Response to the comments of anonymous referee #3

We thank the referee for the valuable comments which have greatly to helped us improve the manuscript. Please find below our responses (in black) after the referee comments (in blue). The changes in the revised manuscript are written in *italic*.

Technical comments:

P1, L19: "This suggests the EESI-TOF apportionment can be approximately taken at face value, despite ion-by-ion differences in relative sensitivity." Perhaps this is too strong of a statement since this environment is under major influence of BB (and little HOA) and not a mix of very different sources as can be common in other environments, especially in the summer.

We have revised this statement to note that it applies specifically to the range of aerosol composition observed in the current study. We agree that similar analyses are required in different environments before a general conclusion can be drawn. However, even in the current study there is significant variation in the chemical composition (e.g., primary vs. secondary biomass burning, as well as SOA factors with terpene-like signatures that comprise nearly 20 % of the EESI-TOF signal).

The revised statement reads as follows (P2, L18-20):

"This suggests that the EESI-TOF source apportionment in the current study can be approximately taken at face value, despite ion-by-ion differences in relative sensitivity."

P6, L3: why were the ions smaller than 135 amu small? Was tuning changed on purpose to increase transmission of larger ions? Or is there something different in the mass spec design compared to that of a typical CIMS/AMS?

For EESI-TOF, we aim to focus on the molecular compositions. The quads were operated such that the transmission decreases rapidly below approximately m/z 150.

P6, L8: Just out of curiosity, how stable was the background?

In this campaign, the background measurement is in the same level (almost the same value) during the whole measurement period.

P8, L2: why were different factors constrained for AMS and EESI-ToF?

Factors may be constrained to overcome a variety of issues compromising an unconstrained PMF solution, including factors with strong temporal correlation, two or more factors with similar chemical signatures, or factors with chemical features that due to the overall chemical variability within the dataset are not clearly mathematically resolved. In the first case (temporal correlation), the reviewer is correct that one would expect similar factors to be constrained between AMS and EESI-TOF (with the exception of HOA_{AMS}, which is primarily composed of hydrocarbon species undetectable by the EESI-TOF). However, the remaining two cases depend on the nature of the chemical measurement by the AMS and EESI-TOF, which are fundamentally different. Therefore, the constrained factors are expected to vary between instruments. For example, in the current analysis, we note that the extensive fragmentation in the AMS results in both the long-chain hydrocarbons observed HOA_{AMS} and the fatty acids in COA_{AMS} yielding $C_xH_y^+$ fragments, which makes these factors appear chemically similar (and requiring constraints). In contrast, the EESI-TOF directly detects cooking-derived fatty acids, making this factor appear chemically unique (and not requiring constraint). Meanwhile, the increased chemical specificity of the EESI-TOF allows identification of a cigarette-smoke related factor based largely on the distinctive $C_{10}H_{14}N_2H^+$ ion, with the separation optimized by factor constraints, whereas the reduced chemical specificity necessitated the incorporation of cigarette smoke into a mixed factor.

We clarify this issue in the manuscript as follows (P8, L10-14):

"Different factors were constrained in the two datasets due to the fundamental differences between the AMS and EESI-TOF measurements. Specifically, the absence of fragmentation in the EESI-TOF allowed clear separation of cooking without the need for constraints, while separation of a cigarette smoke factor was only achieved for the EESI-TOF. In addition, constraining an AMS cigarette smoke factor was attempted but failed."

P10, L1-2: If OOA1 has some of the CxHy fragments, shouldn't that be the more volatile OOA factor?

We agree with this comment.

The OOA1 factor is the less oxygenated factor (LO-OOA), while the current OOA2 factor is more oxygenated OOA (MO-OOA). We had fixed all the corresponding text and figures.

P15, L3: It's surprising that the SOAEESI factor is less oxidized than the oxidized BB factors. At least in the AMS-based PMF factors, the SOA (OOA) factors are quite more oxidized than the BBOA factor. Do the EESI data suggest that AMS OOA factors may contain the aged BB emissions too? Could the authors elaborate on this. After reading the paper, I realize the authors address this in Section 3.5. It will be good to include a sentence in P15 indicating that this surprising result is going to be further examined.

We agree with this suggestion.

Here we add a short sentence to guide readers (P16, L14-15), *"The more detailed comparison between EESI-TOF_SOA factors and AMS_OOA factors will be discussed in Sect. 3.5."*

P17, L27-28: If the slopes of the mass defect vs. m/z points for both less and more aged BB is similar, how can one trust interpreting the slopes to understand types of functional groups added to the molecules included in the other factors?

