

Reviewer #1

Zhang et al. used advanced mass spectrometry tools to measure the primary organic aerosol emitted from burning a variety of biomass fuels and plastic. They reported emission factors of gases and organic aerosol from burning these fuels, and used EESI-ToF measurement to identify unique tracers for different fuels with solid statistical analysis. The very new instrument, EESI-ToF, is used to characterize biomass burning particulate matter for the first time. Given the expanding use of EESI-ToF by the community, I think this work fits the scope of ACP. The manuscript is very clearly written. I recommend this work be published after some minor changes. I have the following comments for the authors to consider.

We would like to thank the reviewer for the comments and suggestions to improve the current work. We will have the reviewer comments in black, address the comments in blue, and modified sentences in blue and italics.

Line 21 in the abstract: From the main text, I found out that the organic gases were measured by a total hydrocarbon analyzer. However, when reading the abstract, I thought that they were measured by AMS or EESI. I would suggest the authors talk about how the hydrocarbon gases were measured before reporting these numbers.

Response: The instruments used for the measurements are added as follows (line 20 to 22).

“The emission factors of organic matter estimated by AMS and hydrocarbon gases estimated by the total hydrocarbon analyzer are $16.2 \pm 10.8 \text{ g kg}^{-1}$ and $30.3 \pm 8.5 \text{ g kg}^{-1}$ for cow dung burning”

Line 25 in the abstract: I don't fully understand what this sentence means. The authors may want to rewrite it.

Response: It has been deleted because PAHs are not the main scope of this paper.

Line 112: Does “THC” here and in Equation 2 include methane?

Response: Yes, THC includes methane as defined throughout this paper. Line 112 in the original manuscript described parallel THC and CH₄ because Horiba APHA-370 measures THC and CH₄ using different channels and displays both concentrations. The calculation of emission factors using the carbon mass balance method needs the overall carbon mass concentration as the denominator, therefore the THC in Equation 2 also includes methane.

Considering that methane data is not used alone in this paper, we remove the methane from Line 112 to avoid misunderstanding as follows on line 120:

“Gas analyzers were used for monitoring the concentration of CO (Horiba APMA-370), CO₂ (LI-COR LI-7000), and total hydrocarbon (THC, including methane) (Horiba APHA-370).”

Line 115&117: The mass resolution of the AMS instruments can be documented here. Same for the EESI-ToF below.

Response: The mass resolution of EESI-TOF has been shown in Line 131 in our original manuscript as follows:

“The EESI-TOF mass analyzer achieved a mass resolution of ~10000 at m/z 173 and 11000 at m/z 323.”

The mass resolutions of the AMS instruments are added as follows from line 123 to line 127:

“A long time-of-flight aerosol mass spectrometer (LTOF-AMS, Aerodyne Research, Inc.) with a mass resolution of ~5000 over the range of m/z 100 to m/z 450 deployed for online, non-refractory particle characterization and a subset of experiments were performed with high-resolution time-of-flight AMS (HTOF-AMS, Aerodyne Research, Inc.) with a mass resolution of ~2000 over the range of m/z 100 to m/z 450.”

Line 138: In Equation 1, as I understand, MassX is the mass flux to the detector, and the authors are not attempting to quantify the compounds. Did the authors assume that all the compounds have the same response factor when making Figure 3?

Response: Yes, we assume that all the measured compounds have the same response due to the lack of commercial standards. The response factor was discussed for secondary organic aerosols (Wang et al., 2021), but so far it is not available for primary organic

aerosols. Intercomparisons with the AMS have shown that the total EESI-TOF signal responds quantitatively to the bulk organic aerosol concentration (Lopez-Hilfiker et al., 2019; Wang et al., 2021).

It has been clarified as follows from line 258 to line 260.

“The EESI-TOF provides an important complement to the highly fragmented mass spectra generated by the AMS, where intact compounds measured by the EESI-TOF from m/z 100 to 400 without assuming specific response factors toward each molecular formula are shown in Figure 3.”

