

Response to Reviewers for “Predicting photooxidant concentrations in aerosol liquid water based on laboratory extracts of ambient particles” by Lan Ma et. al.

Each reviewer comment is listed in italics and our response, in plain text, is directly below it. Line numbers in the revised version are different from the original (e.g., in reviewer’s comment) due to changes in the manuscript.

**Anonymous Referee #1 Received and published: 20 April 2023**

*General comments:*

*The authors collected ambient PM filters from Davis and diluted the extracts to measure the production of photooxidants (OH, 3C\* and 1O2\*) as a function of dilution. Essentially, the authors are extending Figure 5 from their previous contribution on this topic: (Kaur et al., 2019). Despite the apparent simplicity of this task, the experiments are tedious and difficult and require a carefully controlled understanding of the probes used and their reactivities (which was published recently in what could be called a companion paper in (Ma et al., 2023)). The results of this paper are important as our community tries to understand the relevance of 1O2\* and 3C\* photooxidants. I commend the authors for the diligent experiments presented. Yet, there are important revisions required before publication. They are related to additional references, listing of additional controls and restructuring the discussion between the 2 filter types collected.*

*Important issues to address:*

*The authors have a winter filter composite (WIN) taken from Feb 5-28 2020 and a summer filter composite taken from August 21-24 2020, which are part of the dilution series. They then make seasonal comparisons between these two filters. However, there is little basis on a seasonality discussion with so few filters over such a short period of time. Instead, I would recommend that the authors focus their discussion on brown carbon and how brown carbon from wildfires (SUM) produce different photo-oxidants than brown carbon from wintertime burning (WIN). Concretely, the revision I’m suggesting involves removing the discussion between lines 267-288, and instead expanding further the discussion included between lines 288-293, as well as changing*

*the discussion throughout the text/abstract/title to focus on a BrC-type intercomparison (which also nicely compares to the wintertime PM extracts in (Bogler et al., 2022)). This story re-design would enable a deeper discussion on the possible nature of the 3C\* compounds, which I think would be more beneficial to the community and the future reader.*

**Response:** We thank this reviewer for the thoughtful review and encouraging comments. We agree that two samples are not enough for seasonality discussion. While we used the idea of “seasonality” as a short-hand to distinguish between the two samples in this manuscript, we have another manuscript in review (Ma et al., 2023a) that actually compares the seasonality of samples collected over a year and discusses the results relative to those of Bogler et al. (2022). We added this information to Sections 3.1.

*An important reference is missing which includes recommendations on  $R_{abs}$  calculations and how to use wavelengths from 300 to 800 (instead of to 450 like the authors did in table S1): (Ossola et al., 2021) and their Table 4.*

**Response:** Thank you for your suggestion. This is an important reference, indicating that the wavelength range used can significantly affect the  $^1O_2^*$  quantum yield calculation because it alters the calculated rate of light absorption. We report light absorbance over a range of 300 – 450 nm to be consistent with our past work (Kaur et al., 2019) and because the data at longer wavelengths are very noisy for the more dilute extracts. To address this issue, we have added a column to Table S1 that shows the ratio of light absorption calculated for 300 to 450 nm to the light absorption over the full absorbance range (i.e., 300 nm to the wavelength where the absorbance goes to zero). We also added several sentences to the first paragraph of Section 3.3.3 to discuss this issue and the impact on our quantum yields.

*Important references on photoproduced oxidants in PM and rainwater are missing from the paper and really should be included and discussed (and even added as data points to comparison graphs). I don't see any reason to omit these references:*

*(Leresche et al., 2021)*

*(Li et al., 2022a)*

*(Li et al., 2022b) – this reference is also important for the context of trace metals hypothesized by the authors on lines 320-321. And I would also add (Cote et al., 2018) for a discussion on the role of road dust which is rich in transition metals.*

*Rainwater photooxidants: (Albinet et al., 2010; Hong et al., 2018)*

*1O<sub>2</sub>\* reactivity in aqueous extracts (not be plotted on a graph, but worthwhile for the 1O<sub>2</sub> reactivity discussion in section 3.3.3.: (Barrios et al., 2021)*

*Recent review on ALW: (Carlton et al., 2020)*

**Response:** Thank you for the suggestion. We have included these references for discussion.

*I commend the authors on a thorough study of these oxidants which are difficult to measure. The authors have performed a number of important controls. However, I have additional questions related to the experimental procedure that would need to be clarified before publication:*

