Reviewer #3

We would like to thank the Reviewers for their constructive feedback. The reviewer comments are reproduced below in black, and our responses are provided below each comment in blue. We will also be uploading a track-changed version of the manuscript along with all responses as required by ACP.

General comments

The Authors noted a decrease in absorption following photolysis that leveled off. This observation of a longer-lived fraction of BrC is consistent with several measurements in the lab (e.g. Wong et al. (2017)) and real environment (e.g. Forrister et al. (2015) and Di Lorenzo et al. (2017)). The previous work is not effectively reflected in the text of the paper. For example, lines 60-62 suggest that field measurements demonstrate a short lifetime for BrC. While observations of a short-lived fraction have been made, long-lived fractions have also been observed. In addition, the results described leading up to line 406 should be discussed in the context of this literature.

We have added to the introduction that these studies have observed a recalcitrant fraction of BrC, just as we did. This is in two places, on pages 3 and 4.

"However, there is a recalcitrant fraction of BrC that persists even after long aging times. Di Lorenzo et al. 2017 found that the fraction of higher molecular weight chromophores (>500 Da) relative to lower molecular weight chromophores (<500 Da) increased with plume transport time, on the order of hours to days."

"Size exclusion chromatography showed that low molecular weight BrC chromophores (<400 Da) were quickly formed and photodegraded giving yield to a photoenhancement due to the formation of high molecular weight species (>400 Da). They concluded that this high molecular weight fraction was responsible for long-lived light absorption."

We have also added a few sentences in the "Results and Discussion" section stating that other papers have observed the change in molecular composition of BrC chromophores, and this is consistent with our results.

"The results of both photolysis experiments is consistent with work by Di Lorenzo et al. (2017) and Wong et al. (2017) which show that during aging, high molecular weight BrC chromophores are formed after lower molecular weight chromophores are photodegraded. The high molecular weight fraction of BrC chromophores persist even at long aging times and are referred to as the recalcitrant fraction. This theory is one explanation for the short lifetimes of low molecular weight BrC compounds, while observing longer overall BrC absorption lifetimes."

More information should be provided about the solvents chosen for filter extraction. On line 139, the Authors say, "filters were extracted by solvents with a range of polarities". Only two solvent mixtures were used, and these were used to extract different samples.

This is still the introduction section and the purpose of this paragraph is to show the scope of the study and the main goals/results. We explain the choice of extraction solvents in the experimental section where we think it is more appropriate. See the below comment or details.

A mixture of dichloromethane/acetonitrile/hexanes was used to extract samples prior to HPLC/PDA/HRMS analysis, while a mixture of methanol/acetonitrile/hexane was used to extract

PTFE filters following transmission measurements. A justification should be provided for the choice of each solvent mixture. The impact of the solvent choice on the results described in lines 393-395 should also be discussed.

The extraction solvent mixture was altered depending on their advantages and disadvantages for the application: HPLC/PDA/HRMS or UV-Vis spectroscopy. Dichloromethane was avoided in the overall BrC photolysis experiments (UV-Vis experiments) and methanol was used instead. Dichloromethane absorbs strongly at <240 nm, and could interfere in the measurement of BrC absorption at near-UV wavelengths. In addition, from a safety standpoint, DCM is not a convenient solvent for absorption spectroscopy since it needs to be used in the hood due it its high volatility. Regardless of the solvent mixture used, it is impossible to extract all the material from filter with any solvent combination, and this is why the transmission spectroscopy measurements of the entire filter were done. The decay of absorption of visible wavelengths was consistent across both measurements (solution versus filter).

We now have explained the origins of the extraction protocol on page 6. An additional sentence on page 8 discusses why methanol was used in place of DCM.

Specific comments

Line 70: Typo in polycyclic aromatic hydrocarbons.

Thanks, we corrected this.

Line 122-123: Wong et al. showed not just a decrease in WSOC, but also a decrease in BrC absorption.

Indeed. We have clarified the text, which now reads:

"Wong et al. (2017) found that irradiated BBOA water extracts lost water soluble organic carbon (WSOC) when irradiated with 300-400 nm light. Simultaneously, the absorption coefficients at 365 nm and 400 nm first increased, in the latter case to about 0.035 $m^2 g^{-1}$ after 20 minutes of illumination time, and then decreased to nearly zero in 60 minutes."

Line 266: Should be "one fewer methoxy ring substituent".

Done.

Line 318: Saying that PAHs are "stable during atmospheric transport" is an oversimplification. Although they may end up in pristine regions, the conditions that allow them to undergo long range transport are complex. The review from Keyte et al. (2013) and recent work from Zhou et al. (2019), along with other relevant work, should be consulted and discussed in this section.

Thank you. The text has been modified to clarify this point.

"Polycyclic aromatic hydrocarbons (PAHs) are known to be products of incomplete combustion, and they have the potential to be long-lived BrC chromophores despite their reactivity (Keyte et al., 2013). PAHs have been observed in pristine environments, and it has been suggested that this is due to phase separation of particles and slow diffusivity of PAHs to surfaces where they react with atmospheric oxidants (Fernández et al., 2002; Keyte et al., 2013; Macdonald et al., 2000; Sofowote et al., 2011; Zhou et al., 2012, 2019)."

Figure 1: Suggest this figure could be relocated to the SI.

We elected to keep this figure in the main paper for ease of reading since we reference it twice in the Results and Discussion.