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 are provided in *italics* and our responses follow in normal text. Changes to the manuscript are denoted in blue font.

Comment #1

The authors inform a reader about disadvantages of widely used analytical instrumentation for aerosol characterisation and apply EESI and AMS for their study. I agree that EESI technique certainly has some advantages (which the authors briefly listed in the introductory section); however, as any other techniques, it has numerous limitations (e.g. sensitivity), which, I believe (to avoid any biases) need to be reflected in the introductory section. I believe for this reason, off-line organic analysis techniques are still widely applied for aerosol characterisation (Noziere et al., 2015). Another disadvantage of the later technique is that it employs electrospray ionisation which suffers from competitive ionisation and lead to signal enhancement or suppression. This is affected by a compound's functional group (-OH, -COOH) and presence of inorganic salts in the matrix that are important constituents of atmospheric aerosols (Noziere et al., 2015).

For brevity, the original text did not discuss the advantages/disadvantages of offline organic analysis, addressing only continuous and semi-continuous online instrumentation. Offline techniques involve a different set of advantages/disadvantages relative to highly time-resolved online instrumentation such as the EESI-TOF. We have restructured the introduction to include a brief discussion of offline measurements in the discussion of analytical instrumentation.

The reviewer also raises two specific issues here: sensitivity of the EESI-TOF relative to offline techniques (where sensitivity can potentially refer to either the absolute detection limits or molecule-dependent differences in relative sensitivity), and matrix effects. We discuss these points individually below.

A comparison of absolute sensitivity is difficult to assess, due to (1) the large differences in time resolution between the EESI-TOF (typically seconds to a few minutes) and off-line techniques (typically hours to ~1 day), and (2) the potential for ongoing reactions and/or partitioning on the collection substrate to introduce systematic biases in off-line methods, introducing a disconnect between the bench-top and real-world off-line detection limits for affected compounds (Pospisilova et al., 2020; Zhao et al., 2018). As a result, we think it is not helpful to discuss absolute sensitivity in terms of advantages/disadvantages. Rather, this is an area where the different approaches aim at different targets and are thus complementary.

However, it is certainly true that different molecules exhibit different relative sensitivities in systems like the EESI-TOF and FIGAERO-I-CIMS that are based on soft ionization (Lopez-Hilfiker et al., 2019; Wang et al., 2021). Together with the lack of direct structural information, this is a clear limitation of 1-D MS techniques such as the EESI-TOF, AMS, and CHARON-PTR, as opposed to the chromatographic separation and tandem MS approaches possible in the off-line analysis. These points are noted in the revised manuscript.

Finally, the reviewer raises the issue of matrix effects. Although matrix effects do indeed affect conventional electrospray systems, they are well-known to be drastically reduced in EESI (Chen et al., 2006). In our EESI implementation, the combination of dilute analyte concentrations post-extraction in the charged droplets and the presence of high concentrations of Na^+ have been shown to render matrix effects negligible (Lee et al., 2021; Lopez-Hilfiker et al., 2019).

We now discuss this in the text as follows

Page 3, Line 38:

"To overcome these limitations on fragmentation and thermal decomposition, several offline, continuous and semi-continuous instruments have been developed. The offline techniques provide a high degree of chemically specific information with the possibility of molecular identification as well. They, however, have low time

resolution (typically hours to ~1 day) and include possible artifacts from reactions or partitioning on the surface (Pospisilova et al., 2020; Zhao et al., 2018)"

Page 4, line 19:

"The EESI-TOF enables highly time-resolved measurements of a wide range of atmospherically-relevant oxygenated compounds, including sugars, alcohols, acids, and organonitrates (Lopez-Hilfiker et al., 2019; Stefenelli et al., 2019) with detection limits on the order of 1-10 ng m^{-3}. The EESI-TOF detection limits are sufficient to measure these compounds with 5 s time resolution under typical ambient conditions with negligible thermal decomposition, ionization-induced fragmentation, or matrix effects. EESI-TOF provides the near molecular level information (i.e., molecular formula) with lack of direct structural information. This is a clear limitation of 1-D MS techniques such as the EESI-TOF, AMS, and CHARON-PTR, as opposed to the chromatographic separation and tandem MS approaches possible in the off-line analysis. In addition to that, different molecules exhibit different relative sensitivities in systems like the EESI-TOF (Lopez-Hilfiker et al., 2019; Wang et al., 2021)."

Comment #2

The authors need to be more specific what they mean by atmospherically relevant compounds when stating detection limit "in order of 1-10 ng m^{-3} for atmospherically relevant compounds" especially in light with the comments regarding competitive ionisation, selectivity and specificity of the applied technique. For example, PAHs (oxidised PAHs), sugar alcohols and carboxylic acids are atmospherically relevant compounds but have critically different ionisation efficiencies in ESI (and thus in EESI). Do you expect this technique to have the same "in order of 1-10 ng m^{-3}" detection limit for all of these atmospherically relevant compounds? If yes, please provide a reference or data to support this statement.

