

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 1

1.1 This manuscript reports experiments, in which the evolution of brown carbon (BrC) aerosol upon exposure to OH is followed by the optical properties (scattering and absorption) at low (15%) and higher (60%) relative humidity. BrC aerosol was produced from the aqueous photooxidation of solutions containing resorcinol and H<sub>2</sub>O<sub>2</sub>, thus resembling aged biomass burning aerosol with high aromaticity. The results are that at 60% RH, oxidation of this BrC aerosol first induced an enhancement of absorption, followed by bleaching, with an inverse behavior observed for the single scattering albedo (SSA). At 15% RH, only a slowly increasing absorption was observed during the timescale of the experiments. Interpretation of the results is facilitated by a multilayer kinetics model, in which chemistry is lumped into a simple oxidation scheme involving one parent BrC leading to one second and one third generation oxidation product with differing optical properties. Comparison to experimental data in terms of optical properties, indicate that strongly contrasting diffusivity must be assumed between 15% RH and 60% RH to reproduce the experimental data. This allows speculating about different pathways of oligomerization and fragmentation to occur at various time periods. The evolution of BrC properties is a highly relevant topic of atmospheric aerosol chemistry due to ubiquitous presence of BrC compounds in a large variety of primary, aged primary or secondary organic aerosol.

The experiments seem to be well performed and carefully analyzed. Proper control experiments are performed to distinguish between photolysis and OH oxidation. Since the experiments are not accompanied by more detailed chemical analysis, the application of the kinetic model remains poorly constrained, though it provides a useful link between expected chemical processes and the optical properties, as they evolve under different humidity and thus likely differing diffusivity.

The manuscript is well written and structured; the conclusions are adequately supported by the experimental findings; and the kinetic model is presented and used with care and proper caveats. I recommend publication of this work with maybe just a few small revisions, following some specific comments below.

Thank you for these positive comments.

1.2 The model is based on chemical reactions just occurring at the surface, and the bulk only serves as a medium for reactants and products to diffuse; this seems reasonable for the reaction with OH. However, second generation oxidation may involve O<sub>2</sub> or other reactive oxygen species deriving from the first and second step and may also proceed in the bulk. Of course, considering such would rapidly lead to more variables that would need to be tuned and would make the results more ambiguous. But maybe the authors could make an attempt in checking the sensitivity of the model results and parameters towards the experimental observables. I would also expect that O<sub>2</sub> has quite different diffusivity than the large aromatic oligomers.

We agree that radical products of the initial OH reaction likely form RO<sub>2</sub> species by reaction with O<sub>2</sub>. These RO<sub>2</sub> species may be converted to RO and initiate further oxidation of the brown carbon constituents or react with each other in a termination step. They may also facilitate auto-oxidation by causing hydrogen shifts. As the reviewer points out, an attempt to model these processes would introduce other parameters, such as the diffusion coefficient of O<sub>2</sub> in the particles and the absorptivities of any additional products, so we have not added them into our simple multi-phase model. However, we have modified the manuscript to discuss the potential role of RO<sub>2</sub> species in more detail. For example, RO<sub>2</sub> initiated reactions are suggested to contribute to uptake coefficients greater than unity at 60% RH. We have modified the text as follows:

- **“Processes other than directly OH-initiated oxidation also occur. For example, radical products of the initial OH reaction likely form RO<sub>2</sub> species by reaction with O<sub>2</sub>. These RO<sub>2</sub> species may react with each other in a termination step or react with NO, for example, to form RO (Richards-Henderson et al., 2015, 2016), which may initiate further oxidation of the brown carbon constituents. They may also facilitate auto-oxidation by abstracting hydrogen from adjacent groups on the same molecule. We do not consider these processes in our simple multi-phase kinetics model, since many other parameters, such as the diffusion coefficient of O<sub>2</sub> in the particles and the absorptivities of any additional products, would have to be introduced, but they may play a role in the apparent values of uptake coefficients.”** (page 7, lines 20-26)

We take this opportunity to discuss a change to Figure 8. In the original manuscript, the modeled relative absorbance was compared to the inverse of the experimental relative single scattering albedo (SSA). Since the scattering coefficient appears in both the numerator and denominator of SSA and is much larger than the absorption coefficient, this comparison is problematic. To show the changing absorption properties of the particles more clearly, we now compare the modeled relative absorbance to the experimental absorption coefficient divided by that which would be expected if the initial complex refractive index (*m*) did not change during the experiment, accounting for size dependence. The experimental trends, shown in Figure R1, are also corrected for the contribution of photolysis.