- *What was the source of the H<sub>2</sub>SO<sub>4</sub>? Purchased H<sub>2</sub>SO<sub>4</sub> is often brown in color and so addition of the acid (although valid to similar more acidic aerosols) could also be adding chromophores. Could the authors share their controls related to the addition of the acid?*

**Response:** Thank you for your suggestion. The added H<sub>2</sub>SO<sub>4</sub> was diluted from the trace-metal grade concentrated H<sub>2</sub>SO<sub>4</sub>, which is a colorless liquid. Therefore, we don't think that adding minor amount of H<sub>2</sub>SO<sub>4</sub> (e.g. average ( $\pm \sigma$ ) of 40 ( $\pm 47$ )  $\mu$ M) will bring significant additional chromophores. We have added the H<sub>2</sub>SO<sub>4</sub> grade information in the Supporting Information.

- *How were the filters collected and stored in reference to (Paulson et al., 2019) who observed a burst of OH production upon illumination? (The authors do reference this paper in relation to photo-Fenton chemistry on lines 351-352.)*

**Response:** From Paulson et al. (2019), filters after collection were stored in individual Teflon Petri dishes, sealed with Teflon tape, and stored in a freezer at or below 0°C for later analysis. In our work, we wrapped our samples in pre-baked aluminum foil, sealed in a Ziploc bag, and stored at -25 °C. We do sometimes see a “burst” of OH during the initial illumination period; we discuss this observation in Ma et al., 2023a.

- *Did the authors distill their FFA? (Ossola et al., 2021) describes on page 4114 that FFA oxidizes to form a yellow product which can absorb light and lead to inaccurate  $1O_2^*$  interpretations. If the authors didn't, then they could run an experiment with and within distilled FFA and propagate that difference through to the measurements they've already made.*

**Response:** Unfortunately, we did not distill our FFA. We tried to use freshly purchased FFA but it gradually turned yellow once the chemical bottle had been opened. As Ossola et al. suggested, the yellow impurities might sensitize the indirect photodegradation of FFA (Ossola et al., 2021). One way to check if the impurities affected FFA experiments is to compare FFA decay rates in the samples and field blanks. In our most dilute samples (WIN-10 and SUM-10), the pseudo-first order decay rate constant for FFA was roughly  $(2-3) \times 10^{-3} \text{ min}^{-1}$ , while the value was  $1 \times 10^{-4} \text{ min}^{-1}$  under the same photon flux condition in the field blank samples, more than 20 times lower. This suggests that FFA decay caused by impurities is negligible.

- *Were filter blanks subtracted from the result tables in the SI?*

**Response:** No, we did not subtract the field blanks from the sample results. We have clarified this in each table.

- *The inhibition experiments are very good and well described in the SI. What do the authors think is causing the inhibition? Anti-oxidants in DOM? A short discussion in the next would be valuable.*

**Response:** We think that phenols, which are abundant in biomass burning particles and effective reductants (Schauer et al., 2001; Wenk and Canonica, 2012), are primarily responsible for the inhibition. We have added a short discussion about this in the Section 3.3.2.

*I didn't quite follow the discussion on "plateauing" of  $^3\text{C}^*$  for  $^1\text{O}_2^*$  curve shapes on lines 426-431 and in lines 433-438. Where did the 5000 mgC/L come from? Have the authors considered calculating the % contribution of DOC as a sink for  $^1\text{O}_2^*$  in their FFA experiments? If the steady-state concentration is known, the FFA reactivity is known and the water deactivation constant is known, then the authors could potentially quantify the contribution of the DOC as a sink as a percentage. This information could also be discussed along with Figure 6a (a key figure in my opinion!)*

**Response:** Thank you for your suggestion. The curvature observed for  $[\text{}^1\text{O}_2^*]$  in more concentrated extracts of the SUM sample could be explained by two possible reasons. One is that the DOC concentration is high enough to become the dominant sink for  $^1\text{O}_2^*$ . The other possibility is that the plateauing of  $[\text{}^3\text{C}^*]$  in more concentrated extracts causes the production rate of  $^1\text{O}_2^*$  to increase more slowly. To figure out which reason is more consistent with our data, we calculated the minimum DOC concentration required to enable DOC to become the dominant sink for  $^1\text{O}_2^*$  in our samples. The result, a DOC concentration of 5000 mgC/L, is much higher than our extract values, indicating that the first possible reason is unlikely. We have rewritten much of this section to address the reviewer's concerns, including changing from discussing the concentration required for DOC to be the dominant sink of  $^1\text{O}_2^*$ , to instead stating the upper bound on the fraction of  $^1\text{O}_2^*$  loss due to DOC in our extracts.

