESI factors did not influence this selection? It is important to acknowledge how the EESI factor identification has influenced the factor selection for the AMS and vice

versa.

Figure 2a - y-ticks are overlapping, sticks are feint and their thickness needs to be increased. The region above m/z 120 should be magnified to see clearer patterns in the higher m/z ions which are poorly represented in this figure as is.

Figures 2-4 are grainy and need producing at higher quality for ACP.

Description of the AMS factors should refer to the relevant figures, e.g. diurnal, time series or mass spectra. Descriptions of factor time series and diurnals have various inconsistencies. For HOA, the correlation is not shown in the supplement in Fig. S13 as stated in the manuscript. This should be included. You have stated that the factor peaks between 0600 and 0900 which is not what is shown in Figure 3a. This figure shows elevated concentrations overnight, with the increase between 0600 and 0900 only reflected in the standard deviations, not in the mean. It would be useful to see the diurnal variations split between the seasons as it appears that there is a high degree of variability which means that the average diurnal profile does not show the temporal profile described in the manuscript. I would argue that the morning peak from 0700 to 0900 is also missing in your data, given it is only shown in the standard deviations. The caption of Figure 3 needs to be changed, it is not the "grey area" which represents standard deviations, it is the shaded area. The high contribution of PAHs to the CCOA factor referred to need to be shown more explicitly in the mass spectra by enlarging the MS in the high mass regions in Figure 2a as mentioned previously. The aromatic signatures described for CCOA need to be evidenced, there is no references included or explanation of how they have been identified to be aromatic in origin. The description of OOAs previously classified on page 14 lines 36-39 need to be referenced.

Discussion of EESI factors on page 17 onwards is unclear. The author states that "PMF of the EESI-TOF mass spectral time series was conducted on a 7-factor solution". Surely the PMF was conducted to derive 7 factors? There is no explanation here of how those 7-factors were selected. In addition, there is no detail provided on the influence and biases introduced from constraining EESI factor time series to the seven non-HOA factors. As highlighted above, factors derived from near-molecular-level techniques typically have more distinct time series than those derived from AMS studies. It should be better justified why this approach to constrain TS was taken and if any effort was made to run the PMF of the EESI factors without constraining the TS to that of the AMS factors.

AMS and EESI factors should be named more clearly. As in Stefenneli and Qi papers, these were named with EESI or AMS subscripts. This would make studying the figures more clear. Numbering of Figures is incorrect after Figure 5. The text here refers to Figure 7 when presumably it should be when the van krevelen plot shows as Figure 4 and according to the sequence should be Figure 6. References to figures should be checked, corrected and improved throughout. Markers on the van krevelen plot are too small and should be changed. It is stated that the sizing of these markers is related to the z-score, however this cannot be interpreted from the figure.

Defining COA on the basis of it having most of the mass at ions with high m/z needs to be better explained. Particularly as ions at high m/z in AMS are attributed to PAHs. Intense ions in the mass spectra shown in Figure 4 should be labelled. CCOA , figure numbers are not included and are blank and should be included. Figure 4 needs improving, the factor time series are unclear and variations cannot be seen in the aspect ratios the figures have been output in. The x-ticks need to be made more regular. The mass spectra y-ticks are overlapping, and in some cases such as CCOA, the mass spectra cannot be clearly seen due to intense ions. The presentation needs to be improved.

Correspondences between the AMS and EESI SOA factors need to be better justified, with comparisons of time series presented. AMS MO-OOA and EESI-TOF MO-OOA being related to one another is not explained and simply assumed in the manuscript. Have the ions listed in paragraph 2 on page 21 been observed elsewhere, these ions formulas should be explained. Various nitro-aromatics in Beijing have been reported

previously. Can you explain why the ions stated on line 46 of page 21 are relevant from aromatics? This should be justified. Page 22 line 18, has this ion been previously observed and if so, where? Bertrand et al reference has no date, this needs to be corrected.

The description of MO-OOA relies on a discussion of haze and non-haze events, which are not depicted on the figures except the final figure (Figure 9) and even in this case they are not clearly shown. Figures need to be improved so the interpretation of factors can be followed. Small acids can also be derived from aromatic oxidation (Zaytsev et al. 2019, Mehra et al. 2020, Wang et al. 2020). Their attribution to aqueous phase chemistry needs to be better explained. Line 44 page 22, "section x" needs to be replaced by a section number. Discussion of AMS and EESI factors is confusing due to the identical naming, these need to be better distinguished in the text.

Atmospheric Implications:

Values are missing on line 15 page 29 of "concentrations between x and y". Page 29 lines 14-48, the discussion of "minor" and "major" haze events is unclear and Figure 9 which shows the values discussed in this section is poorly put together, it is unclear which events each pie chart represents making it impossible to interpret. This needs to be improved. The events discussed in the text have dates, which cannot be established from looking at the figures or the pie charts.

The conclusion that oxidation of aromatics from SFC is responsible for SOA is poorly evidenced (lines 44-48). The evidence for the aqueous factor is stronger, however, certain aspects need improving as discussed above.

Conclusions: Overall, the chemical resolution of the EESI is not discussed in great detail, many of the ions used in the PMF are not shown or discussed in the manuscript. This should be improved.

Supplement: A more comprehensive list of ions should be presented in the supplement. The correlations of AMS nitrate and EESI shown in Figure S1 are poor for the first 2 time periods and should be discussed further.

Labelling of supplement factors needs to be improved. "Splitted" is not correct English and needs changing in all figures.

References: Check referencing style for journal names - in some cases ACP is Atmos Chem Phys and in others it is Atmos. Chem. Phys. This should be consistent with journal guidelines. The same applies to various other abbreviated journal names.

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