We have clarified this discussion. The main point in these mass defect plots is that the BB-related factors (both LABB and MABB) exhibit slopes (and intercepts) that are significantly lower than those of the other investigated factors, suggesting increased aromaticity. Within the BB-related factors, $\mathrm{LABB2_{EESI}}$ and $\mathrm{MABB\_HIGH_{EESI}}$ have similar slopes, which are slightly higher than $\mathrm{LABB1_{EESI}}$ and $\mathrm{MABB\_LOW_{EESI}}$.

Section 3.4 was revised as follows (P18-19):

"$LABB1_{EESI}$ and $LABB2_{EESI}$ have a lower mass defect and shallower slope than COA_{EESI} and $CS\text{-}OA_{EESI}$, consistent with increased aromaticity. The slopes are $(4.9\pm0.4)\cdot10^{-4}$, $(5.9\pm0.6)\cdot10^{-4}$, $(8\pm0.5)\cdot10^{-4}$ and $(8\pm0.3)\cdot10^{-4}$ for $LABB1_{EESI}$, $LABB2_{EESI}$, COA_{EESI} and $CS\text{-}OA_{EESI}$, respectively. The slopes of the two LABB factors as well as those of COA_{EESI} and $CS\text{-}OA_{EESI}$ are very similar to each other and have a high possibility to be consistent with CH addition for the former (i.e. $C_{10+x}H_{14+x}O_{4\text{-}5}$, theoretical slope $6\cdot10^{-4}$), and CH2 addition for the latter (i.e. $C_{10+x}H_{20+2x}O_{3\text{-}5}$ for COA_{EESI} and $C_{10+y}H_{15+2y}NO_{3\text{-}5}$ for $CS\text{-}OA_{EESI}$ as nearly every CS-OA-specific ion contains a single N atom, theoretical slope $1.1\cdot10^{-3}$).

The MABB and LABB factors have similar slopes, despite different ion lists. The slopes of two MABB factors ($0.9\cdot10^{-3}$), as shown in Fig. 12b, are consistent with the addition of CHO functionality (theoretical slope = $0.1\cdot10^{-2}$). Due to the high variability of the slopes of the MABB factors, it may also contain the other potential possibility for the added functionalities."

Section 3.5: I believe this section should be discussed earlier. As I was reading the paper, I kept thinking what if differences in sensitivity of the EESI to different molecules is playing a role in determining the identified factors, so it is reassuring if one reads this section before getting deep into the EESI-based PMF factors. Perhaps the first paragraph of this section that's not discussing the PMF factors yet can be moved to earlier parts of the paper.

We agree with the reviewer that molecule-dependent sensitivity of the EESI-TOF is an important point and that the reader should be aware from the start that an AMS/EESI-TOF comparison is presented. With that said, we prefer to retain the current order of sections because the bulk AMS/EESI-TOF comparisons cannot be well understood without also considering the factor-by-factor comparisons, and the factor comparisons in turn cannot be understood without first presenting the PMF analysis. However, we have added the following text to the beginning of section 3 to clarify the discussion structure (P9, L21-26):

"Results of AMS and EESI-TOF PMF analyses are presented in sections 3.1 and 3.2, respectively. Section 3.3 focuses on the EESI-TOF PMF results are then exploited to assess the apportionment of specific ions related to key marker compounds (section 3.3) and to identify groups of molecules uniquely characteristic of the retrieved factors (section 3.4). However, quantitative interpretation of the EESI-TOF PMF results is complicated by differences in the relative sensitivity of the EESI-TOF to different molecules. Therefore section 3.5 presents a comparison of the EESI-TOF and AMS results in terms of total signal, bulk atomic composition, and relative apportionment to the different factors."

P18, L7-9: What's the explanation for a lower sensitivity of EESI for the times levoglucosan was low? Based on the AMS factors, the initial period is not dominated by HOA that EESI is blind to.

Laboratory measurements indicate that the EESI-TOF is likely more sensitive to levoglucosan than to typical SOA components (Lopez-Hilfiker et al., 2019). This has been clarified in the text as follows (P19, L16-19):

"An SOA-dominated period with low levoglucosan concentrations (red line) toward the beginning of the campaign exhibits a lower sensitivity than during a period with higher levoglucosan concentrations (black line), which includes the events on 28.01.2017 and 29.01.2017 characteristic of $EVENT_{EESI}$ *(Lopez-Hilfiker et al., 2019)."*

Editorial comments: Some correlation coefficients were presented as R, some as R2. Please use one consistently.

