Reviewer 2:

We thank the reviewer for their insightful comments and have responded to each shown in blue text below each comment. Underlined text is the modification to the manuscript.

This manuscript investigates characteristics and evolution of brown carbon (BrC) using online photoacoustic spectrometer (PAS) that measures dry aerosol absorption of fine particles and offline filter-based approach using liquid spectrophotometric measurements of extracts of particles collected on filters. They compared the measurements at different wavelengths and found that good agreement of BrC absorption at 400 nm. While doing the comparisons, there are several assumptions and limitations, but it still provides useful information and worth publishing. The study claims that investigated samples falls under moderately absorbing class. They also investigated a particular BrC chromophore, 4-nitrocatechol and its evolution with plume ages. Results indicate that 4-nitrocatechol depleted with plume ages, while other BrC was much stable even with increasing temperature in downwind. However, some previous study reported that particulate nitrophenol and nitrocatechol isomers can contribute significantly to BrC absorption at 405 nm in aged wildfire smoke.

This is an interesting study and will be useful for the community. Overall, the manuscript is clearly written, some suggested clarifications are listed below. However, prior to acceptance, the authors should address the following questions/ suggestions and modify the manuscript accordingly.

Specific comments:

The comparison between bap, PASBrc and bap,TSBrC at 405 nm looks good. It might be good to add some discussion why the PAS derived BrC absorption is higher than the TS Brc at higher wavelength. I see that the authors add some discussion about the insoluble chromophores, but it will be good add this discussion in the results section and will be easier for readers to follow.

Response: The first reviewer also had a similar suggestion, so we have added some text for clarity. It now reads: *"Thus, missing non-soluble* chromophores in the extracts, but which are included in the PAS BrC, would lead to increasing bias of lower TS BrC at the higher wavelengths and likely add variability, observed (Figure 6c) as an increasing slope and lower R^2 compared to the lower wavelengths. Based on the regression fits in figures 6b and 6c, this implies that at wavelengths of 532 and 664 nm, methanol soluble BrC misses roughly 65% and 87% of the overall light absorption at those respective wavelengths. (Or methanol insoluble BrC chromophores contribute 65 and 87% to the light absorption at 532 and 664 nm, respectively, which are consistent with the findings of Atwi et al. (2022))."

As for the suggestion to add to the discussion, we have added more details on this to the Summary, which now reads: "This difference may be due to chromophores that were insoluble in the solvents utilized (water and methanol) and these insoluble chromophores absorb light more strongly at higher wavelengths (e.g., lower AAEs) than soluble species. For the parameters we used in this closure analysis, the data suggest that methanol insoluble BrC chromophores contributed roughly 65% and 87% to the light absorption at 532 and 664 nm, respectively".

One of the main concerns of this manuscript is that applied method rely on several assumptions and approximation which can create a large uncertainty in estimation. I appreciate that the authors stated most of the uncertainties for example in extrapolating the wavelength-dependent differences. However, I think the authors should state overall uncertainties in estimating all the absorption values. For example, I think there is a large uncertainty in estimation of the conversion factor itself. How that translate to uncertainties in total absorption?

Response: We have added uncertainties to Fig. 5a. We decomposed the uncertainty for the optical closure analysis into two part: 1. from BC, 2. from BrC ($Abs_{TS\ BrC}$*K). The uncertainty from BC was estimated to be 40%, same as the measurement uncertainty of SP2. The uncertainty from BrC was derived from TS BrC measurement uncertainty and the uncertainty for conversion factor K. Error bars representing uncertainties have been added to Fig. 5a and the Figure caption has been edited (see below).

