The authors thank the reviewer for their insightful comments and useful suggestions. We have provided a point-by-point response below.

Reviewer 1

This manuscript by Wong et al. investigates the evolution of water-soluble brown carbon (BrC) light absorption due to photolysis and OH oxidation for both laboratory generated BrC from the pyrolysis of cherry hardwood and ambient biomass-burning BrC collected in Crete. The results show interesting behavior starting with increase in absorption (photoenhancement) followed by decrease in absorption (photobleaching). The rates of these two stages were observed to depend on molecular weight, with larger molecules (> 400 Da) dominating the contribution to light absorption after several days of UV exposure. This is a well-written manuscript addressing a timely topic, and the findings constitute a step forward in the understanding of the evolution of atmospheric BrC. Therefore, I believe this manuscript is suitable for publication in ACP after the following comments are addressed:

1. It is not clear why both water and methanol extractions were performed for ambient samples and just water for laboratory samples. Please provide justification.

Response: We only focused on water extractions for laboratory sample since results from our previous work (Wong et al., 2017) indicated that the majority (77%) of the light absorption for laboratory generated BrC from wood smoke was contributed by the water-soluble fraction. This was stated in the original manuscript from lines 8-10. We also note that the trends in the evolution of light absorption for the methanol extraction for laboratory samples due to photochemical aging was also observed to be similar to the observations for water-soluble BrC fractions. We have modified section 2.1.1 (experimental section), as follows: "For these laboratory studies, we only focused on the aging of WS BrC, as results from our previous work indicated that the majority of the light absorption of laboratory generated BrC from wood smoke was contributed by the WS fraction (~ 77%) and that the trends in the evolution of light absorption of water-insoluble (i.e., methanol extracted) BrC due to photochemical aging are similar to that of the WS fraction (Wong et al., 2017)."

2. In section 2.1.1, it is stated that the BrC was produced by pyrolysis of cherry hardwood at 210 C and oxygen-free conditions. Is there a rationale behind choosing these conditions? It is known that the physicochemical properties and optical properties of BrC depend strongly on burn conditions (e.g. Chen and Bond (2010); Saleh et al. (2014); Pokhrel et al. (2016), etc.). While this is somehow acknowledged in the last sentence of the manuscript, the limitations of using one fuel and one burn condition should be featured early on when discussing the results (i.e. in section 3.1) as well as the abstract. This is not to take anything away from the interesting findings of this study.

Response: BrC was pyrolysed at 210°C under oxygen-free atmosphere to represent the smoldering conditions of wildfires, which we now have modified section 2.1.1 (experimental section) to mention this, as follows: "Wood smoke BrC was generated in the laboratory using the method described in Wong et al. (2017). Briefly, a small piece of dry cherry hardwood (5 - 10g), placed on the bottom of a cylindrical electronically-heated combustor, was pyrolyzed

under an oxygen-free atmosphere at 210°C, to representing BrC emitted from smoldering combustion (Andreae and Gelencsér, 2006; Chen and Bond, 2010)."

We have also added the following statements in the specified sections of the manuscript to emphasize the use of one fuel type and burn conditions for the laboratory generated BrC:

Abstract: "Here we report laboratory experiments that examined changes in the optical properties of the water-soluble BrC fraction of laboratory generated biomass burning particles from hardwood pyrolysis."

Section 3.2.1 (Results and discussion): "Firstly, the laboratory constrainted atmospheric lifetime represents BrC emitted from the combustion of one biomass fuel type under smoldering conditions, which may not represent ambient fire conditions, as the light absorption properties of BrC have been observed to be dependent on field and burn conditions (Chen and Bond, 2010)."

3. Section 3.1.1: Describe how MAC is calculated. The reference to Wong et al. (2017) is not enough, as this is a central piece of this paper and it will benefit the reader to have at least a brief explanation of how MAC is calculated.

Response: We have now described how the MAC values were calculated in section 2.1.4 (experimental section), as follows: "The measured light absorption for both bulk and molecular weight separated WS-BrC were normalized by the WSOC concentration of the BrC extract to represent the light absorption per water-soluble organic carbon, or mass absorption coefficient (MAC) of the WS-BrC."

We have also added the following to section 2.2.2 to describe the calculation of MAC for WS and MeOH BrC for the ambient filter samples: "The MAC of the WS and MeOH soluble BrC were determined through normalizing by the WSOC concentration (WS BrC/WSOC) or OC concentrations (MeOH BrC/OC), as determined using the TOC and OCEC analyzers, respectively."

4. Also, you need a short discussion of the meaning of MAC in this context. I assume this is a "bulk" MAC, which is related to but not the same as the MAC of suspended particles. See, for example, discussion in section 3.1.2 of Laskin et al. (2015).

Response: We have now added the following to section 3.1.1 to emphasize that the MAC represents the light absorption of the WS-BrC extract, "Note that these MAC values arise from light absorption measurements of water-extracted BrC and not of suspended BrC particles."

