

We thank the reviewers for their helpful comments. In the process of addressing these comments, we have performed supporting experiments and improved the presentation and clarity of the manuscript. Our detailed responses to the individual comments are shown below; quotations from the manuscript are shown with changes in bold. We give line numbers from the tracked-changes manuscript where appropriate.

## Reviewer 2

2.1 Overall, I find this to be an interesting study that looks at how photochemical aging influences the absorptivity of aqueous, secondary brown carbon. The results and interpretation, if correct, are a useful contribution to the literature. I do, however, have two substantial concerns. (i) The photoacoustic method has been experimentally shown to have potential negative biases at elevated RH, despite the references given. (The authors missed a critical reference.) (ii) It is, at times, difficult to understand exactly what conditions were run for the optimized modeling, and thus it was a little difficult to fully understand the interpretation provided. A table and further description may be helpful.

We agree that these are substantial concerns. To address the possibility of negative bias at 60% RH, we have performed a supporting experiment, described in detail in our reply to comment 2.3. We have added the critical reference to the manuscript. We have also modified and clarified our discussion of the modeling results, as described in our replies to comments 1.2 and 2.8-2.10.

2.2 Abstract: It would be good to explicitly state that this study investigates heterogeneous processing of “aqueous, secondary BrC” or something like that, to distinguish from primary BrC.

Done.

2.3 I am concerned that there is a potentially fatal flaw in this study at least with respect to a portion of the data. It may be that there is not, but this needs to be addressed. The authors made some of their absorption measurements with their PAS instrument at elevated RH. They cite two studies saying that they “assume there is no evaporation of water ...” and given two citations, both theoretical. Unfortunately, much more recent experimental evidence has developed that suggests that there can be negative biases that result from evaporation of water vapor. The key paper is by Langridge et al. (AS&T, 2013). The authors do not cite this paper, which is an unfortunate oversight. Unless the authors can demonstrate that their measurements at elevated RH are not impacted by evaporation of water vapor. The apparent bleaching that is observed here could, potentially, simply be a reflection of the particles becoming more hygroscopic upon oxidation, and thus there being a negative bias of increasing magnitude. I believe it is up to the authors to demonstrate that their results are not biased by evaporation effects. If they cannot, then the 60% RH observations should probably be removed.

The reviewer suggests that the particles may become more hygroscopic during oxidation, leading to more water uptake and, upon irradiation in the photo-acoustic spectrometer, water evaporation from the particles. Through evaporation, some of the energy of the absorbed photons would be lost without contributing to the detected pressure wave. In

addition to this instrumental artifact, progressively more water uptake could lead to genuinely greater scattering coefficients, which would also result in apparent bleaching.

To address these concerns, we performed an additional photo-oxidation experiment. Particles were sampled from the chamber to the photo-acoustic spectrometer and scanning mobility particle spectrometer, alternately with and without a diffusion dryer downstream of the chamber. Results of this experiment are illustrated in Figures R2-R3 and the supporting information (Figures S7 and S8 in the supporting information). We note that this experiment was conducted in a different chamber than the original experiments, so some of the conditions (like average OH concentration) may differ. Unlike in the original experiments, some particle growth occurred, leading to a significant increase in the scattering coefficient.

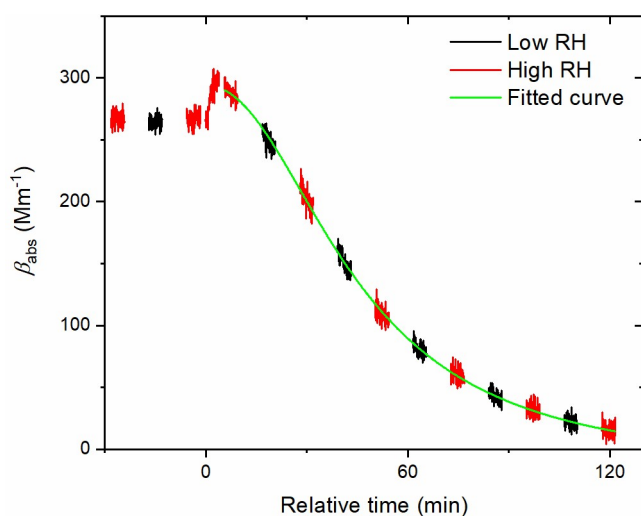


Figure R3. Time series of the absorption coefficient at 405 nm for dried (low RH) and nascent (high RH) particles, measured by alternatively sending the particle flow through a diffusion dryer.

