

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

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Response to Reviewers comments for Photooxidants from Brown Carbon and Other Chromophores in Illuminated Particle Extracts By Richie Kaur et. al.

Each reviewer comment is mentioned and our response is directly below it.

Please note that line numbers in the revised version are different due to changes in the manuscript. _____

Anonymous Referee #1 Received and published: 21 December 2018

This paper reports the results of a study that quantified $\cdot\text{OH}$, IO_2 and triplet states in particulate matter aqueous extracts. As there are few or no studies on the subject, the

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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 $1O_2$ and $3C^*$ data). For these reasons, the manuscript should be revised following the recommendations reported below.

Response: We thank this reviewer for their thorough review and the detailed, helpful comments. We have addressed each of them below.

Regarding probe molecules, while we tried to limit probe concentrations so that they were insignificant scavengers of the transient oxidants, we found that we had one condition (MBO used to measure $[OH]$ in the dilution series of sample PME3D) where the probe was a significant sink. As described below (and in the revised manuscript), we corrected these $[OH]$ values for the influence of MBO. For the other oxidant cases – $1O_2^*$ and $3C^*$, and $[OH]$ measured in the other samples using benzene – our probe concentrations were low enough that they insignificantly perturbed oxidant kinetics. These determinations are also described below.

1. Page 5, bottom. Please specify the degree (approximate) by which the samples were diluted upon addition of H_2SO_4 . Moreover, measuring pH in a small sample might not be totally trivial: please provide details of the pH measurement device.

Response: The dilution of the samples was always kept below 10%. For each sample, we acidified and measured the pH of a 1 mL aliquot using a pH microelectrode (MI-414 series, protected tip needle, 16 gauge, 6 cm length; Microelectrodes, Inc.). We have added this information in Sect. 2.3 (Page 6, top).

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

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Response: Yes. Pathlength was measured in cm. We have clarified this (now Page 6, bottom).

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).

Response: The contributions of NO₂⁻ / NO₃⁻ to light absorption were small and vary by wavelength. Integrated across the solar wavelengths, these species accounted for up to 7% of total absorption. We have added this information to Sect. 2.4 (top of page 7).

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

Response: We apologize for the oversight. We have spelled out the acronyms OM (organic matter) and OC (organic carbon).

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.

Response: To minimize perturbations in the steady-state concentrations of the oxi-

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dants, we used low concentrations of probe compounds for $1O_2^*$ and $3C^*$. The concentrations of FFA and triplet probes (SYR and MeJA) were $10 \mu\text{M}$ each (Sections 2.5.2 and 2.5.3, respectively). The major sink for $1O_2^*$ in our samples is water, with a pseudo-first order rate constant of $2.2 \times 10^5 \text{ s}^{-1}$ (Bilski et al., 1997). In comparison, $10 \mu\text{M}$ of FFA (with a rate constant $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$; Wilkinson et al. (1995)) has a corresponding rate constant of $1.2 \times 10^3 \text{ s}^{-1}$, indicating that it reduces $[1O_2^*]$ by less than 1 %.

For triplets, there are two major natural sinks: O_2 , with a pseudo first-order rate constant, $k_{3C^*+O_2}[O_2]$, of $8.0 \times 10^5 \text{ s}^{-1}$ (see Eqn. 8) and dissolved organic compounds, which have an average pseudo-first-order rate constant with triplets of $\sim (9 \times 10^7 \text{ L mol}^{-1} \text{ C}^{-1})(3 \times 10^{-3} \text{ mol L}^{-1}) = 3 \times 10^4 \text{ s}^{-1}$ in the standard extracts. Together, these two sinks represent a total background rate constant for triplet loss of approximately $8.3 \times 10^5 \text{ s}^{-1}$. In contrast, $10 \mu\text{M}$ of SYR (our most reactive triplet probe) has a pseudo-first-order rate constant of $k_{3C^*+SYR}[SYR] \approx (4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})(1 \times 10^{-5} \text{ M}) = 4 \times 10^4 \text{ s}^{-1}$. Thus the addition of SYR causes, on average, a decrease in the triplet concentration of only $\sim 5\%$.