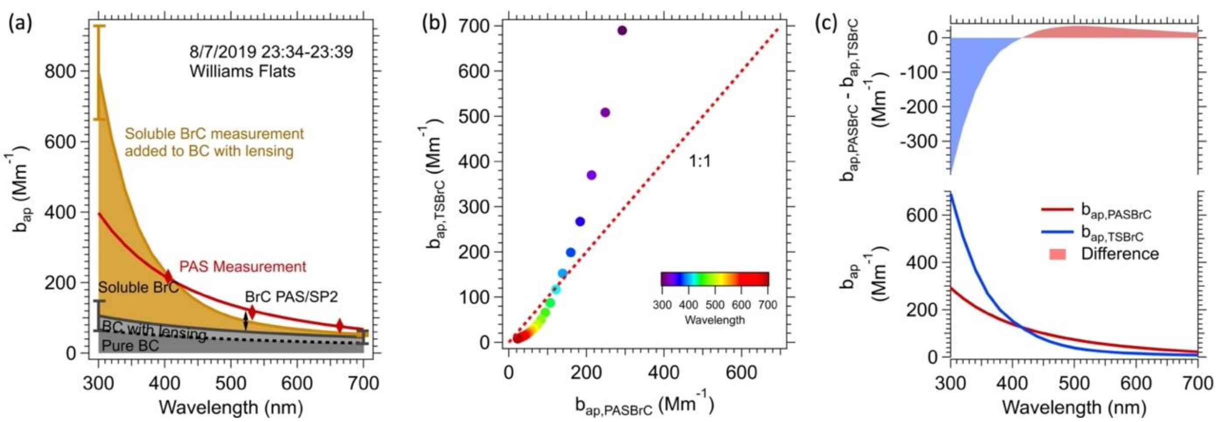

Figure 5. Various light absorption coefficients for the average of the first transect made closest to the Williams Flats fire (23:34–23:39 7 Aug. 2019 UTC). (a) Spectral light absorption closure analysis, where the dashed black line is the light absorption of bare rBC and the solid line is BC considering the coating effect (E_λ). The brown shading is soluble BrC, $b_{ap,TSBrC,\lambda}$, where Abs_λ^{LWCC} was multiplied by the conversion factor K_λ to convert from solution to aerosol particle absorption. The upper part of the brown curve is $b_{ap,predicted,\lambda}$, given by Eqn 4. Uncertainties at two extreme wavelengths (300 nm and 700 nm) for two individual components (1. The effect or rBC coating, $b_{ap,BC,\lambda}$, dark gray in plot (a), estimated to be 40%, the same as the SP2 measurement uncertainty; 2. TS BrC $b_{ap,TSBrC,\lambda}$, brown, from ($Abs_{TS\ BrC}$*K), considering the uncertainty in measurements and K). (b) Comparison between $b_{ap,TSBrC,\lambda}$ (brown shading in plot (a)) and $b_{ap,PASBrC,\lambda}$ (difference between red and the black solid line in plot (a)), color coded by wavelength. (c) Similar to plot (b), but versus wavelength (i.e., the difference between BrC determined from the soluble measurements with the conversion factor K_λ included, and BrC calculated from the PAS data).

Page 12: Some more discussion about the absorption Angstrom exponent (AAE) measured by PAS and WS BrC and MS BrC and in context to previous study would be useful, like lower

AAE value reported by PAS. I'm bit confused with the AAE values from PAS and from TS reported in Figure 3. And how did the authors calculate the modified combustion efficiency?

Response: We have added text to address both these points. We first note that the AAE values reported in Figure 3 are of BrC, which can be obtained in a straightforward manner from the TS BrC data. In this case we fit the log of the bap TS BrC vs the log of the wavelength to determine AAE from the slope. We used data over the full wavelength range. For the PAS, the data must be first converted to PAS BrC, which is done using equation 2, and then the data at the three wavelengths are used to determine the AAE using the same log transformation method discussed above. This sentence has been added to Page 12 Line 69: "The AAE for soluble BrC (either WS BrC or TS BrC) measured in FIREX-AQ is comparable to the result from the ATom study (Zeng et al., 2020) but lower than the DC3 (Liu et al., 2015)." Higher AAE observed in the DC3 might be because that study focused on convective regions. BrC aerosol associated with convective movement (secondary production) may have different optical properties (higher AAE), but this hypothesis needs further investigation. No studies reported the AAE value for BrC aerosol from the PAS measurements using the same analytic methods, therefore no comparison was made.

Regarding the modified combustion efficiency, Reviewer 1 has suggested we use OC/rBC instead due to higher dynamic range, which we have done, so all references to MCE have been removed.

Size distribution data and black carbon data from SP2 are missing in the manuscript but it is important to have this information in the SI.

Response: The SP2 BC size distribution was added, see Supplement Fig. S1

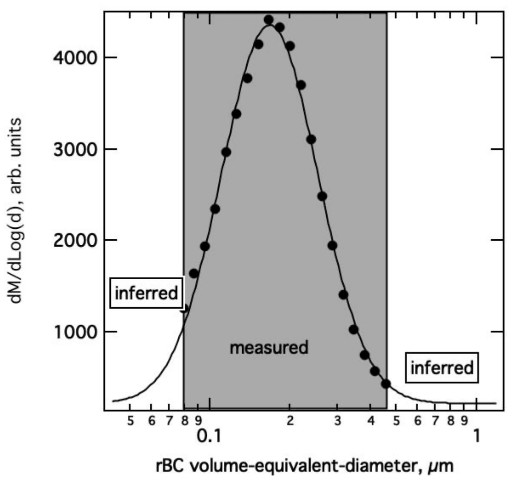

Figure S1. Mass size distribution of rBC measured for a flight. A log normal fit over the valid range of detection is used to infer the rBC mass undetected in the population.