*In figure 2, why do the  $^3\text{C}^*$  in the WIN and SUM measured by syringol collapse onto one another but that's not the case of PTA? I suspect there is an interesting BrC-type specific discussion to be addressed here and how perhaps as a community we ought to be using multiple  $^3\text{C}^*$  probes for our measurements?*

**Response:** This is an interesting question. We think this phenomenon can be attributed to the types of oxidizing triplets captured by SYR and PTA and differences in BrC types in the WIN and SUM samples. We believe SYR captures both weakly and strongly oxidizing triplets (i.e., roughly the entire oxidizing triplet pool), while PTA only captures strongly oxidizing triplets. The similar  $[\text{}^3\text{C}^*]_{\text{SYR}}$  trends for WIN and SUM suggest that the total amount of oxidizing triplets in SUM and WIN are similar. However, the lower  $^3\text{C}^*$  concentration determined by PTA in SUM compared to WIN might be due to a lower fraction of strongly oxidizing triplet in SUM samples. This also can be indicated by the lower ratio of  $[\text{}^3\text{C}^*]_{\text{PTA}}/[\text{}^3\text{C}^*]_{\text{SYR}}$  in SUM (36%) compared to WIN (67%). Different BrC

types might explain the different ratios. Since SUM represent fresh wildfire samples, it might contain more highly aromatic compounds that show a lower triplet reactivity. However, WIN represent more aged samples containing higher fraction of carbonyl or ketone functional groups, enhancing the triplet reactivity (McNeill and Canonica, 2016; Wenk et al., 2011). We added a discussion of these points to the Section 3.3.2.

*I also have some criticism on the length and tone of the manuscript. I spent more time than I had allocated going through this manuscript, and I referred often to the SI, as well as had to reference constantly to (Ma et al., 2023) as well as to (Kaur et al., 2019). It's a difficult read for someone unfamiliar with these types of measurements (like 1<sup>st</sup> year graduate students for example). To improve the more editorial side of this manuscript, the authors could consider:*

- 1. moving more information to the SI and focus on the interpretation of their results.*
- 2. Include more references to measurements in their Figure 2. (Manfrin et al., 2019; Bogler et al., 2022) has measurements of OH and 1O2. (Leresche et al., 2021) et al also has measurements of OH and 1O2.*
- 3. Use the full name of the molecules. I often got confused with DMB, PTA and TMP and had to refer back to the methods a couple of times. (There are no space limits in ACP, so perhaps worth considering writing the compound names in full? "trimethylphenol")*

**Response:** Thank you for your suggestions. It is a difficult balance to decide how information should be distributed between the main text and SI, but we believe the current breakdown is reasonable. For the second suggestion, we recently submitted a separate manuscript on the seasonality of particle photooxidants; when we revise the seasonality manuscript, we will include the additional measurements suggested by the reviewer. For the third point, we have modified the manuscript to use the full name of the chemicals more frequently.

*Specific/technical comments:*

- The title could include the term "brown carbon" to highlight the differences between filters more accurately.*

**Response:** Thank you for the suggestion but we would like to have a focus on photooxidant concentrations.

- *Lines 93-94 refers to the authors' previous work. Why didn't they do these corrections in the past? If the answer is they learned as they went, then they might benefit from "building" upon their work instead of "criticizing" their work.*

**Response:** The reviewer is correct that the inhibition corrections were not made in the past because we did not realize this problem at that time. Thank you for your suggestion. We have revised the sentence in the manuscript.

- *Lines 108 and 109 seem to contradict themselves about which type of PM was collected. PM<sub>2.5</sub> or PM<sub>10</sub>?*

**Response:** PM<sub>10</sub> inlet filtered out the particles with size greater than PM<sub>10</sub>, and then two offsets were used to filter out particles with size greater than PM<sub>2.5</sub>. We modified the text to clarify this.

- *Contrast the statement on lines 419-421 about how DOC is a good predictor of 1O<sub>2</sub>\* (where others have also shown the same like (Cote et al., 2018)) and lines 266-267 on how the water extraction only removes a fraction of BrC.*

**Response:** This is an interesting point. There is a possibility that the similar relationships between DOC and <sup>1</sup>O<sub>2</sub>\* concentration among three samples can be attributed to the extraction method, which only extracted the water-soluble brown carbon. However, since we lack any data about the <sup>1</sup>O<sub>2</sub>\* production from water-insoluble brown carbon, it is difficult to make a comparison.

