Reviewer #2

General comments:

This study estimated the emission factors and characterized the POA with AMS and EESI-TOF from a variety of solid fuels. This topic is interesting and the experiment is well-designed.

However, some typos and misunderstandings were found. More necessary discussions and details are suggested to be provided. The authors should provide more convincing results. I recommend a major revision of this manuscript.

We thank the reviewer for the helpful comments. Below we provide a detailed point-by-point response to the issues raised by the reviewer. We will have the reviewer comments in black, address the comments in blue, and modified sentences in blue and italics.

Major concerns

The abstract part does not stress the importance of this manuscript, only emphasizing that OA is important, biomass burning is the common source of OA, and EESI-TOF is powerful. What is the urgency of measuring OA from the molecular level? What is the breakthrough and highlight of this work?

Response: As we have shown in the abstract, the urgency for molecular-level characterization of particulate matter stems from the inadequacy of chemical fragments to identify particulate matter from similar sources (Line 13-15). Such chemical separation is necessary to provide insight into the sources of air pollution in developing, and polluted, regions. The breakthrough and highlights of this paper are building up the molecular-level mass spectra from burning emissions and providing robust marker for source apportionment to assess the importance of different burning processes. Future measurements in such regions will provide insight into the ability of these markers to assess the importance of different biomass burning sources.

Please add some instrument comparisons in the introduction part. Why is EESI-TOF important? We admit that less decomposition or fragmentation is observed in EESI-TOF measurement, however, the homolog speciation could not be achieved.

Response: More instrument comparison has been added as below on line 76 to line 78.

"*Liquid chromatography-mass spectrometer can avoid thermal desorption and separate mixtures including isomers based their chemical affinity with the mobile and stationary phases (Zhang et al., 2021). However, it requires pre-treatment of samples which could introduce artefacts and lowers the time resolution*."

Is burning plastic bags really important? Please add more details or figures to illustrate this.

Response: The importance of burning plastic bags has been added in the manuscript as follows from line 46 to line 50.

"*Plastic burning has been estimated to contribute 13.4% of fine particulate matter ($PM_{2.5}$) yearly in India (Gadi et al., 2019), 6.8% in wintertime in China (Haque et al., 2019), and 2% to 7% in wintertime in the US (Islam et al., 2022). The toxic pollutants released from plastic burning, including olefins, paraffin, and polycyclic aromatic hydrocarbons, can cause respiratory irritation, and carcinogenic and mutagenic effects (Pathak et al., 2023).*"

The standard deviation of CO, and THC of straw burning and plastic bag burning is extremely high. Please specify. Note that other pollutants are not varied significantly.

Response: There is inherent variability in burn-to-burn. The high standard deviation of CO, CO_2, and THC for straw and plastic bag burning is driven by the combustion efficiency, i.e. MCE. The more flaming (MCE close to 1) the fire is the more emission of CO_2 and less emission of CO and THC. As shown in Table S1, the most flaming experiment of "SO4" with MCE of 1 has the largest emission factor (EF) of CO (97.4 g kg^{-1}) and smallest EF of THC (1366.1 g kg^{-1}) in all straw burning compared to the experiment of "SO6" with MCE of 0.89 (CO EF 0.2 g kg^{-1}, THC EF 1636.4 g kg^{-1}). For the same reason, the standard deviation is also high for plastic bags.

It has been specified from line 196 to line 198 as below.

"Taking straw burning as an example, as shown in Table S1, the EFs of THC vary from 0.7 to 39.3 g kg^{-1}, with the MCE varying from nearly 1.00 to 0.89 correspondingly, resulting in the high standard deviation of the EFs."

Line 229- 239: please add more detail or discussion about WHY PAHs are so different among samples. Does the material or burning styles shape the emission pattern?

Response: To begin with, please note that we corrected the mass spectra for plastic bags as mentioned in Reviewer #1's comments. The updated spectra and PAH peaks are marked in the new Figure S3, and show less difference than the old figure between fuel types.