Authors discussed several other factors that may influence the evolution of BrC. I appreciate this discussion. However, some of the supporting data on this are not shown in the manuscript.

Response: We assume this refers to section 3.4.5. We did not present these results in the paper in detail to keep the manuscript focused, but we still felt that it was important to document what other factors we investigated, even if we could come to no conclusion on their possible effects. We have not modified the manuscript.

Summary section can be improved by proving general applicability of the closure exercise and overall applicability of this study. Another thing I find it difficult to draw some firm conclusions as this study investigated several fires with different scales, while chasing one large fire with sufficient time would help to decipher some of the key aspect of BrC evolution. I think this is still an important study but something to discuss in the summary section so future work can be better designed.

Response: We note that the closure analysis was applied to all the smoke plumes. We showed the detailed spectral comparison in Fig. 5 for one pass through a plume, but did comparisons for all passes through the smoke plumes in Fig. 6. As for overall applicability of this closure exercise to other types of smoke or other studies, we have no insights since this was the first time this type of closure analysis was performed. We did investigate fires of different spatial scales (or age of smoke plumes), but most of the smoke sampled in this study was focused on near the fires. However, we have added some more details on the evolution of more aged smoke (two plots were added to the supplemental material) and we do make suggestions for future work in the last line of the Summary.

Minor comments:

Page 21, line 67: please check the sentence, 405 nm wavelength was mentioned twice

Response: This was corrected by removing the second reference to 405 nm in the sentence.

Overall, there are several acronyms and subscripts, it will be difficult for readers to follow, it will be good to have a table with all the acronyms.

Response: The following table has been added as Table 2.

Table 2. Nomenclature

Nomenclature	Description
$Abs_{x,\lambda}^{LWCC}$	Light absorption coefficient of component x at wavelength λ in liquid solution measured with LWCC
AAE_x	Absorption Ångström Exponents of component x determined from a power law fit over the wavelength range of 300 nm to 500nm.
A_λ	Light absorption measured by the spectrophotometer with the LWCC
$b_{ap,x,\lambda}$	Light absorption coefficient of component x at wavelength λ in aerosol phase
c_{rBC}	Mass concentration of rBC measured by the SP2
E_λ	Absorption enhancement for BC particle due to coating effect
LWCC	Liquid waveguide capillary cell

K_λ	Conversion factor for estimating the particle light absorption coefficient from the solution
$MAC_{x,\lambda}$	Mass absorption cross-section of component x at wavelength λ
$NEMR_x$	Normalized excess mixing ratio of component x
PAS BrC	Brown carbon inferred from the PAS and SP2
rBC	Refractory black carbon concentration measured by the SP2
TS (BrC)	Total-soluble brown carbon determined from the sum of sequential water then methanol extraction of a single filter
WS (BrC)	Water-soluble brown carbon
4-NC	4-Nitrocatechol

Is there a reason to just show one specific fire events for the wavelength dependencies in the main manuscript? I see the value for each fire events but how about combining all the dataset to get a broader picture?

Response: This relates to the question above on including an uncertainty/sensitivity analysis. Our approach was to provide a detailed analysis for one plume transect (Fig. 5) and show similar plots in the supp. material for all the transects of the one plume (Fig. S5). We then made scatter plots summarizing the differences for all plumes (Fig 6). We feel that is sufficient detail for this manuscript and as noted above a much more detailed analysis is planned for a future paper.

Figure 4 can be move to SI. Did you calculate the correction factor for each fire events? I suggest adding some sorts of histograms and combining all the events, so reader can get an idea about the spread of the data.

Response: We have left Fig 4 in the main text because we think it is important for the reader to realize that the correction factor has a wavelength dependance, which has not been discussed in previous publications. The suggestion to do a more complete sensitivity analysis to determine the range of values for this factor (maybe at some specific set of different wavelengths), is a good idea, but again we feel it is beyond the scope of this paper and better suited to a dedicated publication.

Other changes to the manuscript:

Figure 5. An updated Figure 5 was produced where the PAS fit in Fig. 5a was slighted modified (a constant in the fit equation was removed). This results in a very minor change in the red line in Fig. 5a.

Figure 7. An error was found in Figure 7. The PAS fit did not match the same curve shown in Fig 5a. Figure S4 has been corrected, and Figure S5 and the sentence in Page 14 Line 27 has been deleted.

Figure 8. This figure has been updated. We have added the Tucker near fire marker to the legend and corrected the 807 Williams Flats data points, which results in a slight shift to shorter times for a few data points.

We added two figures to the Supplemental material, equivalent to Fig 8, but only showing the RIM and Tucker fires and RIM and Williams Flats fires to help clarify the discussion on the comparisons of these plumes to the RIM fire reported in an earlier study.