#### *References:*

*Albinet, A., Minero, C., and Vione, D.: Photochemical generation of reactive species upon irradiation of rainwater: Negligible photoactivity of dissolved organic matter, Sci. Total Environ., 408, 3367–3373, <https://doi.org/10.1016/j.scitotenv.2010.04.011>, 2010.*

*Barrios, B., Mohrhardt, B., Doskey, P. V., and Minakata, D.: Mechanistic Insight into the Reactivities of Aqueous-Phase Singlet Oxygen with Organic Compounds, Environ. Sci. Technol., 55, 8054–8067, <https://doi.org/10.1021/acs.est.1c01712>, 2021.*

Bogler, S., Daellenbach, K. R., Bell, D. M., Prévôt, A. S. H., El Haddad, I., and Borduas-Dedekind, N.: Singlet Oxygen Seasonality in Aqueous PM<sub>10</sub> is Driven by Biomass Burning and Anthropogenic Secondary Organic Aerosol, *Environ. Sci. Technol.*, *56*, 15389–15397, <https://doi.org/10.1021/acs.est.2c04554>, 2022.

Carlton, A. G., Christiansen, A. E., Flesch, M. M., Hennigan, C. J., and Sareen, N.: Multiphase Atmospheric Chemistry in Liquid Water: Impacts and Controllability of Organic Aerosol, *Acc. Chem. Res.*, *53*, 1715–1723, <https://doi.org/10.1021/acs.accounts.0c00301>, 2020.

Cote, C. D., Schneider, S. R., Lyu, M., Gao, S., Gan, L., Holod, A. J., Chou, T. H. H., and Styler, S. A.: Photochemical Production of Singlet Oxygen by Urban Road Dust, *Environ. Sci. Technol. Lett.*, *5*, 92–97, <https://doi.org/10.1021/acs.estlett.7b00533>, 2018.

Hong, J., Liu, J., Wang, L., Kong, S., Tong, C., Qin, J., Chen, L., Sui, Y., and Li, B.: Characterization of reactive photoinduced species in rainwater, *Environ. Sci. Pollut. Res.*, *25*, 36368–36380, <https://doi.org/10.1007/s11356-018-3499-4>, 2018.

Kaur, R., Labins, J. R., Helbock, S. S., Jiang, W., Bein, K. J., Zhang, Q., and Anastasio, C.: Photooxidants from Brown Carbon and Other Chromophores in Illuminated Particle Extracts, *Atmos Chem Phys*, *19*, 6579, 2019.

Leresche, F., Salazar, J. R., Pfothner, D. J., Hannigan, M. P., Majestic, B. J., and Rosario-Ortiz, F. L.: Photochemical Aging of Atmospheric Particulate Matter in the Aqueous Phase, *Environ. Sci. Technol.*, <https://doi.org/10.1021/acs.est.1c00978>, 2021.

Li, J., Chen, Q., and Guan, D.: Insights into the triplet photochemistry of atmospheric aerosol and subfractions isolated with different polarity, *Atmos. Environ.*, *290*, 119375, <https://doi.org/10.1016/j.atmosenv.2022.119375>, 2022a.

Li, J., Chen, Q., Sha, T., and Liu, Y.: Significant Promotion of Light Absorption Ability and Formation of Triplet Organics and Reactive Oxygen Species in Atmospheric HULIS by Fe(III) Ions, *Environ. Sci. Technol.*, *56*, 16652–16664, <https://doi.org/10.1021/acs.est.2c05137>, 2022b.

Ma, L., Worland, R., Tran, T., and Anastasio, C.: Evaluation of Probes to Measure Oxidizing Organic Triplet Excited States in Aerosol Liquid Water, *Environ. Sci. Technol.*, <https://doi.org/10.1021/acs.est.2c09672>, 2023.

Manfrin, A., Nizkorodov, S. A., Malecha, K. T., Getzinger, G. J., McNeill, K., and Borduas-Dedekind, N.: Reactive Oxygen Species Production from Secondary Organic Aerosols: The Importance of Singlet Oxygen, *Environ. Sci. Technol.*, 53, 8553–8562, <https://doi.org/10.1021/acs.est.9b01609>, 2019.

Ossola, R., Jönsson, O. M., Moor, K., and McNeill, K.: Singlet Oxygen Quantum Yields in Environmental Waters, *Chem. Rev.*, 121, 4100–4146, <https://doi.org/10.1021/acs.chemrev.0c00781>, 2021.

Paulson, S. E., Gallimore, P. J., Kuang, X. M., Chen, J. R., Kalberer, M., and Gonzalez, D. H.: A light-driven burst of hydroxyl radicals dominates oxidation chemistry in newly activated cloud droplets, *Sci. Adv.*, 5, eaav7689, <https://doi.org/10.1126/sciadv.aav7689>, 2019.