Line 154: Would be great to document the (average) densities of aerosol in Table 1 or Table S1.

Response: The densities of particles in the burning emissions are added in Table 1.

Table 1 Average emission factors of CO, CO₂, THC, PM, OM, and BC as well as MCE for 6 types of burning.

Burning type	Carbon content	Particle density (g cm ⁻³)	MCE	Emission factors (g kg ⁻¹ fuel)					
				CO	CO ₂	THC	PM	OM	eBC*
beech logs stove (n=5)	0.46	1.70	0.91±0.03	85.8±25.9	1466.9±65.8	19.3±5.5	7.6±2.2	6.2±2.8	2.43±0.9
spruce and pine logs stove (n=8)	0.46	1.70	0.91±0.02	83.8±26.7	1640.7±58	16.1±4.8	4.9±2.2	2.0±1.3	n.a
spruce and pine branches and needles open (n=4)	0.46	1.70	0.93±0.02	63.5±6.8	1668.9±26.7	14.1±3.4	9.4±2.7	3.8±1.1	n.a
straw open (n=6)	0.45	1.50	0.95±0.04	44.4±34.1	1511.7±103.2	19.1±17	2.8±1.2	2.4±1.3	0.7±0.2
cow dung open (n=6)	0.45	1.54	0.87±0.03	92.3±27.4	1366.2±88.4	30.3±8.5	16.6±10.8	16.2±10.8	0.8±0.3
plastic bags open** (n=4)	0.84	0.45	0.98±0.02	29.3±39.2	2956.6±138.9	18.2±28.6	32.7±1.2	1.1±0.3	1.0±0.3

* The number of burns is indicated by n. BC data is not available for some burns.

** The emission factors of PM and OM are corrected as explained in Supplement.

“The densities could be underestimated because of the non-spherical shape of particles, especially particles from plastic bags burning mainly due to the high contribution of BC.” (Line 164 to line 166)

Line 204: The CHON ions are not included in Figure 1. Is it because they are negligible? Were they fitted in Pika?

Response: Yes, the fragments containing CHO₁N and CHO₂+N are fitted in Pika, but their individual contribution is less than 1%. We added the C_xH_yON_z family in Figure 1 for the concern.