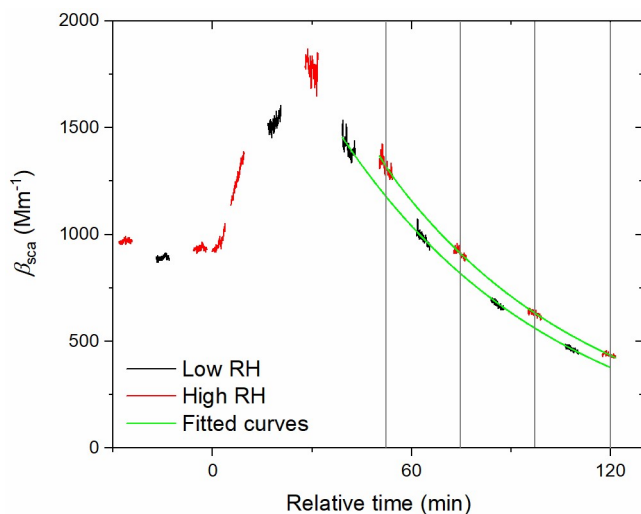


Figure R4. Time series of the scattering coefficient at 405 nm for dried (low RH) and nascent (high RH) particles.

Nonetheless, the trends in absorption and scattering coefficients demonstrate that the results of the original experiments are valid. First, as shown in Figure R3, the decrease in the absorption coefficient following the initial colour enhancement can be well represented by fitting a single logistic function to measurements for both nascent and dried particles. In other words, there is not a significant negative bias from water evaporation. Second, as shown in Figure R4, the relative difference between the scattering coefficients of the nascent and dried particles, based on fitting exponential functions to the measurements after the initial particle growth, is roughly constant across four reaction time intervals from about 50 to 120 min: 11, 10, 11, and 13%. This consistency indicates that the particles are not taking up significantly more water as they react with OH.

We have modified the text as follows:

- **“One potential source of bias in photo-acoustic measurements is evaporation of water from particles (Baker, 1976; Raspert et al., 2003; Langridge et al., 2013); through evaporation, some of the energy of the absorbed photons may be lost and not contribute to the detected pressure wave. On this basis, the higher RH was selected to be lower than the maximum operating RH of the PASS (70%). To verify that evaporation of water did not influence the measurements of absorption coefficients, we alternately sampled with and without a diffusion dryer downstream the chamber in one experiment.”** (page 5, lines 26-30)
- **“As described above, evaporation of water from particles can result in a negative bias in photo-acoustic measurements (Langridge et al., 2013). If heterogeneous OH oxidation significantly increased the hygroscopicity of the particles, the water content of the aerosol would increase during the experiment. The resulting increase in the magnitude of the bias could contribute to apparent bleaching. In addition to this instrumental artifact, progressively more water uptake could lead to genuinely greater scattering coefficients, which would also result in apparent bleaching. We investigated these potential effects by alternately sampling with and without a diffusion dryer downstream of the chamber at 60% RH. As shown in Fig. S7, the absorption coefficient does not depend on the conditioning. The scattering coefficient is about 10% lower for the dried particles (see Fig. S8), but this difference is roughly steady during photo-oxidation. In other words, the particles do not become significantly more hygroscopic, and the changes in absorption and scattering coefficients are indeed due to the chemical evolution of the particles.”** (page 11, lines 1-10)

We thank the reviewer for bringing the paper by Langridge et al. to our attention; we now cite this paper, along with the earlier theoretical papers.