**Anonymous Referee #2 Received and published: 20 April 2023**

*The paper aims at predicting photooxidant ( $^1O_2$ ,  $^3C^*$  and OH) concentrations in brown carbon aerosol liquid water. This is an important issue and relatively challenging to extrapolate from dilute laboratory experiments to the more concentrated aerosol liquid water. Here is a few issues and thoughts on the manuscript:*

*Steady-state concentration of  $^3C^*$  and  $^1O_2$*

*The review by McNeill and Canonica cited in the manuscript indicates that the steady-state concentration of  $^3C^*$  and  $^1O_2$  are roughly equals one to each other. The authors present numbers that are quite higher for  $^1O_2$  than  $^3C^*$ . I think that the authors should make it clearer that the numbers they measure for  $^3C^*$  are only a subset of the triplets (oxidizing triplets). This has implications when the authors compare the steady-state  $^3C^*$  to literature one. The literature concentrations were not necessarily measured with the same probes and are not necessarily the same subset of oxidizing triplets and I do think that one should be careful when comparing  $^3C^*$  numbers.*

**Response:** We thank this reviewer for the thoughtful review and encouraging comments. The reviewer is correct that the  $^3C^*$  we measured in this work is oxidizing triplet, which is only a subset of the total triplet pool. Therefore, the measured oxidizing  $^3C^*$  concentrations are always lower than  $^1O_2^*$ . Another reason that might cause the  $^1O_2^*$  concentration to be higher than  $^3C^*$  is that we used the rate constant of probe with  $^3DMB^*$  to calculate oxidizing triplet concentrations. This value might be higher than the rate constants for natural triplets, leading to an underestimate of oxidizing triplets, as we discussed in Ma et al. (2023). We have added this information in the Method section of 2.4.2.

*Extraction efficiency*

*To investigate [DOC] influence, the authors extracted the collected PM<sub>2.5</sub> in various amounts of water. The authors present convincing evidence that [DOC] reflects the amount of water used in the extraction. Seeing Table S2 and S3, I was left wondering if it is also the case for the inorganics. E.g., Na<sup>+</sup> concentration does not look to reflect well the amount of water used in the extraction. Similarly, the measured OH sinks do not look to reflect well the dilution. Seeing Figure 2, I think that for  $^1O_2$  and  $^3C^*$ , the results do not look to be affected by a potential*

variation in extraction efficiency. But for the OH measurements, I am wondering if the observed increase is real or if it reflects a variation in the inorganics extraction (or eventually a non-ideal behavior of the probe, see below).

**Response:** Thank you for your suggestion. We checked the relationships of ion concentrations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , formate,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) with our concentration factor. All ions show good linearity with concentration factor, with most having  $R^2$  greater than 0.98. We have added this as Figure S2 in the Supporting Information. This indicates that the inorganics extraction efficiencies were consistent with different dilution conditions. Therefore, we do not think the inorganic extraction affect the  $\bullet\text{OH}$  measurement. Unfortunately, we do not know why the measured  $\bullet\text{OH}$  sinks do not exhibit good linearity with dilution.

#### OH Probe

*Benzoic acid is known to have some drawbacks as OH probe. Being relatively less selective towards OH than other OH probes (Environ Chem Lett (2010) 8:95–100). The observed increase in OH concentration could also reflect a non-ideal behavior of the probe (e.g., if the probe starts to react with  $^3\text{C}^*$  at high [DOC]). If the authors have the possibility to do additional control experiments, I would suggest replicating an OH measurement at high [DOC] in the presence of an OH quencher. That would tell the authors if the observed production of *p*-hydroxybenzoic acid is due exclusively to OH reaction.*

**Response:** Unfortunately, we do not have enough sample remaining to do an  $\bullet\text{OH}$  quenching experiment. However, we tested the idea that triplets might interfere with  $\bullet\text{OH}$  determinations by illuminating a mixture of benzoic acid (BA) and a high concentration of DMB. We saw no decay of BA by  $^3\text{DMB}^*$ , consistent with a second-order rate constant below  $10^7 \text{ M}^{-1}\text{s}^{-1}$ . Therefore, BA decay by  $^3\text{C}^*$  should be negligible. Moreover, the mechanism of  $\bullet\text{OH}$  reacting with BA will be different from  $^3\text{C}^*$  reaction. *p*-Hydroxybenzoic acid is the specific reaction product of the OH addition reaction between  $\bullet\text{OH}$  and benzoic acid. For triplet reaction, it undergoes proton-coupled electron transfer, and should not form *p*-hydroxybenzoic acid if there is any reaction between  $^3\text{C}^*$  and BA.