The competition kinetics technique, which was used for most measurements of $\dot{\text{A}}\dot{\text{C}}\text{OH}$, uses a range of probe (benzene) concentrations so that the parameters POH , $k'OH$ and $[\dot{\text{A}}\dot{\text{C}}\text{OH}]$ can be determined under extrapolated conditions of zero added probe. For these cases the probe influence is accounted for in the method.

However, for our final case we found that the probe concentration was indeed too high. This is the dilution series of sample PME3D, where we used $75 \mu\text{M}$ methylbutenol (MBO) (Section S1). We had to use a high concentration because of analytical limitations: the high background absorbance in the standard extract made it difficult to detect MBO in our samples. However, in hindsight we should have adjusted the MBO concentration so that it was lower in the more dilute PM extracts. MBO has a rate constant with $\dot{\text{A}}\dot{\text{C}}\text{OH}$ of $7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Section S1), thus $75 \mu\text{M}$ corresponds to a pseudo-first-order rate constant for $\dot{\text{A}}\dot{\text{C}}\text{OH}$ loss of $5.6 \times 10^5 \text{ s}^{-1}$. With this relatively high value

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MBO is a significant, and in one case dominant, sink for HO_2 in the dilution series of PME3D. MBO is significantly suppressing $[\text{HO}_2]$ in the more dilute extracts, but not as much in the more concentrated extracts: our originally reported $[\text{HO}_2]$ values are too low by factors of 3.3, 1.4, 1.3, 1.2, and 1.1 for samples PME3D10, D2.5, D1.3, D1, and D0.5, respectively. We have added a description of this problem to the manuscript and corrected the $[\text{HO}_2]$ values in the PME3D dilution series. Because we correct our SYR probe results for the contribution of HO_2 , we have also corrected the corresponding 3C^* concentrations for the PME3D dilution samples, as well as our associated Figures and the extrapolations to aerosol liquid water conditions. Because HO_2 was a minor contributor to SYR loss, the corrections for 3C^* are relatively small. We have indicated the problem with MBO determination of HO_2 , and our correction, in the main text and supplemental material.

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 μL aliquots. The reason for this difference should be provided for clarity.

Response: We thank the reviewer for their attention to detail. At the beginning of Sect. 2.3, we mention that the procedure of using a 1 mL sample volume applies to all measurements except “POH measurements” when it should have said “ HO_2 measurements using benzene” – this was an error that we have corrected. For all HO_2 measurements where benzene is used as a probe, we used a larger sample volume (5 mL instead of 1 mL) while withdrawing the same small aliquot for HPLC analysis (100 μL) in order to minimize the headspace in the reaction container. Since benzene is highly volatile, reducing headspace prevents loss of benzene due to volatilization. Since the other probes are less volatile, we were able to use a small volume (1 mL) for those experiments because the additional headspace in the container after a few aliquot withdrawals does not pose a complication, unlike in case of benzene. We have

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added this clarification in Sect. 2.5.1.

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

Response: Thank you, we have corrected this.

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.

Response: Yes, because of the very small pathlength in ambient particles the screening is negligible for our filtered samples. (Insoluble black carbon might cause screening in airborne particles, but our samples were filtered.) Although the particles are much more concentrated than our solutions (by approximately a factor of 103), the pathlength in the particles ($\sim 1 \mu\text{m}$) is smaller than in our solutions by a larger amount (approximately a factor of 104).