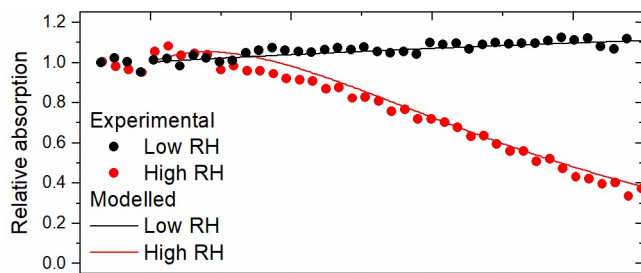


Figure R1. Experimental and modelled trends in relative absorption.

At 60% RH, the final value of the plotted quantity is about 0.40, rather than the value of 0.85 using the comparison plotted in the original Figure 8. To reproduce this trend – in particular, the more significant bleaching – the diffusion coefficient must be increased

from  $1 \times 10^{-16}$  to  $1 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ , at which the particle is well-mixed, not semi-solid. The uptake coefficients and absorptivity were changed slightly, but do not alter the original discussion. At 15% RH, the diffusion coefficient was also increased by two orders of magnitude. At both RH conditions, the product C is set to be non-absorbing, but at 15% RH the uptake coefficient associated with its formation is set to only 0.1. The text was modified by substituting the new parameter values throughout. Other changes include the following:

- **“The parameters also suggest that, as RH decreases, reactivity decreases, and aerosol viscosity increases, such that particles are well-mixed at 60% RH but not at 15% RH, and the aerosol is very viscous, even at 60% RH. At 15% RH, the aerosol will be viscous enough to confine products of fragmentation, leading to their recombination, such that little bleaching is observed on the experimental timescale.”** (page 1, lines 19-22)
- **“This modelled relative absorption is compared to the to the experimental absorption coefficient normalized to that which would be expected if the initial complex refractive index ( $m$ ) did not change during the experiment, accounting for size dependence. Experimental times series of this normalized absorption were derived for photolysis and heterogeneous OH oxidation experiments, and the latter were corrected for the effect of photolysis. During heterogeneous OH oxidation, the evolution of the SSA of the particles incorporates changes in both absorption and scattering. However, the changes in absorption are likely dominant. For example, for fixed values of  $n$  (1.35) and particle diameter (200 nm), a 50% decrease in  $k$  (from 0.04 to 0.02) gives a 10% increase in  $Q_{\text{sea}}$  but almost a 50% decrease in  $Q_{\text{abs}}$ . Consequently, we assume that  $Q_{\text{sea}}$  is steady, and we compare the modelled trends in relative absorption to the experimental trends in the inverse of relative SSA.”** (page 7, lines 11-19)
- We find that the observed trend in relative absorption at 60% RH – **in particular, the significant bleaching** – cannot be reproduced **only** if the aging particles are taken as well-mixed, **so diffusion of A from the bulk to the surface is not restricted**; if  $D_{\text{b,t}}$  is taken as  $1 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$ , the decay in the concentration of A is about the same in all three bulk layers (see Fig. S6a), and the abrupt cessation of absorption enhancement cannot be captured. As shown in Fig. S7, if the absorptivities are fixed, and the uptake coefficient is scanned from 0.2 to 10, the trends in relative absorption have the same shape (simply stretched or compressed along the time axis), because the particles are well-mixed. On the other hand, if  $D_{\text{b,t}}$  is taken as  $1 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ , the fraction of species A at the surface decays faster than in the bulk (see Fig. S6c), the modelled trends cannot be superimposed by scaling along the time axis (see Fig. S8), and the abrupt cessation of absorption enhancement to be captured.” (page 12, lines 8-15)
- **“Though the extent of bleaching is captured by the model, and rapid initial colour enhancement is not. We speculate the other processes, like auto-oxidation, could contribute to this feature.”** (page 12, lines 20-22)

1.3 The estimated diffusivity at 60% RH and also the fact that diffusion limitations are so apparent are a bit surprising. The authors are explaining it with the high aromatic content and the ease with which aromatic oligomers are formed. Can the hygroscopic growth be estimated from the experiment between 15% and 60% RH. The lack of significant water uptake could support the semi-solid character of these particles at 60% RH.