2.4 Abstract: Regarding the conclusion that at 15% RH the particles are viscous enough to “confine products of fragmentation,” if the products are confined, how does the OH reach these molecules in the first place to react with them? The high viscosity would similarly cause the

reactions to occur primarily at the surface, correct? And if so, the products would be in a very good spot for evaporation.

Under the conditions originally proposed for 15% RH – specifically, the very small diffusion coefficient of  $1 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$  – the model products B and C, which form at the surface, do not diffuse appreciably. Even after 180 min, their concentrations in bulk layer 3 are negligible. This observation was the basis of our conclusion that the products are strictly confined to the surface. We agree that the products of fragmentation (i.e., species C) likely evaporate from the particle surface to some extent. In fact, the size distributions at 15% RH shift slightly to smaller sizes at later OH exposures. Since we now assume a larger diffusion coefficient of  $1 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ , as described in our reply to comment 1.2, we have removed the suggestion that recombination may occur, as follows:

- ~~“This equivalence may indicate that, if fragmentation occurs due to reaction of OH with B, the strict confinement of the fragments leads to recombination, such that the absorption persists. It is also possible that stable fragmentation products form, but they volatilize out of the condensed phase to a much greater extent than they diffuse to the bulk phase, because the particles are so viscous; in this case, the decreased molar absorptivity of the products would have little effect on the total particle absorption. In fact, a slight decrease in the mean geometric surface diameter suggests that there is some degree of volatilization.”~~ (page 13, lines 6-11)

2.5 P8/L11: Was only the SSA matched, or were the absolute absorption and scattering also matched during the RI determination? If only the SSA, how can the authors ensure that they have a unique solution? There are a multitude of combinations of  $n$  and  $k$  that can give the same SSA value. Especially given that the  $n$  value determined differs so much from other SOA types.

SSA, rather than the absolute absorption and scattering coefficients, was used to derive an approximate complex refractive index ( $m$ ). In the deposition experiment, the aerosol is unperturbed, so  $m$  is assumed to be constant, while the aerosol distribution and SSA change slightly. We agree that any reasonable combination of  $n$  and  $k$  can give good agreement for an individual distribution, but it cannot reproduce the observed trend in SSA, as shown in Figure R5 and the supporting information (Figure S4).

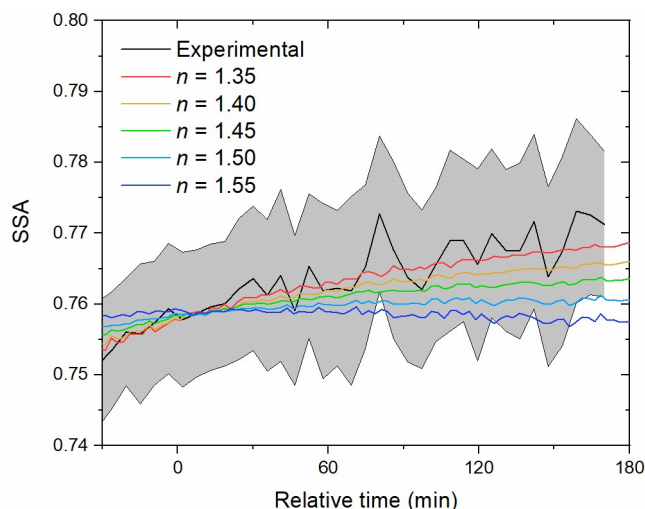


Figure R5. Time series of observed and predicted (based on the size distributions) SSA during a deposition experiment.

We agree that it would be preferable to use the absolute absorption and scattering coefficients. However, we find that the coefficients predicted from the distributions are lower than those observed for all values of  $m$ . Unfortunately, the impactor installed in the DMA had an orifice of 0.0502 cm, but the value was set to 0.0708 cm in the firmware, so the flow rate on the DMA display was too high. As a result, the particles were diluted more than expected before reaching the CPC, leading to lower number and cross sectional area concentrations.