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

Response: The two techniques are not directly comparable. In the benzene technique, we measured the product of the reaction between benzene and OH , i.e., phenol. The yield for phenol from the benzene + OH reaction is 73%; we have added this information to Sect. 2.5.1. On the other hand, when MBO was the probe, we measured the loss of MBO in solution, similar to FFA, SYR and MeJA. Because MBO can also react with HO_2^* and 3C^* , we corrected the MBO decay to account for these contributions and then calculated $[\text{OH}]$ from the fraction of MBO lost due to OH alone (see Section S1.1 in the SI). On average, $55 (\pm 15) \%$ of MBO was lost by reaction with OH in the PME3D dilution samples where MBO was used.

10. Section 2.5.2. Please specify the FFA concentration and the way HO_2 scavenging by added Ffa was accounted for.

Response: The concentration of FFA ($10 \mu\text{M}$) is specified near the beginning of Sect.

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2.5.2. As we describe in our response to comment #5 above, this FFA concentration is low enough that it does not significantly affect the singlet oxygen concentration.

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

Response: Faster (as we had in the text) is correct. Since $^1\text{O}_2^*$ reacts more slowly with D_2O than H_2O , $[^1\text{O}_2^*]$ is higher in the D_2O solutions and thus FFA loss is faster.

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

Response: The probe concentration of $10 \mu\text{M}$ is specified near the beginning of Sect. 2.5.3. As we discussed in our response to comment #5 above, our calculations indicate that the addition of SYR (or MeJA) does not significantly affect the triplet concentration. We have added a mention of this to the text.

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.

Response: The reviewer is correct about how our technique works. We have added some text at the top of page 10 to try to clarify our description.

14. Lines 288-289. Canonica estimated $5 \times 10^{-5} \text{ s}^{-1}$ 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 $[\text{O}_2]$ assumed here in comparison with surface waters? Please explain better.

Response: The triplet deactivation constant (units: s^{-1}) is the product of the second-order rate constant of triplet quenching by O_2 ($k_{3\text{C}^+\text{O}_2}$; units: $\text{M}^{-1} \text{ s}^{-1}$) and the molar concentration of O_2 . We used Canonica's estimates for $k_{3\text{C}^+\text{O}_2}$ (Canonica et al.,

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2000) for 3 model triplets, and to mimic natural triplets, we averaged them to get a value of $2.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (shown in Table S11). We used USGS estimates for dissolved oxygen concentration of $284 \mu\text{M}$ at our experimental temperature of $20 \text{ }^\circ\text{C}$ (USGS, 2018), which yields a triplet deactivation constant of $8 \times 10^5 \text{ s}^{-1}$. It is possible that some of the surface water studies were done at a different temperatures or used $\text{k}3\text{C}+\text{O}_2$ for a single model triplet rather than the average value we used – either or both of those factors could be responsible for that difference. All of these details are given after Equation 8 in the main text.

15. Equation (9) and related discussion. I imagine that also R_{abs} 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 normalized data, that should be explained.

Response: We normalize measured rates of oxidant formation to winter solstice sunlight to correct for daily variations in the output of our lamp; this allows rates in different samples to be directly compared (and averaged). To be consistent, R_{abs} , the rate of light absorption in a sample, is calculated using the winter solstice actinic flux (Equation 2): while we could calculate the rate of light absorption for each experiment, values for different samples couldn't be properly compared because of variations in light output. So, while we are essentially double normalizing, it allows us to put all values on the same photon flux basis.

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

Response: The AAE formula and calculation are described in the footnotes of Table S1 of the SI. In the interest of keeping our main text from getting any larger, we have not added the equation to the main text.

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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).

Response: This is an interesting point. Yes, as shown in Fig. S5 of the SI, the particle extracts had a higher absorbance and mass absorption coefficient at shorter wavelengths. Consequently, the decline of absorbance with wavelength in the extracts was faster than in fog. However, a caveat to this data is that the figure compares the ratios of two specific samples (e.g., median absorbing PM extract with median absorbing fog), so it is unclear how representative each sample is. To better make this comparison we also calculated AAE values for the fog drops: the fog values are generally lower than the PM extract values (consistent with the Fig. S5 result), but the difference is small ($p = 0.56$; Table S1).