The burning fuel and combustion efficiency are both important for the PAHs emission, as PAHs are the pyrolysis products of the burning material. However, the burning style used in this study does not cause a clear difference for PAHs, because the PAHs are very similar between spruce and pine logs stove burning (Figure S2b) and spruce and pine branches and needles open burning (Figure S2c). We note the lack of PAHs in cow dung emissions, which were dominated by smoldering conditions given their low MCE (0.87), nevertheless this difference may still be due to the fuel type.

 More discussion has been added to our manuscript from line 252 to line 256.

"Not many PAHs are observed with the AMS for the plastic bags. The difference in the observed PAH contribution is mainly caused by the burning material, i.e., the precursor of PAH, such as lignin, single-ring compounds, and aliphatic hydrocarbons. The burning of PE has a lower yield of PAHs than lignin (Zhou et al., 2015), resulting in the lower PAH contribution for polyethylene plastic bags."

Line 264-267: add more uncertainty analysis to the quantitative or qualitative measurement.

Response: The standard deviation has been added as below from line 283 to line 284.

"The O/C (calculated as the ratio of total oxygen to total carbon) of the POAs from 5 types of burning measured by the EESI-TOF is 0.32 ±0.07 to 0.41 ±0.02, which is higher than that of the AMS (0.16 ±0.07 to 0.37±0.08)."

Line 273, how could the authors be sure that $C_6H_{10}O_5$ (m/z 162.0523) is levoglucosan (or similar dehydrated sugars)? Is there any GC-MS measurement?

Response: There are no GC-MS measurements associated with our measurements here, but we rely upon the breadth of previous work associated with quantification of the importance of dehydrated sugars (e.g. levoglucosan) present in many different biomass burning emission sources (Fabbri et al., 2008; Engling et al., 2006; Pashynska et al., 2002).

Part 3.3, Levoglucosan is not a good marker. However, $C_{16}H_{32}O_2$ is also not a good marker. Note that cooking emissions could also result in emissions of these so-called "markers" in this work. Please add more details.

Response: Section 3.3 aims to discuss and compare the often-mentioned markers in literature with our measurements instead of defining good markers. To better clarify this, the heading of the section has been changed to "Literature markers for solid-fuel combustion".

These markers are not defined as markers for the studied fuels. The "good" or "not good" marker is difficult to define without conditions. A detailed discussion of markers for specific fuels can be seen in Section 3.4. As the manuscript says, "the $C_6H_{10}O_5$ is a good untargeted marker for biomass burning" and it has been widely used in source apportionment. The cooking source of $C_{16}H_{32}O_2$ in our manuscript has been mentioned in Line 284 in the original manuscript.

Line 370: how could the authors be convinced that most of these markers are reported for the first time in POA emissions from the studied fuels? The investigation of pyrolysis of lignins has lots of results related to sugars, alcohols, and benzaldehydes.

Response: Due to the ubiquitous presence of lignins in the biomass materials, the pyrolysis products of it are less likely to be selected as useful markers for specific fuels. While some of the same markers may have been shown for previous biomass burning results as the chemical composition, our study is the best of our knowledge the first to determine the markers' ability to distinguish between specific fuels, as well as the first demonstration of the EESI-MS in conjunction with organic aerosol produced from biomass burning emissions.

The sentence has been modified as below from line 405 to line 406.

"To the best of our knowledge, most of these markers are reported for the first time in POA emissions from the studied fuels with the EESI-MS, which is becoming more commonly used in the measurement of atmospheric aerosols."

Please add more atmospheric implications in the conclusion part. The current paragraphs are only the common conclusions stated by the authors before.

Response: The implications have been added to the conclusion section from line 441 to line 458.

"This work shows mass spectral profiles of burning emissions on bulk and molecular level, which improves our understanding of POA from different fuels. The markers provided in this study are crucial for distinguishing the sources of aerosols in the atmosphere and enhancing the interpretation of source apportionment. In the future, the volatility and chemical reactivity of the proposed markers should be tested to determine their atmospheric stability and their ability to be a robust marker. More burning fuels such as coal and grass could be conducted to enrich the spectral database.