Done. We change all the R2 to R. R2 is focus on the section 3.2.2, LABB factors.

Quality of some figures was not good when viewed at 100% and the legends/axis labels were blurry.

Done. Fig. 10 and Fig. 12 are changed to the high resolution.

P 1. L15: ": : :was derived: : :"

Done. *"While the AMS attributed slightly over half the OA mass to SOA but did not identify its source, the EESI-TOF showed that most (> 70 %) of the SOA was derived from biomass burning." (P2, L15)*

P1, L21: consider changing "..utilize a: : :." to ": : :utilization of a : : :"

Done. *"The apportionment of specific ions measured by the EESI-TOF (e.g. levoglucosan, nitrocatechol, and selected organic acids), and utilization of a cluster analysis-based approach to identify key marker ions for the EESI-TOF factors are investigated." (P2, L21)*

P2, L14: delete "of" in ": : :fragments typical SOA molecules".

Done. *"The chemical analysis of aerosol online-proton transfer reaction mass spectrometer (CHARON-PTR-MS) has no significant thermal decomposition but the ionization scheme fragments typical SOA molecules." (P3, L15-16)*

P6, L2: change "The total number fitting of 1125 ions: : :." to "The total number of 1125 fitted ions : : :".

Done. *"The total number of 1125 fitted ions (including 882* Na^+ *adducts, one* H^+ *adduct, and 242 unknown ions) between m/z 135 and 400 were identified." (P6, L9-10)*

P6, L9: delete "the" to read " : : :were removed from further analysis."

Done. *"Ions with a mean signal-to-noise ratio (SNR) below 2 were removed from further analysis." (P6, L17-18)*

P6, L19: "An HR-ToF-AMS: : :"

Done. *"An HR-TOF-AMS was deployed for online measurements of non-refractory (NR) $PM_{2.5}$." (P6, L28)*

P6, L21: "spent"

Done. *"The AMS recorded data with 1 min time resolution, of which 30 s was spent recording the ensemble mass spectrum (mass spectrum (MS) mode) and 30 s recording size-resolved mass spectra." (P6, L29-31)*

P14, L4/5: it should be NOAAMS (not NSOAAMS). Related to this, the discussion on NOAAMS and the EESI-based factor is provided after this sentence, not before.

Done. In the section 3.1, the AMS source apportionment, we suggest this factor is a mixed factor, so here we don't include it into the calculation of AMS OOA contribution. *"NOA_{AMS} is excluded from this calculation due to the contribution from primary cigarette smoke discussed above." (P15, L2-3)*

Fig. 6b- unit for precipitation is not included.

Done. The unit for precipitation has been added (*mm/h*).

P14, L12: "period 1" should be move to ": : :.study, period 1, occurs : : :."

Done. *"As shown in Fig. 6b, the coldest part of the study, period 1, occurs from 25 to 27 January." (P15, L9-10)*

P15, L25: I believe you mean EESI-CHON fragments correlate better NSOA_EESI. I don't think AMS_CHON fragments are displayed.

Done. *"Figure S10 shows a comparison of the $NSOA_{EESI}$ time series and CS-OA_{EESI} time series with the CHON ions from the EESI and CHN ions from the AMS, respectively. The group of EESI_CHON ions shows the same temporal variation as the $NSOA_{EESI}$ factor (Fig. S10) while the AMS_CHN group is more correlated to the primary organic group." (P16, L24-26)*

Fig. 12b. Green color for more aged secondary BB factor is too hard to see against the white background.

Done. We change to the black color.

P18, L10: consider replacing "big events" to some other phrase

Done. *"An SOA-dominated period with low levoglucosan concentrations (red line) toward the beginning of the campaign exhibits a lower sensitivity than during a period with higher levoglucosan concentrations (black line), which includes the events on 28.01.2017 and 29.01.2017 characteristic of* $EVENT_{EESI}$*." (P19, L16-19)*

Fig. 13b: intercept of the black line appears to have two negative signs in front

Done. We delete one negative sign.

P18, L31: change "primarily" to "primary"

Done. *"Both AMS and EESI-TOF factors stacked time series (Fig. 14) show clearly that biomass burning is dominated by secondary fractions early in the campaign, mixed fractions in the middle of the campaign, and primary fractions late in the campaign." (P20, L6)*

P18, L34: replace "WB-related" by "BB-related"?

Done. "…, it is hard to define how much of AMS OOA is BB-related as a function of time." (P20, L9)