18. Lines 378,379. This statement means that PME are not more concentrated than for with respect to NO_3^- and NO_2^- . Is there any idea as to the reason for this?

Response: The reviewer is correct, but it's difficult to interpret this result since the gas-particle partitioning of HNO_3 under non-fog conditions is highly dependent upon the availability of ammonia.

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

Response: We have added the range of measured DOC values.

20. Page 14, bottom. It may be interesting to recall that the IO_2 formation QY determined here is also not very distant from typical values found in surface waters.

Response: This is a good point. We have added this comparison to the manuscript (on Page 15).

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

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much better to compare the formation quantum yields.

Response: The reviewer makes a good point. We have added a quantum yield comparison at the end of this section (on Page 16). The concentration comparison we had in the original manuscript (and which we've kept) is for the same winter-solstice sunlight conditions.

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 $1O_2$ formation quantum yields. That could be discussed to place the used results and methodology into a clearer and more complete framework.

Response: As we described earlier, our calculations indicate that our $1O_2^*$ and $3C^*$ probes did not significantly perturb the concentrations of these oxidants, so we do not think there is a problem with our method. It is possible that our PM results for $\Phi 3C^*/\Phi 1O_2^*$ are lower than the surface water results described by the reviewer because of differences in OM chemistry between the two types of samples; our result suggests that $f\Delta$ is lower in atmospheric waters. But we also note that a recent study by Zhou et al. (2019) shows that the ratio $\Phi 3C^*/\Phi 1O_2^*$ for terrestrial NOM is approximately 0.5, similar to our result. The quantum yield for oxidizing triplets probably also depends on the probe used.

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

Response: Liquid water content for particles in California's Central Valley during winter were calculated based on particle composition and the component thermodynamics by Parworth et al. (2017). We used their values as an estimate for our samples, as described in Table S14 of the SI.

24. Line 524. In the case of $1O_2$ production, it is strange that saturation of absorbance

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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?

Response: Our highest absorbing samples had absorption coefficients of less than 0.6 cm⁻¹ at 300 nm (e.g., Fig. 1) but we had a short pathlength (4 mm), so there was no significant screening of light in our experiments. Light screening factors (where a value of 1 indicates no screening) ranged from 0.84 to 0.99 (Table S1) and were accounted for in our calculations.

25. Page 18, 1st half. In the case of surface waters, you need DOC \hat{A} 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.

Response: The DOC values in μ M-C for all PME samples are given in Table S2 of the SI. Converted to mg-C L⁻¹, the values for the PME3D samples range from 4.3 to 86 mg-C L⁻¹. Thus, as the concentration. We have added a statement in the main text to indicate this.

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

Response: Thank you, we have corrected this partially but somehow, we are unable to fix the formatting completely. It now reads “Wenk et al. (2011); (2013)”. We are hoping this can be fixed during typesetting.

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

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(they might tend to highlight $1O_2$ reactions). This issue should be discussed better.

Response: This is an interesting point. We don't think that the duality of our results is because we picked compounds that are not representative, but rather that there are so many compounds (in number and/or quantity) that are reacting with triplets that its steady-state concentration is significantly suppressed in the PM condition (but its formation rate is unaffected). The result is that triplets do not appear to be very significant sinks for individual compounds, but they are significant in aggregate, i.e., when considered over all of the species that react with triplets. We have modified the text to describe this.

28. Line 615. "approximately" should read "approximate".

Response: Thank you, we have corrected this sentence.

29. Line 622. 600 vs. 3000. According to Fig. 5 one has quite parallel increases of both $[1O_2]$ 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.

Response: This is a good observation from the reviewer: while Fig. 5 considered only an extrapolation of the measured aqueous processes, in the text we also considered gas-phase mass transport and the expected organic sinks for oxidants in highly concentrated particles. To eliminate this confusion, we have modified Fig. 5 to show the expected oxidant concentrations in drops and particles considering both our aqueous measurements and the calculated impacts of organic sinks and mass transport from the gas phase. Under these conditions, the concentration of $1O_2^*$ increases by a factor of 2400 from dilute drops to concentrated particles, while the concentration of oxidizing triplets increases by a factor of 30 (best fit) to 2000 (high estimate).