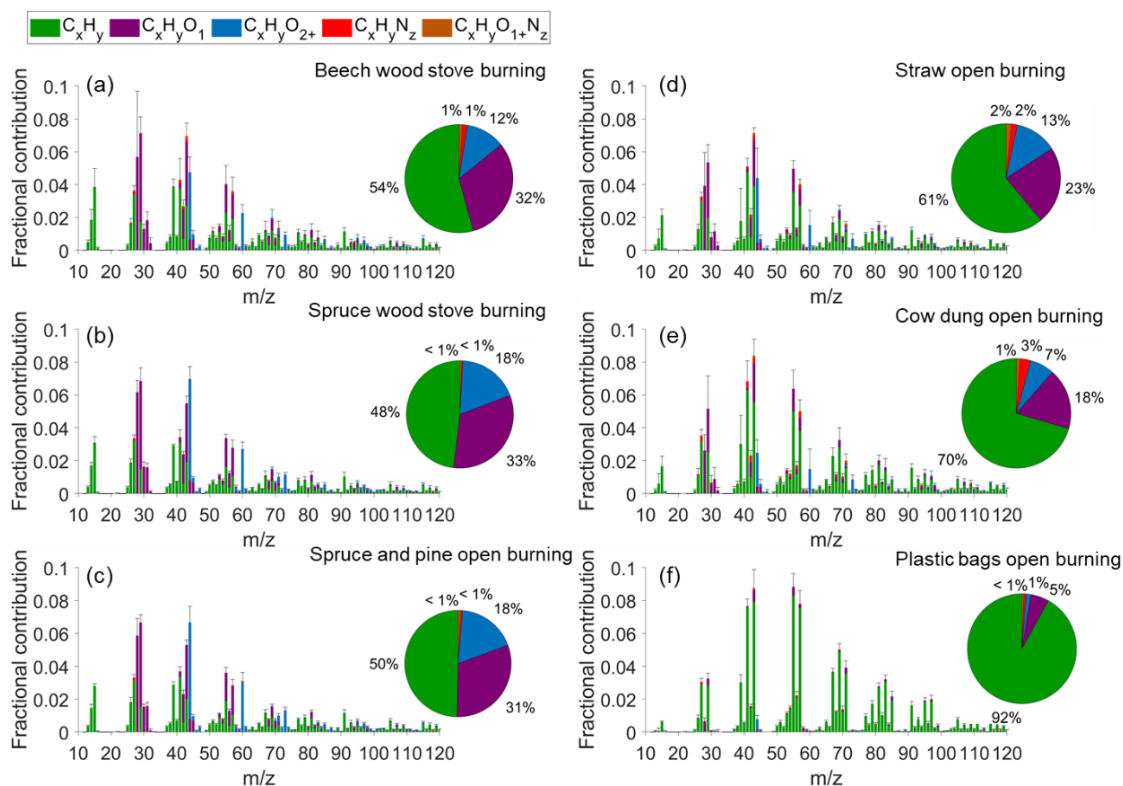


Figure 1 Average AMS POA mass spectral profiles and elemental compositions of (a) beech logs stove burning ($n=6$; n is the number of experiments), (b) spruce and pine logs stove burning ($n=9$), (c) spruce and pine branches and needles open burning ($n=4$), (d) straw open burning ($n=6$), (e) cow dung open burning ($n=5$), and (f) plastic bags burning ($n=4$). The error bar denotes half standard deviation in grey. The pie chart showing the contribution of elemental families is at the right of the mass spectrum.

Line 206: If the ions in the $C_xH_yO_z$ family in the plastic burning spectrum are coming from burning other fuels, then are PM, OM, and BC emission factors reported for burning plastic bags still reliable? Also, did the authors see $C_xH_yO_z$ in all four plastic bag burning experiments?

Response: We observed a high contribution of $C_xH_yO_z$ in 3 out of 4 plastic burning experiments. We accordingly added a corresponding section in the SI where we estimate the contribution of the contamination of the mass spectra of plastic bags. Please find the details we added in the SI on line 11 to line 23 as below. The emission factor has been corrected for the relevant experiments in Table S1 and Table 1.

“Plastic bags burning emission correction. In three out of four plastic bags burning experiments, the mass spectrum at the middle to end burning stages had considerable $C_xH_yO_z$ family contribution (~23%). As the combustion progressed, the chimney was heated, and the volatile substances remaining on the chimney evaporated and were then partitioned to the particles for detection. However, at the early stage, before the chimney got hot, the mass spectra consisted mainly of hydrocarbons (see Figure S2a). Therefore, we take only the early burning stage of these three burning experiments into account for the average mass spectrum in Figure 1(f). The absolute concentration of the three AMS mass spectra derived from the early-stage burning is scaled to the uncontaminated burning experiment ions based on m/z 81 and m/z 83, which are stable and characteristic for hydrocarbons. The difference on average is $0.4\% \pm 1.0\%$ which is very minor as shown in Figure S2b. The mass spectra of three contaminated burning over the whole burning stages indicate that the measured organics was $14.6\% \pm 8.7\%$ overestimated. Correspondingly, the emission factors for PM and OM are corrected for each plastic bags burning.

