

Atmos. Chem. Phys. Discuss., referee comment RC3
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Comment on acp-2021-871

Anonymous Referee #3

Referee comment on "Aqueous chemical bleaching of 4-nitrophenol brown carbon by hydroxyl radicals; products, mechanism, and light absorption" by Bartłomiej Witkowski et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-871-RC3>, 2021

Review of "Aqueous chemical bleaching of 4-nitrophenol brown carbon by hydroxyl radicals; products, mechanism and light absorptivity by Witkowski et al.,

General comments: This manuscript presents results from a series of studies looking at the aqueous phase photochemical removal of 4-NP. The system was measured by tracking the decay of the precursor and the formation of products via GC/MS along with the overall changes in absorption vs. time. It was found that the solution as a whole had a slower decay in absorption compared to the loss of the precursor, due to the formation of products that could also absorb visible light. The influence of pH was also probed and while there were differences in the products at different pH values, the change in absorption vs. pH was a larger factor compared to differences in decay. Overall the manuscript is interesting and it does a very good job of referencing and comparing to previous work. There are numerous places where additional information and possibly some additional experiments/data would help clarify statements made in the manuscript and these are listed below. If these comments are addressed, the manuscript would be a valuable addition to the growing knowledge of BrC aging in the atmosphere and would be acceptable for publication in ACP.

Specific comments:

- It is stated in the abstract "Hence, up to 65% of the organic carbon...". I can see in the

conclusions where this statement comes from, but I don't see how there can be a hence leading to this coming from the sentence before it in the abstract. Please clarify where the 65% value is coming from.

- The experimental set-up uses two 254 lamps. It is stated that this allows for the formation of OH radicals from the added H₂O₂ and that the direct absorption of 4-NP is avoided. Were any experiments done to confirm this? The supplemental refers to section 4.2, but there is no mention of photolysis only experiments with these lamps, or with the 254 nm lamps only, to show the possible role these might play in the rates.
- In figure 1A, what is the inset? Please add labels to the axis and discuss this figure in the caption and in the text.
- In Figure 1A and 1B, what are the linear fits showing? The data does not look linear, especially in Figure 1B, so why is this assumption being made?
- In Figure 1A and 1B, what is the x-axis? Is this the change in 4-NP concentration relative to the initial concentration? Please add this to the caption.
- In Figure 3, you show the change in MAC vs. % 4-NP reacted at different pH values. But, the data also shows different pH levels (colors). I believe that the pH is being adjusted after the aging process to generate this data. If this is the case, please clarify that in either the text or the caption. If not, please clarify what is being plotted.
- Page 13, at the end of the section it is stated that "Also, because of a significant increase in the actinic flux at ...any "brown" products formed efficiently stabilize the Rabs values throughout the course of the reaction..." I don't understand this statement. How do the brown product stabilize the Rabs values? A little more clarity here would be helpful.