Anonymous Referee #2 Received and published: 2 January 2019

General comments This manuscript presents results of measurements of traditional

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and novel oxidants in PM extracts of ambient samples and importantly illustrates the potential for brown carbon to increase oxidant concentrations through the formation of triplet states. While many uncertainties exist, this study lays the groundwork for future studies into the role of brown carbon in generating photooxidants. The study presents a novel technique for measuring oxidants that appears to hold even under diluted conditions of aerosol extracts, and the results and conclusions drawn are supported by the available data. The abstract is concise enough, though it may benefit from further shortening and the title reflects the work as presented. The large volume of supplementary information will allow future work to build on this publication.

This work may help address the measurement/model discrepancies between the O/C ratio of ambient SOA and that predicted by chemical models. The manuscript is well presented with clear writing and legible figures. The work is also highly timely, and represents a step forward in our ability to understand the competing reactions taking place in aerosol and aerosol water (oxidant generation and loss). I have only two minor comments to improve the paper and one technical correction.

Response: We thank this reviewer for their thoughtful review, encouraging comments, and specific suggestions for improvement of the manuscript. We had addressed each of the comments below.

Specific comments:

The abstract was a bit hard to get through, and could benefit from further shortening if the authors feel this is possible. For example, lines 34-38 may be omitted without loss of meaning.

Response: We appreciate the reviewer's comment about the length of the abstract. To make it more concise, we have deleted lines 34-35. We left lines 36-38 as it is to provide an appropriate segue from discussing oxidant concentration measurements in dilute extracts to estimating them in ambient particles.

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Lines 448-451: It was difficult to follow the relationship between $k'SYR,3C^*$ / $k'MeJA,3C^*$, and $k'Probe,3C^*$ ratio. Are these the same thing, but the latter is a general term? Please clarify.

Response: Yes, the reviewer is correct – these refer to the same thing. The latter ($k'Probe,3C^*$ ratio) is a general term whereas $k'SYR,3C^*$ / $k'MeJA,3C^*$ specifically mentions the probes. We have clarified this.

Technical corrections Line 545: missing “is” between “it also”

Response: We thank the reviewer for their attention to detail. We have made this correction.

Anonymous Referee #3 Received and published: 8 January 2019

This work mainly measured the concentrations of three important photooxidants formed from photoexcitation of brown carbon by collecting ambient particles during heavy residential wood-burning period in winter, extracting them in water, and illuminating the acidified aqueous extracts. The results in aqueous extracts were extrapolated to ambient particle water conditions and compared to the corresponding photooxidants in fog. The main conclusion of this work is that hydroxyl radical in particles had similar levels with fog and cloud drops while singlet oxygen and oxidizing triplet excited sites of organic matters are enhanced in particles. Their results indicate that singlet oxygen and oxidizing triplet excited sites of organic matters formed from the photoexcitation of brown carbon can be important sinks for organic compounds in atmospheric particles. Although there are large uncertainties in the extrapolation to ambient particle water conditions, especially for oxidizing triplet excited sites of organic matters, this work provides the first measurement of singlet oxygen and oxidizing triplet excited sites of organic matters, which affect the lifetime of organic compounds in particle liquid water. The results are very helpful for the science community to improve our understanding of photooxidants and inspire more works for different seasons and locations, and implementing in current atmospheric models. I think this is an interesting and important

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work, and recommend for acceptance after comments below are addressed:

Response: We thank this reviewer for their thoughtful review, encouraging comments, and specific suggestions for improvement of the manuscript. We had addressed each of the comments below.