#### 102 vs $^3\text{C}^*$ reactivity

*When comparing  $^1\text{O}_2$  vs  $^3\text{C}^*$ , the surface water literature indicates that  $^3\text{C}^*$  tends to be more important for the degradation of contaminants (Environ. Sci. Technol. 2013, 47, 10781–10790, Environ. Sci. Technol. 2013, 47, 6735–6745). I am not very sure for which class of compounds  $^1\text{O}_2$  reactivity tends to be higher than  $^3\text{C}^*$  but the examination of the compounds presented in Environ. Sci. Technol. 2013, 47, 6735–6745 indicates to me that it may not be electron rich compounds as the authors stated on line 85. Electron rich compounds have very high  $^3\text{C}^*$  reactivity that would dominate  $^1\text{O}_2$  pathway. It may be compounds that are doing Diels-Alder reaction with  $^1\text{O}_2$  that reacts preferentially with  $^1\text{O}_2$ .*

**Response:** The reviewer is correct that not necessarily electron rich compound reacts fast with  $^1\text{O}_2^*$  or dominated by  $^1\text{O}_2^*$  pathway. It also depends on the structure of a compound since the mechanisms of  $^3\text{C}^*$  and  $^1\text{O}_2^*$  reacting with organic compound are different.  $^1\text{O}_2^*$  tends to add to the double bond, for example, via cyclic addition or Diels-Alder reaction as indicated by the reviewer (Barrios et al., 2021), while  $^3\text{C}^*$  undergoes proton-coupled electron transfer (McNeill and Canonica, 2016). However,  $^1\text{O}_2^*$  also reacts rapidly with deprotonated phenols with a rate constant that can be higher than  $10^8 \text{ M}^{-1}\text{s}^{-1}$ , which is not necessarily a cyclic addition reaction (Tratnyek and Hoigne, 1991). We modified the sentence to give some examples of compound classes that react quickly with  $^1\text{O}_2^*$ , rather than trying to summarize the reactants as “electron rich”.

### *Halogens influence*

*A side thought to consider for further works:*

*The authors (Anastasio, C., and J. T. Newberg (2007), Sources and sinks of hydroxyl radical in sea-salt particles, J. Geophys. Res., 112,) and others (Environ. Sci. Technol. 2021, 55, 13152–13163) measured sinks of OH such as Cl<sup>-</sup> and Br<sup>-</sup>. It would have been interesting to evaluate Cl<sup>-</sup> and Br<sup>-</sup> importance as OH sink. Additionally, Cl<sup>-</sup> and Br<sup>-</sup> can quench  $^3\text{C}^*$  (PNAS, 2016, 113, 21, 5868–5873). These reactions would form bromine and chlorine radicals that have some reactivity and could potentially lead to the formation of brominated and chlorinated products. This has some similarities with the formation of disinfection by-products during water treatment and the produced compounds could potentially have a high carcinogenicity.*

**Response:** Cl<sup>-</sup> concentrations in our samples a range from 5 to 190 μM, while Br<sup>-</sup> concentrations were always below the detection limit. In previous work from our group we investigated Cl<sup>-</sup> as a sink for •OH (Kaur et al., 2019), but it was negligible (< 1 % of OH loss) since at the pH of our samples nearly all of the reaction product falls apart to regenerate •OH.

In PNAS' work (Parker and Mitch, 2016), they considered the effect of Cl<sup>-</sup> and Br<sup>-</sup> on quenching <sup>3</sup>C\* in coastal and estuarine surface waters, which contain more than 1000 times higher concentration of Cl<sup>-</sup> and Br<sup>-</sup> than in our samples. The rate constants of Cl<sup>-</sup> and Br<sup>-</sup> quenching <sup>3</sup>C\* are on the order of < 10<sup>5</sup> and 10<sup>5</sup>-10<sup>8</sup> M<sup>-1</sup>s<sup>-1</sup>, respectively (Gemayel et al., 2021). These slow rate constants coupled with the low halide concentrations, make Cl<sup>-</sup> and Br<sup>-</sup> negligible sinks for <sup>3</sup>C\* in our work. Halogens influence might be negligible in our samples, but it will be interesting for sea spray aerosols or marine aerosols that contain high concentrations of halogens and need further investigation.