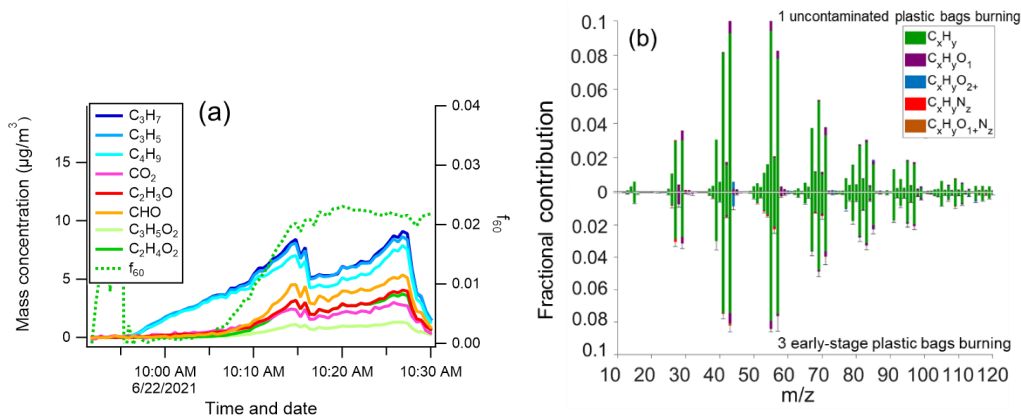


Figure S2 (a) The time series of some ions measured by the AMS during the plastic bags burning for the contaminated case; (b) the mass spectrum comparison of uncontaminated plastic bags burning experiment at the top v.s. the average of 3 early-stage burning at the bottom.”

Line 219: What is the “f₆₀ filter”? Is it 0.003?

Response: The f₆₀ filter is 0.003. The original sentence is modified on line 232 as below.

“..., suggesting the f₆₀ filter (f₆₀ = 0.003) in the ambient is unlikely to miss biomass combustion.”

Line 229: It might be good to label the PAH ions in the mass spectra (Figure S2).

Response: The relevant ions have been marked in Figure S2.

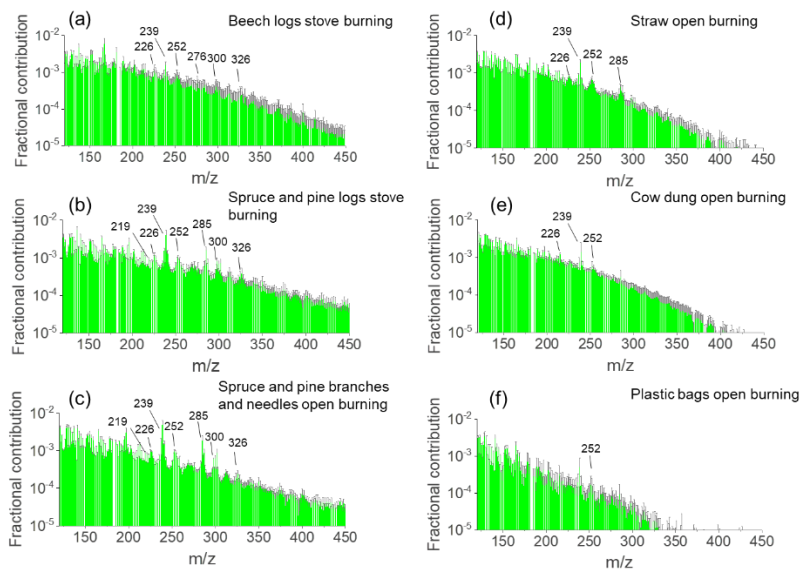


Figure S2. Average AMS POA mass spectral profiles in the range from m/z 120 to 450 of (a) beech logs stove burning (n=6; n is the number of experiments), (b) spruce and pine logs stove burning (n=9), (c) spruce and pine branches and needles open burning (n=4), (d) straw open burning (n=6), (e) cow dung open burning (n=5), and (f) plastic bags open burning (n=4). The m/z for some ions are marked in the figure. The error bar denotes half standard deviation in grey.

Line 230 and 231: The authors may want to double-check what the ion with m/z 239 is. It should not be the parent ion of a hydrocarbon. Also, is the molecular formula of methylbenzofluoranthene C₁₉H₁₂? I think it should be C₂₀H₁₄. I am also curious

whether the authors found a hint of retene in the AMS mass spectra because retene is usually a very abundant PAH emitted from burning conifers. It could have fragmented into smaller ions given its branched structure.