Future studies will probe the usefulness of these markers, if they are long lived enough in the atmosphere to provide useful separation between complex emission sources shown here. This will either focus on online measurements in polluted regions or from offline filter analysis from similar regions. Clearly, the dominant biomass burning markers (levoglucosan and others) are not robust to be used to separate different biomass sources, though they are robust for identification of general biomass burning aerosol. Nitrogen containing compounds emitted from cow dung emissions can provide a very unique set of markers for separating this source from other biomass sources. Additionally, resin acids from observed in the emissions from spruce and pine emissions provide unique species associated with these emissions (and observed previously).

At the present moment, to provide insight into the usefulness of these markers within the context of ambient measurements, or against source apportionment methods, we would require a robust dataset of comparable data to test these markers and average emission profiles against. "

Minor comments

The abstract part is not transparent and brief. See line 17 – 20, I recommend cutting this sentence into two separate sections.

Response: The original sentence has been rewritten into two sentences as shown below on line 17 to 20.

"In this study, we systematically estimated the emission factors and characterized the primary OA (POA) chemical composition with the AMS and the extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF) for the first time. The study was conducted on a variety of solid fuels, including beech logs, spruce and pine logs, spruce and pine branches and needles, straw, cow dung, and plastic bags."

Line 42:45: "… Southeast Asia… developing regions,…India", Please rewrite these sentences, as these regions are involved with each other.

Response: They are rephrased as below on line 43 to 45.

"In Southeast Asia, haze events are mainly attributed to the wildfires, agricultural waste burning, and peatland fires (Adam et al., 2021). In India, more than half of households use inefficient stoves for cooking, burning solid fuels such as firewood, charcoal, crop residues, and cow dung (Census of India, 2011)."

Line 117: high-resolution time-of-flight AMS (HTOF-AMS)? OR H*R*-TOF?

Response: We think both abbreviations are fine as long as it is clear in the manuscript. We prefer to refer it as HTOF-AMS, as it is consistent with the abbreviation form of the name from its producer Aerodyne Research, Inc., which can be found here: https://www.aerodyne.com/product/aerosol-mass-spectrometer.

Line 171, why is $p<0.1$ chosen?

Response: The significance level α typically is 0.1, 0.05, and 0.01. When we choose α = 0.1 to formulate the hypotheses, it means there is 10% chance of rejecting the null hypothesis when the null hypothesis is true (Type I error). In the two-tailed test we used, for each tail (significantly high or significantly low) the α is equivalent to 0.05 in the one-tailed test as the cutoff. This is a practically useful cutoff. When α is set to 0.05, the criteria is too strict to effectively select markers for straw, while, an α higher than 0.1 runs the risk of committing the Type I error.

Line 692, static p?

Response: changed.

Reference

Engling, G., Carrico, C. M., Kreidenweis, S. M., Collett Jr, J. L., Day, D. E., Malm, W. C., Lincoln, E., Min Hao, W., Iinuma, Y., and Herrmann, H.: Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, Atmos. Environ., 40, 299-311, https://www.sciencedirect.com/science/article/pii/S1352231006005802, 2006.

Fabbri, D., Modelli, S., Torri, C., Cemin, A., Ragazzi, M., and Scaramuzza, P.: GC-MS determination of levoglucosan in atmospheric particulate matter collected over different filter materials, J Environ Monit, 10, 1519-1523, https://www.ncbi.nlm.nih.gov/pubmed/19037493, 2008.

Pashynska, V., Vermeylen, R., Vas, G., Maenhaut, W., and Claeys, M.: Development of a gas chromatographic/ion trap mass spectrometric method for the determination of levoglucosan and saccharidic compounds in atmospheric aerosols. Application to urban aerosols, J Mass Spectrom, 37, 1249-1257, https://www.ncbi.nlm.nih.gov/pubmed/12489085, 2002.