Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2022-801-RC1, 2023

Comment on acp-2022-801

Anonymous Referee #1

Referee comment on "Light absorption and molecular characteristics of molecular-specific brown carbon formed in dung combustion in the Tibetan Plateau, China" by Qian Zhang et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-801-RC1, 2023

This manuscript, prepared by Qian Zhang et al., describes an analysis of Brown Carbon (BrC) emitted from burning traditional solid fuels (yak dung, sheep dung, and bitumite) commonly used in the Qinghai Tibet Plateau (TPL) region. With the measurement of light absorptivity and molecular-level information, the authors attempted to identify major light-absorbing species and markers for such combustion. TPL is a climatically sensitive region, and addressing light-absorbing climate forcers, such as BrC, emitted in this region is of paramount importance. Particularly, emissions arising from traditional (but still widely practiced) solid fuels, including dung burning, are significantly understudied in the literature. In this regard, the research topic is important, timely, and fits the scope of ACP. In particular, I find the observation that these emissions are particularly high in BrC emission fascinating.

However, I cannot recommend publishing this manuscript in its current form. I have a number of major scientific concerns, as listed below, and I think parts of the discussion just seem to be incomplete in the current version. It may be potentially publishable after significant rewriting. Last but not least, the literary grade of the manuscript is not excellent, with countless grammatical errors. I would recommend the authors undergo additional editing and proofreading.

Major comment

My biggest concern is that the analytical method used, UHPLC-ToF-MS/MS, has limitations in both quantitation and identification of molecules. Although I acknowledge that the chemical analyses were done carefully, and with much appreciated chemical insights, the authors not only did not carefully discuss these limitations but seem to be unaware of them. Please see my breakdown below.

Completeness of the detected species

There are multiple reasons the method used here can detect only a fraction of BrC emitted. 1) methanol cannot extract all BrC compounds on the filter 2) The column cannot elute all the compounds in MSOC. 3) ESI(-) only detects compounds with an acidic proton, which is far from the entire spectrum of MSOC compounds.

Quantitation

ESI is not a very quantitative method, as the ionization efficiency of molecules varies drastically between compounds due to size and functional group.1 However, the authors employ relative intensity - which I don't think is clearly defined (see minor comment) - as the sole indicator for the abundance and concentration of species in the sample.

Identification

Molecular identification using MS, even with the assistance of MS/MS, is challenging. How can the authors be confident about structure identification (Table 2) down to the isomer level? As the authors stated themselves, there are numerous isomers in this complex sample (Line 206). It seems that the authors have investigated a lot of work into a self-built library (Line 113), but it is not clear in the manuscript.

Combining compleeteness, quantitation, and identification above, many of the authors' conclusions and implications are questionable and should be revised across the manuscript. Some of these include, but may not be limited to:

- The Mbabs values and the relative contribution of each compound class to the total absorption (basically everything in Figure 6).
- The fact that authors consider the observed BrC species are all that contribute to light absorbers. E.g., "The values confirm that CHON compounds were likely to be the dominant light absorbers in solid fuel combustion over the TPL region (Line 254)".
- The conclusion "this work provides exhaustive molecular information" (Line 327)

Burning conditions/scenarios.

One of the conclusions from the paper is that burning type/scenario (i.e., cooking vs heating) significantly affects BrC emissions. The conclusion is valid and interesting, but the authors did not provide further information on how they are different. The readers can only see that they are different, their pictures (SI) and "heating has poor oxygen conditions than cooking" (Line 152), but without further support. I thought the authors measured OC/EC to gauge combustion efficiency, but I was surprised that none of the data had been presented in the manuscript.

Minor Comments

- I don't think Mbabs is clearly defined in the main article (it is in the abstract). As such, the method to determine Mbabs is unclear. Is the PLSR method from line ~118 for Mbabs?
- 'Relative intensity' is not properly defined. Relative to what?
- Line 218 - what is atmospheric conditions? Is it burning conditions instead?
- In the paragraph starting Line 220, the discussion related to Figure 4 does not seem to fully reflect the observations on Figure 4. For example, 'a wide DBE range from 0 to 20' - it seems to be wider. And 'CHON and CHONS compounds (beyond 70%) lies in the potential BrC chromophore range - I don't think its beyond 70%, looking at the data.

Grammatical errors

There are numerous that I believe can be corrected by careful proofreading and editing.

Additionally, certain sentences appear too subjective, and I suggest the authors revise the tone of the writing.

E.g, :

"We all know that burning biofuels of yak and sheep dung is still the most traditional and popular way of heating and cooking over the TPL region. The total consumption of both yak and sheep dung can even possess up to nearly 70% of the total dung fuel consumptions during heating periods (Zhang et al., 2022a)."

'We all know that' , 'still the most traditional and' , 'dung can even possess up to' can all be considered subjective.

Reference

(1) Kenseth, C. M.; Hafeman, N. J.; Huang, Y.; Dalleska, N. F.; Stoltz, B. M.; Seinfeld, J. H. Synthesis of Carboxylic Acid and Dimer Ester Surrogates to Constrain the Abundance and Distribution of Molecular Products in α-Pinene and β-Pinene Secondary Organic Aerosol. *Environ. Sci. Technol.* **2020**, *54* (20), 12829–12839. https://doi.org/10.1021/acs.est.0c01566.