General comment:

The manuscript titled "*Chromophores and chemical compositions of brown carbon aerosol before and after photooxidation of combustion emissions*" investigates the influence of fuel-source and photooxidative aging over the optical and chemical properties of combustion-based brown carbon (BrC). The authors generated fresh and aged brown carbon from a variety of fuels within an oxidative flow reactor and analyzed these aerosols using fluorescence spectroscopy and mass spectrometry. These experiments demonstrated that photooxidation impacted the chemical and fluorescent structures of brown carbon aerosols; where compared to primary aerosols, aged brown carbon displayed a higher fraction of oxygen and nitrogen containing organic matter. The observations from this study may be of interest to the broader atmospheric science community; however, certain elements of the paper (including the written structure, methodology, and discussion) require considerable improvement. I will expand on these issues in the "specific comments" section. As a final note, I encourage the authors to more effectively communicate the scientific significance and implications of their study.

Specific comments:

Lines 20-22: I suggest mentioning that the key analytical methods used in the study (fluorescence, MS). Without this context, the remaining abstract will confuse some readers.

Lines 38-42: The content in this first paragraph is useful; however, I would suggest some restructuring to include a brief statement clearly defining brown carbon. Ie., "diverse range of aerosols consisting of organic compounds capable of absorbing UV-Vis light etc., etc."

Line 39: "The global simulation showed that…" This phasing is confusing. You must first introduce/establish the simulation, as this will contextualize the following discussion.

Line 43: The phrasing in this sentence is somewhat confusing; I would suggest rewording to state: "The sources of BrC primarily consisted of…" Perhaps I am misinterpreting the phrasing, but I'm not sure what the authors mean by this statement – considering that primary emission and secondary formation are effectively the only two pathways for contaminants to enter the atmosphere.

Lines 44-45: Correct to "… in the presence of NOx…".

Line 47: I would suggest rewording: "Field-based measurements have shown that…"

Lines 47-51: This is important context for the study; however, it would be helpful to provide some additional data/stats to help emphasize the relative size of biomass burning emissions? i.e. what percent of BrC was linked to burning in the papers cited?

52: Briefly define the term, "chromophore".

Lines 54-62: I suggest starting this section with a brief sentence establishing to the concept of BrC aging its influence over aerosol fate. I.e., what is BrC aging and why do we care? Then expand on the literature.

Line 63: Reword: "…spectroscopy has been widely used…"

Line 66: Considering that this term is only used twice in the MS, I don't think the acronym "PLOM" is needed here.

Lines 71-72: This sentence is somewhat confusing – please rephrase.

Lines 83-84: It is established here that the study measured BrC emissions from a range of fuel types. This is a good element of the study – but I suggest that the authors establish earlier in the introduction why we are interested in different fuel types. Cite the literature that highlights the influence of burning material over BrC composition.

Lines 81-88: I recommend that the authors restructure this final paragraph. The first sentence should clearly outline the study objectives: "In this study, we investigated the influence of fuel type and photochemical aging over the optical and chemical properties of primary and secondary BrC."... or something along that line. Once the former is established, you can briefly outline how the study design will achieve these objectives.

Lines 92-99: The authors should provide some additional details justifying the selection of these specific burning materials. Some statistics / data describing the prevalence of these fuel types would help.

Lines 96-99: These sentences are somewhat confusing. Do the authors mean to say, "Straw and beech materials were burned in an open stainless-steel cylinder...". Moreover, this is the first time the steel-cylinder has been mentioned in the MS – without initial context these statements will confuse the reader, as it is not clear why the straw and beech were burned in the cylinder, and the dung/plastic on top.

Line 108: Correct: "The particles in the holding tank...". In addition, merge this sentence with the following one.

Lines 108-109: I am curious regarding the QA/QC methods applied in these experiments. For instance, were blank and replicate samples collected for analysis? This information should be available in the MS.

Lines 125-133: It is well established that sample fluorescence can be highly pH-dependant. Did the authors account for this factor? Was sample pH measured? Was sample pH adjustment considered?

Line 134: Could the authors name the software used for EEM / PARAFAC processing?

Lines 142-143: Split-half validation is a useful tool for PARAFAC model selection. However, I have noticed that Fig. S2 mentions the Core consistency and eemqual metrics. These are also valuable tools for model validation; however, I do not see these methods described in the MS or SI files. Could the authors provide brief descriptions of these techniques?

Lines 108-109 & 115: I am somewhat concerned by these methods. Particles generated during these experiments were collected on quartz and Teflon filters - these filter samples were then allocated for EEM and FIGAERO-CIMS analysis, respectively. The parallel EEM and chemical datasets underwent statistical comparison (e.g. Spearman correlation) under the general assumption that the particulates collected on the quartz and Teflon filter were identical. Quartz

and Teflon filters have fundamentally different structures and particle retention capacity – not to mention that quartz filters can retain volatile organics that can lead to an overestimation of aerosol brown carbon. As such, I am worried that the quartz and Teflon filter samples are not as chemically similar as the authors might assume, and this dissimilarity could weaken the comparison of EEM and FIGAERO-CIMS.

Lines 175-176: I'm curious why a Spearman r of 0.643 was selected as the cut-off point? This value seems somewhat arbitrary (and low); why not let the p-value of the Spearman test (at higher significance levels) inform the pairing of FIGAERO-CIMS and PARAFAC components? What methods have previous studies used? I would suggest citing them here.

Line 182: Section 3 first covers the chemical characteristics of sampled aerosols, followed by discussion regarding EEM-PARAFAC. However, section 2 discusses the corresponding methods (CIMS, EEM-PARAFAC) in the reverse order. This is a somewhat pedantic critique, but I would suggest reordering either the methods or results/discussion sections to improve the written flow of the MS.

Line 214: remove "also".

Line 230: Correct phrasing. Perhaps "A PARAFAC model was…".

Lines 232-233: The phrasing in this sentence is somewhat confusing. Do the values "239, 300, and 372 nm represent three separate peaks associated with the C1 fluorophore? Are they representative of the excitation or emission wavelengths? Please clarify.

Line 233-234: Please define "AMS". The phrasing here is somewhat confusing – make sure that it is clear you are comparing C1 to fluorophores from an external study.

Line 236: I'm apprehensive about the decision to compare the methanol-soluble PARAFAC components to water-soluble fluorophores from other studies. I would suggest comparing against other methanol-soluble fluorophores.

Lines 235-236, 238: why not state the specific wavelength here?

Line 302: The header for Table 1 would benefit from some additional detail. For instance, what does "average properties" refer to?

Line 330: The scale of the O/C axis is different between the three plots shown in Figure 4. I would suggest making note of this discrepancy in the figure header (or unify the axis scaling).

Lines 333-334: The authors discuss the possible influence of NOx over PLS oxidation. Does this imply that NOx was included in the flow reactor experiments? Was NOx injected into the reactor? At what concentration? Perhaps I am missing something, but this was not disclosed in the methods section. Please elaborate.

Line 366: Correct to "..component, and a phenolic-like substance…"

Lines 355-383: This section reads more like a summary than a discussion regarding atmospheric implications. In particular, the first two paragraphs repeat key findings reported earlier in the MS. I

strongly suggest the authors revisit this section to consider what their observations tell us regarding the atmospheric chemistry, fate, and source-dependence of combustion based BrC.

Lines 374-376: “The oxidation of volatile organic compounds and degradation of large molecules were smaller organic compounds with higher oxidation state and the high fractions of nitrogen containing chromophore.” I’m not sure I understand this sentence. Please reword.