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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Photooxidants from Brown Carbon and Other Chromophores in Illuminated Particle Extracts” *by* Richie Kaur et al.

Anonymous Referee #1

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REVIEW OF THE MANUSCRIPT “PHOTOOXIDANTS FROM BROWN CARBON…”, BY KAUR ET AL.

This paper reports the results of a study that quantified °OH, 1O2 and triplet states in particulate matter aqueous extracts. As there are few or no studies on the subject, the topic is interesting and deserves publication. However, there are some clarity issues with the present version of the manuscript that should be solved. Moreover, it is not clear whether the procedure to determine the transient species was fully appropriate (in particular, the authors do not specify if and how they dealt with transient scavenging by the probe molecules, which is a confounding factor in this kind of measurements and could possibly explain the inconsistency between the 1O2 and 3C* data). For these reasons, the manuscript should be revised following the recommendations reported

below.

1. Page 5, bottom. Please specify the degree (approximate) by which the samples were diluted upon addition of H2SO4. Moreover, measuring pH in a small sample might not be totally trivial: please provide details of the pH measurement device.

2. Line 177. Is the pathlength measured in cm? Please specify.

3. Page 6, bottom. I suppose that the contributions of nitrate and nitrite to absorption were small. Anyway, that should be specified for completeness (approximately which percentage of absorbance would be accounted for by NO2-/NO3- and which by DOM, of course it varies with wavelength but it is important to have an idea of that).

4. Line 190. Please spell out the “OM” and “OC” acronyms.

5. Section 2.5 and overall. Scavenging of the reactive species by probes can be a problem, because it decreases the transient steady-state concentration. Because of this, the steady-state concentration in the illuminated sample with the probe can be much different from the steady-state concentration in the sample without probe. If an issue like this occurred in the measurements of 1O2 and the triplet states, that could explain the inconsistency of the results (comparison between 1O2 and 3C* should be carried out in the samples without probes, by means of an extrapolation). Experiments with benzene were carried out at different initial concentrations, and by so doing there is a chance of correcting for probe scavenging (although it was not specified whether such a procedure was followed). In the case of FFA and the triplet probes the used concentration is not provided. This issue should be checked, corrected if necessary, and in any case discussed in the manuscript.

6. Lines 199-204. The procedure used here was different from the description of the irradiation experiments provided in section 2.3. Also the irradiated volume is different (5 mL vs. 1 mL), although the same HPLC was used in both cases which required the withdrawal of 100 uL aliquots. The reason for this difference should be provided for

clarity. 7. Line 201. “illuminated” should read “illumination”.

8. Equation (4). Which is the rationale behind this equation? Is it assumed that light screening in ambient particles can be neglected? If so, why (there is a small pathlength there, but concentrations can be very high and compensate)? Please explain for clarity.

9. Page 8, top. To enable comparison between the two methods, please report reaction yields for benzene => phenol and for MBO.

10. Section 2.5.2. Please specify the FFA concentration and the way 1O2 scavenging by added Ffa was accounted for.

11. Line 232. Is it “faster” or slower? Please check.

12. Section 2.5.3. Also in this case, the probe concentration should be specified and its role as 3C* scavenger (or the way scavenging was corrected for) should be discussed, because the presence of the probe alters [3C*].

13. Lines 269-272 and 279. the overall explanation here is not very clear. I imagine that a couple of matching triplets were used and the mole fractions were calculated so that it was possible to exactly match the experimental rate constant ratios. However, this should be explained better because it is definitely not straightforward to derive it from the text.

14. Lines 288-289. Canonica estimated 5x10ˆ5 s-1 as the triplet deactivation rate constant. The data provided here suggest a higher value for the estimated rate constant. Which is the reason? Was a different [O2] assumed here in comparison with surface waters? Please explain better.

15. Equation (9) and related discussion. I imagine that also Rabs was normalised to the winter solstice, otherwise there is no consistency. However, I do not understand the reason for using a double normalization. The quantum yield should be independent from the irradiation conditions, thus it should be the same (and better, to my opinion) to use the raw experimental data. If there are additional reasons for using normalised

data, that should be explained.

16. Line 345. How were the Absorption Angstrom Exponents calculated? Please specify (better by using a formula).

17. Line 362. Do you mean here that absorption declined faster with increasing wavelength? This may have implications for the molecular weight of DOM (higher molecular weight compounds experience a slower decrease of absorption with wavelength).

18. Lines 378,379. This statement means that PME are not more concentrated than for with respect to NO3- and NO2-. Is there any idea as to the reason for this?

19. Line 387. DOC concentration. It would be very useful for the readers to have a range of measured DOC values here.

20. Page 14, bottom. It may be interesting to recall that the 1O2 formation QY determined here is also not very distant from typical values found in surface waters.

21. Page 15, bottom. Comparing steady-state concentrations in different studies is not very significant because they strongly depend on the irradiation conditions. It would be much better to compare the formation quantum yields.

22. Page 16, top and middle (end of section 3.5). if it is not a consequence of unwanted transient scavenging by probes, this puzzling result might mean that the complicated approach followed here to measure 3C* was not very appropriate. In the context of surface waters, the use of 2,4,6-trimethylphenol as probe usually gives consistent results between the 3c* and 1O2 formation quantum yields. That could be discussed to place the used results and methodology into a clearer and more complete framework.

23. Lines 489,490. How is particle moisture estimated? Please specify.

24. Line 524. In the case of 1O2 production, it is strange that saturation of absorbance was not observed even in the most concentrated samples. In the presence of a very high DOM amount, all or almost all incident radiation should be absorbed and a plateau

[1O2] trend should be observed as a consequence. Which was the absorbance in the most concentrated samples that were subject to irradiation?

25. Page 18, 1st half. In the case of surface waters, you need DOC » 20 mgC L-1 to have significant scavenging of 3C* by DOM. What is the situation here? Which were the DOC values of the most concentrated PME samples? It is important to discuss them for comparison.

26. Line 529. “(Wenk et al., 2011;2013) have shown” should read “Wenk et al. (2011; 2013) have shown”.

27. Lines 577 and 597-599. Role of 1O2 vs. 3C* in PM water. There is a potential inconsistency here, because 3C* seem to play a minor role with the chosen model compounds but then one has to admit an important 3C* scavenging by DOM. This seems to suggest that the choice of the five model compounds was not fully representative (they might tend to highlight 1O2 reactions). This issue should be discussed better.

28. Line 615. “approximately” should read “approximate”.

29. Line 622. 600 vs. 3000. According to Fig. 5 one has quite parallel increases of both [1O2] and [3C*] (the latter under the hypothesis of no plateau), while 3000/600 = 5 which is quite a lot as difference. Are these numbers compatible with Figure 5 data? Please add a comment.

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