Response: The m/z 239 could be methylbenzo[ghi]fluoranthene or fragmentation of dehydroabietic acid according to the literature. The parent ion of retene at m/z 243 does not have a significant signal due to the fragmentation, but the main fragment of it at m/z 219 was found in the spruce and pine burning experiment.

Please find the modified sentences below from line 243 to line 250..

“..., parent ions at m/z 226, 252, 276, 300, and 326 correspond respectively to $C_{18}H_{10}$ (benzo[ghi]fluoranthene and cyclopenta[cd]pyrene) $C_{20}H_{12}$ (benzofluoranthene and benzopyrene), $C_{22}H_{12}$ (indenopyrene and benzoperylene), $C_{24}H_{12}$ (coronene), and $C_{26}H_{14}$ (dibenzoperylene). The fragment of m/z 239 could be methylbenzo[ghi]fluoranthene ($C_{19}H_{12}$) (Dzepina et al., 2007; Ji et al., 2010) or a fragment of dehydroabietic acid which has been found in fresh pine resin (Colombini et al., 2005). The m/z 219 and m/z 285 also could arise from the fragmentation of retene and dehydroabietic acid, respectively, which also can be derived from conifer resin (Dzepina et al., 2007; Jen et al., 2019; Zetra et al., 2016).”

Line 262: Compounds with 18-20 carbon atoms could be resin acids (or their decomposition products in biomass burning), which are abundant in conifers. Also, in Line 286, I am curious that did the authors see emission of dehydroabietic acid ($C_{20}H_{28}O_2$) from burning coniferous fuels?

Response: Yes, we observed $C_{20}H_{28}O_2$. We have adapted this in the relevant description as below from line 305 to line 308.

“The corresponding compounds for the $C_{20}H_{30}O_2$ and $C_{20}H_{28}O_2$ are most likely resin acids (e.g., abietic acid and pimaric acid) and dehydroabietic acid, respectively, which have been found in coniferous resin (Holmbom, 1977; Simoneit, 2002) and suggested as biomass burning tracers (Simoneit et al., 1993; Liang et al., 2021).”

Line 298: How is the correlation coefficient calculated? The authors may want to provide more details.

Response: The details of correlation coefficient calculation have been added in the manuscript as follows on line 319 to 321:

“The calculation of Spearman’s coefficient is equivalent to calculating the Pearson correlation coefficient on the rank-ordered data, so it assesses monotonic relationships for ions from two mass spectra.”

Line 409: I am convinced by this analysis that the p-value and FC methods can select tracer compounds from different biomass burning fuels very efficiently. However, in source apportionment studies, there are usually non-biomass burning PM sources. I would suggest that the authors compare the spectra of the biomass burning POA with OA from other common sources in their future study or verify these tracers in future field campaigns to make sure they are exclusively from biomass burning.

Response: Thank you for the forward-looking approach that this method can offer. Indeed we plan to compare these specific markers noted in the future to evaluate the utility of tracers in combination with FC and p -value within the range of studied fuels. Certainly, if we can develop mass spectrum data in a wide range of sources in the future, we can make better use of this method and reduce the uncertainty in its application. Additionally, we plan in the future to assess these markers against secondary organic aerosol formation from the same emissions to assess their stability and continued uniqueness.

Minor Comments

Line 251-253: This seems to be an unfinished sentence.

Response: it is modified as follows on line 270 to 272.

“Of the N-containing species in cow dung POA 95% contain one nitrogen atom and are in a wide range of carbon number between 5 and 22. They are mainly in the O/C range of < 0.15 to 0.5 and the H/C from 1.2 to > 1.7 (Figure S4).”

Line 257: A redundant “%” should be removed.

Response: It is removed from the manuscript.

Line 696: “markers denote”

Response: It is changed as suggested.