We have revised the statement. We now note that the EESI-TOF measures a wide range of atmospherically-relevant oxygenated compounds, including sugars, alcohols, acids, and organonitrates (Lopez-Hilfiker et al., 2019; Stefenelli et al., 2019) The results of Tong et al. (submitted) suggest that on average the sensitivities between these compound classes are broadly consistent with the stated 1-10 ng m^{-3} detection limits. However, variation among individual compounds is likely larger (Wang et al., 2021). We therefore now simply note that EESI-TOF detection limits are sufficient to measure these compounds with 5 s time resolution under typical ambient conditions. The modified text reads (page 4, line 19):

"The EESI-TOF enables highly time-resolved measurements of a wide range of atmospherically-relevant oxygenated compounds, including sugars, alcohols, acids, and organonitrates (Lopez-Hilfiker et al., 2019; Stefenelli et al., 2019) with detection limits on the order of 1-10 ng m^{-3}. The EESI-TOF detection limits are sufficient to measure these compounds with 5 s time resolution under typical ambient conditions"

Comment #3

Including a reference for the following statement would be beneficial or support this by showing data: '' In the configuration of the mass spectrometer and ionization scheme used in this study, one can detect a wide range of molecules present in the organic aerosols, including sugars, alcohols, acids, and organo-nitrates.''

We thank the reviewer for the suggestion. We have now added the following references with the text (page 4, line 19):

"The EESI-TOF enables highly time-resolved measurements of a wide range of atmospherically-relevant oxygenated compounds, including sugars, alcohols, acids, and organonitrates (Lopez-Hilfiker et al., 2019; Stefenelli et al., 2019) with detection limits on the order of 1-10 ng m^{-3}."

Comment #4

The authors report a range of molecular formula detected by the technique and relate them to specific compounds, e.g., levoglucosan. I failed to find the mass accuracy and resolving power of the applied EESI technique to support their molecular assignments. Please add this to the paper and consider how this will impact on the presented results (molecular assignments).

We thank the reviewer for the comment. The resolving power of the time-of-flight (TOF) mass analyser used in this study was ~8000 M/dM. This high resolving power of TOF analyser allowed the separation of isobars and the determination of molecular formula. A point to note here is that the molecular assignments given here are tentative and may also contain isomeric contributions. To clarify this, we have added the following lines to the text (page 6, line 8):

"The mass resolution (M/dM) achieved by the mass analyser in this study was ~8000. This resolution is enough to separate isobars (compounds with same nominal mass) and determine the molecular formula. Due to the lack of direct structural information, the molecular assignments given here are, however, tentative and may include contributions from multiple isomers."

Comment #5

The authors associate $C_2H_4O_2^+$ (m/z 60) and $C_3H_5O_2^+$ (m/z 73) to levoglucosan. It is worth mentioning that other anhydrosugars (levoglucosan isomers) can lead to this fragmentation. These include galactosan and mannosan, which are isomeric compounds of levoglucosan and cannot be distinguished/separated by the applied technique. Again, this caveat needs to be stated in the manuscript.

We agree, and have changed the text in the manuscript as given below (page 14, line 14):

The mass spectrum of primary biomass burning is dominated by $C_6H_{10}O_5$, likely associated with anhydrosugars such as levoglucosan, mannosan and galactosan. $C_6H_{10}O_5$ constitutes 81.1 % of the total mass spectral signal in this factor (Fig. 2a).

Comment #6

*Line 10 (page 12) ''The mass spectra of BBOA-1 and BBOA-2 both have strong signals from $C_2H_4O_2^+$ (m/z 60) and $C_3H_5O_2$ + (m/z73) fragments, which are characteristic of anyhdrosugars like levoglucosan, a product of cellulose pyrolysis (Simoneit et al., 1999).'' needs revising. The work by Simoneit et al., 1999 reports data for TMS esters so the reference to levoglucosan fragments is invalid. If this reference was used to support the second part of the statement i.e., ''*a product of cellulose pyrolysis*'', then the sentence needs revising as well.*

The original text did not clearly link the references to the statements they were intended to support. The revised text reads (page 12, line 27):

The mass spectra of BBOA-1 and BBOA-2 both have strong signals from $C_2H_4O_2^+$ (*m/z* 60) and $C_3H_5O_2^+$ (*m/z* 73) fragments, which are characteristic fragments of anyhdrosugars like levoglucosan (Aiken et al., 2009), a product of cellulose pyrolysis (Hoffmann et al., 2010; Simoneit et al., 1999).

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