

***Interactive comment on* “Laboratory studies of fresh and aged biomass burning aerosols emitted from east African biomass fuels – Part 2: Chemical properties and characterization” by Damon M. Smith et al.**

Anonymous Referee #2

Received and published: 22 June 2020

While the topic of this manuscript is certainly within the scope of ACP, I have significant concerns regarding some of the experimental methods used and how these are presented. Furthermore, several key pieces of experimental data are not included, and many of the results are not clearly discussed and explained. I found it difficult to understand many aspects of the paper. The SI is a spreadsheet of data with several figures that are not discussed. Many of these are important figures that should be presented and discussed in the main paper to understand the experiments (such as the aerosol size distributions). I do not think this submission meets the standards in terms of qual-

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ity or clarity required for ACP and that it would be challenging to revise the paper to meet the standards of ACP. Many of my serious concerns and questions below were raised in pre-review for ACPD and were not addressed by the authors. Therefore I am concerned that they are not taking the peer review processes seriously and am also significantly concerned with the reliability of many their results. I conclude that it will be very challenging to substantially revise this manuscript to meet the standards of ACP and must recommend it be rejected.

The central issue is the experimental design seems poor. Very high aerosol mass concentrations are added to the chamber, and even after 12 hours of aging these only increase by half. This is a lot of time for semi-volatiles to partition to the walls which will cause additional “aging” that does not really simulate atmospheric aging processes; you will lose a lot of the semivolatile components that are strongly involved in atmospheric photooxidaton processes. There is a wide body of information on this specific to the dynamics of BBA and the key roles of dilution and evaporation such as from the FLAME experiments. It is also not clear how much aerosol is left in the chamber after 12 hours of aging, and the aerosol size distributions are not shown in the main paper. In the size distributions in the SI it appears there is substantial aerosol growth, but this is also not discussed. The high aerosol chamber mass concentrations will result in a lot of semi-volatiles being partitioned to the aerosol phase which will affect how they respond to photochemical aging since this occurs quite differently in the gas phase versus in the aerosol phase.

A relationship between BrC components and volatility has been found and would play an important role here though this is never discussed here. See for example the recent work of Rawad Saleh. Many studies on chamber aging and the role of dilution and evaporation of BBA have been reported and need to be discussed and used to interpret these results. See the many papers from the 4 prior FLAME campaigns, such as the work of Andrew May and Allen Robinson, and also the more recent papers from the FIREX lab studies. The chamber studies of BBA aging reported by Ahern et al. from

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FLAME-4 are especially relevant to this work. Jeff Pierce has also examined the key interplay between fire size, dilution, and the resulting gain or loss of OA with “aging”.

ppm levels of a few VOCs also appear to be added to the chamber during the UV aging but the purpose of this is not explained. Thus the aging consists of high mass concentrations with high amounts of a few VOCs added but no additional oxidants added, and UV photochemistry. What type of realistic atmospheric aging does this represent? The high aerosol mass concentrations represent in-plume concentrations while in the atmosphere most photochemical aging will occur under much more dilute conditions as the smoke entrains background air, and possible additional oxidants. Adding such high concentrations of VOCs is also odd as this would not occur as the smoke plume (a large source of VOCs itself) spreads and dilutes. Without a better handle on what specific type of aging is simulated here and how it represents atmospheric processes it is difficult to extrapolate these experiments to understand the real atmosphere. The focus is on understanding the sources, properties, and evolution of brown carbon. Nitration of organics such as aromatics is known to play a prominent role in BrC production yet the role of nitrogen oxide chemistry is not discussed. 12 hours of photochemistry will likely deplete most of the NO_x/NO_y while this would not necessarily be the case under atmospheric conditions.

Allowing the biomass fuel to dry in a hood for a year will drive evaporative loss of a substantial fraction of the organic components that can be emitted or are combusted in biomass burning, thus substantially altering the composition of the BBA measured here compared to realistic biomass burning. This aspect needs to be discussed as it can significantly alter the composition of the resulting BBOA and SOA. See Ahern et al. for a discussion of this: Ahern, A. T.; Robinson, E. S.; Tkacik, D. S.; Saleh, R.; Hatch, L. E.; Barsanti, K. C.; Stockwell, C. E.; Yokelson, R. J.; Presto, A. A.; Robinson, A. L.; et al. Production of Secondary Organic Aerosol During Aging of Biomass Burning Smoke From Fresh Fuels and Its Relationship to VOC Precursors. *J. Geophys. Res. Atmos.* 2019, 124 (6), 3583–3606.