We stress that, here, even an approximate value of the  $m$  is adequate to distinguish changes in the SSA due to changes in the size distribution from those in the chemical composition. For all assumed  $m$  values, for example, the sudden colour enhancement and significant bleaching observed at 60% RH is not predicted, so it must be due to chemical evolution.

The manuscript was modified as follows:

- **“Stepping  $n$  from 1.40 to 1.55 and adjusting  $k$  accordingly demonstrates that the good agreement for this refractive index is unique, as shown in Fig. S9. We stress that even an approximate value of the refractive index is adequate to distinguish whether changes in the SSA are due to changes in the size distribution or chemical composition.”** (page 8, line 33-page 9, line 1)

2.6 P9/L24: Presumably, a difference between 0.040 and 0.041 are within experimental uncertainty.

We agree that such a small difference in  $k$  is within the experimental uncertainty; nonetheless, the respective values give the best agreement with the average values of SSA. We modify the text, acknowledging the values are similar:

- “The initial geometric mean surface diameter was slightly higher than in the photolysis experiment described above (about 196 nm compared to 160 nm), so although the initial aerosol was slightly more scattering (higher SSA), the value of  $k$  required to reproduce the SSA before irradiation is ~~slightly higher~~ **very similar** (0.041 compared to 0.040).” (page 10, lines 24-27)

2.7 P10/L3: it would be helpful if the authors could clarify what they mean when they say they “observed uniform bleaching.” Also, the origin of the red curve in Fig. S5 is a bit unclear, if it does assume a constant  $n$  and  $k$ .

We apologize for a mistake in the legend of the original Figure S5b: the labels for the red and black curves were swapped. Assuming constant values of  $n$  and  $k$  gives the relatively steady predicted curve shown in black. The observed uniform bleaching is evident, beginning at relative time zero, coincident with the cusp of the red curve. The labels have been corrected.

2.8 P10/L21: How large of a MW would be necessary to yield a  $\gamma = 1$ ?

With the current set of parameters for 60% RH, decreasing the uptake coefficient for the initial BrC (i.e., species B) from 5.0 to 1.0 requires increasing the molecular weight from 326 to 1600 g mol<sup>-1</sup>, in order to reproduce the experimental trend in relative absorption. We modify the text as follows:

- **“Scaling the uptake coefficients such that  $\gamma_{\text{OH,A}}$  decreases from 5.0 to 1.0 requires increasing the molecular weight from 326 to 1600 g mol<sup>-1</sup>. It is difficult to rationalize such large oligomers forming during the 4-h aqueous photo-oxidation, so secondary radicals are indeed likely contributing to oxidation.”**  
(page 12, lines 1-3)

2.9 Fig. 8: This figure could probably benefit from additional panels showing the time-evolution of the normalized concentrations of A, B and C. It is difficult to visualize in the model how there is a sudden turnover that occurs with the 60% RH experiment with only two products and a continuous evolution. It would seem, at least to me, that some step change is necessary and the origin of this is not abundantly clear from the text.

We have added two panels to Figure 8, shown below as Figure R6, one for each RH condition. In each, 12 time series are plotted, one for each species in each layer. As shown in the middle panel, the concentrations of the individual species are the same in all four layers at 60% RH; in other words, the particles are well-mixed. In contrast, as shown in the bottom panel, the concentrations of the individual species vary significantly across the layers at 15% RH.