5. Finally, there is an inconsistency between the terminology in the text (MAC) and Figure 2 (AbsWSOC).

Response: We have now modified the Figure 2 such that Abs/WSOC is now referred to MAC.

6. While the molecular-weight separated results are interesting, I believe further discussion is required. First, it would be helpful to include a more detailed description of the SEC technique. In particular, the dependence of MW on elution volume (from Figure 3) seems to be very non-linear. Please elaborate more on this and how it affects the measurements.

Response: We agree that a discussion on the SEC technique would be helpful for readers, and have added a discussion of the SEC technique in section 2.1.4 (experimental section) as follows: "The molecular weight distributions of WS BrC were determined using size exclusion chromatography (SEC), which separates analyte molecules due to differences in the extent of permeation into the column packing material, where larger molecules elute earlier than smaller molecules due to weaker interactions (Strigel et al., 2009). The technique was operated using high-performance liquid chromatography (HPLC; GP40 Dionex), equipped with a SEC column (Polysep GFC P-3000, Phenomenex) that was operated in isocratic mode using a 90:10 *v/v* mixture of water and methanol with 25 mM ammonium acetate as the mobile phase, at 1mL min^{-1}."

We note that the elution time and molecular weight appears to be non-linear for Figure 3 because the relationship is linear for the logarithm of elution time to molecular weight. Since the elution of molecular weight separated BrC requires the use of a mobile phase, these dilution effects need to be account for in order to relate the absorbance of the molecular weight separated BrC to that of the bulk BrC sample. Since we have discussed these calculations in detail in our previous work (Wong et al., 2017), we have now added the following brief description in the section 2.1.4 (experimental section): "The absorbance of the different molecular weight fractions were determined by integrating the absorbance of a specific wavelength over the period of elution that corresponds to the molecular weight fraction ($P_{MW,\lambda}$). Since the coupling of the chromatographic technique to UV-VIS absorption measurements leads to the dilution of the BrC sample due to the use of the mobile phase, the absorbance of the molecular weight separated BrC is related to absorbance of the injected BrC by accounting for the mobile phase flow rate (*f*) and the volume of the injected BrC sample (V_{BrC}) using Eq. (1) :

$$A_{BrC,\lambda} = \frac{P_{MW,\lambda} \cdot f}{V_{BrC}} \qquad (1)"$$

New reference added: Strigel, Andre M., Yau, Wallace W., Kirkland, Joseph J. and Bly, Donald D.: Modern Size-Exclusion Liquid Chromatography, Second Edition., John Wiley & Sons, Inc., 2009.

7. Second, what is the rationale behind a) grouping into just low and high MW (why not low, medium, and high, for example?) and b) choosing 400 Da as the cutoff?

Response: The total light absorption was binned into two groups (high- and low-MW) instead of three because it is more reflective of the SEC separation process and better emphasize the uncertainties associated with the molecular weight information, as the accuracy of the SEC calibration approach, from which the MW information derives from, depends on whether the molecular densities of the calibration standards are representative of that of the BrC molecules. In other words, we feel the resolution of the SEC column combined with

uncertainties in calibration of the molecular weight separation does not warrant a more highly resolved classification then what we have used.

400 Da was designated as the cutoff for high- and low-MW BrC as it represents the penetration limit of the SEC column used.

8. Finally, Figure 3b shows that BrC absorption is mostly due to molecules larger than 10,000 Da. The observation of these large molecules, on its own, should be highlighted and discussed. Have such large molecules been observed in biomass burning BrC before?

Response: Ambient BrC molecules of molecular weights larger than ~10K Da have been previously observed in aged biomass burning aerosols collected at St. John's, Canada by De Lorenzo et al., 2017. We have highlighted this previous observation of high-MW BrC in the introduction and conclusion sections. We also note that given the large molecular weights and solubility in water, the high-MW BrC is likely to be of low-volatility, of which extremely low volatility organic compounds (ELVOCs) have been shown to dominate the light absorptivity of wood smoke BrC (Saleh et al., 2004). We have also added this point to the section 4 (conclusions and atmospheric implication).

References:

Chen Y, Bond TC (2010) Light absorption by organic carbon from wood combustion. Atmos Chem Phys 10(2001):1773–1787.

Saleh R, et al. (2014) Brownness of organics in aerosols from biomass burning linked to their black carbon content. Nat Geosci:DOI: 10.1038/NGEO2220.

Pokhrel RP, et al. (2016) Parameterization of single-scattering albedo (SSA) and absorption Ångström exponent (AAE) with EC/OC for aerosol emissions from biomass burning. Atmos Chem Phys 16(15):9549–9561.

Laskin A, Laskin J, Nizkorodov S a. (2015) Chemistry of Atmospheric Brown Carbon. Chem Rev:DOI: 10.1021/cr5006167.