1. Line 154, please explain “air-saturated”.

Response: The term “air-saturated” refers to the fact that the particle extracts are saturated with O₂ by exposure to air. This is important because O₂ is a sink for triplets, and the lack of oxygen in solutions can artificially enhance the triplet steady-state concentration. During the course of the experiments, we stirred the solutions continuously and exposed the surface of the solution to air each time an aliquot was taken for HPLC analysis.

2. Line 379, the authors mentioned additional source can be photo-Fenton processes, I am wondering if Fe has been/can be measured in the samples. It would be interesting to compare to Fe data.

Response: Unfortunately, we were not able to measure Fe in the solutions due to a lack of sample volumes. However, this is a very valid question that should be addressed in future studies of a similar nature.

3. Line 389-394, suggest adding some literature reviews on the destruction/sinks of OH in this section or in the introduction section.

Response: We have added the references.

4. The authors made a couple comparisons between “standard” and “dilute” extracts throughout the manuscript. From the manuscript, the “standard” extraction was based on extracting particles into 1 mL water and the “dilute” was extracting in 2.5 mL water. It is an effect of dilution. It is not clear to me what is the purpose of comparing “standard” and “dilution” conditions. The authors have already studied extensively the effect of dilution using sample 3 in later experiments, so I don’t understand why repetitive

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comparison were made here or are there additional purposes of comparing “standard” and “dilute” extracts but were not well presented in the manuscript? The authors need to make it clearer.

Response: We appreciate the reviewer’s comments on this. The comparisons between standard and dilute extracts arise mainly because we started out measuring the oxidant concentrations in the dilute extracts. After a few samples, we realized that the “dilute” extracts closely resembled fog samples in terms of oxidant concentrations. We then switched to a higher concentration, i.e, extracting the particles in 1 mL water instead of 2.5 mL and we established this as the “standard” condition. The benefits of showing both results in the paper are to illuminate how even this small concentration factor changes oxidant concentrations and how dilute particle extracts essentially mimic fog droplet photochemistry.

5. Method section: sample extracts were mixed with photooxidant probes and then illuminated in light. The authors will need to address whether illumination will affect the probes or the products formed from probes and targeted photooxidants. For example, benzene traps OH radicals and form phenol. How does illumination experiments affect the product phenol. Do the authors concern about the photodegradation or photoenhancement of phenol, therefore, resulting in underestimation or overestimation of the OH concentration? Same concerns will also be needed to address for singlet oxygen and triplets cases.

Response: This is a good question. Briefly, for measuring $\dot{\text{A}}\text{OH}$, we only illuminated solutions spiked with benzene for time periods where linear increase in phenol concentration was observed (Fig. S1 in the SI). Had there been any secondary chemistry, the concentration of phenol would no longer increase linearly. This is evidence that measuring $\dot{\text{A}}\text{OH}$ from phenol formation within our experimental time frame was not confounded by secondary reactions. Similarly, for 1O_2^* and 3C^* , the loss of the probes follow first order kinetics (Figs. S2 and S8 in the SI).

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6. Line 339, following the last comment, another concern is the effect of illumination on the light absorbance of brown carbon. For example, a recent study by Wong et al. 2017 EST (Changes in Light Absorptivity of Molecular Weight Separated Brown Carbon Due to Photolytic Aging) showed that light Absorptivity of brown carbon changes due to photolytic aging. Please discuss how change of absorptivity affects the conclusions in this work.

Response: This is an interesting question. Part of the photolytic aging of brown carbon are likely the reactions of the dissolved organics with transient oxidants such as HO^\bullet , $^1\text{O}_2$ and $^3\text{C}^\bullet$. With respect to photolytic aging affecting the experimental outcomes, since we are measuring photooxidant formation in approximately the same time frame as the Wong et. al. study cited by the reviewer (i.e. about 2 hours), it is possible that some transformation of organics does occur. However, since the loss of probe compounds followed first-order kinetics in all cases and our probes do not undergo direct photolysis, we don't suspect the aging process to have affected photooxidant formation.

References:

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