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UPLC is used to separate the methanol extract of the BBA filter samples, but no chromatograms are shown. This is critical as BBA is notoriously difficult to separate using a C18 or similar reverse-phase column, and these chromatograms are used here in much of the analysis. Cora Young has a series of paper on the use of size exclusion chromatography that discusses issues in UPLC analysis of BBA that should be consulted and discussed, as well as what they have learned regarding the relationship between BrC and molecular weight. Showing the chromatograms, at least in the SI, is also important as there are some weird baseline correction issues mentioned in the paper. Throughout the paper the properties of BrC obtained from other studies not on these same systems are extrapolated to also describe the BrC/OA in these experiments. This is not a safe assumption.

Di Lorenzo, R. A.; Place, B. K.; VandenBoer, T. C.; Young, C. J. Composition of Size-Resolved Aged Boreal Fire Aerosols: Brown Carbon, Biomass Burning Tracers, and Reduced Nitrogen. *ACS Earth Sp. Chem.* 2018, 2 (3). Di Lorenzo, R. A.; Washenfelder, R. A.; Attwood, A. R.; Guo, H.; Xu, L.; Ng, N. L.; Weber, R. J.; Baumann, K.; Edgerton, E.; Young, C. J. Molecular-Size-Separated Brown Carbon Absorption for Biomass-Burning Aerosol at Multiple Field Sites. *Environ. Sci. Technol.* 2017, 51 (6). Di Lorenzo, R. A.; Young, C. J. Size Separation Method for Absorption Characterization in Brown Carbon: Application to an Aged Biomass Burning Sample. *Geophys. Res. Lett.* 2016, 43 (1), 458–465.

In the non-targeted analysis the use of retention time is not clear to me. Is it used to help propose a chemical formula for a given ion peak? Or page 7 it says similar m/z with different t_r were combined. Also were any standard run to determine the expected retention time? Or is a standard C18 elution program being used and a database of retention times being referenced?

The UV/vis absorption spectra in Fig 5. These very flat featureless spectra do not make sense or provide any information. Even black carbon does not have such a flat wavelength spectrum.

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It seems that the UV/Vis absorption spectrum is averaged over the entire chromatogram. Why? This is throwing away valuable information, and likely explains why the spectra in Fig. 5 are so featureless. If you examine the absorption spectra for specific chromatographic peaks you can then relate the light absorption properties and potential chromophores to the ions observed at that same retention time. This provides molecular-level understanding of the specific compounds that are light absorbing, their sources, and their alteration by aging.

Throughout the paper brown carbon (BrC) is discussed as though it is a distinct component, but it is just the organic carbon that has a significant molar absorptivity or real refractive index in the UV/vis wavelengths of interest. There is plenty of evidence from prior studies that BrC cannot be separated or easily distinguished from the rest of the organic aerosol. It really exists as a spectrum. See for example Rawad Saleh's work on this topic.

The role of catechol is mentioned and there has been much recent work on the role of nitration of catechol as well as other aqueous chemistry in producing BrC. This needs to be discussed and in order to do so a solid understanding of the NO_x/NO_y chemistry in the fresh and aged BBA must be determined and presented. Biomass burning typically emits substantial NO_x, and also NO_y such as HONO.

There are several inappropriate and unsupported statements made regarding particle morphology and its role in the light absorption properties. For example, on page 2 "BrC aerosols are spherical in morphology", and on line 513: "Such an increase in SSA resulting from morphology changes is implausible". Aging can drive the condensation of secondary components that change morphology (how well coated the BC is, for example) that can absolutely alter SSA.

More details on the type of TEM grid and how the sample was collected on it are required. Is it coated with formvar or similar, or a bare metal grid?

Flaming-phase combustion also increases the mass fraction of inorganic components

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present, and nitrogen oxides and chloride can play a role in BrC chemistry (line 331).
Were the inorganic components measured and quantified?

Line 573: What mass fraction of eucalyptol would have to be present to explain the observations? Is this reasonable?

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-1160>, 2020.

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