***Anonymous Referee #3 Received and published: 26 April 2023***

*In this new contribution, Ma et al explore different sources of tropospheric aqueous oxidants, including hydroxyl radical (•OH), singlet molecular oxygen (1O2\*), and oxidizing triplet excited states of organic matter (3C\*), as a function of the aerosol liquid water (ALW) for two distinct samples (i.e., winter vs summer) sampled in California. Obviously, the amounts of oxidants in the tropospheric liquid phase is poorly constrained, and therefore this contribution provides valuable information, that will certainly be subject to discussion. But this is sign of the usefulness of the data provided.*

*This manuscript is well written and illustrated, and reads very well. This reviewer enjoyed reading it, and would recommend its publication subject to minor corrections.*

*Due to the very limited water content of particles, it is difficult to quantify oxidant concentrations in ALW directly. To predict these values, the authors measured photooxidant concentrations in illuminated aqueous particle extracts as a function of dilution and used the resulting oxidant kinetics to extrapolate to ALW conditions. How were such dilution ratios defined? Do they have any atmospheric significance?*

**Response:** We thank this reviewer for the thoughtful review and encouraging comments. We defined dilution using the concentration factor (CF) at the end of Section 2.2, where CF is the inverse of the volume (in mL) used for extraction. Because CF has no inherent atmospheric meaning, for most of the manuscript we report dilutions using the particle mass to water mass ratio, which has atmospheric significance. Aqueous aerosols often have particle mass to water mass ratios near  $1 \mu\text{g PM}/\mu\text{g H}_2\text{O}$ , while cloud/fog drops typically have ratios in the range  $10^{-4} - 10^{-5} \mu\text{g PM}/\mu\text{g H}_2\text{O}$ . Our samples have CF values of 0.3 to 10 and particle mass to water mass ratios range from  $10^{-3}$  to  $10^{-5} \mu\text{g PM}/\mu\text{g H}_2\text{O}$ . This range represents dilute to heavily polluted cloud/fog waters. We have added this information to the Section 3.2.

*Data are reported in the range 0-500 mg C/L. At the higher concentrations, what precautions have been taken to maintain a constant oxygen concentration or is oxygen consumed during the illumination experiments? With regard to the important role played by oxygen, I would suggest to clarify this.*

**Response:** This is an interesting question, which we consider in terms of the likely stoichiometry of oxygen consumption. When taking a sample (after typically 2 min of illumination), we open the quartz tube, remove an aliquot of solution, re-cap the tube, and shake the container several times to ensure re-equilibration with air. We estimate the rate of  $\text{O}_2$  consumption during illumination by summing the rates of  $^1\text{O}_2^*$  and OH formation (assuming that each OH reacts to make an alkyl radical, which then adds oxygen). In the most reactive sample (i.e., our most concentrated extract), the amount of  $\text{O}_2$  consumed in a sampling interval (e.g., 2 min) was around  $20 \mu\text{M}$ , which is less than 10% of the total  $\text{O}_2$  concentration in air-saturated solution (i.e.,  $280 \mu\text{M}$  at  $20^\circ\text{C}$ ). Therefore, the decrease in oxygen concentration during our experiments seems negligible.

*The extraction procedure used is very simple and certainly samples a subset of the brown carbon available. How is this affecting the conclusions of this study? Are the numbers provided to be considered as lower limits only? In fact, would using other extraction conditions (different pH, etc.) enhance the amount of absorbing and reactive material?*

**Response:** The reviewer is correct that the water-soluble brown carbon is only a subset of the total BrC pool. In another manuscript currently under review (Ma et al., 2023a), we

examine this issue by also extracting PM filters with methanol or hexane. We find that the absorbance of the methanol extract can be more than two times higher than the corresponding water extract. This suggests that organic-soluble brown carbon has high potential to produce photooxidants. However, since the oxidant probes are not yet validated for organic solutions, we did not study photooxidant generation in methanol or hexane. Based on the methanol extract absorbance, the numbers provided here can be considered as lower limits.

*It is show that the summer extracts absorb sunlight at approximately twice the rate as winter extracts. Is this expected? Was this sampling affected by strong biomass burning occurring in California over the last years? If yes, this should made clear as the seasonality of the two samples considered would be affected and the overall outcomes of this study as well (it would not correspond to a summer vs winter comparison, but rather to two types of burning processes).*

**Response:** The summer samples were significantly impacted by wildfires. Therefore, they have much higher light absorption than the winter extracts. We named samples based on the seasons in which they were collected, but have modified the manuscript to remove mention of seasonality since the two samples are more reflective of different types of biomass burning. We have added this information in Section 3.2.