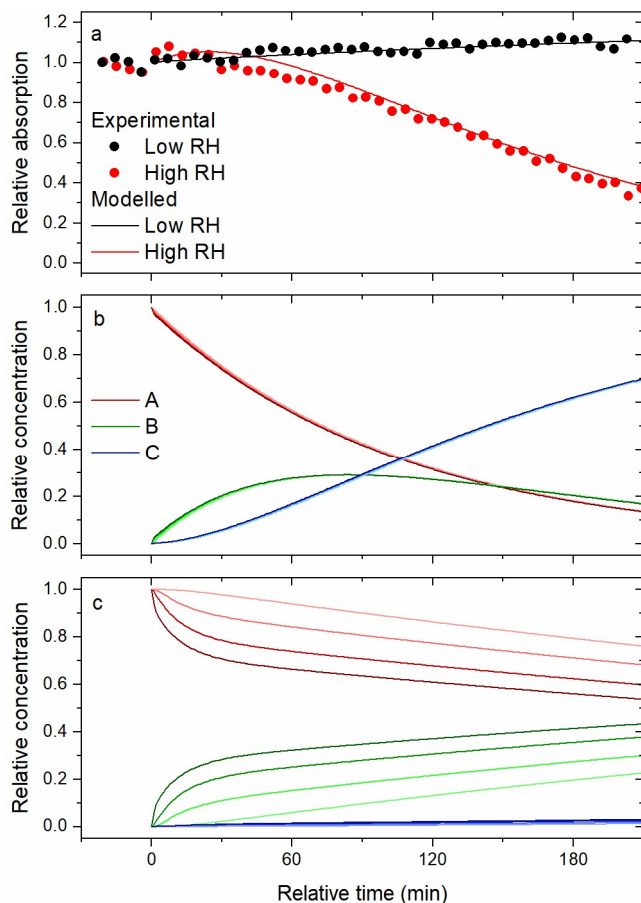


Figure R6. Time series of (a) observed and modelled relative absorption at 60 and 15% RH and the modelled relative concentrations of A, B, and C at (b) 60 and (c) 15% RH. The curves are shaded according to layer, with the darkest curves corresponding to the surface layer.

The text was modified as follows:

- “As shown in Fig. 8b, the concentrations of A, B, and C are the same in all four layers.” (page 12, line 14)
- “On a related note, because the viscosity is so high, the products B and C are much more concentrated at the surface than in the bulk layers (see Fig. 9-8c). Consequently, at 15% RH, the aged-aging particles likely consist of less absorbing cores and highly absorbing shells ~~consist of unchanged BrC cores encased in thin, more-absorptive shells.~~” (page 13, lines 11-14)

2.10 Figures S7/8/9/etc.: It would be very useful if the authors would report the epsilon values assumed for each of these simulations in the caption. It is difficult to understand whether the differences between e.g. Fig. S8 and S9 are the result of differences in the diffusivity alone, or because different assumptions have been made about the evolution of the absorptivity and the absorptivity of the products. I say this because the authors could do a better job of explaining how the evolution of the product species differs between the 60% RH and 15% RH cases, given

that they show that at 60% RH the particles are already fairly viscous, with differential oxidation between the surface layers and the bulk. What happens if all the authors do is drop the diffusivity from  $10^{-16}$  (which worked for RH = 60%) to  $10^{-18}$ , keeping everything else the same? Perhaps this is what Fig. S8 and Fig. S9a are showing, but it is not abundantly clear as written and presented. And I actually think that these figures fundamentally differ in what is assumed about the absorptivity of the products.

To generate these figures,  $\epsilon_B$  was set to 2.5, and  $\epsilon_B$  was set to either zero or 2.5, as well. These are the same conditions that were used to give the original model results in Figure 8, so the supporting figures do not fundamentally differ from what was described about the absorptivities of the products in the text.

However, Figures S7-S9 were intended to illustrate how a low diffusion coefficient was required in the model even at 60% RH. Comparing the modeled relative absorption to the experimental absorption coefficient divided by that which would be expected of a constant refractive index resulted in different values for the model parameters, as described in our reply to comment 1.2. In particular, the diffusion coefficient increased by two orders of magnitude, required to reproduce the significant bleaching. Consequently, we have decided to omit the original Figures S7-S9 from the revised manuscript.

2.11 P12/L16: it might be good to indicate that Sumlin investigated only a handful of biomass sources.

We have modified the text as follows:

- “Recently, Sumlin et al. (2017) observed bleaching due to heterogeneous OH oxidation of primary BrC derived from biomass-burning **of a number of types of biomass fuels**, which lost almost 50% of its absorption at 375 and 405 nm after the equivalent of about 4.5 days in the atmosphere.” (lines )