As described above, the modelled diffusion coefficient at 60% RH increased by two orders of magnitude, upon comparing the modelled relative absorbance to the experimental absorption coefficient divided by that which would be expected of a constant refractive index. Consequently, the particles are no longer estimated to be semi-solid at 60% RH.

Nonetheless, we agree that it would be informative to roughly estimate the extent of hygroscopic growth at 60% RH. Unfortunately, the initial size distributions vary between experiments, including replicates at the same RH, so we cannot directly compare the 15 and 60% RH experiments to evaluate hygroscopic growth at 60% RH.

To address this issue, we performed an additional experiment, in which BrC particles were sampled from the chamber alternately with and without a diffusion dryer upstream of the DMA. The conditioning was alternated every 15 min, allowing time for the RH of the sheath flow to stabilize. As shown in Figure R2 (also Figure S5 in the supporting information), the size distribution slowly shifts to larger mobility diameters, because smaller particles are lost faster than larger particles. Besides this trend, the variation between the conditions appears to be negligible, so there is not significant water uptake. Nonetheless, slight differences in scattering coefficients of nascent and dried particles are observed, as described in our reply to comment 2.3.

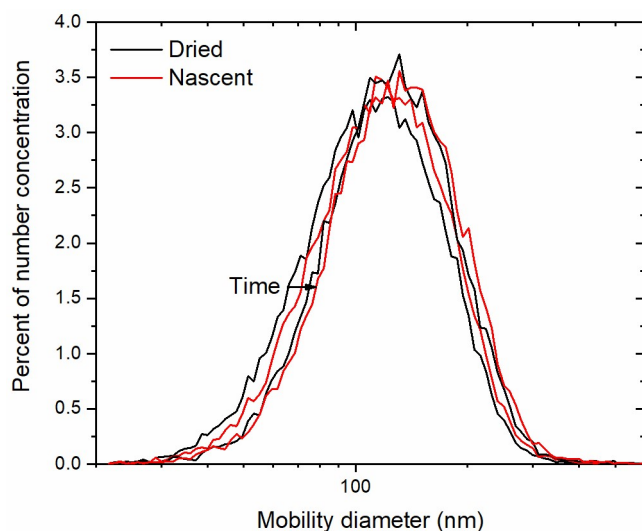


Figure R2. Size distributions of dried and nascent particles, collected alternately in 15 min intervals.

The manuscript was modified as follows:

- **“In one experiment, BrC particles were sampled from the chamber alternately with and without a diffusion dryer upstream of the DMA. The conditioning was alternated every 15 min, allowing time for the RH of the sheath flow to stabilize. As shown in Fig. S6, the size distribution slowly shifts to larger mobility diameters, because smaller particles are lost faster than larger particles. Besides this trend, the variation between the conditions appears to be negligible, so there is not significant water uptake at 60% RH.”** (page 9, lines 6-10)

1.4 Based on the reported results, under the conditions of the experiments, OH oxidation dominated the changes in optical properties in comparison to pure photolysis alone. Could the authors try estimating the relative impact of photolysis and OH under atmospheric conditions. Photolysis of BrC or reactions of their triplet excited states may also lead to later generation radical processes, similar to those initiated by OH; therefore the relative impact of OH versus that of BrC induced photochemistry on aerosol aging may require some attention.

This is a very important issue, and we now address it in the text as follows:

- **“The emission of the UV-B black-lights in the chamber, with a peak at 310 nm, is not representative of natural sunlight, so we do not draw direct comparisons between the timescale of our experiments and that of photolysis in the atmosphere. Rather, we performed photolysis experiments to account for the effects of photolysis during the heterogeneous OH oxidation experiments. Wong et al. (2015) have shown that for this chamber equipped with UV-B bulbs, the photo flux at wavelengths below 310 nm is much greater than for a clear-sky summer day; for example, at 300 nm, the photon flux from the bulbs is close to its peak value of about  $1 \times 10^{14}$  photons  $s^{-1} cm^{-2} nm^{-1}$ , while the photon flux outside is negligible. Light at wavelengths below 310 nm is likely driving most of the photo-chemistry during the photolysis experiments, so we believe the relative impact of photolysis would be small in the atmosphere, even considering that the ambient OH concentration is lower than in the chamber.”** (page 9, lines 13-21)