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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Photochemical processing of aqueous atmospheric brown carbon" *by* R. Zhao et al.

Anonymous Referee #3

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This paper reports on laboratory experiments investigating the stability of BrC. The results are highly important given recent assertions that one can simply assume BrC is stable following emissions and use these emission factors to predict climate impacts. The paper was a delight to read.

Following are a number of things the authors may wish to consider. The main issue is that the experiments could be put in a better context with what is known about ambient BrC, and the results qualified.

Some overview thoughts:

The focus is on water-soluble BrC, which is typically less than half the total ambient BrC observed. This should likely be considered in the introduction and kept in mind when

discussing overall implications of the results. See Washenfelder (2015) and references therein.

The bleaching experiments reported here with "real" BrC (biofuel smoke) seem very different from the single component results (i.e., note the much smaller changes in BrC absorption with time). This may demonstrate how careful one needs to be in making broad conclusions on limited experiments with single components.

Comments on the Introduction:

Much of this paper investigates the bleaching of aldehydes. What is the justification for this? There are many reports on BrC associated with biomass burning based on ambient measurements, but is there actually any ambient data for aldehyde – derived BrC in field studies? You might consider the results of [Washenfelder et al., 2015]. It appears that most of the aldehyde-BrC interest is driven by laboratory experiments. Maybe this could be noted, and then the paper conclude a possible reason for lack of ambient evidence for this is the finding that BrC from this source is essentially not stable so not expected to be found in ambient studies.

One might assess the representativeness of the experiments by comparing the light absorption spectra to that observed in the atmosphere (as noted later in the paper).

Pg 2959 lines 15 to 20. It is not clear why the chemistry of BB OA is discussed. Molecules containing chromophores are likely such a small mass fraction of BB OA that BB OA chemistry is not informative.

In my view the Introduction should also discuss in more detail the actual evidence for BrC in the atmosphere, its sources and prevalence. Since most of the chemical composition of chromophores is unknown (this could be more clearly pointed out in the Intro) there should be a discussion on the limitations of this work, e.g., what are the limitations of picking a few specific compounds to test. How generalizable are the results? (Example, Pg 2962 lines 19 – 23, it is simply stated that the 3 nitrophenols

were chosen to represent primary BB BrC since they have been detected in cloud water). One could start by going over in detail all the papers where BrC chemistry of ambient aerosols is presented and what fraction has been identified. From what I know this includes: [Desyaterik et al., 2013; Mohr et al., 2013; Zhang et al., 2013]. Further, it is worth noting that some specific BrC compounds have been identified in different sources (biomass burning and vehicle emissions).

Why were emissions from agricultural biofuels used as representative of BrC from biomass burning?

Other comments.

Pg 2965 Line 23 to 24. It seems surprising that one could actually see a brown color for the extract solutions if the concentrations were representative of ambient.

Maybe one of the most interesting things from these experiments is that the bleaching does not result in complete loss of the BrC. It is this stable BrC that may be the most optically important and so likely the chemically most interesting. It seems a bit unfortunate that the experiments were not carried out over longer times so the real fractions of stable BrC could be given (i.e., in some cases plots of the time evolution are still dropping when the experiment is ended). Since the curves seem to flatten out with time and not at Absorbance = 0 could the authors estimate the fraction of stable to initial BrC for the various experiments (ie fit the data to extended times)?

Pg 2973 List line of section 3.3.3. Based on limited experiments from two oxidation methods of compounds that make up a fraction of the total BrC maybe it should not be stated so definitively that OH oxidation is the dominant fate of nitrophenols? The subsequent predictions in the following sentences may also need to be qualified.

Pg 2975, Line 12-14, The biofuel BrC may have bleached rapidly, but was there a significant change in the overall light absorption, ie, Fig 10 suggests not. That is, the magnitude of the bleaching seems quite small. When compared to the single compo-

nent results, what are the implications?

References:

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