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Interactive comment on "Heterogeneous OH oxidation of secondary brown carbon aerosol" *by* Elijah G. Schnitzler and Jonathan P. D. Abbatt

Anonymous Referee #2

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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.

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.

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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 The authors do not cite this paper, which is an unfortunate oversight.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.

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.

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.

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

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.

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

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.

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 diffisivity 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 10ˆ-16 (which worked for RH = 60%) to 10ˆ-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.

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

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