*This reviewer had difficult to follow the logic between equations 1 to 6, and would recommend providing more explanations on the arithmetic used here.*

**Response:** We agree that it is difficult to follow the derivation of these equations from the brief description in the Methods section, but it is not worth the space to restate the entire derivation. We fully describe these equations in the Anastasio and McGregor (2001) reference that we cite at the top of section 2.4.

## References

- Barrios, B., Mohrhardt, B., Doskey, P. V. and Minakata, D.: Mechanistic Insight into the Reactivities of Aqueous-Phase Singlet Oxygen with Organic Compounds., *Environ. Sci. Technol.*, 55(12), 8054–8067, doi:10.1021/acs.est.1c01712, 2021.
- Gemayel, R., Emmelin, C., Perrier, S., Tomaz, S., Baboomian, V. J., Fishman, D. A., Nizkorodov, S. A., Dumas, S. and George, C.: Quenching of ketone triplet excited states by atmospheric halides, *Environ. Sci.: Atmos.*, 1(1), 31–44, doi:10.1039/D0EA00011F, 2021.
- Kaur, R., Labins, J. R., Helbock, S. S., Jiang, W., Bein, K. J., Zhang, Q. and Anastasio, C.: Photooxidants from brown carbon and other chromophores in illuminated particle extracts, *Atmos. Chem. Phys.*, 19(9), 6579–6594, doi:10.5194/acp-19-6579-2019, 2019.
- Ma, L., Worland, R., Heinlein, L., Guzman, C., Jiang, W., Niedek, C., Bein, K. J., Zhang, Q. and Anastasio, C.: Seasonal variations in photooxidant formation and light absorption in aqueous extracts of ambient particles, , doi:10.5194/egusphere-2023-861, 2023a.
- Ma, L., Worland, R., Tran, T. and Anastasio, C.: Evaluation of probes to measure oxidizing organic triplet excited states in aerosol liquid water., *Environ. Sci. Technol.*, 57(15), 6052–6062, doi:10.1021/acs.est.2c09672, 2023b.
- McNeill, K. and Canonica, S.: Triplet state dissolved organic matter in aquatic photochemistry: reaction mechanisms, substrate scope, and photophysical properties., *Environ. Sci. Process. Impacts*, 18(11), 1381–1399, doi:10.1039/c6em00408c, 2016.
- Ossola, R., Jönsson, O. M., Moor, K. and McNeill, K.: Singlet oxygen quantum yields in environmental waters., *Chem. Rev.*, 121(7), 4100–4146, doi:10.1021/acs.chemrev.0c00781, 2021.
- Parker, K. M. and Mitch, W. A.: Halogen radicals contribute to photooxidation in coastal and estuarine waters., *Proc. Natl. Acad. Sci. USA*, 113(21), 5868–5873, doi:10.1073/pnas.1602595113, 2016.
- Paulson, S. E., Gallimore, P. J., Kuang, X. M., Chen, J. R., Kalberer, M. and Gonzalez, D. H.: A light-driven burst of hydroxyl radicals dominates oxidation chemistry in newly activated cloud droplets., *Sci. Adv.*, 5(5), eaav7689, doi:10.1126/sciadv.aav7689, 2019.
- Schauer, J. J., Kleeman, M. J., Cass, G. R. and Simoneit, B. R.: Measurement of emissions from air pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood., *Environ. Sci. Technol.*, 35(9), 1716–1728, doi:10.1021/es001331e, 2001.
- Schwartz, S. E. and Freiberg, J. E.: Mass-transport limitation to the rate of reaction of gases in liquid droplets: Application to oxidation of SO<sub>2</sub> in aqueous solutions, *Atmospheric Environment* (1967), 15(7), 1129–1144, doi:10.1016/0004-6981(81)90303-6, 1981.
- Tratnyek, P. G. and Hoigne, J.: Oxidation of substituted phenols in the environment: a QSAR analysis of rate constants for reaction with singlet oxygen, *Environ. Sci. Technol.*, 25(9), 1596–1604, 1991.

Wenk, J. and Canonica, S.: Phenolic antioxidants inhibit the triplet-induced transformation of anilines and sulfonamide antibiotics in aqueous solution, *Environ. Sci. Technol.*, 46(10), 5455–5462, doi:10.1021/es300485u, 2012.

Wenk, J., von Gunten, U. and Canonica, S.: Effect of dissolved organic matter on the transformation of contaminants induced by excited triplet states and the hydroxyl radical., *Environ. Sci. Technol.*, 45(4), 1334–1340, doi:10.1021/es102212t, 2011.