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Comment on acp-2022-70

Rawad Saleh (Referee)

Referee comment on "Characteristics and evolution of brown carbon in western United States wildfires" by Linghan Zeng et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-70-RC1, 2022

General comment:

This manuscript presents an investigation of brown carbon (BrC) from wildfire emissions using aircraft plume measurements as part of the FIREX-AQ study. The manuscript has two main foci. The first involves quantifying BrC light-absorption properties and contribution to wildfire aerosol absorption using an online method (which relies on online measurements of absorption coefficients using a PAS and BC concentrations using an SP2) and an offline method (which relies on solvent extraction using both water and methanol). The second involves investigating the evolution of BrC in the atmosphere including (i) overall change in BrC absorption, (ii) comparison of overall change in BrC absorption to 4-Nitrocatechol, (iii) effect of evaporation, and (iv) the role of ozone.

The manuscript is well-written and presents comprehensive high-quality data and analyses, which constitute an important contribution to the understanding of wildfire BrC. I find the following to be particularly interesting: (i) the comparison between offline and online BrC measurements, (ii) the comparison between 4-NC and overall BrC evolution, and (iii) illustrating the complex dynamics that govern BrC evolution. Below is a list of comments that I believe should be addressed in the revised version of the manuscript.

Major specific comments:

1) The comparison between b_ap_PASBrC and b_ap_TSBrC (Figure 6): The difference in comparison at different wavelength is interesting and should be further discussed. The slope of the comparison increases with wavelength, which indicates that (i) there are

insoluble BrC species and (ii) these species have a smaller AAE than the TSBrC (which leads to the wavelength-dependent comparison). As the authors point out (Page 14 Line 29), the absolute comparisons (i.e. the slopes in Figure 6) are uncertain. However, the trends are still informative. Starting with the theoretical baseline that b_ap_TSBrC cannot exceed b_ap_PASBrC (because PASBrC represents the total BrC), the slopes in Figure 6 are likely underestimates. Nevertheless, the results highlight the importance of methanol-insoluble BrC, which, according to Figure 6b and 6c, contributes an average of ~65% and ~85% of BrC absorption at 532 nm and 664 nm, respectively. This qualitatively agrees with the findings of (Atwi et al., 2022) that biomass-burning BrC can be split into a less-absorbing methanol-soluble fraction (smaller MAC and larger AAE) and a more-absorbing methanol-insoluble fraction (larger MAC and smaller AAE), with the methanol-insoluble fraction dominating mid-visible absorption.

2) Figure 3 and associated discussion: The paragraph on top of Page 13 points out the lack of correlation between MAC and AAE. This is expected because there is no substantial variability in BrC sources and combustion conditions in this study. Due of the usually encountered large spread in BrC data (due to both true variability in optical properties as well as measurement uncertainty), the inverse MAC vs AAE trend becomes apparent only when comparing different BrC categories. For instance, in Figure 1 in Saleh (2020), the inverse MAC vs AAE trend would not be apparent if only looking at one category (e.g. smoldering biomass combustion or SOA from aromatic VOCs).

With that being said, comparing the average MAC and AAE of PASBrC with those of TSBrC would be informative (see (Atwi et al., 2022)). I suggest combining the two panels of Figure 3 in one figure (using different symbols for TSBrC and PASBrC) and showing the average and standard deviation for each group. Doing so will illustrate the inverse MAC vs AAE relation. Specifically, TSBrC will be shown to have a smaller MAC but larger AAE than PASBrC, in agreement with the results of Atwi et al. (2022).

Also, because of the inverse MAC vs AAE relation, the MAC values of different BrC categories start to converge at shorter wavelengths. It is therefore more informative to present Figure 3 at 532 nm, which would better illustrate the difference between TSBrC and PASBrC.

Finally, what is the reason for TSBrC having less data points than PASBrC?

3) There are several studies that pointed out that MCE does not correlate well with aerosol light-absorption properties (e.g. (McClure et al., 2019; Pokhrel et al., 2016)). I suggest

using BC/OA as a proxy for combustion conditions in Figures 3, 5, and 6.

4) The manuscript presents details of uncertainty associated with each measurement / analysis, but the uncertainty is not reflected in the figures. Uncertainties can be added as light-gray error bars, which should not have a substantial effect on the clarity of the figures.

5) The calculation of PAS BrC absorption coefficients (b_ap_PASBrC) and the corresponding MAC_PASBrC include multiple steps that should be presented in the SI. Please show:

- a) rBC size distributions and how they were adjusted to account for rBC outside the detection window of the SP2. Typically, how much rBC was found to be outside of the detection window of the SP2?
- b) Particle size distributions measured with LAS and the corresponding lognormal fits. How much of the particle number was outside the detection window of LAS? Also, Page 8 Line 48 states that the variability in smoke aerosol refractive index causes an uncertainty of 20%. How is this estimated? In addition to this uncertainty, does the fact that the instrument was calibrated using non-absorbing aerosol (ammonium sulfate) cause any systematic uncertainty because the smoke aerosol is light-absorbing?

6) Section 3.4.3 and Figure 11: The data collected over this short period of time (4 minutes) does not provide enough evidence to arrive at the conclusion that (i) 4-NC contribution to absorption dropped from 10% to 3% and (i) there must be BrC production (which contradicts the statement earlier in the section that "chemical aging should be negligible during this time period."). For instance, the variability in 4-NC concentration over a period of 20 s around 1:44 is approximately twice the inferred change over the measurement period (dotted blue line). Also, I would assume that if the difference between NEMR_PASBrC and NEMR_4-NC is plotted on Figure 11, the trend would be very similar to NEMR_PASBrC (i.e. it would not show any increase in non-4-NC BrC absorption).

Minor specific comments:

1) Line 65: This statement necessitates specifying an imaginary part of the refractive index cutoff above which the OA is said to be light-absorbing. I would rephrase this sentence to reflect the fact that OA is made of components with variable light-absorption properties that vary from negligibly absorbing to strongly absorbing.

2) Line 83: By definition, DRE of a certain component is obtained as the difference in radiative balance with and without the component. The statement here that BrC contributed 7 to 48% of DRE is not consistent with this definition because these values were obtained as the difference in radiative balance with and without BrC absorption, and should more accurately be referred to as 'BrC absorption DRE,' not DRE of BrC (see (Saleh, 2020; Wang et al., 2018)).

3) Section 3.4.2: Please provide 4-NC optical properties used to calculate absorption coefficients.

References:

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